SELF-ASSEMBLY OF OLIGOMERIC DIPYRROMETHENE METAL COMPLEXES

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Abstract

The study of metallosupramolecular complexes has become an active research field in recent years. These complexes are formed through self-assembly processes driven by ligand-metal coordination, and they are widely used in molecular electronic, catalyst, host-guest chemistry and gas storage applications. Dipyrromethenes (dipyrins) can act as monoanionic ligands which coordinate with various metals to form charge-neutral metal complexes. In the past decade, $\alpha,\alpha'$-linked and $\beta,\beta'$-linked bis(dipyrromethene)s have drawn considerable attention as building blocks for various supramolecular architectures. Surprisingly, limited work has been done to study meso-substituted dipyrinato metal complexes. The primary objective of this project was to investigate meso-substituted dipyrinato complexes and to synthesize novel meso-bridged bis(dipyrromethene) ligands to explore their capabilities for use in supramolecular systems.

A new type of ligand which incorporates both boron-linked dipyrromethenes and free-base dipyrromethenes was synthesized and treated with various metals to form complexes. These metal complexes exhibit different structural features depending on the central metal or substituents on the dipyrromethenes, and the correlations between the structural features and optical properties were established. Also, a one-side BF$_2$-protected bis(dipyrromethene) ligand was used for stepwise oligomerization to form extended dipyrromethene arrays. Different methods to achieve these linear dipyrrin arrays were explored. Heteroleptic metal dipyrrin complexes can act as both the ligand and metal ion source to coordinate with free-base dipyrrin ligands, leading to the formation of oligomeric linear complexes incorporating the same or different metals.
Further, differently angled spacers were employed to link two dipyrrin moieties at the meso-position. Depending on the angle of the spacer, the coordination reactions between bis(dipyrromethene)s and metals produced self-assembled cyclic oligomers with different core sizes. When the two dipyrrin moieties were oriented 86° apart, the resulting products ranged from trimer to hexamer. The trimeric and pentameric structures were determined by X-ray diffraction analysis, and the macrocycles display channel structures formed through intermolecular π-π or CH/π interactions. In contrast, when the two dipyrrin moieties were 35° apart, the main product was the dimer with trace amounts of tetramer. Finally, the coordination between linear heteroleptic metal dipyrrin complexes and the 35° angled bis(dipyrromethene) ligand produced a mixed-ligand complex.
Preface

This project was initiated by my supervisor, Professor David Dolphin. Following a search of the literature and preliminary investigations, I designed, synthesized and further characterized the linear and angled bis(dipyrрин) ligands which eventually led to the desired linear and cyclic metal complexes.

This work has produced one published paper with another two manuscripts in preparation. Parts of Chapter 2 and Chapter 3 have been published (“Self-assembly of oligomeric linear dipyrrromethene metal complexes”; Miao, Qing; Shin, Ji-Young; Patrick, Brian O.; Dolphin, David; Chemical Communications, 2009, 2541-2543.). I conducted all the benchwork and wrote most of the manuscript. Dr. Ji-Young Shin provided useful suggestions for choosing 2-methylpyrrole as the starting material and for the solvents for crystal growth. Dr. Brian Patrick conducted the X-ray analysis of the crystals. Professor David Dolphin provided invaluable guidance and suggestions during the entire course of research and paper preparation.
Table of Contents

Abstract ........................................................................................................................................ ii
Preface .......................................................................................................................................... iv
Table of Contents .......................................................................................................................... v
List of Tables ................................................................................................................................ x
List of Figures ............................................................................................................................ xii
List of Schemes ........................................................................................................................... xx
List of Abbreviations ................................................................................................................... xxii
Acknowledgements ................................................................................................................... xxv

CHAPTER 1 Introduction ............................................................................................................. 1
  1.1 Supramolecular chemistry and supramolecular metal complexes ......................... 2
  1.2 Synthesis of supramolecular complexes through self-assembly ............................ 3
    1.2.1 Linear coordination supramolecular structures ............................................ 3
    1.2.2 Cyclic coordination supramolecular structures ............................................ 6
      1.2.2.1 Self-assembly of cyclic structures ....................................................... 6
      1.2.2.2 Self-assembly of polygons ................................................................. 7
        1.2.2.2.1 Dinuclear cyclic structures ......................................................... 8
        1.2.2.2.2 Trinuclear cyclic structures ....................................................... 9
        1.2.2.2.3 Tetranuclear cyclic structures ................................................... 11
        1.2.2.2.4 Higher nuclearity complexes .................................................... 13
      1.2.2.3 Three-dimensional metal coordination assemblies ................................ 13
  1.3 Dipyrrromethenes ........................................................................................................ 14
    1.3.1 Dipyrrromethanes and dipyrrromethenes: general background ................. 14
1.3.2 Synthesis of dipyrromethenes....................................................................................16

1.3.3 Dipyrromethenes as ligands.......................................................................................18
  1.3.3.1 Dipyrromethene metal complexes ......................................................................18
  1.3.3.2 Dipyrromethene boron complexes......................................................................19

1.4 Development of dipyrromethenes for supramolecular chemistry through self-assembly 20
  1.4.1 Extensive supramolecular structures based on dipyrromethene metal complexes...21
  1.4.2 Discrete dipyrin metal complexes through self-assembly........................................29

1.5 Goals and scope of the thesis............................................................................................35

CHAPTER 2 Metal complexes of building blocks featuring protected dipyrromethene diads36

2.1 Overview of dipyrromethene metal complexes................................................................37

2.2 Synthetic approach to ligands...........................................................................................38
  2.2.1 Initial design ..............................................................................................................38
  2.2.2 Synthesis of bis(dipyrrin)s capped by BF2 as protecting group ..............................39
  2.2.3 Formation and characterization of BF2 capped bis(dipyrrin)s II-12 and II-14..........41
     2.2.3.1 Preparation of ligands .........................................................................................41
     2.2.3.2 Spectroscopic and structural features of II-12 and II-14 ....................................42

2.3 Formation and characterization of divalent metal complexes ..........................................44
  2.3.1 Synthesis of divalent metal complexes......................................................................44
  2.3.2 NMR spectroscopic analysis of complexes II-15 through II-20..............................45
  2.3.3 Crystal structure discussion .......................................................................................47

2.4 Formation and characterization of trivalent metal complexes ........................................50
  2.4.1 Synthesis of trivalent metal complexes II-21 and II-22 ...........................................50
  2.4.2 NMR Spectroscopic analysis of complexes II-21 and II-22....................................51
  2.4.3 Crystal structure discussion .......................................................................................52
2.5 UV-Vis spectroscopy of dipyrromethene metal complexes .............................................55

2.6 Summary ...........................................................................................................................59

CHAPTER  3 Self-assembled linear oligomers of bis(dipyrrinato) metal complexes ..........60

3.1 Overview of molecular wires ..................................................................................................61

3.2 Synthesis of the dipyrromethene dimer and its polymerization .........................................62

3.3 Formation and characterization of dipyrromethene metal complexes with predetermined
length ...........................................................................................................................................64

  3.3.1 Synthesis and purification of dipyrromethene oligomers with different lengths .....64

  3.3.2 UV-Vis spectroscopic analysis of linear metal complexes ........................................65

  3.3.3 Crystal structure analysis of linear metal complex III-5 ...........................................67

3.4 Alternate approach for linear dipyrrin metal complexes with controlled length ..........68

  3.4.1 Synthesis and characterization of heteroleptic dipyrromethene metal complexes ....68

  3.4.2 Synthesis of linear dipyrrin metal complexes via heteroleptic bis(dipyrrin) metal
complexes ...................................................................................................................................70

3.5 Current progress on the synthesis of linear dipyrrin metal complexes ............................73

  3.5.1 Using simple dipyrrins to replace BF₂-capped bis(dipyrrin)s .............................73

  3.5.2 Linear dipyrrin metal complexes incorporating different metals .........................75

    3.5.2.1 Step 1: synthesis of metal-dipyrrin chains with free ends on both sides .........76

    3.5.2.2 Step 2: synthesis of metal-dipyrrin chains with both ends blocked by metal
acetylacetonate ........................................................................................................................78

    3.5.2.3 Step 3: synthesis of linear dipyrrin metal complexes containing different metals
.................................................................................................................................................80

3.5.3 Attempts to prepare two-dimensional dipyrromethene metal complexes ..........83

  3.5.3.1 Synthesis of dipyrromethene trimer and tri-boron dipyrromethene .................83
3.5.3.1 Formation of two-dimensional dipyrromethene metal complexes .....................85

3.6 Conclusion and outlook ....................................................................................................86

CHAPTER 4 Self-assembled cyclic oligomers of bis(dipyrrinato) metal complexes........88

4.1 Self-assembled cyclic metal complexes ...........................................................................89

4.2 Attempts using dimeric dipyrrin derivatives bridged by phenyl linkers .................91

4.2.1 α-Free dimeric dipyrrin derivatives bridged by phenyl linkers and their metal complexes ......................................................................................................................................91

4.2.2 α-Methyl dimeric dipyrrin derivatives and their metal complexes .........................92

4.2.3 Dimeric dipyrrin derivatives with extended “arms” and their metal complexes ......93

4.3 Carbazole-bridged 3,6-dimeric dipyrrin derivatives and their metal complexes ..........94

4.3.1 Synthetic approach to carbazole bridged 3,6-dimeric dipyrrin ligands and their metal complexes ......................................................................................................................................95

4.3.2 Improved carbazole-bridged 3,6-dimeric dipyrrin ligands and their metal complexes ......................................................................................................................................97

4.3.2.1 Synthesis of carbazole-bridged 3,6-dimeric dipyrrin ligands and their metal complexes ......................................................................................................................................97

4.3.2.2 UV-Vis spectroscopic analysis of metal complexes IV-26 through IV-28 .......99

4.3.2.3 Crystal structure analysis of metal complexes IV-26 and IV-28 .........................99

4.4 Carbazole-bridged 1,8-dimeric dipyrrin ligands and their metal complexes ..........108

4.4.1 Synthesis of carbazole-bridged 1,8-dimeric dipyrrin ligand IV-33 .......................109

4.4.2 Formation of stereoisomers through metal complexation of ligand IV-33 ..........110

4.4.3 NMR spectroscopic analysis of complexes IV-35 ...............................................112

4.4.4 UV-Vis spectroscopic analysis of complexes IV-34 and IV-35 .........................113

4.4.5 Crystal structures of complexes IV-34 and IV-35 .............................................114
List of Tables

Table 2.1 Selected $^1$H NMR data of ligands II-12, II-14, and metal complexes II-15 – II-20.45

Table 2.2 Selected crystal data of metal complexes. Bending angle ($\theta$) as shown in Figure 2.7

Table 2.3 Optical data of the metal-dipyrrin and boron-dipyrrin reference series. .................57

Table 4.1 The distances between CH-$\pi$ interaction donor and accepting planes of the X-ray single crystal structure of IV-26. .................................................................103

Table 4.2 Comparison of selected crystal data between metal complexes IV-28 and II-19. Bending angle ($\theta$) is as shown in Figure 4.9 .................................................................106

Table 4.3 The distances between CH-$\pi$ interaction donor and accepting planes of four neighbouring macrocycles of the X-ray single crystal structure of IV-28. ......................107

Table 4.4 Comparison of selected crystal data between cyclic metal complexes (IV-34 and IV-35) and linear metal complexes (II-19 and II-20). Bending angle ($\theta$) is as shown in Figure 4.18 and Figure 4.19. .................................................................116

Table 4.5 The distances between CH-$\pi$ interaction donor and accepting planes of two neighbouring macrocycles (ring-A and ring-B). .................................................................124

Table 5.1 X-ray crystal structure details for II-6 ..................................................................189

Table 5.2 X-ray crystal structure details for II-12 ................................................................190

Table 5.3 X-ray crystal structure details for II-15 ................................................................191

Table 5.4 X-ray crystal structure details for II-16 ................................................................192

Table 5.5 X-ray crystal structure details for II-17 ................................................................193

Table 5.6 X-ray crystal structure details for II-18 ................................................................194

Table 5.7 X-ray crystal structure details for II-19 ................................................................195

Table 5.8 X-ray crystal structure details for II-20 ................................................................196
Table 5.9 X-ray crystal structure details for II-21 ............................................................... 197
Table 5.10 X-ray crystal structure details for II-22 ............................................................. 198
Table 5.11 X-ray crystal structure details for III-5 ............................................................... 199
Table 5.12 X-ray crystal structure details for III-11 ............................................................ 200
Table 5.13 X-ray crystal structure details for III-31 ............................................................ 201
Table 5.14 X-ray crystal structure details for IV-26 ............................................................ 202
Table 5.15 X-ray crystal structure details for IV-28 ............................................................ 203
Table 5.16 X-ray crystal structure details for IV-34 ............................................................ 204
Table 5.17 X-ray crystal structure details for IV-35 ............................................................ 205
Table 5.18 X-ray crystal structure details for IV-36 ............................................................ 206
## List of Figures

**Figure 1.1** Examples of terpyridyl diruthenium complexes. .......................................................4

**Figure 1.2** Bisporphyrins assembled around ruthenium(II)/iridium(III) bis-terpyridine............5

**Figure 1.3** Bipyridine ligand bridged by ruthenium(II) bis-terpyridine complex.......................5

**Figure 1.4** Illustration of assemblies that can be created from subunits A and B. A is a linear ditopic unit, while B is an angled ditopic unit. They can form a linear oligomer or different polygons........................................................................................................................................6

**Figure 1.5** Molecular library of cyclic polygons created by the assembly of ditopic subunits with predetermined angles............................................................................................................7

**Figure 1.6** Structure of binuclear copper(II) complex ........................................................................8

**Figure 1.7** Two examples of self-assembled binuclear complexes: a) a binuclear helicate structure; b) a hybrid iodonium-transition metal molecular square.................................................................9

**Figure 1.8** Two examples of self-assembled trinuclear cyclic complexes. ......................................10

**Figure 1.9** Another approach to supramolecular triangles............................................................11

**Figure 1.10** Tetranuclear molecular square based on 4,4'-bipyridine and square planar coordination metals................................................................................................................................................12

**Figure 1.11** Two types of tetranuclear molecular squares containing porphyrin subunits.......12

**Figure 1.12** Self-assembled pentameric (a) and hexameric (b) macrocycles. ...............................13

**Figure 1.13** The IUPAC nomenclature for dipyrromethane..............................................................14

**Figure 1.14** The IUPAC numbering system for dipyrromethene and its three possible conformations. .................................................................................................................................................14

**Figure 1.15** General synthetic method and numbering scheme of borondifluoride dipyrrinato complex. ..................................................................................................................................................19
Figure 1.16 Structures of heteroleptic dipyrrin complexes bearing different substituents, and the illustration of hydrogen-bonding in the complex I-2.................................21

Figure 1.17 Hydrogen-bonded networks of different trimeric dipyrrin complexes. a) Structures of two tris(dipyrrinato)cobalt(III) complexes and a tris(dipyrrinato)rhodium(III) complex; b) two types of intermolecular hydrogen-bonding involving DAT (diamino-triazine) groups; c) 1D zig-zag chain of complex I-9 linked by hydrogen-bonds; and the hydrogen-bonded network formed by compound Λ-[I-10] (d) and compound rac-[I-10](e)................................................23

Figure 1.18 Heteroleptic copper(II) dipyrrinato complexes I-11 through I-20.........................24

Figure 1.19 Crystal structures (50% probability ellipsoids) of the coordination polymer formed by complex I-14 (a), discrete dimeric ring formed by complex I-20 (b) and discrete hexameric ring in the solid structure of complex I-13 (c). Hydrogen atoms have been omitted for clarity. ....................................................................................................................................................25

Figure 1.20 Structure of heteroleptic copper(II) dipyrrinato complexes appended with an imidazole (I-21) or a pyrazole (I-22) group. .................................................................26

Figure 1.21 Crystal structures (50% probability ellipsoids) of the coordination polymer chains formed by complex I-21 (a) and I-22 (b). Hydrogen atoms have been omitted for clarity......26

Figure 1.22 List of dipyrrin metalloligands for metal-organic frameworks. .......................27

Figure 1.23 The 3D network of MOF-Co/AgOTf-complex I-23 (a) and the 2D network of MOF-Co/AgPF$_6$-complex I-23 (ORTEP, 50% probability ellipsoids). Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity.................................................27

Figure 1.24 The formation of dipyrrin polymers I-29 through I-32........................................28

Figure 1.25 The structures of bis(dipyrrin) ligands I-33 and I-34, and the copper(II) complex I-35 ..................................................................................................................30
Figure 1.26 The structure of α,α’-linked bis(dipyrromethene) metal complexes, and the crystal structures (50% probability ellipsoids) of the helical structure of complex I-37. One strand is coloured red for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity. .................................................................30

Figure 1.27 The oligomeric ratios of β,β’-linked bis(dipyrromethene) zinc(II) complexes (a), and the crystal structures (50% probability ellipsoids) of the helical structure of complex I-39 (b), I-40 (c) and I-41 (d). One strand of each complex is coloured red for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity. ..............31

Figure 1.28 The structure of bis(dipyrromethene) ligands I-45, I-46 and I-47.........................32

Figure 1.29 Crystal structures of Fe₂L₃ complexes (50% probability ellipsoids). (a) helicate and (b) mesocate. Two strands are coloured red and green for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity. .........................32

Figure 1.30 The structure of β,β’-linked bis(dipyrromethene) ligands I-50 and I-51 (a), and the crystal structure of the triangular helicate I-52 (b) and dimeric circular helical complex I-54 (c) (50% probability ellipsoids). Two strands in I-52 are coloured red and green for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity. ..........33

Figure 1.31 Crystal structure of complex I-55 (50% probability ellipsoids). Solvent molecules have been omitted for clarity. ..............................................................................................................34

Figure 2.1 Structure of compound II-1......................................................................................38

Figure 2.2 Crystal structure of II-6 with partial atom numbering schemes. Thermal ellipsoids are scaled to the 50% probability level.................................................................40

Figure 2.3 Structure of BF₂ capped ligands.............................................................................41

Figure 2.4 ¹H NMR spectra of ligands II-12 and II-14..............................................................43
**Figure 2.5** Crystal structure of **II-12**. The $C_2$ symmetry axis is denoted by the gray line. Thermal ellipsoids are scaled to the 50% probability level.

**Figure 2.6** Comparison of $^1$H NMR Spectra for **II-12**(a) and **II-17**(b), **II-14**(c) and **II-20**(d).

**Figure 2.7** Crystal structures of metal complexes with partial atom numbering schemes (ORTEP, thermal ellipsoids are scaled to the 50% probability level). a) **II-15**; b) **II-16**; c) **II-17**; d) **II-18**; e) **II-19**; f) **II-20**. Solvent molecules and hydrogen atoms in **II-15**, **II-16**, **II-18** and **II-19** have been omitted for clarity.

**Figure 2.8** Comparison between $^1$H NMR Spectra of **II-12** and **II-22**.

**Figure 2.9** ORTEP structures of trivalent metal complexes **II-21** and **II-22**. Thermal ellipsoids are scaled to the 50% probability level. a) top and side view of **II-21**, hydrogen atoms have been omitted for clarity; b) top and side view of **II-22**.

**Figure 2.10** a) Stepwise packing pattern of the individual layers of complexes **II-21** and **II-22**. Top view (b) and side view (c) of packing diagram of **II-21**, and top view of the packing diagram of **II-22**(d). Hydrogen atoms have been omitted for clarity.

**Figure 2.11** Optical spectra of a) ligand **II-12** and its divalent metal complexes; b) ligand **II-14** and its metal complexes; and c) ligand **II-12** and its trivalent metal complexes. All spectra were recorded in CH$_2$Cl$_2$ at room temperature.

**Figure 2.12** Comparison of the experimental and calculated optical spectra. All spectra were recorded in CH$_2$Cl$_2$ at room temperature. The calculated spectrum of compound **II-15** (**II-15 calcd.**) was obtained as shown at the top of the figure. The calculated spectra of compound **II-16** – **II-22** were obtained the same method.

**Figure 3.1** Different molecular wires based on porphyrin/dipyrromethene arrays.

**Figure 3.2** MALDI-TOF spectrum of the crude reaction mixture containing an oligomeric mixture of **II-19**, **III-5** through **III-8** and excess ligand **II-14**.
Figure 3.3 Optical spectra of ligand II-14 and complexes II-19, III-5 and III-6 in CH2Cl2....66

Figure 3.4 Comparison of the experimental and calculated optical spectra of linear metal complexes III-5 and III-6. All spectra were recorded in CH2Cl2 at room temperature..............66

Figure 3.5 Structural diagrams of linear complex III-5 with partial atom numbering scheme (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. .................................................................67

Figure 3.6 1H NMR spectrum (CD2Cl2, 300MHz) of compound III-11..............................69

Figure 3.7 Crystal structure of III-11 with partial atom numbering schemes. Thermal ellipsoids are scaled to the 50% probability level. .................................................................70

Figure 3.8 1H NMR spectra (CDCl3, 400 MHz) for linear metal complexes II-19 (a), III-12 (b) and III-13 (c). .................................................................72

Figure 3.9 1H NMR spectra (CDCl3, 300 MHz) for complexes III-15 (a), III-16 (b) and III-17 (c). ........................................................................................................................75

Figure 3.10 MALDI-TOF spectrum of the step 1 reaction mixture. ........................................77

Figure 3.11 1H NMR spectra for heteroleptic metal complexes III-11 (a), III-18 (b), III-19 (c) and III-20 (d) (CDCl3, 300MHz). .................................................................78

Figure 3.12 Comparison of the experimental and calculated isotopic mass distribution for III-25 (a), III-24 (b) and III-23 (c). For each complex, i) the full spectrum, ii) the enlarged experimental isotopic distribution, and iii) the calculated isotopic distribution..............81

Figure 3.13 Comparison of the experimental and calculated isotopic mass distribution for III-27 (a) and III-26 (b). i) full spectrum; ii) enlarged experimental isotopic distribution; iii) calculated isotopic distribution. ........................................................................82

Figure 3.14 Crystal structure of III-31 with partial atom numbering schemes. (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. 84
Figure 3.15 $^1$H NMR spectrum for two-dimensional dipyrrromethene metal complex III-32. 86

Figure 4.1 Structures of ligand IV-3 (a), IV-4 (b) and illustrations of the zig-zag and cyclic structures (c). ...........................................................................................................................................92

Figure 4.2 Structure and numbering system of carbazole. ..................................................................................94

Figure 4.3 MALDI-TOF spectra of cobalt(II) complexes of IV-24 (a) and IV-25 (b). ...........................98

Figure 4.4 Optical spectra of cyclic complexes of ligand IV-25. All spectra were taken in CH$_2$Cl$_2$ at room temperature.............................................................................................................99

Figure 4.5 Crystal structure of IV-26: a) top view (ORTEP, 50% probability ellipsoids. The C$_2$ symmetry axis is denoted by the gray line); b) side view (ORTEP, 50% probability ellipsoids. The red line indicates the plane through three cobalt atoms); c) stick model and d) space-filling model. Hydrogen atoms and solvent molecules have been omitted for clarity........................................101

Figure 4.6 Molecular space-filling packing of IV-26 (a); top view (b) and side view (c) of the tunnel structures ...............................................................................................................................................102

Figure 4.7 CH-π interactions in the neighbouring macrocycles of the X-ray single crystal structure of IV-26. .................................................................................................................................................103

Figure 4.8 Crystal structure of IV-28: a) top view (ORTEP, 50% probability ellipsoids); b) top view (space-filling model); c) side view (stick model). Hydrogen atoms and solvent molecules have been omitted for clarity. .................................................................................................................................104

Figure 4.9 Stick and space-filling representation of the coordination environment of Co1 in IV-28 shown from different angles. Hydrogen atoms have been omitted in the stick model for clarity. ................................................................................................................................................105

Figure 4.10 CH-π interactions in the neighbouring macrocycles of the X-ray single crystal structure of IV-28. .................................................................................................................................................106
Figure 4.11 Molecular space-filling packing of IV-28 (a), top view (b) and side view (c) of the tunnel structures........................................................................................................................108

Figure 4.12 The angle between the C1-H1 and C8-H8 bonds in a carbazole molecule........108

Figure 4.13 Diagram of the Λ and Δ structures of the tetrahedral dipyrrin metal complex. The dashed-arrow indicates the point of reference............................................................111

Figure 4.14 Diagram of three stereoisomers, a) achiral (meso, ΛΔ), b) chiral (ΔΔ), c) chiral (ΛΛ). These optimized structures were obtained through HyperChem calculation.................111

Figure 4.15 Partial ¹H NMR spectrum of complex IV-35 in CDCl₃. The major (blue solid line) and minor (red solid line) isomers are suggested by the integration. The purple and orange dotted lines indicate the correlation between β-H signals in the major and minor isomers, respectively.................................................................112

Figure 4.16 Optical spectra of ligand IV-33 and its metal complexes. All spectra were recorded in CH₂Cl₂ at room temperature.................................................................113

Figure 4.17 Packing diagrams of the X-ray structures of IV-34 (a) and IV-35 (b). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity....114

Figure 4.18 Crystal structure of IV-34: a) top view (ORTEP, 50% probability ellipsoids). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity; b) top view (stick representation); c) side view (stick representation)......................115

Figure 4.19 Crystal structure of IV-35: a) top view (ORTEP, 50% probability ellipsoids). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity; b) top view (stick representation); c) side view (stick representation)......................116

Figure 4.20 Illustration of the Λ and Δ structures of the seven possible stereoisomers of mixed dipyrrin ligands cyclic metal complex IV-36.................................................................118
Figure 4.21 Partial $^1$H NMR spectrum of IV-36 in CDCl$_3$. The red dotted lines indicate the correlation between the $\beta$-H signals in the major isomer. The blue dotted lines indicate the correlation between the $\beta$-H signals in the minor isomers.

Figure 4.22 Optical spectra of ligand IV-35 and IV-36. Both spectra were recorded in CH$_2$Cl$_2$ at room temperature.

Figure 4.23 Crystal structures of IV-36 with partial atom numbering schemes (ORTEP, thermal ellipsoids are scaled to the 50% probability level). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity.

Figure 4.24 Stick representation of the crystal structure of IV-36. Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted. Different planes are colour-coded for clarity: a) top view; b) side view; c) side view with front half and back half showed separately.

Figure 4.25 Packing diagrams of IV-36: top view (a) and two different side views (b and c) of the layer 1 (1. counterclockwise rotation of layer 1 ninety degrees about the y-axis; 2. clockwise rotation of layer 1 sixty degrees about the y-axis); d) $\pi$-$\pi$ stacking interactions between layer 1 and layer 2.

Figure 4.26 CH-$\pi$ interactions between the neighbouring macrocycles (ring-A and ring-B) of the X-ray single crystal structure of IV-36.

Figure 4.27 Illustration of possible coordination structures of asymmetric dipyrrin ligands. Red and blue represent two different dipyrrin moieties in one ligand. Structure A exhibits “head to tail” connections; Structure B shows “head to head, tail to tail” connections; Structures C and D contain both types of connections.
List of Schemes

Scheme 1.1 Synthesis of hetero-metallic trinuclear terpyridyl complexes. ........................................4
Scheme 1.2 An equilibration between a self-assembled molecular square and triangle...............9
Scheme 1.3 Tautomerization of dipyrrromethene. ........................................................................15
Scheme 1.4 Synthesis of dipyrrromethenes by acid-catalyzed condensation reaction.............16
Scheme 1.5 Synthesis of dipyrrromethenes by oxidation of dipyrrromethanes. ....................16
Scheme 1.6 Synthesis of asymmetrical 5-unsubstituted dipyrrromethanes. ..........................17
Scheme 1.7 Deprotonation of dipyrrromethene and κ² binding in a metal complex.............18
Scheme 1.8 Preparation of dipyrrinato lithium complex and heteroleptic zinc(II) complex....19
Scheme 1.9 Synthesis of homo- and heteroleptic complexes I-4 through I-7. .........................22
Scheme 2.1 Synthetic route to compound II-6. ...........................................................................40
Scheme 2.2 Synthetic route to ligands II-12 and II-14..........................................................42
Scheme 2.3 Synthesis of metal complexes II-15 through II-20. .............................................44
Scheme 2.4 Synthesis of metal complexes II-21 to II-22.......................................................50
Scheme 2.5 Synthesis of reference compounds II-23 through II-40.......................................56
Scheme 3.1 Synthesis of bis(dipyrrin) ligands III-2 and III-4...............................................63
Scheme 3.2 Synthesis of self-assembled oligomers II-19 and III-5 through III-8. ...............64
Scheme 3.3 General approach for synthesis of [Cu(dpm)₂] or [Cu(dpm)(acac)]. ....................68
Scheme 3.4 Synthesis of heteroleptic bis(dipyrrin) metal complexes. .................................69
Scheme 3.5 Reactions between BF₂-capped dipyrrins and heteroleptic bis(dipyrrin) metal complexes. .................................................................................................................71
Scheme 3.6 Reaction between meso-free dipyrrin III-14 and heteroleptic bis(dipyrrin) metal complex III-11. ........................................................................................................74
Scheme 3.7 Alternate strategy for dipyrrin metal complexes...............................................76
Scheme 3.8 Synthesis of metal-dipyrrin chains with free ends on both sides. .................77
Scheme 3.9 Synthesis of long chain heteroleptic metal complexes..............................78
Scheme 3.10 Synthesis of long-chain heteroleptic metal complexes containing different metals .................................................................................................................................79
Scheme 3.11 Synthesis of linear dipyrrin metal complexes containing different metals. ....80
Scheme 3.12 Synthesis of linear dipyrrin metal complexes from III-10..........................82
Scheme 3.13 Synthesis of dipyrrin “trimer” III-30. .........................................................83
Scheme 3.14 Synthesis of tri-chromophoric boron-dipyrrin complex III-31..................84
Scheme 3.15 Synthesis of two-dimensional dipyrromethene metal complex III-32........85
Scheme 3.16 Deprotection of BODIPY with tBuOK via microwave irradiation. ..........87
Scheme 3.17 Reaction of BODIPY metal complex with tBuOK under microwave irradiation. .........................................................................................................................................87
Scheme 4.1 Synthesis of ligand IV-2. ..................................................................................91
Scheme 4.2 Synthesis of cyclic metal complexes from ligand IV-5. .................................93
Scheme 4.3 Synthesis of ligands IV-6 and IV-7, and their metal complexation..............93
Scheme 4.4 Synthesis of carbazole-bridged dimeric dipyrrin ligands IV-14 to IV-16. ....95
Scheme 4.5 Metal complexation reactions of ligands IV-14 through IV-16.................96
Scheme 4.6 Synthesis of ligands IV-23 through IV-25....................................................97
Scheme 4.7 Metal complexation reactions and yields of ligands IV-23 through IV-25. ...98
Scheme 4.8 Synthetic route for ligand IV-33. ................................................................109
Scheme 4.9 Synthesis of metal complexes IV-34 and IV-35.........................................110
Scheme 4.10 Synthesis of cyclic metal complex IV-36..................................................117
Scheme 4.11 Structures of carbazole-bridged asymmetric 3,6-dimeric dipyrrin ligands. ....125
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>three-dimensional</td>
</tr>
<tr>
<td>Ac</td>
<td>acetyl</td>
</tr>
<tr>
<td>acac</td>
<td>acetylacetone</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>BODIPY</td>
<td>4,4-difluoro-4-bora-3a,4a-diaza-s-indacene</td>
</tr>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>Calcd.</td>
<td>calculated</td>
</tr>
<tr>
<td>COSY</td>
<td>correlation spectroscopy</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>DAT</td>
<td>diamino-triazine</td>
</tr>
<tr>
<td>DCTB</td>
<td>2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidene] malononitrile</td>
</tr>
<tr>
<td>dd</td>
<td>doublet-doublet</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-dichloro-5,6-dicyanobenzoquinone</td>
</tr>
<tr>
<td>DIBAL-H</td>
<td>diisobutylaluminum hydride</td>
</tr>
<tr>
<td>DMF</td>
<td>(N, N)-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>dpm</td>
<td>dipyrromethene</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
</tbody>
</table>
hfacac  hexafluoroacetylacetonate
HPLC  high performance liquid chromatography
HREIMS  high resolution electron impact ionization mass spectroscopy
HRESIMS  high resolution electrospray ionization mass spectroscopy
IUPAC  International Union of Pure and Applied Chemistry
LREIMS  low resolution electron impact ionization mass spectroscopy
LRESIMS  low resolution electrospray ionization mass spectroscopy
m  multiplet
MALDI-TOF  matrix-assisted laser desorption/ionization-time of flight
m/e  mass/charge
min  minute(s)
MOF  metal-organic frameworks
nm  nanometer(s)
NMR  nuclear magnetic resonance
ORTEP  Oak Ridge thermal ellipsoid plot
OTf  triflate
ppm  part per million
r. t.  room temperature
s  singlet
SEM  scanning electron microscopy
t  triplet
TFA  trifluoroacetic acid
THF  tetrahydrofuran
TLC  thin-layer chromatography
UV/Vis  ultraviolet/visible
Acknowledgements

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CHAPTER 1

Introduction
In the field of supramolecular chemistry, a large number of the structures are assembled using metal coordination bonds. Metal complexes can bring intrinsic functionalities as well as a variety of coordination geometries to the assemblies. In this thesis, we focus on linear and cyclic supramolecular structures made from dipyrrromethene metal complexes. Dipyrrromethene metal complexes feature neutral charges and interesting photophysical and electrochemical properties. They can be potentially used as molecular wires or as coordination networks in host-guest chemistry. In this chapter, the self-assembly of linear and cyclic supramolecular metal complexes, the synthesis of dipyrrromethene ligands, and their coordination to metals will be reviewed.

1.1 Supramolecular chemistry and supramolecular metal complexes

Supramolecular chemistry refers to chemistry “beyond the molecule” and deals with ‘organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces’. The term was first introduced in 1978 by J. M. Lehn describing ‘the chemistry of molecular assemblies and of the intermolecular bond’. It has been a rapidly growing field since the breakthrough of the synthesis of crown ethers in the 1960’s and further accelerated with the recognition of the Nobel Prize in 1987. Its basic concepts have their origin in chemistry, but its interface with biology, physics and material science has injected new possibilities into those domains of science.

Among the non-covalent interactions, such as hydrogen-bonding, static electronic interactions, coordination bonding, van der Waals forces, π-π interaction, hydrophobic forces, etc., metal coordination bonding plays an important role. It provides a variety of coordination
geometries leading to the construction of different higher order complexes with precisely positioned components. In addition, metal complexes also generate new photophysical, electrochemical, catalytic and magnetic properties within the supramolecular structures. Supramolecular metal complexes have demonstrated their application in nanoelectronics, the construction of molecular wires and dynamic mechanical devices.3

1.2 Synthesis of supramolecular complexes through self-assembly

Self-assembly is a synthetic process that allows the generation of larger structures from their smaller building blocks. It is defined as ‘a spontaneous association of molecules under equilibrium conditions into stable aggregates held together by non-covalent bonds’.4 Using metal coordination bonding, numerous supramolecular metal complexes have been synthesized, including discrete or extended one-, two- and three-dimensional structures.

