Controlled polymerization of organic semiconductor monomers: applications in hierarchical nanostructures and luminescent materials

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Abstract

Emerging methods for the fabrication of multifunctional nanostructures from soft matter have allowed for the synthesis of complex macromolecules with varied morphologies and physical properties. Using organic semiconductors as building blocks, nanostructures with novel emissive properties and interesting charge-transport behaviour are increasingly accessible. Self-assembly processes have been developed to promote nanofiber formation, giving access to previously inaccessible functional nanostructures. However, self-assembly routes to nanofibers are limited by the metastability of the resulting structures, leading to a demand for covalent methodologies for their assembly.

This thesis presents an optimized method for the synthesis of polymeric organic semiconductors via controlled radical polymerization and methods by which these linear polymers can be used to generate complex, covalently bound nanofibers. We proposed that by controlling the composition and ordering of the polymeric components, multiblock bottlebrush copolymers could be prepared with photophysical and electronic properties that could not be achieved in a linear polymer morphology. Using this method, multicomponent fibers were prepared resembling nanoscale organic electronic devices such as two-component diodes. This bottlebrush framework can also be used to control the electronic interaction between multiple organic semiconductors within the brush. This property was exploited to control through-space charge transfer thermally activated delayed fluorescence (TSCT TADF) in bottlebrush fibers.

The polymerization methodologies developed for the synthesis of organic semiconductors were also explored as a method to prepare luminescent copolymers composed of a host monomer and a series of emissive monomers. We propose that using this methodology, low-cost polymers can be prepared that exhibit the photophysical properties of the emissive dopant. This will allow us to prepare polymers that exhibit a range of interesting properties including deep blue electroluminescence, TADF, and ratiometric fluorescent oxygen sensing.

Lastly, a pair of violet emitters were prepared using a novel planarized triphenylamine donor and a sulfone or sulfoxide acceptor. State-of-the-art deep blue emitters typically exhibit low photostability. We propose that stable emitters can be achieved using a planarized hexamethylazatriangulene donor in a donor-acceptor framework. The reduced torsional strain and locked planar rigidity increase the stability of this donor while reducing nonradiative decay resulting in highly emissive compounds with resistance to photobleaching.

Lay Summary

Organic nanofibers have emerged as a promising platform for the preparation of nanomaterials with properties that are not accessible using typical methods. Conventional techniques to make these macromolecules typically rely on self-assembly to combine small building blocks into large fibers. Unfortunately, many nanostructures prepared in this way must be kept in specific solvents and/or temperature ranges to remain stable, making characterization and further applications of these materials difficult to access. In this work, we describe methods for the preparation of polymer-based nanofibers that are composed of a covalently linked backbone polymer and densely packed side chain polymers, with the goal of creating nanofibers that simulate simplified electronic devices. Properties of these nanofibers were then characterized, demonstrating novel material properties that result from well-defined nanoscale organization. Further work was done using more complex monomers to make materials capable of fluorescent oxygen sensing, thermally activated delayed fluorescence, and deep blue electroluminescence.

Preface

The contents of Chapter 2 have been reported previously in two publications: Tonge, C. M.; Sauvé, E. R.; Paisley, N. R.; Heyes, J. E.; Hudson, Z. M. Polymerization of Acrylates Based on N-Type Organic Semiconductors Using Cu(0)-RDRP. *Polym. Chem.* **2018**, *9*, 3359–3367 and Sauvé, E. R.; Tonge, C. M.; Paisley, N. R.; Cheng, S.; Hudson, Z. M. Cu(0)-RDRP of Acrylates Based on p-Type Organic Semiconductors. *Polym. Chem.* **2018**, *9*, 1397–1403. Synthetic work and polymer characterization for both these publications were split between myself and Ethan Sauvé.

The contents of Chapter 3 have been published previously over two publications: Tonge, C. M.; Yuan, F.; Lu, Z. H.; Hudson, Z. M. Cu(0)-RDRP as an Efficient and Low-Cost Synthetic Route to Blue-Emissive Polymers for OLEDs. *Polym. Chem.* **2019**, *10*, 3288–3297 and Tonge, C. M.; Paisley, N. R.; Polgar, A. M.; Lix, K.; Algar, W. R.; Hudson, Z. M. Color-Tunable Thermally Activated Delayed Fluorescence in Oxadiazole-Based Acrylic Copolymers: Photophysical Properties and Applications in Ratiometric Oxygen Sensing. *ACS Appl. Mater. Interfaces* **2020**, *12*, 6525–6535. Computational work (3.3.6) was performed by Nathan Paisley and lowtemperature time-resolved emission measurements were performed by Alex Polgar. Device work (Section 3.2.6) was performed in collaboration with Prof. Zheng-Hong Lu and Fanglong Yuan of the University of Toronto. Polymer dots were prepared in collaboration with Prof. Russ Algar and Kelsi Lix.

The contents of Chapter 4 have been published previously: Tonge, C. M.; Sauvé, E. R.; Cheng, S.; Howard, T. A.; Hudson, Z. M. Multiblock Bottlebrush Nanofibers from Organic Electronic Materials. *J. Am. Chem. Soc.* **2018**, *140*, 11599–11603. Synthetic and characterization work were divided between myself and Ethan Sauvé with assistance from Susan Cheng and Teresa Howard.

The contents of Chapter 5 have been published previously: Tonge, C. M.; Hudson, Z. M. Interface-Dependent Aggregation-Induced Delayed Fluorescence in Bottlebrush Polymer Nanofibers. J. Am. Chem. Soc. 2019, 141, 13970–13976.

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All of the authors listed in the publications below were involved in the discussion and writing of the manuscripts.

All figures, unless otherwise specified, have been created by me or in collaboration with the previously specified authors and are used with permission.

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List of Abbreviations

2PEF	two-photon excited fluorescence
3PCzPFP	3-(9-Phenyl-9H-carbazol-3-yl)furo[2,3-b:5,4-b0]dipyridine
ACQ	aggregation-caused quenching
AEE	aggregation-enhanced emission
AFM	atomic force microscopy
AIE	aggregation-induced emission
ARGET	activators regenerated by electron transfer
ATRA	atom transfer radical addition
ATRP	atom transfer radical polymerization
BBCPs	bottlebrush copolymers
BTB	4,4'-bis(4,6-diphenyl-1,3,5-triazin-2-yl)biphenyl
CCDC	Cambridge Crystallographic Data Centre
CDSA	crystallization driven self-assembly
CIE	Commision Internationale de l'Éclairage
CRP	controlled radical polymerization
DCC	N,N'-dicyclohexylcarbodiimide
DCU	dicyclohexylurea
DFT	density functional theory
DLS	dynamic light scattering
DMAc	dimethylacetamide
DMF	dimethylformamide
DP	degree of polymerization
DPEPO	bis[2-(diphenylphosphino)phenyl] ether oxide
DSC	differential scanning calorimetry
DVB	divinylbenzene
eATRP	electrochemically mediated ATRP
EBiB	ethyl bromoisobutyrate
EQE	external quantum efficiencies
ESI	electrospray ionization
ESIPT	excited-state intramolecular proton transfer
FLIM	fluoresence lifetime imaging
FWHM	full-widths at half-maxima
HATCN	hexaazatriphenylenehexacabonitrile
HMAT	hexamethylazatriangulene
НОМО	highest occupied molecular orbital
HOPG	highly-oriented pyrolytic graphite
HSSA	hierarchical solution self-assembly
ISC	intersystem crossing

LUMO	lowest unoccupied molecular orbital
MA	methyl acrylate
mCP	9,9'-(1,3-phenylene)bis-9H-carbazole
Me ₆ TREN	tris[2-(dimethylamino)ethyl]amine
MMs	macromonomers
NMP	<i>N</i> -methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
NPB	N, N'-bis(naphthalen-1-yl)- N, N' -bis(phenyl)benzidine)
NTA	nanoparticle tracking analysis
OLEDs	organic light emitting diodes
OPVs	organic photovoltaics
OTFTs	organic thin-film transistors
PBD	2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole
PDot	polymer dot
PEDOT:PSS	poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
PLA	polylactide
PLED	polymer light emitting diode
PLQY	photoluminescent quantum yield
PPF	2,8-bis(diphenylphosphoryl)dibenzo[b,d]furan
PS	polystyrene
PS/DVB	polystyrene/divinylbenzene
RAFT	reverse addition-fragmentation chain transfer polymerization
RDRP	reversible-deactivation radical polymerization
RISC	reverse intersystem crossing
ROMP	ring-opening metathesis polymerization
RTP	room-temperature phosphorescence
SCPNs	single chain polymer nanoparticles
SEC	size exclusion chromatography
STED	stimulated emission depletion
TADF	thermally activated delayed fluorescence
TEMPO	2,2,6,6-tetramethylpiperidinyloxyl
TFB	poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine)
TGA	thermogravimetric analysis
TLC	thin layer chromatography
TPBi	2,2',2"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TPD	N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine
TSCT	through-space charge transfer

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From the moments of pain Look how far we done came

Kanye West

Chapter 1: Introduction

1.1 Inspiration for the Work

In the last two decades, significant strides have been made towards preparing functional and hierarchical nanomaterials that exhibit emergent properties, in other words, multicomponent materials that exhibit characteristics that cannot be accounted for by the sum of their component parts. Current methods to prepare multicomponent nanomaterials from soft matter typically rely on self-assembly methods in which a small number of molecular or polymeric building blocks come together through noncovalent interactions. These interactions are controlled not only by the structures of the building blocks themselves, but also the environment with which they are surrounded. Under the right conditions, the negative enthalpy of these interactions can overcome the negative entropy of assembly, giving rise to nanostructures. By careful selection of the building blocks, diverse morphologies such as spheres, rods, platelets, toroids, and more can be prepared, yet the construction of nanomaterials with multiple controlled compartments remains a challenge. Furthermore, maintaining the structural integrity of these nanomaterials under non-ideal conditions, such as temperature, solvent, or mechanical stress, limits their use in widespread applications.

The fabrication of multicompartment nanofibers in particular has attracted significant attention due to their unique applications in electronics,^{8,9} data encoding,^{10–12} and nanomedicine.^{13–15} For example, Manners, Winnik and others have exploited the epitaxial crystallization of specific polymers to produce long nanofibers via crystallization driven self-assembly (CDSA) with unique chemical, photonic, or electronic functionality.^{12,16–19} Conductive nanofibers have also been prepared via living supramolecular polymerization using well-controlled hydrogen bonding interactions, giving fibers up to several hundred nanometers in length.^{20,21} Complex wormlike

materials have also been prepared via hierarchical solution self-assembly by selective step-wise precipitation of multiblock copolymers with differing block solubility.^{22–25} The study of these structures has uncovered new phenomena, including long-range exciton transport through self-assembled nanowires or the control of crystallization-driven self-assembly using light.²⁶ As new morphologies, properties and applications of polymer nanomaterials emerge, the need for robust methods for their fabrication will only continue to rise.

In the course of my graduate work, I have sought to develop methods to prepare robust nanofibers with well-defined structure and electronic functionality. In addition, we aimed to substantially expand the range of materials from which ordered nanofibers can be prepared. Our chosen approach was to generate bottlebrush copolymers, ultrahigh molecular weight polymers composed of a polymeric backbone to which linear polymers are directly appended, decorated with semiconducting small molecules. The steric interactions between these adjacent side-chain polymers leads to reduced chain entanglement, resulting in fiber like morphologies that are typically extended when observed in the solid state. By directly attaching linear polymers to the bottlebrush backbone, this framework allows for facile synthesis of multifunctional polymeric nanoparticles with control over composition over three degrees of hierarchy. These include the identities of the monomers in the linear side-chains, the ordering of these monomers in the sidechains (e.g. homopolymers, block copolymers, random copolymers), and the ordering of the polymeric side chains along the bottlebrush backbone. Furthermore, as all functionalities are attached to the bottlebrush backbone using strong covalent bonds, the stability of the resulting nanofibers is significantly improved relative to fibers assembled by non-covalent means.

Current methods of generating fiber-like nanostructures typically use self-assembly methods such as CDSA, hierarchical solution self-assembly (HSSA), or living supramolecular
self-assembly. While incredibly complex materials have been achieved using these methods, there are significant limitations that we hope to address using bottlebrush copolymers. These methods all depend on non-covalent interactions such as hydrogen-bonding, Van der Waals interactions, or π - π interactions, which are at least an order of magnitude weaker in energy than covalent C-C, C-N or C-O bonds. Furthermore, achieving the desired self-assembly behaviour requires that the target structures represent a local or absolute free energy minimum in a specific environment. This requirement limits the scope of nanomaterials that can be accessed by self-assembly. For example, while long nanofibers are easily prepared, self-assembly methods do not allow for easy access to non-centrosymmetric materials. Furthermore, the metastable nature of the structures prepared limits the range of potential applications for which they can be used.

Through the course of our investigations with BBCPs, new synthetic methodologies for polymerization of organic semiconductors were a key initial target. Once developed, these methods were then used to give optoelectronic materials with a variety of applications. Initially, efforts were focused on the development of a polymerization method with which diverse macromonomer building blocks could be prepared with ease. To be amenable to bottlebrush synthesis, macromonomers must have a high degree of end group functionality as well as narrow dispersity and well-defined molecular weight. It was found that Cu(0)-reversible deactivation radical polymerization (Cu(0)-RDRP), a modified version of atom transfer radical polymerization (ATRP), was optimal for polymerizing the polyaromatic acrylic monomers investigated. Using this method, linear polymers composed of hole-transport, electron-transport, and emissive materials were prepared with polymerizable end groups, which could then be used as macromolecular monomers – or 'macromonomers' – in bottlebrush synthesis. We demonstrate that a bottlebrush architecture can be used to prepare complex nanomaterials with structures that

3

resemble simple organic electronic devices, such as bilayer p-n junctions or multilayer organic light-emitting diodes (OLEDs). A bottlebrush morphology can also be used to control the interface between donor and acceptor monomers within a nanofiber, controlling through-space charge transfer (TSCT) by controlling the degree of donor-acceptor interaction.

This Cu(0)-RDRP methodology was also used to prepare a series of highly emissive doped copolymers based on donor-acceptor triarylamine-oxadiazoles. A series of polymers with tunable emission colour were prepared and characterized, demonstrating potential applications for oxygen sensing, imaging, and electroluminescent devices. Monomers with thermally activated delayed fluorescence (TADF) properties were also prepared which exhibited utility as ratiometric sensors for oxygen concentration.

Lastly, a common limitation in the application of fluorescent emitters is the limited photostability of many of the chromophores used. One way in which this limited photostability can be addressed is by reducing the vibrational degrees of freedom in the material, by bridging and planarizing the emitters. We explored planarization of triarylamine donors to synthesize a highly stabilized deep blue/violet emitter, which exhibits enhanced two-photon absorption and improved resistance to photobleaching. In summary, our overarching goal has been to develop new synthetic techniques and building blocks for optoelectronics, to both expand our fundamental understanding of nanomaterials synthesis and to unlock new applications in sensing and electronics.

1.2 Literature Review

1.2.1 Current Methods for Nanofiber Preparation

Recent work has shown that novel optoelectronic properties can be observed in complex nanomaterials that are not accessible with small molecules or simple structures. One example of properties that are directly linked to the morphology of the material are the recent demonstrations of long-range exciton transport in nanomaterials assembled via CDSA and supramolecular polymerization.²⁶ Exciton transport has been observed over micron length scales, a feature that can be particularly useful in designing high efficiency photovoltaics and light emitting diodes, in these materials, a direct result of the well-defined nanostructures assembled in each case. As such, significant work has focused on preparing nanomaterials containing interesting functionalities which imbue them with novel electronic and photophysical properties.

As implied by the name, crystallization-driven self-assembly takes advantage of block copolymers with a semicrystalline block that is amenable to epitaxial crystallization and a soluble outer block to generate complex nanostructures. Pioneered by Manners and Winnik in 2007,²⁷ this method has been expanded from poly(ferrocenylsilane)-poly(dimethylsiloxane) copolymers to include a variety of semicrystalline core polymers, including poly(3-hexylthiophene),²⁸ polyselenopehene,²⁹ poly(piro[fluorene-9,5'-[1,3]-dioxan]-2'-one),³⁰ and polyethylene,³¹ among others. Using these semicrystalline polymers, complex nanostructures and interesting morphologies have been demonstrated by varying the functionality and size of the core-forming block and the outer block, including scarf-like^{32,33} and dumbbell shaped³⁴ micelles as well as welldefined two-dimensional platelets.^{16,35–37} Furthermore, materials created using these methods have demonstrated novel physical properties, such as unprecedented charge transport properties²⁶ or the control of crystallization driven self-assembly using light,¹⁸ driving further research. Current work in this area, however, is limited due to the relatively few semicrystalline polymers that are amenable to serving as a core-forming block in these systems. As a result of this crystallinity requirement, nanostructures formed by CDSA are unstable outside of specific solvents or

temperature ranges, and there are limitations on the potential functional groups that these structures can incorporate.



Figure 1.1 Tunable hierarchical solution self-assembly achieved via modulating block ratio in triblock linear polymers. (a) Chemical structure of the polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) triblock terpolymer (SBT). (b) Suggested structural control: the length of the soluble PT corona (green chain) controls the micelle geometry to spheres, cylinders, bilayer sheets and vesicles; (c) the block lengths of the insoluble and immiscible blocks, PS (grey) and PB (black), determine the patch morphology to spherical, cylindrical, bicontinuous and lamellar. Reproduced from Ref 23 and licensed under CC BY 4.0.

Hierarchical solution self-assembly has also been demonstrated to allow access to welldefined functional nanostructures from polymeric materials. While HSSA also takes advantage of polymer-polymer interactions to generate complex nanostructures, rather than taking advantage of epitaxial crystallization, this method uses multiblock polymer building blocks with substantially differing solubilities to regulate the self-assembly process. In a typical HSSA protocol, the solvent environment of a multiblock copolymer is modified in a series of steps, causing polymer blocks with differing solubility to collapse in stages. Using this methodology, different morphologies can be directly accessed by simply modifying solvent polarity, block length, and other parameters, as demonstrated by Müller and others (Figure 1.1).^{22,23,38} They were able to directly demonstrate high-level control over the self-assembled morphologies achieved by simply modifying the relative ratio of core and corona blocks.²³ Furthermore, the authors were able to prepare welldefined nanostructures with a high degree of control over periodicity to generate patterned cylinders, spheres, and sheets. Complex wormlike superstructures have also been prepared by restricting the conformational space of multiblock copolymers with differing solubilities in a stepwise fashion. While this method is incredibly powerful in terms of the scale and complexity of the materials that can be generated with it, the dependence on specific conditions (e.g. polarity, temperature, and concentration) to maintain the metastability of these structures makes it very difficult to make use of materials created in this fashion.

Nanostructures that exhibit interesting charge transport properties are also accessible using living supramolecular polymerization. Instead of using polymeric building blocks, supramolecular polymerization uses small-molecule building blocks with hydrogen bonding substituents attached in strategic locations. By precisely balancing the H-bonding interactions with the Van der Waals forces and steric repulsion between adjacent small molecules, highly extended structures can be observed on the length scale of hundreds of nanometers. By using building blocks with complex electronic functionalities such as triaryalmines³⁹ or porphyrins,²¹ emergent electronic properties can also be observed. For example, materials generated via supramolecular polymerization methods have demonstrated metallic behavior³⁹ or enhanced singlet oxygen generation properties.⁴⁰ One method that has been shown to increase the stability of structures generated via this method is to covalently cross link adjacent building blocks after self-assembly.⁴¹ This allows for facile isolation of the nanostructures formed without affecting the stability of the structures, preventing them from dispersing in solution during the isolation process.

1.2.2 Bottlebrush Polymerization as a Route to Nanofibers

Bottlebrush copolymers (BBCPs) are an emerging route to well-defined covalently linked nanofibers, avoiding some of the pitfalls of self-assembly based methods.⁴² Composed of a linear polymeric backbone decorated with many polymeric side chains, BBCPs are particularly interesting due to their highly extended conformation when in solution and in the solid state. Although composed primarily of flexible single bonds, the steric repulsion of adjacent side chains forces backbone units apart, leading to a low-entropy polymeric nanofiber. This extended conformation is particularly interesting as it allows one to generate nanofibers in which opposite termini are held apart in solution, potentially allowing for measurements of interactions over the length of the fiber. BBCPs have been prepared in a variety of morphologies, including multiblock polymers,⁴³ gradient copolymers,⁴⁴ and Janus structures.^{45,46} BBCPs have been shown to demonstrate novel properties that arise directly from their extended structure, forced by the dense side chain packing illustrated in Figure 1.2, and ultrahigh molecular weight, including interesting light-matter interactions^{47–49} as well as applications in biological systems for both sensing⁵⁰ and drug delivery.^{51–53}



Increasing grafting density

Figure 1.2. Effect of side chain grafting density on the conformation of bottlebrush (co)polymers, colors representing distinct macromonomers, showing the enhanced sidechain segregation with high grafting density. Reprinted with permission from Ref 42. Copyright 2020 American Chemical Society.

The rigidity of the bottlebrush backbone combined with their large domain sizes and facile access to multiblock materials has led many groups to explore the properties of BBCPs when selfassembled in a thin-film or from the melt.⁴⁸ One particularly interesting application of selfassembled bottlebrushes is the formation of photonic crystals, arising from lamellar assemblies formed. These lamella result in periodic differences in refractive index that form a onedimensional photonic crystal. This results in partial reflection of light that can be correlated directly to the lamella domain size and the difference in refractive index between the polymers of which these domains are composed. Grubbs and coworkers demonstrated using polylactide (PLA) and poly(*n*-butyl acrylate) BBCPs that domain spacing can be controlled by either backbone length or by side chain length depending on the bottlebrush morphology. By preparing a randomized BBCP of these two macromonomers and a diblock BBCP, it was found that domain size was dependent on side chain length for a random copolymer and dependent on backbone length and block length for a diblock copolymer.⁵⁴ This system was extended using polystyrene in place of poly(*n*-butyl acrylate) to prepare photonic crystal films with selective reflection throughout the entire visible spectrum. Tunable reflectance was observed by directly swelling bottlebrush domains in the film state by codepositing the BBCPs with linear homopolymers, either PLA or polystyrene (PS), resulting in red-shifted reflected light.⁵⁵ Furthermore, as the color of reflected light is directly dependent on domain size, red-shifted reflected emission can be observed for some samples following exposure to solvent vapor, which swells the copolymers.^{56,57}

The utility of high molecular weight BBCPs has also been demonstrated *in vivo* in several studies, either as a framework for drug delivery,^{51–53} as a building block for self-assembled nanoparticles,^{58–61} or as a multifunctional sensing tool.⁵⁰ For example, core-shell BBCPs with a cross-linkable shell and an easily degraded core have been used to make hollow nanoparticles that

can cross the cell membrane for use as a potential drug delivery method.^{62–65} These cylindrical structures with empty cores were demonstrated to be tolerated well by HeLa cells, opening the door to using this bottlebrush morphology as a method to encapsulate and deliver drugs. Alternatively, bottlebrushes can be used for drug delivery by functionalizing them with drug molecules bound directly to the backbone via an easily degraded linker, shielded from the environment by the bottlebrush side chains.⁶⁶ By using a linker that degrades upon light exposure, cytotoxicity of the bottlebrushes was suppressed prior to drug release, increasing 10-fold upon irradiation and the release of the drug. Using a similar bottlebrush framework, Johnson and coworkers also demonstrated the utility of bottlebrush copolymers for in vivo fluorescence and MRI imaging.⁵⁰ They prepared a bottlebrush copolymer that was capable of acting simultaneously as a near IR emitter and as an MRI agent by using a pair of macromonomers composed of a solubilizing poly(ethylene glycol) chain and a stimuli responsive core group, either an NIR emitter or an organic MRI contrast agent respectively. By attaching the dyes directly to the backbone and shielding them with PEG side chains, they were able to maintain biocompatibility of the resulting bottlebrushes. Furthermore, by using a bottlebrush framework for these nanoparticles, residence time *in vivo* was increased significantly due to the ultrahigh molecular weight, allowing for extended utility of these dual-responsive materials for imaging and sensing.

Bottlebrush copolymers are an exciting new avenue to prepare functional nanofibers. Although materials of similar complexity have been prepared via self-assembly based methods such as CDSA, HSSA, and supramolecular polymerization, BBCPs do not rely on noncovalent intramolecular bonding. By covalently bonding adjacent polymer building blocks through a polymeric backbone, these nanostructures have significantly improved stability, especially when removed from solution. Due to their ultrahigh molecular weight, BBCPs give access to structures with macroscale features upon self-assembly if they are used as building blocks. Furthermore, using a bottom-up approach to synthesize BBCPs allows access to nanostructures that are difficult or impossible to achieve with self-assembly, such as non-centrosymmetric structures, while providing well-controlled routes to core-shell and multiblock nanofibers.



1.2.3 Synthetic Routes to Bottlebrush Polymers

Figure 1.3 Methods to prepare bottlebrush copolymers. Reproduced from Ref 67 with permission from The Royal Society of Chemistry.

Bottlebrush copolymers give access to high molecular weight materials with control of composition and organization at three distinct levels of hierarchy via a bottom-up, covalently bound synthetic method. By controlling the monomer identity, the ordering of these monomers on linear side-chains, and the organization of these linear side-chains along a polymeric backbone, complex materials can be designed with a high degree of control along the nanofiber. There are three main methods to generate bottlebrush copolymers. The route used to generate the BBCPs has direct implications on the grafting density of the backbone, the control of side-chain organization, and the backbone length achievable. As illustrated in Figure 1.3, these methods can be categorized into three key methods, "grafting-through" polymerization, "grafting-to" coupling,

or "grafting-from" polymerization, differentiated by the method through which polymeric side chains are attached to the bottlebrush backbone.

In a grafting-to method, a polymeric backbone is synthesized and then functionalized with many coupling partners (*e.g.* alkynes, azides, etc.) along its length. In a separate polymerization, side chain polymers that include an appropriate coupling partner to pair with this backbone are prepared. These polymeric side chains are then coupled with the backbone polymer to give the bottlebrush in a grafting-to procedure. This method tends to lead to low grafting density of linear side-chains as each additional side chain that successfully couples adds significant steric bulk to the immediate surroundings. Furthermore, this method makes the preparation of multiblock bottlebrushes very difficult, as there is little control over side chain placement in the coupling step.

Alternatively, a grafting-from polymerization method can be used to significantly increase grafting density. In this method, a polyinitiator backbone is first synthesized, from which side chains are grown via a second, orthogonal polymerization. Typically, a polymer backbone is first synthesized with an initiator functionality for a second polymerization attached to each backbone monomer unit. The second polymerization gives the bottlebrush polymer, with longer polyinitiators giving rise to longer bottlebrushes. Furthermore, if chain end fidelity is maintained, multiblock side chain polymers can be prepared *in situ* to give fiber-like polymers with a coreshell structure. While this method tends to yield bottlebrush copolymers with a higher grafting density, the steric interactions between adjacent growing chains can limit the growth of these side chains. The preparation of multicomponent bottlebrushes can be achieved by sequential polymerization of two monomers, resulting in core-shell bottlebrush copolymers, or via more complex synthetic methods requiring three or more orthogonal polymerization or protection-

deprotection steps.⁶⁸ It should be noted that the initiation efficiency from these macroinitiators may be limited due to the close spacing of adjacent initiator sites.^{69,70}

To maximize grafting density while also allowing for explicit control over side chain functionality and ordering, grafting-through polymerization is an ideal synthetic route. In a grafting-through bottlebrush synthesis, polymeric building blocks are first synthesized bearing a reactive end group amenable to a second orthogonal polymerization. These macromonomers are then polymerized to generate a bottlebrush, with side chain organization explicitly dictated by the order and timing of macromonomer addition. This method gives the highest degree of control over the distribution of functionality throughout the final bottlebrush structure, allowing for core-shell and multiblock nanofibers. However, the steric interactions of polymeric side chains at the propagating chain end in this second polymerization lead to issues achieving BBCPs with long backbone lengths. As our target structures depend explicitly on control of monomer placement along the bottlebrush backbone, this grafting-through method is ideal.

1.3 Methods to Synthesize Polymeric Organic Semiconductors

Polymeric organic semiconductors are polymers composed of or pi-conjugated monomers that can act as a semiconductor when charge is injected. Current methods to generate semiconducting polymers are typically dependent on transition metal catalyzed coupling methods, free radical polymerizations, and living or controlled polymerization methods. Free radical polymerization is very cheap to implement, especially as polymerizations run in this way typically run to high monomer conversion. However, this method offers limited control over the polymerization reaction, resulting in broad polydispersity. This method is therefore ideal for applications in which these drawbacks have minimal impact. Transition metal catalyzed coupling methods are widely used to synthesize polymers with conjugated backbones, typically proceeding via a polycondensation mechanism using Suzuki,^{71,72} Stille,⁷³ Negishi,^{74,75} Kumada,^{76–78} and other catalyst systems.⁷⁹ These condensation methods can be used to prepare common conjugated polymer semiconductors, including polythiophenes^{80,81} and polyfluorenes.^{82–84} Controlled radical polymerization (CRP) and living polymerization have also emerged in recent years as attractive routes to synthesize polymeric semiconductors, including atom transfer radical polymerization (ATRP),^{85,86} reverse addition-fragmentation chain transfer polymerization (RAFT),^{87,88} and ring-opening metathesis polymerization (ROMP).^{89–91} These methods give facile access to well-defined polymers at the cost of somewhat increased difficulty of monomer synthesis. For our purposes, we required a controlled radical method with mild conditions that was easily generalized to a series of monomers while providing high conversions and low polydispersity. This was particularly challenging as the polyaromatic monomers used were not fully soluble in most reaction solvents, necessitating an improved polymerization method.

The first goal of our work with linear polymers was to optimize a method to synthesize semiconducting polymers that allow access to polymers ranging from 10 kDa to 50 kDa while maintaining end group functionality, low dispersity, and high conversions. While multiple polymerization methods can potentially fulfill these requirements, CRP and ROMP are more amenable to complex functionalities. Other polymerization methods such as anionic or cationic polymerizations are not functional group tolerant, eliminating them from consideration. Once optimized, we then sought to demonstrate that these methods can be adapted to generate semiconducting end-group functionalized polymers for use in synthesizing BBCPs.

1.3.1 Atom Transfer Radical Polymerization (ATRP)

Discovered independently by Mitsuo Sawamoto⁹² and by Krzysztof Matyjaszewski and Jin-Shan Wang in 1995,⁹³ atom transfer radical polymerization (ATRP) is a notable example of a reversible-deactivation radical polymerization (RDRP). Typically governed by a Cu(I)/Cu(II) catalyst system, ATRP allows for facile synthesis of complex polymers using a variety of monomers, including acrylates, acrylamides, acrylonitriles, and styrenes. In these polymerizations, a polymer is grown from a halide- or triflate-functionalized initiator. The polymerization is composed of a reversible equilibrium between dormant chains (polymer halides) and the propagating radical species that is formed by halogen abstraction from the dormant chain end by the Cu(I)X catalyst species. Initiators or polymers with activated end groups can then undergo a radical addition step into the monomer present in solution or be reverted back to the corresponding alkyl halide by the $Cu(II)X_2$ deactivating species. By regulating the relative amount of Cu(I) and Cu(II) in solution, this method can be tuned such that a low concentration of propagating polymer chain ends are present in solution at any given time, limiting termination events and allowing for control over the polymerization kinetics. A generalized scheme of this mechanism is illustrated in Figure 1.4. ATRP relies on a complex, multicomponent reaction to achieve well-controlled polymerization kinetics that, when properly optimized, allow for relatively high conversion with narrow polydispersity. There are five key components of an ATRP that must be considered when optimizing a particular reaction: the monomer, the initiator, the ratio of catalyst to deactivator (i.e. Cu(I) and Cu(II) in a typical system), the ligand used, the reaction solvent, and the reaction temperature.⁹⁶ Each of these factors can play a significant role in the rate of the polymerization as well as the quality of the resulting polymer.



Figure 1.4 Generalized mechanism of ATRP.

While being highly functional group tolerant, traditional ATRP methods have several limitations that have been addressed via modified polymerization protocols. With unoptimized polymerization conditions, ATRP often required high concentrations of copper catalyst which can be hard to remove while also facing some issues with end group fidelity at conversions above 70%. These issues are particularly problematic for the synthesis of semiconducting polymers, as residual copper could significantly impact the charge transfer and fluorescent properties of the polymer, as well as interfere with their function in a final macroscale device. Furthermore, issues with termination at low conversion and loss of end group fidelity make it significantly harder to generate high purity end-functional polymers for use as macromonomers for our target BBCPs. As such, we sought out modified ATRP methods to allow facile polymerization while minimizing these issues. In the two decades since the discovery of ATRP, many modifications of the original polymerization method have been developed to address these issues. These modified methods typically rely on adding an additional component to regenerate active catalyst (Cu(I)) from deactivator (Cu(II)). These methods include direct electronic reduction of the Cu(II) deactivator (electrochemically mediated ATRP or eATRP) or chemical reduction of the deactivator using

additional reducing agent in activators regenerated by electron transfer (ARGET) ATRP. One particularly simple method, Cu(0) reversible-addition radical polymerization (Cu(0)-RDRP) achieves catalyst regeneration via the addition of a reducing Cu(0) source in the polymerization, typically a solid piece of copper to facilitate its removal at the end of the polymerization. Using this method, Cu(I) is generated *in situ* by comproportionation of Cu(II) and Cu(0). The amount of Cu(0) is limited by the surface area of the copper additive but is typically available in excess. This quasi-unlimited supply of reducing copper makes this method particularly resistant to quenching with oxygen or other contaminants. Furthermore, it allows for significantly reduced catalyst loading. However, this method requires a more active ligand for the copper to facilitate the comproportionation of Cu(II) and Cu(0). The combination of these factors results in a polymerization that proceeds to high conversion for a wide range of polymerizable groups including (meth)acrylic, styrenic, and acrylamide-based monomers while maintaining first-order polymerization kinetics with no observed loss of end group fidelity.⁹⁴ This allows for facile synthesis of semiconducting polymers with minimal wasted monomer as well as allowing for easy functionalization of the end group or initiator, opening the door to applications for these polymers in more complex systems.

1.3.2 Ring Opening Metathesis Polymerization (ROMP)



Figure 1.5. Catalytic cycle of ROMP of a norbornene monomer.

While ATRP does provide easy access to the targeted linear polymers, there are other polymerization methods that are functional group tolerant and able to provide low dispersity, end group functionalized polymers such as ring-opening metathesis polymerization (ROMP). This method uses a strained olefin-based monomer in combination with a transition metal catalyst to generate a polymer as illustrated in Figure 1.5. The polymerization is typically initiated via the addition of a transition metal-carbene complex, such as Grubbs' 2nd- or 3rd- generation ruthenium catalysts,^{95–97} followed by rapid association with a olefin monomer in solution. This olefin-ruthenium complex cyclizes to form a metallocyclobutane followed by an elimination step resulting in the (re)formation of a transition metal-carbene complex attached to the propagating end of this polymer.

ROMP has several significant advantages when compared to other polymerization methods. First of all, due to the relatively high stability of the ruthenium catalysts typically used for ROMP, this method is amenable to the production of polymers with a high degree of chainend livingness, barring the presence of impurities in the reaction. This results in polymers with very narrow dispersities at high conversion, and may often be performed at room-temperature. Furthermore, the high degree of chain-end livingness allows for facile synthesis of block copolymers via the injection of a second monomer after the first block has run to conversion. Polymers generated via ROMP have found uses in a variety of applications, including medicine,^{66,98} optoelectronics,⁹⁰ and manufacturing.^{99–102}

While ROMP is highly controlled, allowing access to very well-defined linear polymers with low polydispersity and good control over molecular weight, end group functionalization can be more difficult. Initiator functionalization requires significant modification of the ruthenium catalyst, a process that is prohibitively difficult, while end group functionalization requires the use of complex chain-transfer agents or quenchers that are difficult to implement due to their synthetic complexity. Furthermore, the norbornene monomer handle required to make functional monomers is comparatively expensive (>100x the price for exo-5-Norbornenecarboxylic acid compared to acryloyl chloride, approximately 11,500 \$/mol compared to 108 \$/mol from Sigma Aldrich), without significantly improving the resulting material properties. Given these disadvantages, this high-fidelity polymerization method is well-suited for the synthesis of bottlebrush copolymers, however, it is not amenable to the large-scale synthesis of low molecular weight linear polymers for use as side-chains in a bottlebrush copolymer.

1.3.3 End Group Functionalization of Linear Polymers

End group functionalized polymers are of particular interest for a variety of fields besides the synthesis of bottlebrush copolymers. By allowing for controlled synthesis of well-defined monochelic (single end functionalized polymers) and telechelic (double end functionalized with same group) polymers, it is possible to functionalize polymers with small amounts of fluorescent tags, antibodies, or even coupling partners to generate more complex structures. For example, in work in our lab, we have demonstrated that multifunctional single chain polymer nanoparticles (SCPNs) can be end group functionalized with two different groups to append both biotin and the cancer drug camptothecin to a fluorescent nanoparticle, allowing us to directly observe targeted delivery of the drug payload.¹⁰³ Another application of end group functionalized polymers is the controlled synthesis of block copolymers, by first generating the two desired blocks as separate building blocks, appending the appropriate click-coupling handles, and then assembling the diblock polymers directly.¹⁰⁴ This method allows one to rapidly generate a library of multiblock polymers, particularly useful for exploring self-assembly behavior or other properties dependent on block ratio.

There are multiple methods by which polymers generated via Cu(0)-RDRP can have functionality introduced to either terminus. As the initiator structure is relatively simple, it is straightforward to generate functional initiators for ATRP as long as the appended functionality is tolerant to the polymerization conditions. This method is preferable to post-polymerization functionalization as it ensures that the reactive group will be present on every polymer generated, however, care must be taken to account for this potential for side reactivity. For example, if a norbornene-functionalized initiator is used for ATRP, the norbornene is prone to react via an atom transfer radical addition (ATRA) mechanism. If this occurs, this modified initiator could terminate the propagating chain end, couple multiple chains, or branch the resulting polymer. This can be prevented by selecting initiator modifications and polymerization conditions that minimize this undesired side reactivity.

Furthermore, the catalyst can lead to unwanted addition of acrylate monomers into the end group via ATRA resulting in loss of the desired functionality.¹⁰⁵ Alternatively, if there is potential

for chain-chain coupling events in the polymerization, it is possible to generate some number of polymers with double the targeted molecular weight and two end-group functionalities. This can be particularly problematic when planning to use this functionality in an orthogonal polymerization, as even a small portion of bifunctional macromonomer impurity can act as a potent crosslinker,¹⁰⁶ preventing controlled bottlebrush formation.

If satisfactory results cannot be achieved via initiator functionalization, there are various methods to end group functionalize ATRP polymers post polymerization. If quenched prior to side reactivity of the propagating chain end, a polymer synthesized via ATRP should have an alkyl halide end group.^{107,108} This alkyl halide can be readily functionalized via a substitution reaction with sodium azide to deliver azide-terminated polymers that can be carried forward as a coupling partner for click chemistry. Furthermore, if quenched with an appropriate ATRA agent,¹⁰⁹ one can use the copper catalyst present in the polymerization to directly append a functionality without requiring post-polymerization steps. These methods can be somewhat unreliable as they rely on the polymers in the mixture will remain unfunctionalized. Using a combination of initiator and end-group functionalization, it is possible to generate polymers with complex functionality attached directly to either terminus, or both termini asymmetrically.

1.4 Hole- and Electron-Transport Materials

electron and holes form excitons (recombination region) **Electron blocking** LUMO ΘΘ 77777 HOST Cathode HTL doped-emitters ETL HOMO Ð Œ Energy Hole blocking Anode

1.4.1 Organic Light Emitting Diodes (OLEDs)

Figure 1.6. Simplified diagram of a multilayer organic light emitting diode (OLED). Reproduced with permission from Ref 110. Copyright 2018 American Chemical Society.

An organic light-emitting diode is an electroluminescent device composed of stratified layers of organic semiconductors that are constructed such that light is generated upon applied bias. To reduce the driving voltage required for electroluminescence, a series of hole-transport, electron-transport, and host materials are arranged such that electrons and holes are shuttled to the emissive layer with ease. The emissive layer is typically composed of a multicomponent blended layer composed of a low-cost, high bandgap material and a highly emissive fluorescent or phosphorescent dopant. The low-cost host material funnels excitons into the emitters, allowing for reduced doping concentrations of emitter which results in improved performance and lower cost. In Figure 1.6., a device is illustrated featuring three emissive dopants as is common in a white emissive OLED, by including each dopant in separated layers of host, it is possible to make a device that exhibits the electroluminescent characteristics of the three dopants combined.^{110,111}

This allows for the production of OLEDs that emit light over the visible spectrum, a key development in the development of low-cost lighting solutions.

1.4.2 Design of Hole- and Electron-Transport Materials

Typical hole transport, electron transport, and emissive materials for OLED applications share several common functional groups. For instance, most hole transport materials are composed of a central triarylamine donor as well as pendant functionalities to modulate solubility as well as hole stability on the compounds.¹¹² Typical hole transport materials are composed of electrondonating triarylamine or highly conjugated aryl systems that stabilize the radical cations generated during hole transport.¹¹² There are many factors that affect the performance of a compound as a hole transport material in a device: the ability to form a defect-free film, high hole mobility, high glass transition temperatures (Tg), and chemical stability.¹¹² The film forming ability of hole transport materials is often improved via the addition of bulky alkyl and aromatic groups, or the use of dendritic¹¹³ or polymeric materials.¹¹⁴ Large molecular weight donors improve film-forming properties as they significantly inhibit crystallization and dewetting.^{115–117} The addition of bulky side chains or additional donors also leads to an elevated Tg, leading to further improved performance.^{118–120} Chemical and thermal stability can be improved by functionalization at the para- positions of the arylamine donors used, preventing unwanted reactivity of the stabilized radical cations at these positions.^{121,122} The thermal stability of these molecules must also be sufficient to maintain film integrity upon Joule heating, heat generated by the passage of current through a conductor, in an electroluminescent device.^{123,124} The specific hole transport material used in an OLED can be specifically tuned to match the emissive layer and electron transport layer to ensure proper alignment of the HOMO and LUMO of the layers.

Similarly, electron transport materials are typically characterized by several electronaccepting core functionalities such as triazines,^{125,126} imidazoles,¹²⁷ and oxadiazoles.^{128,129} Similar to hole transporting materials, the function of electron transport materials can be improved significantly by selecting compounds with high glass transition temperature (T_g), high chemical stability, high thermal stability, high electron mobility, and good film forming capabilities. If using low molecular weight electron transport materials to prepare films via thermal evaporation, it is ideal to select for compounds with high T_g and low crystallinity to reduce the occurrence of film defects. These problems can be eliminated to some extent using dendritic or polymeric electron transport materials, however, it is difficult to prepare high-purity films of these materials. Lastly, electron transport materials must be optimized to match the hole transport and emissive layers so as to maximize electron injection efficiency while minimizing the driving voltage required to turn the device on.

1.5 Fluorescence



Figure 1.7. Jablonski diagram illustrating a typical fluorescence process. Reprinted with permission from Ref 130. Copyright 2005 Springer Nature.

Key to the complex optoelectronic properties measured in this work is the concept of fluorescent emission. Fluorescence can be defined simply as emission of light resulting from the radiative decay of a singlet excited state to a singlet ground state, conserving spin.¹³¹ In a typical fluorescence process, photons are absorbed by the fluorophore, exciting the material from its ground state to an excited singlet state (S₀ and S₁/S₂ respectively in the Jablonski diagram illustrated in Figure 1.7.). These excited states rapidly undergo internal conversion, emitting energy nonradiatively and converting to the lowest energy excited state, S₁, according to Kasha's rule. This rule states that emission is observed in appreciable yield only for transitions from the lowest energy excited state (S₁) to the ground state (S₀). This is possible due to the relatively small energy differences between vibrational states of the S₁ excited state and the S₂ or S_n excited states. As illustrated in Figure 1.6, the vibrational states of the S₁ excited state overlap with those of the S₂ state, allowing for very rapid internal conversion. This internal conversion process is significantly faster than fluorescent emission, occurring on the picosecond timescale, and therefore occurs before typical fluorescent emission with nanosecond lifetimes.

A common metric for the efficiency of a fluorescent emission process is quantum yield or Φ . This efficiency is determined by the ratio of the rate at which of photons are absorbed to the rate at which photons are emitted. A high-efficiency emitter can exhibit quantum yields that are within measurement error of unity. The integrated absorption and emission can be readily characterized using an integration sphere paired with a non-emissive scattering standard.

Phosphorescence is a significantly slower emission process, also illustrated in Figure 1.6. This emission mechanism involves emission directly from a triplet excited state. Triplet excited states can be formed either via intersystem crossing (ISC), the energetically favorable conversion of a singlet exciton to a triplet exciton, or as a result of an electroluminescent process in which singlet and triplet excitons are produced in a 1 to 3 ratio according to spin statistics. Phosphorescent emitters typically include a heavy metal dopant, such as platinum or iridium, that facilitates spinorbit coupling leading to partial mixing of the singlet and triplet excited states and increasing the rate of intersystem crossing. If intersystem crossing is energetically favorable and occurs on a similar time scale to fluorescence, then singlet excitons will convert to lower energy triplet excitons that are then emitted via phosphorescence. Phosphorescent emission involves a "forbidden" transition from triplet excited state to singlet ground state. While this "forbidden" transition is unlikely, it is not impossible, resulting in slow emission directly from the triplet state. This can be observed as emission with lifetimes on the microsecond to second time scale.