It is beyond the scope of this thesis to review all the classes of supramolecular metal complexes. The readers are referred to several excellent books and reviews on the subject.5-13 Linear and cyclic complexes will be on the focus here, and some important examples are listed in the following sections.

1.2.1 Linear coordination supramolecular structures

A substantial number of linear metallostructures have been reported, with the focus being primarily on their photophysical properties and electrochemical activity. Terpyridine and porphyrin are commonly used to assemble linear metallostructures.
In a typical approach, the ligand consists of two terpyridine subunits linked by spacers at a 180° angle. Ruthenium atoms are coordinated to both sides of this bridging ligand, with the opposite side of the ruthenium atom capped with a terminal capping ligand (Figure 1.1). A variation of this type of reaction is the pre-introduction of inert metals such as RuII and OsII to the ligand, followed by coordination with FeII or CoII to generate a linear assembly with multiple different metals (Scheme 1.1).¹⁷

![Figure 1.1 Examples of terpyridyl diruthenium complexes.](image)

![Scheme 1.1 Synthesis of hetero-metallic trinuclear terpyridyl complexes.](image)
Sauvage et al. introduced porphyrin into the ruthenium(II) bis-terpyridine complex to construct a linear triad for the study of photophysical and electrochemical properties. In this assembly, one of the termini is a gold(III) porphyrin, which acts as the electron acceptor. The other terminal subunit is a zinc(II) or free-base porphyrin, which acts as the electron donor. The ruthenium(II) bis-terpyridine complex acts as an electron relay between the two porphyrin subunits. Later, they performed a similar study using an iridium(III) bis-terpyridine unit to replace the ruthenium(II) bis-terpyridine complex to exploit its highly energetic excited states (Figure 1.2).

![Bisporphyrins assembled around ruthenium(II)/iridium(III) bis-terpyridine.](image)

Figure 1.2 Bisporphyrins assembled around ruthenium(II)/iridium(III) bis-terpyridine.

In 2007, Constable et al. reported a coordination polymer which employed the ruthenium(II) bis-terpyridine complex as the bridging unit to connect two pyridine units (Figure 1.3). Upon the addition of an aqueous acetonitrile solution of AgNO₃, the ligands assembled into linear 1-D chains through the coordination between the pyridine nitrogens and the [Ag(NO₃)(MeCN)] units.

![Bipyridine ligand bridged by ruthenium(II) bis-terpyridine complex](image)

Figure 1.3 Bipyridine ligand bridged by ruthenium(II) bis-terpyridine complex.
1.2.2 Cyclic coordination supramolecular structures

Closed cyclic complexes formed by metal coordination are also known as metallocycles. This includes polygons, polyhedra and cyclic helicates.

1.2.2.1 Self-assembly of cyclic structures

Practically, a cyclic structure is often achieved through a thermodynamic assembly, leading to a stable product. Kinetically fast and labile interactions are preferred, since they allow self-correction to occur.\textsuperscript{21}

\textbf{Figure 1.4} Illustration of assemblies that can be created from subunits \textit{A} and \textit{B}. \textit{A} is a linear ditopic unit, while \textit{B} is an angled ditopic unit. They can form a linear oligomer or different polygons.

In a system designed for the assembly of a cyclic structure, the formation of linear oligomers or cyclic structures with different sizes are often possible (\textbf{Figure 1.4}). Several studies have been done to address the preference of these products.\textsuperscript{22-24} Compared to a cyclic structure, in which the ligands are fully coordinated, the ligand or metal at the ends of the linear assembly remain uncoordinated, thus the linear structure has fewer bonds formed and is less favoured in an enthalpy driven process. Compared to large cyclic assemblies, small ones will give a higher number of species in the solution, thus increasing the entropy. At low
concentrations, small cycles are favoured, while at high concentrations, the formation of large cyclic systems is entropically favoured.

1.2.2.2 Self-assembly of polygons

Construction of polygons or polyhedrons can be achieved through appropriately oriented donor and acceptor units. Fujita,\textsuperscript{25} Stang\textsuperscript{7, 9, 26} and other scientists have developed a ‘molecular library’ methodology, which states that any polygon can be assembled by the right combination of the ditopic building blocks with predetermined angles (Figure 1.5). It is important to point out that this methodology assumes the value of the directing angle within each ditopic subunit remains unchanged upon coordination.

\begin{center}
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Ditopic Subunit} & \textbf{60°} & \textbf{90°} & \textbf{109.5°} & \textbf{120°} & \textbf{180°} \\
\hline
\textbf{60°} & & & & & \\
\hline
\textbf{90°} & & & & & \\
\hline
\textbf{109.5°} & & & & & \\
\hline
\textbf{120°} & & & & & \\
\hline
\textbf{180°} & & & & & \\
\hline
\end{tabular}
\end{center}

\textbf{Figure 1.5} Molecular library of cyclic polygons created by the assembly of ditopic subunits with predetermined angles (adapted from reference 9).
1.2.2.2.1 Dinuclear cyclic structures

One of the first self-assembled macrocyclic structures was reported by Maverick and Klavetter.\textsuperscript{27, 28} This dinuclear structure was obtained by Cu(II) coordination to an acetylacetonate ligand. This assembly showed a strong binding affinity towards pyrazine, pyridine and diazabicyclooctanes (\textbf{Figure 1.6}). Since then, many other dinuclear structures have been made.\textsuperscript{29-31} Pyridine-type ligands are among the most commonly used ligands in such structures.

\textbf{Figure 1.6} Structure of binuclear copper(II) complex

Depending on the coordination geometry, dinuclear complexes can be considered as essentially helicates, representing the simplest form of such structures. One example is shown in \textbf{Figure 1.7 (a)}, where the ligand has two 2,2’-bipyridine units linked by an aromatic spacer. Two such ligands bind with two metals, either Cu(I) or Zn(II), with a tetrahedral geometry, giving a helicate complex.\textsuperscript{32} Interwoven dinuclear structures which form catenanes were also reported.\textsuperscript{33, 34} The shape of the dinuclear complexes also rests upon the distinct geometric structure of the ligand. One example is a hybrid iodonium-transition metal macrocyclic square made by Stang’s group.\textsuperscript{35, 36} The molecular squares were obtained using a bis(heteroaryl)iodonium species, which gives a near 90° angle. The perpendicularly oriented lone pairs of the nitrogen atoms were then coordinated to Pd(II) or Pt(II) (\textbf{Figure 1.7, b}). A variety of squares were synthesized using similar methods.
1.2.2.2 Trinuclear cyclic structures

Compared to dinuclear complexes or molecular squares, the number of reported trinuclear cyclic structures is small. Because there is no appropriate metal coordination with a 60° angle, the triangle shaped complexes are usually constructed by either distorted metal coordination, or bidentate ligands with near 60° angled binding sites.

Using distorted coordination, there is often an equilibration between the triangle and square forms. One example from Fujita’s group shows that the molecular triangle is a minor
product when they build the Pd$^{II}$ molecular squares using the bidentate pyridine-based ligands (Scheme 1.2). \(^{37}\)

Even using a 60° rigid ligand, the metal coordination can still lead to the formation of a mixture of triangles and squares, as shown by Ziessel and co-workers (Figure 1.8, a). \(^{38}\) In a recently published paper, Sauvage et al. synthesized a rigid ditopic ligand with two coordination sites located perpendicularly. \(^{39}\) Coordinating this ligand with copper(II) led to the formation of both dimeric and trimeric complexes (Figure 1.8, b).

**Figure 1.8** Two examples of self-assembled trinuclear cyclic complexes.

A different approach to the synthesis of trinuclear cyclic complexes has been taken by Schmittel and co-workers (Figure 1.9). Instead of simply mixing a ditopic ligand and a metal ion to generate homometallic moieties, they built a copper(I) complex to act as an angular unit with two phenanthroline termini, followed by reaction with AgPF$_6$ and another bisphenanthroline ligand resulting in the desired heteroleptic triangles. \(^{40}\)
1.2.2.3 Tetranuclear cyclic structures

There are many opportunities to introduce 90° angles in metal coordination chemistry, making tetranuclear complexes among the most studied cyclic structures. Many molecular squares have been reported, using the square planar coordination metals Pt^{II} and Pd^{II} or octahedral coordination metals.{9,10}

Fujita and co-workers assembled molecular squares using Pt^{II}/Pd^{II} and 4,4'-bipyridyl ligands (Figure 1.10).{41} The crystal structure showed an almost perfect square. The cavity in the middle of the square can host neutral aromatic guest molecules. The size of the cavity can be tuned using ligands of different sizes.
Figure 1.10 Tetranuclear molecular square based on 4,4’-bipyridine and square planar coordination metals.

Figure 1.11 Two types of tetranuclear molecular squares containing porphyrin subunits.

Porphyrin is also an attractive subunit for the construction of cyclic structures due to its rich photochemistry and conformational rigidity. Lehn took advantage of different angles between the pyridyl groups (90° or 180°) in the pyridylporphyrin ligand to build porphyrin-containing squares, where the porphyrin lies at the corner or on the side of the squares, respectively (Figure 1.11).42
1.2.2.2.4 Higher nuclearity complexes

Pentameric and hexameric self-assembled macrocycles have also been synthesized. Newkome and colleagues use carbazole as the bridging unit to connect two terpyridine ligands. The two terpyridine ligands were appropriately angled (ca. 105°), and stable metallopentacycles were obtained upon coordination with divalent metals (Figure 1.12, a).43 Instead of the carbazole unit, when two terpyridine ligands were connected at the meta-position of a phenyl ring, the bis(terpyridine) ligand possesses a 120° angle with respect to the two coordination sites. The resulting macrocycle is a hexameric ring (Figure 1.11, b).44

![Figure 1.12](image)

**Figure 1.12** Self-assembled pentameric (a) and hexameric (b) macrocycles.

1.2.2.3 Three-dimensional metal coordination assemblies

In recent years, study of three-dimensional assemblies constructed by metal coordination has been a fast developing field. Discrete 3D structures or extended 3D complexes have been made. These metallostructures can potentially be used as molecular devices with desirable optical, electronic and magnetic properties,8,45 or can be used as hosts to gases such as hydrogen or carbon dioxide for fuel-cell and other applications.46
1.3 Dipyrromethenes

1.3.1 Dipyrromethanes and dipyrromethenes: general background

Dipyrromethanes consist of two pyrrolic rings linked by a methylene bridge (Figure 1.13). Following the historical pyrrole nomenclature, the 1-, 4-, 6- and 9-positions are designated as the α-positions and the 2-, 3-, 7- and 8-positions are designated as the β-positions. The 5-position is referred to as the meso-position. Depending on the position of the methylene bridge, the dipyrromethanes can be classified into three categories: α,α’-linked dipyrromethanes; α,β’-linked dipyrromethanes and β,β’-linked dipyrromethanes. The structures to be discussed in this thesis are limited to the α,α’-linked dipyrromethanes.

![Figure 1.13 The IUPAC nomenclature for dipyrromethane.](image)

Figure 1.13 The IUPAC nomenclature for dipyrromethane.

![Figure 1.14 The IUPAC numbering system for dipyrromethene and its three possible geometrical isomers.](image)

Figure 1.14 The IUPAC numbering system for dipyrromethene and its three possible geometrical isomers.
Dipyrromethenes (dipyrrins) have one more degree of unsaturation compared to
dipyrromethanes. They were first reported by Ploty in 1914.\textsuperscript{47} Fisher’s book \textit{Die Chemie des}
\textit{Pyrrols} then expanded on the application of dipyrromethenes in porphyrin synthesis.\textsuperscript{48} The
recommended nomenclature for dipyrromethenes was published in 1987\textsuperscript{49} and the numbering
scheme is shown in \textbf{Figure 1.14}.

Since the pyrrolyl groups of dipyrromethenes can rotate around the central methine
carbon, three different conformations can exist (\textbf{Figure 1.14}).\textsuperscript{50,51} Among the three types, the
type I conformation is the most common due to the intra-molecular hydrogen bond (N-H···N). In a
dipyrromethene molecule, the two pyrrolic rings and the methine bridge are coplanar to
attain the maximum $\pi$ conjugation, and tautomerization of dipyrromethene can be achieved by
proton transfer between the two nitrogen atoms (\textbf{Scheme 1.3})

\begin{center}
\includegraphics[width=0.5\textwidth]{Scheme1.3.png}
\end{center}

\textbf{Scheme 1.3} Tautomerization of dipyrromethene.

Free-base dipyrromethenes are regarded as relatively strong bases due to a lone pair of
electrons on one of the nitrogens.\textsuperscript{52} The stability of the dipyrromethenes depends on the nature
and the position of substituents. The fully unsubstituted dipyrromethenes are the least stable
due to the vulnerability of the unsubstituted ring to electrophillic and nucleophillic attack.\textsuperscript{52-54}
The stability of dipyrromethenes can be enhanced by introducing aryl substituents at the \textit{meso-}
position.
1.3.2 Synthesis of dipyrromethenes

There are two common methods for the synthesis of dipyrromethenes. The first one is shown in Scheme 1.4. A 5-unsubstituted dipyrromethene can be obtained through a condensation of equimolar 2-formylpyrrole with 2-unsubstituted pyrrole in the presence of a strong acid (typically hydrobromic acid). 5-Unsubstituted dipyrromethenes are less stable than their salts. As a result, 5-unsubstituted dipyrromethenes are usually handled as their hydrobromide salts. The yields of this type of condensation reaction are generally high, and the most common method for the purification is precipitation. This method is ideal for the preparation of asymmetrical dipyrromethenes, while the other method, the oxidation of dipyrromethanes, is best suited for the synthesis of symmetrical 5-substituted dipyrromethenes.

Scheme 1.4 Synthesis of dipyrromethenes by acid-catalyzed condensation reaction.

As shown in Scheme 1.5, this procedure involves two steps: preparation of the dipyrromethanes by the condensation of aldehydes with pyrroles followed by oxidation of the dipyrromethanes. This method is extensively used in the synthesis of α- and β-free, 5-aryl substituted dipyrromethenes. Aldehydes and unsubstituted pyrrole readily undergo acid-catalyzed condensation at room temperature to produce dipyrromethanes. However, when
using equimolar concentrations in the solution, the condensation of aldehydes and pyrrole also yields higher oligomers and the $\alpha,\beta'$-linked dipyrromethanes.\textsuperscript{55, 56} In order to minimize the formation of the side products, Lindsey et al. elegantly optimized the procedure by employing a large excess of pyrrole as both the reactant and the solvent for the pyrrole-aldehyde condensation in the presence of a catalytic amount of a Lewis acid (such as trifluoroacetic acid or InCl$_3$) to achieve the formation of dipyrromethane.\textsuperscript{57-59} The yields of these simple one-flask syntheses are generally over 50% and can be carried out on a large scale.

The asymmetrical 5-unsubstituted dipyrromethanes can also be achieved via the reaction of an appropriately substituted pyrrole carbonyl cation precursor and a 2-unsubstituted pyrrole (Scheme 1.6).

![Scheme 1.6 Synthesis of asymmetrical 5-unsubstituted dipyrromethanes.](image)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and $p$-chloranil are the two most common oxidants for the oxidation of dipyrromethanes to dipyrromethenes.\textsuperscript{60, 61} This oxidation reaction proceeds smoothly for 5-aryl dipyrromethanes at room temperature with moderate yield. The reaction of 5-alkyl or 5-unsubstituted dipyrromethanes with DDQ or $p$-chloranil failed to give the desired dipyrreins, although the starting dipyrromethanes were completely consumed.\textsuperscript{62} The 5-aryl dipyrreins are usually stable in their free-base form and thus can be isolated using column chromatography (silica gel or alumina) and collected in high purity.
1.3.3 Dipyrromethenes as ligands

1.3.3.1 Dipyrromethene metal complexes

Dipyrromethenes have been reported to generate complexes with a wide variety of metal ions. Upon deprotonation, these monoanionic ligands bind metal cations in a chelating $\kappa^2$ manner to form isolable neutral complexes, without requiring a counteranion (Scheme 1.7).

Scheme 1.7 Deprotonation of dipyrromethene and $\kappa^2$ binding in a metal complex.

The majority of known dipyrromethene metal complexes are homoleptic. The coordination geometry of divalent metal complexes is nearly exclusively tetrahedral or a distorted tetrahedral about the complexed metal ion due to the steric repulsion between $\alpha$-substituents, even if these substituents are only hydrogens. For example, instead of their well documented square-planar coordination geometry, dipyrromethene copper(II) complexes take on a distorted tetrahedral coordination geometry due to interligand crowding. Another example is a dipyrren palladium(II) complex reported by Fergusson and his colleagues. In this complex, the palladium center is coplanar with the four nitrogen atoms of the ligands. Because of the steric interaction between the $\alpha$-methyl groups of the ligands and the strong tendency for palladium to achieve square-planar coordination geometry, the two ligands are forced to form a stepped arrangement around the metal center to avoid overcrowding. The dipyrromethenes can also form neutral complexes with different trivalent metals such as Fe$^{III}$, Mn$^{III}$, Co$^{III}$, Ga$^{III}$, In$^{III}$, etc. Previous research shows that when dipyrromethenes coordinate with trivalent metals,
the metal complexes almost exclusively form from α-unsubstituted dipyrrins, and the trivalent metal complexes exhibit highly symmetric octahedral geometries. The only exception was a cobalt(III) dipyrrinato complex reported by Cohen, which contains two α-unsubstituted dipyrrinato ligands and one α-methoxy dipyrrinato ligand. Recently, Thompson reported the first dipyrrinato-alkali metal complex. This dipyrromethene lithium complex was then employed for the formation of a unique heteroleptic zinc(II) complex (Scheme 1.8).

**Scheme 1.8** Preparation of dipyrrinato lithium complex and heteroleptic zinc(II) complex.

### 1.3.3.2 Dipyrromethene boron complexes

Borondifluoride dipyrrinato complexes, commonly referred to BODIPYs or 4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes, have been known for over 40 years. The BODIPYs can be readily obtained by complexation of dipyrromethene and BF₃·OEt₂ in the presence of base, such as triethylamine or N,N-diisopropylethylamine (Figure 1.15). In a recently published review article, Loudet and Burgess covered the synthetic procedures and the variety of the BODIPY structures in detail.

**Figure 1.15** General synthetic method and numbering scheme of borondifluoride dipyrrinato complex.
BODIPYs usually exhibit narrow absorption bands with absorbance maxima greater than 500 nm. The research carried out by Boens et al. also shows that BODIPYs have large molar absorption coefficients (between 40000 to 110000 M⁻¹cm⁻¹), and high fluorescence quantum yields. It also bears mentioning that one of the advantages of BODIPYs are their synthetic adaptability. Upon modification of the α-, β-, or meso-position of the dipyrrin backbone or the boron sites, the photophysical properties change accordingly, which provides the possibility of a variety of applications. Much research has been performed on both fundamental and application studies of BODIPYs in the past decade. The good chemical and photochemical stability of borondifluoride dipyrrinato complexes, along with their distinctive optical properties render them popular candidates for many different applications, such as energy-, electron-, and charge-transfer, chemical sensor and other applications.

1.4 Development of dipyrromethenes for supramolecular chemistry through self-assembly

In the past few decades, coordination-driven supramolecular assemblies have drawn considerable interest. A large body of work has been reported that includes N-heterocycles as classic ligands, such as bipyridine derivatives and terpyridine derivatives. However, the examples of using dipyrromethenes as building blocks are limited. This is partially due to the synthetic and purification difficulties of dipyrromethenes. Over the past few years, with the development of synthetic methods of dipyrrin derivatives, dipyrrin-based supramolecular structures have started receiving more attention. Both extensive networks/polymers and discrete oligomeric species based on dipyrrin metal complexes have been reported.
The ligands of these complexes usually contain at least two interaction sites. Upon coordination with a metal center using one interaction site, a dipyrrin metal complex is formed. The resulting metal complex then forms an extensive or discrete supramolecular structure depending on the chemical and geometric features of the additional site(s).

### 1.4.1 Extensive supramolecular structures based on dipyrrromethene metal complexes

By carefully designing the periphery with additional interaction sites, dipyrrromethene-based extensive supramolecular networks can be formed through coordination bonds solely or through a combination of both metal-ligand binding and hydrogen-bonding.

![Figure 1.16](image)

Figure 1.16 Structures of heteroleptic dipyrrin complexes bearing different substituents, and the illustration of hydrogen-bonding in the complex I-2.

Heinze and Reinhart\textsuperscript{104} synthesized a series of [Cu(dpm)(acac)] (dpm = dipyrrromethene, acac = acetylacetonato) complexes to show the impact of different substituents on the type of interaction in the solid state (Figure 1.16). The solid-state structures show that complex I-1 crystallizes as a discrete molecule with no intermolecular interactions. Complex I-2 bears a
secondary amide group as a hydrogen-bond donor/acceptor group, with the polymeric chains assembled through hydrogen-bonding between the amide groups. By employing a nitro group as a substituent on the phenyl moiety, a coordinative polymer was obtained through oxygen-copper interactions between the nitro moiety and the copper(II) center.

![Scheme 1.9 Synthesis of homo- and heteroleptic complexes I-4 through I-7.](image)

Similarly, Baudron and Hosseini\textsuperscript{105} prepared a dipyrrin ligand bearing a primary amide on the \textit{meso}-phenyl moiety as H-bond donor and acceptor. The ligand was used to react with different metal salts to form homo- and heteroleptic complexes (\textbf{Scheme 1.9}). Depending on the structure of the complexes and the hydrogen-bonding capabilities of competing groups (solvent molecules of crystallization and the capping ligands), different hydrogen-bonding connectivity patterns have been observed.
**Figure 1.17** Hydrogen-bonded networks of different trimeric dipyrrin complexes. a) Structures of two tris(dipyrrinato)cobalt(III) complexes and a tris(dipyrrinato)rhodium(III) complex; b) two types of intermolecular hydrogen-bonding involving DAT (diamino-triazine) groups; c) 1D zig-zag chain of complex I-9 linked by hydrogen-bonds; and the hydrogen-bonded network formed by compound Λ-[I-10] (d) and compound rac-[I-10](e).

Telfer and his colleagues\textsuperscript{106-108} employed tris(dipyrrinato)cobalt(III) complexes as building blocks for further self-assemblies (**Figure 1.17, a**). The Δ and Λ enantiomers of complexes I-8 and I-10 have been resolved. Interestingly, instead of using all three carboxyl groups of complexes I-8 and I-9, only two participate in hydrogen-bonding with neighbouring molecules. This results in the formation of an extensive 1D zigzag chain (**Figure 1.17, c**).
complex I-10, both the racemate and $\Lambda$-enantiomer can form 2-D hydrogen-bonded networks, but with different patterns. As shown in Figure 1.17, there were two types of intermolecular hydrogen-bonding. The $\Lambda$-enantiomer featured type II connectivity only, and the racemic complex contained both types of connectivities, resulting in the different structures.

Instead of hydrogen-bonding driven self-assembly, a variety of supramolecular architectures that utilize metal-ligand interactions as the driving force for assembly were synthesized by Cohen and co-workers. A series of self-assembling heteroleptic copper(II) complexes were used as building blocks to form homometallic coordination solids. As shown in Figure 1.18, these building blocks feature a second donor site, which can bind to the open axial site on a neighbouring copper center.

![Complex Structure](image)

Complex No: I-11 I-12 I-13 I-14 I-15 I-16 I-17 I-18 I-19 I-20

$R = \begin{array}{cccccccccc}
\text{CH}_3 & \text{CH}_3 & \text{CF}_3 & \text{CH}_3 & \text{CF}_3 & \text{CH}_3 & \text{CF}_3 & \text{CF}_3 & \text{CF}_3 & \text{CF}_3 \\
\text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3 & \text{SCH}_3
\end{array}$

Figure 1.18 Heteroleptic copper(II) dipyrrinato complexes I-11 through I-20.

Among these structures, no intermolecular interactions were observed in complex I-11 due to the steric hindrance between the nitrogen donor and a neighbouring copper(II) center. Complexes I-12, I-14, I-17 and I-19 assembled into one-dimensional zigzag polymer chains (Figure 1.19, a).$^{109-111}$ Complexes I-15 and I-18 also form one-dimensional polymer chains but display a double helical topology due to aggregation of the perfluoromethyl groups.$^{110}$

24
Complexes I-16 and I-20 did not generate coordination polymers in the solid state. Instead, they crystallized as discrete hexameric and dimeric rings, respectively (Figure 1.19, b). The crystal structure of complex I-13 is unique. It consists two supramolecular arrangements: a double helix based on intertwined coordination polymers, as well as a discrete hexameric ring (the discrete hexameric ring structure is shown in Figure 1.19, c).

Figure 1.19 Crystal structures (50% probability ellipsoids) of the coordination polymer formed by complex I-14 (a), discrete dimeric ring formed by complex I-20 (b) and discrete hexameric ring in the solid structure of complex I-13 (c). Hydrogen atoms have been omitted for clarity.

Baudron and Hosseini prepared two other heteroleptic copper(II) dipyrrinato complexes I-21 and I-22 (Figure 1.20). The X-ray structure shows, in a similar way to Cu(dpm-m-py)(acac) (I-14), that the imidazolyl group in complex I-21 is coordinated to the copper atom to generate a polymer chain. A different connection pattern was observed in complex I-22,
where the nitrile group of the acacCN is involved in weak coordination with the copper atom (Figure 1.21).

Figure 1.20 Structure of heteroleptic copper(II) dipyrrinato complexes appended with an imidazole (I-21) or a pyrazole (I-22) group.

Figure 1.21 Crystal structures (50% probability ellipsoids) of the coordination polymer chains formed by complex I-21 (a) and I-22 (b). Hydrogen atoms have been omitted for clarity.

Cohen and his group also thoroughly investigated heterometallic dipyrrin metal-organic frameworks (MOF). The terminology of metal-organic frameworks is used to describe crystalline compounds consisting of a rigid organic ligand as linker coordinated to metal ions
or metal clusters to form a framework structure. A large amount of one-, two-, and three-dimensional frameworks have been prepared.\textsuperscript{114,115} As an alternative, an inorganic complex (a ‘metalloligand’), such as neutral dipyrrin metal complexes, can replace the organic ligand as building blocks to integrate into MOFs.

![Chemical structures](image)

**Figure 1.22** List of dipyrrin metalloligands for metal-organic frameworks.

![3D and 2D network structures](image)

**Figure 1.23** The 3D network of MOF-Co/AgOTf-complex \textbf{1-23} (a) and the 2D network of MOF-Co/AgPF\textsubscript{6}-complex \textbf{1-23} (ORTEP, 50% probability ellipsoids). Hydrogen atoms, counterions, and solvent molecules have been omitted for clarity.
When combining pyridine-substituted dipyrrin metal complexes I-23 and I-24 (Figure 1.22) with silver(I) salts, each silver(I) ion coordinates to pyridine ligands of three dipyrrin complexes to form heterometallic MOFs. In order to investigate the templating effect of the silver(I) counteranion, different silver(I) salts were used to coordinate to dipyrrin complexes I-23 and I-24. The results demonstrate that weakly coordinating counterions OTf\(^{-}\) and BF\(_4\)^{-} result in similar three-dimensional networks, while non-coordinating counterions SbF\(_6\)^{-} and PF\(_6\)^{-} form two-dimensional networks (Figure 1.23). The modified dipyrrin metalloligands such as complexes I-25 and I-26 or the main-group metal dipyrrinato complexes I-27 and I-28 have been prepared (Figure 1.22) and incorporated into a variety of silver(I) MOFs. The formation of chiral MOFs based on tris(dipyrrinato) coordination complexes and the mixed metal MOFs which present as both the iron(III) and cobalt(III) dipyrrin complexes have also been reported.

![Diagram](image)

**Figure 1.24** The formation of dipyrrin polymers I-29 through I-32

Instead of using heteroleptic dipyrrinato complexes to generate extensive metal-coordinated dipyrrin polymers, Maeda synthesized a series dipyrrin “dimers” with rigid phenylethynyl linkages. When these dipyrrin dimers were treated with Zn(OAc)$_2$, self-assembled coordination polymers I-29 through I-32 were obtained (Figure 1.24). Scanning
electron microscopy (SEM) shows that nano-sized spherical structures were formed in THF for the polymers **I-30** and **I-31**, while **I-29** and **I-32** gave randomly shaped objects.

**1.4.2 Discrete dipyrrin metal complexes through self-assembly**

The methodology of coordination-driven self-assembly utilizes the steric and binding information contained in the ligands to generate the supramolecular structures. Bearing this tactic in mind, careful design of the ligands and acceptors with fixed bonding directionality and suitable coordination geometries will allow the formation of discrete supramolecules instead of extensive networks.

The self-assembly of discrete structures of several types has been achieved. As mentioned before (Figure 1.19, b and c), discrete cyclic supramolecular architectures based on heteroleptic copper(II) dipyrrin complexes were obtained. More research has been done on designing poly(dipyrromethene) ligands, which can readily coordinate with different metal ions to form discrete homoleptic structures.

In 1966, Dolphin *et al.* suggested two [2+2] bis(dipyrromethene) metal complexes (ligand **I-33** and cobalt(II) and ligand **I-34** with copper (II)) have a helical conformation.\(^{120,121}\) (The ligand **I-34** and copper(II) also formed a mononuclear complex **I-35** due to the preference of Cu\(^{II}\) ions for a planar conformation, as shown in **Figure 1.25**). To investigate potential usage of the bis(dipyrromethene) in self-assembly chemistry and the impact of the spacer between two dipyrromethene moieties, bis(dipyrromethene)s with different spacers were synthesized, and the effect of the length, rigidity and substituted location of the linker was investigated.
Figure 1.25 The structures of bis(dipyrrin) ligands I-33 and I-34, and the copper(II) complex I-35

![Figure 1.25](image)

$$I-33: \quad n=1 \quad R_1=\text{CH}_3 \quad R_2=\text{CH}_2\text{CH}_3$$
$$I-34: \quad n=0 \quad R_1=\text{CO}_2\text{Et} \quad R_2=\text{H}$$

Figure 1.26 The structure of $\alpha,\alpha'$-linked bis(dipyrromethene) metal complexes, and the crystal structures (50% probability ellipsoids) of the helical structure of complex I-37. One strand is coloured red for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity.

![Figure 1.26](image)

A series $\alpha,\alpha'$-linked bis(dipyrromethene)$^{122}$ (Figure 1.26) and $\beta,\beta'$-linked bis(dipyrromethene)$^{123-126}$ were used to coordinate with zinc(II) or cobalt(II) to form complexes. The complexes have been confirmed by X-ray crystallography and by chiral
lanthanide shift $^1$H NMR spectroscopy. The study of $\beta,\beta'$-linked bis(dipyrromethene) ligands shows the spacer between two dipyrromethene moieties is one of the determinant factors in the self-assembly of dipyrromethene based complexes. The dinuclear complexes are the favoured products when using shorter spacers. As the length of the spacer increases, two dipyrroin moieties within one ligand will be able to coordinate with one metal ion due to the increased flexibility of the spacer, and thus the mononuclear complexes become favoured (Figure 1.27).

Figure 1.27 The oligomeric ratios of $\beta,\beta'$-linked bis(dipyrromethene) zinc(II) complexes (a), and the crystal structures (50% probability ellipsoids) of the helical structure of complex I-39 (b), I-40 (c) and I-41 (d). One strand of each complex is coloured red for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity.
Further, the Zn(II) dipyrrromethene helicates were formed diastereoselectively using $\beta,\beta'$-linked bis(dipyrrromethene) ligand **I-45** which contains aromatic amide homochiral auxiliaries, and the M and P helices were resolved by HPLC. The study also shows that double helical bis(dipyrrromethene) complexes are stereochemically stable. In addition, S-linked bis(dipyrrromethene)s **I-46** and **I-47** (**Figure 1.28**) were synthesized to generate double helical complexes.\(^{128}\)

![Figure 1.28](image)

**Figure 1.28** The structure of bis(dipyrrromethene) ligands **I-45**, **I-46** and **I-47**.

![Figure 1.29](image)

**Figure 1.29** Crystal structures of Fe$_2$L$_3$ complexes (50% probability ellipsoids). (a) helicate and (b) mesocate. Two strands are coloured red and green for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity.
Recently, the first dinuclear octahedral poly(dipyrromethene) complexes were reported by Zhang.\textsuperscript{129} Interestingly, during the reaction between the β,β’-linked bis(dipyrromethene) ligands and trivalent cobalt (or iron) metal, both triple-stranded helicates and mesocates were obtained (Figure 1.29).

Figure 1.30 The structure of β,β’-linked bis(dipyrromethene) ligands I-50 and I-51 (a), and the crystal structure of the triangular helicate I-52 (b) and dimeric circular helical complex I-54 (c) (50% probability ellipsoids). Two strands in I-52 are coloured red and green for a clearer representation. Hydrogen atoms and solvent molecules have been omitted for clarity.

Instead of the double-stranded and triple-stranded helicates, the triangular helicates can be formed by employing ligands with a rigid spacer. Thompson successfully obtained the trimeric zinc complex (I-52) and cobalt complex (I-53) by employing ligand I-50 (Figure 1.30).\textsuperscript{123} In a recent published paper by Ma,\textsuperscript{130} a triangular helicate with a large interior cavity
was synthesized by including an extended rigid spacer in the ligand (I-51). Instead of the rigid linear spacer, Ma also took advantage of the directionality of an angled spacer to form dimeric circular helical complexes, such as complex I-54.

In contrast to the breadth of studies on $\alpha,\alpha'$-linked and $\beta,\beta'$-linked bis(dipyrromethene)s, surprisingly, very little research has been done on bis(dipyrromethene)s with spacers linked at the meso-positions. In 2007, Maeda reported the first [2+2]-type macrocycle based on bis(dipyrromethene) ligands with two dipyrrin moieties linked at the meso-position.\textsuperscript{131} The coordination reaction between the ligand and Zn(OAc)$_2$ produces three type of stereoisomers, and the structure of meso-type diastereomer I-55 was identified by X-ray diffraction (Figure 1.31).

**Figure 1.31** Crystal structure of complex I-55 (50% probability ellipsoids). Solvent molecules have been omitted for clarity.
1.5 Goals and scope of the thesis

Over the past few decades, self-assembly has received considerable attention in a number of fields, ranging from chemistry to biology, material science and nanoscience. Self-assembled systems hold promise for various applications such as catalysis, gas storage, drug delivery, molecular electronics, and sensor design and optics. Much work has been done in an effort to generate a variety of one-, two-, and three-dimensional structures, and some progress has been achieved in the design and synthesis of functional supramolecular structures.\textsuperscript{132}

A recently published paper reports the generation of a highly conductive molecular wire which incorporates metal centers into a rigid molecular backbone in a step-wise fashion.\textsuperscript{133} The research shows the nature of the metal centers have an enormous impact on the conductance of the molecular wire. In Chapters 2 and 3, we will discuss in detail the formation and properties of dipyrrinato complexes with different metals and the self-assembly of linear oligomeric dipyrrinato metal complexes incorporating the same or different metals.

Porous supramolecular metal complexes offer potential application in gas storage and host-guest chemistry. Extensive studies have been done in this field. Depending on the pore size, shape and chemical environment, the porous networks show variable binding ability with different guest molecules.\textsuperscript{134} In Chapter 4, the successful self-assembly of cyclic oligomeric complexes of different size and shape is detailed. The experimental procedure and supporting data is presented in Chapter 5.
CHAPTER 2

Metal complexes of building blocks featuring
protected dipyrrromethene diads
2.1 Overview of dipyrromethene metal complexes

Dipyrromethenes (dipyrins) are monoanionic divalent ligands. They have unique properties and possess some distinct advantages in their coordination chemistry. Firstly, upon deprotonation, they chelate various transition metals to form isolable neutral complexes, with no counteranion required. As a result, the complexes can be purified by conventional chromatographic techniques. Secondly, upon modification of the α-, β- or meso-positions, a great range of substituents can be introduced into the dipyrromethene system, facilitating the incorporation of metal complexes into larger and more diverse structures. Thirdly, the ligands and their complexes have favourable spectroscopic properties, which make them potentially useful in the field of electron/energy transfer. It also bears mentioning here that dipyrin metal complexes have a high degree of crystallinity, which renders them amenable to X-ray diffraction analysis.

A great variety of metal ions have been employed to react with dipyrins to obtain homoleptic metal complexes, such as: copper(II), nickel(II), zinc(II), cobalt(II), cobalt(III), iron(III), palladium(II), and lithium(I), to name a few. Coordination geometry studies show that substituents at the 1- and 9-positions of dipyrin ligands have a pronounced effect on the structural geometry of metal complexes due to inter-ligand steric interactions. This typically results in distorted tetrahedral structures for these metal complexes. The metal used has a significant impact on the stereochemistry of the complexes. Regardless of the presence of α-substituents, the preference for tetrahedral coordination geometry for zinc(II) is preferred for these complexes since it minimizes steric hindrance. It is a different story for copper(II) complexes. The α-substituents force the complex to adopt a distorted tetrahedral structure to release the steric repulsion
between two ligands, even though the preferential formation of square-planar coordination geometry for copper(II) is amply documented.\textsuperscript{64} It is even more intriguing for nickel(II) complexes. Depending on the presence of $\alpha$-substituents, the nickel(II) complexes show different coordination geometries and electron distributions.\textsuperscript{61} Instead of using distorted tetrahedral configurations, palladium(II) complexes form a “stepped square planar” structure in order to overcome inter-ligand crowding.\textsuperscript{65}

When coordinating with trivalent metals, only $\alpha$-unsubstituted dipyrrins can form complexes due to steric effects. Previous research shows the copper(II) and iron(II) complexes of $\alpha$-unsubstituted dipyrrins are unstable and not purifiable. In the presence of excess ligand, the complexes readily transform to tris(dipyrrinato) complexes.\textsuperscript{67} The trivalent metal complexes display octahedral coordination geometries. Their highly symmetric geometry and ready modification, along with unique spectroscopic properties, make them ideal candidates for generation of metal-organic frameworks,\textsuperscript{72, 117} which have great potential for use in molecular storage, sensory technology and catalytic applications.\textsuperscript{114, 139}

\textbf{2.2 Synthetic approach to ligands}

\textbf{2.2.1 Initial design}

![Structure of compound II-1](image)

\textbf{Figure 2.1} Structure of compound II-1.

The initial synthetic strategy to generate dipyrrromethene ligands is to synthesize compound \textbf{II-1} (\textbf{Figure 2.1}), which contains a dipyrrromethane moiety and a dipyrrromethene
moiety in one molecule. The anticipated advantage of this ligand design is that after metal coordination with the dipyrrromethene moiety, we can further modify the dipyrrromethane component. For example, generation of a second dipyrrromethene moiety through oxidation, allows further coordination with another metal (same or different) or boron to produce an oligomeric dipyrrromethene complex of controlled length.

Following a published synthetic route,62 II-1 was successfully prepared. This ligand was further reacted using a general dipyrrin metal complexation method. However, the anticipated complex did not form but rather a precipitate was immediately observed upon the addition of the metal salt into a solution of ligand. It is well known that dipyrrromethanes are labile species and prone to atmospheric oxidation reaction.140 It is possible that electrons flow towards the dipyrrin side during the metal complexation, which causes the dipyrrromethane side to become vulnerable to auto-oxidation to form the dipyrrin. The newly formed dipyrrin automatically reacts with excess metals in the solution and eventually leads to an insoluble polymeric product.

2.2.2 Synthesis of bis(dipyrrin)s capped by BF2 as protecting group

In order to control this “uncontrolled” polymerization, we decided to employ a cap to protect one side of the ligand. Boron-dipyrrromethene complexes have properties which combine high molar extinction coefficients and high fluorescence quantum yields, strong chemical and photochemical stabilities in both solution and the solid state, along with remarkable electron-transfer properties78,141 which offer many advantages for future studies. It was seen as an excellent candidate as protecting group for our ligands.
The first successfully synthesized mono-protected dipyrrromethene diad was II-6 (Scheme 2.1), which was fully characterized by mass spectrometry, NMR spectroscopy and X-ray crystal structure analysis. The red needle crystals of II-6 were obtained by slow evaporation from a CH₂Cl₂ solution of the compound (Figure 2.2). The asymmetric ligand exhibits a 70.5° twist angle between the boron dipyrrromethene plane and the free-base dipyrrromethene plane. The two pyrrole interior C-N-C angles (C24-N3-C27 and C29-N4-C32) are 108.3° and 106.0°, respectively.

Scheme 2.1 Synthetic route to compound II-6.

Figure 2.2 Crystal structure of II-6 with partial atom numbering schemes. Thermal ellipsoids are scaled to the 50% probability level.
A series of BF₂-capped ligands were synthesized. These ligands are linked through various spacers (Figure 2.3) and they all readily reacted with various metals to form complexes. Unfortunately, attempts to crystallize the metal complexes containing these ligands by slow evaporation or diffusion were not successful and the acquisition of clear crystal data failed.

![Figure 2.3 Structure of BF₂ capped ligands.](image)

### 2.2.3 Formation and characterization of BF₂ capped bis(dipyrin)s II-12 and II-14

#### 2.2.3.1 Preparation of ligands

2-Methylpyrrole (II-7) was chosen as the starting reagent to form the dipyrromethene and was prepared according to literature methods. Compound II-10 was synthesized by the condensation between p-cyanobenzaldehyde and 2-methylpyrrole and was followed by the reduction of the p-CN group to p-CHO, and finally complexation with boron-difluoride. The CH₂Cl₂ solution of II-10 and pyrrole (or 2-methylpyrrole) was treated with trifluoroacetic acid, and then reacted with DDQ. The reaction mixture was concentrated and column chromatographed. Fluorescent compounds II-12 and II-14 were collected as red solids (Scheme 2.2).
Scheme 2.2 Synthetic route to ligands II-12 and II-14.

2.2.3.2 Spectroscopic and structural features of II-12 and II-14

Ligands II-12 and II-14 were both fully characterized by mass spectrometry and NMR and UV-Vis spectroscopy. II-12 and II-14 exhibited similar absorption spectra with absorbance maxima at 514 nm in CH$_2$Cl$_2$ as a result of boron complexation.

As shown in the $^1$H NMR spectra of these two compounds (Figure 2.4), the $\beta$-protons on the boron dipyrrin side and on the free dipyrrin are well-separated and the characteristic patterns of $\alpha$- and $\beta$- proton peak-splitting can be observed. Because of the electron-withdrawing nature of the BF$_2$ group, the methyl protons (the assignments of methyl protons were done by comparing the $^1$H NMR spectra of II-12 and II-14) on the boron dipyrrin side are distinctly downfield-shifted in comparison to the methyl protons on the free-base dipyrrin side.
Figure 2.4 $^1$H NMR spectra of ligands II-12 and II-14

Figure 2.5 Crystal structure of II-12. The $C_2$ symmetry axis is denoted by the gray line. Thermal ellipsoids are scaled to the 50% probability level.

In addition to full spectroscopic characterization, crystals of II-12 were obtained by the slow evaporation of a CH$_2$Cl$_2$ solution. The resulting X-ray crystal structure of II-12 shows $C_2$ symmetry, where a nitrogen-bound H-atom on the free-base dipyrrromethene unit is shared between two N-atoms N2 and N2' (Figure 2.5, the shared proton is marked as pink circles).
Consequently, the pyrrole interior C-N-C angles exhibit an average angle of 107.5°, which is intermediate between the amino and imino values for this delocalized aromatic system. The two planes of the boron dipyrromethene and the free-base dipyrromethene are essentially planar with an approximate 3° tilting angle.

2.3 Formation and characterization of divalent metal complexes

2.3.1 Synthesis of divalent metal complexes

\[
\text{II-12 (R}^1 = \text{H)} \quad \text{II-14 (R}^1 = \text{CH}_3) \quad \text{II-15 (R}^1 = \text{H, M = Cu}^{II}) \quad \text{II-16 (R}^1 = \text{CH}_3, \text{ M = Cu}^{II}) \quad \text{II-17 (R}^1 = \text{H, M = Ni}^{II}) \quad \text{II-18 (R}^1 = \text{CH}_3, \text{ M = Ni}^{II}) \quad \text{II-19 (R}^1 = \text{CH}_3, \text{ M = Co}^{III}) \quad \text{II-20 (R}^1 = \text{CH}_3, \text{ M = Zn}^{II})
\]

Scheme 2.3 Synthesis of metal complexes II-15 through II-20.

As expected, ligands II-12 and II-14 readily form unique metal complexes with various metals (Scheme 2.3). Dicationic metals, Cu^{II}, Ni^{II}, Co^{II}, and Zn^{II} were introduced into solutions of II-12 (or II-14) in a mixed solvent of CH$_2$Cl$_2$ and MeOH, to form metal complexes. The resulting complexes were purified using chromatography on silica or basic alumina gel.
2.3.2 NMR spectroscopic analysis of complexes II-15 through II-20

Signals for the Cu$^{II}$ complexes II-15 and II-16 were not detected between -20 to +30 ppm, which proves that the complexes are paramagnetic and the central dicationic metals were in the $d^9$ configuration. Similarly, the paramagnetism of the Co$^{II}$ centre resulted in a large range (-20~60 ppm) for the signals of the H-atoms of II-19. Interestingly, the two Ni$^{II}$ complexes II-17 and II-18 exhibited different electron configurations, which implies these two complexes employ different coordination geometries. Complex II-17 showed sharp signals in its $^1$H NMR and $^{13}$C NMR spectra, which suggests it has a low-spin, diamagnetic, distorted square-planar structure. On the other hand, complex II-18 showed broad signals over a large range, correlating with a high-spin, paramagnetic, distorted tetrahedral structure. The differences between the structures were further confirmed by the crystal structure analysis (see 2.3.3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Metal</th>
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<td>II-14</td>
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<td>II-18</td>
<td>Ni$^{II}$</td>
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<td>II-19</td>
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<td>diamagnetic($d^{10}$)</td>
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</table>

Table 2.1 Selected $^1$H NMR data of ligands II-12, II-14, and metal complexes II-15 – II-20.
Figure 2.6 Comparison of $^1$H NMR Spectra for II-12(a) and II-17(b), II-14(c) and II-20(d).
Table 2.1 and Figure 2.6 compare the NMR data between the two ligands and their metal complexes. The β-H signals of Ni\textsuperscript{II} complex II-17 and Zn\textsuperscript{II} complex II-20 were downfield shifted in the \textsuperscript{1}H NMR spectra compared to those of free-base ligands II-12 and II-14 due to the extended π-conjugated system resulting from electron overlap with the metal $d$ orbitals. The α-H signals of II-17 were highly downfield-shifted (from 7.69 ppm for II-12 to 10.31 ppm for II-17) which also correlates to the extension of the π-conjugated system, and as shown in the crystal structure (Figure 2.7), the α-H protons of II-17 experience deshielding effects as they were positioned on the side of the dipyrrinato ring system. On the other hand, the signal of α-methyl groups in II-20 was upfield-shifted (from 2.45 ppm for II-14 to 2.16 ppm for II-20) as the methyl groups are positioned above the ring current of the dipyrrinato system.

2.3.3 Crystal structure discussion

Metal complexes II-15 through II-20 were characterized by X-ray diffraction analysis. Crystals of II-15 and II-20 were obtained as needles by slow evaporation of CH$_2$Cl$_2$ from a CH$_2$Cl$_2$/hexane solution. The plate-shaped crystals of II-16, II-17 and II-19 were grown from solutions of the metal complex in CH$_2$Cl$_2$ with slow diffusion of CH$_3$OH. The tablet crystals of II-18 were obtained via slow diffusion of the CH$_3$OH into a CHCl$_3$ solution. The crystals appear either red and/or green with a metallic luster.

Metal complexes II-15 through II-20 show nearly linear conformations, in which the dipyrrromethene units linked to the central dicationic metal exhibit distorted tetrahedral structures as shown by the different dihedral angles of the inter-ligand planes. The bite angles of the complexes range between $91^\circ$ to $95^\circ$ (Table 2.2). The structures of complexes II-15 and II-17 show $C_2$ symmetry, while the others, II-16, II-18 – II-20, are non-symmetric molecules.
(Figure 2.7). Similar to the planarity shown in ligand \textbf{II-12}, near-planarity was also detected in \textbf{II-15} and \textbf{II-17}, with ca. 4.0° and 5.5° intra-ligand tilting angles, respectively. Interestingly, the two single ligand units of \textbf{II-15} and \textbf{II-17} are bent with 20.5° and 19.2° angles, as shown in Figure 2.7. Compared with other metal complexes having the same ligand unit \textbf{II-17}, the Cu\textsuperscript{II} complex \textbf{II-16} shows significant differences in metal-N bond lengths, resulting from the Jahn-Teller effect. Due to the steric hindrance between the \(\alpha\)-methyl groups, the dihedral angles of the metal complexes of \textbf{II-14} were larger than those of the metal complexes of \textbf{II-12}, which are represented by the different coordination geometries and electron distributions in the two Ni\textsuperscript{II} complexes \textbf{II-17} and \textbf{II-18}. The relatively shorter N-Ni bond lengths in complex \textbf{II-17} (1.89-1.90 Å), compared with those in complex \textbf{II-18} (1.96-1.97 Å), were considered to be the result of lower steric hindrance owing to the absence of \(\alpha\)-substituents and the reduced radius of the \(d^8\) low-spin state central metal ion. These differences in the coordination and electron distribution are consistent with the NMR spectroscopic results.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bite angle (°)</th>
<th>Inter-ligand dihedral angle (°)</th>
<th>Bending angle (\theta) (°)</th>
<th>Metal-N bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{II-15}</td>
<td>92.0</td>
<td>58.4</td>
<td>20.5</td>
<td>1.92-1.93</td>
</tr>
<tr>
<td>\textbf{II-16}</td>
<td>94.0, 94.8</td>
<td>70.5</td>
<td>8.4</td>
<td>1.95-1.99</td>
</tr>
<tr>
<td>\textbf{II-17}</td>
<td>92.7</td>
<td>54.5</td>
<td>19.2</td>
<td>1.89-1.90</td>
</tr>
<tr>
<td>\textbf{II-18}</td>
<td>91.3, 91.4</td>
<td>78.5</td>
<td>2.0</td>
<td>1.96-1.97</td>
</tr>
<tr>
<td>\textbf{II-19}</td>
<td>92.9, 93.1</td>
<td>84.0</td>
<td>3.4</td>
<td>1.96-1.98</td>
</tr>
<tr>
<td>\textbf{II-20}</td>
<td>93.8, 94.0</td>
<td>84.7</td>
<td>3.4</td>
<td>1.97-1.98</td>
</tr>
</tbody>
</table>

Table 2.2 Selected crystal data of metal complexes. Bending angle (\(\theta\)) as shown in Figure 2.7.
Figure 2.7 Crystal structures of metal complexes with partial atom numbering schemes (ORTEP, thermal ellipsoids are scaled to the 50 % probability level). a) II-15; b) II-16; c) II-17; d) II-18; e) II-19; f) II-20. Solvent molecules and hydrogen atoms in II-15, II-16, II-18 and II-19 have been omitted for clarity.
2.4 Formation and characterization of trivalent metal complexes

2.4.1 Synthesis of trivalent metal complexes II-21 and II-22

Trivalent metal salts can also be used in coordination reactions to form dipyrrin complexes. Here, we chose Co$^{III}$ and Fe$^{III}$ to react with ligands II-12 and II-14. As mentioned previously, only $\alpha$-unsubstituted dipyrrins can coordinate with trivalent metals to form complexes due to steric hindrance. In our case, only ligand II-12 formed trivalent metal complexes (Scheme 2.4). Ligand II-14 shows no reaction with Fe$^{III}$ and Co$^{III}$ even with increased temperature and prolonged reaction time.

![Scheme 2.4 Synthesis of metal complexes II-21 to II-22](image)

The ligand was dissolved in a mixture of CHCl$_3$ and MeOH. Following the addition of triethylamine, a MeOH suspension of the metal salt was added to the reaction solution. After reflux overnight under an argon atmosphere, the solvent was removed and the desired complexes were purified by flash silica chromatography. Both tris(dipyrrinato) coordination complexes were confirmed by MALDI-TOF mass spectrometry.
2.4.2 NMR Spectroscopic analysis of complexes II-21 and II-22

![NMR Spectra of complexes II-21 and II-22](image)

**Figure 2.8** Comparison between $^1$H NMR Spectra of II-12 and II-22

NMR signals of Fe$^{III}$ complex II-21 were not detected due to its paramagnetism. Co$^{III}$ complex II-22 exhibits sharp NMR signals as shown in **Figure 2.8**. As expected, the three ligands chelated to cobalt only show one set of NMR signals due to the $C_3$ symmetry of the
complex. The $\alpha$-H signal of cobalt complex was upfield-shifted compared to the free dipyrrin ligand due to the shielding effect of the conjugated dipyrrinato ring system. One set of $\beta$-H signals of the cobalt complex was downfield-shifted as the protons were positioned on the side of the dipyrrinato ring, while the other set of $\beta$-Hs, boron dipyrrin protons and the phenyl protons remain relatively unperturbed in the complex.

2.4.3 Crystal structure discussion

Several trivalent metal complexes of $\alpha,\beta$-unsubstituted dipyrrins have been reported previously and are without a three-fold axis due to the central metal distortion. In the past few years, the Cohen group has synthesized dipyrrin metal complexes with high symmetry in the solid state. In this work, crystals of complexes II-21 and II-22 were obtained as red prisms by the slow diffusion of CH$_3$OH into a CH$_2$Cl$_2$ solution of the complex. As shown in Figure 2.9, in both the Fe$^{\text{III}}$ and Co$^{\text{III}}$ complexes, six pyrrole nitrogen atoms exhibit perfect octahedral coordination geometry with the metal occupying the central position, and the three ligands displayed the expected 3-fold symmetry about the metal center.

In both the II-21 and II-22 crystals, the planarity between two intra-ligand dipyrrin systems are well preserved and the tilting angles between the two dipyrrin moieties are 2.89° for the Fe$^{\text{III}}$ complex and 2.95° for the Co$^{\text{III}}$ complex. The average Fe-N distance is 1.937Å, and the bite angle is 91.6°. The selected Co$^{\text{III}}$ complex crystal was twinned about a hexagonal axis, with an average Co-N bond length of 1.940Å, and a bite angle of 92.7°.
Figure 2.9 ORTEP structures of trivalent metal complexes II-21 and II-22. Thermal ellipsoids are scaled to the 50% probability level. a) top and side view of II-21, hydrogen atoms have been omitted for clarity; b) top and side view of II-22.

The two crystals show similar packing patterns. The stepwise packing pattern model and three-dimensional packing structure of each complex is shown in Figure 2.10. The fourth layer of each complex superimposes with the first layer with a 60° twist angle to minimize steric hindrance, resulting in a six-petal flower-like packing pattern. The distance between the
mean planes of layer 1 and layer 4 is 8.85Å for Fe\textsuperscript{III} complex \textbf{II-21} and 8.93Å for Co\textsuperscript{III} complex \textbf{II-22}.

\textbf{Figure 2.10} a) Stepwise packing pattern of the individual layers of complexes \textbf{II-21} and \textbf{II-22}. Top view (b) and side view (c) of packing diagram of \textbf{II-21}, and top view of the packing diagram of \textbf{II-22} (d). Hydrogen atoms have been omitted for clarity.
2.5 UV-Vis spectroscopy of dipyrromethene metal complexes

Some research regarding the optical spectra of simple dipyrromethenes and their metal complexes has been performed in the past. A. I. V’yugin et al.\textsuperscript{135} examined solvent effects and showed that the $\lambda_{\text{max}}$ is determined by the polarization of the $\pi$ system, which in turn is governed by electronic nature and the coordination properties of the metal ions. Our group has also shown that hyperconjugation of peripheral alkyl groups results in bathochromic shifts and Motekaitis-Martell MO theory allows for the calculation of dihedral angles for metal complexes.\textsuperscript{61} On the other hand, the optical spectra, especially fluorescence, have been thoroughly studied for the boron complexes of dipyrromethenes.\textsuperscript{78, 141}

The optical properties of dipyrromethene metal complexes II-15 through II-20 bear great similarity to one another which indicates comparable stereochemistry for these complexes. The absorbance maximum (514 nm) band for ligands II-12 and II-14 in CH$_2$Cl$_2$ remains as a shoulder or with minor shifts upon metallation (513 nm for II-15, II-17, II-21 and II-22, as shoulders for II-16, II-18, II-19 and II-20) (\textbf{Figure 2.11}). As expected, new bands appeared at 420-510 nm in accordance with metal complexation.
Figure 2.11 Optical spectra of a) ligand II-12 and its divalent metal complexes; b) ligand II-14 and its metal complexes; and c) ligand II-12 and its trivalent metal complexes. All spectra were recorded in CH$_2$Cl$_2$ at room temperature.

Scheme 2.5 Synthesis of reference compounds II-23 through II-40
Table 2.3 Optical data of the metal-dipyrrin and boron-dipyrrin reference series.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}} \text{ (nm)}$ / $\log \varepsilon$</th>
<th>Compound</th>
<th>$\lambda_{\text{max}} \text{ (nm)}$ / $\log \varepsilon$</th>
<th>$R^1$</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-23</td>
<td>517.9 / 4.85</td>
<td>II-24</td>
<td>510.6 / 4.89</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II-25</td>
<td>471.1 / 4.82</td>
<td>II-31</td>
<td>466.0 / 4.80</td>
<td>H</td>
<td>Cu$^{II}$</td>
</tr>
<tr>
<td>II-26</td>
<td>510.0 / 4.72</td>
<td>II-32</td>
<td>504.0 / 4.85</td>
<td>CH$_3$</td>
<td>Cu$^{II}$</td>
</tr>
<tr>
<td>II-27</td>
<td>480.0 / 4.59</td>
<td>II-33</td>
<td>466.0 / 4.57</td>
<td>H</td>
<td>Ni$^{II}$</td>
</tr>
<tr>
<td>II-28</td>
<td>515.0 / 4.70</td>
<td>II-34</td>
<td>513.0 / 4.79</td>
<td>CH$_3$</td>
<td>Ni$^{II}$</td>
</tr>
<tr>
<td>II-29</td>
<td>500.5 / 5.05</td>
<td>II-35</td>
<td>497.5 / 5.15</td>
<td>CH$_3$</td>
<td>Co$^{II}$</td>
</tr>
<tr>
<td>II-30</td>
<td>494.5 / 5.08</td>
<td>II-36</td>
<td>491.0 / 5.14</td>
<td>CH$_3$</td>
<td>Zn$^{II}$</td>
</tr>
<tr>
<td>II-37</td>
<td>493.0 / 4.55</td>
<td>II-39</td>
<td>491.5 / 4.56</td>
<td>H</td>
<td>Fe$^{III}$</td>
</tr>
<tr>
<td>II-38</td>
<td>507.1 / 4.69</td>
<td>II-40</td>
<td>503.9 / 4.66</td>
<td>H</td>
<td>Co$^{III}$</td>
</tr>
</tbody>
</table>

In this study, we also prepared two series of metal complexes as reference compounds with different substituents on the meso-aryl rings (II-23 - II-40, Scheme 2.5) to provide the electronic spectra of the uncoupled metal-dipyrrins and boron-dipyrrins. The optical spectra show a correlation between the inter-ligand dihedral angles and the maximum absorption bands (Table 2.3). For the same metal, with an increase of the inter-ligand dihedral angles (data based on Table 2.2), the absorption bands show significant bathochromic shifts (38.9 nm and 38.0 nm for two sets of Cu$^{II}$ complexes (II-25, II-26 and II-31, II-32); 35.0 nm and 47.0 nm for two sets of Ni$^{II}$ complexes (II-27, II-28 and II-33, II-34), respectively. The bathochromic shift also occurs with a cyano group on the meso-aryl instead of a methyl group. The influence of the electron-withdrawing cyano group is particularly obvious in Ni$^{II}$ complexes of the $\alpha$-free dipyrrromethenes, where the distorted square-planar structures exhibit a large bathochromic shift (14 nm, compare II-27 with II-33). In contrast, the two distorted tetrahedral Ni$^{II}$ complexes of $\alpha$-methyl dipyrrromethenes (compare II-28 with II-34) show only a relatively small bathochromic shift (2 nm). Interestingly, the optical spectra of all of the metal
complexes II-15 through II-22 approximate the sum of the individual boron-dipyrrins and metal dipyrrins, which suggests a minimal overlap between the π systems (Figure 2.12).

**Figure 2.12** Comparison of the experimental and calculated optical spectra. All spectra were recorded in CH₂Cl₂ at room temperature. The calculated spectrum of compound II-15 (II-15 calcd.) was obtained as shown at the top of the figure. The calculated spectra of compound II-16 – II-22 were obtained the same method.
2.6 Summary

Novel ligands which contain boron-linked dipyrrromethenes on one side and free-base dipyrrromethenes on the other were successfully synthesized and the structure of ligand II-12 was determined by X-ray diffraction analysis. Various dicationic and tricationic metals form complexes with the ligands and new peaks corresponding to these metalations were observed in the optical spectra. All of the metal complexes were defined by X-ray diffraction analysis. The crystal structures of metal complexes were investigated and the correlation between structural features and optical properties was established. Porphyrins, which can be considered as cyclic bis(dipyrrin)s, have been introduced as molecular wires via linkage with boron-dipyrrromethene. Here, we introduce new molecular systems that can potentially act as molecular wires generated between boron-dipyrrin and metal-dipyrrin. With this said, the energy transfer processes between metal dipyrrromethene and boron dipyrrromethene is still a relatively new area of investigation. At the same time, these systems are correlated with self-assemblies. Studies on similar systems with greater length will be discussed in detail in the next chapter.
CHAPTER 3

Self-assembled linear oligomers of bis(dipyrrinato) metal complexes
3.1 Overview of molecular wires

One of the main objectives in nanotechnology is the manufacture of well-organized functional architectures through molecular self-assembly. Recently, the study of molecular electronic and photonic wires, which are considered to be one-dimensional nanostructures, has become an active platform. Molecular wires involve the use of single or small bundles of molecules as building blocks for energy transport and electronic applications.\textsuperscript{145, 146} In addition, molecular photonics and electronics have attracted much interest due to the potential of storing vast amounts of information in very small volumes.\textsuperscript{147} A perfect example is using DNA as a building block for self-organized molecular wires. The two complementary DNA helical strands readily form a double helix upon self-assembly according to base-pairing rules. However, the ability of DNA as a molecular wire to conduct electricity is still in dispute.\textsuperscript{148} At the same time, some studies show that conjugated molecular systems dramatically increase conductivity.\textsuperscript{149}

Different approaches to generate molecular wires by employing unsaturated $\pi$-bonded metal-organic systems have been studied. Porphyrins can be considered as cyclic bis-dipyrrromethenes. Crossley and Burn have synthesized tetrakisporphyrin with a fully-conjugated polyporphyrin backbone (Figure 3.1, a).\textsuperscript{150} The molecule is close to 65Å in length and the \textit{meso}-positions of the porphyrin backbones are substituted with \textit{tert}-butyl groups to insulate the conjugated core as well as to increase solubility in common organic solvents. Wagner and Lindsey have introduced a molecular wire where a porphyrin array is linked to a boron-dipyrromethene complex at one end of the assembly (Figure 3.1, b).\textsuperscript{60} In this case, the boron-dipyrromethene acts as an optical input while the porphyrin array plays the role of the transmission element of the molecular photonic device. Similarly, Weiss and his colleagues
have designed a self-assembled porphyrin photonic wire which performs a stepwise energy transfer (Figure 3.1, c).\textsuperscript{88} In 2006, Maeda et al. employed phenylethynyl-bridged dipyrrins as scaffolds to form metal-coordinated dipyrrin polymers which exhibited spherical nanoarchitectures.\textsuperscript{118} (Figure 3.1, d)

![Figure 3.1](image_url)

**Figure 3.1** Different molecular wires based on porphyrin/dipyromethene arrays.

### 3.2 Synthesis of the dipyromethene dimer and its polymerization

In Maeda’s work, the self-assembled dipyrrin metal oligomer structures have diameters ranging from 100nm to 0.3µm, and contain at least $10^5$-10$^6$ dipyrrin units in one polymer sphere. We have prepared similar dipyrrin “dimers” III-2 and III-4 (Scheme 3.1), but instead
of “uncontrolled” polymerization, we have attempted to control the oligomerization using a dipyrrin dimer monoprotected as the BF$_2$ complex. The condensation between freshly distilled pyrrole (or 2-methyl pyrrole) and terephthalaldehyde and a subsequent DDQ oxidation afforded a dark red precipitate, which is a self-assembled system that incorporates a protonated dipyrrromethene with a deprotonated dichloro-dicyano-quinone (DDQ). The reaction mixture was directly poured onto a basic alumina column, and THF was used as eluent to flush through the crude product. The crude product was evaporated to dryness and further purified by silica gel column chromatography. Pure dipyrrin derivatives III-2 and III-4 were collected as brown powders in 16% and 23% overall yields, respectively (Scheme 3.1). The structures of both dipyrrin “dimers” were confirmed by $^1$H NMR, $^{13}$C NMR and mass spectrometry.

![Scheme 3.1 Synthesis of bis(dipyrrin) ligands III-2 and III-4.](image)

The dipyrrin dimer ligands were dissolved in a mixture of CH$_2$Cl$_2$ and CH$_3$OH. The precipitation occurs immediately upon the addition of one equivalent of metal acetate salt (Cu(OAc)$_2$, Co(OAc)$_2$ or Zn(OAc)$_2$). The polymer particles were red in colour and spherically shaped. Decreasing the amount of the metal salt or lowering the reaction temperature did not prevent the polymerization.

Instead of these “uncontrolled” polymerizations, we attempted to control the oligomerization using a dipyrrin dimer monoprotected with a BF$_2$ group.
3.3 Formation and characterization of dipyrromethene metal complexes with predetermined length

3.3.1 Synthesis and purification of dipyrromethene oligomers with different lengths

Scheme 3.2 Synthesis of self-assembled oligomers II-19 and III-5 through III-8.

In order to achieve longer linear dipyrromethene oligomers, mono-BF$_2$-protected ligand II-14 and dipyrrin dimer III-4 were mixed with metal salts for coordination. The reaction produced a mixture, which contains self-assembled oligomers of different length (Scheme 3.2). The formation of these self-assembled oligomers was confirmed by MALDI-TOF mass spectrometry (Figure 3.2) and were then separated using size exclusion chromatography. The reaction was also carried out using different proportions of ligand II-14, ligand III-4 and the metal salt as well as at various temperatures. The resulting ratio of the various length metal complexes did not significantly change.
Figure 3.2 MALDI-TOF spectrum of the crude reaction mixture containing an oligomeric mixture of II-19, III-5 through III-8 and excess ligand II-14.

A similar reaction was also performed between II-12, III-2 and Cu(OAc)$_2$. Unfortunately, MALDI-TOF mass analysis shows only homoleptic copper(II) dipyrrin complex II-15 was formed.

3.3.2 UV-Vis spectroscopic analysis of linear metal complexes

As shown in Figure 3.3, the sharp absorption at 514 nm resulting from boron-complexation with the ligand still remains as a shoulder in metal complex II-19. With increasing length and increasing number of metal ions, the electronic absorption spectra of the complexes show a hypsochromic shift, with the sharp boron-complexation band gradually disappearing beneath the enhanced metal-dipyrrin absorption band.
Figure 3.3 Optical spectra of ligand II-14 and complexes II-19, III-5 and III-6 in CH$_2$Cl$_2$.

Figure 3.4 Comparison of the experimental and calculated optical spectra of linear metal complexes III-5 and III-6. All spectra were recorded in CH$_2$Cl$_2$ at room temperature.
The comparisons between experimental and calculated optical spectra was performed using the same method described in Chapter 2, and the resemblance between the sum of the spectra of the boron-dipyrrromethene and metal dipyrrromethene and the experimental data indicates minimal overlap between the $\pi$ systems (Figure 3.4).

3.3.3 Crystal structure analysis of linear metal complex III-5

In addition to spectroscopic characterization, linear metal complex III-5 was crystallized and the structure was determined by X-ray diffraction. The red needle crystals of complex III-5 were grown from a solution of the complex dissolved in CHCl$_3$ with diffusion of CH$_3$OH. The complex co-crystallized with one molecule of CHCl$_3$ in the asymmetric unit. The crystal structure of III-5 has an inversion center. It shows similar metal-N bond lengths (1.96-1.98\,Å) and inter-ligand dihedral angle (84.9°) to the mono-cobalt metal complex II-19. The straight line distance between two boron atoms is 3.6 nm (Figure 3.5).