1.5.1 Design of Fluorescent Emitters

Fluorescent compounds have a similar set of design principles, whether for OLED applications or otherwise.¹³² While material properties of fluorescent emitters are different for imaging applications, traditional OLEDs require emissive layers with high chemical and thermal stability, high T_g, and good film-forming capabilities. Emissive layers are typically composed of multiple components that are blended with a low-cost host material to maximize the efficiency of the device. These host compounds are specifically designed such that the HOMO and LUMO of the emitter are contained within the HOMO and LUMO of the host so as to funnel excitons to the emitters. Furthermore, a host material should also be selected such that the T₁ energy of the emitter is lower than that of the host, especially key for emitters that are able to harvest triplet excitons. These host materials can be composed of a variety of materials, typically carbazole-based small molecules or dendrimers with high band gaps so as to accommodate a large range of emitters. Recent work has shown promising results using ambipolar host compounds. These are composed

of a donor acceptor system that enhances charge transport by enhancing both hole and electron mobility through the host while also giving a large bandgap appropriate for deep-blue emitters. An OLED emissive layer is therefore typically composed of a high quantum yield dopant dispersed into these host materials.

Since the first demonstration of a practical OLED by Tang and Van Slyke in 1987,¹³³ many groups have focused on developing highly emissive fluorescent dopants to improve the efficiency of electroluminescent devices. In a typical emitter, fluorescence can be attributed to excitation of an electron from a singlet ground state to a singlet excited state, followed by radiative decay back to the ground state with emission of a photon. In an electroluminescent device, however, excitons are generated by the recombination of hole and electron pairs inject ed at opposite electrodes, leading to a mix of 25% singlet excitons and 75% triplet excitons as dictated by spin statistics.¹³⁴ This means that while fluorescent emitters may be able to achieve high quantum yields in a photoexcitation processes, only 25% of excitons generated in an electroluminescent device can decay radiatively. This is because while singlet excitons can decay radiatively without issue from the S₁ excited state to the S₀ ground state, transitions from T₁ to S₀ are forbidden according to quantum mechanical selection rules, dictating that transitions between two states are disallowed. As these excitons are unable to decay radiatively, they undergo a series of nonradiative transitions to relax to the S₀ ground state, releasing the energy as heat. Due to the limitations of outcoupling efficiency in an electroluminescent device, only ~20% of the photons generated are observed, leading to underwhelming external quantum efficiencies (EQE, measured by finding the ratio of the number of photons emitted per second to the number of electrons flowing into the device per second)¹³⁵ of approximately 6%. The 80% loss in efficiency in a completed device is due to several processes that absorb light during electroluminescence, including coupling to the waveguide

modes in the substrate on which the device is built, other layers in the device, or the anode, coupling to the phonons in the cathode, or reabsorption of the emitted photons by the organic layers. As a result, a 1st generation fluorescent OLED can exhibit an EQE of at most 6% (assuming typical outcoupling efficiencies).¹¹⁶

As a potential solution to this triplet exciton utilization problem, phosphorescent organometallic complexes have been explored for their utility in OLEDs. Composed of organic ligands paired with a heavy metal such as iridium or platinum, phosphorescent emitters enable full exciton utilization by allowing emission directly from the triplet excited state. The addition of a heavy metal dopant in these systems enables emission via "forbidden" transitions from T₁ to S₀. This is due to spin-orbit coupling, a process by which singlet and triplet states are able to interconvert due to their overlapping energy levels, enhanced by the inclusion heavy atoms, leading to partial mixing of the singlet and triplet states.¹³⁴ This also leads to facile conversion of singlet excitons to triplet excitons, allowing for up to 100% of the excitons generated to be used for radiative emission processes. While phosphorescent emitters have successfully been used to make OLEDs with internal quantum efficiencies up to 100%, they also have several drawbacks. Using high value metals as a key component of these emitters significantly increases the cost of production while also complicating their synthesis. Phosphorescent emitters also face significant challenges when attempting to access blue-emitting complexes, as these complexes typically exhibit low color purity, stability, and quantum yield.¹²³ The mechanism for this poor performance is linked to triplet-polaron annihilation leading to the accumulation of high energy polarons, localized electrons or holes propagating through the OLED, and radical cations on the emitters.



Figure 1.8. Illustration of the mechanistic differences between 1st, 2nd, and 3rd generation OLED emitters in an electroluminescent device. Reproduced from Ref 132 and licensed under <u>CC BY 4.0</u>.

In an effort to address the limitations of phosphorescent OLEDs, thermally-activated delayed fluorescence has emerged as a potential solution for obtaining 100% internal quantum efficiency using purely organic emitters. Since the first OLEDs using TADF were reported in 2011, significant progress has been made towards developing highly efficient TADF compounds with emission spanning the visible spectrum. TADF emitters function by specifically designing chromophores with a very small singlet-triplet energy gap (ΔE_{ST}), typically < 0.2 eV. This allows ambient thermal energy to convert triplet excitons to emissive singlet excitons by reverse intersystem crossing (RISC), illustrated in Figure 1.8. The design of TADF emitters can be challenging, however, as the emitter must typically be designed with distinct donor and acceptor (D and A) regions to minimize exchange interactions and give a small ΔE_{ST} . Low overlap between donor and acceptor portions of an emitter molecule is often achieved by intentionally forcing large dihedral angles between donors and acceptors via the addition of bulky alkyl groups or the use of

bridging groups.¹³⁶ Using donors and acceptors of differing strength, high-efficiency emitters have been prepared with emission covering the visible spectrum with external quantum efficiencies rivaling those achieved using phosphorescent dopants (e.g. DMAC-DPS = 464 nm, DMAC-TRZ = 495 nm, 4CzIPN = 507 nm, PXZ-TRZ = 545 nm, and TPA-DCPP = 708 nm as illustrated in Figure 1.9).



Figure 1.9. Representative donor and acceptor functionalities used in the synthesis of TADF emitters and representative TADF emitters over the visual spectrum. Reprinted with permission from Ref 136. Copyright 2018 Springer Nature.

Although TADF has demonstrated significant improvements over phosphorescence in electroluminescent devices, there are still several challenges that must be overcome to commercialize this technology. As these emitters must by definition emit via a charge transfer mechanism, they typically have broader emission profiles resulting in low color purity. Furthermore, as these emitters also rely on the comparatively rapid interconversion of triplet and singlet excitons followed by slow emission from the triplet, they suffer from a buildup of triplet excitons, especially if their rate of phosphorescent emission is low. This triplet exciton buildup in the emissive layer leads to significantly reduced device lifetime, which makes these emitters challenging to implement in a commercial device even if their efficiencies rival those of phosphorescent OLEDs.



Figure 1.10. Illustration of energy transfer processes in a hyperfluorescent OLED, using a TADF emitter as an assistant dopant to allow for conversion of triplet excitons to singlet excitons followed by transfer to a series of fluorescent dyes. FRET = Förster resonance energy transfer, TBPe = 2,5,8,11-Tetra-tert-butylperylene, TTPA = 9,10-Bis[N,N-di-(p-tolyl)-amino]anthracene, TBRb = 2,8-Di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene, DBP = 5,10,15,20-Tetraphenylbisbenz[5,6]indeno[1,2,3-cd:1',2',3'-Im]perylene.Reproduced with permission from Ref 137. Copyright 2014 Springer Nature.

Adachi and coworkers have also explored the use of multicomponent emissive layers in

which a TADF emitter is paired with a high quantum yield fluorescent emitter and a traditional 31

host matrix.¹³⁷ Systems using this architecture are typically referred to as TADF-sensitized emissive layers or hyperfluorescent emitters. Using a multicomponent system allows for the use of high efficiency TADF emitters to convert triplet excitons to singlet excitons, illustrated in Figure 1.10. These singlet excitons are then funneled to a high-stability fluorescent emitter that also typically has improved color purity compared to the broad charge transfer emission exhibited by the TADF emitter. Using this series of emitters allows for the use of a high-efficiency fluorescent emitter paired with a TADF emitter that would otherwise decompose rapidly in an electroluminescent device. This seems to be the most efficient way to commercialize TADF technology barring significant progress in the synthesis of TADF emitters with vastly improved stability and color purity.

1.6 Decomposition of Organic Semiconductors

When designing a high-efficiency emissive compound or semiconducting material, a key issue is the long-term stability of these materials. Whether to be used for bioimaging applications or for use in electroluminescent devices, the stability of the emitter is critical for commercial application to be realized. Current high-efficiency OLEDs are significantly limited by the stability of the emitters used, especially in the case of deep blue and deep red emitters. Deep blue emissive compounds are particularly prone to decomposition as they require high energy excitation to generate light and tend to accumulate high energy excitons during use, populating high energy excited states that may result bond breaking or emitter isomerization upon relaxation.¹³⁸



Figure 1.11. Phosphole oxide dyes explored by Yamaguchi and coworkers.^{141,142}

Several studies have shown that a potential route to improve the photostability of luminescent materials involves rigidification of the emitters, resulting in narrower emission spectra, higher quantum yields, and reduced rate of decomposition due to the suppression of vibrational motion in both the ground and excited states.^{139,140} Using this method, Yamaguchi and coworkers have prepared a series of ultrastable phosphole-based dyes for stimulated emission depletion (STED) imaging,^{141,142} two of which are illustrated in Figure 1.11. By rigidifying the core of these dyes with a simple carbon-based bridge (C-Bphox), they are able to achieve dramatic reduction in the rate of decay of fluorescent intensity due to photobleaching.



Figure 1.12. a) An unbridged triarylamine donor; b) planarized triarylamine donor using a bridging group between the *ortho*- positions of adjacent aryl rings; c) increased stability from the increased effective π -conjugation. Reproduced with permission from Ref 143. Copyright 2019 American Chemical Society.

The increased stability via rigidification is attributed to the stabilization of the weakest intermolecular bonds in the respective dyes. In many donor-acceptor systems in which a triarylamine donor is employed, the weakest bond has been identified as the highly twisted C-N sp² bonds between the amine center and the pendant aryl groups. The weak nature of these bonds is a particular issue when making emitters for OLEDs as the donor-acceptor dyes common to these systems typically take advantage of triarylamine donors that are rich in C-heteroatom bonds. By linking adjacent aryl groups using *ortho*-bridges, Bryce and coworkers managed to achieve stabilization of the C-N sp² bonds in a series of donor-acceptor dyes using a hexamethylazatriangulene (HMAT) core in place of an unbridged triarylamines.¹⁴⁴ This HMAT core is composed of three arylamines that are linked to the adjacent arylamines via an sp³ hybridized isopropenyl bridge (Figure 1.11). The alkyl linker planarizes the resulting donor, reducing torsion between adjacent aryl groups while also reducing the length of the C-N bonds, significantly improving their stability. We hoped to apply this C-N bond encapsulation method in other OLED emitters to achieve highly fluorescent dyes with significantly improved stability.

1.7 Goals of the Thesis

In order to study the electronic properties of semiconducting nanofibers, we sought to first develop high-fidelity methods of synthesizing BBCPs with a high degree of control over the photophysical and electronic properties of the appended side chains. By generating nanostructures with complex electronic properties, we hoped to use BBCPs as a substrate through which novel charge transfer processes can be directly observed. Using this template, we also sought to generate multiblock structures simulating the arrangement of semiconducting layers in a series of electronic devices, including simple diodes and organic light-emitting diodes. To achieve these highly

organized structures, a grafting-through method was a clear necessity as only this method gives direct access to both multiblock and core-shell bottlebrush copolymers. The first step in generating functional bottlebrush copolymers is to first develop a polymerization method to allow highyielding synthesis of macromonomers composed of semiconducting and highly fluorescent monomers.

The second chapter of this thesis, discusses efforts towards optimizing Cu(0)-RDRP for the synthesis of semiconducting p- and n- type polymers. I synthesized a series of four p-type monomers, and 3 n-type monomers on multigram scale. These monomers were then polymerized to generate polymers with molecular weights from 10 kDa to 50 kDa with dispersities as low as 1.12 and conversions from 92% to 99%. Furthermore, we demonstrated that end group functionality was maintained using this polymerization method, providing potential routes to end group functionalized polymers and multiblock polymers.

The third chapter of this thesis discusses work with highly fluorescent emissive monomers based on a triarylamine-oxadiazole donor-acceptor pair. Using this framework, a series of monomers and polymers were made with both fluorescent and thermally activated delayed fluorescence properties with emission over the visible spectrum. The utility of these polymers for electroluminescent applications was demonstrated using a deep blue fluorescent emitter. Furthermore, one of the TADF-active monomers was shown to have distinct dual emission properties, enabling ratiometric oxygen sensing in the solid state and when embedded in polymer nanoparticles.

The fourth chapter of this thesis discusses the synthesis of bottlebrush copolymers composed of semiconducting monomers. Macromonomers functionalized with p-type, n-type, host, and fluorescent emissive monomers were prepared. These monomers were then ordered into

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a series of nanostructures simulating multilayer semiconducting devices. These materials are characterized by AFM to demonstrate their fiber-like morphology and extended conformation in the solid state. The electrochemical and photophysical properties of these materials were also characterized. This work demonstrates that using a bottlebrush framework, it is possible to directly prepare ordered nanostructures with complexity rivalling what has been achieved using state-ofthe-art self-assembly methods.

The fifth chapter of this thesis discusses the synthesis of mixed bottlebrush copolymers that were synthesized to directly probe the effect of polymer morphology on charge transport phenomena. Using a set of donor and acceptor monomers that are known to emit via a throughspace charge transfer (TSCT) mechanism, a series of copolymers was prepared in which the degree of donor-acceptor blending was directly controlled via morphology of the bottlebrushes prepared.

The sixth chapter covers a series of donor-acceptor fluorescent compounds with structural modifications added to improve the stability of the emitters. Several compounds were prepared in which a stabilized HMAT donor was used in place of an unbridged donor. This donor was stabilized by the addition of three methylene bridges between the aryl rings that planarizes the amine, reducing strain along the C-N bonds. This planarization leads to significantly improved photostability as well as enhanced two-photon absorption properties when compared to the analogous unbridged compounds. Using this approach, a deep blue/violet emitter was developed with enhanced photostability and two-photon cross-section. Furthermore, proof-of-concept deep blue OLEDs were fabricated with this emitter to demonstrate the utility of these emitters in an electroluminescent device.

Chapter 2: Polymerization of Acrylic Organic Semiconductors by Cu(0)-RDRP

2.1 Motivation

In pursuit of a robust synthesis of organic semiconductor nanofibers via a bottlebrush polymerization, a high-yielding, well-controlled polymerization method is a necessity. As the BBCPs targeted required a high degree of control over composition along the side chains as well as along the backbone, a grafting-through method was selected. This method requires the synthesis of low molecular weight polymeric side chains, typically < 10kDa, with polymerizable groups appended to either terminus. Furthermore, the polymerization must be compatible with polyaromatic organic semiconductor monomers with limited solubility in many solvents. As the complex monomers used in these materials are costly to synthesize, the polymerization method selected must deliver end-group functionalized polymers without requiring quenching at low conversion to prevent monomer wastage. Here, the development of stable p- and n- type monomers on scales up to 50 g is described, followed by the optimization of controlled radical polymerization methods to generate linear polymers. We propose that via these methods, a novel series of electron and hole transporting polymers can be prepared with material properties similar to the small molecule materials off of which they are based.

The work described in this chapter has been published in two publications: Tonge, C. M., Sauvé, E. R., Paisley, N. R., Heyes, J. E. and Hudson, Z. M., *Polym. Chem.* **2018**, *9*, 3359-3367, and Sauvé, E. R., Tonge, C. M., Paisley, N. R., Cheng, S., and Hudson, Z. M., *Polym. Chem.* **2018**, *9*, 1397-1403.

2.2 Methods for the Synthesis of Polymeric Semiconductors

Research has focused on developing novel polymers with conducting properties since the report of the first polymers with significant conductivity in 1977.¹⁴⁵ There are many ways of making organic polymer semiconductors, including free radical polymerization,¹⁴⁶ transition metal mediated coupling,¹⁴⁷ and living methods.^{148–150} These methods each have their own benefits and drawbacks, balancing control over polymer characteristics, harsh reaction conditions, and low conversions. Free radical methods typically do not involve expensive catalysts or monomers, yet also typically do not provide a high degree of control over the dispersity of the polymers.^{151–153} This method is ideal for simple thin films and other applications that do not require low dispersity polymers with controlled morphology and end group functionality. Transition metal coupling methods are widely used to make polymers with conjugated backbones via polycondensation reactions, using Suzuki,^{154,155} Negishi,¹⁵⁶ Kumada,^{157–159} or other transition metal couplings.^{160–162} These methods are used to generate the most common conjugated polymers, including polythiophenes,¹⁶³ polyfluorenes,¹⁶⁴ and poly(*p*-phenylenes).¹⁶⁵ These polymers can be functionalized easily, but often require conditions or reagents that are incompatible with many potential monomers and end group functionalities. While organic semiconductors often require extensive conjugation through the polymer backbone, useful electronic properties can also be achieved with π -conjugated pendant side chains connected to a styrenic, (meth)acrylic, or norbornene-based all-carbon main chain.^{114,148,149,166} Previous work exploring the reversible deactivation radical polymerization (RDRP) of triarylamines has examined their polymerization $(ATRP)^{150}$ light-mediated transfer radical polymerization by atom reversible addition/fragmentation chain transfer polymerization (RAFT),^{167–171} ATRP,^{148,149} and free radical polymerization.¹⁴⁶ These side-chain functionalized polymers had several benefits over their
conjugated counterparts, including facile solvent processability, milder reaction conditions, and multiple methods to introduce chain-end functionality.

For our work, we required a controlled radical method with mild and general conditions which could be run to high conversion while maintaining low dispersity and end group fidelity. Furthermore, a method that generated polymers that were soluble in typical organic solvents would also simplify further post-polymerization modifications, and the subsequent synthesis of nanostructures. Cu(0)-RDRP emerged as an ideal solution as it provides a high degree of control over polymer properties, low cost, and high scalability. This method provides access to welldefined materials with low PDI while also minimizing waste of expensive monomer by maintaining these characteristics at high conversion. Cu(0)-RDRP polymerizations also proceed rapidly at room temperature in relatively dilute solution, making them significantly more amenable to complex monomers with potentially unstable functional groups. Furthermore, the crystalline semiconducting monomers were sparingly soluble in the polar solvents required for typical controlled radical polymerization methods, so methods allowing a higher degree of dilution were favorable. Moreover, this technique facilitates the synthesis of many materials in which the functionality of the polymer end group is retained at high conversion, making it a useful tool for the synthesis of block copolymers.^{172–175}

Side-chain functionalized non-conjugated polymers have been used in a variety of applications as organic semiconductors, using p-type, n-type, and emissive materials. Polymers bearing electron-rich triarylamine side chains, for example, have found widespread use as p-type materials in organic electronics, including OLEDs,^{150,176–178} solar cells,^{148,179–183} and organic thin-film transistors.¹⁸⁴ These materials offer flexible, lightweight alternatives to inorganic semiconductors which can be easily processed over large areas at low cost. Similarly, polymers

with pendant electron-poor heterocyclic moieties with electron transport properties have demonstrated favorable charge transport properties in organic light-emitting diodes (OLEDs),^{185,186} organic thin-film transistors (OTFTs),¹⁸⁷ and organic photovoltaics (OPVs).¹⁸¹ As these polymers have demonstrated advantageous bulk properties, a low-cost method to generate these polymers with a high degree of control is desirable. Furthermore, as the monomers used typically require multiple synthetic steps, a method that minimizes monomer waste is key. This frames Cu(0)-RDRP as an obvious candidate, however, investigations to date on Cu(0)-RDRP of optoelectronic materials have been limited. Recently, Gohy and coworkers demonstrated the utility Cu(0)-RDRP the synthesis of electroactive polymers of in based on 2,2,6,6tetramethylpiperidinyloxyl (TEMPO) radicals.¹⁸⁸ As this technique is very well-suited to the polymerization of many of the classes of π -conjugated organic semiconductors used in plastic electronics, we sought to implement it and optimize it in our particular monomer system.

2.3 Designing Semiconducting Monomers to Emulate OLED Materials



Figure 2.1 Example of commercial hole-transport (TPD), electron-transport (BTB), and host materials (CBP) and acrylate monomers derived via structural modification.

To generate a series of monomers with electronic properties similar to common small molecule organic semiconductors, inspiration was taken directly from the small molecules themselves. Often these molecules are composed of dimers of common electron donating groups (such as triarylamines) or electron withdrawing groups (such as triazines). These polyaromatic moieties are dimerized as the increased molecular weight serves to improve film quality due to their amorphous solid-state arrangement. We proposed generating a series of monomers by taking these dimeric small molecules and synthesizing small molecules that have a polymerizable handle attached, where the two halves of the molecules would otherwise be connected. Some examples

of this method are illustrated in Figure 2.1. Although these monomers will not likely be amenable to high quality film formation prior to polymerization, by attaching them to a long polymeric backbone, their film-forming properties should be vastly improved. Furthermore, the Tg values of the resulting semiconducting polymers should also be favorable, even when compared to the dimeric parent compounds. This is ideal as a high Tg value prevents morphological changes upon Joule heating during use in an electroluminescent device.¹⁸⁹ As these polymers will be densely packed, the π - π interactions between adjacent monomers along the backbone should be sufficient to ensure large-scale charge delocalization along the length of the polymer, hopefully improving charge transport properties. Furthermore, using these monomers, copolymers are easily accessible, potentially allowing for the synthesis of multicomponent emissive materials doped with small amounts of high-cost fluorophores for use as single-component emissive layers. By attaching a series of highly donating triarylamines to this benzyl acrylate framework, we hope to deliver several viable hole transport materials. Similarly, to target electron transport materials, a variety of aromatic heterocycles were appended to this benzyl acrylate framework, including triazine, oxadiazole, and phenylbenzimidazole moieties.

2.4 Optimization of Polymerization of P-type monomers



2.4.1 Monomer Synthesis



To generate a series of p-type polymer semiconductors via Cu(0)-RDRP, four triarylaminefunctionalized benzyl acrylate monomers were synthesized. Triarylamine donors are among the cheapest and highest-performing organic hole transport materials, used in the hole transport layer of OLEDs^{190,191} and as the donor material in organic photovoltaic devices and TFTs.¹⁸⁴ Furthermore, carbazole-based arylamines have also shown utility as hole-transport or host materials in OLEDs.^{191,192} These monomers were designed using common small molecule donors and hosts (such as CBP) as templates, desymmetrizing along the central C-C bond, then appending a benzyl acrylate functionality. Benzyl acrylate was chosen as the polymerizable handle as it separates the donor moiety completely from the polymer backbone, preventing unwanted electronic communication and limiting charge transport to through-space π - π interactions.

These monomers were synthesized via a four-step procedure (illustrated in Figure 2.2) that begins with a simple *N*-arylation method, using a Goldberg reaction from the diarylamine starting

material (2.1a-2.3a) to give the parent triarylamines (2.1b-2.3b). This triarylamine was then functionalized via a Vilsmeier-Haack formylation using POCl₃ and DMF to selectively monoformylate the triarylamines to give 2.1c-2.3c. 4-(9H-carbazol-9-yl)benzaldehyde (2.4c) was synthesized via an alternate, high yielding procedure via a nucleophilic aromatic substitution using carbazole and 4-fluorobenzaldehyde. From the donor-functionalized benzaldehydes (2.1c-2.4c), the corresponding benzyl alcohols (2.1d-2.4d) were delivered in high yield via a reduction with sodium borohydride, followed by a simple acrylation in dichloromethane using acryloyl chloride to deliver the targeted monomers NpHTL, tBuHTL, tolHTL, and CzBA. These monomers were purified by chromatography to yield high-purity monomers on scales greater than 50 grams. The addition of *p*-alkyl moieties to the donor monomers (tBuHTL and tolHTL) significantly improves the stability of the monomers during acrylation, purification, and later storage when compared to the highly donating naphthyl-functionalized monomer **NpHTL**. The phenylcarbazole monomer (CzBA) was found to be highly crystalline, facilitating the preparation of very high-purity monomer on large scales by recrystallization from hexanes and dichloromethane. Overall yields for the monomers prepared were relatively high over several steps, 49% for NpHTL, 66% for tBuHTL, 34% for tolHTL, and 69% for CzBA.

2.4.2 Polymer Synthesis and Kinetics



Figure 2.3. Scheme of typical Cu(0)-RDRP of p-type acrylate monomers.

Once large quantities of donor and host monomers were prepared in high purity, the next step towards delivering polymeric organic hole transport materials was the optimization of the polymerization conditions. Typically, Cu(0)-RDRP proceeds most efficiently in highly polar solvents⁹⁴ such as DMF, DMSO, isopropanol, or even water,¹⁹³ as these solvents facilitate the disproportionation of Cu(I) to Cu(0) and Cu(II). These solvents, however, are not amenable to solubilizing these highly aromatic systems, especially upon polymerization, leading us to work with less polar solvents with solubilizing methyl groups such as *N*-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc). The polymerizations were tested at a variety of concentrations, but approximately 200 mg mL⁻¹ was found to give a relatively high polymerization rate while maintaining full solubility of both monomer and polymer throughout the reaction. The polymerizations (were performed in a nitrogen atmosphere glovebox using dry, degassed solvent (Figure 2.3). Monomer, initiator (ethyl bromoisobutyrate, EBiB), CuBr₂, and tris[2-(dimethylamino)ethyl]amine (Me₆TREN) were combined in the glovebox along with the solvent of choice. The polymerization was then initiated via the addition of copper wire that had been freshly treated with hydrochloric acid and washed prior to introducing it to the glovebox. The molecular weight of the polymers generated was controlled by varying the ratio of initiator to monomer, while keeping the ratio of initiator to CuBr₂ and Me₆TREN constant.

Entry ^a	$k_p (10^{-5} \text{ s}^{-1})$	t (h)	$M_{n, SEC}^{c}$	$M_{n, \text{ theory}}$	Đ	$\frac{\text{Conv.}^d}{(\%)^d}$
NpHTL _{10k} ^a	1.14	70	10800	9900	1.23	99
NpHTL _{10k} ^b	5.6	18	10100	9700	1.43	97
tBuHTL _{10k} ^a	3.78	26	9500	9400	1.13	94
tBuHTL _{10k} ^b	8.42	9	10900	9300	1.14	93
tolHTL _{10k} ^a	8.56	26	9400	9000	1.28	90
$\mathbf{tolHTL}_{10k}^{b}$	15.5	6	9900	9700	1.15	97
\mathbf{CzBA}_{10k}^{a}	6.93	26	9800	9700	1.12	97
\mathbf{CzBA}_{10k}^{b}	14.7	8	10100	9600	1.11	96

Table 2.1. Synthesis of p-type semiconducting polymers via Cu(0)-RDRP

^{*a*} Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **NMP** = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (**NpHTL**: M = 26, **tBuHTL**: M = 23, **tolHTL**: M = 28, **CzBA**: M = 30).

^{*b*} Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **DMAc** = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (**NpHTL**: M = 26, **tBuHTL**: M = 23, **tolHTL**: M = 28, **CzBA**: M = 30).

^c Determined by triple-detection SEC in THF.

^{*d*} Determined by ¹H NMR in CDCl₃.

To explore the scope of this polymerization method as well as the importance of the solvent selected, a series of experiments were conducted where polymer kinetics were compared. First, we sought to improve the polymerization kinetics as the reaction reached high conversion. In NMP, all monomers show linear first-order behaviour up to ~85% conversion with propagation rates (k_p) between 1.14×10^{-6} and 8.56×10^{-5} s⁻¹ when targeting polymers of 10 kDa (

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Table 2.1). Beyond 85% conversion, the linear first order behavior fell off somewhat (Figure 2.4), implying that the concentration of active species was not constant as the reaction reached conversion. Literature precedent implied that this loss of linearity is likely a result of loss of chainend livingness at higher conversions.^{194,195} Furthermore, it should be noted that an induction period was observed for the polymerization of **NpHTL**, the napthyl-functionalized monomer, however, we attributed this induction period to difficulties in isolating high-purity monomer due to its propensity to decompose at room temperature. These stability issues were ameliorated by the addition of alkyl moieties to the nucleophilic *para*-positions (in monomers **tBuHTL** and **tolHTL**) or the use of a significantly less donating arylamine (in monomer **CzBA**).



Figure 2.4. Comparison of the polymerization kinetics of NpHTL_{10k} (a), tBuHTL_{10k} (b), tolHTL_{10k} (c), and CzBA_{10k} (d) in NMP and DMAc by Cu(0)-RDRP: ln([M0]/[M]) vs. time plot.

When these polymerizations were performed in DMAc instead of NMP, improved polymerization kinetics were observed. These polymerizations were shown to follow first order linear polymerization kinetics up to 93-97% conversion with more rapid propagation rates (k_p) between 5.6×10^{-5} and 14.7×10^{-5} s⁻¹ when targeting polymers with molecular weights of 10 kDa. Moreover, polymerization in DMAc seemed to significantly reduce the induction period observed in the polymerization of **NpHTL**.



Figure 2.5. Molecular weight distribution plots of NpHTL_{10k} and NpHTL_{50k} (a), tBuHTL_{10k} and tBuHTL_{50k}(b), tolHTL_{10k} and tolHTL_{50k} (c), CzBA_{10k} and CzBA_{50k} (d). (e) Molecular weight distribution plots of CzBA_{50k} polymerized in DMAc (black) and NMP (red) demonstrating broadened dispersity and inability to reach targeted 50 kDa molecular weight (43.0 kDa and 1.22 PDI in DMAc, 15.7 kDa and 1.77 PDI in NMP).

The ratio of monomer to initiator was increased to test the suitability of this method to the synthesis of larger polymers with target M_n values of 50,000 Da. While the polymerizations of **NpHTL**, **tolHTL**, and **CzBA** all proceeded to high conversion (84-99%), the polymerization of **tBuHTL** reached a maximum conversion of only 63% even with the use of four times the solvent and four times the Cu(0) wire to solubilize the growing polymer and increase the amount of active catalyst in solution. This lower final conversion was attributed to the low solubility of the polymer in the reaction medium due to the more hydrophobic structure of this monomer. These high molecular weight polymers also showed broadening in polydispersity (Table 2.2), increasing from 1.11-1.43 for the 10 kDa polymers to 1.34-1.87 for the high molecular weight tests. Furthermore, when dimethylacetamide (DMAc) was used as a polymerization solvent for a polymerization of

CzBA targeting 50 kDa, significantly higher conversion (89% in DMAc compared to 31% in NMP) and narrower polydispersity (D = 1.22 in DMAc compared to 1.77 in NMP) were observed (Figure 2.5). These polymerizations demonstrated that this Cu(0)-RDRP method is applicable to the synthesis of high molecular weight polymers using a variety of p-type semiconducting acrylate monomers, and that the use of DMAc as a reaction solvent served to improve livingness of the polymerization as well as the quality of the polymers produced.

Table 2.2 Synthesis of high molecular weight donor-type polymers by Cu(0)-RDRP

Entry	$k_p (10^{-5} \text{ s}^{-1})$	t (h)	$M_{n, SEC}^{c}$	$M_{n, \text{ theory}}$	Đ	Conv. (%) ^{d}
NpHTL _{50k} ^a	0.53	96	43200	42200	1.87	84
tBuHTL _{50k} ^b	1.14	24	29800	31400	1.44	63
tolHTL _{50k} ^a	1.99	30	43300	43800	1.34	88
$CzBA_{50k}^{a}$	1.22	48	43000	44400	1.34	89

^{*a*} Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **DMAc** = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (**NpHTL**: M = 132, **tolHTL**: M = 140, **CzBA**: M = 152).

^b Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **DMAc** = 4.6 mL; 18 gauge Cu(0) wire = 4.6 cm (**tBuHTL**: M = 23).

^{*c*} Determined by triple-detection SEC in THF.

^{*d*} Determined by ¹H NMR in CDCl₃.



Figure 2.6. GPC chromatogram of diblock copolymer PMA_{10k}-CzBA_{10k} (red) and the PMA_{10k} (black) polymer from which this diblock was grown. Chemical structure of the polymer generated shown on the right.

In order to demonstrate the utility of this method for the synthesis of block copolymers, a

diblock copolymer of CzBA and methyl acrylate was prepared. Using our optimized conditions, a

10 kDa methyl acrylate polymer was first grown from an EBiB initiator (MA:EBiB:CuBr₂:Me₆TREN = 100:1:0.065:0.068) giving a polymer with PDI = 1.03. This polymerization was allowed to run for 8 hours, reaching 90% conversion by NMR, at which point a second monomer was added to the reaction mixture, **CzBA**, along with additional CuBr₂/Me₆TREN catalyst and Cu(0) wire. The resulting block copolymer, shown in Figure 2.6, demonstrated a monomodal distribution and a low PDI of 1.11. This demonstrates that chain extension of the methyl acrylate block occurred upon addition of **CzBA** without quantifiable chain-termination events. This indicates that this optimized Cu(0)-RDRP method should be amenable to the preparation of multiblock acrylate polymers that could find use in a variety of applications, including the synthesis of core-shell bottlebrush copolymers or the generation of luminescent polymer dots.¹⁹⁶

2.4.3 Electronic Properties

		HOMO (eV)		LUMO (eV)	
Entry	E ^{ox} _{1/2} ^a	Calc.	Exp. ^b	Calc.	Exp. ^c
NpHTL _{10k}	0.412	-5.15	-5.21	-1.57	-1.10
tBuHTL _{10k}	0.419	-5.21	-5.21	-0.86	-0.99
tolHTL _{10k}	0.417	-5.21	-5.22	-0.89	-1.13
CzBA _{10k}	0.535	-5.66	-5.34	-1.09	-1.11

Table 2.3. Simulated and experimental electronic properties of polymers 1_{10k}-4_{10k}.

^{*a*} In CH₂Cl₂ relative to FeCp₂^{0/+}.

^b Calculated from $E_{1/2}^{ox}$ relative to the FeCp2^{0/+} HOMO level (4.80 eV).

^c Calculated from the HOMO level and the optical energy gap, E_g . E_g was determined from the low-energy UV- vis absorption band edge.

All four polymers, **NpHTL**_{10k}, **tBuHTL**_{10k}, **tolHTL**_{10k}, and **CzBA**_{10k}, showed reversible one-electron oxidations by cyclic voltammetry, detailed in Table 2.3 and illustrated in Figure 2.7. These measurements were performed in dichloromethane using tetrabutylammonium

hexafluorophosphate as an electrolyte. The strongest donor polymer, **NpHTL**_{10k}, demonstrated a reversible oxidation at 0.41 V relative to $FeCp_2^{0/+}$, corresponding to HOMO level of -5.21 eV with the rest of the polymers demonstrating slightly lower highest occupied molecular orbital (HOMO) levels. The carbazole-based donor demonstrated two reversible oxidation waves in dichloromethane as well as the lowest HOMO level of approximately -5.34 eV.



Figure 2.7. Cyclic voltammograms of polymers NpHTL_{10k}, tBuHTL_{10k}, tolHTL_{10k}, and CzBA_{10k}, relative to $FeCp_2^{0/+}$, recorded at a rate of 50 mV s⁻¹ in CH₂Cl₂ containing 2 mg mL⁻¹ of analyte and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

Reduction waves were not observed via cyclic voltammetry, however, the lowest occupied

molecular orbital (LUMO) levels were estimated using the measured HOMO values and the optical

energy bandgap that was determined from the low-energy UV absorption band-edge.



Figure 2.8. Calculated HOMO and LUMO values and for the *sec*-butyl analogues of monomers NpHTL (a), tBuHTL (b), tolHTL (c), and CzBA (d).

The trends in the electrochemical behaviour were confirmed via density functional theory calculations at the B3LYP/6-31+g(d) level of theory. These calculations were performed on individual monomers in which the polymerizable acrylate functionality was substituted for a *sec*-butyl analogue to more accurately simulate the electronic properties of these monomers once they are attached to a saturated polyacrylate backbone. These calculations predicted HOMO levels between -5.15 eV and -5.66 eV with significant electron density on the nitrogen atom of the HOMO (Figure 2.8) in all cases, as would be expected in a p-type organic semiconductor. The combination of the experimental electrochemical characterization and the calculations performed imply that these materials should be useful as hole transport materials as they should be able to reversible oxidize and stabilize a positive hole on the electron-rich triarylamine moiety present in each monomer in this series

2.4.4 Photophysical Properties



Figure 2.9. Normalized absorbance (solid) and photoluminescence (PL, dashed) spectra of polymers NpHTL_{10k} (a), tBuHTL_{10k} (b), tolHTL_{10k} (c), CzBA_{10k} (d) measured at 0.01 mg mL⁻¹ in CH₂Cl₂.

The photophysical properties of polymers NpHTL_{10k}, tBuHTL_{10k}, tolHTL_{10k}, and CzBA_{10k} were also characterized (Figure 2.9). These polymers all showed strong absorption in the UV region as expected for triarylamine-functionalized polymers, with absorption maxima ranging from 293 nm (CzBA_{10k}) to 303 nm (tolHTL_{10k}). Polymers NpHTL_{10k} and CzBA_{10k} were found to have fluorescent emission in the blue ($\lambda_{max} = 431$ nm) and ultraviolet ($\lambda_{max} = 347$ nm) in dichloromethane with relatively high quantum yields of 0.29 and 0.20 respectively, while tBuHTL_{10k} and tolHTL_{10k} demonstrated much lower quantum yields of 0.02 and <0.01 respectively. The dimmer triarylamine polymers, tBuHTL_{10k} and tolHTL_{10k}, both demonstrated interesting emission behavior when measured in dichloromethane, resulting in broad emission peaks with maxima centered at 543 and 548 nm respectively. The low quantum yields recorded

for these polymers in dichloromethane coupled with minor structured emission bands observed at 345 and 367 nm respectively imply that the red-shifted emission is likely the result of excimer formation along the polymer backbone. The structured emission bands observed in these two polymers closely resemble those found in the emission spectrum of $CzBA_{10k}$. The lower-energy blue emission observed for NpHTL_{10k} is likely due to the addition of lower-bandgap naphthyl substituent resulting in this polymer behaving more like a conventional blue emitter with π - π * character.





Figure 2.10. TGA of polymer NpHTL_{10k} (a, 1.25 mg), tBuHTL_{10k} (b, 2.76 mg), tolHTL_{10k} (c, 12.06 mg), CzBA_{10k} (d, 4.01 mg), run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen from 25 to 800 °C and DSC traces of polymers NpHTL_{10k} (e), tBuHTL_{10k} (f), tolHTL_{10k} (g), and CzBA_{10k} (h), run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen. Three consecutive heating and cooling cycles were performed, the second (h) or third (e, f, g) is shown.

Lastly, the thermal properties of these p-type polymers were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), the results of which are shown in Figure 2.10. All polymers were shown to be somewhat stable up to approximately 200 °C, however there were some differences between the four polymers analyzed. Polymer NpHTL_{10k} was the least thermally stable of the four, showing a two-step decomposition process, a first step from 200 to 490 °C involving a mass loss of 34 % and a second step from 490

to 800 °C with a further mass loss of 35%, leaving the remaining 31% as char yield. When characterized by DSC, this polymer demonstrated a Tg of approximately 109 °C, an acceptable value for use in an OLED. Polymer $tBuHTL_{10k}$ was found to be the most stable of the series, remaining stable up to 287 °C at which point 92% of the mass was lost in a single step resulting in an 8% char yield. DSC measurements on these two polymers demonstrated a relatively high T_g of 109 °C, high enough to avoid any potential issues due to Joule heating in a device. TGA showed that polymer tolHTL_{10k} was also stable to high temperature (259 °C), decomposing in a two-step process in which 19% mass loss was recorded from 260 to 360 °C and 68% mass loss was recorded from 360 to 800 °C to give a char yield of 13%. DSC measurements for this polymer demonstrated a somewhat lower T_g of 71 °C, likely high enough for most applications but notably lower than the previous two polymers. Lastly, polymer CzBA_{10k} was characterized by TGA and DSC, demonstrating thermal stability up to 256 °C followed by a two-step degradation process, losing 35% of its mass from 255 to 500 °C and a further 25% mass loss from 500 to 800 °C to give an overall char yield of 40%. DSC measurements also revealed a relatively low Tg value of 76 °C. The T_g values for NpHTL_{10k} and tBuHTL_{10k} were high enough that there would likely not be any issues with changes in film quality during normal device operation, however polymers tolHTL_{10k} and CzBA10k had low enough Tg values that there could potentially be some issues in highertemperature use cases.

2.5 Optimization of Polymerization of N-type Monomers

2.5.1 Monomer Design and Synthesis



Figure 2.11. Small molecule inspiration for n-type semiconducting acrylate monomers TRZ, ODA, and PBI.

Alongside the development of p-type semiconducting polymers, we also sought to develop a series of n-type monomers that could be used as electron transport materials in OLEDs. The design for these n-type monomers followed a similar thought process to that used in the design of the p-type monomers discussed above. The three n-type monomers targeted in this work draw direct inspiration from currently commercialized electron transport layer materials: 2,2',2"-(1,3,5benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI)¹⁹⁷, 4,4'-Bis(4,6-diphenyl-1,3,5-triazin-2yl)biphenyl (BTB),¹⁹⁸ and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD),¹⁹⁹ shown in Figure 2.11. Unlike p-type semiconductors, a large range of electron deficient heterocycles have found applications as n-type semiconducting materials rather than the arylamine structures typical to the p-type monomers explored previously. As a result, three structurally diverse acceptor monomers were explored, taking advantage of different aromatic heterocycle cores to achieve the electron deficiency that is required in an electron transport material. These differing monomer structures resulted in variations in polymerization kinetics and the resulting polymer properties due to potential undesired interactions between the monomer and the catalyst.



Figure 2.12. Synthetic route to n-type organic semiconductor monomers TRZ, ODA, and PBI.

Due to the structural diversity of the acceptor monomers targeted, a unique synthetic route was developed for each TRZ, ODA, and PBI (Figure 2.11). The triphenyltriazine core of **TRZ** can

be prepared using a variety of methods, however to add an asymmetric benzyl acrylate functionality, relatively harsh chemistry was required. Using two equivalents of *p*-tolunitrile and an equivalent of *p*-bromobenzoyl chloride, an asymmetric ditolylbromotriazine (**2.5a**) was delivered by a two-step procedure that begins by cyclizing these starting materials using SbCl₅. This cyclization yields an oxadiazinium intermediate that is converted in high yield to triazine **2.5a** upon treatment with aqueous ammonia. The resulting triazine bromide is then modified via a Suzuki coupling using 4-formylphenylboronic acid to give **2.5b** in good yield. The resulting triazine-functionalized benzaldehyde is then converted to the corresponding benzyl acrylate via a quantitative reduction to the benzyl alcohol (**2.5c**) using sodium borohydride followed by a mild acrylation procedure using acryloyl chloride in the presence of triethylamine. The monomer (**TRZ**) was isolated as a white solid with an overall yield of 68% over four steps.

The oxadiazole-based monomer, **ODA**, was produced from relatively simple starting materials on very large scale (>100 g) via a four-step synthesis detailed in Figure 2.11. The key step in this synthesis is the cyclization of hydrazide **2.6b** with 4-(hydroxymethyl)benzoic acid in the presence of 2-chloro-1,3-dimethylimidazolinium chloride. This reaction proceeds in high yield if moisture is rigorously excluded by using freshly distilled solvent and triethylamine and by transferring solid reagents in a nitrogen atmosphere glovebox.²⁰⁰ The resulting benzyl alcohol (**2.6c**) is converted to **ODA** via a mild acrylation procedure with an overall yield of 59%.

The third n-type acrylate monomer, **PBI**, is based on a benzimidazole acceptor. This monomer is prepared using commercially available 2-phenylbenzimidazole that is functionalized using a nucleophilic aromatic substitution with 4-fluorobenzaldehyde. This procedure is easily scalable and proceeds with high yields even when wet and nondegassed solvents are used. This

procedure is particularly advantageous as it does not require the use of a transition metal catalyst and it delivers the benzaldehyde-functionalized benzimidazole **2.7a** in a single high-yielding step. This benzaldehyde is then converted to the corresponding benzyl alcohol, **2.7b**, via a high-yielding sodium borohydride reduction followed by an acrylate to yield monomer **PBI** in 61% overall yield.

2.6 Polymer Synthesis

As was the case for the p-type monomers discussed in Section 2.4, solvent selection for the Cu(0)-RDRP polymerization was of critical importance. The n-type monomers prepared in this section suffered significantly lower solubility in both polar and non-polar solvents, leading to significant difficulty finding a suitable system in which monomer and polymer solubility was maintained without compromising catalyst activity. Similar to the p-type monomers, DMAc and NMP were found to provide the best balance of solubility and catalyst activity, albeit with lower concentrations required to fully solubilize some of the n-type monomers explored.

Entry ^a	$k_p (10^{-5} \text{ s}^{-1})$	t (h)	$M_{n, SEC}^{c}$	<i>Mn</i> , theory	Ð	Conv. (%) ^d
TRZ _{10k} ^a	3.30	26	9600	9200	1.30	92
TRZ10k ^b	1.26	72	12200	9700	1.26	97
$\mathbf{ODA_{10k}}^a$	10.5	26	9800	9700	1.25	97
ODA_{10k}^b	9.47	18	12800	9400	1.14	94
PBI_{10k} ^a	5.49	40	13200	9300	1.39	93
PBI _{10k} ^b	10.5	12	23900	9200	1.39	92

Table 2.4. Synthesis of n-type semiconducting polymers via Cu(0)-RDRP.

^{*a*} Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **NMP** = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (5: M = 20, 6: M = 27, 7: M = 28).

^b Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068; **DMAc** = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (**5**: M = 26, **6**: M = 23, 7: M = 28).