Figure 3.5 Structural diagrams of linear complex III-5 with partial atom numbering scheme (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.
3.4 Alternate approach for linear dipyrrin metal complexes with controlled length

3.4.1 Synthesis and characterization of heteroleptic dipyrrromethene metal complexes

In 2004, a paper published by the Cohen group described the formation of homoleptic or heteroleptic copper(II) complexes with dipyrrromethene ligands by adding different amounts of Cu(acac)$_2$ (acac = acetylacetonato) to the dipyrrin$^{109}$. When 0.4 equivalents (relative to the initial dipyrrromethene) of Cu(acac)$_2$ were added, the homoleptic product [Cu(dpm)$_2$] (dpm = dipyrrromethene) was produced. When 1.0 equivalent of Cu(acac)$_2$ was employed to react with dipyrrromethene, the product was a heteroleptic complex [Cu(dpm)(acac)] (Scheme 3.3). In light of this study, we synthesized different heteroleptic dipyrrromethene metal complexes. These metal complexes can act as metal salt precursors and further react with the same or different dipyrrromethene ligands to form more complicated metal complexes.

![Scheme 3.3 General approach for synthesis of [Cu(dpm)$_2$] or [Cu(dpm)(acac)].](image)

As described in Cohen’s research, the products of the reaction between dipyrrin ligands and metal acetylacetonates were dependent on the metal-ligand stoichiometry. In our case, when dipyrrin dimer III-2 or III-4 was mixed with substoichiometric amounts of metal acetylacetonate, dipyrrin-metal polymers were formed. However, combination of ditopic ligands with an excess of metal acetylacetonate results in the formation of the desired heteroleptic bis(dipyrrin) metal complexes (Scheme 3.4).
Scheme 3.4 Synthesis of heteroleptic bis(dipyrrin) metal complexes.

All three complexes were obtained in modest yields and are stable in solution. Complex III-9 was isolated by flash silica column chromatography as a red compound. Complexes III-10 and III-11 were found to decompose rapidly when exposed to silica gel. Complex III-10 was purified using size exclusion chromatography. The collected solution was evaporated in vacuo to afford a maroon compound. Pure III-11 was obtained by recrystallization from CH$_2$Cl$_2$/ethyl ether as bright red crystals. These heteroleptic bis(dipyrrin) metal complexes were confirmed by MALDI-TOF mass spectrometry and absorption spectroscopy. Furthermore, complex III-11 was characterized by $^1$H NMR (Figure 3.6) and X-ray diffraction (Figure 3.7).

Figure 3.6 $^1$H NMR spectrum (CD$_2$Cl$_2$, 300MHz) of compound III-11.
Figure 3.7 Crystal structure of III-11 with partial atom numbering schemes. Thermal ellipsoids are scaled to the 50% probability level.

The crystal structure of III-11 has an inversion center. It displays tetrahedral metal environments with the two O atoms from acac and the two N atoms from dipyromethene occupying the four vertices. The average Zn-O and Zn-N bond lengths are 1.955 and 1.953Å, respectively. The dihedral angle between the two chelators (acetylacetonate and dipyrrin) is 86.3°. The two dipyrrin systems are essentially planar with a 2.4° tilting angle, and the phenyl group in the middle is twisted out of plane by 24.1°.

Attempts to crystallize III-9 and III-10 only produced microcrystalline material not suitable for X-ray diffraction.

3.4.2 Synthesis of linear dipyrrin metal complexes via heteroleptic bis(dipyrrin) metal complexes

After successfully synthesizing and purifying metal heteroleptic complexes III-9 through III-11, we tried to employ them as metal salt precursors for the self-assembly of linear dipyrrin metal complexes.

The first attempt involves the reaction between heteroleptic bis(dipyrrin) copper(II) complex III-9 and BF₂-capped ligand II-12. Unfortunately, when 0.5 equivalents of III-9 were
combined with 1 equivalent \( \text{II-12} \) and stirred at room temperature, the only product obtained was homoleptic dipyrrin copper(II) complex \( \text{II-15} \). When heteroleptic bis(dipyrrin) cobalt(II) complex \( \text{III-10} \) was treated with BF\(_2\)-capped bis(dipyrrin) ligand \( \text{II-14} \), the complexes \( \text{II-19} \) and \( \text{III-5} \) were formed. Compared to the yields in the straightforward reaction as shown in Scheme 3.2 (53% and 21% for \( \text{II-19} \) and \( \text{III-5} \), respectively), the product yields here are much lower (33% for \( \text{II-19} \) and 4.6% for \( \text{III-5} \)) (Scheme 3.5).

Scheme 3.5 Reactions between BF\(_2\)-capped dipyrrins and heteroleptic bis(dipyrrin) metal complexes.

The reaction between heteroleptic bis(dipyrrin) zinc(II) complex \( \text{III-11} \) and ligand \( \text{II-14} \) yielded some positive results. A solution of \( \text{III-11} \) was cooled to -15 °C, and treated with \( \text{II-14} \) and kept stirring for 3 hours at -15 °C. The reaction mixture was filtered through a basic alumina column, and the resultant mixture was further purified using a size exclusion column. Three complexes were collected and the MALDI-TOF spectra suggest they are linear
complexes of different length (Scheme 3.5). Unfortunately, attempts to obtain a crystal suitable for X-ray analysis failed. $^1$H NMR was used to support the structures of these complexes.

Figure 3.8 $^1$H NMR spectra (CDCl₃, 400 MHz) for linear metal complexes II-19 (a), III-12 (b) and III-13 (c).
The $^1$H NMR spectra clearly show the formation of metal complexes with different lengths (Figure 3.8). In the spectrum of compound II-19, the protons of the aryl ring between the boron-dipyrrin and zinc-dipyrrin show a characteristic doublet-doublet splitting pattern. This splitting pattern was well preserved in the spectra of III-12 and III-13, and a new peak was observed in the resonance region for aryl group protons, which correlates to the aryl-ring(s) between two zinc-dipyrrins, and the integration for the protons confirms the different number of aryl rings. At the same time, new signals for $\beta$-protons appeared in the spectra of III-12 and III-13 due to introduction of ligand III-4 into the linear metal complexes, and the integration for $\beta$-protons varied accordingly. In all three metal complexes, the integrations for the methyl group on the boron-dipyrrin sides are the same ($\delta = 2.7$ ppm, 12H), and the integrations for the methyl group on the zinc-dipyrrin side are 12(II-19), 24(III-12) and 36(III-13), respectively.

To further support the assignment of the protons of these metal complexes, $^1$H-$^1$H COSY NMR experiments were carried out for complex III-12.

3.5 Current progress on the synthesis of linear dipyrrin metal complexes

3.5.1 Using simple dipyrrins to replace BF$_2$-capped bis(dipyrrin)s

As shown in Scheme 3.5, the major products of the reaction between the heteroleptic bis(dipyrrin) metal complexes and BF$_2$-capped ligands are homoleptic metal complexes II-15, II-19 and II-20, which suggests that instead of using these acac-derived complexes (III-9 through III-11) as metal sources, there are some subtle forces driving the metal-N bond-breakage in the heteroleptic bis(dipyrrin) metal complexes. The BF$_2$-group of ligands II-12 and II-14 perhaps has some impact on the metal center due to its strong electron-withdrawing nature, resulting in the stripping of metal atoms from the heteroleptic metal complexes and the
subsequent formation of the homoleptic metal complexes. The tedious synthesis and purification process of ligands II-12 and II-14, and their relatively overall low yield did not help matters. As a result, instead of BF$_2$-capped bis(dipyrrin)s II-12 and II-14, we used lab-made meso-free dipyrrin salt III-14 as a replacement in the reactions (Scheme 3.6).

Scheme 3.6 Reaction between meso-free dipyrrin III-14 and heteroleptic bis(dipyrrin) metal complex III-11.

The reaction between III-11 and III-14 followed the same procedure as the reaction between III-11 and II-14. A series of products were again formed but in much better yields for the desired complex III-16. All three complexes were characterized by mass spectrometry and NMR (Figure 3.9).
3.5.2 Linear dipyrrin metal complexes incorporating different metals

Mixed ligand coordination reactions can produce controlled-length metal complexes, but there are disadvantages. Firstly, the longest detectable chain contains five metal atoms and is produced in only trace yield and, secondly, only one type of metal is present in each complex. With these issues in mind, new approaches toward synthesizing linear metal complexes were designed and investigated.
As shown in Scheme 3.7, the reaction between heteroleptic bis(dipyrrin) metal complex III-11 and dipyrrin “dimer” III-4 produces a dipyrrin metal chain with free dipyrrins attached at both ends for further coordination reaction with other metals (step 1). Following treatment with metal acetylacetonates, the linear heteroleptic metal complexes contain the same or different metals in one molecule depending on the metal acetylacetonate used (step 2). Both sides can be blocked with dipyrromethene to form the desired linear metal complexes (step 3), or a repetition of steps 1 and 2 lead to even longer metal-dipyrrin chains. When this strategy is employed, the results are much more complete.

**Scheme 3.7** Alternate strategy for dipyrrin metal complexes.

### 3.5.2.1 Step 1: synthesis of metal-dipyrrin chains with free ends on both sides

A mixture of dipyrrin dimer III-4 and heteroleptic metal complex III-11 was dissolved in CH$_2$Cl$_2$ and stirred overnight at room temperature (Scheme 3.8). Red precipitates were formed during the reaction. The precipitates also have very poor solubility in toluene, which
causes difficulties for purification using size exclusion chromatography. The MALDI-TOF spectrum of the reaction mixture shows it contains unreacted starting material III-4 and a series of metal complexes with different lengths (Figure 3.10). Due to the difficulties of separation and purification, the mixture was carried forward to the next step.

Scheme 3.8 Synthesis of metal-dipyrrin chains with free ends on both sides.

Figure 3.10 MALDI-TOF spectrum of the step 1 reaction mixture.
3.5.2.2 Step 2: synthesis of metal-dipyrrin chains with both ends blocked by metal acetylacetonate

Scheme 3.9 Synthesis of long chain heteroleptic metal complexes.

Figure 3.11 $^1$H NMR spectra for heteroleptic metal complexes III-11 (a), III-18 (b), III-19 (c) and III-20 (d) (CDCl$_3$, 300MHz).
The reaction mixture from step 1 was divided into two equal portions, and the solvent was removed *in vacuo*. One portion was suspended in CHCl₃, and added drop-wise to a CHCl₃ solution of excess Zn(acac)₂. The reaction mixture was stirred at room temperature for 5 hours. After the excess Zn(acac)₂ was removed by recrystallization from CH₂Cl₂/ethyl ether, the residue was further purified by size exclusion chromatography to produce a series of metal complexes with different lengths (Scheme 3.9). These complexes were confirmed by ¹H NMR spectroscopy (Figure 3.11) and MALDI-TOF spectrometry. The resulting complexes can be further reacted to produce longer dipyrrin metal complexes.

Excess Co(acac)₂ was employed to react with the other portion of the reaction mixture from step 1. After stirring at room temperature overnight, the solvent was removed *in vacuo*. The burgundy coloured mixture was dissolved in toluene and loaded onto a size exclusion column. Three fractions were collected (Scheme 3.10). The MALDI-TOF spectra show the formations of bis(dipyrrin) metal complexes that contain both zinc and cobalt metals.

**Scheme 3.10** Synthesis of long-chain heteroleptic metal complexes containing different metals
3.5.2.3 Step 3: synthesis of linear dipyrrin metal complexes containing different metals

Each of the three products of step 2 (III-10, III-21 and III-22) was then reacted with simple dipyrromethene III-14. The products were collected and purified by size exclusion chromatography (Scheme 3.11). The MALDI-TOF spectra show the formation of linear dipyrrin metal complexes which contain different metals. In each of the three reactions, the main product is a metal complex of III-14. The yields of the desired linear complexes are relatively low (ca. 8%). Because NMR study is not effective due to the paramagnetism of Co^II in the molecule, and suitable single crystals for X-ray diffraction could not be obtained, isotope mass distribution modelling was used to confirm the formation of the desired linear dipyrrin metal complex. As shown in Figure 3.12, for the isotopic mass distribution of each metal complex, the experimental data and its corresponding theoretical calculation are well matched.

Scheme 3.11 Synthesis of linear dipyrrin metal complexes containing different metals.
Figure 3.12 Comparison of the experimental and calculated isotopic mass distribution for III-25 (C_{114}H_{110}Co_{2}Zn_{2}N_{16}) (a), III-24 (C_{86}H_{86}Co_{2}ZnN_{12}) (b) and III-23 (C_{58}H_{62}Co_{2}N_{8}) (c). For each complex, i) the full spectrum, ii) the enlarged experimental isotopic distribution, and iii) the calculated isotopic distribution.

Similar reactions were also carried out by starting with heteroleptic cobalt(II) dipyrrin complex III-10 and dipyrrin dimer III-4. Excess zinc(II) acetylacetonate was added into the solution of the complexes and the reaction was finished by capping both sides of the complexes.
with **III-14**. The resulting complexes were purified by size exclusion chromatography and confirmed by MALDI-TOF mass spectrometry (Scheme 3.12 and Figure 3.13).

**Scheme 3.12** Synthesis of linear dipyrrin metal complexes from **III-10**.

**Figure 3.13** Comparison of the experimental and calculated isotopic mass distribution for **III-27** (C_{114}H_{110}Co_{2}Zn_{2}N_{16}) (a) and **III-26** (C_{86}H_{86}CoZn_{2}N_{12}) (b). i) full spectrum; ii) enlarged experimental isotopic distribution; iii) calculated isotopic distribution.
3.5.3 Attempts to prepare two-dimensional dipyrromethene metal complexes

3.5.3.1 Synthesis of dipyrromethene trimer and tri-boron dipyrromethene

The formation of linear oligomeric species by combination of metal dipyrrin fragments with boron dipyrromethene naturally leads to the following question: instead of linear structures (one-dimensional expansion), is it possible to build a two-dimensional structure, with the ultimate goal of achieving a 2D net architecture? In an effort to explore the possibility of building a two-dimensional structure for potential electron/energy transfer applications, we prepared dipyrrin “trimer” III-30. The preparation of the dipyrrin trimer III-30 began with Suzuki coupling between 1,3,5-tribromobenzene and 4-formylphenylboronic acid, followed by condensation with 2-methyl pyrrole and a subsequent oxidation by DDQ (Scheme 3.13). Structures III-28 through III-30 were confirmed by NMR and mass spectrometry.

Scheme 3.13 Synthesis of dipyrrin “trimer” III-30.

Compound III-30 reacts with an excess of boron trifluoride etherate to afford the trichromophoric boron-dipyrromethene complex III-31 (Scheme 3.14), which has potential use in various applications such as biological labelling, light-harvesting antennae and fluorescent sensors. The Blanchard-Desce group has synthesized a similar boron complex and investigated its absorption properties previously; however, no crystal structure was given.
Scheme 3.14 Synthesis of tri-chromophoric boron-dipyrrin complex III-31

Compound III-31 was confirmed by $^1$H NMR, $^{13}$C NMR and mass spectrometry. Red crystals suitable for X-ray diffraction were grown from a solution of the complex dissolved in CH$_2$Cl$_2$ diffused with cyclohexane. The complex co-crystallized with two molecules of cyclohexane in the asymmetric unit. The crystal structure of III-31 shows it is a non-symmetric molecule with N-B bond distances of 1.53-1.55 Å. The meso-phenyl group is rotated ~51° from the dipyrrin moiety (Figure 3.14).

Figure 3.14 Crystal structure of III-31 with partial atom numbering schemes. (ORTEP, 50% probability ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity.
3.5.3.1 Formation of two-dimensional dipyrromethene metal complexes

Unlike the reaction between the dipyrrin dimer III-4 and BF₂-capped ligand II-14 (Scheme 3.2), which produced a series of linear metal complexes, the reaction between dipyrrin trimer III-30 and ligand II-14 only generated an inseparable mixture. In order to obtain the desired two-dimensional dipyrrin metal complex, Zn(acac)₂ was used to cap the tris(dipyrrin) III-30 to obtain the heteroleptic zinc(II) dipyrrin complex, which was further reacted with BF₂-capped ligand II-14 to obtain the tri-metal, tri-boron product III-32 in an overall 11% yield (Scheme 3.15). The final product was confirmed by ¹H NMR (Figure 3.15) and mass spectrometry.

Scheme 3.15 Synthesis of two-dimensional dipyrromethene metal complex III-32
3.6 Conclusion and outlook

A series of linear oligomeric species containing both metal dipyrrin fragments and boron dipyrrromethenes were synthesized from mixed-ligand coordination reactions. Complexes of different lengths were separated, characterized and their optical properties were investigated. In addition, a new synthetic methodology employing heteroleptic bis(dipyrrin) metal complexes as metal sources was explored, and these heteroleptic complexes $[\text{M(dpm)(acac)}]$ can be used to produce linear dipyrrin metal complexes (incorporating the same or different metals in one molecule) in a step-wise fashion. The resulting complexes were confirmed by NMR and mass spectrometry. Furthermore, a two-dimensional dipyrrromethene metal complex $\text{III-32}$ was synthesized and the strategy of employing heteroleptic dipyrrin metal complexes was shown to have potential use in the preparation of coordination networks.
In a recently published paper, Thompson described a one-step method for removing BF$_2$ from BODIPY (Scheme 3.16) to generate dipyrrins via microwave irradiation. Combination of this method with the use of heteroleptic bis(dipyrrin) metal complexes may be a new approach for developing a dipyrrin metal molecular wire, which can incorporate different metals and dipyrromethenes (Figure 3.16). Unfortunately, treatment of dipyrrin zinc complex II-20 with the described deprotection conditions results only in the formation of free dipyrrin dimer III-4 (Scheme 3.17). The potential utility of this synthetic methodology still needs to be explored further by investigation and optimization of the reaction conditions.

As mentioned previously, architecture construction is not the only application of linear dipyrrin metal complexes. The versatility of the chemistry and the unique physical and optical properties of these systems ensures a healthy future for research in this area.
CHAPTER 4

Self-assembled cyclic oligomers of bis(dipyrrinato) metal complexes
4.1 Self-assembled cyclic metal complexes

Study of metal-coordinated macrocycles has become an active research field in recent years. Metallosupramolecular complexes can be formed through a self-assembly process driven by ligand-metal coordination, and are widely used in host-guest chemistry and gas storage.

The thermodynamic factors of metallocyclic complex formation have been studied, and two conclusions may be drawn: i) compared with linear complexes, cyclic compounds increase the number of coordinate bonds formed and are thus more enthalpically favourable; ii) as Le Chatelier’s principle states that any perturbation in a system at equilibrium results in a shift of equilibrium in the direction which counteracts the change. In a dilute solution, small cyclic structures are preferred over larger ones from the entropic point of view.

The most common ligands used in metallomacrocyclic structures are oligopyridyl derivatives. Stang, Lehn and many other researchers have constructed a wide range of macrocycles by employing oligopyridyl ligands as building blocks. A vast range of self-cyclized triangles, squares, rectangles, hexagons and other metallocyclic polygons are known and their practical application is being studied.

Compared to the extensive study of metallomacrocyclic structures based on oligopyridyl ligands, only limited research has occurred with dipyrrromethene derivatives. Dipyrrromethenes can provide neutral oligomers when coordinated to various metals and thus can be used to construct uncharged supramolecular cyclic architectures. Various oligomeric structures have been reported. Previous investigations in our group involved using β,β'-linked bis(dipyrrin)s as scaffolds in metal chelation. Thompson et al. investigated the oligomer ratios between the monomer, dimer and trimer when altering the length of spacer. X-ray diffraction
confirmed the triangular shape of the trimer. By employing a longer rigid spacer to link two dipyrromethenes, Ma et al.\textsuperscript{130} managed to produce a trinuclear complex containing a larger core size. They also employed angled spacers to bridge two dipyrrinato units of $\beta,\beta'$-bis(dipyrren). By doing so, dimeric complexes were formed with the structures confirmed by X-ray diffraction analysis. Nabeshima\textsuperscript{166} introduced a catecholyl group into a boron-dipyrrin complex to form a series of self-assembled cyclic oligomers through boron complexation between the catecholyl moiety and the dipyrrinato moiety. Cohen’s group reported the synthesis of discrete cyclic dipyrrin metal complexes by using pyridine-substituted dipyrrin ligands. Cu(hfacac)$_2$ (hfacac = hexafluoroacetylacetonate) was utilized as the metal source to form a heteroleptic dipyrrin metal complex. The pyridyl nitrogen atom then acted as the second donor site and coordinated to a neighbouring copper(II) center to generate the cyclic species.\textsuperscript{112} Maeda and his colleague also reported the formation of dimeric structures of bis(dipyrrinato) metal complexes.\textsuperscript{131} Instead of $\beta,\beta'$-linked bis(dipyrren), two dipyrrinato units were linked at the $sp^2$-meso position using an elaborate spacer. The complexation reaction yielded meso stereoisomers as the major product. At the same time, chiral coordination macrocycles were also formed as minor products. The neutral macrocycles, based on the “dimeric” dipyrrin derivatives in Maeda’s work, have a diagonal of about 1.6 nm. Herein, we detail the design and synthesis of a series of dimeric dipyrrin derivatives in which two dipyrrin units were bridged rigidly by various linkers. These ligands then further self-assembled to give metallomacrocyclic structures.
4.2 Attempts using dimeric dipyrrin derivatives bridged by phenyl linkers

4.2.1 α-Free dimeric dipyrrin derivatives bridged by phenyl linkers and their metal complexes

Since the isophthalaldehyde and pyrrole are readily available, we used them as starting materials and followed a general procedure to synthesize the dipyrrin dimer IV-2, in which the angle of the two dipyrrinato moieties is ca. 120° (Scheme 4.1). Further, we sought to explore the possibility of fabricating metallomacrocycles by employing this ligand.

Scheme 4.1 Synthesis of ligand IV-2.

Ligand IV-2 is a dark brown powder. After dissolving it in CH$_2$Cl$_2$, a solution of Zn(OAc)$_2$ in CH$_3$OH was slowly added into the reaction mixture by syringe pump. Upon the addition of Zn(OAc)$_2$, a dark red precipitate was formed. The UV spectrum of the reaction mixture shows the disappearance of the original absorption peak of the ligand (430 nm in CH$_2$Cl$_2$) and the appearance of two new peaks at 461 nm and 480 nm which indicate the formation of the zinc metal complex. Similar shifts in the UV spectra are also observed in the reactions with other metal salts (Co$^{II}$, Cu$^{II}$ and Ni$^{II}$).

Thinking that the poor solubility of ligand IV-2 was the cause of precipitation, we introduced a hexyloxy group and a $t$-butyl group, respectively, into the ligand to improve solubility (ligand IV-3 and IV-4, Figure 4.1 a and b). Unfortunately, during the coordination reactions with different metals, the precipitation still occurred. Even though the absorption
spectra exhibited the formation of metal complexes, the mass spectra showed no desired discrete cyclic complexes. This can be explained by the formation of zig-zag shaped metal complexes instead of the desired cyclic products (Figure 4.1, c).

![Image](image_url)

**Figure 4.1** Structures of ligand IV-3 (a), IV-4 (b) and illustrations of the zig-zag and cyclic structures (c).

### 4.2.2 α-Methyl dimeric dipyrrin derivatives and their metal complexes

During the exploration of cyclic metal complex synthesis, the use of 2-methylpyrrole produced some positive results. The synthesis of ligand IV-5 followed a procedure similar to the synthesis of IV-2. The reaction between IV-5 and Co$^{II}$ generated some products with $R_f$ values of ca. 1 ($\text{CH}_2\text{Cl}_2$), which indicates the formation of the low polarity cyclic complexes. Strong peaks were observed in the MALDI-TOF spectrum at $m/z$ 2376.5, 2852.4 and 3328.2, which corresponded to the pentamer, hexamer and heptamer of the ligand-cobalt complexes. After filtration through a silica column, the crude products were further purified by gel permeation chromatography (GPC). The separation was not ideal. The pentamer and the heptamer were collected in very low yield (1-2%). No pure hexamer were obtained due to the
low yield. The reaction between ligand IV-5 and Ni$^{II}$ exhibits a similar result again with very low yield of pentamer and heptamer.

![Scheme 4.2 Synthesis of cyclic metal complexes from ligand IV-5.](image)

**Scheme 4.2** Synthesis of cyclic metal complexes from ligand IV-5.

4.2.3 Dimeric dipyrrin derivatives with extended “arms” and their metal complexes

![Scheme 4.3 Synthesis of ligands IV-6 and IV-7, and their metal complexation.](image)

**Scheme 4.3** Synthesis of ligands IV-6 and IV-7, and their metal complexation.

The ligands with longer “arms” were also synthesized to further explore their effect on the geometry of the metal complexes. Synthesis of the ligands involved Suzuki coupling of 1,3-dibromobenzene and (4-formylphenyl)boronic acid, condensation with pyrrole (or 2-
methylpyrrole), and oxidation with DDQ (Scheme 4.3). Similar to ligand IV-2, the reaction between α-free dimeric dipyrin derivative IV-6 and Co(OAc)$_2$ formed a precipitate and no low polarity cyclic complexes were detected. For the reaction between α-methyl dimeric dipyrin derivative IV-7 and Co(OAc)$_2$, the formations of the self-assembled pentamer and hexamer were suggested by the MALDI-TOF mass spectrum. After GPC column purification, the pentamer was isolated and collected. No pure hexamer was separated due to the low yield. Unfortunately, no suitable single crystals of the cyclic metal complexes of ligand IV-5 or IV-7 could be obtained.

4.3 Carbazole-bridged 3,6-dimeric dipyrin derivatives and their metal complexes

![Figure 4.2 Structure and numbering system of carbazole.](image)

Because the metal complexes of phenyl-linked dimeric dipyrin ligands have several disadvantages: low yields, difficulty in purification, and the lack of suitable crystals for X-ray diffraction, we proceeded to design and synthesize a dimeric dipyrin system with a different linker to replace the phenyl group. Carbazole and its derivatives are widely used in luminescence chemistry as photosensitizing materials. It is commercially available, and can be easily functionalized at its 3-, 6- or 9-positions (Figure 4.2). By modifying the 3- and 6-positions of carbazole, the two ligand units can be appropriately directed (the angle between
the C3-H3 and C6-H6 bonds is \( \text{ca. } 86^\circ \)). We synthesized a series of dimeric dipyrrin ligands based on the carbazole unit, and then further formed metallomacrocycles with different core sizes.

**4.3.1 Synthetic approach to carbazole bridged 3,6-dimeric dipyrrin ligands and their metal complexes**

**Scheme 4.4** Synthesis of carbazole-bridged dimeric dipyrrin ligands IV-14 to IV-16.

Ligand synthesis began with commercially available 9\( H \)-carbazole. Following the published method\(^4\), the \( N \)-alkylated carbazoles were converted to the corresponding diiodo compounds using \( N \)-iodosuccinimide. Palladium-catalyzed Suzuki coupling reactions then afforded dialdehydes IV-8 through IV-10. The condensation between the dialdehyde (IV-8 through IV-10) with pyrrole (or 2-methylpyrrole), followed by oxidation with DDQ generated the corresponding dimeric dipyrrins (IV-14 through IV-16) as the desired angular building blocks (Scheme 4.4).
The structures of ligands IV-14 through IV-16 were confirmed by $^1$H NMR and mass spectrometry. The reaction with Co(OAc)$_2$ was carried out following the general procedure of metal complexation (Scheme 4.5). The MALDI-TOF spectra of the reaction mixture show the formation of trimer, tetramer and pentamer. Because the directing angle of the carbazole bridge (ca. 86°) is close to a right angle, the tetrameric complex was considered to produce the least geometric strain and thus to be the main product. To our surprise, the more strained trimeric and pentameric complexes were generated in better yields than the tetramer, which could not be isolated due to its low yield. Even though the pure trimer and pentamer were isolated and collected by gel permeation chromatography, crystals for the trimer, tetramer and pentamer suitable for X-ray diffraction study were not obtained.

Scheme 4.5 Metal complexation reactions of ligands IV-14 through IV-16.
4.3.2 Improved carbazole-bridged 3,6-dimeric dipyrrin ligands and their metal complexes

4.3.2.1 Synthesis of carbazole-bridged 3,6-dimeric dipyrrin ligands and their metal complexes

In a variation of carbazole-based ligands IV-14, IV-15 and IV-16, we synthesized another series of dimeric dipyrrin ligands, which are smaller but still maintained the two rigidly angled dipyrrin moieties (ca. 86°) at the 3- and 6-positions.

Dicarboxaldehydes IV-17, IV-18 and IV-19 were prepared through a double lithium halogen exchange, followed by a double formylation reaction. The dicarboxaldehyde and 2-methylpyrrole were then treated with trifluoroacetic acid, followed by oxidation with DDQ to afford the corresponding dimeric dipyrrin ligands IV-23, IV-24 and IV-25 (Scheme 4.6). The three ligands were characterized by mass spectrometry and NMR spectroscopy.

![Scheme 4.6 Synthesis of ligands IV-23 through IV-25.](image)

Scheme 4.6 Synthesis of ligands IV-23 through IV-25.
Scheme 4.7 Metal complexation reactions and the isolated yields (%) of ligands IV-23 through IV-25.

Each ligand was reacted with Co(OAc)$_2$. After stirring overnight followed by purification using gel permeation chromatography, cyclic metal complexes with different core sizes were separated. The yields of these metallomacrocycles are listed in Scheme 4.7. For ligands IV-24 and IV-25, the MALDI-TOF spectra also show the formation of hexamer, heptamer and octamer, but no heptamer or octamer were isolated due to the very low yield (Figure 4.3).

Figure 4.3 MALDI-TOF spectra of cobalt(II) complexes of IV-24 (a) and IV-25 (b).
4.3.2.2 UV-Vis spectroscopic analysis of metal complexes IV-26 through IV-28

The optical spectra of the cyclic metal complexes of ligand IV-25 are shown in Figure 4.4. The absorbance maxima (493 nm for trimer and 495 nm for tetramer, pentamer and hexamer) are the result of metal complexation. As expected, the extinction coefficients of the cyclic metal complexes increase in accordance with the increase in core size.

![Optical spectra of cyclic complexes of ligand IV-25. All spectra were taken in CH$_2$Cl$_2$ at room temperature.](image)

**Figure 4.4** Optical spectra of cyclic complexes of ligand IV-25. All spectra were taken in CH$_2$Cl$_2$ at room temperature.

4.3.2.3 Crystal structure analysis of metal complexes IV-26 and IV-28

In addition to the spectroscopic studies, two complexes IV-26 and IV-28 were also crystallized and the structures were determined by X-ray diffraction analysis.

The dark red crystals of IV-26 were obtained by slow evaporation of a CHCl$_3$/n-hexane solution. The X-ray crystal structure of the trinuclear complex shows $C_2$ symmetry (Figure 4.5,
a). Each cobalt center has a distorted tetrahedral geometry with inter-ligand dihedral angles of 71.7° for Co1 and 76.8° for Co2 and Co3. The metal-N bond lengths (1.96-1.98 Å) are similar to those in the linear CoII complex II-19. Complex IV-26 is nearly planar (Figure 4.5, b), and the distance between the metal centers in one molecule are 11.75 Å and 12.37 Å (Figure 4.5, c). Around each metal center, the bending angles of two ligand units are much larger (10.7° for Co1 and 18.9° for Co2 and Co3) than the bending angle of the linear CoII complex II-19 (3.4°). Compared to the ring-strain free structure of the linear complex, the trimeric complex has to adopt larger bending angles in order to permit the triangular arrangement. The space-filling model of the crystal (Figure 4.5, d) clearly shows a triangle shaped cavity with an approximate 9.6 Å × 11.4 Å dimension.
Figure 4.5 Crystal structure of IV-26: a) top view (ORTEP, 50% probability ellipsoids. The $C_2$ symmetry axis is denoted by the gray line); b) side view (ORTEP, 50% probability ellipsoids. The red line indicates the plane through three cobalt atoms); c) stick model and d) space-filling model. Hydrogen atoms and solvent molecules have been omitted for clarity.

The space-filling diagram shows a tunnel-like structure resulting from the overlapped IV-26 molecules (Figure 4.6). The inter-layer distance between two Co$^{II}$ ions is 12.45 Å.
Because of the complete overlap, the tunnel maintains the triangle shape and the dimensions are similar to the cavity in a single molecule.

**Figure 4.6** Molecular space-filling packing of IV-26 (a); top view (b) and side view (c) of the tunnel structures.

In the same layer, the intermolecular CH-π interactions are considered to be the driving force for crystal stacking. In the same layer, each macrocycle ring interacts with four neighbouring rings (**Figure 4.7**. Ring-B’ and ring C’ were omitted due to the C₂ symmetry of IV-26). The methyl groups on the dipyrrin moieties (C1 and C46 of ring-A, C1 of ring-B, and C46 of ring-C) are the donating sites and the carbazole moieties are the accepting planes. The detailed donor/acceptor pairs and the distance between donors and acceptors are listed in **Table 4.1**.
Figure 4.7 CH-π interactions in the neighbouring macrocycles of the X-ray single crystal structure of IV-26.

<table>
<thead>
<tr>
<th>Donors</th>
<th>Acceptors</th>
<th>Distances between donor and their corresponding accepting plane (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)H₃ (ring-A)</td>
<td>carbazole plane with N3 (ring-B)</td>
<td>3.440 (C1) 2.865 (H1A), 2.912(H1B), 4.175(H1C)</td>
</tr>
<tr>
<td>C(1)H₃ (ring-B)</td>
<td>carbazole plane with N3 (ring-A)</td>
<td>3.440 (C1) 2.865 (H1A), 2.912(H1B), 4.175(H1C)</td>
</tr>
<tr>
<td>C(46)H₃ (ring-A)</td>
<td>carbazole plane with N8 (ring-C)</td>
<td>3.639 (C46) 3.269 (H46A), 2.944(H46B), 4.387(H46C)</td>
</tr>
<tr>
<td>C(46)H₃ (ring-C)</td>
<td>carbazole plane with N8 (ring-A)</td>
<td>3.639 (C46) 3.269 (H46A), 2.944(H46B), 4.387(H46C)</td>
</tr>
</tbody>
</table>

Table 4.1 The distances between CH-π interaction donor and accepting planes of the X-ray single crystal structure of IV-26.
The green crystals of **IV-28** were obtained via slow diffusion of *n*-hexane into a CH$_2$Cl$_2$ solution. This is the first report of a dipyrrin pentameric complex crystal structure. The structure of the complex shows it is a non-symmetric molecule with a large core size. The side view (**Figure 4.8**, c) of the structure shows the complex is folded with a folding angle of 91.8°.