^c Determined by triple-detection SEC in THF.

^d Determined by ¹H NMR in CDCl₃.

The initial polymerization tests using NMP provided promising results for these n-type

polymers. Similar to the Cu(0)-RDRP polymerizations of the p-type monomers in the first part of 59

this chapter, the polymerizations were performed in a nitrogen atmosphere glovebox using [EBiB]:[CuBr₂]:[Me₆TREN] in 1 : 0.065 : 0.068 molar ratios, an appropriate amount of monomer to give polymers with number-average molecular weights of 10 kDa at full conversion, and a freshly cleaned piece of 18 gauge Cu(0) wire that is used to initiate the polymerization. As summarized in Table 2.4, polymerization of monomers **TRZ** and **ODA** delivered polymers with relatively narrow PDIs of 1.25 and 1.30 at 92% and 97% conversion respectively. These polymerizations proceeded with rate constants k_p of 3.31 31 × 10⁻⁵ s⁻¹ and 1.05 × 10⁻⁴ s⁻¹ respectively, although **ODA** exhibited a short induction period prior to the beginning of the polymerization. These polymerizations showed deviation from the expected kinetics at higher conversions as the semilogarithmic plot of $\ln([M_0]/[M])$ no longer exhibits the same linear behaviour when plotted against time (Figure 2.13). This suggests that at higher conversions, the concentration of active species is no longer constant, implying that the reaction conditions are unable to support a controlled polymerization at higher conversions.^{194,195}



Figure 2.13. Kinetic data for the Cu(0)-RDRP of TRZ_{10k} (a, b), ODA_{10k} (c, d), and PBI_{10k} (e, f): in NMP (top) and DMAc (bottom).

The polymerization of **PBI**, however, deviated significantly from the kinetics previously observed for the other monomers. This monomer exhibited an extended induction period followed by first-order polymerization similar to those observed for other p- and n-type monomers. The resulting polymers also displayed significantly broadened polydispersities, increasing to 1.39 compared to 1.14 for **ODA**_{10k} and 1.30 for **TRZ**_{10k}. It was hypothesized that the induction period observed followed by the rapid polymer growth could be attributed to interaction between the benzimidazole nitrogen and the Cu(I) and Cu(II) species in the reaction mixture due to the propensity for copper to form complexes with benzimidazole ligands.^{201–204} This would result in competition between the desired Me₆TREN ligand and the significantly higher concentration of benzimidazole monomer in solution.



Figure 2.14. Molecular weight distribution plots of TRZ_{10k} (a), ODA_{10k} (b), PBI_{10k} (c) synthesized in NMP (black) and DMAc (red).

Based on the improvements in polymerization kinetics observed using DMAc as a solvent for our other benzyl acrylate monomers, this solvent was also evaluated for these n-type monomers. It was found, however, that by switching from NMP to DMAc, the rate of polymerization was essentially unchanged for monomer ODA but was retarded somewhat for monomers **TRZ** and **PBI**. This slowed rate of polymerization of **TRZ** was attributed to the poor solubility of the triazine monomer and polymer in DMAc that resulted in a cloudy appearance for the duration of the reaction, even though near-quantitative conversion was reached after 72 hours (97%). The slowed polymerization rate of monomer **PBI** was likely due to similar solubility issues as well as altered interaction between monomer and the copper catalyst with differing solvent polarity. Furthermore, significant induction periods were observed for the polymerization of monomers **ODA** and **PBI**, persisting even after multiple recrystallizations, implying that impurities were likely not the cause. These induction periods were attributed to the presence of σ donating nitrogen atoms that are capable of coordinating to the Cu species present in the reaction, interfering with the initial portion of the polymerization until more copper becomes available from the Cu(0) wire. The lack of induction period with monomer **TRZ** is likely due to the large steric bulk of the aryl groups on the triazine preventing the copper from complexing with this monomer easily. Interestingly, although polymerization rates were only affected slightly by using DMAc

instead of NMP, the molecular weight distributions of the polymers generated in DMAc were significantly narrower than those prepared in NMP in all cases, as shown in Figure 2.14, with significant improvements noted in the case of monomer **PBI**.

Entry ^a	$k_p (10^{-5} \text{ s}^{-1})$	t (h)	$M_{n, SEC}^{b}$	$M_{n, \text{ theory}}$	Đ	Conv. (%) ^{<i>c</i>}
\mathbf{TRZ}_{50k}^{a}	0.26	64.5	39900	26500	1.30	53
\mathbf{ODA}_{50k}^{a}	1.19	48	54600	43400	1.26	87
PBI 50k ^a	0.39	64.5	42200	31000	1.25	62

 Table 2.5. Synthesis of high molecular weight n-type polymers by Cu(0)-RDRP.

^{*a*} Reaction conditions: Monomer/EBiB/CuBr₂/Me₆TREN = M/1/0.065/0.068.

DMAc = 1.15 mL; 18 gauge Cu(0) wire = 1.15 cm (1: M = 132, 2: M = 140, 3: M = 28).

^b Determined by triple-detection SEC in THF.

^{*c*} Determined by ¹H NMR in CDCl₃.

Given these results, further experiments were performed to determine whether Cu(0)-RDRP could be used to generate larger n-type acrylate polymers without an increase in dispersity. By modifying the ratio of monomer to EBiB initiator, significantly larger polymers were prepared, albeit these polymerizations were not able to reach the high conversions observed with the p-type monomers (Table 2.5). Polymers **TRZ**_{50k} and **PBI**_{50k} reached only 53% and 62% conversion at 64.5 hours and did not proceed further, even with significantly extended reaction times up to 120 hours. The high molecular weight polymer of monomer **ODA**, **ODA**_{50k}, reached a somewhat higher conversion of 87% after 48 hours. It should be noted that significant broadening of the polydispersity was observed (1.51 to 1.92), likely due to monomer interacting with the copper catalyst, acting as excess ligand and leading to premature chain death early in the polymerization.



Figure 2.15. Solid-state structure of CuBr₂(PBI)₂, depicted with 50% thermal ellipsoids. A disordered benzene molecule and the minor disordered ester fragment were removed for clarity. Selected bond lengths: Br1- Cu1 2.4353(5), N1-Cu1 1.965(3).

In an attempt to elucidate the mechanism for the induction period and broadened polymer dispersities observed with these n-type monomers, we attempted to prepare and isolate copper complexes of these monomers. When 0.5 equiv of CuBr₂ was added to a sample of monomer **PBI** in NMP, a dark brown solution was observed. When the solution was diluted with benzene and layered with hexane, crystals of the resulting copper (II) complex were easily obtained. These crystals were paramagnetic and therefore not characterizable via NMR spectroscopy, however, they were suitable for X-ray crystallography. The crystal structures show a clear copper complex in which a single CuBr₂ center is surrounded by two benzimidazole ligands with Cu-N bond lengths of 1.965 Å in the P21/c space group (Figure 2.15). This behaviour was expected as phenylbenzimidazoles have been shown to form complexes with a variety of metals including Fe(III), Cu(I), and Cu(II).^{201,205} While stable complexes of **TRZ** and **ODA** were not easily prepared, it is likely that the interaction between the σ -donating nitrogen atoms on these n-type monomers are leading to significant complications in the polymerization leading to the induction periods and larger dispersities observed.

Entry	HOMO _{Calc} ^a (eV)	LUMO _{Calc} ^a (eV)	$\Delta \mathrm{E}_{\mathrm{g, Calc}}^{a}$	$\Delta E_{g, Exp}^{b}$
TRZ _{10k}	-6.38	-2.15	4.23	4.23
ODA _{10k}	-6.30	-1.92	4.38	4.32
PBI10k	-6.03	-1.43	4.60	4.23

Table 2.6. Simulated and experimental electronic properties of polymers TRZ10k, ODA10k, and PBI10k.

^{*a*} Calculated via density functional theory calculations at the B3LYP/6-31+g(d) level of theory ^{*b*} E_g was determined from $\lambda_{max, abs}$ from the UV-vis absorption spectrum.

To confirm the utility of these n-type acrylate monomers as electron transport materials, the electronic properties were characterized via cyclic voltammetry and simulated using density functional theory (DFT) at the B3LYP/6-31G+(d) level of theory (Table 2.6). The cyclic voltammetry data did not yield useful results as the polymers were sparingly soluble in any solvents suitable to measure the reversible reduction of these heterocycle-functionalized monomers and no response was recorded upon oxidation of these three polymers.



Figure 2.16. Calculated HOMO and LUMO for the sec-butyl analog of TRZ (a), ODA (b), and PBI (c).

Instead, DFT was used to simulate the expected HOMO and LUMO energy levels of polymers **TRZ**_{10k}, **ODA**_{10k}, and **PBI**_{10k} by performing these calculations on the *sec*-butyl analogs of the corresponding monomers (Figure 2.16). DFT predicted LUMO levels of -2.15, -1.92, and -65

1.43 eV respectively. In all cases, the HOMO–LUMO transition was determined to be largely π – π^* in character, accounting for the strong absorption bands seen for all three materials. Polymer **PBI**_{10k} showed the most charge-transfer character by DFT, likely due to the highly electron-deficient triazine heterocycle and its large orbital contribution to the LUMO, accounting for the comparatively large Stokes shift observed in this material.



Figure 2.17. Thermogravimetric analysis of polymer TRZ_{10k} (a, 7.79 mg), ODA_{10k} (b, 4.20 mg), and PBI_{10k} (c, 2.55 mg), run at 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen from 25 to 800 °C and DSC traces of polymers TRZ_{10k} (d), ODA_{10k} (e), and PBI_{10k} (f), run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen. Three consecutive heating and cooling cycles were performed, the second is shown above.

The thermal properties of polymer TRZ_{10k} , ODA_{10k} , and PBI_{10k} were also evaluated by thermogravimetric analysis and differential scanning calorimetry, shown in Figure 2.17. Polymer TRZ_{10k} was found to be the most stable, only demonstrating degradation beginning at 320 °C after which the polymer rapidly decomposed in one step resulting in a mass loss of 83% and an overall char yield of 17%. Furthermore, the T_g recorded for this polymer was found to be 109.7 °C, sufficiently high to preclude issues when used in an electrically driven device. Polymer **ODA**_{10k} was found to be the least stable of the n-type polymers, demonstrating thermal stability up to 277 °C at which point rapid degradation proceeded resulting in a mass loss of 91% to give a char yield of 9%. This polymer also had the least favorable glass transition temperature, T_g , of 85.1 °C. This T_g is low enough to potentially result in loss of film integrity upon Joule heating. The last polymer, **PBI**_{10k}, demonstrated thermal stability and T_g values in between the other two n-type polymers. Polymer **PBI**_{10k} exhibited thermal stability up to 286 °C at which point rapid degradation resulted in a mass loss of 91% to give a char yield of 9%. DSC revealed a T_g of 103.8 °C, high enough to likely preclude any negative interactions upon Joule heating.



Figure 2.18. Normalized absorbance (solid) and photoluminescence (PL, dashed) spectra of polymers TRZ_{10k} (a) (5.6 x 10⁻⁷ M), ODA_{10k} (b) (3.3 x 10⁻⁷ M), and PBI_{10k} (c) (2.7 x 10⁻⁷ M) in CH₂Cl₂.

The absorption and emission properties of these three n-type polymers were also characterized, showing strong absorption in the UV region with minimal absorption in the visible range (Figure 2.18). Polymers TRZ_{10k} , ODA_{10k} , and PBI_{10k} demonstrated absorption maxima of 293 nm, 287 nm, and 293 nm respectively. Polymers ODA_{10k} and PBI_{10k} are highly fluorescent in toluene, demonstrating deep blue fluorescence with quantum yields of 0.78 and 0.24 respectively. Polymer TRZ_{10k} shows only weak fluorescence with a quantum yield below 0.01 when measured in toluene.



Figure 2.19. Emission spectra of TRZ_{10k} (a), ODA_{10k} (b), and PBI_{10k} (c) at concentrations of 0.02 mg/ml in THF/water mixtures with f_w (water fraction, % by volume) ranging from from 0% (yellow) to 90% (red).

Aggregation-enhanced emission (AEE) and aggregation-induced emission (AIE) materials have found broad applications in a variety of optoelectronic applications including chemical sensing,^{206,207} OLEDs,^{208–210} and stimuli responsive materials.^{211,212} While polymer **TRZ**_{10k} only exhibits weak fluorescence in solution, this polymer demonstrates a dramatic increase in fluorescence emission upon aggregation (Figure 2.19). As this polymer is aggregated via the addition of water to a THF solution of polymer **TRZ**_{10k}, fluorescence intensity increases by approximately 300% as the fraction of water f_w increases from 0 to 90% by volume. In contrast, polymers **ODA**_{10k} and **PBI**_{10k} exhibit only aggregation-caused quenching, a well-documented phenomenon that is typical in normal fluorescent emitters.²¹³ Due to the relative ease of synthesis by the described methods and narrow polydispersity, polymers **TRZ**_{10k}, **ODA**_{10k}, and **PBI**_{10k} may find utility in materials in which AIE/ACQ behaviour is sought, particularly as components of block copolymers as significant emission changes are observed between the aggregated and dissolved acceptor polymers.

2.7 Conclusions

In summary, the utility of Cu(0)-RDRP for the polymerization of polymeric organic semiconductors based on both p- and n-type monomers has been demonstrated. The monomers

investigated have been prepared on >10 gram scale in all cases with efficient synthetic methods that minimize the cost of the final materials. Furthermore, many of these materials are highly crystalline which facilitates the preparation of ultra-high purity monomer via recrystallization paired with column chromatography. These polymerizations demonstrate first-order kinetics up to high conversions, allowing access to polymers with a high degree of control over molecular weight and dispersity. As these polymerizations proceed to high conversion, these methods also reduce monomer waste, a key feature when using expensive monomers that require multistep syntheses to prepare. Homopolymers with a range of molecular weights were prepared from all the monomers explored, demonstrating the accessibility of higher molecular weight polymers that are often difficult to prepare in a controlled fashion. A diblock polymer was also prepared to confirm that end-group fidelity is maintained in these polymers even when approaching high conversions. The ability to functionalize both initiator and the polymer chain-end will be explored in later chapters for post-polymerization modifications as well as the assembly of multicomponent polymeric nanostructures. Finally, the polymers generated demonstrated electronic properties analogous to those observed in small molecule hole- and electron-transport materials.

2.8 Experimental

2.8.1 General Considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. Tris[2-(dimethyl- amino)ethyl]amine (Me₆TREN), ethyl α -bromoisobutyrate (EBiB), and dry dimethylformamide (DMF) were degassed by three freeze-pump-thaw cycles, then stored under a nitrogen atmosphere. Compound 1b was prepared according to literature procedures.²¹⁴ 4-(9H-Carbazol-9-yl)benzaldehyde (2.4c) was prepared according to literature procedures.^{215,216} Compounds 2.6a, 2.6b, and 2.6c were prepared according to literature procedures.²⁰⁰ N-Methyl-2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc) were dis- tilled, then degassed and stored under N₂ atmosphere. CH₂Cl₂ was freshly distilled from P₂O₅ prior to use. Et₃N was dried by distillation on CaH₂ onto activated molecular sieves then degassed and stored under an N₂ atmosphere. The ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with chloroform-d (CDCl₃) or dichloromethane- d_2 (CD_2Cl_2) as the solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; CH₂Cl₂ was used as the solvent and the optical density at λ_{ex} was kept between 0.05–0.15. Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization.

2.8.2 Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 2.5– 5 mg mL⁻¹ using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly (styrene-co-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array, and light scattering (90° and 7°) detectors. Interdetector volume was calibrated using a single polystyrene standard with $M_n = 101\ 000$ and PDI = 1.04, and absolute molecular weights were calculated using triple detection after measuring the refractive index increment (dn/dc) in THF of each polymer.

2.8.3 Thermal Analysis

Thermal degradation studies were performed using a NETZSCH TG 209F1 Libra instrument. Samples were placed in an Al₂O₃ crucible and heated at a rate of 10 °C min⁻¹ from 25 to 800 °C under a flow of nitrogen (50 mL min⁻¹). Glass transition temperatures were determined using differential scanning calorimetry on a NETZSCH DSC 214 Polyma instrument. The polymer samples were placed in an aluminum pan and heated from 25 to 200 °C at 10 °C min⁻¹ under a flow of nitrogen for 3 heating/cooling cycles.

2.8.4 Electrochemical Methods

Cyclic voltammograms were recorded using a CH Instruments 660D potentiostat at room temperature using a standard three-electrode configuration (working electrode: 2 mm diameter Pt disc; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ ferrocenium (0.519 V vs. Ag/AgCl in CH₂Cl₂; 0.591 in tetrahydrofuran)²¹⁷; counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluoro-phosphate in dichloromethane or tetrahydrofuran. Experiments were run at a scan rate of 100 mV s⁻¹ in dry degassed electrolyte solution with ~2 mg mL⁻¹ of analyte.

2.8.5 **Density Functional Theory**

Calculations were performed using the Gaussian 09 software package.²¹⁸ Ground state geometries and energies were calculated at the B3LYP/6-31+g(d) level of theory. To simulate electronic properties of these polymeric materials, analogous versions of each monomer were calculated in which the vinyl end group of the acrylate functionality is replaced with a *sec*-butyl group to more closely mimic the structure of the corresponding polymer chain. If this approximation is not made, the LUMO lies on the acrylate moiety in all cases.

2.8.6 X-Ray Crystallography

Single brown plate-shaped crystals of $CuBr_2(PBI)_2$ were recrystallised from a mixture of DCM and benzene by slow evaporation. Initial crystals were prepared via precipitation and larger crystals were grown via this method. A suitable crystal (0.44×0.22×0.09) mm³ was selected and mounted on a mylar loop with oil on a Bruker APEX II area detector diffractometer. The crystal was kept at T = 90(2) K during data collection. Using Olex2,²¹⁹ the structure was solved with the XT²²⁰ structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of **XL**²²¹ (Sheldrick, 2015) using Least Squares minimisation. CCDC 1830669.

2.8.7 General Procedure for Cu(0)-RDRP of a Polymer with $M_n = 10000$

In a nitrogen atmosphere glovebox, a 4 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was filled with monomer (230 mg), 89.7 μ L of a solution of ethyl α -bromoisobutyrate in NMP or DMAc (C_{EBiB} = 50 mg mL⁻¹; EBiB: 4.49 mg, 2.3 × 10⁻² mmol, 1 equiv), 89.0 μ L of a solution of CuBr₂/Me₆TREN in NMP or DMAc (C_{Cu} = 3.75 mg mL⁻¹)

¹; CuBr₂: 0.334 mg, 1.5×10^{-3} mmol, 0.065 equiv; Me₆TREN: 0.362 mg, 1.57×10^{-3} mmol, 0.068 equiv), and 1,3,5-trimethoxy- benzene (3 equiv) as an internal standard. The total polymerization volume was kept to 1.15 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 1.15 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried in vacuo, and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. The polymerization was stirred until completion (monitored via ¹H NMR), then quenched by addition of water followed by centrifugation. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated in vacuo. The residue was purified by SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by GPC analysis. All fractions containing polymer were collected and dried in vacuo overnight. Alternatively, polymers can be purified by reprecipitation into MeOH (NpHTL, tBuHTL, tolHTL, and TRZ) or hexanes (CzBA, ODA, PBI). Higher molecular weight polymers were generated by modifying the ratio of monomer to EBiB initiator accordingly.

2.8.8 Chain Extension of Methyl Acrylate (MA) with CzBA

The general procedure for the homopolymerization of a 10k MW polymer by Cu (0)-RDRP was followed as given above. Homopolymerization of MA was allowed to proceed for 8 h (~90% conversion by ¹H NMR) before addition of a mixture of **CzBA** (0.23 g, 0.70 mmol, 30 equiv), DMAc (1 mL), 0.10 mL of a solution of CuBr₂/Me₆TREN in DMAc ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 0.39 mg, 1.7×10^{-3} mmol, 0.065 equiv; Me₆TREN: 0.42 mg, 1.8×10^{-3} mmol, 0.068 equiv), and 1.2 cm Cu(0) wire. Samples were taken at 2 h intervals for a total of 10 h and passed through a

short column of neutral alumina to remove dissolved copper salts prior to analysis by ¹H NMR and GPC.

2.8.9 Synthetic Procedures

General Goldberg Reaction (A):

Modified from a previously reported procedure.²²² Diarylamine (10 mmol, 1.0 equiv), copper (I) iodide (0.19 g, 1.0 mmol, 0.10 equiv), and 1,10-phenanthroline (0.18 g, 1.0 mmol, 0.10 equiv) were added to a three-neck round bottom flask with an attached condenser and magnetic stir bar. The headspace was evacuated and backfilled with N₂ three times. *p*-xylene (10 mL) and iodobenzene (2.5 g, 12 mmol, 1.2 equiv) were added and the reaction mixture was heated to reflux. KOH (3.9 g, 70 mmol, 7.0 equiv) was then ground to a fine powder using a mortar and pestle and added at reflux. The reaction was stirred at reflux until complete by thin-layer chromatography (TLC) (approximately 24 h), then neutralized with 1 M acetic acid until the aqueous layer reached pH 7. The mixture was then extracted into CH₂Cl₂ (3 x 200 mL), after which the organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The crude residue was purified on silica and the product was recrystallized from MeOH.

General Vilsmeier-Haack Formylation (B):

Modified from a previously reported procedure.²²² Triarylamine (10 mmol) was added to a 100 mL round bottom flask equipped with a magnetic stir bar. The headspace was evacuated and backfilled with N₂ three times. DMF (6.2 mL, 80 mmol, 8.0 equiv) and chlorobenzene (12 mL) were added and the flask was heated to 65 °C in an oil bath. At 65 °C, POCl₃ (5.6 mL, 60 mmol, 6.0 equiv) was added dropwise to the reaction mixture. The reaction was stirred overnight and then quenched by pouring the solution onto ice. The remaining acid was neutralized with solid K₂CO₃, added in small portions, until the pH reached 7, and extracted into CH₂Cl₂ (3 x 100 mL). The
organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The crude residue was purified on silica.

General NaBH₄ Reduction (C):

Modified from a previously reported procedure.²²³ Pure aldehyde-functionalized compound (10 mmol) was added to a round bottom flask and dissolved in CH_2Cl_2 . Once all starting material was dissolved, one part EtOH was added for every three parts CH_2Cl_2 . Solid NaBH₄ (0.45 g, 12 mmol, 1.2 equiv) was then added to the solution and the reaction was monitored by TLC. When no starting material remained by TLC (approximately 24 h) the reaction was quenched by addition of water followed by extraction using CH_2Cl_2 (3 x 50 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The crude residue was then purified on a short silica column.

General Acrylation (D):

The alcohol-functionalized compound (10 mmol) and a magnetic stir bar were added to a flame dried round bottom flask which was evacuated and backfilled three times with N₂. CH₂Cl₂ (100 mL) and triethylamine (1.8 mL, 13 mmol, 1.3 equiv) were then added to the round bottom flask and stirred until all solid had dissolved. The reaction flask was cooled to 0 °C in an ice bath for 30 minutes, then acryloyl chloride (0.96 mL, 1.2 mmol, 1.2 equiv) was added to the reaction mixture dropwise over 10 minutes. The reaction was then protected from light using foil and allowed to stir in the ice bath for 6, 8 or 24 hrs as indicated below. The reaction was quenched by addition of water and extracted with CH₂Cl₂ (3 x 50 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo* without added heat. The crude residue was purified on a short silica column, taking care to elute the product as quickly as possible to avoid decomposition on silica.



4-(naphthalen-1-yl(phenyl)amino)benzaldehyde (2.1c)

Prepared according to general reaction B, using **2.1b** as the starting material. Purified on silica using CH₂Cl₂. Yield 75%. ¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁴



(4-(naphthalen-1-yl(phenyl)amino)phenyl)methanol (2.1d)

Prepared according to general reaction C using **2.1c** as the starting material. Purified on silica using a gradient from 2% to 10% MeOH in CH₂Cl₂. Yield 95%.

¹**H NMR (400 MHz, Chloroform-***d*): δ 7.92 (ddt, *J* = 16.1, 8.2, 0.9 Hz, 2H), 7.79 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.31 (m, 2H), 7.22 (ddd, *J* = 8.7, 4.7, 2.3 Hz, 4H), 7.08 – 7.00 (m, 4H), 6.99 – 6.93 (m, 1H), 4.63 (s, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 148.4, 147.9, 143.5, 135.4, 134.5, 131.2, 129.1,
128.4, 128.1, 127.3, 126.5, 126.4, 126.3, 126.1, 124.0, 121.8, 121.7, 121.6, 64.8 ppm.

HRMS (EI) *m/z*: [M⁺] calcd for [C₂₃H₁₉NO] ⁺, 325.14666; found, 325.14626; difference: 1.3 ppm.



4-(naphthalen-1-yl(phenyl)amino)benzyl acrylate (NpHTL)

Prepared according to general reaction D (8 h) using **2.1d** as the starting material. Purified on silica using 6:1 hexanes/ethyl acetate. Yield 97%.

¹**H NMR (400 MHz, Methylene Chloride**-*d*₂): δ 7.96 (ddd, *J* = 7.6, 4.5, 1.1 Hz, 2H), 7.88 – 7.82 (m, 1H), 7.57 – 7.32 (m, 4H), 7.29 – 7.19 (m, 4H), 7.12 – 7.05 (m, 2H), 7.04 – 6.88 (m, 3H), 6.43 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.18 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.86 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.12 (s, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Methylene Chloride-*d*₂): δ 166.0, 148.7, 148.2, 143.4, 135.5, 131.4, 130.7, 129.6, 129.3, 128.9, 128.6, 127.5, 126.8, 126.5, 126.3, 124.1, 122.4, 122.3, 121.1, 66.2 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₂₆H₂₁NO₂] ^{+•}, 379.15727; found, 379.15723; difference: – 0.1 ppm.



4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-phenylaniline (2.2b)

Prepared according to general reaction A, using bis(4-(*tert*-butyl)phenyl)amine, **2.2a**, as the diarylamine. Purified on silica using 1:3 CH₂Cl₂/hexane. Yield 81%. ¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁵



4-(bis(4-(*tert*-butyl)phenyl)amino)benzaldehyde (2.2c)

Prepared according to general reaction B, using **2.2b** as the starting material. Purified on silica using CH₂Cl₂. Yield 95%. ¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁶



(4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)methanol (2.2d)

Prepared according to general reaction C using **2.2c** as the starting material. Purified on silica using 1% MeOH in CH₂Cl₂. Yield 90%. ¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁷



4-(bis(4-(*tert*-butyl)phenyl)amino)benzyl acrylate (tBuHTL)

Prepared according to general reaction D (24 h) using **2.2d** as the starting material. Purified on silica using CH₂Cl₂. Yield 96%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.39 (s, 1H), 7.33 – 7.20 (m, 6H), 7.10 – 7.00 (m, 6H), 6.48 (dd, J = 17.3, 1.5 Hz, 1H), 6.19 (dd, J = 17.3, 10.4 Hz, 1H), 5.87 (dd, J = 10.4, 1.5 Hz, 1H), 5.16 (s, 2H), 1.34 (s, 18H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.2, 148.4, 145.9, 144.9, 130.9, 129.5, 128.6, 128.5, 128.3, 126.1, 124.1, 122.5, 66.3, 34.3, 31.5 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₃₀H₃₅NO₂] ^{+•}, 441.26678; found, 441.26711; difference: -0.8 ppm.



4-methyl-*N*-phenyl-*N*-(*p*-tolyl)aniline (2.3b)

Prepared according to general reaction A, using di-*p*-tolylamine, **2.3a**, as the diarylamine. Purified on silica using 1:4 CH₂Cl₂/hexane. Yield 62%. ¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁴



4-(di-*p*-tolylamino)benzaldehyde (2.3c)

Prepared according to general reaction B, using **2.3b** as the starting material. Purified on silica using a gradient from 1:1 CH₂Cl₂/hexane to CH₂Cl₂. Yield 80%.¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁴



(4-(di-p-tolylamino)phenyl)methanol (2.3d)

Prepared according to general reaction C using **2.3c** as the starting material. Purified on silica using CH₂Cl₂. Yield 93%.¹H NMR and ¹³C{¹H} NMR spectra match literature values.²²⁸



4-(di-p-tolylamino)benzyl acrylate (tolHTL)

Prepared according to general reaction D (8 h) using **2.3d** as the starting material. Purified on silica using CH₂Cl₂. Yield 73%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.28 – 7.20 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 4H), 7.07 – 6.99 (m, 6H), 6.49 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.21 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.88 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.16 (s, 2H), 2.35 (s, 6H) ppm.

¹³C{¹H } NMR (101 MHz, Chloroform-*d*): δ 166.2, 148.4, 145.1, 132.8, 130.9, 129.9, 129.5, 128.5, 128.4, 124.8, 122.1, 66.3, 20.9 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₂₄H₂₃NO₂] ^{+•}, 357.17293; found, 357.17288; difference: -0.1 ppm.



(4-(9*H*-carbazol-9-yl)phenyl)methanol (2.4d)

Prepared according to general reaction C using **2.4c** as the aldehyde. Purified on silica using CH₂Cl₂. Yield 90%. ¹H NMR and ¹³C{¹H} NMR match literature values.²²⁹



4-(9*H*-carbazol-9-yl)benzyl acrylate (CzBA)

Prepared according to general reaction D (6 h) using **2.4d** as the starting material. Purified on silica using CH_2Cl_2 and recrystallized twice from CH_2Cl_2 /hexanes. Yield 96%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.18 (d, J = 7.7 Hz, 2H), 7.63 (q, J = 8.5 Hz, 4H), 7.48 – 7.38 (m, 4H), 7.32 (ddd, J = 8.0, 5.1, 3.1 Hz, 2H), 6.56 (dd, J = 17.3, 1.4 Hz, 1H), 6.27 (dd, J = 17.3, 10.4 Hz, 1H), 5.95 (dd, J = 10.4, 1.4 Hz, 1H), 5.36 (s, 2H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 166.0, 140.8, 137.7, 135.1, 131.5, 129.8, 128.2, 127.2, 126.0, 123.4, 120.4, 120.1, 109.8, 65.8 ppm.

HRMS (EI) *m*/*z*: [M^{+•}] calcd for [C₂₂H₁₇NO₂] ^{+•}, 327.12576; found, 327.12593; difference: 0.5 ppm.



2-(4-bromophenyl)-4,6-di-p-tolyl-1,3,5-triazine (2.5a)

Prepared according to modified literature procedure.²³⁰ All steps were performed under a nitrogen atmosphere in flame-dried glassware. First, p-bromobenzoyl chloride (5.5 g, 25 mmol, 1.0 equiv) was combined with p-tolunitrile (5.9 g, 50 mmol, 2.0 equiv) and a magnetic stir bar in a three neck 100 mL round-bottom flask equipped with a reflux condenser. The flask was evacuated and backfilled three times with nitrogen followed by the addition of freshly distilled CH₂Cl₂ (50 mL). Once completely dissolved, the reaction mixture was allowed to cool for 30 minutes in an ice bath. SbCl₅ (7.5 g, 3.2 mL, 25 mmol, 1.0 equiv) was weighed into an addition funnel in a nitrogen atmosphere glovebox. CAUTION: SbCl₅ is highly corrosive and should be handled with extreme care. Once measured, the SbCl₅ was removed from the glovebox and added dropwise to the reaction mixture at 0 °C, then the reaction was removed from the ice bath and stirred for one hour at 20 °C. Following this, the reaction was heated to reflux for 8 hours. After

this reflux was complete, the reaction was filtered through a glass microfiber filter under a nitrogen atmosphere and washed with dry, degassed CH₂Cl₂. The resulting yellow solid was removed from the filter and dried in vacuo. Once dry, this intermediate was cooled to 0 °C in an ice bath and converted to the final product by slow addition of 150 mL of 28% NH₃ in water under air while stirring. Once addition is complete, the mixture was stirred for 1 hour. The resulting aqueous slurry was then vacuum filtered, collected, and purified by Soxhlet extraction for 48 hours using chloroform. Once complete, the product was collected by precipitation from the concentrated chloroform solution by the addition of methanol followed by filtration. Yield 9.1 g, 87%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.79 (dd, J = 8.0, 1.7 Hz, 2H), 8.73 – 8.67 (m, 4H), 7.66 – 7.53 (m, 2H), 7.46 – 7.35 (m, 4H), 2.51 (s, 6H) ppm.

¹³C{¹H}NMR (101 MHz, Chloroform-*d*): δ 171.6, 170.6, 143.2, 135.4, 133.4, 131.8, 130.4, 129.4, 128.9, 127.2, 21.8 ppm.

HRMS (EI) m/z: [M^{+•}] calcd for [C₂₃H₁₈N₃⁷⁹Br] ^{+•}, 415.06841; found, 415.06859; difference: -0.4 ppm.



4'-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (2.5b)

Prepared according to modified literature procedure, using **2.5a** and 4-formylphenyl boronic acid.²³¹ To a 500 mL three neck round bottom flask was added **2.5a** (1.0 g, 2.4 mmol, 1 equiv), 4- formylphenyl boronic acid (0.43 g, 2.9 mmol, 1.2 equiv), and Pd(PPh₃)₄ (0.10 g, 0.12 mmol, 0.050 equiv). The flask was then evacuated and backfilled with N₂ three times. In a separate 250 mL round bottom flask, 120 mL of toluene and 50 mL of EtOH were mixed and sparged with nitrogen gas for 30 minutes. Similarly, 70 mL of 2N Na₂CO₃ in water was sparged in a third 100 mL round bottom flask. First, the organics were cannula transferred to the 500 mL three neck flask, followed by the aqueous base solution. The reaction was then heated to reflux overnight. The reaction was then quenched by opening to atmosphere, then extracted to EtOAc. The organic layer was washed three times with 150 mL portions of distilled water, dried on MgSO₄, and concentrated in vacuo. The crude residue was purified on silica using hexane and CH₂Cl₂. Yield 0.90 g, 85%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.08 (s, 1H), 8.81 (d, J = 8.4 Hz, 2H), 8.65 (d, J = 8.2 Hz, 4H), 7.98 (d, J = 8.2 Hz, 2H), 7.81 (dd, J = 16.4, 8.3 Hz, 4H), 7.36 (d, J = 8.0 Hz, 4H), 2.48 (s, 6H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 191.9, 171.5, 170.8, 146.3, 143.2, 143.1, 136.5, 135.6, 133.5, 130.3, 129.5, 129.4, 129.0, 127.8, 127.5, 21.8 ppm.

HRMS (EI) *m/z*: [M⁺⁺] calcd for [C₃₀H₂₃N₃O] ⁺⁺, 441.18344; found, 441.18411; difference: 1.5 ppm.



(4'-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-yl)methanol (2.5c)

Prepared according to general reaction C using **2.5b** as starting material. Purified on silica using 2% MeOH in CH₂Cl₂. Yield 99%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.85 (d, J = 8.4 Hz, 2H), 8.70 (d, J = 8.2 Hz, 4H), 7.82 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.2 Hz, 2H), 7.48 – 7.35 (m, 5H), 4.81 (d, J = 6.0 Hz, 2H), 2.51 (s, 6H), 1.72 (t, J = 6.0 Hz, 1H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 171.5, 171.2, 144.6, 143.0, 140.6, 139.9, 135.5, 133.7, 129.5, 129.4, 129.0, 127.5, 127.5, 127.2, 65.1, 21.8 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₃₀H₂₅N₃O] ^{+•}, 443.19976; found, 443.19969; difference: 0.2 ppm.



(4'-(4,6-di-p-tolyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-4-yl)methyl acrylate (TRZ) Prepared as general reaction D using 2.5c as starting material. Purified on silica using CH₂Cl₂. Yield 93%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.86 (d, J = 8.4 Hz, 2H), 8.75 – 8.67 (m, 4H), 7.81 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.0 Hz, 4H), 6.51 (dd, J = 17.3, 1.4 Hz, 1H), 6.23 (dd, J = 17.3, 10.4 Hz, 1H), 5.91 (dd, J = 10.4, 1.4 Hz, 1H), 5.31 (s, 2H), 2.51 (s, 6H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 171.5, 171.1, 166.1, 144.4, 143.0, 140.5, 135.6,
133.7, 131.3, 129.5, 129.4, 129.0, 128.9, 128.3, 127.5, 127.3, 66.1, 21.8 ppm.

HRMS (EI) *m*/*z*: [M^{+•}] calcd for [C₃₃H₂₇N₃O₂]^{+•}, 497.21033; found, 497.20999; difference: 0.7 ppm.



(4-(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (2.6c)

Prepared according to a literature procedure.²⁰⁰ Purified on silica using 4:1 CH₂Cl₂:EtOAc. Yield 89%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.16 – 8.04 (m, 4H), 7.57 (dd, J = 8.2, 6.0 Hz, 4H), 4.82 (s, 2H), 1.40 (s, 9H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 162.1, 155.4, 145.1, 127.2, 127.0, 126.8, 126.1, 123.0, 121.1, 64.5, 35.1, 31.1 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₁₉H₂₀N₂O₂] ^{+•}, 308.15248; found, 308.15203; difference: 1.5 ppm.



4-(5-(4-(tert-butyl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (ODA)

Prepared as general reaction D using **2.6c** as starting material. Purified on silica using CH_2Cl_2 with 2% ethyl acetate. Yield 73%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.21 – 8.12 (m, 2H), 8.13 – 8.06 (m, 2H), 7.58 (dd, J = 8.2, 5.3 Hz, 4H), 6.52 (dd, J = 17.3, 1.4 Hz, 1H), 6.24 (dd, J = 17.3, 10.4 Hz, 1H), 5.93 (dd, J = 10.5, 1.4 Hz, 1H), 5.31 (s, 2H), 1.41 (s, 9H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 165.8, 164.0 155.4, 139.6, 131.6, 128.5, 128.0, 127.1, 126.8, 126.1, 123.9, 121.1, 65.6, 35.1, 31.1 ppm.

HRMS (EI) m/z: [M^{+•}] calcd for [C₂₂H₂₂N₂O₃]^{+•}, 362.16304; found, 362.16257; difference: 0.5 ppm.



4-(2-phenyl-1H-benzo[d]imidazol-1-yl)benzaldehyde (2.7a)

Prepared according to modified literature procedure.²³² A Teflon-capped, 20 mL vial equipped with a magnetic stir bar was charged with 2-phenylbenzimidazole (0.18 g, 0.93 mmol, 1.0 equiv), K_3PO_4 (0.98 g, 4.6 mmol, 5.0 equiv), and 15 mL DMF. The reaction was sealed and heated to 150 °C with stirring. 4- fluorobenzaldehyde (0.20 mL, 1.85 mmol, 2 equiv) was then added and the reaction was stirred overnight. Ethyl acetate (20 mL) was added and the organic layer was washed with water (4 x 50 mL), dried over MgSO₄, and concentrated in vacuo. The crude residue was purified on a silica column (1:3 ethyl acetate/hexane) to afford **2.7a** as a white solid. Yield 0.20 g (72%).

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.10 (s, 1H), 8.08 – 7.99 (m, 2H), 7.93 (dt, J = 8.0, 1.0 Hz, 1H), 7.60 – 7.46 (m, 4H), 7.45 – 7.29 (m, 6H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 190.8, 152.3, 143.2, 142.1, 136.4, 135.7, 131.1, 129.8, 129.5, 128.6, 128.2, 127.8, 123.8, 123.5, 120.2, 110.2 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₂₀H₁₄N₂O]^{+•}, 298.11061; found, 298.10998; difference: 2.1 ppm.



(4-(2-phenyl-1H-benzo[d]imidazol-1-yl)phenyl)methanol (2.7b)

Prepared according to general reaction C using **2.7a** as starting material. Purified on silica using EtOAc. Yield 96%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.91 (dt, J = 8.0, 0.9 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.56 – 7.44 (m, 2H), 7.41 – 7.24 (m, 8H), 4.84 (d, J = 5.5 Hz, 2H), 2.20 (t, J = 5.8 Hz, 1H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 152.4, 142.8, 141.6, 137.2, 136.0, 129.8, 129.5, 129.5, 128.4, 128.2, 127.4, 123.4, 123.1, 119.8, 110.5, 64.4 ppm.

HRMS (EI) *m*/*z*: [M^{+•}] calcd for [C₂₀H₁₆N₂O]^{+•}, 300.12626; found, 300.12586; difference: 1.3 ppm.



4-(2-phenyl-1H-benzo[d]imidazol-1-yl)benzyl acrylate (PBI)

Prepared according to general reaction D using **2.7b** as starting material. Purified on silica using CH₂Cl₂. Yield 88%.

¹**H NMR (400 MHz, Methylene Chloride**-*d*₂): δ 7.88 (dt, J = 8.0, 1.0 Hz, 1H), 7.67 – 7.53 (m, 4H), 7.48 – 7.33 (m, 6H), 7.37 – 7.27 (m, 2H), 6.53 (dd, J = 17.3, 1.5 Hz, 1H), 6.27 (dd, J = 17.3, 10.4 Hz, 1H), 5.95 (dd, J = 10.4, 1.4 Hz, 1H), 5.34 (s, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Methylene Chloride-*d*₂): δ 166.1, 152.7, 143.6, 137.7, 137.2, 137.1,
131.6, 130.6, 129.9, 129.8, 129.7, 128.7, 128.5, 127.9, 123.6, 123.2, 120.1, 110.8, 65.8 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₂₃H₁₈N₂O₂]^{+•}, 354.13683; found, 354.13622; difference: 1.7 ppm.



Bis(4-(2-phenyl-1H-benzo[d]imidazol-1-yl)benzyl acrylate) copper(II) bromide (CuBr₂(PBI)₂)

CuBr₂ (16 mg, 0.070 mmol, 0.50 equiv) and **PBI** (50 mg, 0.14 mmol, 1.0 equiv) were added to a 2 mL vial equipped with a magnetic stir bar. 0.20 mL of NMP was added, resulting in the immediate formation of a dark brown solution and the reaction was stirred overnight. To isolate CuBr₂(**PBI**)₂, 1 mL of benzene was added to the mixture, stirring was turned off and the NMP/benzene solution was layered with approximately 2 mL of hexane. After 24 hours dark brown crystals suitable for X-ray crystallography were obtained. Yield 46 mg (70%). Crystals were paramagnetic and not suitable for analysis by ¹H or ¹³C NMR spectroscopy.

HRMS (ESI) *m/z*: [M–2Br]^{+•} calc'd for [C₄₆H₃₆N₄O₄⁶³Cu]^{+•}, 771.2033; found, 771.2029; difference: -0.5 ppm.

2.8.10 Crystallographic Data

Formula	$C_{58}H_{48}Br_2CuN_4O_4$			
$D_{calc.}/g \text{ cm}^{-3}$	1.449			
μ/mm^{-1}	2.091			
Formula Weight	1088.36			
Colour	brown			
Shape	plate			
Size/mm ³	0.44×0.22×0.09			
T/K	90(2)			
Crystal System	monoclinic			
Space Group	P2 ₁ /c			
a/Å	16.4411(18)			
b/Å	8.8490(10)			
c/Å	18.948(2)			
<i>α</i> /°	90			
β /°	115.172(2)			
γ/°	90			
V/Å ³	2495.0(5)			
Ζ	2			
Ζ'	0.5			
Wavelength/Å	0.71073			
Radiation type	MoKα			
$\Theta_{min}/^{\circ}$	2.375			
$\Theta_{max}/^{\circ}$	28.299			
Measured Refl.	25174			
Independent Refl.	6173			
Reflections Used	4845			
Rint	0.0462			
Parameters	372			
Restraints	313			
Largest Peak	1.535			
Deepest Hole	-1.293			
GooF	1.107			
wR2 (all data)	0.1264			
wR ₂	0.1164			
R_1 (all data)	0.0811			
$R_1(I > 2(I))$	0.0585			

Table 2.7. Crystallographic data for solid-state structure of compound CuBr₂(PBI)₂, CCDC 1830669.

Chapter 3: Oxadiazole-Based Donor-Acceptor Acrylic Polymers and their Applications

3.1 Motivation

Having developed high-efficiency methods to polymerize organic semiconducting acrylate monomers, we next sought to expand this system to include doped copolymers composed of a host and a highly emissive dopant. Typical host materials in OLED emissive layers are composed of carbazole-functionalized aromatic compounds with electronic properties tuned so as to properly funnel excitons to the emitters that they contain. To achieve this, host materials are typically designed such that the HOMO energy of the host sits slightly below that of the adjacent hole transport layer while the LUMO sits at a slightly higher energy than that of the electron transport layer. This serves to reduce the driving voltage required to bring holes and electrons to the emissive layer. To favor efficient exciton transfer to the dopant, emitters must be chosen such that their S_1 energies are lower in energy than that of the host. In the case of emitters in which triplet excitons are harvested, the emitter must have a lower T_1 energy than the host as well.

Using the Cu(0)-RDRP methods described in Chapter 2, we sought to design a series of highly fluorescent doped copolymers with potential applications in OLEDs, polymer dots, and sensing. We proposed that low-cost emissive polymers can be generated via copolymerization of an emissive monomer and a bulk, exciton-funneling host material, resulting in materials that demonstrate the photophysical and electronic properties of their emissive dopants. A series of donor-acceptor monomers were prepared using a range of triarylamine donors paired with an

The work described in this chapter has been published in two publications: Tonge, C. M., Yuan, F., Lu, Z.-H., and Hudson, Z. M., *Polym. Chem.* **2019**, *10*, 3288-3297, and Tonge, C. M., Paisley, N. R., Polgar, A. M., Lix, K., Algar, W. R., and Hudson, Z. M., *ACS Appl. Mater. Interfaces* **2020**, *12*, 6525-6535.

oxadiazole acceptor. Using these monomers, a proof-of-concept electroluminescent device was prepared using a simple blue fluorescent emitter monomer, demonstrating the potential utility of these polymers for polymer-based OLEDs. Using other monomers prepared in this series, polymers were also prepared with TADF properties to develop materials with the ability to more efficiently harvest triplet excitons. The oxygen sensitivity of the emission exhibited by these TADF materials was also used to generate films and polymer dots with ratiometric oxygen sensing properties. This demonstrates the potential utility of these doped copolymers to prepare polymer dots for use in imaging applications. In this chapter, I will be focusing on my work synthesizing and characterizing a series of fluorescent acrylic monomers and demonstrating their utility in the synthesis of electroluminescent devices and oxygen sensing.