All cobalt centers have tetrahedral coordination with various dihedral angles of the inter-ligand planes and different metal-N bond lengths (**Table 4.2**). In contrast to the linear Co$^{II}$ complex II-19, around each metal center, the two dipyrrin moieties adopt a bent or twisted orientation in
order to permit the formation of the pentameric structure. For example, as shown in Figure 4.9, the relatively small dihedral angles of the inter-ligand plane (67.1°) and the large bending angle (18.7°) around Co1 in IV-28 cause steric repulsion between the two methyl groups. To minimize the repulsion, the pyrrole rings of the dipyrrromethene ligands are forced out of the mean plane. The dihedral angles between two pyrrole units in one dipyrrromethene are 13.6° (between N1-pyrrole ring and N2-Pyrrole ring) and 18.4° (between N24-pyrrole ring and N25-Pyrrole ring), respectively, which is much larger than the corresponding angles in the linear CoII complex II-19 (3.3° and 6.0°).

Figure 4.9 Stick and space-filling representation of the coordination environment of Co1 in IV-28 shown from different angles. Hydrogen atoms have been omitted in the stick model for clarity.
<table>
<thead>
<tr>
<th>Metal Center</th>
<th>Inter-ligand dihedral angle (°)</th>
<th>Bending angle θ (°)</th>
<th>Dihedral angle between two pyrrole units in one DPM (°)</th>
<th>Metal-N bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV-28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co1</td>
<td>67.1</td>
<td>18.7</td>
<td>18.4 and 13.6</td>
<td>1.91 - 2.00</td>
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<tr>
<td>Co2</td>
<td>81.2</td>
<td>7.5</td>
<td>8.0 and 4.7</td>
<td>1.90 - 1.98</td>
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<td>Co3</td>
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<td>11.6</td>
<td>1.3 and 0.6</td>
<td>1.88 - 2.00</td>
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<tr>
<td>Co4</td>
<td>89.6</td>
<td>17.4</td>
<td>11.5 and 4.8</td>
<td>1.92 - 2.00</td>
</tr>
<tr>
<td>Co5</td>
<td>81.9</td>
<td>3.4</td>
<td>11.3 and 9.8</td>
<td>1.91 - 1.97</td>
</tr>
<tr>
<td>II-19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>84.0</td>
<td>3.4</td>
<td>6.0 and 3.3</td>
<td>1.96 - 1.98</td>
</tr>
</tbody>
</table>

**Table 4.2** Comparison of selected crystal data between metal complexes **IV-28** and **II-19**.

Bending angle (θ) is as shown in **Figure 4.9**.

**Figure 4.10** CH-π interactions in the neighbouring macrocycles of the X-ray single crystal structure of **IV-28**.

The intermolecular donor/acceptor CH-π interactions are observed between four neighbouring rings (**Figure 4.10**). The aryl-Hs of ring-A (C156-H, C172-H, C173-H and C24-H) act as donating sites to interact with the dipyrrin planes or carbazole plane in ring-B, ring-C and ring-D. The C156-H of ring-B, C93-H of ring-C and C24-H of ring-D then interact with
the acceptor π planes in the ring-A. The distance between donors and acceptors are listed in Table 4.3. These four rings then further connected with other macrocycles to form the crystal stacking structure.

<table>
<thead>
<tr>
<th>Donors</th>
<th>Acceptors</th>
<th>Distances between donor and accepting planes (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(156)H (ring-A)</td>
<td>dipyrrin plane with N21 and N22 (ring-B)</td>
<td>3.380 (C156-plane) 2.637 (H156-plane)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(156)H (ring-B)</td>
<td>dipyrrin plane with N21 and N22 (ring-A)</td>
<td>3.380 (C156-plane) 2.637 (H156-plane)</td>
</tr>
<tr>
<td>C(172)H (ring-A)</td>
<td>carbazole plane with N13 (ring-C)</td>
<td>3.569 (C172-plane) 2.860 (H172-plane)</td>
</tr>
<tr>
<td>C(173)H (ring-A)</td>
<td>carbazole plane with N13 (ring-C)</td>
<td>3.584 (C173-plane) 2.886 (H173-plane)</td>
</tr>
<tr>
<td>C(93)H (ring-C)</td>
<td>carbazole plane with N23 (ring-A)</td>
<td>3.480 (C93-plane) 3.156 (H93-plane)</td>
</tr>
<tr>
<td>C(24)H (ring-A)</td>
<td>dipyrrin plane with N4 and N5 (ring-D)</td>
<td>3.463 (C24-plane) 2.787 (H24-plane)</td>
</tr>
<tr>
<td>C(24)H (ring-D)</td>
<td>dipyrrin plane with N4 and N5 (ring-D)</td>
<td>3.463 (C24-plane) 2.787 (H24-plane)</td>
</tr>
</tbody>
</table>

Table 4.3 The distances between CH-π interaction donor and accepting planes of four neighbouring macrocycles of the X-ray single crystal structure of IV-28.

As shown in Figure 4.11, the molecules of IV-28 at different layers are completely overlapped which results in large tunnels with approximate dimensions of 16.9 Å × 17.5 Å running along the crystallographic y-axis. To the best of our knowledge, this is the largest ring structure based on dipyrrin derivatives ever reported. The distance between two Co^{II} ions between two layers is 10.17 Å. There is a large amount of disordered solvent occupying the tunnel, but the extent of the disorder made it impossible to properly model any of the solvent molecules.
4.4 Carbazole-bridged 1,8-dimeric dipyrrin ligands and their metal complexes

As mentioned before, the angle between C3-H3 bond and C6-H6 bond in a carbazole is \textit{ca.} 86°. Attaching dipyrrin ligands to the C3 and C6 positions followed by metal complexation,
results in trimeric to pentameric main products. Here, we synthesized another series of carbazole-bridged dimeric dipyrrin ligands by modifying the 1- and 8-positions of carbazole (the angle between C1-H1 bond and C8-H8 bond is ca. 35°, Figure 4.12), and their metal complexation reactions were studied.

4.4.1 Synthesis of carbazole-bridged 1,8-dimeric dipyrrin ligand IV-33

Scheme 4.8 Synthetic route for ligand IV-33.

1,8-diformyl-3,6-dimethylcarbazole (IV-31) was synthesized following the published literature. The starting material is commercially available 3,6-dibromo-9H-carbazole. 3,6-dimethyl-9H-carbazole (IV-29) was synthesized by protecting the N-H proton with trimethylsilane during the dilithiation, followed by quenching the intermediate product with methyl iodide. IV-29 was obtained as a white powder in over 90% yield. 1,8-dibrominated carbazole (IV-30) was obtained as an off-white solid by bromination with N-bromosuccinimide (NBS) in the dark. The N-H proton was protected again with trimethylsilane during the dilithiation, followed by formylation with excess DMF leading to the product, 1,8-diformyl-
3,6-dimethyl-9\textit{H}-carbazole (IV-31), as a yellow solid. Following the general procedure for the synthesis of dipyrromethane, IV-32 was obtained by the condensation of dialdehyde IV-31 with 2-methylpyrrole. The oxidation with DDQ generates the final ligand IV-33 as a red-brown powder (Scheme 4.8), which was fully characterized by mass spectrometry and NMR spectroscopy.

4.4.2 Formation of stereoisomers through metal complexation of ligand IV-33

Considering the angle between two dipyrrin moieties in one molecule (\textit{ca.} 35°), the products of metal complexation should be a dimeric complex, with the possibility of a small amount of trimeric or tetrameric complex. Dicationic metals Co\textsuperscript{II} and Zn\textsuperscript{II} were introduced into a solution of ligand IV-33 to form metal complexes (Scheme 4.9). As predicted, the MALDI-TOF spectra show the resulting crude products contain dimeric and tetrameric complexes. After purification using gel permeation chromatography, only dimeric complexes IV-34 and IV-35 were isolated and collected with relatively low yield (14 % for IV-34 and 13 % for IV-35).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=0.8\textwidth]{scheme4_9.png}};
\end{tikzpicture}
\end{center}

\textbf{Scheme 4.9} Synthesis of metal complexes IV-34 and IV-35.
As seen in the literature, as well as in the cobalt (II) and zinc(II) complexes IV-19 and IV-20 in Chapter 2, the two dipyrrin planes around the metal center are not perfectly perpendicular, which results in the chirality of the metal centers of these [2+2] complexes. Maeda and his group observed the formation of different stereoisomers of a zinc(II) dipyrrin macrocycle and used two dipyrrin moieties and the adjacent meso-aryl to define the configurations \( \Lambda \) and \( \Delta \) (as shown in Figure 4.13).131

![Figure 4.13 Diagram of the \( \Lambda \) and \( \Delta \) structures of the tetrahedral dipyrrin metal complex. The dashed-arrow indicates the point of reference.](image)

**Figure 4.13** Diagram of the \( \Lambda \) and \( \Delta \) structures of the tetrahedral dipyrrin metal complex. The dashed-arrow indicates the point of reference.

![Figure 4.14 Diagram of three stereoisomers, a) achiral (meso, \( \Lambda\Delta \)), b) chiral (\( \Delta\Delta \)), c) chiral (\( \Lambda\Lambda \)). These optimized structures were obtained through HyperChem calculation.](image)

**Figure 4.14** Diagram of three stereoisomers, a) achiral (meso, \( \Lambda\Delta \)), b) chiral (\( \Delta\Delta \)), c) chiral (\( \Lambda\Lambda \)). These optimized structures were obtained through HyperChem calculation.
Hence, there should be three stereoisomers of cyclic metal complex of ligand IV-33: an achiral one (meso, Figure 4.14, a) and two chiral ones (ΔΔ and ΛΛ Figure 4.14, b and c). The formation of these various stereoisomers was further supported by their NMR spectra.

### 4.4.3 NMR spectroscopic analysis of complexes IV-35

![Partial ¹H NMR spectrum of complex IV-35 in CDCl₃](image)

**Figure 4.15** Partial ¹H NMR spectrum of complex IV-35 in CDCl₃. The major (blue solid line) and minor (red solid line) isomers are suggested by the integration. The purple and orange dotted lines indicate the correlation between β-H signals in the major and minor isomers, respectively.

The ¹H NMR spectrum of complex IV-35 clearly shows two sets of signals with an integration ratio of β-H signals of 1.85:1, which indicates that two types of diastereomers were formed during the coordination reaction. The ¹H-¹H COSY spectrum reveals the correlations between adjacent β-protons (as shown in the Figure 4.15). For the linear dipyrrin zinc complex, the chemical shifts (δ) of β1 and β1’ (also β2 and β2’) are the same due to the free rotation of
the dipyrrin plane. The formation of the cyclic complex results in a different local chemical environment for \( \beta_1 \) (external of the complex ring) and for \( \beta_1' \) (internal of the complex ring), which further causes the split in the chemical shifts. For the major isomer, \( \Delta \delta \) is 0.3 for \( \beta_1\)-H and \( \beta_1'\)-H, and 0.42 for \( \beta_2\)-H and \( \beta_2'\)-H. For the minor isomer, the \( \Delta \delta \) is 0.40 and 0.66 for the two sets of \( \beta\)-H signals.

4.4.4 UV-Vis spectroscopic analysis of complexes IV-34 and IV-35

![Figure 4.16 Optical spectra of ligand IV-33 and its metal complexes. All spectra were recorded in CH\(_2\)Cl\(_2\) at room temperature.](image)

The UV-Vis absorption spectrum of ligand IV-33 exhibits an absorbance maximum at 437 nm in CH\(_2\)Cl\(_2\). Upon metallation, the absorbance maximum shows a significant bathochromic shift (48 nm for IV-34 and 27 nm for IV-35). Also new bands appeared at 522 nm for IV-34 and 529 nm for IV-35 (Figure 4.16).
4.4.5 Crystal structures of complexes IV-34 and IV-35

Complexes IV-34 and IV-35 were also characterized by X-ray diffraction analysis. Both were obtained as red needles. The crystals of IV-34 were grown from a CH$_2$Cl$_2$ solution of the complex with slow diffusion of CH$_3$OH, and the crystals of IV-35 were obtained via slow evaporation of a CHCl$_3$/n-hexane solution.

![Packing diagrams of the X-ray structures of IV-34 (a) and IV-35 (b). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity.](image)

The structures of both complexes are achiral (meso) stereoisomers and have inversion centers. They also possess nearly identical packing patterns as shown in Figure 4.17 with inter-layer distances of 12.4 Å for IV-34 and 12.3 Å for IV-35.

Both macrocycles form distorted rectangular cavities. The distance between two metals and two inner hydrogens (H3n-H3n’) are 6.95 Å (Co-Co) and 7.0 Å (H3n-H3n’) for IV-34 and 7.06 Å (Zn-Zn) and 6.88 Å (H3n-H3n’) for IV-35, respectively. Compared to the linear cobalt
complex (II-19) and zinc complex (II-20), the inter-ligand dihedral angles between two dipyrrin moieties are much smaller (69.4° for IV-34 compared to 84.0° for II-19, and 71.4° for IV-35 compared to 84.7° for II-20), but the bending angles are much larger than their linear counterparts (34.0° for IV-34 and 25.1° for IV-35 compared to 3.4° for II-19 and II-20). These may be caused by the steric repulsions resulting from the generation of these relatively small cyclic structures. The dihedral angles between the dipyrrin moieties and carbazole moiety (a-c and b'-c) are 56.2° and 61.3° for IV-34 and 56.5° and 58.7° for IV-35. The side view of the crystals show the two dipyrrin moieties (a-a’ and b-b’) are parallel with average distances of 6.55 Å and 6.65 Å for IV-34 and 6.24 Å and 6.72 Å for IV-34 (Figure 4.18, Figure 4.19 and Table 4.4).

**Figure 4.18** Crystal structure of IV-34: a) top view (ORTEP, 50% probability ellipsoids). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity; b) top view (stick representation); c) side view (stick representation).
Figure 4.19 Crystal structure of IV-35: a) top view (ORTEP, 50% probability ellipsoids). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity; b) top view (stick representation); c) side view (stick representation).

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Inter-ligands dihedral angle (°)</th>
<th>Bending angle θ (°)</th>
<th>Metal-N bond length (Å)</th>
<th>Metal-metal distance (Å)</th>
<th>H3n-H3n’ distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV-34</td>
<td>69.4</td>
<td>34.0</td>
<td>1.96-1.99</td>
<td>7.0</td>
<td>6.95</td>
</tr>
<tr>
<td>II-19</td>
<td>84.0</td>
<td>3.4</td>
<td>1.96-1.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IV-35</td>
<td>71.4</td>
<td>25.1</td>
<td>1.98-2.07</td>
<td>7.06</td>
<td>6.88</td>
</tr>
<tr>
<td>II-20</td>
<td>84.7</td>
<td>3.4</td>
<td>1.97-1.98</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.4 Comparison of selected crystal data between cyclic metal complexes (IV-34 and IV-35) and linear metal complexes (II-19 and II-20). Bending angle (θ) is as shown in Figure 4.18 and Figure 4.19.
4.5 Self-assembled cyclic metal complexes with mixed ligands.

Due to the fixed angle limitation of carbazole-bridged 1,8-dimeric dipyrin ligand IV-33, the self-assembled coordination reaction only gave the dimeric structure as the main cyclic product with trace amounts of the tetramer. In order to expand the size of the cavity, instead of the simple metal salt, the heteroleptic dipyrromethene zinc complex III-11 was employed as metal source for the complexation.

4.5.1 Formation of the metal complexes

![Scheme 4.10 Synthesis of cyclic metal complex IV-36.](image)

Ligand IV-33 and heteroleptic zinc(II) dipyrin complex III-11 were dissolved in the solvent (CH$_2$Cl$_2$:CH$_3$OH=1:1) and stirred at room temperature overnight. The crude products were passed through a basic alumina column and further purified by gel permeation chromatography. The MALDI-TOF spectrum shows the formation of dimeric zinc(II) complex
IV-35, along with the cyclic metal complex IV-36, which contains two different ligands (Scheme. 4.10).

Due to the tetrahedral geometry of the zinc(II) iron, the metal complexes of mixed ligands are expected to have four chiral centers; therefore, there should be a total of seven stereoisomers (five diastereomers): three different achiral (meso) stereoisomers (Figure 4.20, a, b and c) and two pairs of chiral stereoisomers (Figure 4.20, d and e, f and g).

4.5.2 NMR and UV-Vis spectroscopic analysis of IV-36

The $^1$H NMR spectrum supports the formation of the macrocycles with mixed ligands. Three sets of signals with an integration ratio of 4.1:1.3:1 were observed (the ratio was obtained from the integration of the dipyrrin $\beta$-Hs). $^1$H-$^1$H COSY was used to show the
correlations between the $\beta$-Hs of the dipyrrins (Figure 4.21). The formation of the ring structure causes the change in chemical shifts and peak splitting between the $\beta$-Hs located inside and outside of the ring.

Figure 4.21 Partial $^1$H NMR spectrum of IV-36 in CDCl₃. The red dotted lines indicate the correlation between the $\beta$-H signals in the major isomer. The blue dotted lines indicate the correlation between the $\beta$-H signals in the minor isomers.

Figure 4.22 Optical spectra of ligand IV-35 and IV-36. Both spectra were recorded in CH₂Cl₂ at room temperature.
The optical spectrum of complex IV-36 is shown in Figure 4.22. It exhibits two intense absorption bands. Compared to the optical spectrum of complex IV-35, one of the absorption bands shows a small bathochromic shift (468 nm for IV-36 compared to 464 nm for IV-35), while the other band shows a hypsochromic shift (512 nm for IV-36 compared to 529 nm for IV-35) with an increase in extinction coefficient in accordance with the increase in metal complexation.

4.5.3 Crystal structure of complex IV-36

The red plate shape crystals were grown from the mixture of the stereoisomers using liquid-liquid diffusion (CHCl₃/n-hexane) in a NMR tube. X-ray diffraction analysis confirmed the proposed mixed ligand product and revealed the structure has an inversion center (Figure 4.23).

Figure 4.23 Crystal structures of IV-36 with partial atom numbering schemes (ORTEP, thermal ellipsoids are scaled to the 50% probability level). Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted for clarity.
The crystal structure shows that two carbazole based ligands (IV-33) are connected by two linear ligands (III-4) through metal complexation. The distance between two N-Hs (H3n and H3n’) is 19.51 Å. The distances between metals are 7.61 Å between Zn1 and Zn2, and 12.45 Å between Zn1 and Zn2’. Similar to IV-35, the dipyrromethene units linked to the dicationic zinc center exhibit distorted tetrahedral structures due to the steric hindrance present in the cyclic structure, with inter-ligand dihedral angles of 73.72° and 73.44° for Zn1 and Zn2, respectively. The relatively shorter zinc-N bond lengths (varying from 1.96 Å to 2.01 Å) and the smaller bending angles (Figure 4.24, a: $\theta_1 = 12.0°$ and $\theta_2 = 11.6°$) indicate the structure of IV-36 has less steric hindrance compared to that of IV-35 (the Zn-N bond lengths vary from 1.98 Å to 2.07 Å, and the bending angle is 25.1°).

**Figure 4.24** Stick representation of the crystal structure of IV-36. Solvent molecules and hydrogen atoms (except the N-H hydrogens) have been omitted. Different planes are colour-coded for clarity: a) top view; b) side view; c) side view with front half and back half showed separately.
The side view of the crystal structure (Figure 4.24, b and c) clearly shows the structure is one of the meso diastereomers (Figure 4.20, type a). The two carbazole moieties (b and b’) and two dipyrrin moieties from ligand III-11 (d and d’) actually fall in the same plane, while the rest of the dipyrrin moieties are parallel in pairs (a-a’, c-c’, and f-f’). The dihedral angles are 54.8˚ (between a and b), 71.4˚ (between c and b), and 55.3˚ (between f’ and b), respectively. The two meso-aryl moieties (e and e’) are also parallel with an average distance of 7.55 Å.

Figure 4.25 Packing diagrams of IV-36: top view (a) and two different side views (b and c) of the layer 1 (1. counterclockwise rotation of layer 1 ninety degrees about the y-axis; 2. clockwise rotation of layer 1 sixty degrees about the y-axis); d) π-π stacking interactions between layer 1 and layer 2.
The crystal packing pattern of IV-36 is shown in Figure 4.25. Intermolecular CH-π interactions are observed and are considered as a driving force for the observed crystal packing. As shown in Figure 4.26, a macrocycle (ring-A (red)) interacts with four neighbouring macrocycles (ring-B (maroon) and ring-C (purple)) in the same layer to form a 2-D network. The methyl groups attached to the dipyrrin moieties (C1 and C37 of ring-A, C26 and C54 of ring-B) are the hydrogen-bonding donation sites, and dipyrrin plane (a and d of ring-B, c and f of ring-A) are the accepting π-planes. Similar donor/acceptor-type CH-π interactions also exist between the aryl-Hs (C50-H of ring-A and C53-H of ring-B) and the dipyrrin planes (f of ring-B and d of ring-A). The distances between donor and accepting planes are listed in Table 4.5. Ring-C interacts with ring-A the same way, with its C1, C37 and C50 as donors and c, d, and f as acceptors. The macrocycles in one layer are stacked with those in other layers by π-π stacking interactions between the parallel-arranged carbazole moieties with a stacking distance of 3.5Å (Figure 4.25, d).

Figure 4.26 CH-π interactions between the neighbouring macrocycles (ring-A and ring-B) of the X-ray single crystal structure of IV-36.
Donors | Acceptors | Distances between donor and accepting planes (Å)
---|---|---
C(1)H₃ (ring-A) | plane a (ring-B) | 3.449 (C1-a) 4.072 (H1A-a), 2.844(H1B-a), 2.926 (H1C-a)
C(37)H₃ (ring-A) | plane d (ring-B) | 3.481 (C37-d) 2.772 (H37A-d), 3.155 (H37B-d), 4.259 (H37C-d)
C(50)H (ring-A) | plane f (ring-B) | 3.455 (C50-f) 2.694 (H50-f)
C(26)H₃ (ring-B) | plane c (ring-A) | 3.415 (C26-c) 3.753 (H26A-c), 2.620 (H26B-c), 3.180 (H26C-c)
C(54)H₃ (ring-B) | plane f (ring-A) | 3.833 (C54-f) 4.292 (H54A-f), 2.864 (H54B-f), 4.099 (H54C-f)
C(53)H (ring-B) | plane d (ring-A) | 3.317 (C53-d) 2.550 (H53-d)

Table 4.5 The distances between CH-π interaction donor and accepting planes of two neighbouring macrocycles (ring-A and ring-B).

4.6 Conclusions and outlook

In summary, a variety of meso-substituted dimeric dipyrrin ligands were prepared. The self-assembled complexation of these ligands generated metallomacrocyclic structures with various core sizes. The cobalt(II) complexes of carbazole-bridged 3,6-dimeric dipyrrins were successfully separated according to ring size. The pentameric coordination macrocycle reported here, to the best of our knowledge, is the largest ring structure with a promising guest-binding cavity based on dipyrrin derivatives.

Further, coordination macrocycles based on carbazole-bridged 1,8-dimeric dipyrrin ligands were synthesized. Due to the tetrahedral geometry of the Zn(II) ion, three types of stereoisomers (two diasteromers) were formed and confirmed by NMR spectroscopy.
solid-state structure of the meso-type diastereomer was also revealed by X-ray diffraction analysis.

Finally, by introducing heteroleptic bis(dipyrrin) metal complexes as the metal source to react with carbazole-bridged 1,8-dimeric dipyrrin ligands, a coordination macrocycle containing two different ligands was obtained. The macrocycle is expected to have four chiral centers and seven types of stereoisomers (four diasteromers) are possible. The NMR spectrum shows three sets of signals and X-ray diffraction analysis reveals the structure to be one of the meso-stereoisomers.

![Diagram of meso-substituted dimeric dipyrrin ligands](image)

**Scheme 4.11** Structures of carbazole-bridged asymmetric 3,6-dimeric dipyrrin ligands.

All the meso-substituted dimeric dipyrrin ligands mentioned here are symmetric. To study whether asymmetric dimeric dipyrrin ligands act the same way, we also synthesized ligands IV-37, IV-38 and IV-39, on which the carbazole linker bears two different dipyrrin moieties (**Scheme 4.11**). The preliminary studies of these dipyrrin ligands with metal ions also show the formation of the ring structure, but with tetrameric macrocycles as the major product. Due to the lack of symmetry of the ligands, several possible tetrameric structures may be obtained through self-assembled complexation (**Figure 4.27**). Investigation of the preferred structure of the reaction and the driving force behind it should prove interesting.
Figure 4.27 Illustration of possible coordination structures of asymmetric dipyrrin ligands. Red and blue represent two different dipyrrin moieties in one ligand. Structure A exhibits “head to tail” connections; Structure B shows “head to head, tail to tail” connections; Structures C and D contain both types of connections.
CHAPTER 5

Experimental section
5.1 Instrumentation and general materials

All chemicals for syntheses were purchased from Fisher Scientific, Aldrich Chemical Co. or Alfa Aesar. Unless otherwise noted, the chemicals were used without further purification. Pyrrole was freshly distilled. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel aluminum plates containing a fluorescent indicator (Merck Silica Gel 60 F254). Column chromatography was performed using basic (or neutral) alumina from Fisher (Brockman activity I, 60-325 mesh, deactivated with 3% water to activity II or 6% water to activity III), silica gel from Silicycle Chemical Division (230-400 mesh), and gel permeation on Bio-Beads S-X1 beads (Bio-Rad Laboratories, Inc., porous styrene and divinylbenzene copolymer beads, 200-400 mesh; eluent: toluene). Deuterated solvents for NMR measurements were purchased from Cambridge Isotope Laboratories. $^1$H NMR and $^{13}$C NMR data were collected in DMSO-$d_6$, CD$_2$Cl$_2$ or CDCl$_3$ on a Bruker Avance 300 MHz or a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to the residual solvent proton or carbon resonance (DMSO-$d_6$ at 2.50 ppm for $^1$H NMR; CD$_2$Cl$_2$ at 5.32 ppm and 54.00 ppm for $^1$H NMR and $^{13}$C NMR, respectively; CDCl$_3$ at 7.27 ppm and 77.23 ppm for $^1$H NMR and $^{13}$C NMR, respectively). Elemental analyses were performed by UBC Chemistry Department Mass Spectrometry lab on a Carlo Erba Elemental Analyzer EA 1108. Low and high resolution mass spectra were determined by UBC Chemistry Department Mass Spectrometry lab on a Micromass LCT mass spectrometer, a Kratos MS-50 mass spectrometer, or a Kratos Concept IIHQ hybrid mass spectrometer, with only molecular ions ([M]$^+$, [M+H]$^+$, [M+Na]$^+$) being reported. High resolution ESI mass spectrometry (HRESIMS) measurements are valid to ± 5 ppm. The mass spectra of metal complexes were acquired by MALDI-TOF in the presence of an added matrix (DCTB) on a Bruker Biflex IV. The UV-Visible spectra were
recorded in CH$_2$Cl$_2$ at room temperature on a Varian Cary 50 spectrophotometer or a Varian Cary 5000 spectrophotometer. The X-ray data were obtained on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K$_\alpha$ radiation. The structures were solved by direct methods and refined with the SHELXTL crystallographic software package of Bruker-AXS.

5.2 General procedure for synthesis of dipyrromethanes and dipyrromethenes

5.2.1 General procedure for synthesis of dipyrromethanes via condensation of the corresponding aldehyde and pyrrole under TFA catalysis

Aldehyde and pyrrole were dissolved in CH$_2$Cl$_2$ and degassed with argon for 10 min. Trifluoroacetic acid (TFA, 10 to 15%) was added. The solution was stirred at room temperature under argon. CH$_2$Cl$_2$ was then added to dilute the reaction mixture. The reaction was quenched with 0.1 M NaOH. The mixture was extracted with CH$_2$Cl$_2$ and dried over anhydrous Na$_2$SO$_4$. The Na$_2$SO$_4$ was removed by vacuum filtration and the filtrate was evaporated to remove CH$_2$Cl$_2$. The product was purified by column chromatography (Silica, CH$_2$Cl$_2$) to give an off-white solid.

5.2.2 General procedure for synthesis of dipyrrins by oxidation of dipyrromethane

A solution of dipyrromethane was treated with $p$-chloranil (or DDQ). After stirring at room temperature overnight, the entire reaction mixture was poured onto and filtered through a basic alumina column (eluent: CH$_2$Cl$_2$, then THF). The crude product was then purified by column chromatography (Silica, CH$_2$Cl$_2$ : CH$_3$OH = 100:2) to afford a brown powder.
5.3 Experimental data for Chapter 2

5-[4-(Dipyrrin-5-yl)phenyl]dipyrromethane (II-1)

II-1 was prepared according to a literature method.  

$\text{H NMR (300 MHz, CDCl}_3\text{)} \delta = 8.02 \text{ (br. s., 2H, 2NH), 7.65 (m, 2H, } \alpha\text{-dipyrrin), 7.47 (d, } J = 8.22 \text{ Hz, 2H, Ar-H), 7.31 (d, } J = 8.22 \text{ Hz, 2H, Ar-H), 6.73-6.79 (m, 2H, } \alpha\text{-dipyrromethane), 6.63 (dd, } J = 1.14, 4.34 \text{ Hz, 2H, } \beta\text{-dipyrrin), 6.41 (dd, } J = 1.60, 4.34 \text{ Hz, 2H, } \beta\text{-dipyrrin), 6.17-6.23 (m, 2H, } \beta\text{-dipyrromethane), 5.94-5.99 (m, 2H, } \beta\text{-dipyrromethane), 5.58 (s, 1H, meso-H);}

\text{LRESIMS(m/z): 365.2 [M+H]+, calcd. for C24H22N4: 365.2;}

\text{UV/Vis (CH2Cl2) } \lambda_{\text{max}} \text{ nm: 434}

3-(tert-Butyl)-1H-pyrrole (II-2)

II-2 was prepared according to a literature method.  

$^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta = 8.08 \text{ (br. s., 1H), 6.73-6.79 (m, 1H), 6.59-6.64 (m, 1H), 6.20-6.25 (m, 1H), 1.31 (s, 9H)}$
2,8-Di-tert-butyl-5-(4-formylphenyl)dipyrromethane (II-3)

Following the general procedure for the synthesis of dipyrromethanes, a mixture of terephthalaldehyde (0.237 g, 1.77 mmol) and II-2 (0.88 g, 7.1 mmol) in CH₂Cl₂ (10 mL) was flushed with argon for 10 min and treated with TFA (14 µL, 0.18 mmol). The reaction mixture was stirred at r.t. for 1.5 hrs. Column chromatography (silica, CH₂Cl₂) afforded a pale yellow solid (0.335 g, 52%).

¹H NMR (300 MHz, DMSO-\textit{d₆}) \(\delta = 10.19\) (br. s., 2H, 2NH), 9.95 (s, 1H, CHO), 7.83 (d, \(J = 8.22\) Hz, 3H, Ar-H), 7.39 (d, \(J = 8.22\) Hz, 2H, Ar-H), 6.34-6.41 (s, 2H, α-H), 5.70 (s, 2H, β-H), 5.34 (s, 1H, \(meso\)-H), 1.14 (s, 18H, \(tert\)-Bu)

4,4-Difluoro-2,6-di-tert-butyl-8-(4-formylphenyl)-4-bora-3a,4a-diaza-s-indacene(II-4)

\(p\)-Chloronil (269 mg, 1.09 mmol) was added to the solution of II-3 (330 mg, 0.91 mmol) in THF (50 mL). After stirring for 24 hrs at room temperature, a dark red solid precipitated from the reaction mixture. After adding triethylamine (0.63 mL, 4.52 mmol) to the reaction mixture, the precipitate dissolved. The reaction mixture was then treated with boron trifluoride etherate (0.56 mL, 4.52 mmol). After stirring for another 16 hrs, the entire reaction mixture was filtered
through a basic alumina column (eluent: CH₂Cl₂). The crude product was then purified by column chromatography (silica, CH₂Cl₂), which afforded a red solid (270 mg, 72%).

\(^1\)H NMR (300 MHz, CDCl₃) \(\delta = 10.15\) (s, 1H, CHO), 8.06 (d, \(J = 8.22\) Hz, 2H, Ar-H), 7.86 (s, 2H, α-H), 7.71 (d, \(J = 8.22\) Hz, 2H, Ar-H), 6.53 (s, 2H, β-H), 1.22 (s, 18H, tert-Bu);

UV/Vis (CH₂Cl₂) \(\lambda_{\text{max}}\) nm: 539 and 343

4,4-Difluoro-2,6-di-tert-Butyl-8-[4-(dipyrromethane-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-5)

Following the general procedure for the synthesis of dipyrromethanes, II-4 (270 mg, 0.66 mmol) was dissolved in 3.4 ml of pyrrole (49 mmol). The mixture was degassed with argon for 10 min and treated with TFA (0.08 mL, 0.10 mmol), then stirred at room temperature for 10 mins. Column chromatography (silica, CH₂Cl₂) afforded a red solid (145 mg, 42%).

\(^1\)H NMR (300 MHz, CDCl₃) \(\delta = 8.07\) (br. s., 2H, NH), 7.83 (s, 2H, α-BODIPY), 7.52 (d, \(J = 8.22\) Hz, 2H, Ar-H), 7.41 (d, \(J = 8.22\) Hz, 2H, Ar-H), 6.80 (s, 2H, β-BODIPY), 6.64 (s, 2H, α-dipyrromethane), 6.17-6.27 (m, 2H, β-dipyrromethane), 6.01 (s, 2H, , β-dipyrromethane), 5.62 (s, 1H, meso-H), 1.25 (s, 18H, tert-Bu);

UV/Vis (CH₂Cl₂) \(\lambda_{\text{max}}\) nm: 533 and 376
4,4-Difluoro-2,6-di-tert-Butyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-6)

A solution of II-5 (141 mg, 0.27 mmol) in THF (20 mL) was treated with p-chloranil (100 mg, 0.4 mmol) for 24 hrs at room temperature. The solvent was removed and the residue was column chromatographed (silica, CH2Cl2 : CH3OH = 100:2) to afford a red solid (67 mg, 48%).

$^1$H NMR (300 MHz, CD2Cl2) $\delta$ = 7.85 (s., 2H, $\alpha$-BODIPY), 7.67-7.73 (m, 6H, Ar-H and $\alpha$-dipyrrin), 6.78 (s, 2H, $\beta$-H), 6.71 (d, $J = 4.11$ Hz, 2H, $\beta$-H), 6.47 (d, $J = 4.57$ Hz, 4H, $\beta$-H), 1.28 (s, 18H, tert-Bu);

$^{13}$C NMR (101 MHz, CD2Cl2) $\delta$ = 146.4, 145.3, 144.6, 142.2, 141.3, 141.0, 140.0, 135.2, 135.1, 131.4, 130.4, 129.1, 126.8, 118.5, 37.0, 31.5;

LRESIMS (m/z): 523.3 [M+H]$^+$;

HRESIMS: 523.2853 [M+H]$^+$, calcd. for C$_{32}$H$_{34}$BF$_2$N$_3$: 523.2845;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm: 534, 438 and 371

2-Methyl-1H-pyrrole (II-7)

II-7 was prepared according to a literature method.$^{142}$

$^1$H NMR (400MHz, CD$_2$Cl$_2$) $\delta$ = 7.96 (br. s., 1H), 6.67-6.59 (m, 1H), 6.08 (q, $J = 2.7$ Hz, 1H), 5.88 (br. s., 1H), 2.28 (s, 3H);
$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta = 128.0, 116.6, 108.8, 106.3, 13.1$; 
LREIMS(m/z): 81 (M$^+$)

**1,9-Dimethyl-5-(4-cyanophenyl)dipyrromethane (II-8)**

Following the general procedure for the synthesis of dipyrromethane, a mixture of $p$-cyanobenzaldehyde (2.62 g, 20 mmol) and 2-methylpyrrole (3.57 g, 44 mmol) in CH$_2$Cl$_2$ (100 mL) was flushed with argon for 10 min and treated with TFA (0.223 mL, 3 mmol). The reaction mixture was stirred at r.t. for 3 hrs. Column chromatography (silica, CH$_2$Cl$_2$) afforded a pale yellow solid (4.26 g, 77%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.78$ (br. s, 2H, 2NH), 7.61 (d, $J = 8.2$ Hz, 2H, Ar-H), 7.35 (d, $J = 8.2$ Hz, 2H, Ar-H), 5.78 (t, $J = 2.5$ Hz, 2H, $\beta$-H), 5.68 (t, $J = 3.0$ Hz, 2H, $\beta$-H), 5.41 (s, 1H, meso-H), 2.21 (s, 6H, CH$_3$); 

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 148.9, 132.8, 130.4, 129.7, 128.3, 119.4, 111.0, 108.1, 106.6, 44.7, 13.3$; 
HRESIMS: 298.1318 [M+Na]$^+$, calcd. for C$_{18}$H$_{17}$N$_3$Na: 298.1320.

**1,9-Dimethyl-5-(4-formylphenyl)dipyrromethane (II-9)**

A solution of DIBAL-H (1 M in hexanes, 31.0 mL, 31.0 mmol) was added drop-wise to a solution of II-8 (4.26 g, 15.5 mmol) in CH$_2$Cl$_2$ (150 mL). The reaction mixture was stirred at
room temperature for 4 hrs and then quenched with 200 mL of saturated aq. NH₄Cl and stirred for another 2 hrs. After the aqueous layer was removed, 10% aq. NaOH (200 mL) was added to the organic layer which formed an emulsion. The aqueous phase was extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried over Na₂SO₄. Column chromatography (silica, CH₂Cl₂) afforded a pale yellow solid (2.99 g, 69%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 9.97 (s, 1H, CHO), 7.83 (br. s, 2H, 2NH), 7.82 (d, J = 8.2 Hz, 2H, Ar-H), 7.41 (d, J = 8.2 Hz, 2H, Ar-H), 5.77 (br. s, 2H, β-H), 5.70 (t, J = 3.0 Hz, 2H, β-H), 5.43 (s, 1H, meso-H), 2.21 (s, 6H, CH₃);

¹³C NMR (75 MHz, CD₂Cl₂): δ = 192.4, 150.4, 135.8, 130.7, 130.4, 129.5, 128.2, 108.0, 106.5, 44.8, 13.3;

HRESIMS: 301.1314 [M+Na]⁺, calcd. for C₁₈H₁₈N₂ONa: 301.1317

4,4-Difluoro-3,5-dimethyl-8-(4-formylphenyl)-4-bora-3a,4a-diaza-s-indacene (II-10)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.66 g, 7.3 mmol) was added to a solution of II-9 (1.85 g, 6.65 mmol) in CH₂Cl₂ (50 mL). After stirring for 1.5 hrs at room temperature, a dark red solid precipitated from the reaction mixture. After adding triethylamine (4.63 mL, 33.3 mmol) to the reaction mixture, the precipitate dissolved. The reaction mixture was then treated with boron trifluoride etherate (4.10 mL, 33.3 mmol). After stirring for another 2 hrs, the entire reaction mixture was filtered through a basic alumina column (eluent: CH₂Cl₂). The crude product was then purified by column chromatography (silica, CH₂Cl₂), which afforded a red solid (0.98 g, 45%).
$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 10.12 (s, 1H, CHO), 8.00 (d, $J$ = 8.2 Hz, 2H, Ar-H), 7.68 (d, $J$ = 8.2 Hz, 2H, Ar-H), 6.70 (d, $J$ = 4.1 Hz, 2H, $\beta$-H), 6.33 (d, $J$ = 4.1 Hz, 2H, $\beta$-H), 2.64 (s, 6H, CH$_3$);

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ = 192.0, 159.0, 141.2, 140.2, 137.9, 134.7, 131.6, 130.7, 129.8, 120.5, 15.3;

HRESIMS: 347.1151 [M+Na]$^+$, calcd. for C$_{18}$H$_{15}$BF$_2$N$_2$ONa: 347.1143

4,4-Difluoro-3,5-dimethyl-8-[4-(dipyrromethane-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-11)

Following the general procedure for the synthesis of dipyrromethane, II-10 (588 mg, 1.81 mmol) was dissolved in 6.5ml of pyrrole (91 mmol). The mixture was degassed with argon for 10 min and treated with TFA (0.021 mL, 0.27 mmol), then stirred at room temperature for 3 hrs. Column chromatography (silica, CH$_2$Cl$_2$) afforded a red solid (503 mg, 63%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 8.12 (br. s, 2H, NH), 7.48 (d, $J$ = 8.1 Hz, 2H, Ar-H), 7.35 (d, $J$ = 8.1 Hz, 2H, Ar-H), 6.78 (d, $J$ = 4.1 Hz, 2H, $\beta$-BODIPY), 6.69-6.75 (m, 2H, $\alpha$-dipyrromethane), 6.31 (d, $J$ = 4.1 Hz, 2H, $\beta$-BODIPY), 6.16 (q, $J$ = 2.9 Hz, 2H, $\beta$-dipyrromethane), 5.92 (br. s, 1H, $\beta$-dipyrromethane), 5.55 (s, 1H, meso-H), 2.62 (s, 6H, CH$_3$);

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$ = 158.0, 145.4, 143.0, 135.0, 133.2, 132.6, 131.4, 131.0, 128.7, 119.9, 118.1, 108.9, 107.9, 44.4, 15.2;

HRESIMS: 463.1891 [M+Na]$^+$, calcd. for C$_{26}$H$_{23}$BF$_2$N$_4$Na: 463.1882
4,4-Difluoro-3,5-dimethyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-12)

A solution of II-11 (503 mg, 1.14 mmol) in CH₂Cl₂ (60 mL) was treated with DDQ (285 mg, 1.26 mmol) for 1 hr at room temperature. The solvent was removed and the residue was column chromatographed (silica, CH₂Cl₂ : CH₃OH = 100:2) to afford a red solid (257 mg, 51%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.69 (s, 2H, α-dipyrrin), 7.64 (s, 4H, Ar-H), 6.86 (d, J = 3.7 Hz, 2H, β-BODIPY), 6.67 (d, J = 3.2 Hz, 2H, β-dipyrrin), 6.46 (dd, J = 4.3 Hz, J = 1.6 Hz, 2H, β-dipyrrin), 6.37 (d, J = 4.1 Hz, 2H, β-BODIPY), 2.65 (s, 6H, CH₃);

¹³C NMR (75 MHz, CD₂Cl₂): δ = 158.5, 144.5, 142.4, 141.3, 141.1, 139.6, 135.3, 135.0, 131.2, 131.0, 130.4, 129.3, 120.2, 118.4, 15.3;


UV/Vis (CH₂Cl₂) λ_max nm (ε × 10⁴): 514 (6.89), 486 (2.53), 444 (2.44) and 345 (2.39)

4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrromethane-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-13)

Following the general procedure for the synthesis of dipyrromethanes, a mixture of II-10 (747 mg, 2.3 mmol) and 2-methylpyrrole (414 mg, 5.1 mmol) in 30 mL CH₂Cl₂ was degassed with
argon for 10 min and treated with TFA (0.027 mL, 0.35 mmol). The reaction mixture was stirred at room temperature for 1 hr. The crude product was purified by column chromatography (silica, CH₂Cl₂) affording a red solid (556 mg, 52%).

\[ \text{H NMR (300 MHz, CD₂Cl₂): } \delta = 7.82 \text{ (br. s, 2H, NH), 7.49 (d, } J = 8.1 \text{ Hz, 2H, Ar-H), 7.37 (d, } J = 8.1 \text{ Hz, 2H, Ar-H), 6.80 (d, } J = 3.9 \text{ Hz, 2H, } \beta\text{-BODIPY), 6.32 (d, } J = 4.1 \text{ Hz, 2H, } \beta\text{-BODIPY), 5.71-5.83 (m, 4H, } \beta\text{-dipyrrromethane), 5.44 (s, 1H, meso-H), 2.62 (s, 6H, CH₃-boron dipyrinn), 2.23 (s, 6H, CH₃-dipyrromethane);} \]

\[ \text{13C NMR (75 MHz, CD₂Cl₂): } \delta = 158.0, 145.8, 143.2, 135.0, 133.0, 131.3, 131.2, 131.0, 128.7, 128.1, 119.9, 107.9, 106.5, 44.6, 15.2, 13.3; \]

HRESIMS: 467.2235 [M+H]⁺, calcd. for C₂₈H₂₆BF₂N₄: 467.2219

4,4-Difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene (II-14)

II-13 (556 mg, 1.19 mmol) was dissolved in 60 mL CH₂Cl₂ and 296 mg of DDQ (1.30 mmol) was added. The mixture was stirred at room temperature for 1 hour. Removal of solvent and column chromatography (silica, CH₂Cl₂ : CH₃OH = 100:2) afforded a red solid (442 mg, 80%).

\[ \text{H NMR (300 MHz, CD₂Cl₂): } \delta = 7.60 \text{ (s, 4H, Ar-H), 6.86 (d, } J = 4.1 \text{ Hz, 2H, } \beta\text{-BODIPY), 6.51 (d, } J = 4.1 \text{ Hz, 2H, } \beta\text{-dipyrrin), 6.36 (d, } J = 4.1 \text{ Hz, 2H, } \beta\text{-BODIPY), 6.22 (d, } J = 4.1 \text{ Hz, 2H, } \beta\text{-dipyrrin), 2.64 (s, 6H, CH₃-BODIPY), 2.46 (s, 6H, CH₃-dipyrinn);} \]

\[ \text{13C NMR (75 MHz, CD₂Cl₂): } \delta = 158.3, 154.8, 142.7, 140.3, 139.9, 137.4, 135.0, 134.8, 131.2, 131.0, 130.3, 129.1, 120.1, 118.3, 16.6, \text{ and 15.3;} \]
HRESIMS: 467.2215 [M+H]^+, calcd. for C_{28}H_{26}BF_{2}N_{4}: 467.2219;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4})\text{: } 514 (6.75), 481 (3.44), 455 (2.85) \text{ and } 348 (2.26).

General procedure for synthesis of metal complexes II-15 through II-20

A solution of ligand \textbf{II-12} or \textbf{II-14} (1 equiv.) in CH_{2}Cl_{2} was treated with a solution of M(OAc)$_2$·xH$_2$O (0.7 equiv.) in methanol. The reaction mixture was stirred overnight at room temperature. Removal of the solvent and purification on a flash silica (or basic alumina) column afforded the desired metal complexes (yields 30%-40%).

\textbf{Bis[4,4-difluoro-3,5-dimethyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]copper(II) (II-15)}

MALDI-TOF: 937.5, calcd. for C_{52}H_{40}B_{2}CuF_{4}N_{8}: 937.3;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4})\text{: } 513 (12.82), 478 (7.98) \text{ and } 350 (4.97)

\textbf{Bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]copper(II) (II-16)}

MALDI-TOF: 993.3, calcd. for C_{56}H_{48}B_{2}CuF_{4}N_{8}: 993.3;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4})\text{: } 511 (12.61) \text{ and } 351 (3.61)
Bis[4,4-difluoro-3,5-dimethyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]nickel(II) (II-17)

\[ \begin{align*}
&\text{\H NMR (300 MHz, CD2Cl2): } \delta = 10.31 \text{ (br. s, 4H, } \alpha\text{-nickel dipyrrin), } 8.03 \text{ (d, } J = 3.7 \text{ Hz, 4H, } \\
&\beta\text{-nickel dipyrrin), } 7.57 \text{ (q, } J = 8.2 \text{ Hz, 8H, Ar-H), } 6.88 \text{ (dd, } J = 15.5 \text{ Hz, } J = 4.1 \text{ Hz, 4H, } \\
&\beta\text{-nickel dipyrrin), } 6.37 \text{ (d, } J = 3.7 \text{ Hz, 4H, } \beta\text{-BODIPY), } 2.65 \text{ (s, 12H, CH3- BODIPY); } \\
&\text{\C NMR (75 MHz, CD2Cl2): } \delta = 179.6, 158.5, 153.0, 142.8, 142.3, 141.2, 140.3, 138.86, \\
&135.5, 134.9, 131.0, 131.0, 130.2, 120.2, 15.3; \\
&\text{MALDI-TOF: 932.4, calcd. for C}_{52}\text{H}_{40}\text{B}_{2}\text{F}_{4}\text{N}_{8}\text{Ni: 932.3; } \\
&\text{UV/Vis (CH2Cl2) } \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4}\text{): 513 (13.80), 487 (7.37) and 350 (4.72) } \\
\end{align*} \]

Bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-y1)phenyl]-4-bora-3a,4a-diaza-s-indacene]nickel(II) (II-18)

\[\begin{align*}
&\text{MALDI-TOF: 988.5, calcd. for C}_{56}\text{H}_{48}\text{B}_{2}\text{F}_{4}\text{N}_{8}\text{Ni: 988.4; } \\
&\text{UV/Vis (CH2Cl2) } \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4}\text{): 511 (14.45) and 353 (4.40) } \\
\end{align*}\]
Bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene|cobalt(II) (II-19)

MALDI-TOF: 989.7, calcd. for C_{56}H_{48}B_{2}CoF_{4}N_{8}: 989.4;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm} (\varepsilon \times 10^{-4}): 501 (12.29) and 349 (3.53)

Bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene|zinc(II) (II-20)

{\textsuperscript{1}}H NMR (300 MHz, CD_{2}Cl_{2}): \delta = 7.64 (m, 8H, Ar-H), 6.90 (d, J = 4.1 Hz, 4H, \beta- BODIPY), 6.63 (d, J = 4.1 Hz, 4H, \beta- zinc dipyrrin), 6.38 (d, J = 4.1 Hz, 4H, \beta- BODIPY), 6.27 (d, J = 3.7 Hz, 4H, \beta- zinc dipyrrin), 2.66 (s, 12H, CH_{3}- BODIPY), 2.16 (s, 12H, CH_{3}- zinc dipyrrin);

{\textsuperscript{13}}C NMR (75 MHz, CDCl_{3}): \delta = 160.0, 158.1, 143.3, 142.2, 141.4, 139.1, 134.7, 134.2, 133.2, 130.8, 130.6, 129.4, 119.7, 117.6, 16.8, 15.2;

MALDI-TOF: 993.7, calcd. for C_{56}H_{48}B_{2}F_{4}N_{8}Zn: 994.3;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm} (\varepsilon \times 10^{-4}): 493 (13.32) and 350 (3.75)
General procedure for synthesis of metal complexes II-21 and II-22

A solution (CHCl₃:CH₃OH=1:1) of ligand II-12 (1 equiv.) was treated with a suspension of 0.3 equiv. FeCl₃ (or Na₃Co(NO₃)₆) in methanol. After adding triethylamine (5 equiv.) to the reaction, the mixture was degassed with argon for 10 min, and then refluxed overnight under argon. Removal of the solvent and purification on a flash silica column afforded the desired metal complexes (yields: 80% for II-21 and 76% for II-22).

Tris[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]iron(III) (II-21)

MALDI-TOF: 1367.5, calcd. for C₇₈H₆₀B₃F₆FeN₁₂: 1367.5;
UV/Vis (CH₂Cl₂) λ_{max} nm (ε × 10⁻⁴): 513 (20.00) and 350 (6.67)

Tris[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]cobalt(III) (II-22)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.63 (s, 8H, Ar-H), 6.83-6.88 (m, 8H, α-cobalt dipyrrin and β-BODIPY), 6.52 (s, 4H, β-cobalt dipyrrin), 6.41-6.47 (m, 4H, β-cobalt dipyrrin), 6.36 (d, J = 4.11 Hz, 4H, β-BODIPY), 2.64 (s, 12H, CH₃-BODIPY);
$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ = 158.2, 152.4, 145.2, 141.9, 139.9, 135.7, 134.7, 134.6, 133.2, 130.5, 129.6, 119.9, 119.8, 119.3, 15.2;
MALDI-TOF: 1370.4, calcd. for C$_{78}$H$_{60}$B$_3$F$_6$CoN$_{12}$: 1370.5;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 513 (20.65) and 349 (6.93)

**General procedure for synthesis of II-23 to II-40**

Following the general procedure, the desired dipyrromethanes were obtained by TFA catalyzed condensation of 1 equiv. $p$-cyanobenzaldehyde (or $p$-tolualdehyde) and 2.2 equiv. 2-methylpyrrole (or 100 equiv. pyrrole) in CH$_2$Cl$_2$. The desired dipyrrins were obtained by oxidation of the corresponding dipyrromethane with DDQ. Boron complexes II-23 and II-24 were prepared following the synthetic procedure for II-10. Divalent metal complexes II-25 to II-36 were prepared following the synthetic procedure for II-15. Trivalent metal complexes II-37 to II-40 were prepared following the synthetic procedure for II-21 (overall yield: 30%-50%).

![II-23, II-24](image_url)

**4,4-Difluoro-3,5-dimethyl-8-(4-cyanophenyl)-4-bora-3a,4a-diaza-s-indacene (II-23)**

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 7.80 (d, $J$ = 8.22 Hz, 2H, Ar-H), 7.63 (d, $J$ = 8.22 Hz, 2H, Ar-H), 6.65 (d, $J$ = 4.11 Hz, 2H, $\beta$-BODIPY), 6.33 (d, $J$ = 4.11 Hz, 2H, $\beta$-BODIPY), 2.62 (s, 6H, CH$_3$-BODIPY);
LREIMS(m/z): 321 (M$^+$), calcd. for C$_{18}$H$_{14}$BF$_2$N$_3$:321.1
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 518 (7.14) and 328 (1.41)
4,4-Difluoro-3,5-dimethyl-8-(p-tolyl)-4-bora-3a,4a-diaza-s-indacene (II-24)

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 7.42 (d, $J$ = 8.22 Hz, 2H, Ar-H), 7.31 (d, $J$ = 7.77 Hz, 2H, Ar-H), 6.76 (d, $J$ = 4.11 Hz, 2H, $\beta$-BODIPY), 6.30 (d, $J$ = 4.11 Hz, 2H, $\beta$-BODIPY), 2.61 (s, 6H, CH$_3$-BODIPY), 2.45 (s, 3H, CH$_3$-Ar);

LREIMS(m/z): 310 (M$^+$), calcd. for C$_{18}$H$_{17}$BF$_2$N$_2$: 310.1

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 511 (7.63) and 352 (1.43)

Bis[5-(4-cyanophenyl)dipyrrinato]copper(II) (II-25)

MALDI-TOF: 551.4, calcd. for C$_{32}$H$_{20}$CuN$_6$: 551.1;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 503 (3.38), 471 (6.65) and 376 (1.28)

Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]copper(II) (II-26)

MALDI-TOF: 607.3, calcd. for C$_{36}$H$_{28}$CuN$_6$: 607.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 510 (5.25), 457 (3.21) and 301 (1.49)

Bis[5-(4-cyanophenyl)dipyrrinato]nickel(II) (II-27)

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 11.79 (s, 4H, $\alpha$-dipyrrin), 8.79 (s, 4H, $\beta$-dipyrrin), 7.71 (d, 4H, $J$ = 8.0 Hz, Ar-H), 7.46 (d, $J$ = 7.9 Hz, 4H, Ar-H), 6.78 (s, 4H, $\beta$-dipyrrin);
MALDI-TOF: 546.4, calcd. for C$_{32}$H$_{20}$N$_6$Ni: 546.1;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 480 (3.86) and 316 (1.93)

**Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]nickel(II) (II-28)**

MALDI-TOF: 602.3, calcd. for C$_{36}$H$_{28}$N$_6$Ni: 602.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 515 (4.94), 452 (2.35) and 319 (1.73)

**Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]cobalt(II) (II-29)**

MALDI-TOF: 603.3, calcd. for C$_{36}$H$_{28}$CoN$_6$: 603.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 501 (11.24) and 314 (1.67)

**Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]zinc(II) (II-30)**

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.77$ (d, 4H, $J = 8.3$ Hz, Ar-H), 7.62 (d, $J = 8.3$ Hz, 4H, Ar-H), 6.46 (d, $J = 4.0$ Hz, 4H, $\beta$-dipyrrin), 6.24 (d, $J = 4.0$ Hz, 4H, $\beta$-dipyrrin), 2.12 (s, 12H, CH$_3$-dipyrrin);

MALDI-TOF: 608.3, calcd. for C$_{36}$H$_{28}$N$_6$Zn: 608.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 495 (12.12) and 309 (1.56)

**Bis[5-(p-tolyl)dipyrrinato]copper(II) (II-31)**

MALDI-TOF: 529.1, calcd. for C$_{32}$H$_{26}$CuN$_4$: 529.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 499 (3.28), 466 (6.32) and 341 (2.11)

**Bis[1,9-dimethyl-5-(p-tolyl)dipyrrinato]copper(II) (II-32)**

MALDI-TOF: 585.2, calcd. for C$_{36}$H$_{34}$CuN$_4$: 585.2;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 504 (7.08), 454 (4.13) and 328 (1.70)

**Bis[5-(p-tolyl)dipyrinato]nickel(II) (II-33)**

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ = 9.70 (br. s, 4H, $\alpha$-dipyrrin), 7.67 (br. s, 4H, $\beta$-dipyrrin), 7.32 (d, $J = 8.0$ Hz, 4H, Ar-H), 7.25 (d, $J = 7.9$ Hz, 4H, Ar-H), 6.80 (d, $J = 3.7$ Hz, 4H, $\beta$-dipyrrin), 2.44 (s, 6H, CH$_3$);
MALDI-TOF: 523.9, calcd. for C$_{32}$H$_{26}$N$_4$Ni: 524.1;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 466 (3.71) and 337 (2.03)

**Bis[1,9-dimethyl-5-(p-tolyl)dipyrinato]nickel(II) (II-34)**

MALDI-TOF: 580.2, calcd. for C$_{36}$H$_{34}$N$_4$Ni: 580.2;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 513 (6.05), 447 (2.42) and 330 (2.10)

**Bis[1,9-dimethyl-5-(p-tolyl)dipyrinato]cobalt(II) (II-35)**

MALDI-TOF: 581.1, calcd. for C$_{36}$H$_{34}$CoN$_4$: 581.2;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 498 (14.02) and 330 (2.08)

**Bis[1,9-dimethyl-5-(p-tolyl)dipyrinato]zinc(II) (II-36)**

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 7.39 (d, 4H, $J = 8.0$ Hz, Ar-H), 7.26 (d, $J = 7.8$ Hz, 4H, Ar-H), 6.57 (d, $J = 3.9$ Hz, 4H, $\beta$-dipyrrin), 6.20 (d, $J = 4.0$ Hz, 4H, $\beta$-dipyrrin), 2.47 (s, 6H, CH$_3$-Ar), 2.11 (s, 12H, CH$_3$-dipyrrin);
MALDI-TOF: 586.2, calcd. for C$_{36}$H$_{34}$N$_4$Zn: 586.2;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 491 (13.89) and 328 (1.86)
Tris[5-(4-cyanophenyl)dipyrrinato]iron(III) (II-37)

MALDI-TOF: 788.0, calcd. for C_{48}H_{30}FeN_{9}: 788.2;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm} (\varepsilon \times 10^{-4}): 493 (3.49) and 444 (4.61)

Tris[5-(4-cyanophenyl)dipyrrinato]cobalt(III) (II-38)

\(^1\)H NMR (300 MHz, CD_{2}Cl_{2}): \delta = 7.77 (d, J = 8.22 Hz, 6H, Ar-H), 7.57 (d, J = 8.68 Hz, 6H, Ar-H), 6.66 (dd, J = 1.37, 4.11 Hz, 6H, \beta\text{-dipyrrin}), 6.45 (s, 6H, \alpha\text{-dipyrrin}), 6.40 (dd, J = 1.83, 4.57 Hz, 6H, \beta\text{-dipyrrin});

MALDI-TOF: 791.1, calcd. for C_{48}H_{30}CoN_{9}: 791.2;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm} (\varepsilon \times 10^{-4}): 508 (5.17), 471 (5.93) and 402 (2.13)

Tris[5-(p-tolyl)dipyrrinato]iron(III) (II-39)

MALDI-TOF: 754.9, calcd. for C_{48}H_{39}FeN_{6}: 755.2;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{ nm} (\varepsilon \times 10^{-4}): 492 (3.66), 442 (4.90) and 330 (2.51)

Tris[5-(p-tolyl)dipyrrinato]cobalt(III) (II-40)

\(^1\)H NMR (300 MHz, CD_{2}Cl_{2}): \delta = 7.36 (d, J = 8.22 Hz, 6H, Ar-H), 7.26 (d, J = 7.77 Hz, 6H, Ar-H), 6.76 (dd, J = 1.37, 4.11 Hz, 6H, \beta\text{-dipyrrin}), 6.40 (s, 6H, \alpha\text{-dipyrrin}), 6.35 (dd, J = 1.60, 4.34 Hz, 6H, \beta\text{-dipyrrin}), 2.45 (s, 9H, CH_{3}\text{-Ar});
MALDI-TOF: 758.0, calcd. for C\textsubscript{48}H\textsubscript{39}FeN\textsubscript{6}: 758.3;

UV/Vis (CH\textsubscript{2}Cl\textsubscript{2}) \( \lambda_{\text{max}} \text{ nm (} \varepsilon \times 10^{-4} \): 504 (4.54), 467 (5.23), 398 (1.74) and 334 (2.43)

5.4 Experimental data for Chapter 3

1,4-Bis(dipyrromethane-5-yl)benzene (III-1)

Following the general procedure for the synthesis of dipyrromethanes, 3.353 g (25 mmol) terephthalaldehyde was dissolved in 87 ml of pyrrole (1.25 mol, 50 equiv.). The mixture was degassed with argon for 10 min and treated with TFA (0.28 mL, 3.75 mmol, 0.15 equiv.). After stirring at room temperature 10 mins, 1.0 M aq. NaOH solution (80 mL) was added to quench the reaction. The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} and dried (anhydrous Na\textsubscript{2}SO\textsubscript{4}). Column chromatography (silica, CH\textsubscript{2}Cl\textsubscript{2}) afforded an off-white solid (3.74 g, 41%).

\textsuperscript{1}H NMR (300MHz, CD\textsubscript{2}Cl\textsubscript{2}): \( \delta = 8.04 \) (br. s, 4H, 4NH), 7.18 (s, 4H, Ar-H), 6.64 - 6.71 (m, 4H, \( \alpha \)-dipyrromethane), 6.08 - 6.13 (m, 4H, \( \beta \)-dipyrromethane), 5.87 (s, 4H, \( \beta \)-dipyrromethane), 5.45 (s, 2H, \textit{meso}-H);

Anal. Calcd. for C\textsubscript{24}H\textsubscript{22}N\textsubscript{4}·1/4H\textsubscript{2}O: C, 77.71; H, 6.11; N, 15.10. Found: C, 77.90; H, 5.96; N, 15.15
1,4-Bis(dipyrrin-5-yl)benzene (III-2)

Following the general procedure for synthesis of dipyrrins with DDQ, 5.1 g DDQ (22.5 mmol) was added to a solution of III-1 (3.74 g, 10.2 mmol) in CH$_2$Cl$_2$ (250 mL). After stirring overnight at r.t., a dark brown solid precipitate formed. The crude product was purified by column chromatography to afford a dark brown solid (1.46 g, 40%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.56-7.76$ (m, 8H, $\alpha$-dipyrrin and Ar-H), 6.67-6.73 (m, 4H, $\beta$-dipyrrin), 6.43 - 6.49 (m, 4H, $\beta$-dipyrrin);

LRESIMS (m/z): 363.5 [M+H]$^+$;

HRESIMS: 363.1597 [M+H]$^+$, calcd. for C$_{24}$H$_{19}$N$_4$: 363.1610;

UV/Vis (CHCl$_3$) $\lambda_{max}$ nm: 478

1,4-Bis(1,9-dimethyl-dipyrromethane-5-yl)benzene (III-3)

Following the general procedure for the synthesis of dipyrromethanes, 1.96 g (14.6 mmol) terephthalaldehyde and 5.23g (64.5 mmol) 2-methylpyrrole were dissolved in 50ml CH$_2$Cl$_2$ and degassed by bubbling with argon for 10 min. 0.163 mL (2.2 mmol) trifluoroacetic acid (TFA) was added and the solution was stirred at r.t. for 2 hours. The crude product was purified by column chromatography (silica, CH$_2$Cl$_2$) affording an off-white solid (1.87 g, 30%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.73$ (br. s, 4H, 4NH), 7.19 (s, 4H, Ar-H), 5.71-5.75 (m, 8H, $\beta$-dipyrromethane), 5.30 (s, 2H, meso-H), 2.19 (s, 12H, CH$_3$);
$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 141.95, 131.81, 128.95, 127.72, 107.54, 106.31, 44.44, 13.28$;

LRESIMS(m/z): 445.2 [M+Na]$^+$;


1,4-Bis(1,9-dimethyl-dipyrrin-5-yl)benzene (III-4)

Following the general procedure for synthesis of dipyrrins with DDQ, 2.21 g DDQ (9.7 mmol) was added to the solution of III-3 (1.87 g, 4.4 mmol) in CH$_2$Cl$_2$ (50 mL). After stirring overnight at r.t., a dark red solid precipitate formed. The crude product was purified by column chromatography, which afforded a dark brown solid (1.44 g, 77%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 7.51$ (s, 4H, Ar-H), 6.53 (d, $J = 2.9$ Hz, 4H, $\beta$-dipyrrin), 6.20 (d, $J = 2.9$ Hz, 4H, $\beta$-dipyrrin), 2.45 (s, 12H, CH$_3$);

$^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta = 154.56, 140.35, 138.25, 138.10, 130.54, 129.26, 118.10, 16.57$;

Anal. Calcd. for C$_{28}$H$_{26}$N$_4$·H$_2$O: C, 77.04; H, 6.46; N, 12.83. Found: C, 76.62; H, 6.09; N, 12.50;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^{-4}$): 442 (4.83) and 321 (1.58)
Synthesis of metal complexes III-5 through III-8

67 mg of BF₂ capped dipyrromethene II-14 (0.144 mmol) and 30 mg of dipyrrin “dimer” III-4 (0.072 mmol) were dissolved in 40 ml CH₂Cl₂. A solution of Co(OAc)₂·4H₂O (39 mg, 0.156 mmol) in methanol (3 mL) was then added into the reaction mixture. The mixture was stirred overnight at r.t. Removal of the solvent and purification on a GPC column afforded the metal complexes II-19, III-5 through III-8.

\[[\text{II-14}][\text{III-4}]\text{Co}_2\text{ (III-5)}\]

MALDI-TOF: 1464.7, calcd. for C₈₄H₇₂B₂Co₂F₄N₁₂: 1464.5;
UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \text{ nm} (\varepsilon \times 10^{-4}) \): 497 (24.95) and 347 (6.15)

\[[\text{II-14}][\text{III-4}]\text{Co}_3\text{ (III-6)}\]

MALDI-TOF: 1940.9, calcd. for C₁₁₂H₉₆B₂Co₃F₄N₁₆: 1939.6;
UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \text{ nm} (\varepsilon \times 10^{-4}) \): 496 (32.40) and 343 (7.25)

\[[\text{II-14}][\text{III-4}]\text{Co}_4\text{ (III-7)}\]

MALDI-TOF: 2415.7, calcd. for C₁₄₀H₁₂₀B₂Co₄F₄N₂₀: 2414.8;
UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \text{ nm} \): 493 and 342

\[[\text{II-14}][\text{III-4}]\text{Co}_5\text{ (III-8)}\]

MALDI-TOF: 2890.7, calcd. for C₁₆₈H₁₄₄B₂Co₅F₄N₂₄: 2889.9
General procedure for synthesis of heteroleptic bis(dipyrinato) metal complexes III-9 through III-11

Dipyrrin dimer (III-2 or III-4) was dissolved in CHCl₃, and was added drop-wise into a CHCl₃ solution of metal acetylacetonate. The reaction mixture was stirred at r.t. for 4 hours to form the heteroleptic bis(dipyrinato) metal complexes. The solution was evaporated to dryness and the product was further purified.

[III-2]Cu₂(acac)₂ (III-9)

Following the general procedure, Cu(acac)₂ (1.11 g, 4.24 mmol) and compound III-2 (257 mg, 0.71 mmol) were dissolved in 100 ml CHCl₃ and stirred for 2 hours at room temperature. The solvent was removed \textit{in vacuo}. The crude product was purified by column chromatography (Silica; CHCl₃ with 0.5% MeOH) to afford 151 mg of a red powder (yield: 31%).

MALDI-TOF: 684.1, calcd. for C₃₄H₃₀Cu₂N₄O₄: 684.1;
UV/Vis (CH₂Cl₂) \textit{λ}_{max} \text{nm}: 469, 339

[III-4]Co₂(acac)₂ (III-10)

Following the general procedure, Co(acac)₂ (1 g, 3.9 mmol) and compound III-4 (110 mg, 0.26 mmol) were dissolved in 100 ml CHCl₃ and stirred for 4 hours. The crude product was
dissolved in toluene and purified by a GPC column to afford 153 mg of the maroon complex (yield: 79%).

MALDI-TOF: 732.2, calcd. for C_{38}H_{38}Co_{2}N_{4}O_{4}: 732.2;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm: 489}

\[ \text{III-4} \text{Zn}_{2}(\text{acac})_{2} \text{ (III-11)} \]

Following the general procedure, Zn(acac)_{2} (1.03 g, 3.9 mmol) and compound \text{III-4} (110 mg, 0.26 mmol) were dissolved in 100 ml CHCl_{3} and stirred for 4 hours and the solvent was removed \textit{in vacuo}. The crude product was purified by recrystallization from CH_{2}Cl_{2}/ethyl ether to afford bright red crystals (147 mg, yield: 75%).