3.2 Synthesis of Fluorescent Copolymers

3.2.1 Molecular Design and Synthesis of a Fluorescent Dopant

As demonstrated in Chapter 2, benzyl acrylate polymers are a promising framework with which semiconducting polymers can be assembled with a high degree of control. The Cu(0)-RDRP of these monomers has been shown to proceed at room temperature with a robust Cu(0)/Cu(II) catalyst system that allows for limited sensitivity to air and water as well as maintaining tolerance to a wide range of functional groups. Furthermore, our work optimizing the polymerization of p- and n-type semiconducting benzyl acrylate monomers has demonstrated that minimal modifications are necessary to accommodate a wide range of π -conjugated monomers. Moreover, these methods can be applied to polymerization at larger scale (50 - 200 g monomer) with no change in polymerization kinetics or the dispersity of the polymers generated. Given these

favorable properties, I sought to exploit this polymerization to make a highly scalable, low-cost polymeric emissive layer for use in an electroluminescent device.

We began this work by selecting the phenylcarbazole monomer detailed in chapter 2, CzBA, as a host material. Given its favorable polymerization behavior, its facile synthesis, and its electronic properties, this monomer was an ideal choice to use as a bulk host material for this work. To pair with this host material, we developed a fluorescent monomer composed of an oxadiazole acceptor and a t-butyl functionalized triphenylamine donor to generate a deep blue emissive donoracceptor monomer. The oxadiazole acceptor was selected as it exhibited a lower degree of interaction with the copper catalyst system during polymerization while maintaining significantly better solubility than the triazine acceptor. The *t*-butyl functionalized triphenylamine was selected for its low cost, high solubility, and electron donating ability. Furthermore, the addition of alkyl groups at the *para*- positions of the donor moiety also serve to prevent undesired reactivity of the triarylamine at the electron-rich *para*- positions during purification and polymerization. Similar donor-acceptor compounds composed of a triphenylamine donor and oxadiazole acceptor are wellknown in the literature, with related compounds having found applications as fluorescent materials for OLEDs due to their quantum yields approaching unity.^{233–235} Triarylamine-oxadiazole compounds have also been used in luminescent liquid crystals²³⁶ and as ambipolar host materials for phosphorescent emitters.²³⁷ Besides having demonstrated utility for a variety of applications, triarylamine-oxadiazole compounds are also well-suited for use as fluorescent monomers as they are easily asymmetrically functionalized while maintaining high overall yields.



Figure 3.1. Synthesis of tBuODA monomer.

The blue donor-acceptor monomer explored in this work, **tBuODA**, requires a multistep synthesis, however these steps are all high yielding with many reactions not requiring column chromatography to purify (Figure 3.1). Starting from a benzaldehyde-functionalized di-*t*-butyl triarylamine (**2.2c**), this monomer can be prepared in seven steps with all but one step demonstrating yields above 80%. This synthetic route diverges from the route used previously in Chapter 2 to synthesize an oxadiazole acceptor to allow for scalability without incurring the

expense and complication incurred using 2-chloro-1,3-dimethylimidazolinium chloride. First, the benzaldehyde is converted to the corresponding aryl nitrile (3.1a) in a quantitative reaction with hydroxylamine hydrochloride. This nitrile can be used without purification, or easily purified via chromatography or recrystallization in ethanol on larger scales. This benzonitrile is then converted to the corresponding tetrazole (3.1b) using sodium azide and ammonium chloride in refluxing dimethylformamide.²³⁸ Without further purification, this triarylamine-functionalized tetrazole is converted to an oxadiazole via a key ring-forming step using stoichiometric $N_{,N}$ dicyclohexylcarbodiimide (DCC) and benzoic acid. This reaction results in the coupling of the benzoic acid moiety to the tetrazole, generating an oxadiazole with a pendant aryl group. For this synthesis, para-iodobenzoic acid was selected as the coupling partner to deliver an oxadiazole intermediate with an aryl iodide moiety for facile functionalization (3.1c). This aryl iodide was then coupled to 4-formylphenyl boronic acid via a palladium-catalyzed Suzuki coupling to deliver **3.1d** in 91% yield.²³⁹ This benzaldehyde-functionalized donor-acceptor was then converted to the corresponding benzyl acrylate via a two-step procedure whereby 3.1d was first reduced using sodium borohydride²²³ to yield **3.1e** in 85% yield then acrylated using a mild procedure with acryloyl chloride²⁴⁰ to yield the target monomer, tBuODA, in 78% yield. This procedure allowed us to prepare multigram quantities of **tBuODA** monomer in an overall yield of 49% while limiting the necessity for expensive and time-consuming column chromatography. Once purified, both the CzBA host monomer and the tBuODA dopant monomer were further recrystallized to ensure high purity.

3.2.2 Polymer Design and Synthesis



Figure 3.2. Cu(0)-RDRP of blue fluorescent copolymers for single component polymeric emissive layers using tBuODA and CzBA.

With these two monomers in hand, prepared in high purity on multigram scale, the next step was to design and synthesize a series of polymers to optimize the performance of the fluorescent tBuODA dopant used. To do this, four polymers were prepared, poly(CzBA), poly(CzBA_{0.90}-*co*-tBuODA_{0.10}), poly(CzBA_{0.825}-*co*-tBuODA_{0.175}), and poly(CzBA_{0.75}-cotBuODA_{0.25}), where poly(CzBA) was an undoped homopolymer of the CzBA host to serve as a standard, while the three doped copolymers were named according to their composition (by mass % of each component) with quantities of tBuODA ranging from 10% to 25% by mass and target M_n values of 20 kDa. To prepare these polymers, the optimized polymerization procedure for the host monomer, CzBA, was adapted to account for the addition of dopant monomer. The monomers were weighed into a small, 4 mL Teflon-capped vial, then dissolved in DMAc under inert atmosphere. To this mixture was added ethyl α -bromoisobutyrate (EBiB) as initiator and a stock solution containing CuBr₂ and tris[2-(dimethylamino)ethyl]amine (Me₆TREN). The polymerization was then initiated via the addition of a Cu(0) wire, generating active Cu(I) in situ (Figure 3.2). Polymers with 20 kDa molecular weight were targeted to ensure sufficiently high

molecular weight to form high-quality films via wet processing methods. These polymerizations proceeded cleanly, resulting in conversions as high as 98% in 12-18 hours while maintaining low dispersities between 1.17 and 1.30.

3.2.3 Polymer Properties

Table 3.1. Synthesis of polymers poly(CzBA), poly(CzBA0.90-*co*-tBuODA0.10), poly(CzBA0.825-*co*-tBuODA0.175), and poly(CzBA0.75-*co*-tBuODA0.25).

Polymer	Conv.	Yield	M_n (kDa) ^a	M_n (kDa) ^b	Đ	Targeted Doping ^c	Measured Doping ^{b,c}
poly(CzBA)	87%	85%	19.5	22.4	1.23	0%	0%
poly(CzBA _{0.90} - <i>co</i> - tBuODA _{0.10})	96%	75%	20.1	21.5	1.17	10%	10.6%
poly(CzBA _{0.825} -co- tBuODA _{0.175})	97%	78%	22.9	20.2	1.20	17.5%	16.8%
poly(CzBA _{0.75} -co- tBuODA _{0.25})	98%	85%	22.2	20.0	1.30	25%	24.8%

^{*a*} Determined by SEC in THF using triple detection after purification. Interdetector volume was calibrated with a polystyrene standard.

^b Determined by ¹H NMR.

^c By mass percent, doping percentage of tBuODA in CzBA.

Using this Cu(0)-RDRP polymerization method a series of four polymers were synthesized as outlined above with targeted molecular weights of 20 kDa and varied quantities of the blue fluorescent dopant, **tBuODA**. To confirm the doping concentration of the blue emitter in the host matrix, ¹H NMR was performed on the purified polymers. By comparing the integration of the dopant peaks (*e. g.* 8.18 ppm) to the broad peak corresponding to the backbone protons (5.1 ppm), we demonstrated that the doping concentration measured for these polymers closely matched the targeted doping concentrations (Table 3.1). As such, the mass ratio of the monomers can be used as an accurate guide as to the composition of the final polymers. While this does not prove completely random emitter distribution in the polymer, the lack of significant emitter concentration

in the residual monomer post-polymerization implies that the monomers are polymerized at a similar rate and that they are likely included at comparable rates along the polymer backbone.



Figure 3.3. Size exclusion chromatography data for a) poly(CzBA), b) poly(CzBA_{0.90}-*co*-tBuODA_{0.10}), c) poly(CzBA_{0.825}-*co*-tBuODA_{0.175}), and d) poly(CzBA_{0.75}-*co*-tBuODA_{0.25}), refractive index trace shown.

These polymers were also characterized by size exclusion chromatography to quantify the molecular weight and polydispersity of the polymers prepared. The four polymers generated via Cu(0)-RDRP were found to have consistently low dispersities with molecular weights close to the targeted value, 20 kDa (Table 3.1, Figure 3.3). At higher doping concentrations, the polydispersity of the resulting polymer was somewhat broadened, (1.30 for **poly(CzBA_{0.75}-co-tBuODA_{0.25})** compared to 1.17-1.23 for the lower doping concentrations). This broadened dispersity can be attributed to the lower solubility of the dopant monomer that are exacerbated at higher doping concentrations. Even with high doping concentrations of the blue fluorescent dopant, high conversions and acceptable polymer properties were achieved.



Figure 3.4. TGA (top) run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen from 25 to 800 °C and DSC (bottom) run at a rate of 10 °C min⁻¹ under a 50 mL min⁻¹ flow of nitrogen for polymers a) poly(CzBA), b) poly(CzBA0.90-*co*-tBuODA0.10), c) poly(CzBA0.825-*co*-tBuODA0.175), and d) poly(CzBA0.75-*co*-tBuODA0.25). DSC was measured over three consecutive heating and cooling cycles, the second is shown above.

The behavior of these emitter-doped acrylate copolymers upon exposure to heat is a key property to characterize if they are to be used in an electroluminescent device. When current is applied, Joule heating can lead to significant temperature fluctuations. If the materials reach temperatures high enough to lead to degradation or are higher than the glass transition temperature. the integrity of the emissive film can be lost leading to significant loss of efficiency. All 4 polymers demonstrated high thermal stability (Figure 3.4). The undoped host polymer, poly(CzBA), was stable up to 244 °C, with 10% mass loss at this point. The doped copolymers were somewhat more stable, demonstrating 10% mass loss at 321 °C, 295 °C, and 333 °C for poly(CzBA0.90-cotBuODA_{0.10}), poly(CzBA_{0.825}-*co*-tBuODA_{0.175}), and poly(CzBA_{0.75}-co-tBuODA_{0.25}) respectively (Figure 3.4). This is sufficiently high that degradation upon exposure to heat was not a likely route for efficiency loss in devices using these polymers. The glass transition temperature (T_g) was also measured for these four polymers using DSC. Glass transition temperatures of 92 °C, 130 °C, 111 °C, and 112 °C were recorded for polymers poly(CzBA), poly(CzBA0.90-co-

tBuODA_{0.10}), poly(CzBA_{0.825}-co-tBuODA_{0.175}), and poly(CzBA_{0.75}-co-tBuODA_{0.25})

respectively, high enough to be suitable for use in EL devices. .



Figure 3.5. AFM height images of spin-coated films of a) $poly(CzBA_{0.90}$ -*co*-tBuODA_{0.10}) and b) a 9:1 blend of host monomer and tBuODA monomer (scale bar = 1 μ m). c) Photographs of the films showing the homogeneous nature of $poly(CzBA_{0.90}$ -*co*-tBuODA_{0.10}) (bottom) compared to the corresponding monomer blend when spin-cast (top), scale bar = 1 cm.

One of the main reasons for developing polymeric materials for OLEDs is the significantly improved film forming properties of higher molecular weight materials when processed via wet processing methods (Figure 3.5). The improved film forming capabilities of these polymers are typically attributed to the random orientation of semiconducting side groups along the alkyl backbone, inhibiting their crystallization. To demonstrate the enhanced film forming properties of these materials, pair of films were prepared, one with the 10% doped polymer **poly(CzBA0.90-co-tBuODA0.10)** and a second film prepared from a 9:1 blend of **CzBA** and **tBuODA** monomers. The films prepared are shown in Figure 3.5c, demonstrating an amorphous, featureless film for the film of **poly(CzBA0.90-co-tBuODA0.10)**, and a lower quality film when prepared from the monomer blend. The RMS roughness (Sq) of this amorphous film was measured via AFM, and found to be approximately 0.29 nm, a value that is well within the acceptable range for high-performance organic electronics. The film prepared from a blend of **CzBA** and **tBuODA** monomers, on the

other hand, did not form a high-quality film. Instead, this film rapidly dewetted, forming a rough and inhomogenous coating that did not present any homogenous areas large enough to merit measuring the RMS roughness (Figure 3.5).





Figure 3.6. Normalized photoluminescence of films of a) poly(CzBA), b) poly(CzBA_{0.90}-*co*-tBuODA_{0.10}), c) poly(CzBA_{0.825}-*co*-tBuODA_{0.175}), and d) poly(CzBA_{0.75}-*co*-tBuODA_{0.25}) spin-cast from 2:1 chlorobenzene/chloroform on a 1 in. x 1 in. glass slide.

The efficiency of charge transfer from host to dopant monomer was characterized by measuring the fluorescent emission of these polymers in the solid state. This allows us to select the lowest doping concentration that exhibits only dopant emission, optimizing for high efficiency electroluminescence without wasting the high-cost dopant monomer. To determine the degree of charge transfer, the ratio of host emission to dopant emission was measured. Shown in Figure 3.6,

it was found that even the lowest doping concentration, $poly(CzBA_{0.90}-co-tBuODA_{0.10})$, demonstrated complete charge transfer.

Entry	$\lambda_{\max, abs}{}^a$	$\lambda_{\max, em}^{a}$	$\Phi_{\mathrm{F}}{}^{a,b}$	$CIE_{tol} (x,y)^a$	CIE _{ss} (x,y)
poly(CzBA)	293	348	0.31	(0.18, 0.03)	(0.23, 0.22)
poly(CzBA _{0.90} - <i>co</i> - tBuODA _{0.10})	293	444	1.02	(0.15, 0.09)	(0.17, 0.14)
poly(CzBA _{0.825} - <i>co</i> - tBuODA _{0.175})	293	444	0.97	(0.15, 0.09)	(0.16, 0.14)
poly(CzBA _{0.75} - <i>co</i> - tBuODA _{0.25})	293	444	0.98	(0.15, 0.09)	(0.15, 0.13)

Table 3.2. Photophysical properties of a) poly(CzBA), b) poly(CzBA0.90tBuODA0.10), c) poly(CzBA0.825tBuODA0.175), and d) poly(CzBA0.75tBuODA0.25).

^{*a*} Measured in toluene at 0.01 mg ml⁻¹.

^b Quantum yields measured using an integration sphere, +/- 0.05.

Furthermore, it was observed that the doping concentration of **tBuODA** in the **CzBA** host did not significantly impact the absorbance maximum (293 nm) or emission maximum (444 nm). The absorbance maximum in all polymers was attributed to the host monomer. The CIE coordinates measured for the three doped polymers demonstrated a slight blue shift in the solid state as doping concentration increases, shifting from $CIE_x = 0.17$ to 0.15 and $CIE_y = 0.14$ to 0.13. As the emission maximum does not shift, this can be attributed to slightly narrowed emission spectra for the polymers with higher emitter doping concentration. All three doped polymers, **poly(CzBA**_{0.90}-*co*-**tBuODA**_{0.10}), **poly(CzBA**_{0.825}-*co*-**tBuODA**_{0.175}), and **poly(CzBA**_{0.75}-*co***tBuODA**_{0.25}), demonstrated photoluminescent quantum yields approaching unity, as shown in Table 3.2.



Figure 3.7. Fluorescence decay of polymers a) poly(CzBA), b) poly(CzBA_{0.90}-*co*-tBuODA_{0.10}), c) poly(CzBA_{0.825}-*co*-tBuODA_{0.175}), and d) poly(CzBA_{0.75}-*co*-tBuODA_{0.25}) at 1 x 10⁻⁵ M in toluene sparged with nitrogen for 5 minutes prior to measurement. Green trace = decay, grey trace = scattering standard, red trace = fit line generated using Horiba DAS6 software.

To confirm that the high fluorescence efficiencies were the result of only a standard fluorescence emission process, the fluorescence lifetime was measured via time correlated single photon counting (Figure 3.7). The polymers synthesized all exhibited exclusively short emission lifetimes, less than 5 ns in all cases, as is typical for purely fluorescent emitters. The host polymer **poly(CzBA)** has a decay lifetime of 1.8 ns while the doped copolymers have a slightly longer fluorescence lifetime of 2.8 ns (**poly(CzBA_{0.90}-co-tBuODA_{0.10}**)), 3.0 ns (**poly(CzBA_{0.825}-co-tBuODA_{0.175}**)), and 3.0 ns (**poly(CzBA_{0.75}-co-tBuODA_{0.25}**)). The slight variations between the doped copolymers is likely due to differences in doping concentration affecting intermolecular charge transfer process between host and emitter on the same chain.



Figure 3.8. Solvatochromic response of polymer poly(CzBA_{0.75}-*co*-tBuODA_{0.25}) to solvents of different polarity.

After characterizing the time-resolved fluorescence properties of these polymers, we further probed the nature of this fluorescent emission by measuring the response of these emitters to solvent polarity (Figure 3.8). It was found that there was a slight red shift of the emission peak of polymer **poly(CzBA**_{0.75}-*co*-tBuODA_{0.25}) from $\lambda_{max} = 447$ nm in toluene to $\lambda_{max} = 481$ nm in dichloromethane. This red shift is characteristic of the charge transfer nature of the excited state that is typical in donor-acceptor emitters.



Figure 3.9. a) Aggregation-induced emission and b) photographs of poly(CzBA_{0.75}-*co*-tBuODA_{0.25}) in THF/water at a concentration of 20 μ g mL⁻¹ with f_w from 10% to 98%.

The fluorescence response of these emitter functionalized polymers to aggregation was also measured and quantified (Figure 3.9). If the fluorescent emission of these doped polymers is significantly quenched in the solid state, it could preclude these emitters from use in an efficient

OLED. To measure the effect of aggregation on emission properties, the fluorescence intensity at peak was recorded for a series of solutions of equal concentration in THF with a water fraction (f_w) ranging from 0% to 98%. The emission of polymer **poly(CzBA**_{0.75}-*co*-tBuODA_{0.25}) was found to increase somewhat at peak, increasing 20% from 0% to 98% f_w . The emission also narrowed somewhat with FWHM narrowing from 84 nm to 73 nm upon aggregation, resulting in a slight blue shift of the CIE 1931 coordinates from (0.16, 0.19) to (0.15, 0.15). This lack of ACQ and mild aggregation enhanced emission demonstrates that upon inclusion in a solid-state device, there will not be significant emission quenching due to aggregation effects.

3.2.5 Electronic Properties of Doped Acrylic Polymers



Figure 3.10. Cyclic voltammograms of polymers poly(CzBA) (black) and poly(CzBA_{0.75}-*co*-tBuODA_{0.25}) (blue) relative to FeCp₂^{0/+}, recorded at a rate of 50 mV s⁻¹ in *o*-difluorobenzene containing 4 mg mL⁻¹ of analyte and 0.2 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.²¹⁷

The electrochemical properties of host polymer **poly**(**CzBA**) as well as poly(**CzBA**_{0.75}-*co***tBuODA**_{0.25})were measured to help select appropriate hole and electron transport materials in a test electroluminescent device. In the neat **poly**(**CzBA**) sample in Figure 3.10, a quasi-reversible oxidation is clearly observable, allowing us to estimate the HOMO of this host polymer. The LUMO was then estimated using the low-energy UV-vis absorption band edge, giving us an estimated HOMO of -5.66 eV and an estimated LUMO of -2.14 eV, slightly different from those reported in Chapter 2 as these samples were measured in *o*-difluorobenzene rather than dichloromethane.



LUMO = -1.94 eV

HOMO = -5.26 eV



It was difficult to directly measure the oxidation potential of the dopant monomer, tBuODA, as the neat monomer tends to polymerize during the measurement, giving inconsistent results. It was possible to estimate the oxidation potential of the **tBuODA** dopant via cyclic voltammetry on the doped copolymer with the highest doping concentration, poly(**CzBA**_{0.75}-*co*-**tBuODA**_{0.25}). Using this method, it was estimated that the **tBuODA** monomer has a HOMO and LUMO of -5.26 eV and -2.31 eV respectively. These measured HOMO and LUMO values fit comfortably into the bandgap of the **poly(CzBA**) host, demonstrating that the electronics of this host/dopant pair are properly aligned to funnel excitons to the **tBuODA** dopant were also calculated using DFT (B3LYP, 6-31+G*, Figure 3.11). These values are surprisingly close to the experimental values recorded for this emitter. The favorable electronic and photophysical

properties of the doped fluorescent copolymers led us to pursue preparing a proof-of-concept electroluminescent device.



3.2.6 Electroluminescent Properties of Doped Acrylic Polymers

Figure 3.12. a) Device structure and b) energy levels of each layer in PLEDs tested using poly(CzBA_{0.90}-*co*tBuODA_{0.10}). c) electroluminescence spectra from 3 V to 9 V and image of device using poly(CzBA_{0.90}-*co*tBuODA_{0.10}) in operation (inset).

Given that **poly(CzBA**_{0.90}-*co*-t**BuODA**_{0.10}) showed a photoluminescent quantum yield (PLQY) as high as the other copolymers prepared while minimizing usage of the costly **tBuODA** monomer, this polymer was selected to carry forward for testing in electroluminescent devices. The devices were fabricated using **poly(CzBA**_{0.90}-*co*-t**BuODA**_{0.10}) as a single component emissive layer in a polymer OLED (PLED)illustrated in Figure 3.12. The devices were composed of a series of organic semiconductors that were assembled by first spin-casting a PEDOT:PSS (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate) hole injection layer (35 nm) on an ITO anode. This was then followed by a a 40 nm thick layer of poly(9,9-dioctylfluorene-alt-*N*-(4-secbutylphenyl)-diphenylamine) (TFB) deposited via a spin-casting method as a hole transport layer. Polymer **poly(CzBA**_{0.90}-*co*-t**BuODA**_{0.10}) was then deposited onto this hole transport layer via a
spin casting. The device was completed by thermally evaporating TPBi (60 nm) as an electron transport layer followed by LiF/Al as a cathode (1 nm of LiF followed by 150 nm of Al). Using this simple device structure, a series of devices were prepared to determine the optimal emitter film thickness to maximize EQE and minimize turn-on voltage.

Concentration (mg mL ⁻¹)	V _{on} (V)	L_{max} (cd m ⁻²)	EQE _{max} (%)	$\eta_c \ (cd \ A^{-1})$
30	7.5	521	1.27	1.63
20	4	954	1.50	1.74
10	3	2790	2.63	3.28
5	3.1	2082	2.56	2.83

 Table 3.3. Effect of spin-coating conditions on PLED performance of polymer poly($CzBA_{0.90}$ -co-tBuODA_{0.10}).

 Concentration

Four devices were prepared to determine the optimum emissive layer thickness to maximize device efficiency (Table 3.3). It was found that optimum luminescence ($L_{max} = 2790 \text{ cd m}^{-2}$), external quantum efficiency (EQE_{max} = 2.63%), and current efficiency ($\eta_c = 3.28 \text{ cd/A}$) were achieved when the emissive layer was cast from a solution of concentration 10 mg mL⁻¹. While these efficiencies are not record-setting for polymer-based OLEDs, they are relatively high for a device in which the emitter does not harvest triplet excitons. As a typical fluorescent emitter, these devices can only harvest 25% of excitons generated in an electroluminescent device. If we consider further inefficiencies due to outcoupling in a non-ideal device, the maximum efficiency expected for this device is approximately 5% EQE. Given these restraints, an EQE of 2.63% is a very positive result, demonstrating that with optimization of the device structure and a higher efficiency dopant monomer that is able to harvest triplet excitons, this acrylate polymer framework is promising for generating high efficiency polymer-based OLEDs.

3.3 Acrylic Polymers with Thermally Activated Delayed Fluorescence Properties

Having demonstrated the utility of doped acrylic polymers for generating all-in-one emissive materials to serve as a single component emissive layer for polymer-based OLEDs, we next sought to expand this method to include more complex, higher-efficiency emitters. To achieve this end, it was necessary to develop a monomer that is capable of radiatively harvesting triplet excitons, either via a phosphorescent or TADF mechanism. To achieve TADF in a doped acrylic copolymer, the oxadiazole-triarylamine framework developed in Section 3.1 was adapted to incorporate donors with varying strength and geometry. In this way, polymeric TADF materials were achieved with emission colors from blue to orange with quantum yields as high as 96%. Furthermore, these materials can be prepared using high yielding syntheses, low-dispersity polymerizations, and potential utility for oxygen sensing both as an optode or for biological imaging applications.

3.3.1 Synthesis of Donor-Acceptor TADF Acrylate Monomers

Using a similar synthetic route to the blue emissive monomer, **tBuODA**, five donoracceptor oxadiazole-based benzyl acrylates were prepared, illustrated in Figure 3.13, to be used in a series of acrylic TADF polymers. First, a series of five arylamine functionalized aryl nitriles were prepared (**3.2b-3.6b**) by literature methods,^{3,238} typically starting from the corresponding benzaldehyde (**3.2a-3.6a**). These aryl nitriles were converted to the corresponding tetrazole (**3.2c-3.6c**) via reaction with sodium azide and ammonium chloride at 140 °C in DMF.²³⁸ These tetrazoles were collected in quantitative yield and carried forward either without purification or after a short silica plug to remove residual salts.



Figure 3.13. Synthetic route to donor-acceptor acrylate monomers: ACRODA, PXZODA, PTZODA, PAZODA, and TTACODA.

The oxadiazole moiety was installed by cyclization of this tetrazole with a benzoic acid facilitated by DCC in toluene.²⁴¹ By using an aldehyde-functionalized benzoic acid, 4-carboxybenzaldehyde, we were able to easily install an aldehyde handle directly to the donor-acceptor framework, giving compounds **3.2d** to **3.6d**. This benzaldehyde handle was converted to a benzyl acrylate by first reducing the aldehyde with sodium borohydride²²³ then acrylating the resulting benzyl alcohol (**3.2e-3.6e**) with acryloyl chloride and triethylamine in dichloromethane.²⁴⁰ Some monomers in this series suffered low yields in this final acrylation step, which we attributed to their decreased solubility leading to incomplete elution from the final silica column as well as potential side reactivity during the acrylation, particularly in the case of stronger

donors such as the phenothiazine and methyl-phenazine donor-acceptor monomers. All monomers were purified by column chromatography on silica followed by recrystallization to give each monomer in high purity with reasonable overall yields: ACRODA = 37%, PXZODA = 49%, PTZODA = 23%, PAZODA = 11%, and TTACODA = 12%.

To generate a series of monomers that emit over the visible spectrum, donor moieties with varying degrees of donating strength were selected, with a range from the relatively weak 9,9dimethylacridine donor to N-methyl-N-phenazine, a strongly donating moiety that has lately been reported in several examples of deep red TADF emitters.²⁴² Donor moieties were chosen with a bridging group between the two aryl groups not attached to the oxadiazole acceptor. These aryl groups were bridged by a series of heteroatoms (S, O, N-Me) as well as an isopropenyl bridge in the case of the acridine-functionalized emitter. A final dendritic carbazole donor was included as an alternative to the other diarylamine donors. This donor is composed of a carbazole core to which two ditolylamine functionalities were appended, *para*-tolyl amines were used to prevent potential side reactivity at the nucleophilic *para*-positions as discussed in Chapter 2. Similar dendritic donors have been used in previous work by Adachi and coworkers with a triazine acceptor,²³⁹ resulting in high solubility, high donor strength, and high quantum yield TADF. These five donors use linkages at the *ortho* positions of the *N*-aryl rings to induce rigidity and twisted conformations that are typical in TADF emitters. The main differentiation between the methods used for these emitters and that used in for the tBuODA monomer is the use of a phenyl linker between the oxadiazole for these monomers as opposed to the biphenyl used for the tBuODA emitter. The second phenyl is omitted in these monomers so as to eliminate the Suzuki coupling used in the earlier synthesis, allowing for the production of these TADF active emitters without the use of any transition metal catalysis while increasing overall yields by eliminating unnecessary steps.

3.3.2 Polymer Design and Synthesis



Figure 3.14. Generalized route to doped TADF copolymers.

These donor-acceptor benzyl acrylate monomers were then embedded in the same carbazole-based host monomer, CzBA, that was used with the tBuODA dopant via Cu(0)-RDRP (Figure 3.14). Once these five emissive dopant monomers had been synthesized on half-gram to two-gram scale, a series of doped copolymers was prepared to characterize the performance of the resulting doped copolymers. As previous polymers were found to perform optimally around 10% doping concentration (by mass), three concentrations were selected in a closer range surrounding this value, 5%, 10%, and 15% dopant. Polymers with targeted M_n of 20 kDa were synthesized using each monomer giving a total of 15 doped copolymers. These polymers were generated using the same Cu(0)-RDRP method described in Section 3.1, running at approximately 25 °C without the use of harsh polymerization conditions. The polymerizations were run to approximately 90% conversion (measured by ¹H NMR), at which point they were quenched by exposing to air and precipitating into deionized water to remove the majority of the DMAc solvent. The resulting crude polymers were purified via preparatory size exclusion chromatography (SEC) on a crosslinked polystyrene/divinylbenzene (PS/DVB) resin to remove residual monomer, catalyst, and solvent. These resins do not bind any portion of the reaction mixture permanently, allowing for a single column to be reused hundreds of times without cross contamination. Similar purity can be achieved

by reprecipitation from dichloromethane into methanol, albeit with somewhat lower yields unless performed on scales above 200 mg.

3.3.3 Polymer Properties

	A: 5 wt.% dopant			B: 10 wt.% dopant			C: 15 wt.% dopant		
Emitter	Conv. (%) ^{<i>a</i>}	M_n (kDa) ^b	\mathbf{D}^{b}	Conv. (%) ^a	M_n (kDa) ^b	\mathbf{D}^{b}	Conv. (%) ^a	M_n (kDa) ^b	\mathbf{D}^{b}
ACRODA	97	19.5	1.15	98	19.8	1.10	95	19.7	1.11
PXZODA	85	19.5	1.16	93	20.8	1.13	80	18.2	1.21
PTZODA	95	21.9	1.15	96	25.0	1.37	91	24.3	1.45
PAZODA	94	19.8	1.12	92	20.6	1.15	91	20.8	1.16
TTACODA	93	20.3	1.22	78	23.7	1.37	79	24.7	1.43

Table 3.4. Properties of TADF copolymers.

^{*a*} Measured by ¹H NMR.

^b Measured by SEC in THF.

As with the other Cu(0)-RDRP polymerizations involving CzBA, copolymers of these materials proceeded without issue, delivering polymers with accurate doping concentrations while maintaining the low polydispersity and observed in an undoped host homopolymer. As shown in Table 3.4, copolymers using this series of emissive dopants were relatively consistent. Most of the polymerizations gave materials with M_n very close to the targeted 20 kDa, with the exception of polymers of **PTZODA** and **TTACODA**. While these polymers proceeded smoothly at 5% doping concentration, at higher doping levels, the polymerizations slowed somewhat, delivering polymers with broader dispersities (1.37-1.45 vs 1.10-1.21 for the analogous polymers of **ACRODA**, **PXZODA**, and **PAZODA**). Furthermore, polymerizations of **PTZODA** and **TTACODA** at 10% and 15% doping concentrations also delivered polymers with somewhat higher molecular weights

than targeted (23.7 to 25 kDa). This deviation from the expected is likely a result of the low solubility of these two monomers in DMAc, especially at higher doping concentrations.

3.3.4 Steady State Photophysical Properties

	A: 5 wt.% dopant			B: 10 wt.% dopant			C: 15 wt.% dopant		
Emitter	$\lambda_{\mathrm{em},max}$ (nm) ^a	Φ^{a}	$\Phi^{ \mathfrak{b}}$	$\lambda_{em,max}$ (nm) ^a	Φ^{a}	$\Phi^{ \mathfrak{b}}$	$\lambda_{em,max}$ (nm) ^a	Φ^{a}	$\Phi^{ \mathfrak{b}}$
ACRODA	449	0.33	0.29	453	0.24	0.24	457	0.33	0.27
PXZODA	496	0.56	0.35	504	0.50	0.58	507	0.41	0.51
PTZODA	510	0.32	0.28	512	0.35	0.27	517	0.28	0.19
PAZODA	566	0.04	0.04	580	0.03	0.05	584	0.02	0.05
TTACODA	490	0.43	0.79	499	0.40	0.96	502	0.42	0.77

Table 3.5. Photo	physical Pro	perties of TADF	' acrylate co	opolymers.
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^{*a*} Measured as a neat film spin-cast on a glass slide, excited at 313 nm, under inert atmosphere. ^{*b*} Measured in degassed toluene at 10⁻⁵ M.

To find the optimum doping concentration of each dopant monomer in our **CzBA** host, polymers with 5%, 10%, and 15% dopant concentration were prepared (Table 3.5). The minimum concentration with full energy transfer was determined by measuring the steady state fluorescence spectrum of the emitter-doped copolymers and determining when the host emission peak around 400 nm was fully quenched. To further confirm that optimum doping concentration was achieved for each dopant, the solid state and solution state quantum yields were measured. It was found that the optimum doping concentration for all monomers barring **ACRODA** was 10%. Both the 5% and 15% doped polymers for these four dopants demonstrated somewhat lower quantum yields in the solid state due to partial host emission and aggregation-caused quenching respectively. The

ACRODA polymer instead showed highest emission efficiencies at 5% doping concentrations in **CzBA**, with a $\Phi_F = 0.33$ in the solid state.



Figure 3.15. Solution-state absorbance and fluorescence spectra measured at 0.01 mg mL⁻¹ in CH₂Cl₂ and toluene respectively for polymers a) poly(CzBA_{0.85}-*co*-ACRODA_{0.15}), b) poly(CzBA_{0.85}-*co*-PXZODA_{0.15}), c) poly(CzBA_{0.85}-*co*-PTZODA_{0.15}), d) poly(CzBA_{0.85}-*co*-PAZODA_{0.15}), and e) poly(CzBA_{0.85}-*co*-TTACODA_{0.15}), excited at 313 nm. Inset: solutions in toluene under 365 nm irradiation. (f) CIE diagram showing the chromaticity of the fluorescence of the aforementioned polymers.

The optimally doped polymers had quantum yields ranging from $\Phi_F = 0.96$ for **TTACODA** to $\Phi_F = 0.046$ for **PAZODA** when measured in degassed toluene solution, shown in Figure 3.15. Highest photoluminescence quantum yields were achieved when using the dendritic carbazole donor (**TTAC**), as expected from the previous reports using this donor.²³⁹ Somewhat lower quantum yield was observed for the phenothiazine-based monomer, **PTZODA**, which was attributed to increased probability of nonradiative decay of the more flexible sulfur-bridged diarylamine donor. This lowered quantum yield is ameliorated somewhat for **PTZODA** when

measured in the solid state as molecular motion is restricted compared to the same emitter in solution. The low quantum yield of the methyl-phenazine donor, **PAZODA**, could be a result of multiple factors, including low stability of the donor as well as increased probability of nonradiative transition by the energy gap law,²⁴³ as is typical for red-emissive compounds.²⁴⁴



Figure 3.16. Solvatochromic response of polymers a) poly(CzBA_{0.85}-*co*-ACRODA_{0.15}), b) poly(CzBA_{0.85}-*co*-PXZODA_{0.15}), c) poly(CzBA_{0.85}-*co*-PTZODA_{0.15}), d) poly(CzBA_{0.85}-*co*-PAZODA_{0.15}), and e) poly(CzBA_{0.85}-*co*-TTACODA_{0.15}). Measured at 0.01 mg mL⁻¹ in the respective solvents labeled above.

Further steady-state photophysical characterization was used to confirm the charge-transfer nature of the emission observed. Solvatochromic response was recorded for the 15% doped example of each donor-acceptor monomer, shown in Figure 3.16. In all cases but the **PAZODA** polymer, a small bathochromic shift of the emission was observed as solvent polarity was increased. The **PAZODA**_{0.15} polymer displayed very weak emission in all solvents characterized, so measurements of these polymers were difficult to measure reliably, likely due to competing decomposition and quenching processes with this highly donating arylamine.



Figure 3.17. Top: Aggregation-induced emission of a) poly(CzBA_{0.85}-*co*-ACRODA_{0.15}), b) poly(CzBA_{0.85}-*co*-PXZODA_{0.15}), c) poly(CzBA_{0.85}-*co*-PTZODA_{0.15}), d) poly(CzBA_{0.85}-*co*-PAZODA_{0.15}), and e) poly(CzBA_{0.85}-*co*-TTACODA_{0.15}), measured at 0.02 mg mL⁻¹, normalized such that the maximum intensity at $f_w = 0\%$ is set to 1 and all other spectra are scaled accordingly. Bottom: photographs of the above solutions under illumination at 365 nm, ranging from 0% water (left) in 10% increments to 90% water in THF (right).

The fluorescence response of the five 15% doped donor-acceptor polymers to aggregation was quantified in a similar fashion to previous aggregation-induced emission measurements described in Section 3.2. To ensure high-performance electroluminescence it is necessary to demonstrate a lack of aggregation-caused quenching (ACQ) that could potentially limit emission efficiency in a device. Aggregation-induced emission (AIE) has also been demonstrated to have significant utility for imaging applications, enhancing brightness and minimizing quenching of the dye at higher concentrations.^{245–247} The 15% doped polymers were used as these polymers present the highest concentration of TADF dopant and will therefore show the largest response to emitteremitter interactions upon aggregation. The fluorescent intensity of each of the five polymers tested increased significantly as the solvent was changed from THF to various water fractions (f_w) in THF from 0% water to 90% water, shown in Figure 3.17. Aggregation-enhanced emission ranged in magnitude from a 270% increase in emission intensity at peak from dissolved to aggregated in the case of poly(CzBA_{0.85}-co-ACRODA_{0.15}), to 1900% increase in emission in the case of poly(CzBA_{0.85}-co-PXZODA_{0.15}). These favorable emissive properties in the aggregated state bode well for the potential applicability of this series of polymers both in polymer-based OLEDs as well as for use in time-resolved fluorescent imaging.^{248,249}



3.3.5 Time-Resolved Fluorescence Measurements

Figure 3.18. (Top) Time-resolved fluorescence emission for a) poly(CzBA_{0.85}-*co*-ACRODA_{0.15}), b) poly(CzBA_{0.85}-*co*-PXZODA_{0.15}), c) poly(CzBA_{0.85}-*co*-PXZODA_{0.15}), d) poly(CzBA_{0.85}-*co*-PAZODA_{0.15}), and e) poly(CzBA_{0.85}-*co*-TTACODA_{0.15}), under N₂ (Inert) and air. (Bottom) Temperature dependence of the time-resolved fluorescence emission for the corresponding monomers at 1 wt% in poly(methyl methacrylate) film. In the bottom row, decay traces have been corrected for phosphorescence build-up by manual subtraction of background emission. Measured in the solid state, spin-cast on glass slides and excited at 313 nm.

To confirm the thermally activated delayed fluorescent nature of the emission observed for these five structurally constrained donor-acceptor emitters, it was necessary to measure the emission lifetimes of these doped polymers and dopants at room temperature as well as at cryogenic temperatures. These measurements are illustrated in Figure 3.18, demonstrating multicomponent fluorescence at room temperature in the solid state as well as disappearance of the delayed fluorescence at cryogenic temperatures. As explained previously, the two-component emission process observed for TADF emitters is due to the significantly different rates for the two processes at play here, the rate of emission directly from $(S_1 \rightarrow S_0)$, typically with lifetimes on the ns timescale, and the rate of reverse intersystem crossing $(T_1 \rightarrow S_1)$, typically exhibiting longer (μ s) lifetimes that are dependent primarily on the temperature and ΔE_{ST} .

Emitter	$ au_p$ (ns) ^a	$ au_d (\mu s)^b$	ΔE_{st} (eV) ^e	HOMO (Exp., eV) ^c	LUMO $(Exp., eV)^d$	HOMO (Calc., eV) ^e	LUMO (Calc., eV) ^e
poly(CzBA _{0.85} - <i>co</i> - ACRODA _{0.15})	26.0	566	0.0070	-5.94	-2.72	-5.25	-2.19
poly(CzBA _{0.85} - <i>co</i> - PXZODA _{0.15})	14.8	362	0.0073	-5.73	-2.91	-5.09	-2.26
poly(CzBA _{0.85} - <i>co</i> - PTZODA _{0.15})	6.75	5100	0.011	-5.69	-2.59	-5.34	-2.24
poly(CzBA _{0.85} -co- PAZODA _{0.15})	3.58	_ <i>f</i>	0.0046	-5.16	-2.40	-4.74	-2.17
poly(CzBA _{0.85} - <i>co</i> - TTACODA _{0.15})	16.8	142	0.21	-5.51	-2.73	-4.72	-1.86

Table 3.6. Fluorescent Lifetimes and Electronic Properties of TADF acrylate polymers.

^{*a*} Measured in the solid state on 1 µs time scale under inert atmosphere.

^b Measured in the solid state between 8ms and 80 ms scale under inert atmosphere.

^c Measured at 2 mg mL⁻¹ in in 1,2-difluorobenzene with 0.2 M tetrabutylammonium hexafluorophosphate.

^{*d*} Calculated from the HOMO level and the optical energy gap, E_g . E_g was determined from the low-energy UV-vis absorption band edge of the dopant monomer.

^e Calculated via TD-DFT.

^{*f*} Not observed.

All emitters, barring **poly**(CzBA_{0.85}-*co*-PAZODA_{0.15}), demonstrated a significant delayed fluorescence component when measured at room temperature in the solid state under inert atmosphere. These emitters showed a two-component fluorescent lifetime, with a short lifetime (corresponding to the $S_1 \rightarrow S_0$ transition) from 6.8 ns to 26 ns, and a second longer lifetime (corresponding to the RISC process) from 142 µs to 5100 µs (Table 3.6). When measured under air, these extended lifetimes were significantly suppressed in all cases, implying quenching of fluorescence upon exposure to oxygen. This oxygen sensitivity confirms that triplet excited states are likely involved in the emission process, as would be the case in all TADF emitters. The significant fluorescence quenching observed (illustrated in Figure 3.18) is likely due to the extended lifetimes of the second component of the fluorescent emission at room temperature. This long-lived triplet state can easily be quenched by oxygen due to the increased amount of time for which the triplet excited state persists.

Dopant	% Prompt $(\varphi_p)^a$	% Delayed $(\varphi_d)^a$	$\Delta E_{ST} (eV)^b$
ACRODA	83.4 (0.28)	16.6 (0.05)	0.315
PXZODA	78.5 (0.32)	21.5 (0.09)	0.219
PTZODA	45.8 (0.13)	54.2 (0.15)	0.336
PAZODA	100 (0.020)	-	0.136
TTACODA	80.3 (0.34)	19.7 (0.34)	0.320

Table 3.7. Ratios of prompt and delayed fluorescence in the 15% doped polymers and ΔE_{ST} of the monomers at 77 K.

^{*a*}Measured by the method of Dias *et al.* in the solid state.²⁵⁰ φ_p and φ_d are the quantum yields of prompt and delayed fluorescence, respectively.

^bMeasured as the energetic difference in the onsets of the prompt fluorescence and phosphorescence spectra of the monomers at 77 K in 2-methyltetrahydrofuran.

These data are consistent with the experimentally measured ΔE_{ST} values (<0.35 eV, Table 3.7). The singlet-triplet energy gap measured for these compounds is low enough to allow for efficient triplet to singlet upconversion via a rapid RISC process, albeit with somewhat lower rates for some compounds as these energy gaps are relatively large for TADF. The relative ratio of prompt to delayed fluorescence was also characterized to demonstrate the enhanced emission enabled by the TADF process. Upon cooling the emitter monomers used in this work to cryogenic temperatures (under inert atmosphere, in a poly(methyl methacrylate) matrix), delayed fluorescence rapidly quenches, but is replaced by extended, microsecond-long phosphorescence, demonstrated in Figure 3.18. The acridine based emitter, **ACRODA**, did not demonstrate significant phosphorescence even at 77 K. While a secondary emission process is observed for these materials at lower temperature, the TADF nature of the emission can again be confirmed by the reduction in emission intensity as temperature is decreased, as opposed to the increased emission intensity expected if this process were proceeding via a room-temperature phosphorescence (RTP) mechanism.

3.3.6 Electronic Properties of Doped Acrylic Polymers



Figure 3.19. Cyclic voltammograms of the donor-acceptor monomers measured at 2 mg mL⁻¹ in *o*-difluorobenzene.

The electronic properties of these polymers were then simulated using time-dependent density functional theory calculations at the B3LYP/6-31+G(d) level of theory, the results of which are summarized in Table 3.7. While these calculations predicted very low singlet-triplet energy gaps of <0.015 eV for all donor-acceptor monomers except for the **TTACODA** emitter (0.2 eV), delayed fluorescence was still observed with the slightly higher singlet triplet energy gaps measured experimentally. The HOMO and LUMO levels for the monomers calculated via this method showed similar trends to the energy levels measured via cyclic voltammetry. While the simulated and experimental bandgaps showed close similarities, there was a ~0.5 eV discrepancy between calculated and measured values. Cyclic voltammetry was used to directly observe the oxidation of the donor-acceptor monomers, measured in *o*-dichlorobenzene (Figure 3.19). Each donor acceptor monomer demonstrated reversible oxidation (**ACRODA** = 0.969 V, **PXZODA** =

0.893 V, **PTZODA** = 0.899 V, **PAZODA** = 0.358 V, and **TTACODA** = 0.700 V relative to Fc^{0/+}). The reduction wave observed for the unpolymerized monomers is likely due to electropolymerization or decomposition of the acrylate handle, however, even at 15% doping concentration in a polymer, it is difficult to differentiate the host oxidation or reduction process from that of the host monomer matrix. LUMO levels were therefore estimated using the band gap determined using the low energy absorption band edge combined with the HOMO estimated by referencing the above oxidations to ferrocene (Table 3.7).

3.3.7 Oxygen Sensing using TADF Acrylate Polymers



Figure 3.20. Illustration of pseudoaxial and pseudoequatorial conformers of PTZODA and their respective emission wavelengths.

Over the course of the preliminary photophysical characterization of these donor-acceptor emitters, it was noted that the phenothiazine-functionalized emitter, **PTZODA**, demonstrated dual emissive properties. This dual emission property has been observed in several other phenothiazine-based donor-acceptor emitters. The phenomenon is attributed to the multiple stable conformations that the sulfur bridge can be found in, a pseudoaxial conformation in which the sulfur atom is buckled out of plane and a psuedoequatorial conformation in which the phenothiazine donor is perpendicular to the third aryl ring (Figure 3.20).^{230,251,252} As both conformations are similar in stability, it is expected that ground state phenothiazine-functionalized compounds will exist in a

mix of these two conformations, dependent on any additional external factors that may favor one conformation over the other. In the case of a phenothiazine-functionalized donor-acceptor, it is proposed that these two conformations have substantially different fluorescent properties, with the pseudoequatorial conformation exhibiting efficient charge-transfer emission characterized by a broad emission profile centered around 516 nm, while the pseudoaxial conformation exhibits only fluorescence from the extended π -conjugated system, resulting in a higher energy emission at 396 nm and somewhat lower intensity emission. This property has been used for a variety of applications, specifically involving the synthesis of single-emitter white OLEDs.^{253,254}

In the case of this particular emitter, **PTZODA**, the lower energy emission arising from the charge-transfer emission from the pseudoequatorial conformation exhibits distinct TADF properties, but the higher energy peak from the pseudoaxial conformation does not participate in the delayed fluorescence emission. This means that when oxygen concentration is increased, the higher energy peak remains constant, but the charge-transfer emission will be quenched significantly. Furthermore, the lifetime of the TADF emission from this emitter is also quenched significantly upon exposure to oxygen. Using the constant emission intensity at 396 nm as an internal calibrant, the concentration of oxygen can be directly probed by comparing the ratio of these two peaks. This property was characterized fully to determine the utility of these compounds for ratiometric oxygen sensing both as an independent device and embedded in nanoparticles for oxygen sensing for imaging applications.



Figure 3.21. (a) Stern-Volmer plot comparing the ratio of emission intensity at 516 nm to emission intensity at 396 nm (I_{516}/I_{396}) at various partial pressures of O₂ for a film of poly(CzBA_{0.85}-*co*-PTZODA_{0.15}); (b) Fluorescence emission response of poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) to O₂ concentration. PF = prompt fluorescence.

The key property that enables this ratiometric sensing is the insensitivity of the fluorescent peak at 396 nm to oxygen. Using this peak as a reference, oxygen sensing can be achieved without requiring an additional reference dye. To demonstrate the utility of this compound as an oxygen sensor, a thin-film was prepared on a quartz slide by spin-casting a concentrated solution of poly(CzBA_{0.85}-co-PTZODA_{0.15}) polymer onto the substrate. When measured in the solid state using the same settings for each emission scan, a very small decrease in emission intensity is observed for the peak at 396 nm (<3% variation) that was attributed to photobleaching processes. A series of spectra was recorded over a variety of oxygen concentrations in nitrogen to quantify the fluorescent response of this emitter, ranging from 0% oxygen to 100% oxygen (Figure 3.21). When scaled to the peak at 396 to remove any error due to photobleaching, it was found that the intensity of the emission at 516 nm varied inversely with the oxygen concentration. However, it was also found that this oxygen sensitivity saturated at approximately 50% oxygen atmosphere, after which point the emission intensity did not decrease significantly. We found that this oxygenbased fluorescence quenching process could be modeled effectively by the Stern-Volmer equation: 255-257

$$\frac{R_0}{R} = 1 + K_{SV} * pO_2$$

Where R_0 and R are the fluorescence intensity ratios of the intensity at peak, 516 nm, scaled by the intensity of the fluorescent emission at 396 nm, under anaerobic and oxygenated atmospheres respectively. In this case, K_{SV} and pO_2 refer to the Stern-Volmer constant and the partial pressure of O₂ respectively. Below 50% oxygen concentration, there is a linear relationship ($R^2 = 0.97$) between R_0/R and pO_2 , plotted in Figure 3.21a, allowing us to extract a value K_{SV} of 0.0057 mmHg⁻¹. Using this K_{SV} value, one can directly convert any measured fluorescence response to a corresponding oxygen concentration over the response range of this material. While this model is only accurate up to approximately 50% oxygen concentration, this deviation from linearity is common when saturation is reached. It would be ideal to include oxygen sensing over a wider range; however, this compound does provide a linear response over the concentrations most commonly observed in biological systems.

3.3.8 Oxygen Sensing Polymer Dots



Figure 3.22. (a) Illustration of PDot nanostructures (green = poly(CzBA_{0.85}-*co*-PTZODA_{0.15}), blue = PSMA; (b) Image of a solution of poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) nanoparticles at 0.02 mg mL⁻¹ in water under illumination at 365 nm.

As this **poly(CzBA**_{0.85}-*co*-**PTZODA**_{0.15}) polymer demonstrated ratiometric oxygen sensing over a broad range of oxygen concentrations as a thin film, we sought to demonstrate the

scope of these oxygen sensing abilities by also measuring the oxygen response of this polymer doped into a polymer dot (PDot). PDots are emerging as highly-emissive, easily-modified probes for imaging applications, with many examples of PDots modified with antibodies and other tags for targeted imaging.^{258–260} PDots were prepared by coprecipitating a water soluble, amphiphilic polymer into vortexing water with the emissive material of choice, in this case: **poly(CzBA_{0.85}-***co***-PTZODA_{0.15})**. The particles generated then exhibit the properties of the emissive material chosen as well as any material properties granted by the polymer into which the emissive polymers are embedded (Figure 3.22).



Figure 3.23. (a) Absorbance and emission spectra for poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) PDots recorded at 0.02 mg mL⁻¹ in water; (b) NTA size distribution (green bars) and lognormal fit (black dotted trace) measured in water at 0.02 mg mL⁻¹.

It was therefore expected that PDots of **poly(CzBA**_{0.85}-*co*-**PTZODA**_{0.15}) should exhibit oxygen sensitivity similar to that of the films generated of the same polymer. Furthermore, by coprecipitating with an amphiphilic polymer, the PDots formed should also exhibit high water solubility, as demonstrated in Figure 3.22b. Typically PDots are composed of semiconducting polymers with fully conjugated backbones, however, side-chain functionalized polymers such as the ones we are working with improve processability of the resulting polymers while also increasing the tunability of the photophysical properties. Coprecipitation was performed using a

polystyrene/maleic anhydride copolymer (PS₁₁-*co*-MA₄, $M_n = 1700$) to generate PDots that are fully soluble in water at 0.02 mg mL⁻¹. The particles generated were characterized by dynamic light scattering (DLS) and nanoparticle tracking analysis (NTA) and were found to have average diameters of 71± 38 nm and 82 ± 38 nm by each method respectively, plotted in Figure 3.23. The fluorescence emission of the **PTZODA**_{0.15} polymer is largely unchanged when embedded in this polymeric matrix, demonstrating a similar ratio of low and high energy emission peaks as in the thin-film samples, with a minor enhancement in the charge-transfer peak at 516 nm that can be attributed to the difference in polarity between the neat polymer and the amphiphilic polymer matrix used for the PDots (Figure 3.23a).



Figure 3.24. (a) Emission intensity at λ_{max} (516 _{nm}) scaled to the emission intensity at 396 nm at various O₂ concentrations for poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) embedded in PDots; (b) Lifetime measurements for poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) PDots in O₂-saturated and N₂-saturated water; (c) Stern-Volmer plot recorded for poly(CzBA_{0.85}-*co*-PTZODA_{0.15}) PDots from 0 to 42 ppm O₂ in water, red fit line over the linear range (0 to 10.4 ppm), black fit line showing nonlinear response at high concentration O₂.

The response of these PDots to oxygen concentration was characterized in a similar fashion to the thin-films characterized in Section 3.2.6 (Figure 3.24). To measure the oxygen response in water, the ratio of oxygen to nitrogen was modulated by sparging a solution of **poly(CzBA_{0.85}-co-PTZODA_{0.15})** PDots with a series of oxygen/nitrogen blends. When plotted against R_0/R , a somewhat less linear relationship was observed, with significant nonlinearity at oxygen concentrations above 10.4 ppm oxygen. Concentrations lower than this can be modeled relatively accurately with a linear fit giving a $K_{SV} = 0.068$ ppm⁻¹ and R² = 0.90 over the oxygen 130 concentrations below 10.4 ppm, illustrated by the plot in Figure 3.24c. The emission quenching observed at higher oxygen concentrations is common when the quenching process nears saturation.²⁶¹ Besides just the emission change upon exposure to oxygen, a significant decrease in the fluorescence lifetime is observed upon exposure to O_2 , with the lifetime decreasing from 5.2 ms when in solution saturated with nitrogen to 29.4 µs in an oxygen-saturated environment. This lifetime modulation can be used to enable oxygen sensing using fluorescence lifetime imaging. The curved oxygen response curve may also be partially due to a range accessibilities for the emitters, with dyes located closer to the center of the PDots being less accessible to dissolved oxygen, giving a delayed or diminished oxygen response. Regardless, a mostly linear response was observed over the oxygen concentrations typically relevant in most biological systems, demonstrating the potential utility of this emitter as an oxygen sensor for imaging applications using both intensity and lifetime changes upon exposure to oxygen.

3.4 Conclusions

Using the Cu(0)-RDRP methods developed in Chapter 2, we have generated a series of doped copolymers for use as a single component emissive layer in a polymer-based OLED. This method uses mild conditions, low-cost catalysts, and relatively short reaction times while maintaining a high degree of control over polymer characteristics. By using a controlled radical polymerization method, we are able to control the molecular weight and polydispersity easily, allowing for a high degree of batch-to-batch reproducibility. Furthermore, this polymerization method is highly functional group tolerant and scalable, allowing easy access to multigram quantities of doped copolymer.

In this chapter, we expanded this polymerization method to include doped copolymers composed of a carbazole-based host monomer, **CzBA**, and a series of oxadiazole-based donor-acceptor acrylate monomers. We were able to clearly demonstrate that copolymers composed of an exiton-shuttling host and a series of novel emitter monomers would possess the photophysical properties of the emissive monomers even when only composed of a small portion of said dopant. First, a deep-blue fluorescent emitter was synthesized using an inexpensive *tert*-butyl functionalized diarylamine. The bulky alkyl groups on the arylamine donor improve the solubility of the acrylate monomer while minimizing side-reactivity at the aryl *para*- positions. This monomer was found to be highly scalable while providing high quantum yields in the solid state. Even though this compound only emits radiatively using singlet excitons, limiting its maximum electroluminescent efficiency, a proof-of-concept device was prepared to demonstrate the utility of this framework. We found that the electroluminescent device using this **tBuODA** doped polymer delivered acceptable external efficiencies, driving us to develop emitters with improved emissive properties.

Using a variety of donors and an oxadiazole acceptor, we were able to achieve TADF in a series of acrylate monomers with emissive colours from blue to orange. Furthermore, we noted that one of the monomers, **PTZODA**, exhibited dual emission that could be exploited to develop a ratiometric oxygen sensor. This emitter was demonstrated both in the solid state as well as embedded in a polymeric nanoparticle, lending itself to direct oxygen sensing for use in an optode or for use as an oxygen sensor for imaging applications. High quantum yield TADF emitters generated will be tested in electroluminescent devices in the future.

3.5 Experimental

3.5.1 General Considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. Host monomer CzBA was prepared according to procedures described in Chapter 2. Tetra-*p*-tolyl-9*H*-carbazole-3,6-diamine,²⁶² **3.1a**,²⁴¹ **3.1b**,²⁴¹ **3.2a**,⁶ methylphenazine,²⁴² and 3.4a²⁶³ were prepared according to literature procedures. Dimethylacetamide (DMAc) was distilled, then degassed and stored under an N₂ atmosphere. CH₂Cl₂ was freshly distilled from P₂O₅ prior to use. Et₃N was dried by distillation on CaH₂ onto activated molecular sieves then degassed and stored under an N₂ atmosphere. The ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with chloroform-d (CDCl₃) or dichloromethane- d_2 (CD₂Cl₂) as the solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; toluene was used as the solvent and spectra obtained at concentrations of 0.01 mg mL⁻¹. Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization. Molecular weights by NMR were estimated by comparing the integration of the broad peak from the benzylic CH₂ on each monomer unit (approximately 4.5 to 5.5 ppm in deuterated chloroform) to the integration of the ethyl CH₂ peak

on our EBIB (ethyl α -bromoisobutyrate) initiator, a small peak at approximately 4.0 ppm in deuterated chloroform.

3.5.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.44 Hz. Samples were prepared by spincoating solutions of polymer or small molecule blends onto freshly cleaved mica at 2000 rpm for 30 s at concentrations of 10 mg mL⁻¹. For best results, 2:1 chloroform/chlorobenzene was used as the solvent for solutions. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al probes, with typical resonance frequency f = 160 kHz and spring constant k = 5 N/m.

3.5.3 Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 -2 mg mL^{-1} using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right-angle and low angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (*dn/dc*) were determined using 100% mass recovery methods from Malvern OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

3.5.4 Thermal Analysis

Thermal degradation studies were performed using a NETZSCH TG 209F1 Libra instrument. Samples were placed in an Al₂O₃ crucible and heated at a rate of 10 °C min⁻¹ from 25 to 800 °C under a flow of nitrogen (50 mL min⁻¹). Glass transition temperatures were determined using differential scanning calorimetry (DSC) on a NETZSCH DSC 214 Polyma instrument. The polymer samples were placed in an aluminum pan and heated from 25 to 200 °C at 10 °C min⁻¹ under a flow of nitrogen for 3 heating/cooling cycles.

3.5.5 Electrochemical Methods

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene);²¹⁷ counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene. Experiments were run at a scan rate of 50 mV s⁻¹ in dry degassed electrolyte solution with ~4 mg mL⁻¹ of analyte. The HOMO level was found by referencing the oxidation peak to ferrocene and using the known HOMO of ferrocene (–4.80 eV) to calculate HOMO of CzBA and of the dopant monomer in **poly(CzBA**0.75-*co*-**tBuODA**0.25). The LUMO level was calculated by subtracting the optical energy bandgap (Eg) from the HOMO value determined above. Eg was determined from the low-energy UV-absorption band edge. The same method was used to measure the HOMO of the dopant monomer in the 15% doped polymers **poly(CzBA**0.85-*co*-**ACRODA**0.15), **poly(CzBA**0.85-*co*-**PXZODA**0.15), **poly(CzBA**0.85-*co*-**PXZODA**0.15), **poly(CzBA**0.85-*co*-**PXZODA**0.15), **poly(CzBA**0.85-*co*-**PXZODA**0.15),

PAZODA_{0.15}), and **poly**(**CzBA**_{0.85}-*co*-**TTACODA**_{0.15}). Unpolymerized dopant monomers (**ACRODA**, **PXZODA**, **PTZODA**, **PAZODA**, and **TTACODA**) were also characterized via the same procedure to confirm that polymerization did not drastically modify HOMO levels. The LUMO level was calculated by subtracting the optical energy bandgap (E_g) from the HOMO value determined above. E_g was determined from the low-energy UV-absorption band edge.

3.5.6 Density Functional Theory

Calculation for **tBuODA** were performed using the Gaussian 09 software package.²¹⁸ Quantum-mechanical calculations for **ACRODA**, **PXZODA**, **PTZODA**, **PAZODA**, and **TTACODA** were performed using the Gaussian 16 Rev. B.01 computational package using default settings.²⁶⁴ Ground state geometries and energies were calculated at the B3LYP/6-31+g(d) level of theory. To simulate electronic properties of these polymeric materials, analogous versions of each monomer were calculated in which the vinyl end group of the acrylate functionality was replaced with a *sec*-butyl group to more closely mimic the structure of the corresponding polymer chain. If this approximation is not made, the LUMO lies on the acrylate moiety in all cases.

For ACRODA, PXZODA, PTZODA, PAZODA, and TTACODA, geometries were optimized to a minimum and frequency calculations were performed at the same level of theory to verify the absence of imaginary frequencies. Vertical excitation (absorption) energies of the first singlet and triplet excited states were calculated using the Tamm-Dancoff approximation (TDA) scheme of time-dependent density functional theory (TDDFT).

3.5.7 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.44 Hz. Samples were prepared by spincoating solutions of polymer or small molecule blends onto freshly cleaved mica at 2000 rpm for 30 s at concentrations of 10 mg mL⁻¹. For best results, 2:1 chloroform/chlorobenzene was used as the solvent for solutions. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al probes, with typical resonance frequency f = 160 kHz and spring constant k = 5 N/m.

3.5.8 Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 -2 mg mL^{-1} using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right-angle and low angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (*dn/dc*) were determined using 100% mass recovery methods from Malvern OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

3.5.9 PDot Synthesis

Nanoparticles were synthesized by the nanoprecipitation method.²⁶⁵ (Polymer) (100 μ L of a 1 mg/mL stock in THF) and 10 μ L of PSMA (2 mg/mL stock in THF) were diluted to 1 mL with 137

THF to final concentrations of 100 μ g/mL and 20 μ g/mL respectively. This precursor solution was sonicated for ~30 s to ensure complete mixing. The precursor solution was injected by syringe into 10 mL of ultrapure water under sonication. The solution was sonicated for an additional 2 min. THF was removed and the solution concentrated by partial rotary evaporation until *ca*. 5 mL of solution remained. The solution was passed through a 0.22 μ m syringe filter to remove any aggregates.

3.5.10 Nanoparticle Tracking Analysis (NTA)

Nanoparticle size and size distribution were determine by NTA (NanoSight NS300, Malvern Panalytical, Malvern, UK). (Nanoparticle) samples were diluted 100-fold in 0.22 µm filtered ultrapure water prior to measurements. Measurements were recorded in scattering mode using a 488 nm laser. Raw data were fit with a lognormal function to determine mean and mode particle sizes and the standard deviation of the distribution.

3.5.11 Dynamic Light Scattering (DLS)

Intensity-weighted DLS measurements performed using a NanoBrook Omni particle size analyzer (Brookhaven Instruments Corporation, Holtsville, NY) using a 659 nm laser wavelength.

3.5.12 Spectroscopic Measurements for Nanoparticle Solutions

Absorbance spectra and fluorescence emission and excitation spectra were recorded using an M1000 multifunction fluorescence plate reader (Tecan, Morrisville, NC). Emission spectra were recorded between 320–850 nm with an excitation wavelength of 296 nm and monochromator bandwidths of 5 nm. Excitation spectra were recorded between 300-580 nm with an emission wavelength of 600 nm and 5 nm monochromator bandwidth.

3.5.13 Device fabrication

Thin films of PEDOT:PSS were prepared by spin-casting the precursor solution onto prewashed patterned ITO-glass substrates. PEDOT:PSS (Clevios PVP AI 4083) solution was spincast in air at 4000 r.p.m. for 60 s followed by annealing in air at 150 °C for 30 min. For the deposition of the TFB layer, TFB/Toluene (20 mg mL⁻¹) solution was spin-cast on the top of the PEDOT:PSS layer at 3000 r.p.m. for 45 s, and annealed at 150 °C for 30 min in a nitrogen-filled glovebox. The polymer emissive layer **poly(CzBA**_{0.75}-*co*-tBuODA_{0.25}) in chlorobenzene (5-30 mg mL⁻¹) was spin-cast on the top of the TFB layer at 3000 r.p.m. for 45 s, and annealed at 100 °C for 10 min in a nitrogen-filled glovebox. TPBi (60 nm) and LiF/Al electrodes (1 nm/150 nm) were deposited using a Kurt J. Lesker LUMINOS Cluster Tool evaporation system through a shadow mask under a high vacuum of less than 10^{-4} Pa. The device active area was 6.14 mm² as defined by the overlapping area of the ITO and Al electrodes

3.5.14 Device characterization

The luminance-current density-voltage characteristics were collected by using a HP4140B picoammeter. The absolute EL power spectra of the devices were collected using an integrating sphere and an Ocean Optics USB4000 spectrometer by the mounting of the devices on the wall of the integrating sphere. The EQEs were then calculated through the measured absolute power spectra and the current density.

3.5.15 Synthetic Procedures

General Procedure A: Conversion of Aryl Aldehydes to Aryl Nitriles

Aryl nitriles were prepared according to a modified literature procedure.^{3,238} To a Teflon capped 20 mL glass vial equipped with a magnetic stir bar was added 2.0 mmol of aryl aldehyde, 0.42 g (6.0 mmol, 3.0 equiv) of NH₂OH·HCl, and 10 mL of *N*-methyl pyrrolidinone. The reaction was conducted under air. The sealed 20 mL vial was heated to 120 °C for 24 hours. Upon completion, the reaction was cooled to room temperature then diluted with 100 mL of ethyl acetate. This organic mixture was extracted three times with distilled water (3 x 50 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was then purified by column chromatography on silica gel using dichloromethane followed by recrystallization to yield aryl nitrile nearly quantitatively.

General Procedure B: Conversion of Aryl Nitriles to Aryl Tetrazoles

Aryl tetrazoles were prepared according to a modified literature procedure.²³⁸ To a Teflon capped 40 mL glass vial equipped with a magnetic stir bar was added 2.0 mmol of aryl nitrile, 2.1 g (32 mmol, 16 equiv) of NaN₃, 1.7 g (32 mmol, 16 equiv) of NH₄Cl, and 10 mL of DMF. The reaction was conducted under air. The sealed 40 mL vial was heated to 130 °C for 24 hours. Upon completion, the reaction was cooled to room temperature and filtered to remove precipitated salts. The collected salts were rinsed with ethyl acetate (50 mL) then discarded. The organic filtrate was diluted with 50 mL of ethyl acetate then washed three times with distilled water (3 x 50 mL), dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude product was either used as isolated or purified slightly over a short silica plug (ethyl acetate) to remove residual salts.

General Procedure C: Conversion of Aryl Tetrazoles to Aldehyde-Functionalized Oxadiazoles

Aldehyde functionalized oxadiazoles were prepared according to a modified literature procedure.²⁴¹ To a Teflon capped 40 mL glass vial equipped with a magnetic stir bar was added 2.0 mmol of aryl tetrazole, 0.30 g (2.0 mmol, 1.0 equiv) of 4-formylbenzoic acid, 0.41 g (2.0 mmol, 1.0 equiv) of N,N'-dicyclohexylcarbodiimide (DCC), and 10 mL of toluene. The reaction was conducted under air. The sealed 40 mL vial was heated to 105 °C for 24 hours. Upon completion, the reaction was cooled to room temperature. Once cool, 10 mL of dichloromethane was added to the crude reaction to precipitate the dicyclohexylurea (DCU) byproduct. The crude reaction was chilled to -20 °C in the freezer for 1 hour followed by filtration of the crude reaction to remove the DCU byproduct. The organic filtrate was then concentrated *in vacuo*. The crude residue was purified by column chromatography over silica gel using a gradient from pure dichloromethane to 10% ethyl acetate in dichloromethane to yield pure oxadiazole aldehyde product.

General Procedure D: Sodium Borohydride Reduction of Aryl Aldehydes to Benzyl Alcohols

Prepared according to literature procedure.²²³ Pure aldehyde-functionalized starting material (1.0 equiv) was added to a round bottom flask and dissolved in CH₂Cl₂. Once all starting material was dissolved, one part EtOH was added for every three parts CH₂Cl₂ to dissolve the solid. Solid NaBH₄ (1.2 equiv) was then added to the solution and the reaction was monitored by TLC. When no starting material remained by TLC (approximately 24 h) the reaction was quenched by addition of saturated NH₄Cl in water followed by extraction using water and CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. The crude residue was then purified on a short silica column.

General Procedure E: Acrylation of Benzyl Alcohols

Prepared according to literature procedure.²⁴⁰ The benzyl alcohol-functionalized starting material (1.0 equiv) and a magnetic stir bar were added to a flame dried round bottom flask which was evacuated and backfilled three times with N₂. CH₂Cl₂ was then added to dissolve the solid, triethylamine (1.3 equiv) was added with stirring. The reaction flask was cooled to 0 °C in an ice bath for 30 minutes, then acryloyl chloride (1.2 equiv) was added to the reaction mixture dropwise over 10 minutes. The reaction was then protected from light using foil and allowed to stir in the ice bath until completed, monitoring via TLC (typically less than 2 hours). The reaction was quenched by addition of water and extracted with CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo* without heating. The crude residue was purified on a short silica column, taking care to elute the product as quickly as possible to avoid decomposition on silica.

General Procedure for Cu(0)-RDRP

To a 4 mL vial under N₂ atmosphere capped with a Teflon-lined lid and equipped with a magnetic stir bar was added host monomer (**CzBA**), (0.20 g, 0.62 mmol, 61 equiv), 39 μ L of a solution of ethyl α -bromoisobutyrate (**EBIB**) in dimethylacetamide (DMAc) (C_{EBIB} = 50 mg mL⁻¹ ; **EBIB**: 2.0 mg, 0.010 mmol, 1.0 equiv), and 39 μ L of a solution of CuBr₂/ Me₆TREN in DMAc (C_{Cu} = 3.8 mg mL⁻¹ ; CuBr₂: 0.14 mg, 6.6 × 10⁻⁴ mmol, 0.065 equiv; Me₆TREN: 0.16 mg, 6.8 × 10⁻⁴ mmol, 0.068 equiv). The total polymerization volume was kept to 1.0 mL of solvent, so 0.92 mL of DMAc was added to this mixture. To add emitter comonomers, dopants were added in the desired weight percent, removing a corresponding mass of host monomer from the reaction mixture to maintain a total monomer mass of 0.20 g. The amount of initiator and copper catalyst

was adjusted to maintain a target molecular weight of 20 kDa as well as target catalyst loadings described above.

The mixture was stirred at room temperature for 10 minutes in a nitrogen atmosphere glove box to allow all reagents to fully dissolve. A 1.0 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried in vacuo and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. The polymerization was allowed to proceed for 12 hours before a 25 μ L aliquot was removed and diluted with CDCl₃ to characterize conversion by NMR. Once conversion passed approximately 90%, the polymerization was quenched by addition of the reaction mixture to 50 mL of deionized water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO4 and concentrated in vacuo. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. The purified polymer was dissolved in CH₂Cl₂ and precipitated once more into methanol to remove any residual inhibitor from the preparatory SEC purification and collected by filtration to yield purified polymer.



4-(*tert*-butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(4-(5-(4-iodophenyl)-1,3,4-oxadiazol-2yl)phenyl)aniline (3.1c)

Prepared according to a modified literature procedure.²⁴¹ Compound **3.1b** (2.0 g, 4.7 mmol, 1.0 equiv), 4-iodobenzoic acid (1.17 g, 4.7 mmol, 1.0 equiv), and N,N'-dicyclohexylcarbodiimide (0.97 g, 4.7 mmol, 1.0 equiv) were added to a 40 mL vial equipped with a Teflon stir bar and a Teflon screw top. To this vial, 20 mL of toluene was added. The vial was then sealed and heated to 140 °C for 3 h. Once complete, the reaction was allowed to cool to room temperature. Once cool, the reaction mixture was diluted with 20 mL of DCM and cooled to -20 °C in the freezer. The crude reaction was then filtered over a paper filter. The solids were washed with 50 mL of CH₂Cl₂. The filtrate was collected and concentrated *in vacuo*. The crude residue was then purified on a short silica column using CH₂Cl₂. Yield 2.4 g, 81%.

¹H NMR (400 MHz, CDCl₃): δ 8.00 – 7.71 (m, 6H), 7.36 (d, J = 7.8 Hz, 4H), 7.13 (d, J = 7.8 Hz, 4H), 7.09 (d, J = 8.4 Hz, 2H) 1.33 (s, 18H) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 165.0, 163.3, 151.4, 147.5, 143.8, 138.3, 128.1, 128.0, 126.4, 125.4, 123.7, 112.0, 114.8, 98.1, 34.5, 31.4 ppm.

HRMS (EI) *m/z*: [M+Na]⁺ calcd. for [C₃₄H₃₄IN₃ONa]⁺, 650.1644; found, 650.1648; difference: 0.6 ppm.



4'-(5-(4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4carbaldehyde (3.1d)

Prepared according to a modified literature procedure.²³⁹ Compound **3.1c** (1.5 g, 2.4 mmol, 1.0 equiv), 4-formylphenylboronic acid (0.72 g, 4.8 mmol, 2.0 equiv), $Pd_2(dba)_3$ (0.11 g, 0.12 mmol, 0.050 equiv, SPhos (0.20 g, 0.48 mmol, 0.20 equiv), and K_3PO_4 (1.0 g, 4.8 mmol, 2 equiv) were added to a 250 mL three-neck round-bottom flask equipped with a Teflon stir bar and a reflux condenser. The flask was evacuated and back-filled with nitrogen three times with N₂. In a separate 250 mL round-bottom flask, 120 mL of toluene and 4.0 mL of water were combined and sparged with N₂ for 30 mins. Once degassed, the mixture was transferred to the reaction vessel via cannula. The reaction mixture was then stirred and heated to 110 °C for 48 h. Once complete, the reaction was cooled to room temperature, diluted with 150 mL of water, and extracted to CH₂Cl₂ (3 x 100 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo*. 145

The crude residue was then purified on a short silica column using 20% ethyl acetate in hexane. Yield 1.3 g, 91%.

¹**H NMR (400 MHz, CDCl₃):** δ 10.00 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.8 (d, *J* = 8.0 Hz, 2H), 7.72 (t, *J* = 8.8 Hz 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.07 – 6.95 (m, 6H), 1.26 (s, 18H) ppm.

¹³C{¹H} (101 MHz, CDCl₃): δ 191.8, 165.0, 163.5, 151.4, 147.5, 145.8, 143.8, 142.5, 135.8, 130.4, 128.0, 127.8, 127.4, 126.5, 125.4, 124.1, 120.9, 112.0, 114.9, 34.5, 31.4. ppm.

HRMS (EI) m/z: [M+H]⁺ calcd. for [C₄₁H₄₀N₃O₂]⁺, 606.3121; found, 606.3115; difference: - 1.0 ppm.


(4'-(5-(4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4yl)methanol (3.1e) Prepared according to general procedure D using 3.1d (1.3 g, 2.2 mmol, 1.0 equiv) as a starting material. The crude residue was purified on a short silica column using 25% ethyl acetate in hexane. Yield 1.1 g, 85%.

¹**H NMR (400 MHz, CDCl₃):** δ 8.15 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.73 (d, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.9 Hz, 4H), 7.10 (m, 6H), 4.77 (s, 2H), 1.34 (s, 18H).

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 151.3, 147.5, 143.8, 143.8, 141.0, 139.2, 129.6, 128.0, 127.6, 127.3, 127.2, 126.4, 125.4, 124.4, 123.0, 120.1, 118.1, 115.0, 64.9, 34.5, 31.4 ppm.

HRMS (EI) *m/z*: [M+Na]⁺ calcd. for [C₄₁H₄₁N₃O₂Na]⁺, 630.3096; found, 630.3106; difference: 1.6 ppm.



(4'-(5-(4-(bis(4-(*tert*-butyl)phenyl)amino)phenyl)-1,3,4-oxadiazol-2-yl)-[1,1'-biphenyl]-4yl)methyl acrylate (tBuODA) Prepared according to general procedure E using 3.1e (0.90 g, 1.48 mmol, 1.0 equiv) as a starting material. The crude residue was purified on a short silica column using 5% ethyl acetate in CH₂Cl₂, taking care to elute the product as quickly as possible to avoid decomposition on silica. Yield 0.76 g, 78%.

¹**H NMR (400 MHz, CDCl₃):** δ 8.18 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.33 (d, J = 7.8 Hz, 4H), 7.17 – 7.02 (m, 6H), 6.48 (d, J = 17.3 Hz, 1H), 6.20 (dd, J = 17.4, 10.4 Hz, 1H), 5.88 (d, J = 10.3 Hz, 1H), 5.27 (s, 2H), 1.34 (d, J = 1.8 Hz, 18H) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.0, 164.8, 163.7, 151.3, 147.4, 143.8, 143.5, 139.9, 135.8, 131.3, 128.9, 128.3, 128.0, 127.7, 127.4, 127.3, 126.4, 125.4, 123.2, 120.1, 115.1, 66.0, 34.5, 31.4 ppm.

HRMS (ESI) *m*/*z*: [M+H]⁺ calcd. for [C₄₄H₄₄N₃O₃]⁺, 662.3383; found, 662.3385; difference: 0.3 ppm.



4-(9,9-dimethylacridin-10(9*H*)-yl)benzonitrile (3.2b)

Prepared according to general procedure A using **3.2a** as a starting material. Purified on silica gel using a gradient from hexanes to CH₂Cl₂. Recrystallized from hexanes/CH₂Cl₂. Yield 84%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.58 – 7.43 (m, 4H), 7.08 – 6.94 (m, 4H), 6.39 – 6.24 (m, 2H), 1.69 (s, 6H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 146.2, 140.2, 134.8, 131.6, 131.1, 126.5, 125.5, 121.7, 118.4, 114.9, 111.4, 36.2, 30.9 ppm.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for ([C₂₂H₁₈N₂]+H)⁺, 311.1548; found, 311.1547; difference: - 0.32 ppm.



10-(4-(1*H*-tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (3.2c)

Prepared according to general procedure B using **3.2b** as a starting material. Purified on a short silica gel plug using EtOAc to remove residual salts and used without further characterization. Yield is quantitative.



4-(5-(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (3.2d)

Prepared according to general procedure C using **3.2c** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to 10% EtOAc in CH_2Cl_2 . Recrystallized from hexanes and CH_2Cl_2 . Yield 62%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.14 (s, 1H), 8.43 (d, *J* = 8.5 Hz, 2H), 8.37 (d, *J* = 8.3 Hz, 2H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.49 (dd, *J* = 7.4, 1.9 Hz, 2H), 7.05 – 6.93 (m, 5H), 6.32 (dd, *J* = 7.8, 1.6 Hz, 2H), 5.30 (s, 1H), 1.71 (s, 6H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 191.2, 164.8, 163.9, 145.2, 140.4, 138.4, 132.1, 130.7, 130.4, 129.7, 128.8, 127.6, 126.5, 125.5, 123.2, 121.2, 114.2, 36.1, 31.2 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₃₀H₂₃N₃O₂]^{+•}, 457.1790; found, 457.1793; difference: -0.52 ppm.



(4-(5-(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (3.2e) Prepared according to general procedure D using 3.2d as a starting material. Purified on silica gel using a gradient from CH₂Cl₂ to 10% EtOAc in CH₂Cl₂. Yield 80%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.41 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.2 Hz, 2H), 7.56 (dd, *J* = 11.3, 8.3 Hz, 5H), 6.98 (pd, *J* = 7.2, 1.7 Hz, 5H), 6.32 (dd, *J* = 7.9, 1.6 Hz, 2H), 4.84 (s, 2H), 1.71 (s, 6H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 145.0, 144.7, 140.5, 132.1, 130.5, 129.7, 129.6, 127.4, 127.3, 126.5, 125.4, 123.6, 123.0, 121.1, 114.2, 64.7, 36.1, 31.2, 31.0 ppm.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for ([C₃₀H₂₅N₃O₂]+H)⁺, 460.2025; found, 460.2024; difference: -0.22 ppm.



4-(5-(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate(ACRODA)

Prepared according to general procedure E using **3.2e** as a starting material. Purified on silica gel in 20:1 CH₂Cl₂:EtOAC. Yield 88%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.41 (d, *J* = 8.5 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 2H), 7.63 – 7.39 (m, 6H), 6.98 (pd, *J* = 7.2, 1.9 Hz, 4H), 6.50 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.32 (dd, *J* = 7.8, 1.7 Hz, 2H), 6.27 – 6.17 (m, 1H), 5.91 (dd, *J* = 10.5, 1.4 Hz, 1H), 5.31 (s, 2H), 1.71 (s, 6H) ppm.

¹³C{¹H} (101 MHz, Chloroform-*d*): δ 165.9, 164.6, 164.2, 144.8, 140.5, 140.0, 132.1, 131.6, 130.5, 129.6, 128.6, 128.0, 127.3, 126.5, 125.4, 123.6, 121.1, 115.3, 114.1, 65.5, 36.1, 31.2 ppm.

HRMS (ESI) *m*/*z*: [M]^{+•} calcd for [C₃₃H₂₇N₃O₃]^{+•}, 513.2052; found, 513.2049; difference: - 1.0 ppm.



4-(10*H*-phenoxazin-10-yl)benzonitrile (3.3b)

Prepared according to modified literature procedure.²³² To a 250 mL round bottom flask was added 2.0 grams of phenoxazine (11 mmol, 1.0 equiv), 12.0 grams of K₃PO₄ (55 mmol, 5.0 equiv), and 170 mL of dimethylformamide. This mixture was heated to 150 °C, then 2.7 grams of 4-fluorobenzonitrile (22 mmol, 2.0 equiv) was added. The reaction was stirred at 150 °C overnight, cooled to room temperature, then filtered over celite. The celite was rinsed 3 times with 50 mL of ethyl acetate, then the filtrate was concentrated in vacuo. The resulting residue was purified on silica gel using a gradient from hexane to CH_2Cl_2 to yield 3.0 grams of pure **3.3b**, yield 97%. Characterization data matches literature values.²⁶⁶

¹**H NMR (400 MHz, Benzene-***d*₆**):** δ 7.28 (t, J = 1.2 Hz, 4H), 7.03 (d, J = 8.4 Hz, 1H), 6.88 (dd, J = 7.8, 1.5 Hz, 2H), 6.67 – 6.62 (m, 2H), 6.62 – 6.53 (m, 4H), 5.76 (dd, J = 8.0, 1.5 Hz, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆) δ: 144.5, 143.1, 134.6, 133.8, 131.6, 123.6, 122.5, 118.1, 116.2, 113.7, 112.5 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₁₉H₁₂N₂O]^{+•}, 284.0950; found, 284.0957; difference: - 0.66 ppm.



10-(4-(1*H*-tetrazol-5-yl)phenyl)-10*H*-phenoxazine (3.3c)

Prepared according to general procedure B using **3.3b** as a starting material. Purified on a short silica gel plug using EtOAc to remove residual salts and used without further characterization. Yield is quantitative.



4-(5-(4-(10H-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (3.3d)

Prepared according to general procedure C using **3.3c** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to 5% EtOAc in CH_2Cl_2 . Recrystallized from hexanes and CH_2Cl_2 . Yield 84%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.03 (s, 1H), 8.28 (dd, J = 17.6, 8.4 Hz, 4H), 7.98 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 6.65 – 6.50 (m, 6H), 5.89 (dd, J = 7.9, 1.4 Hz, 2H) ppm. 154 ¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 191.2, 164.6, 163.9, 144.0, 142.8, 138.4, 133.7,
131.9, 130.3, 129.9, 128.7, 127.6, 123.5, 123.3, 122.0, 115.8, 113.3 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₂₇H₁₇N₃O₃]^{+•}, 431.1270; found, 431.1273; difference: -0.68 ppm.



(4-(5-(4-(10*H*-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (3.3e)

Prepared according to general procedure D using **3.3d** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to 10% EtOAc in CH_2Cl_2 . Yield 74%.

¹**H NMR (400 MHz, Benzene-***d*₆**):** δ 8.20 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.01 (d, J = 8.2 Hz, 2H), 6.93 – 6.86 (m, 2H), 6.64 (m, 6H), 6.02 (d, J = 8.3 Hz, 2H), 4.35 (d, J = 4.6 Hz, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 165.0, 163.8, 146.2, 145.9, 144.7, 144.1, 141.5, 134.9,
131.5, 129.8, 127.2, 127.2, 123.7, 121.8, 116.0, 113.8, 64.2 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₂₇H₁₉N₃O₃]^{+•}, 433.1426; found, 433.1434; difference: -1.69 ppm.



4-(5-(4-(10H-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (PXZODA)

Prepared according to general procedure E using **3.3e** as a starting material. Purified on silica using a gradient from CH_2Cl_2 to 10% EtOAc in CH_2Cl_2 . Yield 82%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.28 (d, J = 8.3 Hz, 2H), 8.08 (d, J = 8.3 Hz, 2H), 7.58 – 7.40 (m, 4H), 6.66 – 6.50 (m, 6H), 6.40 (dd, J = 17.3, 1.4 Hz, 1H), 6.12 (dd, J = 17.3, 10.4 Hz, 1H), 5.89 (d, J = 7.9 Hz, 2H), 5.81 (dd, J = 10.4, 1.4 Hz, 1H), 5.20 (s, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 165.8, 164.6, 164.0 144.0, 142.5, 140.0, 133.7, 131.8, 131.6, 129.7, 128.6, 128.0, 127.3, 123.9, 123.6, 123.3, 121.9, 115.8, 113.3, 65.5 ppm.
HRMS (ESD *m/z*: [M]^{+•} calcd for [CarHuzNaOa]^{+•} 487 1532; found 487 1542; difference: -

HRMS (ESI) m/z: [M]^{+•} calcd for [C₂₇H₁₇N₃O₃]^{+•}, 487.1532; found, 487.1542; difference: -1.99 ppm.



4-(10*H*-phenothiazin-10-yl)benzonitrile (3.4b)

Prepared according to general procedure A using **3.4a** as a starting material. Purified on silica gel using a gradient from hexanes to CH_2Cl_2 . Recrystallized from hexanes/ CH_2Cl_2 . Yield 55%. ¹H and ¹³C{¹H} NMR matches literature data.²⁶⁷

HRMS (ESI) m/z: $[M]^{+\bullet}$ calcd for $[C_{19}H_{12}N_2S]^{+\bullet}$, 300.0721; found, 307.0729; difference: - 2.74 ppm.



10-(4-(1*H*-tetrazol-5-yl)phenyl)-10*H*-phenothiazine (3.4c)

Prepared according to general procedure B using **3.4b** as a starting material. Purified on a short silica gel plug using EtOAc to remove residual salts and used without further characterization. Yield is quantitative.



4-(5-(4-(10*H*-phenothiazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (3.4d)

Prepared according to general procedure C using **3.4c** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to 5% EtOAc in CH_2Cl_2 . Recrystallized from hexanes and CH_2Cl_2 . Yield 92%.

¹**H NMR (400 MHz, Benzene**-*d*₆): δ 9.66 (s, 1H), 8.00 (d, J = 8.5 Hz, 4H), 7.56 (d, J = 8.3 Hz, 2H), 7.17 (dd, J = 7.6, 1.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.89 (dd, J = 7.9, 1.6 Hz, 2H), 6.81 (dd, J = 7.5, 1.3 Hz, 2H), 6.67 (dd, J = 8.1, 1.3 Hz, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 190.4, 164.8, 163.6, 146.4, 143.3, 138.4, 130.0, 129.2, 129.0, 128.1, 127.9, 127.2, 126.7, 125.4, 124.6, 120.9, 120.8 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₂₇H₁₇N₃O₂S]^{+•}, 447.1041; found, 447.1053; difference: - 2.54 ppm.



(4-(5-(4-(10*H*-phenothiazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (3.4e)

Prepared according to general procedure D using **3.4d** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to EtOAc in CH_2Cl_2 . Yield 73%.

¹**H NMR (400 MHz, Benzene-***d*₆**):** δ 8.07 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.6 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 4H), 7.04 (dd, J = 7.6, 1.6 Hz, 2H), 6.76 (td, J = 7.7, 1.6 Hz, 2H), 6.67 (td, J = 7.5, 1.3 Hz, 2H), 6.44 (dd, J = 8.1, 1.3 Hz, 2H), 5.43 (s, 1H) ppm.

¹³C{¹H} NMR data could not be obtained due to the poor solubility of this compound in many common solvents.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₂₇H₁₉N₃O₂S]^{+•}, 449.1198; found, 449.1206; difference: - 1.68 ppm.



4-(5-(4-(10*H*-phenothiazin-10-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (PTZODA)

Prepared according to general procedure E using **3.4e** as a starting material. Purified on silica using 30:1 CH₂Cl₂:EtOAc. Yield 62%.