\textsuperscript{1}H NMR (300 MHz, CD_{2}Cl_{2}): \delta = 7.45 (s, 4H, Ar-H), 6.58 (d, J = 3.88 Hz, 4H, \beta\text{-dipyrrin}), 6.25 (d, J = 4.11 Hz, 4H, \beta\text{-dipyrrin}), 5.55 (s, 2H, CH\text{-acetylacetonate}), 2.31 (s, 12H, CH_{3}\text{-dipyrrin}), 2.06 (s, 12H, CH_{3}\text{-acetylacetonate});

\textsuperscript{13}C NMR (75 MHz, CD_{2}Cl_{2}) \delta = 194.8, 160.0, 144.7, 139.7, 139.4, 134.3, 129.9, 117.7, 100.5, 28.5, 17.2;

MALDI-TOF: 746.3, calcd. for C_{38}H_{38}N_{4}O_{4}Zn_{2}: 745.5;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm: 491}
Synthesis of metal complexes III-12 and III-13

III-11 (20 mg, 0.027 mmol) was dissolved in a mixture of CHCl₃ (15 ml) and MeOH (15ml). The solution was allowed to cool to -15°C and then a solution (15 ml, CHCl₃:MeOH=1:1) of II-14 (25 mg, 0.054 mmol) was gradually added. The reaction mixture was stirred at -15°C for 3 hrs. The solution was evaporated to dryness and the product was further purified of a GPC column to afford the complexes II-20, III-12 and III-13.

[II-14]₂[III-4]Zn₂ (III-12)

₁H NMR (600 MHz, CDCl₃): δ = 7.65 (d, J = 8.22 Hz, 4H, Ar-H), 7.57 - 7.63 (m, 8H, Ar-H), 6.85 (d, J = 4.11 Hz, 4H, β-BODIPY), 6.70 (d, J = 4.11 Hz, 4H, β-zinc dipyrrin), 6.62 (d, J = 4.11 Hz, 4H, β-zinc dipyrrin), 6.34 (d, J = 4.11 Hz, 4H, β-BODIPY), 6.28 (dd, J = 3.81, 7.63 Hz, 8H, β-zinc dipyrrin), 2.70 (s, 12H, CH₃-BODIPY), 2.18 (s, 12H, CH₃-zinc dipyrrin), 2.18 (s, 12H CH₃-zinc dipyrrin);
MALDI-TOF: 1474.2, calcd. for C₈₄H₇₂B₂Zn₂F₄N₁₂: 1474.5


₁H NMR (400 MHz, CDCl₃): δ = 7.66 (d, J = 8.19 Hz, 4H, Ar-H), 7.57 - 7.63 (m, 12H, Ar-H), 6.85 (d, J = 4.10 Hz, 4H, β-BODIPY), 6.71 (d, J = 4.10 Hz, 8H, β-zinc dipyrrin), 6.62 (d, J = 3.75 Hz, 4H, β-zinc dipyrrin), 6.34 (d, J = 4.10 Hz, 4H, β-BODIPY), 6.25 - 6.30 (m, 12H, β-
zinc dipyrrin), 2.70 (s, 12H, CH$_3$-BODIPY), 2.19 (s, 12H, CH$_3$-zinc dipyrrin), 2.19 (s, 12H, CH$_3$-zinc dipyrrin), 2.18 (s, 12H, CH$_3$-zinc dipyrrin);
MALDI-TOF: 1954.5, calcd. for C$_{112}$H$_{96}$B$_2$Zn$_3$F$_4$N$_{16}$: 1954.6

1,2,3,7,8,9-Hexamethyl dipyrromethene hydrochloride (III-14)

\[
\text{III-14} \quad \text{was synthesized by a former colleague. The purity was checked by } ^1\text{H NMR.}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 13.50$ (s, 1H, NH), 6.99 (s, 1H, meso-H), 2.58 (s, 6H, CH$_3$), 2.23 (s, 6H, CH$_3$), 1.96 (s, 6H, CH$_3$);
LRESIMS(m/z): 229.1 [M-HCl+H]$^+$; calcd. for C$_{15}$H$_{21}$N$_2$: 229.2

Synthesis of metal complexes III-15, III-16 and III-17

30 mg III-11 (0.04 mmol) and 23.6 mg III-14 (0.089 mmol) were dissolved in 20 ml CH$_2$Cl$_2$.
After a MeOH solution (2 ml) of NaOAc (66 mg, 0.8 mmol) was added, the reaction mixture was stirred overnight at r.t.. Removal of the solvent and purification on a GPC column afforded the metal complexes III-15, III-16 and III-17.

[III-14]$_2$Zn (III-15)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 6.97$ (s, 2H, meso-H), 2.22 (s, 12H, CH$_3$), 1.91 (s, 24H, CH$_3$);
MALDI-TOF: 518.4, calcd. for C$_{30}$H$_{38}$ZnN$_4$: 518.2;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 504 and 368

[III-14]$_2$[III-4]Zn$_2$ (III-16)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.56$ (s, 4H, Ar-H), 7.01 (s, 2H, meso-H), 6.64 (d, $J = 3.84$ Hz, 4H, $\beta$-dipyrrin), 6.21 (d, $J = 3.84$ Hz, 4H, $\beta$-dipyrrin), 2.24 (s, 12H, CH$_3$), 2.09 (s, 12H, CH$_3$), 1.99 (s, 12H, CH$_3$), 1.94 (s, 12H, CH$_3$);

MALDI-TOF: 998.5, calcd. for C$_{58}$H$_{62}$Zn$_2$N$_8$: 998.4;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 487 and 331

[III-14]$_2$[III-4]$_2$Zn$_3$ (III-17)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.58$ (s, 8H, Ar-H), 7.02 (s, 2H, meso-H), 6.66 (d, $J = 3.84$ Hz, 4H, $\beta$-dipyrrin), 6.70 (d, $J = 3.84$ Hz, 4H, $\beta$-dipyrrin), 6.22 (d, $J = 4.12$ Hz, 4H, $\beta$-dipyrrin), 6.27 (d, $J = 3.84$ Hz, 4H, $\beta$-dipyrrin), 2.25 (s, 12H, CH$_3$), 2.18 (s, 12H, CH$_3$), 2.10 (s, 12H, CH$_3$), 2.00 (s, 12H, CH$_3$), 1.95 (s, 12H, CH$_3$);

MALDI-TOF: 1478.4, calcd. for C$_{86}$H$_{86}$Zn$_3$N$_{12}$: 1478.5;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 486 and 331

**Synthesis of metal complexes III-18, III-19 and III-20**

30 mg **III-11** (0.04 mmol) and 50 mg **III-14** (0.12 mmol) were dissolved in 50 ml CH$_2$Cl$_2$.

After stirring at r.t. overnight, a red precipitate was formed. The solvent was removed in vacuo
to obtain a dark red solid. Half of the dark red solid was suspended in 30 ml CHCl₃, and added dropwise into a CHCl₃ solution of Zn(acac)₂ (264 mg, 1 mmol). The reaction mixture was then stirred for another 5 hours, followed by recrystallization from CH₂Cl₂/ethyl ether to afford the crude products. Purification was achieved via chromatography over GPC column to give the metal complexes III-18, III-19, III-20 and unreacted III-11.

[III-4]₂Zn₃(acac)₂ (III-18)

¹H NMR (300 MHz, CDCl₃): δ = 7.45-7.62 (m, 8H, Ar-H), 6.67 (d, J = 4.12 Hz, 4H, β-H), 6.59 (d, J = 3.84 Hz, 4H, β-H), 6.25 (t, J = 3.70 Hz, 8H, β-H), 5.55 (s, 2H, CH-acetylacetonate), 2.35 (s, 12H, CH₃-dipyrrin), 2.17 (s, 12H, CH₃-dipyrrin), 2.10 (s, 12H, CH₃-acetylacetonate);

MALDI-TOF: 1222.2, calcd. for C₆₆H₆₂Zn₃N₈O₄: 1222.3;

UV/Vis (CH₂Cl₂) λ_max nm: 487 and 329

[III-4]₃Zn₄(acac)₂ (III-19)

¹H NMR (400 MHz, CDCl₃): δ = 7.61 (br. s., 4H, Ar-H), 7.46-7.57 (m, 8H, Ar-H), 6.65-6.73 (m, 8H, β-H), 6.59 (d, J = 3.91 Hz, 4H, β-H), 6.23 - 6.31 (m, 12H, β-H), 5.55 (s, 2H, CH-acetylacetonate), 2.35 (s, 12H, CH₃-dipyrrin), 2.15-2.22 (m, 24H, CH₃-dipyrrin), 2.10 (s, 12H, CH₃-acetylacetonate);

MALDI-TOF: 1702.6, calcd. for C₉₄H₈₆Zn₄N₁₂O₄: 1702.4;

UV/Vis (CH₂Cl₂) λ_max nm: 487 and 327

[III-4]₄Zn₅(acac)₂ (III-20)

¹H NMR (300 MHz, CDCl₃): δ = 7.61 (s, 8H, Ar-H), 7.46-7.59 (m, 8H, Ar-H), 6.64-6.75 (m, 12H, β-H), 6.59 (d, J = 3.84 Hz, 4H, β-H), 6.22-6.34 (m, 16H, β-H), 5.55 (s, 2H, CH-
acetylacetonate), 2.35 (s, 12H, CH$_3$-dipyrrin), 2.14-2.25 (m, 36H, CH$_3$-dipyrrin), 2.10 (s, 12H, CH$_3$-acetylacetonate);
MALDI-TOF: 2182.7, calcd. for C$_{122}$H$_{110}$Zn$_5$N$_{16}$O$_4$: 2182.5;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 486 and 329

**Synthesis of metal complexes III-21 and III-22**

30 mg **III-11** (0.04 mmol) and 50 mg **III-14** (0.12 mmol) were dissolved in 50 ml CH$_2$Cl$_2$.
After stirring at r.t. overnight, red precipitates were formed. The solvent was removed *in vacuo* to obtain a dark red solid. Half of the dark red solid was suspended in 30 ml CHCl$_3$, and added drop-wise into a CHCl$_3$ solution of Co(acac)$_2$ (257 mg, 1 mmol). The reaction mixture was then stirred for another 5 hours, followed by purification via GPC column to give the metal complexes **III-21**, **III-22** and excess **III-10**.

**[III-4]$_2$ZnCo$_2$(acac)$_2$ (III-21)**
MALDI-TOF: 1212.2, calcd. for C$_{66}$H$_{62}$Co$_2$ZnN$_8$O$_4$: 1212.3

**[III-4]$_3$Zn$_2$Co$_2$(acac)$_2$ (III-22)**
MALDI-TOF: 1692.5, calcd. for C$_{94}$H$_{86}$Co$_2$Zn$_2$N$_{12}$O$_4$: 1692.4

13 mg III-10 (0.018 mmol) and 9.5 mg III-14 (0.036 mmol) were dissolved in 20 ml CH₂Cl₂. After a MeOH solution (2 ml) of NaOAc (30 mg, 0.36 mmol) was added, the reaction mixture was stirred overnight at r.t. Removal of the solvent and purification on a GPC column afforded the desired product III-23 (1.5 mg, 8%) and complex [III-14]₂Co.

MALDI-TOF: 988.4, calcd. for C₅₈H₆₂Co₂N₈: 988.4;
UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \) nm: 497

Synthesis of complexes III-24 and III-25

Following the same procedure for the synthesis of III-23, 1 equiv. III-21 (or III-22) and 1 equiv. III-14 was treated with 20 equiv. NaOAc. After stirring overnight at r.t., purification on a GPC column afforded the desired products III-24 and III-25, respectively, along with the side product [III-14]₂Co.


MALDI-TOF: 1468.7, calcd. for C₈₆H₈₆Co₂ZnN₁₂: 1468.5;
UV/Vis (CH₂Cl₂) \( \lambda_{\text{max}} \) nm: 493
[III-4\_2CoZn\_2[III-14\_2 \ (III-26)

MALDI-TOF: 1973.6, calcd. for C\_{86}H\_{86}CoZn\_2N\_12: 1473.5;

UV/Vis (CH\_2Cl\_2) \(\lambda_{\text{max}}\) nm: 490 and 333

[III-4\_3CoZn\_2[III-14\_2 \ (III-27)

MALDI-TOF: 1948.7, calcd. for C\_{114}H\_{110}CoZn\_2N\_16: 1948.6;

UV/Vis (CH\_2Cl\_2) \(\lambda_{\text{max}}\) nm: 492 and 318
1,3,5-Tri(4-formylphenyl)benzene (III-28)

The mixture of 1,3,5-tribromobenzene (315 mg, 1 mmol), 4-formylphenylboronic acid (495 mg, 3.3 mmol) and tetrakis(triphenylphosphine)palladium (23 mg, 0.02 mmol) were suspended in 5 ml toluene. 829 mg K$_2$CO$_3$ (6 mmol) was dissolved in 3 ml water and introduced into the suspension. The mixture was then sealed into a microwave reactor vial and irradiated to 140 °C for 30 mins. After cooling to room temperature, the mixture was diluted with CH$_2$Cl$_2$ (50 mL) and washed with water. The layers were separated and the aqueous layer was washed with CH$_2$Cl$_2$ (3 x 15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and the solvent was removed in vacuo, followed by chromatography on silica column eluting with CH$_2$Cl$_2$, to give the compound as a white powder (194 mg, 50%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ = 10.09 (s, 3H, CHO), 8.02 (d, $J$ = 8.22 Hz, 6H, Ar-H), 7.96 (s, 3H, Ar-H), 7.86-7.94 (d, $J$ = 8.22 Hz, 6H, Ar-H);

LREIMS(m/z): 390 (M$^+$), calcd. for C$_{27}$H$_{18}$O$_3$: 390.1
1,3,5-Tri[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]benzene (III-29)

Following the general procedure for the synthesis of dipyrrin with DDQ, 410 mg DDQ (1.8 mmol) was added to the solution of III-29 (450 mg, 0.55 mmol) in CH$_2$Cl$_2$ (40 mL). After stirring
overnight at r.t., a dark red solid precipitate formed. The crude product was purified by column chromatography to afford the product (330 mg, 73%).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 8.02$ (s, 3H, Ar-H), 7.86 (d, $J = 8.15$ Hz, 6H, Ar-H), 7.62 (d, $J = 8.17$ Hz, 6H, Ar-H), 6.57 (d, $J = 3.98$ Hz, 6H, $\beta$-H), 6.22 (d, $J = 4.04$ Hz, 6H, $\beta$-H), 2.47 (s, 18H, CH$_3$);  
UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm: 446 and 324

1,3,5-Tri[4-(1,9-dimethyl-BODIPY-5-yl) phenyl]benzene (III-31)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 8.00$ (s, 3H, Ar-H), 7.88 (d, $J = 8.22$ Hz, 6H, Ar-H), 7.65 (d, $J = 8.22$ Hz, 6H, Ar-H), 6.83 (d, $J = 3.91$ Hz, 6H, $\beta$-H), 6.33 (d, $J = 4.30$ Hz, 6H, $\beta$-H), 2.63 (s, 18H, CH$_3$);  
$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 158.1, 142.9, 142.6, 142.2, 134.9, 134.0, 131.7, 130.8, 127.6, 126.2, 120.1, 15.2;  
LRESIMS(m/z): 961.4 [M+H]$^+$, calcd. for C$_{57}$H$_{46}$B$_3$F$_6$N$_6$: 961.4;  
MALDI-TOF: 960.4, calcd. for C$_{57}$H$_{45}$B$_3$F$_6$N$_6$: 960.4  
UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm ($\varepsilon \times 10^4$): 512 (20.92) and 365 (5.22)
Following the same procedure for the synthesis of \textbf{III-11}, Zn(acac)$_2$ (548 mg, 2.1 mmol) and compound \textbf{III-30} (82 mg, 0.1 mmol) was dissolved in 40 ml CHCl$_3$ and was stirred for 4 hours and the solvent was removed \textit{in vacuo}. After recrystallization from CH$_2$Cl$_2$/ethyl ether to remove the excess Zn(acac)$_2$, the result product was dissolved in 20 ml CH$_2$Cl$_2$, and then treated with \textbf{II-14} (187 mg, 0.4 mmol). The mixture was stirred at r.t for overnight. The solvent was evaporated under reduced pressure and the crude product was further purified via GPC column (26 mg, 11 \%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 8.10$ (s, 3H, Ar-H), 7.91 (d, $J = 8.45$ Hz, 6H, Ar-H), 7.68 (d, $J = 8.45$ Hz, 6H, Ar-H), 7.63 (d, $J = 3.20$ Hz, 12H, Ar-H), 6.89 (d, $J = 3.88$ Hz, 6H, $\beta$-BODIPY), 6.70 (d, $J = 4.11$ Hz, 6H, $\beta$-zinc dipyrrin), 6.63 (d, $J = 4.11$ Hz, 6H, $\beta$-zinc dipyrrin), 6.37 (d, $J = 4.11$ Hz, 6H, $\beta$-BODIPY), 6.27 (d, $J = 4.11$ Hz, 12H, $\beta$-zinc dipyrrin), 2.65 (s, 18H, CH$_3$-BODIPY), 2.17 (s, 18H, CH$_3$-zinc dipyrrin), 2.16 (s, 18H, CH$_3$-zinc dipyrrin);

MALDI-TOF: 2400.3, calcd. for C$_{141}$H$_{117}$B$_3$F$_6$Zn$_3$N$_{18}$: 2400.8;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 491 and 345
5.5 Experimental data for Chapter 4

1,3-Bis(dipyrromethane-5-yl)benzene (IV-1)

Following the general procedure for the synthesis of dipyrromethanes, 1.34 g (10 mmol) isophthalaldehyde was dissolved in 25 ml of pyrrole. The mixture was degassed with argon for 10 min and treated with TFA (110 µL, 1.5 mmol, 0.15 equiv.). After stirring at room temperature 10 min, 1.0 M aq. NaOH solution (50 mL) was added to quench the reaction. The mixture was extracted with CH₂Cl₂ and dried (anhydrous Na₂SO₄). Column chromatography (silica, CH₂Cl₂) afforded an off-white solid (1.34 g, 37 %).

\(^1\)H NMR (300 MHz, CDCl₃) δ = 7.90 (br. s., 4H, NH), 7.06-7.31 (m, 4H, Ar-H), 6.64 - 6.73 (m, 4H, α-dipyrromethane), 6.10 - 6.20 (m, 4H, β-dipyrromethane), 5.89 (br. s., 4H, β-dipyrromethane), 5.42 (s, 2H, meso-H)

1,3-Bis(dipyrrinato-5-yl)benzene (IV-2)

Following the general procedure for synthesis of dipyrrins with p-chloranil, IV-1 (1.33 g, 3.64 mmol) and p-chloranil (1.79 g, 7.28 mmol) were dissolved in THF (25 mL) and stirred at r.t. for 24 hrs. The crude product was purified by column chromatography (silica, CH₂Cl₂ : CH₃OH = 100:2), which afforded a dark brown solid (0.61 g, 46%).
1H NMR (300 MHz, CDCl₃) δ = 7.71 (s, 4H, α-dipyrrin), 7.52-7.67 (m, 4H, Ar-H), 6.65 (d, J = 4.4 Hz, 4H, β-dipyrrin), 6.44 (dd, J = 1.8, 4.4 Hz, 4H, β-dipyrrin)

LRESIMS(m/z): 363.4 [M+H]⁺, calcd. for C₂₄H₁₉N₄: 363.2

1,3-Bis(dipyrrin-5-yl)-5-(hexyloxy)benzene (IV-3)

Following the general procedure for the synthesis of dipyrromethanes and dipyrrins, 0.937 g (4 mmol) 5-(hexyloxy)isophthalaldehyde (synthesized according to the procedure described in the literature¹⁷⁵) was dissolved in 20 ml of pyrrole. The mixture was degassed with argon for 10 min and treated with TFA (37 µL, 0.48 mmol, 0.12 equiv.), then stirred at room temperature 1 h. Column chromatography (silica, CH₂Cl₂) afforded the dipyrromethane (0.84 g, 45 %). The dipyrromethane and DDQ (0.899 g, 3.96 mmol) were then dissolved in THF (30 mL). After stirring at r.t. for 5 hrs, the crude product was purified by column chromatography (silica, CH₂Cl₂ : CH₃OH = 100:2), which afforded a dark brown solid (0.22 g, 26%).

¹H NMR (300 MHz, CDCl₃) δ = 7.65 (t, J = 1.37 Hz, 4H, α-dipyrrin), 7.24 (t, J = 1.60 Hz, 1H, Ar-H), 7.18 (d, J = 1.37 Hz, 2H, Ar-H), 6.70 (dd, J = 1.14, 4.34 Hz, 4H, β-dipyrrin), 6.42 (dd, J = 1.37, 4.11 Hz, 4H, β-dipyrrin), 4.03 (t, J = 6.40 Hz, 2H, OCH₂CH₂CH₂CH₂CH₂CH₃), 1.76-1.89 (m, 2H, CH₂CH₂CH₂CH₂CH₂CH₃), 1.46-1.54 (m, 2H, OCH₂CH₂CH₂CH₂CH₂CH₃), 1.30-1.42 (m, 4H, OCH₂CH₂CH₂CH₂CH₂CH₃), 0.92 (t, J = 6.85 Hz, 3H, O(CH₂)₅CH₃);

¹³C NMR (75 MHz, CD₂Cl₂) δ = 158.4, 144.4, 141.4, 138.4, 131.5, 129.3, 129.0, 125.8, 118.3, 69.1, 32.1, 29.8, 26.2, 23.2, 14.4;

LRESIMS(m/z): 463.3 [M+H]⁺;
HRESIMS: 463.2509 [M+H]^+, calcd. for C_{30}H_{31}N_{4}O: 463.2498;

UV/Vis (CH_2Cl_2) \lambda_{\text{max}} \text{nm}: 432

5-(tert-Butyl)-1,3-bis(dipyrrin-5-yl)benzene (IV-4)

Following the general procedure for the synthesis of dipyrromethanes and dipyrrins, 1.33 g (7 mmol) 5-(tert-butyl)Isophthalaldehyde (synthesized according to the procedure described in the literature\textsuperscript{176}) was dissolved in 24.2 ml of pyrrole. The mixture was degassed with argon for 10 min and treated with TFA (81 \mu L, 1.05 mmol, 0.15 equiv.), then stirred at room temperature 10 min. Column chromatography (silica, hexanes : ethyl acetate = 4:1) afforded the dipyrromethane (2.2 g, 74 %). The dipyrromethane and DDQ (2.84 g, 12.5 mmol) were then dissolved in CH_2Cl_2 (80 mL). After stirring at r.t. for 5 hrs, the crude product purified by column chromatography (Silica, CH_2Cl_2 : CH_3OH = 100:2), which afforded a dark brown solid (0.75 g, 34%).

^1H NMR (400 MHz, CD_2Cl_2) \delta: 7.65 (s, 6H, Ar-H and \alpha-dipyrrin), 7.46 (d, J = 1.24 Hz, 1H, Ar-H), 6.66 (d, J = 4.15 Hz, 4H, \beta-dipyrrin), 6.43 (d, J = 4.15 Hz, 4H, \beta-dipyrrin), 1.41 (s, 9H, CH_3);

^13C NMR (101 MHz, CD_2Cl_2) \delta: 150.6, 144.2, 142.2, 141.6, 136.9, 130.7, 129.2, 129.1, 118.2, 35.2, 31.6;

LRESIMS(m/z): 419.2 [M+H]^+, calcd. for C_{28}H_{27}N_{4}: 419.2;
Anal. Calcd. for C$_{28}$H$_{26}$N$_4$·1/2H$_2$O: C, 78.66; H, 6.37; N, 13.10. Found: C, 78.72; H, 6.33; N, 13.27.

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 430

1,3-Bis(1,9-dimethyl-dipyrromethene-5-yl)benzene (IV-5)

Following the general procedure for the synthesis of dipyrromethanes and dipyrrins, 0.94 g (7 mmol) isophthalaldehyde and 2.5 g 2-methylpyrrole (30.8 mmol) were dissolved in 50 ml CH$_2$Cl$_2$. The mixture was degassed with argon for 10 min and treated with TFA (78 µL, 1.05 mmol, 0.15 equiv.), then stirred at room temperature for 10 min. Column chromatography (silica, CH$_2$Cl$_2$) afforded the dipyrromethane (1.83 g, 61%). The dipyrromethane and DDQ (2.16 g, 9.53 mmol) were then dissolved in CH$_2$Cl$_2$ (200 mL). After stirring at r.t. for 24 h, the crude product purified by column chromatography (Silica, CH$_2$Cl$_2$: CH$_3$OH = 100:2), which afforded a dark brown solid (1.15 g, 65%).

$^1$H NMR (400MHz, CD$_2$Cl$_2$) $\delta$ = 7.57-7.46 (m, 4 H, Ar-H), 6.47 (d, $J$ = 3.8 Hz, 4 H, $\beta$-dipyrrin), 6.17 (d, $J$ = 4.1 Hz, 4 H, $\beta$-dipyrrin), 2.42 (s, 12 H, CH$_3$-dipyrrin);

$^{13}$C NMR (101MHz, CD$_2$Cl$_2$) $\delta$ = 154.5, 140.4, 137.9, 137.4, 133.3, 131.3, 129.1, 127.3, 118.1, 16.5;

LRESIMS: 419.3 [M+H]$^+$;

HRESIMS: 419.2249 [M+H]$^+$, calcd. for C$_{28}$H$_{27}$N$_4$: 419.2236;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm: 439
Synthesis of IV-6 and IV-7

Following the same procedure as for III-28, 1,3-dibromobenzene (1 equiv.), 4-formylphenylboronic acid (2.2 equiev.), tetrakis(triphenylphosphine)palladium (0.08 equiev.) and K2CO3 (5 equiv.) were heated to 140 °C for 25 mins in the microwave reactor. After the workup and chromatography on silica column eluting with CH2Cl2, 1,3-bis(4-formylphenyl)benzene was obtained as white solid. Following the general procedure for the synthesis of dipyrromethanes and dipyrrins, 1,3-bis(4-formylphenyl)benzene was then dissolved in 100 equiv. pyrrole (or dissolved in CH2Cl2 with 4.5 equiv. 2-methylpyrrole). The mixture was degassed with argon for 10 min and treated with TFA (0.15 equiv.), then stirred at room temperature. Column chromatography (silica, CH2Cl2) afforded the corresponding dipyrromethanes. The dipyrromethane and DDQ (2.5 equiv.) were then dissolved in CH2Cl2 (200 mL). After stirring at r.t. overnight, the crude product purified by column chromatography (Silica, CH2Cl2 : CH3OH = 100:2), which afforded desired dipyrrins (overall yield 28 % for IV-6, 35 % for IV-7).

1,3-Bis(4-(dipyrrin-5-yl)phenyl)benzene (IV-6)

1H NMR (300 MHz, CD2Cl2) δ = 8.01 (s, 1H, Ar-H), 7.80 (d, J = 8.22 Hz, 4H, Ar-H), 7.57-7.76 (m, 11H, Ar-H and α-dipyrrin), 6.70 (dd, J = 0.91, 4.11 Hz, 4H, β-dipyrrin), 6.44 (dd, J = 1.60, 4.34 Hz, 4H, β-dipyrrin);
LRESIMS: 515.4 [M+H]+;
HRESIMS: 515.2249 [M+H]+, calcd. for C36H27N4: 515.2236;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm: 435, 342

**1,3-Bis(4-(1,9-dimethyl-dipyrrin-5-yl)phenyl)benzene (IV-7)**

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.99 (s, 1H, Ar-H), 7.51 - 7.80 (m, 11H, Ar-H), 6.53 (d, $J$ = 4.11 Hz, 4H, $\beta$-dipyrrin), 6.20 (d, $J$ = 3.65 Hz, 4H, $\beta$-dipyrrin), 2.45 (s, 12H, CH$_3$);

LRESIMS: 571.4 [M+H]$^+$;

HRESIMS: 571.2849 [M+H]$^+$, calcd. for C$_{40}$H$_{35}$N$_4$: 571.2862;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm: 444, 326

**9-Alkylcarbazole (IV-8)**

![Chemical Structure](image)

R = nC$_4$H$_9$, CH$_2$CH$_3$ or H$_2$C

9-Alkylcarbazoles were prepared according to literature method.$^{43}$

**9-Butylcarbazole**

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 8.14 (d, $J$ = 7.85 Hz, 2H), 7.59 (d, $J$ = 8.19 Hz, 2H), 7.44 (td, $J$ = 1.37, 7.68 Hz, 2H), 7.19 (t, $J$ = 7.34 Hz, 2H), 4.38 (t, $J$ = 7.00 Hz, 2H), 1.68-1.80 (m, 2H), 1.23-1.37 (m, 2H), 0.87 (t, 3H, $J$ = 7.34 Hz);

LREIMS(m/z): 223 (M$^+$), calcd. for C$_{16}$H$_{17}$N:223.1

**9-Ethylcarbazole**

$^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 8.15 (d, $J$ = 7.85 Hz, 2H), 7.59 (d, $J$ = 8.19 Hz, 2H), 7.45 (td, $J$ = 1.02, 7.68 Hz, 2H), 7.19 (t, $J$ = 7.51 Hz, 2H), 4.43 (q, $J$ = 7.17 Hz, 2H), 1.30 (t, $J$ = 7.17 Hz, 3H);
LREIMS (m/z): 195 (M⁺), calcd. for C\textsubscript{14}H\textsubscript{13}N: 195.1

**9-Benzylcarbazole**

\(^1\)H NMR (400 MHz, DMSO-\textit{d}6) \(\delta = 8.18 \text{ (d, } J = 7.85 \text{ Hz, 2H)}, 7.63 \text{ (d, } J = 8.19 \text{ Hz, 2H)}, 7.43 \text{ (t, } J = 7.68 \text{ Hz, 2H)}, 7.13 - 7.30 \text{ (m, 7H)}, 5.66 \text{ (s, 2H)};\)

LREIMS (m/z): 257 (M⁺), calcd. for C\textsubscript{19}H\textsubscript{15}N: 257.1

**3,6-Diiodo-9-alkylcarbazole (IV-9)**

![Structure of 3,6-Diiodo-9-alkylcarbazole](image)

3,6-Diiodo-9-alkylcarbazoles were prepared according to a literature method.\(^{169}\)

**3,6-Diiodo-9-butylcarbazole**

\(^1\)H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta = 8.34 \text{ (s, 2H)}, 7.73 \text{ (d, } J = 8.77 \text{ Hz, 2H)}, 7.23 \text{ (d, } J = 8.77 \text{ Hz, 2H)}, 4.24 \text{ (t, } J = 7.02 \text{ Hz, 2H)}, 1.71-1.89 \text{ (m, 2H)}, 1.20-1.43 \text{ (m, 2H)}, 0.92 \text{ (t, } J = 7.45 \text{ Hz, 3H)};\)

LREIMS (m/z): 474.9 (M⁺);

HREIMS (m/z): 474.9302, calcd. for C\textsubscript{16}H\textsubscript{15}I\textsubscript{2}N: 474.9294

**3,6-Diiodo-9-ethylcarbazole**

\(^1\)H NMR (300 MHz, DMSO-\textit{d}6) \(\delta = 8.60 \text{ (s, 2H)}, 7.73 \text{ (d, } J = 9.65 \text{ Hz, 2H)}, 7.49 \text{ (d, } J = 8.77 \text{ Hz, 2H)}, 4.41 \text{ (q, } J = 7.02 \text{ Hz, 2H)}, 1.26 \text{ (t, } J = 7.45 \text{ Hz, 3H)};\)

LREIMS (m/z): 446.8 (M⁺);

HREIMS (m/z): 446.9302, calcd. for C\textsubscript{16}H\textsubscript{15}I\textsubscript{2}N: 446.9294

**3,6-Diiodo-9-ethylcarbazole**

\(^1\)H NMR (300 MHz, DMSO-\textit{d}6) \(\delta = 8.60 \text{ (s, 2H)}, 7.73 \text{ (d, } J = 9.65 \text{ Hz, 2H)}, 7.49 \text{ (d, } J = 8.77 \text{ Hz, 2H)}, 4.41 \text{ (q, } J = 7.02 \text{ Hz, 2H)}, 1.26 \text{ (t, } J = 7.45 \text{ Hz, 3H)};\)

LREIMS (m/z): 446.8 (M⁺);

HREIMS (m/z): 446.9302, calcd. for C\textsubscript{16}H\textsubscript{15}I\textsubscript{2}N: 446.9294
3,6-Diiodo-9-benzylcarbazole

$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta = 8.64$ (d, $J = 1.71$ Hz, 2H), 7.72 (dd, $J = 1.71, 8.53$ Hz, 2H), 7.51 (d, $J = 8.53$ Hz, 2H), 7.18 - 7.30 (m, 3H), 7.08 - 7.15 (m, 2H), 5.65 (s, 2H)

LREIMS(m/z): 509 (M$^+$), calcd. for C$_{19}$H$_{13}$I$_2$N: 508.9

3,6-Bis(4-formylphenyl)-9-alkylcarbazole (IV-10)

Following the same procedure as for III-28, 3,6-diiodo-9-alkylcarbazole (1 equiv.), 4-formylphenylboronic acid (2.2 equiv.), tetrakis(triphenylphosphine)palladium (0.08 equiv.) and K$_2$CO$_3$ (5 equiv.) were heated to 140 °C for 25 min. in the microwave reactor. After the workup and chromatography on silica column eluting with CH$_2$Cl$_2$, 3,6-bis(4-formylphenyl)-9-alkylcarbazole was obtained as a white solid (yields 50%-60%).

3,6-Bis(4-formylphenyl)-9-butylcarbazole

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 10.07$ (s, 2H, CHO), 8.83 (s, 2H, carbazole-H), 8.00-8.13 (m, 8H, Ar-H), 7.95 (d, $J = 8.77$ Hz, 2H, carbazole-H), 7.78 (d, $J = 8.77$ Hz, 2H, carbazole-H), 4.50 (t, $J = 7.02$ Hz, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.74-1.88 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.25-1.43 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 0.90 (t, $J = 7.45$ Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$)
3,6-Bis(4-formylphenyl)-9-ethylcarbazole

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ = 10.09 (s, 2H, CHO), 8.87 (s, 2H, carbazole-H), 7.99-8.11 (m, 8H, Ar-H), 7.93 (d, $J$ = 9.02 Hz, 2H, carbazole-H), 7.73 (d, $J$ = 8.70 Hz, 2H, carbazole-H), 4.48 (q, $J$ = 7.20 Hz, 2H, $\text{CH}_2\text{CH}_3$), 1.41 (t, $J$ = 7.20 Hz, 3H, $\text{CH}_2\text{CH}_3$)

3,6-Bis(4-formylphenyl)-9-benzylcarbazole

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 10.06 (s, 2H, CHO), 8.52 (s, 2H, carbazole-H), 7.86-8.09 (m, 8H, Ar-H), 7.81 (d, $J$ = 8.77 Hz, 2H, carbazole-H), 7.54 (d, $J$ = 7.89 Hz, 2H, carbazole-H), 7.13-7.38 (m, 5H, Ar-H), 5.62 (s, 2H, CH$_2$)

3,6-Bis(4-(1,9-dimethyl-dipyrrin-5-yl)phenyl)-9-butylcarbazole (IV-11)

Following the general procedure for the synthesis of dipyrromethanes, 660 mg (1.53 mmol) 3,6-bis(4-formylphenyl)-9-butylcarbazole and 558 mg (6.88 mmol) 2-methylpyrrole were dissolved in 40ml CH$_2$Cl$_2$. The mixture was degassed with argon for 10 min and treated with TFA (17 $\mu$L, 0.23 mmol, 0.15 equiv.), then stirred at room temperature for 30 min. Column chromatography (silica, CH$_2$Cl$_2$) afforded 790 mg product (72%).