¹**H NMR (400 MHz, Benzene-***d*₆): δ 7.95 (dd, J = 29.7, 8.5 Hz, 4H), 7.11 (d, J = 8.1 Hz, 2H), 7.04 (dd, J = 7.6, 1.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.77 (td, J = 7.8, 1.6 Hz, 2H), 6.68 (td, J = 7.5, 1.3 Hz, 2H), 6.47 (dd, J = 8.1, 1.3 Hz, 2H), 6.32 (dd, J = 17.3, 1.5 Hz, 1H), 5.98 (dd, J = 17.3, 10.4 Hz, 1H), 5.27 (dd, J = 10.4, 1.5 Hz, 1H), 4.94 (s, 2H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 165.4, 164.3, 164.3, 145.5, 143.6, 139.9, 131.0, 129.1, 128.8, 128.1, 127.9, 127.2, 127.2, 126.9, 125.3, 124.4, 124.2, 122.0, 119.7, 65.5 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₃₀H₂₁N₃O₃S]^{+•}, 503.1304; found, 503.1306; difference: - 0.37 ppm.



4-(10-methylphenazin-5(10H)-yl)benzonitrile (3.5b)

Prepared according to modified literature procedure.²³² To a 500 mL round bottom flask was added 2.5 grams of *N*-methylphenazine (12 mmol, 1.0 equiv), 13 grams of K₃PO₄ (60 mmol, 5 equiv), and 0.23 L of dimethylformamide. This mixture was heated to 150 °C, then 3.0 grams of 4-fluorobenzonitrile (24 mmol, 2.0 equiv) was added. The reaction was stirred at 150 °C overnight, cooled to room temperature, then filtered over celite. The celite was rinsed 3 times with 50 mL of ethyl acetate, then the filtrate was concentrated in vacuo. The resulting residue was purified on silica gel using a gradient from hexane to CH₂Cl₂ to yield 1.5 grams of pure **3.5b**, yield 40%.

¹**H NMR (400 MHz, Benzene-***d*₆): δ 6.93 (d, J = 8.3 Hz, 2H), 6.81 – 6.70 (m, 4H), 6.57 (t, J = 7.6 Hz, 2H), 6.24 (d, J = 7.9 Hz, 2H), 6.12 (d, J = 7.8 Hz, 2H), 2.47 (s, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 146.8, 139.6, 135.4, 133.9, 125.2, 123.7, 120.8, 118.4, 117.5, 112.2, 108.8, 31.5 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₂₀H₁₅N₃]^{+•}, 297.1266; found, 297.1271; difference: 1.74 ppm.



5-(4-(1*H*-tetrazol-5-yl)phenyl)-10-methyl-5,10-dihydrophenazine (3.5c)

Prepared according to general procedure B using **3.5b** as a starting material. Purified on a short silica gel plug using EtOAc to remove residual salts and used without further characterization. Yield is quantitative.



4-(5-(4-(10-methylphenazin-5(10H)-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzaldehyde (3.5d) Prepared according to general procedure C using **3.5c** as a starting material. Purified on silica gel using a gradient from CH₂Cl₂ to 5% EtOAc in CH₂Cl₂. Recrystallized from hexanes and CH₂Cl₂. Yield 66%.

¹**H NMR (400 MHz, Benzene**-*d*₆): δ 9.55 (s, 1H), 7.91 (dd, J = 11.7, 7.8 Hz, 4H), 7.46 (d, J = 7.9 Hz, 2H), 7.12 – 7.06 (m, 2H), 6.74 (t, J = 7.7 Hz, 2H), 6.57 (t, J = 7.6 Hz, 2H), 6.23 (d, J = 7.8 Hz, 2H), 6.13 (d, J = 7.8 Hz, 2H), 2.52 (s, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 190.1, 164.4, 163.3, 145.2, 138.4, 138.1, 137.1, 129.7,
129.3, 128.7, 128.6, 126.9, 122.9, 121.9, 120.8, 115.0, 111.8, 31.6 ppm.

HRMS (ESI) *m/z*: [M+H]⁺ calcd for[M]^{+•} calcd for [C₂₈H₂₀N₄O₂]^{+•}, 444.1586; found, 444.1569; difference: -3.86 ppm.



(4-(5-(4-(10-methylphenazin-5(10*H*)-yl)phenyl)-1,3,4-oxadiazol-2-yl)phenyl)methanol (3.5e) Prepared according to general procedure D using 3.5d as a starting material. Purified on silica gel using a gradient from CH₂Cl₂ to EtOAc in CH₂Cl₂. Yield 98%.

¹**H NMR (400 MHz, Benzene-***d*₆**):** δ 8.07 (d, J = 7.8 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 7.09-7.01 (m, 4H), 6.71 (t, J = 7.7 Hz, 2H), 6.54 (t, J = 7.8 Hz, 2H), 6.20 (d, J = 7.9 Hz, 2H), 6.04 (d, J = 7.8 Hz, 2H), 4.20 (s, 2H), 2.52 (s, 3H) ppm.

¹³C{¹H} NMR data could not be obtained due to the poor solubility of this compound in many common solvents.

HRMS (ESI) *m*/*z*: [M]^{+•} calcd for [C₂₈H₂₂N₄O₂]^{+•}, 446.1743; found, 446.1722; difference: - 4.76 ppm.



4-(5-(4-(10-methylphenazin-5(10*H*)-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (PAZODA)

Prepared according to general procedure E using **3.5d** as a starting material. Purified on silica using 30:1 CH₂Cl₂:EtOAc. Yield 44%.

¹**H NMR (400 MHz, Benzene**-*d*₆): δ 7.98 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.70 (d, J = 7.7 Hz, 2H), 6.55 (d, J = 7.9 Hz, 2H), 6.31 (dd, J = 17.3, 1.5 Hz, 1H), 6.21 (d, J = 7.8 Hz, 2H), 6.05 (dd, J = 7.8, 1.4 Hz, 2H), 5.97 (dd, J = 17.3, 10.4 Hz, 1H), 5.26 (dd, J = 10.4, 1.5 Hz, 1H), 4.93 (s, 2H), 2.52 (s, 3H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 165.1, 164.0, 163.9, 144.4, 139.6, 137.9, 137.4, 133.0, 130.7, 130.4, 129.3, 128.5, 126.8, 124.0, 122.7, 122.6, 120.8, 114.3, 111.6, 65.2, 31.6 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₂₇H₁₇N₃O₃]^{+•}, 500.1848; found, 500.1838; difference: - 2.01 ppm.



4-(3,6-bis(di-*p*-tolylamino)-9*H*-carbazol-9-yl)benzonitrile (3.6b)

Prepared according to modified literature procedure.²³² To a 250 mL round bottom flask was added 1.5 grams of tetra-*p*-tolyl-9*H*-carbazole-3,6-diamine (2.7 mmol, 1.0 equiv), 2.9 grams of K_3PO_4 (14 mmol, 5.0 equiv), and 1.2 L of dimethylformamide. This mixture was heated to 150 °C, then 1.0 gram of 4-fluorobenzonitrile (8.1 mmol, 2.0 equiv) was added. The reaction was stirred at 150 °C overnight, cooled to room temperature, then filtered over celite. The celite was rinsed 3 times with 50 mL of ethyl acetate, then the filtrate was concentrated in vacuo. The resulting residue was purified on silica gel using a gradient from hexane to CH_2Cl_2 to yield 0.98 g of pure **3.6b**, yield 55%.

¹**H NMR (400 MHz, Benzene**-*d*₆): δ 7.82 (d, J = 2.1 Hz, 2H), 7.28 (dd, J = 8.8, 2.2 Hz, 2H), 7.15 (m, 8H), 7.00 (dd, J = 11.9, 8.6 Hz, 4H), 6.93 (d, J = 8.2 Hz, 8H), 6.84 (d, J = 8.6 Hz, 2H), 2.11 (s, 12H) ppm.

¹³C{¹H} NMR (101 MHz, Benzene-*d*₆): δ 146.9, 142.6, 141.5, 137.4, 133.6, 131.4, 130.2, 126.4,
126.3, 125.4, 123.3, 118.8, 118.4, 110.9, 110.7, 20.7 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₄₇H₃₈N₄]^{+•}, 658.3096; found, 658.3102; difference: - 0.91 ppm.



9-(4-(1*H*-tetrazol-5-yl)phenyl)-tetra-*p*-tolyl-9*H*-carbazole-3,6-diamine (3.6c)

Prepared according to general procedure B using **3.6b** as a starting material. Purified on a short silica gel plug using EtOAc to remove residual salts and used without further characterization. Yield is quantitative.



4-(5-(4-(3,6-bis(di-p-tolylamino)-9H-carbazol-9-yl)phenyl)-1,3,4-oxadiazol-2-

yl)benzaldehyde (3.6d)

Prepared according to general procedure C using **3.6c** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to 5% EtOAc in CH_2Cl_2 . Recrystallized from hexanes and CH_2Cl_2 . Yield 87%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 10.14 (s, 1H), 8.38 (t, J = 8.6 Hz, 4H), 8.09 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H), 7.72 (s, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.20 (dd, J = 8.8, 2.2 Hz, 2H), 7.05 – 6.94 (m, 16H), 2.29 (s, 12H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 191.2, 164.7, 163.8, 146.2, 141.9, 138.3, 137.2, 131.3, 130.3, 129.8, 128.8, 128.8, 127.5, 127.5, 126.9, 125.3, 124.6, 123.0, 121.7, 117.7, 110.6, 20.7 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₅₅H₄₃N₅O₂]^{+•}, 805.3417; found, 805.3423; difference: - 0.73 ppm.



(4-(5-(4-(3,6-bis(di-*p*-tolylamino)-9*H*-carbazol-9-yl)phenyl)-1,3,4-oxadiazol-2yl)phenyl)methanol (3.6e)

Prepared according to general procedure D using **3.6d** as a starting material. Purified on silica gel using a gradient from CH_2Cl_2 to EtOAc in CH_2Cl_2 . Yield 64%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.41 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 8.1 Hz, 2H), 7.88 – 7.65 (m, 4H), 7.61 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.24 (dd, J = 8.8, 2.1 Hz, 2H), 7.05 (t, J = 13.4 Hz, 16H), 4.87 (s, 2H), 2.35 (dd, J = 7.9, 4.2 Hz, 7H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 164.7, 164.0, 146.2, 145.0, 141.7, 137.3, 131.3, 129.7, 128.6, 127.3, 127.2, 126.8, 125.3, 124.6, 123.1, 122.9, 122.2, 121.3, 117.7, 110.6, 64.7, 20.7 ppm.

HRMS (ESI) m/z: [M]^{+•} calcd for [C₅₅H₄₅N₅O₂]^{+•}, 807.3573; found, 807.3584; difference: - 1.37 ppm.



4-(5-(4-(3,6-bis(di-*p*-tolylamino)-9*H*-carbazol-9-yl)phenyl)-1,3,4-oxadiazol-2-yl)benzyl acrylate (TTACODA)

Prepared according to general procedure E using **3.6e** as a starting material. Purified on silica using 30:1 CH₂Cl₂:EtOAc. Yield 40%.

¹**H NMR (400 MHz, Chloroform-***d***):** δ 8.29 (d, J = 8.3 Hz, 2H), 8.11 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.64 (s, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 7.12 (dd, J = 8.8, 2.2 Hz, 2H), 7.02 – 6.78 (m, 16H), 6.43 (dd, J = 17.3, 1.4 Hz, 1H), 6.14 (dd, J = 17.3, 10.4 Hz, 1H), 5.84 (dd, J = 10.4, 1.4 Hz, 1H), 5.22 (s, 2H), 2.22 (s, 12H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 165.9, 164.5, 164.1, 146.1, 145.2, 141.7, 139.9, 137.3, 131.6, 131.2, 129.7, 128.6, 128.0, 127.3, 126.9, 125.4, 124.6, 123.6, 123.0, 122.1, 121.3, 117.7, 110.6, 65.6, 20.7 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₅₈H₄₇N₅O₃]^{+•}, 861.3679; found, 861.3686; difference: - 0.78 ppm.

Chapter 4: Multiblock Bottlebrush Nanofibers from Organic Electronic Materials

4.1 Motivation

Encouraged by the advancements demonstrated in Chapters 2 and 3, we sought to use the well-controlled Cu(0)-RDRP of semiconducting acrylate monomers to prepare more complex hierarchical structures from organic semiconductor materials. In the past 15 years, numerous techniques have emerged for the assembly of complex nanomaterials from soft matter, opening the door to new applications of nanotechnology. Methods such as crystallization-driven selfassembly (CDSA),^{12,16–18,26,268} living supramolecular polymerization,^{20,21,269–271} and hierarchical solution self-assembly (HSSA)^{22,23,38} have leveraged low-cost solution processing to address scalability challenges, while the complexity of materials prepared in these ways continues to improve. Despite these achievements, synthetic methods that rely on self-assembly continue to face several challenges. Most importantly, self-assembly can be highly dependent on conditions such as solvent and temperature, which must be kept within certain ranges if the integrity of the nanomaterial is to be maintained. Furthermore, methods for the precise synthesis of soft-matter nanomaterials often require building blocks with highly specific properties. For example, CDSA makes use of polymers amenable to epitaxial crystallization, supramolecular polymerization must precisely balance Van der Waals forces, and HSSA uses building blocks with differing solubilities to achieve complex, well-defined nanomaterials. While each has been used to prepare

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nanomaterials with impressive complexity and function, the chemical requirements of each technique narrow the potential scope of materials that might be investigated.

We therefore sought to apply the efficient covalent chemistry developed in Chapters 2 and 3 alongside orthogonal polymerization methods, in order to prepare covalent nanostructures with well-defined components. Multiblock bottlebrush copolymers provide a compelling bottom-up approach to the synthesis of hierarchical nanostructures from soft material. Their block-by-block synthesis allows for the preparation of multicompartment structures that remain nanosegregated by virtue of their covalent chemistry, irrespective of environmental conditions such as temperature or solvent. Furthermore, bottlebrush copolymers may be used to form nanostructures from a vast array of monomers, removing the need to consider factors such as crystallization or selective solvation that a self-assembly approach might require. This would facilitate the preparation of hierarchical materials with complex functionalities difficult to achieve by existing methods. More importantly, bottlebrush synthesis could provide a route to customizable nanofibers made from multiple organic electronic materials.



Figure 4.1. Schematic illustration of a diblock bottlebrush copolymer composed of p-type (blue) and n-type (orange) organic semiconductors.

Here we prepare bottlebrush copolymers which mimic the structure of multilayer organic electronic devices on single polymer chains. We proposed that using a series of macromonomers 171 prepared from p- and n-type organic semiconductors highlighted previously, fiber-like nanomaterials can be prepared with a high degree of control over fiber length, composition, and ordering. Furthermore, we propose that this approach can also be used to access diblock nanofibers analogous to organic p-n junctions, which display the reversible electrochemistry of each of their components (Figure 4.1). Finally, we propose that even more complex bottlebrush copolymers can prepared in which individual polymer chains exhibit the multilayer structure of four-component phosphorescent organic light-emitting diodes (OLEDs), such that the photophysical properties of each of the four organic semiconductors can be independently observed.

4.2 Bottlebrush Polymers from Semiconducting Acrylic Monomers

4.2.1 Initiator Design and Synthesis

To generate these bottlebrush structures, it was first necessary to establish a robust method to generate complex macromonomers – a macromolecule which can itself undergo a second polymerization reaction. Using Cu(0)-RDRP, organic semiconductor polymers functionalized with a second reactive handle amenable to an orthogonal polymerization method could be prepared. Ring-opening metathesis polymerization (ROMP) was chosen as an orthogonal polymerization, using norbornene-terminated polymers as macromonomer building blocks.

End-group functionalization with a norbornene handle can be achieved by either functionalizing the initiator or by post-polymerization modification. These methods each present their own challenges, especially when it is ideal that all polymers are end-group functionalized while minimizing side reactions. Initiator functionalization requires that the moiety appended to the initiator is stable to the conditions used in the first polymerization, which presents a challenge as the norbornene olefin has the potential to react with the propagating radical during Cu(0)-RDRP

by atom-transfer radical addition (ATRA). After extensive efforts investigating both methods, higher degrees of functionalization were achieved using an ATRP initiator modified with a norbornene handle at the α -terminus. In this case, ATRA to the norbornene during Cu(0)-RDRP could be minimized by quenching the polymerization at < 60% conversion.



Figure 4.2. Synthesis of norbronene functionalized initiator, NbInit.

The norbornene-functionalized initiator is prepared via a facile two-step sequence (Figure 4.2) starting from 11-aminoundecan-1-ol and *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride. These two compounds are condensed to form the corresponding dicarboximide product, **4.1**, in 76% yield. This alcohol is then converted to an ATRP initiator via reaction with α -bromoisobutyryl bromide and triethylamine in dichloromethane to yield **NbInit** as a viscous oil in 84% yield.

This initiator structure was selected specifically to deliver the maximum possible backbone length without complicating macromonomer preparation. Although there are more active norbornene handles used for bottlebrush polymerizations,²⁷² these more reactive norbornene moieties undergo rapid ATRA under Cu(0)-RDRP conditions. This norbornene dicarboximide handle was selected to provide high reactivity during ROMP, with minimal reactivity towards ATRA during Cu(0)-RDRP. Additionally, the extended C11 alkyl linker used to join the norbornene handle to the isobutyryl bromide initiator moiety is used to improve bottlebrush synthesis. By increasing the distance between the propagating norbornene and the bulky polymer

side chains, steric crowding of the propagating end-group is relieved significantly.²⁷³ Increasing this alkyl linker length from a short two-carbon linker to the 11-carbon linker used here allowed us to increase the maximum degree of polymerization (DP) in the bottlebrush backbones we prepared from DP = 50 up to DP = 400.

4.2.2 Macromonomer Synthesis



Figure 4.3. Synthesis of macromonomers HTL-MM, EML-MM, and ETL-MM.

Once the norbornene-functionalized initiator was prepared, it was possible to prepare a series of macromonomers (MMs) using this initiator and our optimized Cu(0)-RDRP conditions. Three macromonomers were prepared using representative semiconducting monomers from Chapter 2, **tBuHTL** as a hole-transport material, **CzBA** as a host type material, and **TRZ** as an electron-transport material (Figure 4.3). These monomers were selected for their favorable polymerization kinetics, facile scalability, and low cost. Furthermore, these monomers were specifically chosen for their electronic properties, closely match those of the respective layers they are imitate in a simplified three-layer OLED. As such, the resulting macromonomers were named 174

accordingly, with the suffix '-MM' denoting the structure as a macromonomer: HTL-MM composed of tBuHTL and simulating a hole-transport layer (HTL), EML-MM composed of CzBA and simulating the host of an emissive layer (EML), and ETL-MM composed of TRZ and simulating an electron-transport layer (ETL). Macromonomers were then prepared via direct growth from NbInit via Cu(0)-RDRP, and quenched below 60% conversion to minimize ATRA. Residual monomer is then rigorously removed by precipitation followed by preparatory size exclusion chromatography. A final precipitation is then performed to remove any BHT or other small molecule impurities that may interfere in the subsequent ROMP. The monomers removed from the polymerization can be easily recycled via chromatography followed by crystallization where applicable. This method gives access to macromonomers with well-controlled molecular weights and dispersities, summarized in Figure 4.3.

4.2.3 Homopolymer Bottlebrush Synthesis



Figure 4.4. Generalized ring-opening metathesis polymerization to assemble macromonomers into bottlebrush (co)polymers.

Using these macromonomers, the homopolymer bottlebrushes of each organic semiconductor were first prepared (Figure 4.4). These are denoted with the suffix -BB, with the subscript indicating the target backbone DP. Using this grafting-through method, bottlebrush polymers with backbone DP = 100 were easily accessible using each macromonomer, proceeding

to 71-83% conversion (determined via SEC post-polymerization) while maintaining narrow dispersities (1.12 to 1.17) and molecular weights close to the theoretical molecular weights as shown in Table 4.1.

Entry ^a	$M_{n, SEC}^{b}$ (kDa)	$M_{n, \text{theory}}(\text{kDa})$	Ð	Conv. (%) b
HTL ₁₀₀ -BB	570	499	1.14	78
EML100-BB	701	500	1.17	83
ETL100-BB	473	504	1.12	71
HTL400-BB	1530	1770	1.35	69
EML ₄₀₀ -BB	1990	2040	1.32	85
ETL400-BB	2050	1620	1.31	57

 Table 4.1. Synthesis of bottlebrush homopolymers.

^a Subscript indicates target DP.

^b Determined by SEC in THF after purification by preparatory SEC.

Significantly longer bottlebrush homopolymers were then targeted with target backbone DP = 400. These polymerizations were surprisingly successful, proceeding to conversions from 57-85% dependent on the bottlebrush solubility at high backbone DP. Consistent with literature precedent,²⁷² as targeted bottlebrush backbone length increases, macromonomer conversion decreases while polydispersity of the bottlebrushes generated broadens somewhat to 1.31-1.35. This limited conversion and broadened dispersity can be attributed to the considerable steric bulk of the semiconducting macromonomers used as well as the crowding of the propagating ruthenium as backbone DP increases. Importantly, we determined that residual macromonomer can be completely removed from these mixtures by passing the reaction over a reusable methacrylic resin in THF. This purification is critical if the properties of individual nanowires are to be directly interrogated.



Figure 4.5. Schematic illustrations and AFM height images of a) HTL₄₀₀-BB, b) EML₄₀₀-BB and c) ETL₄₀₀-BB (right) on HOPG substrates (scale bars = 200 nm).

The bottlebrush morphology was then confirmed in each case via atomic force microscopy (AFM) demonstrating extended fiber-like structures (Figure 4.5). Prior to imaging, all residual macromonomer must be removed to facilitate the imaging of isolated extended bottlebrushes. Individual bottlebrush polymers were imaged by spin-casting solutions with a concentration of approximately 0.001 mg mL⁻¹ of each 400-length bottlebrush. As shown above, all semiconducting macromonomers used in this work exhibit distinct fiber-like morphologies up to several hundred nanometers in length.



Figure 4.6. Normalized absorbance (solid) and photoluminescence (PL, dashed) for a) HTL₁₀₀-BB, b) EML₁₀₀-BB, and c) ETL₁₀₀-B at 0.01 mg mL⁻¹ in toluene.

The emissive properties of these bottlebrush homopolymers were found to be nearly identical to the corresponding linear homopolymers reported in Chapter 2 (Figure 4.6). When 177

measured in dilute, degassed toluene, HTL_{100} -BB, EML_{100} -BB, and ETL_{100} -BB each exhibited emission maxima of 469, 347, and 412 nm and quantum yields of 0.56, 0.21, and 0.02 respectively. As these values closely mirror their linear analogues, we conclude that there is little impact on photophysical properties of these fluorophores when incorporated into a bottlebrush.

4.2.4 Synthesis of Diblock Bottlebrush Copolymers

Entry	$M_{n, B1}^{a}$ (kDa)	DP B1 ^{<i>a,b</i>}	DP B2 b,c	M_n , total ^d (kDa)	Ð	Conv. (%) ^a
(ETL ₇₅ - <i>b</i> -HTL ₇₅)-BB	475	67	75	956	1.24	70
(EML ₇₅ - <i>b</i> -ETL ₇₅)-BB	419	70	45	740	1.17	76
(EML75-b-HTL75)-BB	441	74	61	834	1.21	82

 Table 4.2. Synthesis of diblock bottlebrush copolymers by ROMP.

^a Determined by SEC in THF.

 b B1 = first block added, B2 = second block added, DP = degree of polymerization of poly(norbornene) backbone.

^c Determined by ¹H NMR using the degree of polymerization determined for the first block by SEC.

^{*d*} Determined based on $M_{n, \text{SEC}}$ for HTL-MM = 6400, EML-MM = 6000, and ETL-MM = 7100.

After demonstrating the well-controlled ROMP of the HTL-MM, ETL-MM, and EML-MM macromonomers using Grubbs' third generation catalyst with backbone DPs as high as 400, we sought to demonstrate that this method could also be used to generate diblock copolymers. As outlined in Table 4.2, three diblock BBCPs were prepared with target backbone DPs of 150, composed of 75 of each component macromonomer. These polymers were prepared by simply initiating the polymerization with the first portion of macromonomer, allowing the ROMP to proceed to conversion, monitoring with ¹H NMR, then adding the second block of macromonomer in a single portion. The polymerizations were quenched with one drop of ethyl vinyl ether upon consumption of the second macromonomer to yield diblock polymers of each semiconducting monomer pair. These diblock polymers possess two blocks of differing electronic properties, analogous to a nanoscale junction between organic semiconductors, similar to what is found in a typical diode.



Figure 4.7. SEC chromatograms of diblock bottlebrushes (a) (EML₇₅-*b*-ETL₇₅)-BB (b) (EML₇₅-*b*-HTL₇₅)-BB (c) (ETL₇₅-*b*-HTL₇₅)-BB showing the RI response after the addition of each block, and following purification by preparatory SEC.

As shown in Figure 4.7, this method was quite successful for (EML₇₅-*b*-ETL₇₅)-BB and (EML₇₅-*b*-HTL₇₅)-BB, delivering bottlebrush copolymers with monomodal molecular weight distributions and dispersities of 1.21 and 1.17 respectively. In the case of (HTL₇₅-*b*-ETL₇₅)-BB, this method was somewhat less efficient, with significant chain death observed upon addition of the ETL block. This ETL macromonomer is the least soluble of the macromonomers used, likely impacting its reactivity in this ROMP. This indicates that macromonomer steric bulk and solubility play a key role in generating well-defined diblock bottlebrush copolymers, especially when using complex macromonomers such as these.



Figure 4.8. Cyclic voltammogram of HTL100-BB (blue) (ETL75-b-HTL75)-BB (grey) and ETL100-BB (orange).

Each diblock BBCP demonstrates both the oxidation and reduction of their semiconductor components. This is demonstrated in Figure 4.8, in which (ETL₇₅-*b*-HTL₇₅)-BB exhibits a combination of the electronic properties of its component parts. This is particularly interesting as it suggests that bottlebrush copolymers can be used as a framework for generating thin-films for ambipolar charge transport or as a method to assemble nanoscale diode-like structures composed of a single polymer chain.

4.2.5 Triblock Bottlebrush Copolymer



Figure 4.9. Simplified structure of four component triblock bottlebrush, (ETL₅₀-*b*-(EML-*co*-Ir)₃₀-*b*-HTL₅₀)-BB.

This method was then extended to an even more complex triblock bottlebrush copolymer (illustrated in Figure 4.9). In an attempt to generate a bottlebrush nanofiber with electronic properties reminiscent of a multilayer OLED, a triblock bottlebrush was synthesized with a hole-transport, electron-transport, and host functionalized macromonomer to simulate the layers in an electroluminescent device. In this example, we added one further level of complexity, adding an additional phosphorescent iridium dopant monomer to the host layer.²⁷⁴ Using this bottlebrush framework, it is possible to assemble polymer nanofibers with control at three levels of hierarchy: (1) the structures of the monomers used; (2) the arrangement of these monomers within macromonomer strands, and (3) the arrangement of macromonomer strands into a multiblock bottlebrush, mimicking the structure of macroscopic devices.



Figure 4.10. Structure of Ir(ppy)₂(acac) acrylate monomer used in the synthesis of EML-co-Ir-MM.

A fourth macromonomer was synthesized to allow the synthesis of the targeted fourcomponent triblock bottlebrush copolymer. This macromonomer, **EML**-*co*-**Ir**-**MM**, is composed of the same **CzBA** host monomer as the undoped host macromonomer, **EML-MM**, with the addition of 8% by weight of an Ir(ppy)₂(acac)-based monomer, **Ir-mono** (Figure 4.10).²⁷⁴ These two monomers were copolymerized under the same conditions as the other macromonomers prepared for this project using Cu(0)-RDRP and a functionalized initiator, **NbInit**. This doping concentration was selected based on several test blends to determine minimum emitter concentration while maintaining full energy transfer in a similar process to the one described in Chapter 3. This macromonomer was prepared on 500 mg scale and was found to exhibit slightly higher molecular weight than the homopolymeric macromonomers (M_n = 9300, D = 1.22).



Figure 4.11. a) SEC RI chromatograms after the addition of each block; b) Cyclic voltammogram of (ETL₅₀*b*-(EML-*co*-Ir)₃₀-*b*-HTL₅₀)-BB showing the reduction of the ETL block (orange) and oxidation of the HTL block (blue); c) PL decay of this triblock BBCP ($\lambda_{ex} = 340$ nm) showing the phosphorescent decay of the Ir dopant.
This triblock bottlebrush was then prepared via the sequential ROMP of ETL-MM, (EML*co*-Ir)-MM, and HTL-MM to give (ETL₅₀-*b*-(EML-*co*-Ir)₃₀-*b*-HTL₅₀)-BB. This complex polymerization proceeded relatively efficiently, as illustrated in Figure 4.11a. Even with the added complexity of this polymerization, 75% overall macromonomer conversion was achieved with a final molecular weight of 794 kDa and a polydispersity of 1.21. When measured by ¹H NMR, this sequential polymerization gave a bottlebrush with a DP = 42 for the first block, ETL-MM, DP = 24 for the middle block, (EML-*co*-Ir)-MM, and DP = 43 for the final block composed of HTL-MM.

The inclusion of each of these components was confirmed using several methods. First of all, cyclic voltammetry was performed on the final BBCP to demonstrate that this triblock shows the reversible reduction and oxidation behaviour of the ETL and HTL blocks at -2.32 and +0.48 V vs FeCp2^{+/0}, respectively (Figure 4.11b). The inclusion of the phosphorescent central block was demonstrated by measuring the extended phosphorescence lifetime of the triblock polymer in the solid state (Figure 4.11c). This extended lifetime is not observed in the undoped macromonomers. The extended emission lifetime as well as the green photoluminescence of the triblock BBCP clearly demonstrate that this emitter is included in the bottlebrush nanofiber.



Figure 4.12. a) AFM height images of (ETL₅₀-*b*-(EML-*co*-Ir)₃₀-*b*-HTL₅₀)-BB on HOPG (scale bar = 200 nm); b) Energy level diagram for the four components of this triblock BBCP.

The resulting triblock BBCP represents a single polymer chain composed of well-defined, discrete domains with interfaces that remain nanosegregated due to the bottlebrush framework. The size and morphology of the nanowires created via this second polymerization is shown in Figure 4.12a, measured via AFM. The triblock nanofibers were characterized by spin-casting from a solution with an approximate concentration of 0.001 mg mL⁻¹ onto a freshly cleaved highly-oriented pyrolytic graphite (HOPG) so as to be able to find and measure their size via atomic force microscopy. The distinct worm-like appearance of these polymers is persistent in solution due to the steric demands of adjacent side chains resulting in a minimum energy conformation in which the polymers are somewhat extended. The aspect ratio of these nanofibers is determined by the side chain length and the degree of polymerization of the bottlebrush backbone.

The monomers used to assemble these nanofibers were carefully selected to form a typical "staircase" energy level arrangement from the HOMO and LUMO of the four components of which this system is comprised (Figure 4.12b). This arrangement is typically used in OLEDs to facilitate charge transport through the multilayer assembly while minimizing the driving voltage required. The iridium dopant is specifically selected such that the iridium bandgap is narrower than the encompassing host layer while the HTL HOMO is slightly higher than that of the host HOMO

while the ETL LUMO is slightly lower than the host LUMO. In this way, these bottlebrush nanostructures can be thought to closely resemble the macroscale structure of OLEDs on single nanofibers.

4.3 Conclusion

In summary, benzyl acrylate monomers based on acrylic semiconductors have been used to prepare a series of organic semiconducting nanofibers. Using macromonomer building blocks synthesized using Cu(0)-RDRP, a series of bottlebrush copolymers were generated. Homopolymeric bottlebrushes were prepared with backbone degree of polymerizations of up to 400 and molecular weights from 470 to 2050 kDa, giving nanofibers with lengths up to 200 nm while maintaining control over bottlebrush length, composition, and ordering. This polymerization method was then used to generate a series of diblock nanofibers analogous to organic p-n junctions. These two-component diblock polymers demonstrate the reversible electrochemistry of each of the component macromonomers. Finally, a triblock BBCP was prepared, composed of four components organised into a multilayer assembly analogous to a simple phosphorescent OLED such that the photophysical properties of these components can be independently observed. This work opens the door to research on nanoscale wires and junctions from arbitrary organic semiconductors regardless of their crystallinity or solvophilicity, providing methods for the incorporation of diverse optoelectronic materials into hierarchical nanofibers.

4.4 **Experimental Details**

4.4.1 General Considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves.



Figure 4.13. Monomers prepared for use in this chapter.

All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. Monomers **tBuHTL**,² **CzBA**,² **TRZ**,¹ and **Ir-mono**²⁷⁴ (shown above in Figure 4.13) as well as 11-aminoundecan-1-ol,²⁷⁵ and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(pyridine) ruthenium(II)²⁷⁶ (**G3**) were prepared according to literature procedures. *N*-methyl-2-pyrrolidone (NMP) was distilled, then degassed and stored under an N₂ atmosphere. CH₂Cl₂ was freshly distilled from P₂O₅ prior to use. Et₃N was dried by distillation on CaH₂ onto activated molecular sieves then degassed and stored under an N₂ atmosphere. The ¹H and ¹³C {¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with chloroform-*d* (CDCl₃) or dichloromethane-*d*₂ (CD₂Cl₂) as the solvent. Absorbance measurements were made on a Cary 60 spectrometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments

SC-30 Integrating Sphere Module; toluene was used as the solvent and spectra obtained at concentrations of 0.01 mg mL^{-1} . Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization.

4.4.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.1 Hz. Samples were prepared by spincoating solutions of polymer onto freshly cleaved highly-oriented pyrolytic graphite (HOPG) at 2500 rpm for 30 s at concentrations of ~0.001 mg mL⁻¹. For best results, 1,2-dichloroethane was used as the solvent for HTL400-BB, ETL400-BB, and (ETL50-*b*-(EML-*co*-Ir)30-*b*-HTL50)-BB while 2:1 chloroform/chlorobenzene was used as the solvent for EML400-BB. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al or HQ:NSC19/No Al probes, with typical resonance frequencies f and spring constants k of (f = 160 kHz, k = 5 N/m) and (f = 65 kHz, k = 0.5 N/m) respectively.

4.4.3 Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 -2 mg mL^{-1} using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right-angle and low angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (dn/dc) were determined using 100% mass recovery methods from Malvern

OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

4.4.4 Thermal Analysis

Glass transition temperatures were determined using differential scanning calorimetry (DSC) on a NETZSCH DSC 214 Polyma instrument. The polymer samples were placed in an aluminum pan and heated from 25 to 175 °C at 10 °C min⁻¹ under a flow of nitrogen for 3 heating/cooling cycles.

4.4.5 Electrochemical Methods

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene)²¹⁷; counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene. Experiments were run at a scan rate of 100 mV s⁻¹ in dry degassed electrolyte solution with ~4 mg mL⁻¹ of analyte. Polymers ETL₁₀₀-BB, EML₁₀₀-BB, and (EML₇₅-*b*-ETL₇₅)-BB were sparingly soluble and run as saturated solutions.

4.4.6 Synthetic Procedures



Synthesis of N-(hydroxyundecanyl)-cis-5-norbornene-exo-2,3-dicarboximide (4.1)

Prepared according to a modified literature procedure.²⁷³ A 100 mL round-bottomed flask equipped with a magnetic stir bar, a Dean-Stark trap and a condenser was charged with *cis*-5norbornene-*exo*-2,3-dicarboxylic anhydride (0.96 g, 5.8 mmol, 1.0 equiv), 1-aminoundecan-1-ol (1.2g, 6.4 mmol, 1.1 equiv) and Et₃N (59 mg, 0.58 mmol, 0.10 equiv) and 20 mL toluene. The mixture was heated to reflux and left for 22 h before cooling back to room temperature. The reaction was extracted with CH_2Cl_2 and washed with 0.1 M HCl (20 mL) and brine (20 mL), dried over MgSO₄, filtered and concentrated *in vacuo* to yield **4.1** as a yellow oil. Yield = 1.6g (76 %).

¹**H NMR (400 MHz, Chloroform-***d***)**: δ 6.29 (t, J = 1.9 Hz, 2H), 3.65 (t, J = 6.6 Hz, 2H), 3.46 (t, J = 7.3 Hz, 2H), 3.28 (t, J = 1.8 Hz, 2H), 2.68 (d, J = 1.5 Hz, 2H), 1.59 – 1.51 (m, 5H), 1.35 – 1.20 (m, 16H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 178.3, 138.0, 63.2, 47.9, 45.3, 42.8, 38.9, 32.9, 29.6, 29.5, 29.5, 29.5, 29.2, 27.9, 27.1, 25.8 ppm.

HRMS (EI) *m/z*: [M⁺•] calcd for [C₂₀H₃₁NO₃]•, 333.23039; found, 333.23014; difference: 0.8 ppm.



Synthesis of *N*-(undecanyl 2-bromo-2-methylpropionate)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (NbInit)

Prepared according to a modified literature procedure.²⁷³ A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with **4.1** (1.4 g, 4.2 mmol, 1.0 equiv), Et₃N (59 mg, 0.58 mmol, 0.10 equiv) and 50 mL dry CH₂Cl₂. The solution was sparged with N₂ for 10 min and cooled to 0 °C in an ice bath. α -Bromoisobutyryl bromide (1.2 g, 6.4 mmol, 1.1 equiv) was added dropwise with a syringe over 2 min. The reaction was warmed to room temperature slowly, then left stirring under N₂ overnight. A colour change from light yellow to orange was observed. To quench the reaction 20 mL of H₂O was added. The organic layer was collected and washed with 20 mL brine, dried over MgSO₄, filtered and concentrated *in vacuo*. The crude residue was purified with silica gel chromatography (3:1 CH₂Cl₂/Hexanes) to yield **NbInit** as a colourless oil. Yield = 0.81 g (84 %).

¹**H NMR (400 MHz, Chloroform-***d*): δ 6.29 (t, J = 1.9 Hz, 2H), 4.17 (t, J = 6.6 Hz, 2H), 3.46 (d, J = 7.5 Hz, 2H), 3.28 (t, J = 1.8 Hz, 2H), 2.68 (d, J = 1.3 Hz, 2H), 1.94 (s, 6H), 1.67 (dt, J = 8.0, 6.5 Hz, 2H), 1.60 – 1.49 (m, 3H), 1.42 – 1.20 (m, 15H) ppm.

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 178.1, 171.7, 137.8, 66.2, 56.0, 47.8, 45.2, 42.7, 38.7, 30.8, 29.5, 29.4, 29.4, 29.1, 29.1, 28.3, 27.8, 26.9, 25.8 ppm.

HRMS (EI) *m/z*: [M^{+•}] calcd for [C₂₄H₃₆NO₄⁷⁹Br][•], 481.18277; found, 481.18310; difference: 0.7 ppm.



Synthesis of HTL-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added tBuHTL² (2.0 g, 4.5 mmol, 23 equiv), 1.9 mL of a solution of NbInit in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; NbInit: 97 mg, 0.20 mmol, 1.0 equiv), and 0.78 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 2.9 mg, 1.3 x 10⁻² mmol, 0.065 equiv; Me₆TREN: 3.1 mg, 1.4 x 10⁻² mmol, 0.068 equiv). The total polymerization volume was kept to 7.3 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 10 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried in vacuo and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 μ L aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. At approximately 50 % conversion, the polymerization was quenched by addition of water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried in *vacuo* overnight. Yield = 0.95 g.



Synthesis of EML-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added CzBA² (2.0 g, 6.1 mmol, 31 equiv), 1.9 mL of a solution of NbInit in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; NbInit: 97 mg, 0.20 mmol, 1.0 equiv), and 0.78 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 2.9 mg, 1.3 x 10⁻² mmol, 0.065 equiv; Me₆TREN: 3.14 mg, 1.4 x 10⁻² mmol, 0.068 equiv). The total polymerization volume was kept to 9.2 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 10 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 μ L aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. At approximately 50 % conversion, the polymerization was quenched by addition of water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried in *vacuo* overnight. Yield = 0.75 g.



Synthesis of ETL-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 40 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **TRZ**¹ (2.0 g, 4.0 mmol, 20 equiv), 1.9 mL of a solution of **NbInit** in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; **NbInit**: 97 mg, 0.20 mmol, 1.0 equiv), and 0.78 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 2.9 mg, 1.3 x 10⁻² mmol, 0.065 equiv; Me₆TREN: 3.1 mg, 1.4 x 10⁻² mmol, 0.068 equiv). The total polymerization volume was kept to 17 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow reagents to dissolve, however the polymerization can be initiated before all **TRZ** is in solution. A 20 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 µL aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. At approximately 50 % conversion, the polymerization was quenched by addition of water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated *in vacuo*.

and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 0.97 g.



Synthesis of (EML-co-Ir)-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **CzBA**² (0.92 g, 2.8 mmol, 40 equiv), **Ir-mono**²⁷⁴ (80 mg, 0.11 mmol, 1.1 equiv), 0.97 mL of a solution of **NbInit** in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; **NbInit**: 48 mg, 0.10 mmol, 1 equiv), and 0.39 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 1.5 mg, 6.5 x 10⁻³ mmol, 0.065 equiv; Me₆TREN: 1.5 mg, 6.8 x 10⁻³ mmol, 0.068 equiv). The total polymerization volume was kept to 4.6 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 5 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 µL aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. At approximately 60 % conversion, the polymerization was quenched by addition of water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated *in vacuo*.

The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 0.50 g.



Synthesis of HTL₁₀₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **HTL-MM** (0.10 g, 1.6 x 10⁻² mmol, 100 equiv) and 0.40 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 28 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 0.11 mg, 1.3 x 10⁻⁴ mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 64 mg.

Synthesis of HTL₄₀₀-BB by ROMP:

Prepared as above, using $C_{G3} = 1.0 \text{ mg mL}^{-1}$. Yield = 43 mg.



Synthesis of EML₁₀₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **EML-MM** (75 mg, 1.3 x 10^{-2} mmol, 100 equiv) and 0.19 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 23 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 0.092 mg, 1.3 x 10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 57 mg.

Synthesis of EML₄₀₀-BB by ROMP:

Prepared as above, using $C_{G3} = 1.0 \text{ mg mL}^{-1}$. Yield = 52 mg.



Synthesis of ETL₁₀₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ETL-MM** (0.10 g, 1.4×10^{-2} mmol, 100 equiv) and 0.50 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 26 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 0.10 mg, 1.4×10^{-4} mmol, 1.0 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 41 mg.

Synthesis of ETL₄₀₀-BB by ROMP:

Prepared as above, using $C_{G3} = 1.0 \text{ mg mL}^{-1}$. Yield = 20 mg.



Synthesis of (HTL₇₅-*b*-ETL₇₅)-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ETL-MM** (50 mg, 7.0 x 10^{-3} mmol, 75 equiv) and 0.25 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 34 μ L of a solution of **G3** in THF ($C_{G3} = 2.0 \text{ mg mL}^{-1}$; **G3**: 0.070 mg, 9.3 x 10^{-5} mmol, 1.0 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **HTL-MM** (47 mg, 7.0 x 10^{-3} mmol, 75 equiv) dissolved in 250 μ L of THF. The mixture was stirred at room temperature for an additional 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 60 mg.



Synthesis of (EML₇₅-*b*-HTL₇₅)-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **EML-MM** (53 mg, 8.8 x 10^{-3} mmol, 75 equiv) and 0.25 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 44 μ L of a solution of **G3** in THF ($C_{G3} = 2.0 \text{ mg mL}^{-1}$; **G3**: 0.090 mg, 1.2 x 10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **HTL-MM** (59 mg, 8.8 x 10^{-3} mmol, 75 equiv) dissolved in 0.25 mL of THF. The mixture was stirred at room temperature for an additional 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 62 mg.



Synthesis of (EML₇₅-*b*-HTL₇₅)-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **EML-MM** (47 mg, 7.8 x 10^{-3} mmol, 75 equiv) and 0.25 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 40 μ L of a solution of **G3** in THF ($C_{G3} = 2.0 \text{ mg mL}^{-1}$; **G3**: 0.080 mg, 1.0 x 10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **ETL-MM** (55 mg, 7.8 x 10^{-3} mmol, 75 equiv) dissolved in 0.25 mL of THF. The mixture was stirred at room temperature for an additional 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 63 mg.



Synthesis of (ETL₅₀-b-(EML-co-Ir)₃₀-b-HTL₅₀)-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ETL-MM** (50 mg, 7.0 x 10^{-3} mmol, 50 equiv) and 0.25 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 26 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 1.0 mg, 1.0 x 10^{-4} mmol, 1.0 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **(EML-***co***-Ir)-MM** (40 mg, 4.3 x 10^{-3} mmol, 30 equiv) dissolved in 0.25 mL of THF. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **(EML-***co***-Ir)-MM** (40 mg, 4.3 x 10^{-3} mmol, 30 equiv) dissolved in 0.25 mL of THF. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for 1 h. Two 5 μ L aliquots were taken for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, before addition of **(EML-***co***-Ir)-MM** (47 mg, 7.0 x 10^{-3} mmol, 50 equiv) dissolved in 0.25 mL of THF. The mixture was stirred at room temperature for an additional 1 h. Two 5 μ L aliquots were taken

for ¹H NMR and SEC analysis, the polymerization was removed from the glove box and quenched with one drop of ethyl vinyl ether. The polymer was collected and dried *in vacuo* overnight. Yield = 0.13 g. 2.5 mg of this polymer was further purified for AFM analysis using the silylated Toyopearl HW-55F resin described below.

Silylation of HW-55F Resin:

To a 250 mL Erlenmeyer flask was added 50 mL of THF-saturated Toyopearl HW-55F resin followed by a further 50 mL of THF. Et₃N (0.80 g, 1.1 mL, 7.9 mmol) and trimethylsilyl chloride (0.86 g, 1.0 mL, 7.9 mmol) were then added sequentially with gentle mixing. The mixture was left to stand for 16 h, then transferred to a filtration funnel with glass frit and washed with 200 mL THF:EtOH (1:1 v/v) followed by 200 mL THF. This re-usable resin can then be used to purify (ETL₅₀-*b*-(EML-*co*-Ir)₃₀-*b*-HTL₅₀)-BB with no observed retention of the iridium complex.

Chapter 5: Interface-Dependent Aggregation-Induced Delayed Fluorescence in Bottlebrush Polymer Nanofibers

5.1 Motivation

Having demonstrated the utility of the rigid bottlebrush framework to assemble organic semiconductors along a nanoscale fiber, we sought to use a similar framework to explore charge transfer processes within these fibers. Lixiang Wang and coworkers have recently reported several examples of highly emissive polymers for use in electroluminescent applications that generate light via a through-space charge transfer (TSCT) mechanism.^{151,277} Using random copolymers composed of distinct donor- and acceptor-functionalized monomers, materials are obtained which exhibit TSCT upon excitation of the donor-acceptor pair (Figure 5.1). By tuning the electronics of the donor and acceptor fragments used, it is possible to generate donor-acceptor pairs with low singlet-triplet energy gaps (ΔE_{ST}) that enable triplet emission via a TADF mechanism. This is an attractive alternative to the typical synthesis of TADF emitters, which requires care to prepare distinct donor and acceptor functionalities on a single molecule with minimal orbital overlap.



Figure 5.1. Illustration of a) TSCT polymers prepared by Lixiang Wang and coworkers b) a bottlebrush copolymer with TSCT properties with dashed line representing the shared bottlebrush backbone linking adjacent side chains. Adapted with permission from Ref 6. Copyright 2019 American Chemical Society.

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We propose that the precise ordering possible in bottlebrush nanofibers allows for a high degree of control over TSCT in these polymers, generating materials that are not accessible using traditional linear polymer morphologies. Here we prepare bottlebrush nanofibers exhibiting the TSCT TADF effect and demonstrate that this effect is highly dependent on the interface between D and A within the nanofiber by controlling their bottom-up architecture (Figure 5.1). In particular, we find that the brush-like structure of the BBCP enables inter-strand CT from all-donor side chains to all-acceptor side chains, due to the inability of these chains to phase separate when bound to a common backbone. In this way, miktoarm-type ('mixed-arm') nanofibers exhibit TSCT TADF in much the same manner as fully random D-A copolymers. TSCT can further be activated by aggregation of the nanofibers into a globular form in solution, resulting in a dramatic enhancement in TADF.

5.2 Bottlebrush Copolymers with TSCT Properties

5.2.1 Monomer Design and Synthesis





The first step to generate bottlebrush copolymers with TSCT properties is to prepare a pair of donor and acceptor monomers with which these polymers will be built. Based on the work of Lixiang Wang and coworkers, a dimethylacridine-based donor monomer was selected to pair with a 1,3,5,-triphenyltriazine-based acceptor monomer.^{151,277} In their system, these donors and acceptors are included in linear random copolymers using a styrene-based handle rather than the benzyl acrylate handle used in our work. Having already prepared a triazine-functionalized acrylate monomer (**TRZ**) for our earlier studies, the additional acridine-functionalized monomer (**ACR**) was prepared as shown in Figure 5.2.

The **ACR** monomer was synthesized on 20-gram scale via a three-step procedure starting from commercially available 9,9-dimethyl-9,10-dihydroacridine. First, nucleophilic aromatic substitution under atmospheric conditions using *p*-fluorobenzaldehyde delivered **5.1b** in 98% yield. This benzaldehyde is then converted to the corresponding benzyl alcohol (**5.1c**) via a sodium borohydride reduction. This benzyl alcohol is then converted to the corresponding acrylate monomer via the same mild acrylation method used for previously prepared monomers, using triethylamine and acryloyl chloride in cold dichloromethane to yield crystalline **ACR** monomer that is purified by the combination of chromatography and crystallization in hexane.



5.2.2 Macromonomer Design and Synthesis

Figure 5.3. Synthesis of ACR-MM, TRZ-MM, and ACRTRZ-MM.

Similar to the macromonomers prepared in Chapter 4, a norbornene-functionalized initiator (NbInit) is used to generate a series of semiconducting linear polymers with a polymerizable end group. These macromonomers were prepared using Cu(0)-RDRP^{1-3,94} to ensure a high degree of control over polymer dispersity and molecular weight. To explore the effect of bottlebrush morphology on TSCT behavior, three macromonomers were prepared using donor- and acceptorfunctionalized acrylate monomers. First, a pair of homopolymers were prepared, composed entirely of donor (ACR-MM) or acceptor (TRZ-MM) with targeted molecular weights of approximately 5 kDa. A third macromonomer was also prepared, composed of a 50/50 blend of donor and acceptor monomers (by weight) that are copolymerized to achieve a macromonomer with slightly higher molecular weight of 6 kDa (ACRTRZ-MM). Macromonomers were prepared on 500-750 mg scale, running the polymerization to approximately 50% conversion to prevent ATRA between the norbornene handle and the propagating chain end, and gave low dispersities between 1.15 and 1.21 (Figure 5.3). These macromonomers were then purified by sequentially precipitating into water/methanol to remove the high-boiling solvent and catalyst, followed by preparatory size exclusion chromatography, then a final precipitation in methanol to remove residual BHT from the size exclusion process.

5.2.3 Bottlebrush Synthesis and Characterization



Figure 5.4. Illustration of monomer and macromonomer organization for ACRTRZ₁₅₀-BB (random), ACR₇₅-co-TRZ₇₅-BB (miktoarm), and ACR₇₅-b-TRZ₇₅-BB (block).

Bottlebrush copolymers (BBCPs) were then prepared using these macromonomers and Grubbs'

third generation catalyst,²⁷⁶ via a grafting-through ROMP (

Table 5.1). Bottlebrushes with backbone length of 150 units were prepared to generate a series of copolymers with varying degrees of donor/acceptor blending as illustrated in Figure 5.4. Control over the donor-acceptor interface was achieved by preparing the following BBCPs: (1) a bottlebrush homopolymer **ACRTRZ**₁₅₀-**BB** composed entirely of the randomly blended macromonomer **ACRTRZ-MM**, giving a fully randomized donor/acceptor distribution along both the bottlebrush backbone and the linear side chains; (2) a miktoarm bottlebrush **ACR**₇₅-*co*-**TRZ**₇₅-**BB** composed of a 50/50 blend of **ACR-MM** and **TRZ-MM** randomly copolymerized along the bottlebrush backbone, giving a bottlebrush with homopolymeric side chains with donor-acceptor interfaces between adjacent side chains, and (3) a diblock bottlebrush copolymer **ACR**₇₅-*b*-**TRZ**₇₅-**BB**that is generated by first polymerizing 75 units of **ACR-MM** followed by the addition of a second block of **TRZ-MM** to give a BBCP with interfacial interactions only found at the interface of the two blocks.

Entry	$M_{n,a}(kDa)$	DP^a	\mathbb{D}^{a}	Conv. (%) ^{<i>a</i>}
ACR ₁₅₀ -BB	763	150	1.18	86
TRZ ₁₅₀ -BB	812	138	1.35	78
ACRTRZ ₁₅₀ -BB	619	104	1.24	81
ACR75-co-TRZ75-BB	778	142	1.37	82
ACR75- <i>b</i> -TRZ75-BB	604	$66/52^{b}$	1.38	81

Table 5.1. Synthesis of Donor-Acceptor Bottlebrush Copolymers.

^{*a*} Determined by SEC in THF using triple detection.

^b Block 1/Block 2. DP (B2) determined by ¹H NMR.

Two homopolymeric bottlebrushes (ACR₁₅₀-BB and TRZ₁₅₀-BB) were also prepared, composed of only donor and only acceptor macromonomers respectively. These were prepared to demonstrate that any emergent photophysical properties of the BBCPs were due entirely to the donor-acceptor interactions rather than due to aggregation effects of the donor or acceptor monomers on their own. Following polymerization, bottlebrush copolymers were purified via a similar sequence of precipitation, then preparatory SEC in THF over a methacrylic resin suited to this molecular weight range (detailed in Section 5.4), followed by a final precipitation to remove residual BHT and deliver the polymers as high purity, dry powders. The BBCPs prepared were characterized via GPC using triple detection, giving polymers with molecular weights ranging from 604 kDa to 812 kDa with dispersities ranging from 1.18 to 1.38 and conversions between 78% and 86% (Table 5.1). There is some mild broadening of the dispersity of polymers prepared using TRZ-MM that is attributable to the steric bulk and poor solubility of the triazine macromonomer and any (co)polymers thereof.



Figure 5.5. Atomic force microscopy height traces (scale bar = 100 nm) of isolated fibers of polymers ACRTRZ₁₅₀-BB (a), ACR₇₅-co-TRZ₇₅-BB (b), and ACR₇₅-b-TRZ₇₅-BB (c), where the ACR and TRZ chromophores are represented in teal and purple, respectively. Inset: photographs of the respective BBCP powders excited with 365 nm light.

These BBCPs were the cast onto highly-oriented pyrolytic graphite (HOPG) from dilute chloroform/chlorobenzene solution and studied by atomic force microscopy as individual fibers. As shown in Figure 5.5, the three blended copolymers all demonstrate distinct worm-like conformations with lengths on the expected 100-200 nm scale corresponding to the 150-unit backbone length targeted.

This methodology emphasizes the utility of a bottlebrush framework for generating multicomponent nanostructures with explicit control over the interface between optoelectronic components on length scales from tens to hundreds of nanometers. Using this framework, it is possible to control polymer composition at three levels of hierarchy: (1) the structures of the donor and acceptor monomers used; (2) the blending of these monomers within macromonomer strands; and (3) the interpolymer contact of macromonomer strands attached to a common bottlebrush backbone.

5.2.4 Electronic Properties



Figure 5.6. a) Cyclic voltammograms (CVs) of the BBCPs relative to FeCp2^{0/+} at a concentration of 2 mg mL⁻¹ of analyte in 1,2-difluorobenzene with 0.2 M tetrabutylammonium hexafluorophosphate.

Cyclic voltammetry was used to demonstrate that inclusion of these donor and acceptor monomers into the bottlebrush morphology imposes minimal changes on the electronic properties of the monomers. To do this, cyclic voltammograms were recorded for all five polymers in 1,2difluorobenzene (Figure 5.6). As shown above, the acridine-functionalized homopolymer (**ACR**₁₅₀-**BB**) exhibits two reversible oxidations at 0.79 and 1.03 V relative to $FeCp_2^{0/+}$, while demonstrating no response upon reduction. Conversely, the triazine-functionalized homopolymer (**TRZ**₁₅₀-**BB**) demonstrates only a single reversible reduction at -1.73 V relative to $FeCp_2^{0/+}$, while not demonstrating any response upon oxidation. As shown in Figure 5.6, all three blended bottlebrush copolymers demonstrate nearly identical electronic properties, with both a reversible reduction wave from the triazine acceptor and the two oxidation waves observed from the acridine donor.



Figure 5.7. Cyclic voltammograms (CVs) of ACR-MM (a) and TRZ-MM (b) relative to FeCp2^{0/+} run using 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene at a concentration of 2 mg mL⁻¹ of analyte.

Furthermore, there is negligible electrochemical difference between the redox behaviour of the donor and acceptor macromonomers (Figure 5.7) when compared to the homopolymeric bottlebrushes (Figure 5.6). This implies that while there are potentially significant differences in photophysical properties when copolymerized in a bottlebrush framework, there is little modulation of the HOMO and LUMO of the individual donor and acceptor groups. This also implies that any emergent properties of the blended copolymers are due to donor-acceptor interactions exclusively and not a result of the dense packing on a bottlebrush backbone.

5.2.5 Steady-State Fluorescence Properties



Figure 5.8. Solid state fluorescent emission spectra for BBCPs excited at 313 nm, prepared by spin casting onto a glass slide.

The steady-state fluorescent behaviour of all five bottlebrushes was then explored to determine the impact of interfacial blending. In contrast to the cyclic voltammetry data, the fluorescent properties of these polymers are highly dependent on the degree of donor-acceptor blending in each bottlebrush (Figure 5.8). Most notably, significant TSCT emission is observed in the solid state for ACRTRZ₁₅₀-BB and ACR₇₅-*co*-TRZ₇₅-BB, with $\lambda_{max} = 490$ nm. In the solid state, the other three bottlebrushes exhibit only the expected monomer emission, even in the case of the diblock bottlebrush copolymer ACR₇₅-*co*-TRZ₇₅-BB, implying that in the solid state this monomer ordering prevents donor-acceptor contact and the TSCT that results from their close proximity. Similar emission trends are observed when measured in dilute toluene solution, summarized in Table 5.2, with a slight red-shift observed for the TSCT emission when measured in solution.

Entry	$\lambda_{ m max, \ abs}{}^a$	$\lambda_{\max, em}{}^{b}$	${\Phi_{ ext{F}}}^b$	$\Phi_{\text{F}}{}^{c}$
ACR ₁₅₀ -BB	288	330	0.01	0.03
TRZ ₁₅₀ -BB	292	417	0.001	0.02
ACRTRZ ₁₅₀ -BB	292	519	0.47	0.12
ACR75- <i>co</i> -TRZ75	292	519	0.15	0.07
ACR75- <i>b</i> -TRZ75	292	417	0.01	0.03

Concentrations = 0.01 mg mL^{-1} .

^{*a*}Measured in CH₂Cl₂.

^bMeasured in degassed toluene to reduce excimer formation.

^{*c*}Measured in the solid state under inert atmosphere.

Interestingly, although TSCT emission is observed for both the random (ACRTRZ₁₅₀-BB) and miktoarm (ACR₇₅-*co*-TRZ₇₅-BB) copolymers when measured in toluene and in the solid state, there is a significant difference in quantum yield between the two polymers. The random copolymer exhibits quantum yields of 0.47 in degassed toluene and 0.12 when measured in the solid state, while the miktoarm polymer demonstrates quantum yield of only 0.15 in degassed toluene and 0.07 in the solid state. This can be attributed to the lower degree of mixing in the miktoarm polymer leading to incomplete energy transfer and a concomitant decrease in quantum yield.



Figure 5.9. Fluorescence spectra of thin films of ACR₇₅-*b*-TRZ₇₅-BB (top), a 1:1 mixture of ACR-MM and TRZ-MM (middle) and ACR₇₅-*co*-TRZ₇₅-BB (bottom) prepared by spin-coating on glass substrates. $\lambda_{ex} =$ 313 nm. (PF = Prompt fluorescence)

To determine the effect of the bottlebrush backbone on emission behaviour in the solid state, a film was prepared that was composed of a 1:1 mixture of **ACR-MM** and **TRZ-MM**. This film exhibits a blend of prompt monomer fluorescence and delayed TSCT emission, as illustrated in Figure 5.9. When compared to films of the diblock bottlebrush (showing only prompt monomer emission) and films of the miktoarm polymer (showing almost exclusively TSCT emission), we can see that the bottlebrush morphology either forces or prevents contact between donor and acceptor chains, allowing for improved control over the photophysical properties. This may also provide a mechanism by which TSCT can be adjusted according to environmental stimuli if these donor and acceptor side chains are incorporated into a stimulus-responsive matrix. Furthermore, these results demonstrate that TSCT is the dominant emission mechanism for miktoarm-type

bottlebrush nanofibers, indicating that the larger interchain spacing is still amenable to TSCT, even when solvated.

Entry	Prompt (%) ^a	Delayed $(\%)^a$
ACR ₁₅₀ -BB	100	-
TRZ ₁₅₀ -BB	100	-
ACRTRZ ₁₅₀ -BB	39.7	60.3
ACR75- <i>co</i> -TRZ75	42.6	57.4
ACR75- <i>b</i> -TRZ75	100	-

 Table 5.3. Delayed fluorescence and prompt fluorescence ratios of bottlebrush polymers measured in solid state.

^{*a*} Measured according to $\frac{\phi_{PF} + \phi_{DF}}{\phi_{PF}} = 1 + \frac{\phi_{DF}}{\phi_{PF}}$ by measuring quantum yield in film state under oxygen and under inert conditions.²⁵⁰

As the TSCT emission observed in the polymers reported by Lixiang Wang and coworkers demonstrated clear TADF properties, we also measured the quantum yield of the polymers in the solid state under inert atmosphere and air. In this way, it is possible to quantify what portion of the emission is due to the prompt component of the TADF process and what portion is due to the delayed component. As shown in Table 5.3, the larger average donor-acceptor spacing in the miktoarm polymer results in a small reduction in the relative ratio of delayed fluorescence to prompt fluorescence, decreasing from 60.3% delayed emission for the random copolymer to 57.4% in the miktoarm copolymer.



Figure 5.10. Solvatochromic response for a) ACR₁₅₀-BB, b) TRZ₁₅₀-BB, c) ACRTRZ₁₅₀-BB, d) ACR₇₅-*co*-TRZ₇₅-BB, and e) ACR₇₅-*b*-TRZ₇₅-BB measured at 0.01 mg mL⁻¹, excited at 313 nm.

The solvatochromic response of all five bottlebrushes was also characterized to further demonstrate that the low energy emission observed in the random and miktoarm bottlebrushes is due to TSCT. These two BBCP samples demonstrate strong positive solvatochromism (Figure 5.10), although the miktoarm bottlebrush (**ACR**₇₅-*co*-**TRZ**₇₅-**BB**) shows a small degree of residual monomer emission in some solvents. This can be attributed to increased donor-acceptor separation when the miktoarm polymer is solvated, resulting in decreased charge transfer efficiency and resulting emission from the individual monomers. The remaining bottlebrush polymers, the two homopolymers (**ACR**₁₅₀-**BB** and **TRZ**₁₅₀-**BB**) and the diblock polymer (**ACR**₇₅-*b*-**TRZ**₇₅-**BB**) demonstrate minimal change over the range of solvents used, with most changes observed resulting from aggregation effects.

5.2.6 Time-Resolved Fluorescence Properties



Figure 5.11. Solid-state lifetime data for a) ACR₁₅₀-BB, b) TRZ₁₅₀-BB, c) ACRTRZ₁₅₀-BB, d) ACR₇₅-*co*-TRZ₇₅-BB, and e) ACR₇₅-*b*-TRZ₇₅-BB measured at 0.01 mg mL⁻¹ measured on thin films spin-cast on glass.

The time resolved emission properties of these five polymers were then measured to confirm the TADF nature of the TSCT emission observed for the random and miktoarm polymers, as well as to demonstrate the lack of extended emission lifetimes for the remaining bottlebrushes. These lifetimes were measured both in the solid state (Figure 5.11) and in toluene solution (Figure 5.12). The two homopolymers, **ACR**₁₅₀-**BB** and **TRZ**₁₅₀-**BB**, exhibit only prompt fluorescence (<11 ns) in toluene solution. In the solid state, this prompt fluorescence is somewhat slower for these two homopolymers (<42 ns), although increased lifetimes in the solid state are often observed due to restriction of molecular motion.²⁷⁸


Figure 5.12. Lifetimes in toluene for a) ACR₁₅₀-BB, b) TRZ₁₅₀-BB, c) ACRTRZ₁₅₀-BB, d) ACR₇₅-*co*-TRZ₇₅-BB, and e) ACR₇₅-*b*-TRZ₇₅-BB, measured at 0.01 mg mL⁻¹ in toluene excited at 313 nm with and without sparging with nitrogen.

In contrast, the random copolymer (ACRTRZ₁₅₀-BB) and the miktoarm polymer (ACR₇₅*co*-TRZ₇₅-BB) demonstrate significantly extended fluorescence lifetimes, particularly in the solid state (>100 μ s). The multicomponent nature of the emission observed, summarized in Table 5.4, implies that these two polymers are likely participating in a TADF process, with a long secondary lifetime corresponding to the slow rate of RISC compared to prompt fluorescence. Upon exposure to oxygen, these delayed lifetimes are dramatically reduced in both length and magnitude as is expected in a TADF emitter. In the case of the block copolymer ACR₇₅-*b*-TRZ₇₅-BB with its compartmentalized donor and acceptor regions, the delayed fluorescence was completely absent as this bottlebrush copolymer does not exhibit TSCT and therefore should not exhibit TADF emission.

	Solution ^{<i>a</i>}			Solid		
Entry	$\tau_{,air}(ns)$	$\tau_{,inert}(ns)$	$ au_{p,air}\left(ns ight)$	$\tau_{d,air}(\mu s)$	$\tau_{p,inert}(ns)$	$\tau_{d,inert}(\mu s)$
ACR ₁₅₀ -BB	2.6, 8.9	2.9, 11.0	5.3, 41.7		5.5, 42.1	
TRZ ₁₅₀ -BB	1.6, 6.0	1.8, 7.6	2.8, 39.4		3.0, 40.2	
ACRTRZ ₁₅₀ -BB	32.0, 56.7	66.0, 126	33.9, 137	1.8, 33.7	43.1, 157	23.0, 129
ACR75-co-TRZ75-BB	29.7, 130	30.3, 132	30,132	6.8, 59.9	30.2, 132	5.8, 75.5
ACR75-b-TRZ75-BB	0.8, 4.4	0.8, 5.1	3.9, 40.7		3.3, 39.7	

Table 5.4. Fluorescent lifetimes of bottlebrush copolymers.

^{*a*} Fluorescence on a microsecond time scale was not observed in solution for all samples.

As shown in Table 5.4, the majority of these bottlebrush samples exhibited emission lifetimes that were highly complex and challenging to fit with a typical exponential reconvolution fit. It is likely that a result of the varying environment along the length of a bottlebrush nanofiber composed of organic semiconductors. Emitters located on the sides of the backbone will exhibit different emission behaviour to those at either end of the backbone. Furthermore, along each side chain, the environment of the chromophores will vary with respect to the proximity to other emitters, exposure to solvent, or potential interdigitation with another nearby bottlebrush. As there is such a wide range of potential microenvironments in which the donor-acceptor pairs can exist, the complex lifetimes observed are not unexpected.

5.2.7 Aggregation-Induced Emission



Figure 5.13. a) Illustration of change in conformation in the aggregated state. Aggregation induced emission of ACRTRZ₁₅₀-BB (b), ACR75-*co*-TRZ75-BB (c), and ACR75-*b*-TRZ75-BB (d) measured at 0.02 mg mL⁻¹, normalized such that the maximum intensity at $f_w = 0\%$ is set to 1 and all other spectra are scaled accordingly, with images of the fluorescent emission of the corresponding aggregated samples under 365 nm UV light shown below.

To determine the effect of interchain separation on TSCT behaviour, the response of each of the bottlebrush copolymers to aggregation was measured. Aggregation-induced emission properties were measured by beginning with a solution of polymer in pure THF and then preparing a series of solutions with water fractions (f_w) increasing in increments of 10% (v/v) to give a series of solutions from $f_w = 0\%$ to 90%. When fully solubilized, there is significant solvent interpenetration between side arms that results in an increased spacing between semiconducting groups on adjacent side chains. Upon aggregation, the side chains are rapidly desolvated, leading to significantly decreased interchain distances and enhanced charge transfer, observed as an increase in the TSCT emission (Figure 5.13). In the case of the random copolymer, ACRTRZ₁₅₀-

BB and Figure 5.13b, a significant enhancement of the TSCT emission peak is observed, with emission intensity increasing by a factor of 8.0 upon aggregation with no observable increase in monomer emission. Interestingly, the miktoarm bottlebrush (**ACR**₇₅-*co*-**TRZ**₇₅-**BB**, Figure 5.13c) exhibits both monomer (405 nm) and TSCT (540 nm) emission in neat THF with approximately equal intensity. As the polymer is aggregated and interchain spacing decreases, the intensity of the TSCT emission increases significantly by a factor of 15.8 while the residual monomer emission remained at a similar intensity. This implies that interchain TSCT is significantly enhanced upon aggregation as one would expect from this bottlebrush in which donor and acceptor functionalities are not found on the same side chain. As expected from previous measurements, the diblock polymer remains nanosegregated upon aggregation, demonstrating almost no TSCT emission (Figure 5.13d) when solvated and when fully desolvated, implying that the steric bulk of the densely packed side chains on the bottlebrush prevents significant interpenetration of bottlebrush side chains.



Figure 5.14. Aggregation-induced delayed fluorescence emission of ACR₇₅-*co*-TRZ₇₅-BB from $f_w = 0$ to $f_w = 0.9$.

Beyond the large enhancement in emission intensity upon aggregation, a significant increase in the fluorescence lifetime was also observed as the random and miktoarm BBCPs transitioned from solution to an aggregated state. The lengthened emission lifetimes were most

notable in the case of the miktoarm bottlebrush, **ACR**₇₅-*co*-**TRZ**₇₅-**BB** (Figure 5.14). The emission lifetime was measured for the charge transfer emission peak of the miktoarm bottlebrush in degassed solutions of THF and water. When fully solvated in dilute THF, the long-lived emission that is observed in the solid state is suppressed. However, as f_w is increased from 0% to 90%, a dramatic increase in the two-component fluorescence lifetime is observed increasing from from $\tau_d = (5.6 \ \mu s, 54.5 \ \mu s)$ to $(52.0 \ \mu s, 162 \ \mu s)$, respectively.



Figure 5.15. DLS data for ACRTRZ₁₅₀-BB measured in 100% THF and 10% THF / 90% water; a) the intensity weighted size distribution for this polymer in 100% THF (top) and 10% THF (bottom); b) autocorrelation intensity, cumulant and regularization fits for this polymer in 100% THF (top) and 10% THF (bottom).

To gain further insight into the aggregation behaviour of these polymers, their sizes were measured using DLS (Figure 5.15) in both neat THF and the fully aggregated sample ($f_w = 90\%$). The data shown above implies that rather than forming isolated collapsed bottlebrush particles, the polymers are forming small aggregates with mean radius of approximately 365 nm. This is significantly larger than the solution state mean radius of 14.5 nm. This implies that the photophysical properties observed upon aggregation are the result of many bottlebrush fibers interacting in a small nanoparticle, reinforcing the conclusion that this framework allows for the persistent nanosegregation of adjacent blocks in a diblock polymer with minimal interdigitation of side chains.

5.3 Conclusions

Grafting-through ROMP of donor- and acceptor- functionalized macromonomers has been demonstrated to be an effective method to control charge-transfer processes in a bottlebrush nanofiber. The morphology of the donor-acceptor interface was shown to determine the degree of TSCT emission. Furthermore, the degree of donor-acceptor blending could be easily controlled via covalent synthesis, allowing for monomer organization both along polymer side chains and along the bottlebrush backbone. The donor-acceptor contact controlled by the polymer ordering was shown to persist in the solid state, resulting in no TSCT emission from the diblock bottlebrush polymer. This control over the degree of blending allowed for the preparation of materials that were not accessible with linear semiconducting polymers, forcing complete demixing or mixing in films that would otherwise emit a combination of fluorescence and TSCT. These investigations open the door to further studies on multicompartment nanoscale wires with donor/acceptor properties, including nanomaterials with exciplex-type emission and stimuli-responsive fluorescence. Furthermore, a bottlebrush strategy may be used to either force, or prevent, interactions between chemically dissimilar optoelectronic polymers using either a miktoarm or block morphology. This may prove to be an effective method for preparing blended, multicomponent films from organic semiconductors, where maximizing D-A interactions or

preserving the individual properties of each component of a blend may be necessary – for example, in organic photovoltaics, or ambipolar films for charge-transport.

5.4 Experimental Details

5.4.1 General Considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. **TRZ**¹ **NbInit**⁵ **5.1a**²⁷⁹ and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2imidazolidinylidene](benzylidene)bis(pyridine)ruthenium(II)²⁷⁶ (G3) were prepared according to literature procedures. N-methyl-2-pyrrolidone (NMP) was distilled, then degassed and stored under an N₂ atmosphere. CH₂Cl₂ was freshly distilled from P₂O₅ prior to use. Et₃N was dried by distillation on CaH₂ onto activated molecular sieves then degassed and stored under an N₂ atmosphere. The ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with chloroform-d (CDCl₃) or dichloromethane- d_2 (CD_2Cl_2) as the solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; toluene was used as the solvent and spectra obtained at concentrations of 0.01 mg mL⁻¹. Mass spectra were recorded on a Kratos MS-50 instrument using electron impact ionization.

5.4.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images were obtained using an Asylum Instruments Cypher S AFM system in tapping mode at scan rates of 0.1 Hz. Samples were prepared by spincoating solutions of polymer onto freshly cleaved highly-oriented pyrolytic graphite (HOPG) at 2500 rpm for 30 s at concentrations of ~0.001 mg mL⁻¹. For best results, 1,2-dichloroethane was used as the solvent for spin coating for all bottlebrush polymers. Samples were placed in a vacuum oven (60 °C) for at least 2 h before images were obtained using Mikromasch HQ:NSC14/No Al or HQ:NSC19/No Al probes, with typical resonance frequencies f and spring constants k of (f = 160 kHz, k = 5 N/m) and (f = 65 kHz, k = 0.5 N/m) respectively.

5.4.3 Size Exclusion Chromatography (SEC)

SEC experiments were conducted in chromatography-grade THF at concentrations of 0.5 -2 mg mL^{-1} using a Malvern OMNISEC GPC instrument equipped with a Viscotek TGuard guard column (CLM3008), and Viscotek T3000 (CLM3003) and T6000 (CLM3006) GPC columns packed with porous poly(styrene-*co*-divinylbenzene) particles regulated at a temperature of 35 °C. Signal response was measured using differential viscometer, differential refractive index, photodiode array and right-angle and low angle light scattering detectors. Calibration of interdetector distances was performed using a polystyrene standard from Malvern Inc. Refractive index increments (*dn/dc*) were determined using 100% mass recovery methods from Malvern OMNISEC software version 10.2 with each polymer sample being run at least five times to ensure reproducibility of the calculated refractive index increment.

5.4.4 Electrochemical Methods

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene)²¹⁷; counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene. Experiments were run at a scan rate of 100 mV s⁻¹ in dry degassed electrolyte solution with ~4 mg mL⁻¹ of analyte. Bottlebrush polymers containing triazine functionality were sparingly soluble and run as saturated solutions (TRZ₁₅₀-BB, ACRTRZ₁₅₀-BB, ACR75-*co*-TRZ75-BB, and ACR75-*b*-TRZ75-BB).

5.4.5 Synthetic Procedures – Monomers



4-(9,9-dimethyl-10(9*H*)-acridinyl)-benzaldehyde (5.1b)

This compound was prepared according to modified literature procedure.²³² To a 3-neck, 3 litre round bottom flask was added **5.1a** (26.0 g, 0.12 mol, 1 equiv), K₃PO₄ (0.13 kg, 0.62 mol, 5.0 equiv), and 2.2 litres of DMF as well as a magnetic stir bar. A reflux condenser was attached to the flask, then the reaction mixture was heated to reflux. Once refluxing, 4-fluorobenzaldehyde (27 mL, 0.25 mol, 2.0 equiv) was added to the reaction mixture gradually. The reaction was allowed to progress overnight. Once complete by TLC, the crude reaction mixture was filtered to remove excess K_3PO_4 . The filtrate was then concentrated *in vacuo* then dissolved in 500 mL ethyl acetate. This organic layer was washed three times with 250 mL of deionized water, dried over magnesium sulfate, then filtered and concentrated *in vacuo*. This crude mixture was purified by column chromatography using a gradient of hexane and CH₂Cl₂ (100% hexane to 100% CH₂Cl₂) on silica. Yield 38 g (98%).

¹**H NMR (400 MHz,** *Chloroform-d***):** δ 10.16 (s, 1H), 8.17 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.03 (m, 4H), 6.42 – 6.35 (m, 2H), 1.73 (s, 6H) ppm.

¹³C{¹H} NMR (101 MHz, *Chloroform-d*): δ 191.2, 147.5, 140.4, 135.4, 132.2, 131.4, 130.8, 126.5, 125.4, 121.5, 114.9, 36.2, 30.9 ppm.

HRMS (ESI) *m*/**z**: [M+H] calcd. for [C₂₂H₁₉NO]+H, 314.1544; found, 314.1545; difference: 0.3 ppm.



(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)methanol (5.1c)

This compound was prepared according to modified literature procedure.²²³ Compound **5.1b** (15 g, 48 mmol, 1.0 equiv) was added to a round bottom flask and dissolved in 0.40 L CH₂Cl₂. Once dissolved, 0.13 L EtOH was added to the reaction mixture. Solid NaBH₄ (2.7 g, 72 mmol, 1.5 equiv) was then added to the solution and the reaction was monitored by TLC. When no starting material remained by TLC (approximately 24 h) the reaction was quenched by addition of 1 N NH₄Cl followed by extraction using CH₂Cl₂ (3 x 50 mL). The organic fractions were combined, dried over MgSO4, and concentrated in vacuo. The crude residue was then purified on a short silica column using CH₂Cl₂ and hexane. Yield 13 g (85%).

¹**H NMR (400 MHz,** *Chloroform-d***):** δ 7.65 (d, J = 8.2 Hz, 2H), 7.48 (dd, J = 7.5, 1.8 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.01 – 6.91 (m, 5H), 6.29 (dd, J = 8.0, 1.5 Hz, 2H), 4.86 (s, 2H), 1.72 (s, 6H) ppm.

¹³C{¹H} NMR (101 MHz, *Chloroform-d*): δ 141.1, 141.0, 140.7, 131.6, 130.2, 129.5, 126.5, 125.4, 120.7, 114.2, 65.1, 36.1, 31.4 ppm.

HRMS (EI) *m*/*z*: [M+H] calcd. for [C₂₂H₂₁NO]+H, 316.1700; found, 316.1701; difference: 0.3 ppm.



4-(9,9-dimethylacridin-10(9H)-yl)benzyl acrylate (ACR)

This compound was prepared according to a modified literature procedure.²⁴⁰ Compound **5.1c** (5.0 g, 5.9 mmol, 1.0 equiv) and a magnetic stir bar were added to a flame-dried 250 mL round-bottom flask which was evacuated and backfilled three times with N₂. CH₂Cl₂ (100 mL) and triethylamine (3.1 mL, 22 mmol, 1.4 equiv) were then added to the round bottom flask and stirred until all solid had dissolved. The reaction flask was cooled to 0 °C in an ice bath for 30 minutes, then acryloyl chloride (1.6 mL, 19 mmol, 1.2 equiv) was added to the reaction mixture dropwise over 10 minutes. The reaction was then protected from light using foil and allowed to stir in the ice bath for 24 h. The reaction was quenched by addition of water and extracted with CH₂Cl₂ (3 x 50 mL). The organic fractions were combined, dried over MgSO₄, and concentrated *in vacuo* without added heat. The crude residue was purified on a short silica column using CH₂Cl₂, taking care to elute the product as quickly as possible to avoid decomposition on silica. This pure material was then recrystallized from hexane/CH₂Cl₂. Yield 3.4 g (58%).

¹**H NMR (400 MHz,** *Chloroform-d***):** δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 7.5, 1.9 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.05 – 6.92 (m, 4H), 6.57 (dd, *J* = 17.3, 1.4 Hz, 1H), 6.36 – 6.26 (m, 3H), 5.96 (dd, *J* = 10.4, 1.4 Hz, 1H), 5.38 (s, 2H), 1.73 (s, 6H) ppm.

¹³C{¹H} NMR (101 MHz, *Chloroform-d*): δ 166.1, 141.2, 140.8, 136.0, 131.6, 131.5, 130.5, 130.0, 128.2, 126.4, 125.3, 120.6, 114.0, 65.8, 36.0, 31.3 ppm.

HRMS (EI) *m*/z: [M+H] calcd for [C₂₅H₂₃NO₂]+H, 392.1626; found, 392.1626; difference: 0.5 ppm.

5.4.6. Synthetic Procedures – Macromonomers



Synthesis of ACR-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ACR** (1.0 g, 2.7 mmol, 24 equiv), 1.07 mL of a solution of **NbInit** in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; **NbInit**: 54 mg, 0.11 mmol, 1 equiv), and 0.43 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 1.6 mg, 7.2 x 10⁻³ mmol, 0.065 equiv; Me₆TREN: 1.8 mg, 7.6 x 10⁻³ mmol, 0.068 equiv). The total polymerization volume was kept to 5 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 5 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 µL aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. After 6 hours of polymerization, at approximately 50 % conversion, the polymerization was quenched by precipitation into 200 mL of deionized water followed by filtration. The polymer was taken up in CH₂Cl₂, dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF

and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 0.47 g.



Synthesis of TRZ-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **TRZ** (1.0 g, 2.0 mmol, 18 equiv), 1.1 mL of a solution of **NbInit** in NMP ($C_{NbInit} = 50 \text{ mg mL}^{-1}$; **NbInit**: 54 mg, 0.11 mmol, 1.0 equiv), and 0.43 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8 \text{ mg mL}^{-1}$; CuBr₂: 1.6 mg, 7.2 x 10⁻³ mmol, 0.065 equiv; Me₆TREN: 1.8 mg, 7.6 x 10⁻³ mmol, 0.068 equiv). The total polymerization volume was kept to 10 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 10 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 µL aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. After 8 hours of polymerization, at approximately 50 % conversion, the polymerization was quenched by precipitation into 200 mL of deionized water 232

followed by filtration. The polymer was taken up in CH_2Cl_2 , dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 0.44 g.



Synthesis of ACRTRZ-MM by Cu(0)-RDRP:

In a nitrogen atmosphere glovebox, to a 20 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added a mixture of **TRZ** (0.50 g, 1.0 mmol, 9.0 equiv), **ACR** (0.50 g, 1.4 mmol, 12 equiv), and 1.1 mL of a solution of **NbInit** in NMP ($C_{NbInit} = 50$ mg mL⁻¹; **NbInit**: 54 mg, 0.11 mmol, 1 equiv), and 0.43 mL of a solution of CuBr₂/Me₆TREN in NMP ($C_{Cu} = 3.8$ mg mL⁻¹; CuBr₂: 1.6 mg, 7.2 x 10⁻³ mmol, 0.065 equiv; Me₆TREN: 1.8 mg, 7.6 x 10⁻³ mmol, 0.068 equiv). The total polymerization volume was kept to 7 mL of solvent. The mixture was stirred at room temperature for 10 minutes to allow all reagents to fully dissolve. A 7 cm piece of 18-gauge copper (0) wire was soaked in concentrated HCl for 15 minutes to remove surface impurities, then washed with water followed by acetone, dried *in vacuo* and taken into the glovebox. The wire was added to the mixture to initiate the polymerization. Each hour a 25 µL aliquot was taken and diluted with CDCl₃, and the conversion monitored by ¹H NMR. After 7 hours of polymerization, at approximately 50 % conversion, the polymerization was quenched by 233

precipitation into 200 mL of deionized water followed by filtration. The polymer was taken up in CH_2Cl_2 , dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by preparatory SEC (Bio-Rad Bio-Beads S-X1 Support) in THF and fractions containing polymer were determined by SEC analysis. All fractions containing polymer were collected and dried *in vacuo* overnight. Yield = 0.54 g.

5.4.7. Synthetic Procedures – Bottlebrush Copolymers



Synthesis of ACR₁₅₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ACR-MM** (0.10 g, 1.9×10^{-2} mmol, 150 equiv) and 0.50 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 23 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 0.092 mg, 1.3×10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF to remove any residual macromonomer. Fractions containing polymer were identified by spotting on a TLC plate (visualized with 254 nm UV light) and analyzed by SEC analysis to determine whether they

contained residual macromonomers or bottlebrush polymers. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight. Yield = 64.5 mg.



Synthesis of TRZ₁₅₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **TRZ-MM** (0.10 g, 1.7×10^{-2} mmol, 150 equiv) and 0.50 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 21 μ L of a solution of **G3** in THF ($C_{G3} = 4.0 \text{ mg mL}^{-1}$; **G3**: 0.083 mg, 1.2×10^{-4} mmol, 1.0 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 μ L aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF to remove any residual macromonomer. Fractions containing polymer were identified by spotting on a TLC plate (visualized with 254 nm UV) and analyzed by SEC analysis to determine whether they contained residual macromonomers or bottlebrush polymers. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight. Yield = 58 mg.



Synthesis of ACRTRZ₁₅₀-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ACRTRZ-MM** (0.10 mg, 1.8 x 10^{-2} mmol, 150 equiv) and 0.50 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 21 µL of a solution of **G3** in THF ($C_{G3} = 4.0$ mg mL⁻¹; **G3**: 0.085 mg, 1.2 x 10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 µL aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF to remove any residual macromonomer. Fractions containing polymer were identified by spotting on a TLC plate (visualized with 254 nm UV) and analyzed by SEC analysis to determine whether they contained residual macromonomers or bottlebrush polymers. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight. Yield = 54 mg.



Synthesis of ACR₇₅-co-TRZ₇₅-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ACR-MM** (50 mg, 9.4×10^{-3} mmol, 75 equiv), **TRZ-MM** (55 mg, 9.4×10^{-3} mmol, 75 equiv) and 0.50 mL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 23 µL of a solution of **G3** in THF ($C_{G3} = 4.0$ mg mL⁻¹; **G3**: 0.092 mg, 1.3 x 10⁻⁴ mmol, 1.0 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 µL aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF to remove any residual macromonomer. Fractions containing polymer were identified by spotting on a TLC plate (visualized with 254 nm UV) and analyzed by SEC analysis to determine whether they contained residual macromonomers or bottlebrush polymers. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight. Yield = 73 mg.



Synthesis of ACR₇₅-*b*-TRZ₇₅-BB by ROMP:

In a nitrogen atmosphere glovebox, to a 2 mL vial capped with a Teflon-lined lid and equipped with a magnetic stir bar was added **ACR-MM** (50 mg, 9.4 x 10^{-3} mmol, 75 equiv) and 0.25 µL of THF (dry, degassed, filtered through basic alumina). Using a glass microsyringe 23 µL of a solution of **G3** in THF (*C*_{**G3**} = 4.0 mg mL⁻¹; **G3**: 0.092 mg, 1.3 x 10^{-4} mmol, 1 equiv) was added to the dissolved polymer rapidly in one portion. The mixture was stirred at room temperature for 1 h. Two 5 µL aliquots were taken for ¹H NMR and SEC analysis, before addition of **TRZ-MM** (55 mg, 9.4 x 10^{-3} mmol, 75 equiv) dissolved in 0.25 µL of THF. The mixture was stirred at room temperature for an additional 1 h. Two 5 µL aliquots were taken for ¹H NMR and SEC analysis, and the polymerization was removed from the glove box, quenched with one drop of ethyl vinyl ether, and immediately purified by preparatory SEC (Toyopearl HW-55F resin) in THF to remove any residual macromonomer. Fractions containing polymer were identified by spotting on a TLC plate (visualized with 254 nm UV) and analyzed by SEC analysis to determine whether they contained residual macromonomers or bottlebrush polymers. All fractions containing bottlebrush polymer were collected and dried in vacuo overnight. Yield = 54 mg.

Chapter 6: Bis(hexamethylazatriangulene)sulfone: A high-stability deep blueviolet fluorophore with 100% quantum yield and CIE_y < 0.07

6.1 Introduction

While there have been significant advances made in the development of high quantum yield deep-blue emitters,^{280,281} developing fluorescent emitters for use in OLEDs faces challenges beyond improving quantum efficiency. Specifically, emitters must also be stable so as not to decompose upon electroluminescence while also maintaining color purity.²⁸² The problem of decomposition is particularly notable in the case of high-energy deep-blue emitters, defined by having Commision Internationale de l'Éclairage (CIE) coordinates with (x,y) values such that CIE_x + CIE_y \leq 0.3. As this high-energy emission necessitates a large bandgap (>3.0 eV), devices that emit deep-blue light require a high driving voltage to generate excitons. These high-energy excitons are prone to undesired reactivity, making these emitters significantly more susceptible to decomposition when excited than red or green emitters, either via a photoexcitation process or electroluminescence.²⁸³ Devices using deep-blue emitters can also be particularly challenging to design as they require specially designed host, hole-, and electron-transport materials to accommodate the large bandgap needed.

Beyond deep-blue emitters, compounds that are violet emissive, with emission peaks as low as 400 nm and CIE_y values < 0.10, are even less well-studied. These materials are sought for applications in biological and chemical sensing,^{284,285} electroluminescent devices,^{286–289} and organic lasers.^{290,291} The loss in stability due to the large bandgaps required for this violet emission

⁵ The work described in this chapter has been published as Tonge, C. M., Zeng, J., Zhao, Z., Tang, B. Z., Hudson, Z. M., *J. Mater. Chem. C*, **2020**, *8*, 5150 - 5155.

(≥3.2 eV) makes developing high-efficiency emitters with extended photobleaching lifetimes particularly challenging.



Figure 6.1. Orientation of a) unbridged and b) bridged triarylamine donors; c) illustration of the increased orbital overlap when the triarylamine donor is structurally constrained. Reproduced with permission from Ref 143. Copyright 2019 American Chemical Society.

One method that has been used recently to achieve emitters with high photostability involves synthesizing donor-acceptor emitters in which molecular motion is restricted. This is typically achieved by the addition of a bridge between adjacent aryl rings, as illustrated in Figure 6.1. The reduced intermolecular motion that results from the locked planarity of these emitters allows for enhanced quantum yields while simultaneously narrowing the emission spectrum and decreasing the rate of photobleaching. This enhanced stability can be attributed to the reduced intramolecular motion that reduces potential nonradiative decay pathways. For example, Yamaguchi and coworkers have taken advantage of this planarization strategy to synthesize ultrastable dyes that use a planarized phosphole *P*-oxide for stimulated emission-depletion (STED) imaging.^{141,292} In this work, they demonstrated significantly reduced photobleaching over a twohour period by addition of a carbon-based bridge between a triarylamine donor and a phosphole acceptor. Similarly, Hatakeyama¹³⁹ and Lee²⁹³ have demonstrated the utility of this strategy to synthesize emissive materials with enhanced stability as well as narrowed emission.^{144,294} These authors have used this planarization method to achieve TADF without the use of a traditional twisted donor-acceptor framework, instead using a planarized boron acceptor as a framework to 240

rigidify their emitters. This limits molecular motion, resulting in enhanced photoluminescent quantum yield and narrowed emission. Adachi and coworkers have also explored the use of locked planarity as a tool to create electroluminescent materials. In one recent report, Adachi explored the use of a rigid framework with enhanced planarity as well as spatially separated donor and acceptor functionalities²⁹⁵ to generate excited-state intramolecular proton transfer (ESIPT). Proton-transfer upon excitation ensures spatial separation of the HOMO and LUMO, allowing for access to planarized compounds with TADF properties. In another publication, Adachi and coworkers took advantage of the planarized triarylamine hexamethylazatriangulene (HMAT) to generate a novel donor-acceptor emitter composed of this HMAT donor and a triazane acceptor²⁹⁴ with an emission spectrum that is narrowed significantly when compared to an identical molecule with a lower degree of donor bridging.²⁹⁶ This donor was also used in more recent work by Bryce and coworkers in which the same azatriangulene core was used with several acceptor functionalities to generate charge-transfer materials with stability enhanced by the planarized donor.¹⁴⁴ This planarized donor enhances the stability of the emitter by increasing the strength of aryl C-N bonds, by reducing torsion as well as reducing the C-N bond length.²⁹⁷ This is a key method to enhance the stability of compounds based on triarylamine donors as these C-N sp² bonds have been identified as the weakest bond in several twisted donor-acceptor emitters. In all cases, enhanced molecular rigidity has been shown to increase stability of donor-acceptor emitters while narrowing the emission spectrum and enhancing color purity.

In this chapter, I will describe my work towards developing ultra-deep blue-violet chromophores using a planarized (HMAT) donor and a sulfone acceptor. I developed HMAT₂SO₂ as a fully planarized analogue of state-of-the-art blue fluorescent emitters such as record-setting TADF emitter DMAC-DPS.¹³⁸ We proposed that planarizing these sulfone-based emitters will

result in increased resistance to photobleaching while maintaining high quantum yield and blueviolet emission similar emitters in the literature. Furthermore, we proposed that the emitters studied in this chapter should demonstrate enhanced two-photon excited fluorescence (2PEF) due to the planarization of the donor triarylamine generating an enhanced two-photon cross-section.

6.2 Planarized Sulfone Emitter

6.2.1 Molecular Design

Sulfone acceptors have found numerous applications in the design and synthesis of a wide variety of chromophores due to its strong electron-accepting ability. It has found recent utility for the synthesis of TADF emitters as the tetrahedral geometry around the SO₂ center is amenable to the twisted donor-acceptor orientations that are typically required to achieve small singlet-triplet energy gaps. Diphenylsulfone-based emissive materials have been extensively studied by Adachi,^{138,278,298} Wang,²⁹⁹ Yang,^{300,301} and others³⁰² as deep-blue emissive materials. Many of these examples also demonstrated strong TADF, for instance, DMAC-DPS demonstrated an EQE of 19.5% in devices, competitive with phosphorescent blue OLEDs.¹³⁸ Sulfone-based acceptors have also been used in polymeric OLED materials by Bryce and Ren. In this work, they were able to demonstrate polymers with TADF properties and colour-tunable emission that was used to achieve high efficiency white light emission.^{303,304} Furthermore, Wolf has made used of symmetric arylsulfone emitters in photoswitchable materials which have been used for photomediated encryption and encoding.^{305–307} Using a sulfone acceptor to develop a fluorescent emitter that exhibits deep-blue emission as well as high photostability still remains an active area of research.



Figure 6.2. Blue fluorescent emitters developed by Adachi and the proposed planarized analogue explored in this chapter.

Our design strategy focused on improving the photostability of emitters that have been demonstrated to exhibit high efficiency blue emission, such as TBPA-DPS²⁷⁸ or DMAC-DPS,¹³⁸ by using a donor moiety with increased rigidity and planarity as demonstrated in Figure 6.2. Using the HMAT donor fragment, we hoped to generate a deep-blue emitter with enhanced stability and narrowed emission spectrum without significantly reducing the solubility of the resulting emitter. While HMAT-containing materials have demonstrated utility in generating high-efficiency TADF emitters, this donor has also been used for applications in two-photon excited fluorescence (2PEF).¹⁴⁴ These materials remain underexplored due to the complexity of the synthesis of HMAT itself, requiring a multistep procedure with very low yields that complicate purification and scalability.³⁰⁸ HMAT represents an ideal donor for two-photon absorption due to its strong electron-donating ability combined with the large optical and two-photon cross-section (σ_2) of molecules composed of this large planar donor.^{309,310} The bridging of the adjacent aryl rings in this donor orients these phenyl rings such that they form a single plane with delocalized electron density. This planarization has been demonstrated by several groups^{311–313} to significantly improve two-photon absorption, with HMAT-based materials demonstrating impressive cross sections as 243

high as $\sigma_2 = 6100$ GM in the case of a dendritic material composed of six HMAT donors organized in a fully-conjugated dendrimer with all donors arranged in the same plane.^{308,312}

The hexamethylazatriangulene donor also serves to improve the stability of the emitters to which it is appended. The planarized triarylamine structure vastly increases the stability of unstable radicals or charged states that are formed upon excitation, especially in electroluminescent systems. These excited states can often lead to emitter or charge transport material degradation when they are running due to the high energy nature of these excited states.²⁹⁷ This means that molecules used for electroluminescence must be stable both in the neutral form and as a radical state upon hole- or electron-transport. By planarizing the donor functionality, these radicals are able to delocalize over the full π -system of the molecule, reducing their reactivity and limiting decomposition, resulting in emitter stabilization.

In computational work by Song and Lee²⁹⁷ predict that twisted sp² C-N bonds are typically the weakest bonds in triarylamine-containing OLED materials. This instability is particularly notable in the unstable charged excited states observed in highly twisted donor-acceptor TADF emitters.¹⁴⁴ The reduction in torsion, reduced bond length, and increased bond strength achieved via the planarization of the HMAT donor over a traditional triarylamine serves to stabilize both the neutral and charged donor moiety. Several methods can be used to bridge these adjacent *ortho*aryl positions, however, the isopropenyl bridges chosen in this work serve to increase solubility of the donor-acceptor emitter generated via the inclusion of six out of plane methyl groups while avoiding potential side reactivity and low solubility as in the case of oxo-bridged or carbonylbridged arylamines known in the literature.¹⁴³ The radical stabilization properties of HMAT as a hole-transport material have been demonstrated via direct measurement of the electrochemical properties of these materials, demonstrating an oxidation potential ~ 0.2 eV lower in the bridged arylamine compared to its unbridged counterparts.³¹⁴

6.2.2 Synthesis of HMAT₂SO and HMAT₂SO₂



Figure 6.3. Synthetic route to HMAT₂SO and HMAT₂SO₂.

To prepare the proposed compounds, first a brominated HMAT building block is synthesized according to literature methods.³⁰⁸ This involves first generating the HMAT core itself via a three-step procedure in which methyl anthranilate and methyl iodobenzoate are reacted via a copper-catalyzed Ullman condensation to generate the corresponding *ortho*-functionalized triarylamine. These three *ortho*-esters are then reduced to the corresponding tris(tertiary isopropanol)-functionalized triarylamine via a Grignard addition using excess methyl magnesium iodide. These three alcohols are then dehydrated in the presence of neat H₃PO₄ to cyclize this precursor to give the HMAT core. This sequence of reactions, although simple, has an overall yield of approximately 2-4%, causing significant difficulties when attempting to prepare this donor on appreciable scale. The monobrominated HMAT compound **6.1** is prepared in a single step via a stoichiometric bromine addition with one equivalent of *N*-bromosuccinamide followed by purification via chromatography and recrystallization in hexanes.

This brominated building block is then used to synthesize the two emitters studied in this chapter: **HMAT₂SO** and its oxidized analogue, **HMAT₂SO**₂. These compounds are synthesized via a high-yielding two-step process detailed in Figure 6.3. First, **6.1** (1.0 equiv) is reacted at -78 °C with *n*-butyllithium (1.1 equiv), followed by the addition of 0.5 equiv of dimethylsulfite. The

lithiated HMAT in solution then adds via a nucleophilic attack on the dimethylsulfite to yield **HMAT₂SO** in 91% yield. Further oxidation to the sulfone can be achieved via a variety of oxidative methods; in this case, *m*-CPBA in CH_2Cl_2 was used to give the final product in 93% yield. The sulfoxide and sulfone can be readily differentiated by ¹H NMR spectroscopy as the protons *ortho*- to the sulfur-based acceptor shift from 7.64 to 7.90 ppm in CD_2Cl_2 upon oxidation from the sulfoxide to the sulfone.

6.2.3 Crystal structure of HMAT₂SO₂



Figure 6.4. Crystal structure of HMAT₂SO₂ plotted with 50% probability ellipsoids. H atoms have been omitted for clarity.

Following purification via column chromatography, it was noted that the target compound was only sparingly soluble in hexanes. Using this information, crystals of **HMAT₂SO₂** suitable for X-ray crystallographic analysis were obtained by slow evaporation from hexanes/CH₂Cl₂ (Figure 6.4). The compound crystallizes in the $P2_1/c$ space group, with the structure revealing a slightly asymmetric bowl-shaped geometry for the HMAT fragment. An angle of 179.5° is observed from C1 (bonded to sulfur), to C2 (the methylene opposite sulfur) through the central nitrogen atom and an angle of 160.2° from C3 (opposite C1, bonded to sulfur) to C4 (methylene opposite C2). S-C and S-O bond lengths of 1.76 and 1.44 Å are observed, consistent with similar diphenylsulfone-based molecules.²⁷⁸





Figure 6.5. Solution state absorbance (dotted) and emission (solid) for a) HMAT₂SO and b) HMAT₂SO₂ measured at 1 x 10⁻⁵ mg mL⁻¹, c) CIE 1931 diagram showing HMAT₂SO and HMAT₂SO₂.

As expected based off of the strong donor and acceptors used for these two emitters, both **HMAT₂SO** and **HMAT₂SO₂** show bright blue-violet fluorescence, with emission peaks at 392 nm and 401 nm respectively. This is very similar to the emission color of the unmodified donor, however, the addition of an acceptor to the electronic system results in significantly enhanced photoluminescence quantum yields. In fact, such strong fluorescence was noted from the sulfoxide intermediate that both compounds were characterized for their fluorescent properties. In toluene, these compounds were found to have quantum yields of 0.41 and 1.0 respectively, a relatively rare feat for such deep-blue emission. Furthermore, the rigidity enhancement in the donor led to significantly narrowed emission spectra, with full-widths at half-maxima (FWHM) of 39.5 nm and 42.5 nm respectively, significantly narrower than the emission shown for either DMAC-DPS (67 nm).³¹⁵

r J r - r				
Emitter	HMAT ₂ SO	HMAT ₂ SO ₂		
$\lambda_{max,abs}{}^a$	303; 354 nm	293; 371 nm		
$\lambda_{max,em}{}^a$	392 nm	401 nm		
Φ^a	0.41	1.0		
CIE^{a}	(0.165,0.027)	(0.163,0.021)		
FWHM ^a	42.5 nm	39.5 nm		
$E_g^{\ b}$	3.26 eV	3.11 eV		
$\varepsilon (\mathrm{M}^{-1}\mathrm{cm}^{-1})^a$	50500; 38700	25200; 20700		
HOMO _{exp} ^c	-5.53 eV	-5.92 eV		
$LUMO_{exp}^{d}$	-2.27 eV	-2.81 eV		
HOMO _{calc} ^e	-5.10 eV	-5.21 eV		
LUMO _{calc} ^e	-1.06 eV	-1.40 eV		
_				

Table 6.1. Photophysical properties of HMAT₂SO₂ and HMAT₂SO.

^{*a*} Measured in toluene at 10^{-5} M.

 ${}^{b}E_{g}$ was determined from the low-energy UV-vis absorption band edge.

^c Measured by CV at 2 mg mL⁻¹ with 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene.

^d Calculated from the HOMO level and the optical energy gap, $E_{\rm g}$.

^e Calculations were performed at the B3LYP/6-31+G(d) level of theory.

As summarized in Table 6.1, besides demonstrating narrow emission profiles, both of these compounds demonstrate highly favorable emission color and purity. The sulfoxide and sulfone each demonstrate blue-violet emission with CIE coordinates of (0.163, 0.021) and (0.165, 0.027) respectively, well below the cut-off for a deep-blue emitter defined by $CIE_x + CIE_y \le 0.3$. These CIE coordinates represent emission near the lower vertex of the CIE 1931 diagram, illustrated in Figure 6.5, as well as a blue shift of 59 nm relative to DMAC-DPS.¹³⁸ These compounds are among the most blue/violet high quantum yield emitters reported in the literature,^{316,317} lending them to potentially interesting applications in imaging and for electroluminescent devices.



Figure 6.6. a) Aggregation induced emission spectra for HMAT₂SO₂ from 0% water in THF to 90% water in THF, measured at 0.025 mg mL⁻¹; b) Plot of I/I₀ for HMAT₂SO₂ from $f_w = 0$ to $f_w = 0.9$ where I₀ is the intensity at λ_{max} when $f_w = 0$ and I is intensity at λ_{max} .

Next, the response of the sulfone emitter, **HMAT₂SO₂**, to aggregation was characterized to ensure no significant aggregation-caused quenching (ACQ) is observed upon precipitation of the emitter in a THF/water mixture. This is particularly important for both potential applications of these compounds for imaging and for use in nondoped OLEDs. As only the sulfone emitter demonstrated PLQY near unity, the aggregation properties were only measured for this compound. As shown in Figure 6.6, relatively little quenching is observed for this sulfone-based emitter, implying a lack of ACQ. While there are mild variations in the emission intensity, the general trend is a very mild reduction in emission intensity as water fraction is increased.



Figure 6.7. Photoluminescence spectra for HMAT₂SO₂; measured at 0.01 mg mL⁻¹ in the respective solvents labeled above.

The solvatochromic response of the **HMAT₂SO₂** emitter was also characterized as a method to demonstrate the charge-transfer nature of the emission process. As shown in Figure 6.7, a mild bathochromic shift is observed as solvent polarity is increased, as is characteristic of fluorescence from a donor-acceptor emitter. The bathochromic shift from the most polar to the least polar solvent only results in a change in $\lambda_{max,em}$ of 20 nm, likely due to only minor stabilization of the excited state, even in a highly polar solvent such as dichloromethane.

6.2.5 Time-Resolved Fluorescence



Figure 6.8. Temperature-dependent fluorescence lifetimes of a) HMAT₂SO₂ and b) HMAT₂SO measured as spin-cast neat films, excited at 340 nm.

Following the steady-state fluorescence measurements, a series of time-resolved measurements were performed to elucidate the mechanism of photoluminescence observed in both the sulfone- and sulfoxide-based emitters (Figure 6.8). This characterization was performed to determine whether the emission was proceeding via a TADF mechanism (similar to the DMAC-DPS emitter upon which **HMAT₂SO₂** is based) or via a traditional fluorescence mechanism. As shown above, however, these samples exhibited only typical fluorescence, maintaining identical lifetimes over a range of temperatures from 77 K to 300 K. Although fits were assigned to these curves with multiple components, no component was larger than 50 ns for either emitter, implying that it is unlikely for TADF to be contributing to this emission process. The lifetime data for these two emitters is summarized below in Table 6.2.

	HMAT ₂ SO			HMAT ₂ SO ₂			
Temperature	$oldsymbol{ au}_{ ext{total}}{}^{a}$	$oldsymbol{ au}_1{}^a$	$ au_2^a$	$oldsymbol{ au}_{ ext{total}}{}^{a}$	$oldsymbol{ au}_1{}^a$	$ au_2^a$	$ au_{3}^{a}$
77K	1.18	0.820	3.25				
100K	1.17	0.828	3.23	10.2	1.37	3.25	43.9
150K	1.22	0.819	3.12	10.0	1.16	3.25	41.2
200K	1.21	0.815	3.08	10.6	1.06	3.17	43.3
250K	1.25	0.792	3.32	9.90	0.935	3.26	42.1
300K	1.16	0.760	3.12	9.48	1.25	3.25	46.7

Table 6.2. Fluorescence lifetimes vs. temperature for HMAT₂SO and HMAT₂SO₂ measured as a neat film under nitrogen atmosphere.

^{*a*} All lifetimes reported in nanoseconds.

6.2.6 Electronic Properties



Figure 6.9. a) Oxidation waves for HMAT₂SO₂ and HMAT₂SO relative to FeCp^{0/+} measured at 2.0 mg mL⁻¹ in *o*-dichlorobenzene. Calculated HOMO and LUMO orbital distributions for HMAT₂SO (b) and HMAT₂SO₂ (c).

Next, the electronic properties for **HMAT₂SO** and **HMAT₂SO₂** were characterized. To determine the HOMO experimentally, cyclic voltammetry was performed on each compound vs $FeCp_2^{0/+}$ in *o*-difluorobenzene, as shown in Figure 6.9a. For each compound, a reversible oxidation peak was observed at 0.73 and 1.12 V respectively, which correspond to HOMO_{exp} energies of - 5.53 and -5.92 eV respectively. To determine the LUMO level experimentally, the optical bandgap

was measured in toluene (3.26 and 3.11 eV respectively). This value was then subtracted from the HOMO_{exp} value, gives LUMO_{exp} values of -2.27 for **HMAT₂SO** and -2.81 for **HMAT₂SO**₂. These experimentally derived values differed somewhat from those determined via DFT (Figure 6.9), but a similar trend in bandgap energies was observed, with a slightly larger optical bandgap of 4.04 eV for **HMAT₂SO** compared to 3.81 eV for **HMAT₂SO**₂. Furthermore, using DFT, the singlet-triplet energy gaps (ΔE_{ST}) of these compounds were estimated to be 0.57 and 0.42 eV respectively, confirming that TADF is likely not possible in this system as this gap is too large to be overcome with thermal energy at room temperature. All values are summarized above in Table 6.1, as well as illustrated in the cyclic voltammetry traces and orbital diagrams in Figure 6.9.





Figure 6.10. a) HMAT₂SO₂ OLED in operation, b) Electroluminescence spectra, c) luminance-voltage-current density curves and d) external quantum efficiency data for OLEDs using a HMAT₂SO₂ emitter.

Having demonstrated that $HMAT_2SO_2$ exhibits a quantum yield near unity and an emission spectrum close to the bluest point accessible on the CIE 1931 diagram, we sought to demonstrate the utility of this emitter as a fluorescent dopant in an OLED. When generating an OLED with this emitter, however, the large bandgap responsible for the blue-violet emission presented its own challenge. This ultra-large bandgap (>3.0 eV) required special care in the selection of appropriate host and charge-transport materials. A proof-of-concept device was

prepared (Figure 6.10) with the following structure: ITO/HATCN (5 nm)/NPB (40 nm)/mCP (10 nm)/x wt% **HMAT₂SO₂**: PPF (20 nm)/PPF (10 nm)/TPBi (40 nm)/LiF (1 nm)/Al, varying the dopant percentage from 3% to 12%.



Figure 6.11. Diagram of the device structure used for OLEDs I-IV.

In these devices based on $HMAT_2SO_2$, hexaazatriphenylenehexacabonitrile (HATCN) was a hole-injection material; *N*,*N*'-bis(naphthalen-1-yl)-*N*,*N*'-bis(phenyl)benzidine) (NPB) and 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) acted as hole- and electron-transporting materials, respectively; 9,9'-(1,3-phenylene)bis-9H-carbazole (mCP) could transport holes and block electrons; 2,8-bis(diphenylphosphoryl)dibenzo[b,d]furan (PPF) functioned as host and hole-blocking material; indium tin oxide (ITO) and LiF/Al worked as anode and cathode. The device structure is illustrated in Figure 6.11.
	Doping Conc.	$\lambda_{\text{EL}}(\operatorname{nm}_{c})$	V_{on} (V) ^b	$L (cd/m^2)^a$	$\eta_{\rm C}$ $({\rm cd/A})^a$	$\eta_{ m P} \ (m lm/W)^a$	η_{ext} (%) ^a	CIE $(x, y)^c$
Ι	3%	416	4.8	338	0.74	0.47	1.48	(0.157, 0.060)
Π	6%	416	4.7	344	0.84	0.55	1.97	(0.158, 0.063)
III	9%	416	4.7	310	0.89	0.58	2.08	(0.159, 0.060)
IV	12%	420	4.6	352	0.99	0.68	2.15	(0.159, 0.064)

Table 6.3. Electroluminescent Data for HMAT₂SO₂.

^{*a*} The luminance (*L*), current efficiency (η_c), power efficiency (η_P) and external quantum efficiency (η_{ext}) are the maximum values of the devices.

^{*b*} V_{on} is the turn-on voltage at 1 cd/m².

^c Emission peak and CIE coordinates collected at 1 mA/cm².

The electroluminescence data is summarized between Figure 6.10 and Table 6.3, demonstrating that device IV had the best performance examined at an emitter doping concentration of 12%. This device had a maximum external quantum efficiency of 2.15% with CIE coordinates of (0.159, 0.064), giving it emission that is squarely in the deep-blue segment of the CIE 1931 plot. Furthermore, we note that the FWHM of the emission peak only broadens slightly to 53 nm in this electroluminescent device when measured at 1 mA cm⁻² current density. At lower doping concentrations, slightly blue-shifted electroluminescence was observed, although the reduced external quantum efficiencies at these lower doping concentrations is not ideal.

6.2.8 **Two-Photon Excited Fluorescence**



Figure 6.12. Overlay of UV absorbances (solid) and two-photon cross section (dotted) of a) HMAT₂SO and b) HMAT₂SO₂; c) stacked two photon cross section of HMAT₂SO₂, TBPA-DPS, and HMAT₂SO.

After demonstrating the utility of the **HMAT₂SO₂** emitter in an electroluminescent device, we sought to explore the two-photon fluorescence of these emitters. As shown in Figure 6.12, large two-photon cross sections are observed, especially in the case of **HMAT₂SO₂**. The **HMAT₂SO₂** emitter was compared to a control compound with similar solubility and molecular weight, bis(*-p*-(di*-p-tert*-butylphenylamino)phenyl)sulfone (**TBPA-DPS**), a fully unbridged analog. **HMAT₂SO₂** demonstrates a two-photon cross-section of 626 GM at 710 nm (the lower wavelength limit of our laser system), a 250% increase over the nonplanar analogue (Figure 6.12c). **HMAT₂SO** shows a comparatively lower two-photon cross section of only 125 GM at 710 nm, a consequence of its comparatively lower quantum yield as well as less coplanar arrangement of the two HMAT donors in the less oxidized emitter. This is in line with previous studies that have found that donor-acceptor emitters based on a sulfur bridge to the sulfoxide and a further enhancement upon oxidation to the sulfone.³¹⁸



6.2.9 Photobleaching of HMAT₂SO₂

Figure 6.13. a) Relative photobleaching measured over 90 minutes for HMAT₂SO₂ (purple trace), HMAT₂SO (pink trace), and an unbridged analog of HMAT₂SO₂, TBPA-DPS (blue trace) at 0.01 mg mL⁻¹ in DMSO under constant irradiation; b) Color change of HMAT₂SO after 14 hours of irradiation at 365 nm (left) compared to freshly prepared solution in CD₂Cl₂.

The photostability of both the HMAT-functionalized sulfone and sulfoxide emitters was characterized by submitting them to extended irradiation and observing the evolution of the fluorescence intensity over time. As shown in Figure 6.13, the fully unbridged sulfone emitter, **TBPA-DPS**, demonstrates significant bleaching after 90 minutes of irradiation with 350 nm UV light with an estimated excitation power of 98 mW at the sample, retaining only 43% of its original emission intensity, with a significant drop in emission intensity in the first 20 minutes of irradiation. The bridged sulfone emitter, **HMAT₂SO₂**, is significantly more stable under the same conditions, retaining 74% of its original emission intensity over the same period. This enhanced stability is likely due to the previously mentioned C-N bond stability enhancement that arises from the reduced C-N bond length and torsional strain in the planarized donors.^{144,297} Interestingly, the sulfoxide-bridged emitter, **HMAT₂SO**, exhibits significant photobrightening when irradiated for 90 minutes, increasing to a maximum of 145% compared to the initial emission intensity over 70 minutes of irradiation time.



Figure 6.14. Time series progression of NMR aliquots of HMAT₂SO while continuously irradiating at 365 nm. Measurements were taken every 15 minutes for 90 minutes and again after 14 hours. Spectra were measured in CD₂Cl₂ at a concentration of 2 mg mL⁻¹.

To more fully characterize this photobrightening effect, a sample of HMAT₂SO was dissolved in CD₂Cl₂ and irradiated with a 4W handheld 365 nm UV lamp from 3 cm away. This sample was monitored by ¹H NMR every 15 minutes up to the 90 minutes observed during the previous experiment followed by a time point measured after 14 hours of irradiation, shown in Figure 6.14. By monitoring the relative integration of the signals that correspond the protons adjacent to the sulfoxide (7.64 ppm) and the integration of the peaks that correspond to the same protons on the HMAT₂SO₂ emitter at 7.90 ppm, we are able to observe conversion of approximately 28% of the sulfoxide to sulfone over 90 minutes via an undetermined mechanism. Due to the significantly higher quantum yield of the HMAT₂SO₂ emitter over the sulfoxide (approximately 250% brighter), we hypothesize that the photobrightening effect observed may be

due to this conversion during the photobleaching experiment. This reaction does not cleanly deliver a single product, instead delivering a darkly colored mixture of products as observed in Figure 6.13b.

6.3 Conclusions

In conclusion, we have prepared a sulfone-based fluorescent emitter using a fully planarized triarylamine donor, HMAT, to deliver two blue-violet emitters with quantum yields as high as unity. These compounds demonstrate highly desirable deep-blue photoluminescence and electroluminescence, with CIE_x < 0.17 and CIE_y < 0.03 in toluene solution. The fully oxidized **HMAT₂SO₂** emitter was characterized in a proof-of-concept device, demonstrating narrow electroluminescence and acceptable external quantum efficiencies with CIE_x < 0.16 and CIE_y < 0.07 for all doping concentrations examined. **HMAT₂SO₂** shows significant resistance to photobleaching due to the rigidified HMAT donor increasing the stability of C-N aryl bonds. Furthermore, both emitters demonstrated enhanced two-photon cross-sections due to the enhanced coplanarity of the rigidified HMAT donor. Lastly, the **HMAT₂SO₂** emitter also demonstrated minimal aggregation-caused quenching making these compounds amenable to applications in the solid state. Taken together, these materials show promise for applications as high-stability deep-blue/violet emitters for electroluminescence and imaging applications.

6.4 Experimental Details

6.4.1 General Considerations

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk or glove box techniques unless otherwise stated. Dry solvents were obtained from Caledon Laboratories, dried using an Innovative Technologies Inc. solvent purification system, collected under vacuum, and stored under a nitrogen atmosphere over 4 Å molecular sieves. All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received unless otherwise stated. 6.1 was synthesized according to literature procedures.³⁰⁸ The ¹H and ¹³C{¹H} nuclear magnetic resonance (NMR) spectra were measured on a Bruker AV III HD 400 MHz spectrometer with dichloromethane- d_2 (CD₂Cl₂) as the solvent. Absorbance measurements were made on a Cary 60 spectrometer and fluorescence measurements were made on an Edinburgh Instruments FS5 spectrofluorometer. Absolute photoluminescence quantum yields were determined using an Edinburgh Instruments SC-30 Integrating Sphere Module; toluene was used as the solvent and spectra obtained at concentrations of 10^{-5} M. Two-photon cross-sections (σ_2) were calculated using the two-photon excited fluorescence method. Two-photon cross-section (σ_2) values from 710-850 nm were measured with an inverted two-photon fluorescence scanning microscope (Zeiss LSM 510 MP). Samples (3 mL) were measured in quartz cuvettes and concentrations were adjusted to give similar 2PEF intensities (HMAT₂SO₂, 6.0×10^{-5} M; **HMAT₂SO**, 6.0×10^{-5} mg mL⁻¹; **TBPA-DPS**, 1.3×10^{-4} M in toluene) and Rhodamine B in MeOH $(2.1 \times 10^{-4} \text{ M in MeOH})$ was used as the reference.³¹⁹ The cuvette was illuminated at a depth of 0.6 mm from the bottom of the cuvette and imaged with a 10x/0.3 objective lens and femtosecond laser with a tuning range of 710-850 nm. The dichroic mirror had a cut-off at 660. The squaredependence of the fluorescence intensity on laser power was periodically confirmed for all

measured and σ_2 was calculated using the quantum yield obtained from one-photon excitation experiments. Transient PL decay spectra were measured using Quantaurus-Tau fluorescence lifetime measurement system (C11367-03, Hamamatsu Photonics Co., Japan). Mass spectra were recorded on a Bruker HCTultra PTM Discovery System using electrospray ionization.

6.4.2 Electrochemical Methods

Cyclic voltammograms were recorded using a BASi Epsilon Eclipse potentiostat at room temperature using a standard three-electrode configuration (working electrode: 3 mm diameter glassy carbon; reference electrode: RE-5B Ag/AgCl electrode in saturated aqueous KCl (BASi Inc.), referenced externally to ferrocene/ferrocenium (0.543 V in 1,2-difluorobenzene)²¹⁷; counter electrode: Pt wire) in 0.2 M tetrabutylammonium hexafluorophosphate in 1,2-difluorobenzene with 2 mg mL⁻¹ of sample. Experiments were run at a scan rate of 50 mV s⁻¹ in dry degassed electrolyte solution with ~4 mg mL⁻¹ of analyte. The HOMO level was found by referencing the oxidation peak to ferrocene and using the known HOMO of ferrocene (-4.80 eV) to calculate HOMO of **HMAT₂SO** and **HMAT₂SO₂** The LUMO level was calculated by subtracting the optical energy bandgap (Eg) from the HOMO value determined above. Eg was determined from the low-energy UV-absorption band edge.

6.4.3 Density Functional Theory

Quantum-mechanical calculations were performed using the Gaussian 16 Rev. B.01 computational package²⁶⁴ using default settings unless stated otherwise. All calculations were performed at the B3LYP/6-31+G(d) level of theory.

6.4.4 X-Ray Crystallography

Single colorless flake-shaped crystals of **HMAT₂SO₂** were recrystallized from CH_2Cl_2 by slow evaporation. A suitable crystal $0.28 \times 0.15 \times 0.03$ mm³ was selected and mounted on a mylar

loop in oil on a Bruker APEX II area detector diffractometer. The crystal was kept at a steady T = 100(2) K during data collection. The structure was solved with the XT^{220} structure solution program using the Intrinsic Phasing solution method and by using $Olex2^{219}$ as the graphical interface. The model was refined with version 2017/1 of XL^{221} using Least Squares minimization. CCDC 1960706.

6.4.5 Photobleaching

Photobleaching measurements were done on an inverted microscope. Sample aliquots (5 μ L) were measured in a clear flat-bottom 1536-well plate (Greiner Bio One, Kremsmünster, Austria) with the wells covered with universal optical sealing tape (#6575, Corning). Sample concentrations were adjusted to obtain similar initial fluorescence intensities (**HMAT₂SO₂**, 0.001 mg mL⁻¹; **HMAT₂SO**, 0.0005 mg mL⁻¹; **TBPA-DPS**, 0.001 mg mL⁻¹). A 2 × 2 array of wells was illuminated and imaged with a 4× objective lens (NA 0.16). The excitation filter was 350/50 (center wavelength and bandwidth in nm), the dichroic mirror had a cut-off at 425 nm, and no emission filter was used. The excitation power was estimated to be ~98 mW at the sample. Samples were continuously illuminated using the above conditions and images were acquired at 1 min intervals for 90 min and analyzed using ImageJ³²⁰ software with the Time Series Analyzer V3 plugin. The initial intensity for each sample was normalized to a value of unity.

6.4.6 OLED Fabrication and Characterization

Glass substrates with 90-nm indium tin oxide (ITO) with a sheet resistance of $15\sim 20 \Omega$ per square were successively cleaned in ultrasonic bath of acetone, isopropanol, detergent and deionized water, respectively, taking 10 minutes for each step, and then dried in a 70°C oven. Before the fabrication processes, the substrates were treated by O₂ plasma for 10 minutes. The

OLED devices were fabricated under a pressure of $< 5 \times 10^{-4}$ Pa. Organic materials, LiF and Al were deposited at rates of 1~2 A s⁻¹, 0.1 A s⁻¹ and 5 A s⁻¹, respectively.

The luminance–voltage–current density characteristics and electroluminescence spectra were obtained via a Photo Research PR-745 SpectraScan Spectroradiometer with a Keithley 2450 Source Meter. The external quantum efficiencies were estimated assuming that the devices are Lambertian emitters. The effective emitting area of the devices was 9 mm², determined by the overlap between anode and cathode. All the characterizations were conducted at room temperature in ambient conditions without any encapsulation, as soon as the devices were fabricated.

6.4.7 Synthetic Procedures



Synthesis of HMAT₂SO:

Prepared according to modified literature procedure.³⁰⁵ A 250 ml Schlenk flask was charged flame dried then charged with 0.40 g (0.90 mmol, 1 equiv) of compound 6.1. The flask was sealed then evacuated and back filled three times with nitrogen. To this flask was added 0.10 L of dry, degassed THF. The mixture was stirred at room temperature until all materials were fully dissolved. This mixture was then cooled to -78 °C using a dry ice-acetone bath and allowed to equilibrate for 1 hour. Then, 0.62 mL of *n*-BuLi (1.6 M in hexane, 0.99 mmol, 1.1 equiv) was added dropwise. The solution was then stirred for 1 h at -78 °C. To this lithiated mixture was added 50 mg of dimethyl sulfite (0.45 mmol, 0.50 equiv) dissolved in 5 mL of dry, degassed THF. The dimethyl sulfite was added dropwise over the course of 30 min. The reaction was allowed to stir for 1 hour at -78 °C then allowed to warm to room temperature for 2 hours. The reaction was then quenched by dropwise addition of 10 mL of saturated aqueous NH₄Cl. The crude reaction mixture was then diluted with 200 mL of deionized water then extracted with dichloromethane (3 x 50 mL). The organic layer was pooled, dried on MgSO₄, filtered, then dried *in vacuo*. The crude mixture was purified on silica gel using a gradient from hexane to 1:1 hexane in dichloromethane. Yield 325 mg, 91%.

¹**H NMR (400 MHz, Methylene Chloride**-*d*₂): δ 7.64 (s, 4H), 7.41 – 7.34 (m, 8H), 7.14 (t, *J* = 7.7 Hz, 4H), 1.60 (s, 12H), 1.58 (s, 24H) ppm.

¹³C{¹H} NMR (101 MHz, Methylene Chloride-*d*₂): δ 139.3, 134.9, 131.6, 131.1, 130.7, 130.1,
124.5, 124.0, 123.8, 120.5, 36.2, 35.8, 33.7, 32.9 ppm.

HRMS (EIS) *m*/*z*: [M]^{+•} calcd for [C₅₄H₅₂N₂OS]^{+•}, 776.3800; found, 776.3805; difference: - 0.58 ppm.



Synthesis of HMAT₂SO₂:

To a dry 100 mL round bottom flask was added 0.66 g (0.83 mmol, 1 equiv) of **HMAT₂SO** and 50 mL of dry dichloromethane. To this flask was added 0.43 g of *m*-CPBA (2.5 mmol, 3.0 equiv) once all starting material was dissolved. The reaction was monitored by TLC to determine at what point the reaction was complete. Once complete, the reaction was quenched by addition of 30 mL of saturated Na_2CO_3 in water followed by diluting the crude reaction with 100 mL of deionized water. The mixture was then extracted three times with 50 mL of dichloromethane. The organic layer was then dried over MgSO₄, filtered, and dried in vacuo. The crude reaction mixture was then purified over silica gel using a gradient from hexane to 1:1 hexane:dichloromethane to yield the desired product. X-ray quality crystals were prepared by slow evaporation from hexanes/CH₂Cl₂. Yield 0.61 g, 93%.

¹**H NMR (400 MHz, Methylene Chloride**-*d*₂): δ 7.90 (s, 4H), 7.43 – 7.34 (m, 8H), 7.16 (t, *J* = 7.7 Hz, 4H), 1.60 (d, *J* = 1.8 Hz, 36H) ppm.

¹³C{¹H} NMR (101 MHz, Methylene Chloride-*d*₂): δ 136.5, 135.8, 131.2, 130.9, 130.5, 130.2, 124.7, 124.3, 123.7, 122.5, 36.1, 35.7, 33.9, 32.6 ppm.

HRMS (ESI) *m/z*: [M]^{+•} calcd for [C₅₄H₅₂N₂O₂S]^{+•}, 792.3749; found, 792.3758; difference: - 1.02 ppm.

6.4.8 Crystallographic Data

Table 6.4 Crystallographic data for solid-state structure of compound HMAT2SO2, CCDC 1960706

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Formula	C54H52N2O2S
D _{calc.} / g cm ⁻³	1.301
μ/mm ⁻¹	0.127
Formula Weight	793.03
Colour	colourless
Shape	flake
Size/mm ³	0.28×0.15×0.03
T/K	100(2)
Crystal System	monoclinic
Space Group	P21/c
a/Å	14.6045(6)
b/Å	10.5284(4)
<i>c</i> /Å	26.4015(11)
α/ °	90
$\beta/^{\circ}$	94.3480(10)
γ/°	90
V/Å ³	4047.9(3)
Ζ	4
Ζ'	1
Wavelength/Å	0.71073
Radiation type	ΜοΚα
$\Theta_{min}/^{\circ}$	1.398
$\Theta_{max}/^{\circ}$	28.308
Measured Refl.	46632
Independent Refl.	10051
Reflections with I >	6835
2(I)	
Rint	0.0673
Parameters	637
Restraints	1627
Largest Peak	0.598
Deepest Hole	-0.404
GooF	1.005
wR2 (all data)	0.1417
wR ₂	0.1249
R1 (all data)	0.0962
<i>R</i> 1 (I>2(I))	0.0567

Chapter 7: Conclusions and Future Directions

7.1 Conclusions

This work began with the development of a polymerization method by which linear polymers could be easily prepared from a series of π -conjugated acrylic monomers. This Cu(0)-RDRP polymerization method was demonstrated to work well for monomers with both p- and n-type properties, giving access to polymers with molecular weights up to 50 kDa with narrow dispersities and high degrees of chain-end livingness. The p- and n-type polymers were shown to exhibit favorable thermal properties that would make them amenable to use in an organic device. Furthermore, the polymerization method used allowed for facile end group functionalization, allowing us to use this method to generate end group functionalized polymers to use as building blocks in later projects. Most notably, polymerization of these p- and n-type monomers gave rise to polymers whose electronic properties closely matched those of their component monomers, giving insight into expected properties of future semiconducting benzyl acrylate monomers and polymers that has proven invaluable in our research group.

In Chapter 3, it was demonstrated that this polymerization method was also amenable to the synthesis of doped copolymers composed of a large, complex emissive dopant monomer and a low-cost host monomer that serves as a matrix for the emitter. Efficient energy transfer in solid films was demonstrate by carefully selecting the host and emitter monomers used, giving polymers whose emissive properties were entirely the result of emission from the dopant. By generating a series of emissive dopants, materials were generated that demonstrated deep blue electroluminescence, ratiometric oxygen sensing, and thermally activated delayed fluorescence. Furthermore, these emissive properties persisted when these polymers were measured in solution, as a film, and when precipitated as polymer dots. This demonstrates the potential utility of these 268

emissive copolymers for imaging applications via their incorporation into polymer dots with appended handles to bind specific targets. It was therefore demonstrated that by using Cu(0)-RDRP and an appropriate host and emitter monomer, it is possible to generate materials composed almost entirely of host monomer that exhibit the photophysical properties of the emissive dopant.

Having demonstrated the ability to prepare end group functionalized linear polymers via Cu(0)-RDRP, I next sought to use this as a tool to synthesize bottlebrush copolymers. In Chapter 4, we demonstrated how several macromonomers were prepared using the organic semiconductor monomers prepared in Chapter 2 paired with a norbornene-based initiator. Using this method, side chain polymers of approximately 5 kDa molecular weight were prepared and purified, then these macromonomers were polymerized by a second, orthogonal polymerization, ROMP, to generate the bottlebrush copolymers targeted. The composition of the resulting bottlebrushes can be controlled via the order of addition of different macromonomers. Using multiblock ROMP of the π -conjugated macromonomers, we prepared a series of bottlebrush copolymers with multilayer morphologies reminiscent of simple organic electronics such as a two-layer p-n junction or a simplified three-layer OLED. Characterization via AFM confirmed the extended conformations taken by these bottlebrush copolymers, as expected due to the high degree of steric crowding due to the close proximity of adjacent side chains.

This bottlebrush framework was then used for a second project, detailed in Chapter 5. Using the same bottlebrush framework paired with a different set of macromonomers, it was demonstrated that bottlebrush morphology could be used to directly control solid state mixing of a two-component copolymer. To demonstrate the degree to which the two components are blended, donor and acceptor monomers were selected that exhibit through-space charge transfer emission when they are close in proximity but only typical fluorescent emission when separated. Using this method, it was possible to demonstrate the importance of nanoscale ordering on the photophysical properties of bottlebrush nanofibers formed from organic semiconductors. Furthermore, it was shown that this nanoscale control over component mixing and demixing can be used to access materials whose properties are not accessible using traditional linear polymers.

Lastly, in Chapter 6, a highly planarized triphenylamine donor, hexamethylazatriangulene, was prepared to be used as an improved donor group in conjunction with sulfone and sulfoxide acceptors. It was demonstrated that when this HMAT donor is substituted for commonly used triarylamine donors, photostability is increased significantly while still producing blue emission. Besides increasing photostability, the restricted molecular motion of this HMAT donor results in diminished nonradiative decay pathways. This results in higher quantum yield relative to the unbridged analogues. Lastly, enhanced two-photon absorption was also noted for emitters using the HMAT donor, an interesting property for these dyes if imaging applications are explored further.

7.2 Future Work

The work presented in this thesis presents a framework by which complex emissive or charge transporting polymers can be assembled, both low molecular weight linear polymers and large multicomponent bottlebrush copolymers. While a large series of oxadiazole-based donor-acceptor emitters were explored in this work, if these polymers are to be used in high efficiency polymer-based devices, there will need to be significant optimization in terms of host identity, polymerizable handle, and emitter structure. To explore this, I would first explore several alternative host monomers, for example a bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) based monomer to accommodate deep blue TADF emitters^{278,321,322} or 3-(9-phenyl-9H-carbazol-

3-yl)furo[2,3-b:5,4-b0]dipyridine (3PCzPFP) for deep red TADF emitters.³²³ Furthermore, current state-of-the-art OLED devices are using three component emissive layers, using a host, TADF dopant for triplet harvesting, and a high-stability fluorescent emitter in a "hyperfluorescent" device.¹³⁷ A potential route forward would be to prepare fluorescent dopants with enhanced photostability and high color purity and use them in a "hyperfluorescent" three-component polymer system. Our group has begun work exploring this as a potential method to generate OLEDs with high color purity. Other potential applications of linear emissive polymers prepared via Cu(0)-RDRP could also take advantage of stimuli-responsive monomers such as *N*-isopropylacrylamide or acrylic acid. These responsive monomers change in volume at a specific temperature or pH respectively, which could result in enhanced charge transfer when condensed and decreased charge transfer when fully dissolved if luminophores were incorporated.

Based on our initial work developing multiblock bottlebrush copolymers with block structures analogous to simple organic electronic devices, our group plans to explore methods by which these multicomponent fibers can be directly electronically addressed. We would like to explicitly demonstrate exciton transfer through a single polymer fiber using conductive AFM or other suitable methods with a final goal of measuring any electroluminescence produced during this process. As an extension of this, if we are able to demonstrate charge transport in a single chain, we are also interested in potential self-assembly methods with which macroscale organic devices can be assembled in a single self-assembly step. Our group also has interest in investigating responsive bottlebrush polymers achieved via the addition of pH- or temperature-responsive macromonomers. Simply adding a responsive component will likely imbue the nanofiber with similar properties, however, by adding a secondary responsive element, we would be able to synthesize dual-responsive polymers. Materials with optical properties that respond to various stimuli can be particularly useful for imaging applications.

The planarized HMAT donor used here with a sulfoxide and sulfone acceptor has broad applicability to a large range of unexplored acceptors. While this donor has been explored for several TADF emitters,^{144,294} there are many typical acceptor functionalities that have not been explored with this donor. While the sulfone acceptor did not give a sufficiently small ΔE_{ST} to allow for efficient RISC, it is likely that other, weaker acceptors may have potential. If any donoracceptor compounds using this HMAT donor result in efficient TADF, it would be possible to characterize the effect of planarization on the stability of these emitters during electroluminescence and determine whether the stabilization of the triarylamine C-N bonds will result in longer device lifetimes.



Figure 7.1. Proposed structures of several HMAT based emitters spanning the visible spectrum.

Furthermore, dyes composed of HMAT and additional acceptors could also find applications as in imaging, especially time-resolved fluorescence imaging (FLIM) or for twophoton imaging. By modifying the acceptor strength or by adding electron donating/withdrawing substituents on the HMAT core, it should be possible to generate a series of compounds with emission spanning the visible spectrum (Figure 7.1).

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