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 8.37 (s, 2H, carbazole-H), 7.60-7.92 (m, 10H, NH, Ar-H and carbazole-H), 7.51 (d, $J$ = 8.22 Hz, 2H, carbazole-H), 7.35 (d, $J$ = 7.77 Hz, 4H, Ar-H), 5.78 (d, $J$ = 2.28 Hz, 8H, $\beta$-dipyrrromethane), 5.39 (s, 2H, meso-H), 4.37 (t, $J$ = 7.08 Hz, 2H,
CH₂CH₂CH₂CH₃), 2.21 (s, 12H, CH₃-dipyrromethane), 1.78-1.98 (m, 2H, CH₂CH₂CH₂CH₃), 1.34-1.48 (m, 2H, CH₂CH₂CH₂CH₃), 0.97 (t, 3H, J = 7.31 Hz, CH₂CH₂CH₂CH₃);
LRESIMS: 720.5 [M+H]⁺, calcd. for C₅₀H₅₀N₅: 720.4

3,6-Bis(4-(1,9-dimethyl-dipyrromethane-5-yl)phenyl)-9-ethylcarbazole (IV-12)
Compound IV-12 was prepared according to the procedure used for compound IV-11. IV-12 was obtained as a white solid (26 %).
¹H NMR (300 MHz, CD₂Cl₂) δ = 8.37 (s, 2H, carbazole-H), 7.61-7.87 (m, 10H, NH, Ar-H and carbazole-H), 7.52 (d, J = 8.68 Hz, 2H, carbazole-H), 7.35 (d, J = 8.22 Hz, 4H, Ar-H), 5.78 (d, J = 2.74 Hz, 8H, β-dipyrromethane), 5.39 (s, 2H, meso-H), 4.43 (q, J = 7.31 Hz, 2H, CH₂CH₃), 2.21 (s, 12H, CH₃-dipyrromethane), 1.50 - 1.55 (m, 3H, CH₂CH₃)

3,6-Bis(4-(1,9-dimethyl-dipyrromethane-5-yl)phenyl)-9-benzylcarbazole (IV-13)
Compound IV-13 was prepared according to the procedure used for compound IV-11. IV-13 was obtained as a white solid (65 %).
¹H NMR (300 MHz, CD₂Cl₂) δ = 8.40 (s, 2H, carbazole-H), 7.61-7.90 (m, 10H, NH, Ar-H and carbazole-H), 7.47 (d, J = 8.22 Hz, 2H, carbazole-H), 7.14-7.40 (m, 9H, Ar-H), 5.78 (d, J = 2.28 Hz, 8H, β-dipyrromethane), 5.58 (s, 2H, CH₂), 5.39 (s, 2H, meso-H), 2.21 (s, 12H, CH₃-dipyrromethane)
3,6-Bis(4-(1,9-dimethyl-dipyrromethene-5-yl)phenyl)-9-butylcarbazole (IV-14)

Following the general procedure for synthesis of dipyrins, DDQ (548 mg, 2.41 mmol) was added to the solution of IV-11 (790 mg, 1.10 mmol) in CH$_2$Cl$_2$ (80 mL). After stirring at r.t. for 12 hrs, the crude product purified by column chromatography (silica, CH$_2$Cl$_2$ : CH$_3$OH = 100:2), which afforded a dark brown solid (417 mg, 53 %).

$^1$H NMR (300MHz, DMSO-d$_2$) $\delta = 8.77$ (d, $J = 1.8$ Hz, 2H, carbazole-H), 8.00-7.86 (m, 6H, Ar-H and carbazole-H), 7.74 (d, $J = 8.7$ Hz, 2H, carbazole-H), 7.54 (d, $J = 8.2$ Hz, 4H, Ar-H), 6.49 (d, $J = 4.1$ Hz, 4H, $\beta$-dipyrrin), 6.25 (d, $J = 4.1$ Hz, 4H, $\beta$-dipyrrin), 4.48 (t, $J = 6.6$ Hz, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 2.41 (s, 12H, CH$_3$-dipyrrin), 1.90-1.74 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 1.44-1.27 (m, 2H, CH$_2$CH$_2$CH$_2$CH$_3$), 0.92 (t, $J = 7.3$ Hz, 3H, CH$_2$CH$_2$CH$_2$CH$_3$)

LRESIMS: 716.4 [M+H]$^+$;

HRESIMS: 716.3772 [M+H]$^+$, calcd. for C$_{50}$H$_{46}$N$_5$: 716.3772;

UV/Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm: 478

3,6-Bis(4-(1,9-dimethyl-dipyrromethene-5-yl)phenyl)-9-ethylcarbazole (IV-15)

Compound IV-15 was prepared according to the procedure used for compound IV-14, and was used for metal complexation without further purification.
3,6-Bis(4-(1,9-dimethyl-dipyrromethene-5-yl)phenyl)-9-benzylcarbazole (IV-16)

Compound IV-16 was prepared according to the procedure used for compound IV-14, and was used for metal complexation without further purification.

\[
\text{IV-17 } R = \text{H}
\]

\[
\text{IV-18 } R = \text{CH}_2\text{CH}_3
\]

\[
\text{IV-19 } R = \text{CH}_3
\]

9-Benzylcarbazole-3,6-dicarbaldehyde (IV-17)

\[n\text{-Butyllithium (4 equiv.) was added to a solution of 3,6-diiodo-9-benzylcarbazole (1 equiv.) in dry THF. The reaction mixture was stirred for 2 h at -78°C under an argon atmosphere. DMF (5 equiv.) was then added to the solution. After the mixture was stirred for 1 h and hydrolysed with 3N HCl, the reaction mixture was allowed to warm to room temperature. Recrystallization from ethanol afforded the white product.}

\[^{1}\text{H NMR (300 MHz, CDCl}_3\text{)} \delta = 10.15 \text{ (s, 2H, CHO), 8.72 (d, } J = 1.14 \text{ Hz, 2H, carbazole-H), 8.07 (dd, } J = 1.60, 8.68 \text{ Hz, 2H, carbazole-H), 7.54 (d, } J = 8.45 \text{ Hz, 2H, carbazole-H), 7.28–7.12 \text{ (m, 5H, Ar-H), 5.63 (s, 2H, CH}_2\text{);}

\text{LREIMS(m/z): 313 (M^+);}

\text{HREIMS(m/z): 313.1101, calcd. for C}_{21}\text{H}_{15}\text{O}_2\text{N: 313.1103}

9-Ethylcarbazole-3,6-dicarbaldehyde (IV-18)

Compound IV-18 was prepared according to the procedure used for compound IV-17.

\[^{1}\text{H NMR (300 MHz, DMSO-}d_6\text{)} \delta = 10.10 \text{ (s, 2H, CHO), 8.90 (s, 2H, carbazole-H), 8.08 (d, } J = 9.65 \text{ Hz, 2H, carbazole-H), 7.90 (d, } J = 7.89 \text{ Hz, 2H, carbazole-H), 4.58 (q, } J = 7.02 \text{ Hz, 2H, CH}_2\text{CH}_3\text{), 1.37 (t, } J = 7.02 \text{ Hz, 3H, CH}_2\text{CH}_3\text{);}

\]
LREIMS(m/z): 251 (M⁺), calcd. for C₁₆H₁₃O₂N: 251.1

9-Methylcarbazole-3,6-dicarbaldehyde (IV-19)

3,6-Diiodo-9-methylcarbazole was prepared according to the procedure used for IV-9. Followed the same procedure as for IV-17, IV-19 was obtained as a white powder.

1H NMR (300 MHz, CD₂Cl₂) δ = 10.10 (s, 2H, CHO), 8.61 (s, 2H, carbazole-H), 8.06 (d, J = 8.77 Hz, 2H, carbazole-H), 7.54 (d, J = 8.77 Hz, 2H, carbazole-H), 3.90 (s, 3H, CH₃);
13C NMR (101MHz, CD₂Cl₂) δ = 191.8, 145.8, 130.3, 128.3, 124.3, 123.6, 110.2, 30.3;
Anal. Calcd. for C₁₅H₁₁NO₂, C: 75.94; H: 4.67; N: 5.90. Found, C: 76.32; H: 5.15; N: 5.70;
LREIMS(m/z): 237 (M⁺);
HREIMS(m/z): 237.0785, calcd. for C₁₅H₁₁O₂N: 237.0790

3,6-Bis(1,9-dimethyl-dipyrromethane-5-yl)-9-benzylcarbazole (IV-20)

Following the general procedure for the synthesis of dipyrromethane, 724 mg IV-17 (2.31 mmol) and 844 mg 2-methylpyrrole (10.4 mmol) were dissolved in 40ml CH₂Cl₂. The mixture was degassed with argon for 10 min and treated with TFA (26 µL, 0.35 mmol, 0.15 equiv.), then stirred at room temperature for 2 h. Column chromatography (silica, CH₂Cl₂) afforded the product (514 mg, 37 %).
$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.93 (s, 2H, 4,5-carbazole), 7.74 (br. s., 4H, NH), 7.10-7.39 (m, 9H, 1,2,7,8-carbazole and Ar-H), 5.75 (d, $J$ = 2.74 Hz, 8H, $\beta$-dipyrromethane), 5.50 (s, 2H, CH$_2$), 5.48 (s, 2H, meso-H), 2.18 (s, 12H, CH$_3$); LRESIMS: 602.5 [M+H]$^+$, calcd. for C$_{41}$H$_{40}$N$_5$: 602.3

3,6-Bis(1,9-dimethyl-dipyrromethane-5-yl)-9-ethylcarbazole (IV-21)

Compound IV-21 was prepared according to the procedure used for compound IV-20. IV-21 was obtained at 51 % yield.

$^1$H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ = 7.90 (s, 2H, 4,5-carbazole), 7.75 (br. s., 4H, NH), 7.22-7.47 (m, 4H, 1,2,7,8-carbazole), 5.75 (d, $J$ = 2.28 Hz, 8H, $\beta$-dipyrromethane), 5.48 (s, 2H, meso-H), 4.36 (q, $J$ = 7.31 Hz, 2H, CH$_2$CH$_3$), 2.18 (s, 12H, CH$_3$-dipyrromethane), 1.40 (t, $J$ = 7.08 Hz, 3H, CH$_2$CH$_3$)

3,6-Bis(1,9-dimethyl-dipyrromethane-5-yl)-9-methylcarbazole (IV-22)

Compound IV-22 was prepared according to the procedure used for compound IV-20. IV-22 was obtained at 45 % yield.

$^1$H NMR (400MHz, CD$_2$Cl$_2$) $\delta$ = 7.90 (s, 2H, 4,5-carbazole), 7.74 (br. s., 4H, NH), 7.37 (s, 4H, 1,2,7,8-carbazole), 5.81-5.65 (m, 8H, $\beta$-dipyrromethane), 5.48 (s, 2H, meso-H), 3.83 (s, 3H, CH$_3$-carbazole), 2.18 (s, 12H, CH$_3$-dipyrromethane); $^{13}$C NMR (101MHz, CD$_2$Cl$_2$) $\delta$ = 141.1, 134.1, 132.7, 127.5, 126.9, 123.2, 120.3, 109.2, 107.4, 106.3, 44.8, 29.8, 13.3; HREIMS(m/z): 525.2896 (M$^+$), calcd. for C$_{35}$H$_{35}$N$_5$:525.2893
3,6-Bis(1,9-dimethyl-dipyrrin-5-yl)-9-benzylcarbazole (IV-23)

Following the general procedure for synthesis of dipyrins, DDQ (415 mg, 1.83 mmol) was added to the solution of IV-20 (500 mg, 0.83 mmol) in CH₂Cl₂ (50 mL). After stirring at r.t. for 12 hrs, the crude product purified by column chromatography (silica, CH₂Cl₂ : CH₃OH = 100:2), which afforded a dark brown solid (331 mg, 67 %).

¹H NMR (300 MHz, CD₂Cl₂) δ = 8.20 (s, 2H, 4,5-carbazole), 7.53-7.62 (m, 2H, H-carbazole), 7.44 - 7.52 (m, 2H, H-carbazole), 7.24 - 7.38 (m, 5H, Ar-H), 6.49 (d, J = 3.65 Hz, 4H, β-dipyrrin), 6.16 (d, J = 4.11 Hz, 4H, β-dipyrrin), 5.63 (s, 2H, CH₂), 2.43 (s, 12H, CH₃-dipyrrin); LRESIMS: 598.3 [M+H]+;
HRESIMS: 598.2986 [M+H]+, calcd. for C₄₁H₃₆N₅: 598.2971

3,6-Bis(1,9-dimethyl-dipyrromethene-5-yl)-9-ethylcarbazole (IV-24)

Compound IV-24 was prepared according to the procedure used for compound IV-23. IV-24 was obtained at 53 % yield.

¹H NMR (400MHz, CD₂Cl₂) δ = 8.18 (s, 2H, 4,5-carbazole), 7.62 (dd, J = 1.5, 8.4 Hz, 2H, H-carbazole), 7.52 (d, J = 8.5 Hz, 2H, H-carbazole), 6.51 (d, J = 4.1 Hz, 4H, β-dipyrrin), 6.17 (d, J = 4.1 Hz, 4H, β-dipyrrin), 4.49 (q, J = 7.2 Hz, 2H, CH₂CH₃), 2.45 (s, 12H, CH₃-dipyrrin), 1.54 (t, J = 7.2 Hz, 3H, CH₂CH₃);
¹³C NMR (101MHz, CD₂Cl₂) δ = 153.9, 141.2, 140.9, 139.8, 129.8, 129.6, 129.1, 123.8, 122.7, 117.8, 108.3, 38.6, 16.5, 14.3;
LRESIMS: 536.4 [M+H]^+;
HRESIMS: 536.2820 [M+H]^+, calcd. for C_{36}H_{34}N_{5}: 536.2814;
UV/Vis (CH_{2}Cl_{2}) \lambda_{max} \text{nm}: 445

3,6-Bis(1,9-dimethyl-dipyrrromethene-5-yl)-9-methylcarbazole (IV-25)

Compound IV-25 was prepared according to the procedure used for compound IV-23. IV-25 was obtained at 65 % yield.

$^1$H NMR (300 MHz, CD_{2}Cl_{2}): \delta = 8.18 (d, 2H, J=1.4 \text{ Hz}, 4,5-carbazole), 7.63 (dd, J=8.9, 1.38 Hz, 2H, 2,7-carbazole), 7.51 (d, J=8.7 Hz, 2H, 1,8-carbazole), 6.49 (d, J=4.1 Hz, 4H, \beta-dipyrrin), 6.17 (d, J=4.1 Hz, 4H, \beta-dipyrrin), 3.97 (s, 3H, CH_{3}-carbazole), 2.45 (s, 12H, CH_{3}-dipyrrin);

$^{13}$C NMR (75MHz, CD_{2}Cl_{2}) \delta = 153.4, 141.8, 140.5, 139.3, 129.4, 129.1, 128.7, 123.2, 122.1, 117.4, 107.8, 29.5, 16.1;
LRESIMS: 522.2 [M+H]^+;
HRESIMS: 522.2651 [M+H]^+, calcd. for C_{35}H_{32}N_{5}: 522.2658

Synthesis of macrocycles IV-26, IV-27 and IV-28

A solution (CH_{2}Cl_{2}) of ligand IV-25 (80 mg, 0.153mmol) was treated with a solution (CH_{3}OH) of Co(OAc)$_2$\cdot4H_{2}O (57.3 mg, 0.23mmol). The reaction mixture was stirred overnight at room
temperature. Removal of the solvent and purification on a flash silica column afforded the crude metal complex mixture. The mixture was further purified on a GPC column. IV-26, IV-27 and IV-28 were isolated as red solids from the fourth, the third and the second fractions of the column, respectively (IV-26: 10.1 mg, 11 %; IV-27: 2.0 mg, 2.3 %; IV-28: 11.0 mg, 12 %).

[IV-25]$_3$Co$_3$ (IV-26)
MALDI-TOF: 1734.5, calcd. for C$_{105}$H$_{87}$Co$_3$N$_{15}$: 1734.5;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 493 (9.27)

[IV-25]$_4$Co$_4$ (IV-27)
MALDI-TOF: 2312.8, calcd. for C$_{140}$H$_{116}$Co$_4$N$_{20}$: 2312.7;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 495 (23.2)

[IV-25]$_5$Co$_5$ (IV-28)
MALDI-TOF: 2890.7, calcd. for C$_{175}$H$_{145}$Co$_5$N$_{25}$: 2890.9;
UV/Vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ nm ($\varepsilon \times 10^4$): 496 (41.5)

3,6-Dimethyl-9H-carbazole (IV-29)

![3,6-Dimethyl-9H-carbazole](image)

IV-29 was prepared according to a literature method.$^{171}$

$^1$H NMR (300MHz, CD$_2$Cl$_2$) $\delta = 7.95$ (br. s., 1H, NH), 7.87-7.82 (m, 2H, 4,5-carbazole), 7.32 (d, $J = 8.5$ Hz, 2H, 1,8-carbazole), 7.23 (dd, $J = 1.3$, 8.3 Hz, 2H, 2,7-carbazole), 2.52 (s, 6H, CH$_3$);
$^{13}$C NMR (75MHz, CD$_2$Cl$_2$) $\delta$ = 138.7, 129.1, 127.6, 123.8, 120.5, 110.8, 21.7;

LREIMS: 195.1 (M$^+$);

HREIMS: 195.10479 (M$^+$), calcd. for C$_{14}$H$_{13}$N: 195.10480

1,8-Dibromo-3,6-dimethyl-9H-carbazole (IV-30)

IV-30 was prepared according to a literature method.$^{171}$

$^1$H NMR (300MHz, CD$_2$Cl$_2$) $\delta$ = 8.10 (br. s., 1H, NH), 7.67 (s, 2H, 4,5-carbazole), 7.40 (s, 2H, 2,7-carbazole), 2.48 (s, 6H, CH$_3$);

$^{13}$C NMR (75MHz, CD$_2$Cl$_2$) $\delta$ = 136.8, 131.5, 130.2, 125.2, 120.2, 104.3, 21.5;

LREIMS: 352.9 (M$^+$);

HREIMS: 352.92360 (M$^+$), calcd. for C$_{14}$H$_{11}$NBr$_2$: 352.92378

1,8-Diformayl-3,6-dimethyl-9H-carbazole (IV-31)

IV-31 was prepared according to a literature method.$^{171}$

$^1$H NMR (400MHz, CD$_2$Cl$_2$) $\delta$ = 11.20 (br. s., 1H, NH), 10.10 (s, 2H, CHO), 8.00 (s, 2H, 4,5-carbazole), 7.62 (s, 2H, 2,7-carbazole), 2.56 (s, 6H, CH$_3$);

$^{13}$C NMR (101MHz, CD$_2$Cl$_2$) $\delta$ = 193.3, 137.2, 133.2, 130.0, 127.5, 123.8, 120.5, 21.4;

LREIMS: 251.1 (M$^+$);

HREIMS: 251.09450 (M$^+$), calcd. for C$_{16}$H$_{13}$NO$_2$: 251.09463
1,8-Bis(1,9-dimethyl-dipyrromethane-5-yl)-3,6-dimethyl-9H-carbazole (IV-32)

Following the general procedure for the synthesis of dipyrromethanes, 315 mg IV-31 (1.25 mmol) and 447 mg 2-methylpyrrole (5.52 mmol) were dissolved in 30 ml CH₂Cl₂. The mixture was degassed with argon for 10 min and treated with TFA (14 µl, 0.19 mmol, 0.15 equiv.), then stirred at room temperature for 2 h. Column chromatography (silica, CH₂Cl₂ : hexanes = 3:1) afforded the product (480 mg, 71%).

¹H NMR (400MHz, CD₂Cl₂) δ = 7.81 (s, 1H, NH-carbazole), 7.75 (s, 2H, 4,5-carbazole), 7.71 (br. s., 4H, NH-dipyrromethane), 7.02 (s, 2H, 2,7-carbazole), 5.78 (s, 4H, β-dipyrromethane), 5.77 (s, 4H, β-dipyrromethane), 5.40 (s, 2H, meso-H), 2.48 (s, 6H, CH₃-carbazole), 2.17 (s, 12H, CH₃-dipyrromethane);

¹³C NMR (101MHz, CD₂Cl₂) δ = 137.1, 130.4, 129.4, 128.0, 127.4, 125.4, 124.7, 119.3, 107.6, 106.5, 42.2, 21.7, 13.4;

HREIMS: 539.30484 (M⁺), calcd. for C₃₆H₃₇N₅: 539.30490

1,8-Bis(1,9-dimethyl-dipyrrin-5-yl)-3,6-dimethyl-9H-carbazole (IV-33)

Following the general procedure for synthesis of dipyrrins, DDQ (426 mg, 1.88 mmol) was added to a solution of IV-32 (460 mg, 0.85 mmol) in CH₂Cl₂ (60 mL). After stirring at r.t. for 3
hrs, the crude product was purified by column chromatography (silica, CH₂Cl₂ : CH₃OH = 100:2), which afforded the desired product (323 mg, 71 %).

¹H NMR (300MHz, CD₂Cl₂) δ = 7.94 (d, J = 0.7 Hz, 2H, 4,5-carbazole), 7.82 (br. s., 1H, NH), 7.23 (d, J = 0.9 Hz, 2H, 2,7-carbazole), 6.31 (d, J = 4.1 Hz, 4H, β-dipyrrin), 6.04 (d, J = 4.1 Hz, 4H, β-dipyrrin), 2.56 (s, 6H, CH₃-carbazole), 2.39 (s, 12H, CH₃-dipyrrin);

¹³C NMR (75MHz, CD₂Cl₂) δ = 154.5, 139.9, 137.8, 134.4, 130.2, 128.8, 126.0, 123.8, 120.9, 120.7, 118.3, 21.6, 16.5;

ESIMS: 536.5 [M+H]^⁺;

HRESIMS: 536.2808 [M+H]^⁺, calcd. for C₃₆H₃₄N₅: 536.2814;

UV/Vis (CH₂Cl₂) λ_max nm (ε × 10⁻⁴): 437 (3.81)

**Synthesis of macrocycles IV-34 and IV-35**

A solution (CH₂Cl₂) of ligand IV-33 (1 equiv.) was treated with a solution of M(OAc)₂·4H₂O (1.5 equiv.) in CH₃OH. The reaction mixture was stirred overnight at room temperature. Removal of the solvent and purification on a flash silica column afforded the crude metal complex mixture. The mixture was further purified on a GPC column. The desired dimeric complex was isolated as a red powder from the second fraction of the column (14 % for IV-34 and 13 % for IV-35).
[IV-33]_2Co_2 (IV-34)

MALDI-TOF: 1184.6, calcd. for C_{72}H_{62}Co_{2}N_{10}: 1184.4;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm}: 522 and 485

[IV-33]_2Zn_2 (IV-35)

^1_H NMR (major product) (400 MHz, CDCl_3) \delta = 7.97 (s, 4H, carbazole), 7.58(s, 2H, NH), 7.43 (s, 4H, carbazole), 6.89 (d, J = 3.75 Hz, 4H, \beta-dipyrrin), 6.47 (d, J = 4.10 Hz, 4H, \beta-dipyrrin), 6.25 (d, J = 3.75 Hz, 4H, \beta-dipyrrin), 5.95 (d, J = 4.10 Hz, 4H, \beta-dipyrrin), 2.61 (s, 12H, CH_3-carbazole), 2.30 (s, 12H, CH_3-dipyrrin), 1.41 (s, 12H, CH_3-dipyrrin);

MALDI-TOF: 1194.6, calcd. for C_{72}H_{62}Co_{2}N_{10}: 1194.4;

UV/Vis (CH_{2}Cl_{2}) \lambda_{\text{max}} \text{nm (\varepsilon \times 10^{-4})}: 529 (2.88), 464 (5.02) and 309 (0.94)

[IV-33]_2[III-4]_2Zn_4 (IV-36)

Compound IV-33 (25 mg, 0.047 mmol) and III-11 (35 mg, 0.047 mmol) were dissolved in 30 ml solvent (CH_{2}Cl_{2} : CH_{3}OH = 1:1) and stirred at r.t. overnight. Removal of the solvent and purification on a basic alumina column afforded the crude metal complex mixture. The mixture was further purified on a GPC column. IV-35 and IV-36 were isolated as red solids from the third and the second fractions of the column, respectively (IV-35: 6 mg, 21 %; IV-36: 4 mg, 7.9 %).
Synthesis of asymmetric bis(dipyrrin) ligands IV-37, IV-38 and IV-39

Following the general procedure for the synthesis of dipyrromethanes and dipyrrins, 1 equiv. IV-19 and 3 equiv. 2-arylpurrole (the 2-arylpurrole was prepared according to a literature method\textsuperscript{177, 178}) were dissolved in CH\textsubscript{2}Cl\textsubscript{2}. The mixture was degassed with argon for 10 min and treated with TFA (0.15 equiv.), then stirred at room temperature for 5 h. Workup was done as before followed by the addition of 1.5 equiv. DDQ. After stirring at r.t. for 2 h, the solvent was removed and column chromatography gave the 3-(1,9-diaryl-dipyrrin-5-yl)-6-formyl-9-methylcarbazole as product, which was then dissolved in CH\textsubscript{2}Cl\textsubscript{2}. 2-methylpurrole and TFA were introduced into the solution. The reaction mixture was stirred at r.t. for 2 hrs, followed by the addition of DDQ. Workup and column chromatography gave the final product 3-(1,9-diaryl-dipyrrin-5-yl)-6-(1,9-dimethyl-dipyrrin-5-yl)-9-methylcarbazoles IV-37, IV-38 and IV-39.
3-[1,9-Bis(4-acetylphenyl)-dipyrin-5-yl]-6-(1,9-dimethyl-dipyrin-5-yl)-9-ethylcarbazole
(IV-37)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 8.31$ (s, 1H, carbazole-H), 8.22 (s, 1H, carbazole-H), 8.11 (d, $J = 8.53$ Hz, 4H, Ar-H), 8.04 (d, $J = 8.53$ Hz, 4H, Ar-H), 7.75 (dd, $J = 1.37$, 8.19 Hz, 1H, carbazole-H), 7.66 (dd, $J = 1.54$, 8.36 Hz, 1H, carbazole-H), 7.51-7.63 (m, 2H, carbazole-H), 6.98 (d, $J = 4.10$ Hz, 2H, $\beta$-dipyrrin), 6.84 (d, $J = 4.44$ Hz, 2H, $\beta$-dipyrrin), 6.52 (br. s., 2H, $\beta$-dipyrrin), 6.21 (br. s., 2H, $\beta$-dipyrrin), 4.01 (s, 3H, CH$_3$-carbazole), 2.66 (s, 6H, COCH$_3$), 2.48 (br. s., 6H, CH$_3$-dipyrrin);

ESIMS: 730.6 [M+H]$^+$;

HRESIMS: 730.3201 [M+H]$^+$, calcd. for C$_{49}$H$_{40}$N$_5$O$_2$: 730.3182

3-[1,9-Bis(4-fluorophenyl)-dipyrin-5-yl]-6-(1,9-dimethyl-dipyrin-5-yl)-9-ethylcarbazole
(IV-38)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta = 8.29$ (d, $J = 1.37$ Hz, 1H, carbazole-H), 8.22 (d, $J = 1.37$ Hz, 1H, carbazole-H), 7.86-7.96 (m, 4H, Ar-H), 7.73 (dd, $J = 1.71$, 8.19 Hz, 1H, carbazole-H), 7.65 (dd, $J = 1.71$, 8.53 Hz, 1H, carbazole-H), 7.54 (d, $J = 8.53$ Hz, 1H, carbazole-H), 7.57 (d, $J = 8.19$ Hz, 1H, carbazole-H), 7.16-7.26 (m, 4H, Ar-H), 6.80-6.86 (d, $J = 4.44$ Hz, 2H, $\beta$-dipyrrin), 6.74-6.80 (d, $J = 4.44$ Hz, 2H, $\beta$-dipyrrin), 6.50 (d, $J = 4.10$ Hz, 2H, $\beta$-dipyrrin), 6.18 (d, $J = 4.10$ Hz, 2H, $\beta$-dipyrrin), 3.99 (s, 3H, CH$_3$-carbazole), 2.45 (s, 6H, CH$_3$-dipyrrin);

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta = 164.9$, 162.4, 154.0, 153.1, 142.9, 142.6, 142.4, 141.6, 130.9, 130.3, 130.3, 130.0, 129.4, 128.7, 128.5, 128.4, 123.9, 123.7, 122.8, 122.5, 117.9, 116.7, 116.5, 115.8, 108.6, 108.4, 30.0, 16.5
3-[1,9-Bis(4-tolyl)-dipyrrin-5-yl]-6-(1,9-dimethyl-dipyrrin-5-yl)-9-methylcarbazole (IV-39)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ = 8.30 (d, $J = 1.37$ Hz, 1H, carbazole-H), 8.22 (d, $J = 1.02$ Hz, 1H, carbazole-H), 7.86 (d, $J = 8.19$ Hz, 4H, Ar-H), 7.74 (dd, $J = 1.37$, 8.53 Hz, 1H, carbazole-H), 7.64 (dd, $J = 1.54$, 8.36 Hz, 1H, carbazole-H), 7.57 (d, $J = 8.53$ Hz, 1H, carbazole-H), 7.54 (d, $J = 8.53$ Hz, 1H, carbazole-H), 7.34 (d, $J = 7.85$ Hz, 4H, Ar-H), 6.85 (d, $J = 4.10$ Hz, 2H, $\beta$-dipyrrin), 6.75 (d, $J = 4.44$ Hz, 2H, $\beta$-dipyrrin), 6.53 (d, $J = 3.75$ Hz, 2H, $\beta$-dipyrrin), 6.20 (d, $J = 4.10$ Hz, 2H, $\beta$-dipyrrin), 4.00 (s, 3H CH$_3$-carbazole), 2.48 (s, 6H, CH$_3$-Ar), 2.44 (s, 6H, CH$_3$-dipyrrin);

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$) $\delta$ = 154.3, 154.1, 142.8, 142.6, 142.5, 140.8, 139.6, 131.1, 130.5, 130.3, 130.2, 130.1, 129.3, 129.0, 126.6, 124.0, 123.9, 122.7, 122.6, 117.8, 115.7, 108.6, 108.4, 30.0, 21.7, 16.3;

ESIMS: 674.7 [M+H]$^+$;

HRESIMS: 674.3266 [M+H]$^+$, calcd. for C$_{47}$H$_{40}$N$_5$: 674.3284
### 5.6 Detailed crystal data

#### Table 5.1 X-ray crystal structure details for II-6

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<td>Formula Weight</td>
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<td>Crystal Dimensions</td>
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<td>Crystal System</td>
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<td>Lattice Parameters</td>
<td>$a = 22.619(2)$ Å, $b = 13.246(1)$ Å, $c = 19.252(1)$ Å, $\alpha = 90.0^\circ$, $\beta = 97.125(3)^\circ$, $\gamma = 90.0^\circ$</td>
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<td>Reflection/Parameter Ratio</td>
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Table 5.2 X-ray crystal structure details for II-12

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<td>Crystal Dimensions</td>
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<td>Crystal System</td>
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<td>Lattice Parameters</td>
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<td>( a )</td>
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<td>( b )</td>
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<td>( c )</td>
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<td>( \beta )</td>
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<td>( \gamma )</td>
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<td>( V )</td>
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<td>( C 2/c ) (#15)</td>
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Table 5.3 X-ray crystal structure details for II-15

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<td>Crystal Dimensions</td>
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<td>Temperature</td>
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<td>Lattice Parameters</td>
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<td>b = 8.569(2) Å</td>
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<td></td>
<td>c = 27.299(6) Å</td>
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<td></td>
<td>α = 90.0°</td>
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<td>β = 90.0°</td>
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<td>Property</td>
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### Table 5.5 X-ray crystal structure details for II-17

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<td>Crystal System</td>
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<td>Lattice Parameters</td>
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<td>b = 8.5705(7) Å</td>
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<td>c = 27.197(2) Å</td>
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<td>β = 90.0°</td>
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<td>γ = 90.0°</td>
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Table 5.6 X-ray crystal structure details for II-18

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<tr>
<td>Crystal System</td>
<td>triclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>a = 10.840(1) Å</td>
</tr>
<tr>
<td></td>
<td>b = 14.501(2) Å</td>
</tr>
<tr>
<td></td>
<td>c = 19.830(2) Å</td>
</tr>
<tr>
<td></td>
<td>α = 109.761(6)°</td>
</tr>
<tr>
<td></td>
<td>β = 104.839(6)°</td>
</tr>
<tr>
<td></td>
<td>γ = 93.027(6)°</td>
</tr>
<tr>
<td></td>
<td>V = 2802.2(5) Å³</td>
</tr>
<tr>
<td>Space Group</td>
<td>P -1 (#2)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.455 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>1260.00</td>
</tr>
<tr>
<td>$\mu$(MoKα)</td>
<td>6.93 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 30194</td>
</tr>
<tr>
<td></td>
<td>Unique: 9772 (R$_{\text{int}}$ = 0.045)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00σ(I))</td>
<td>9772</td>
</tr>
<tr>
<td>No. Variables</td>
<td>720</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>13.57</td>
</tr>
<tr>
<td>Residuals (refined on $F^2$, all data): R1; wR2</td>
<td>0.128; 0.230</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.04</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00σ(I))</td>
<td>4940</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.075; 0.204</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0084 Å</td>
</tr>
</tbody>
</table>
Table 5.7 X-ray crystal structure details for II-19

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>$C_{58}H_{52}B_2N_8F_4Cl_4Co$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1159.43</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>$0.05 \times 0.25 \times 0.30 \text{ mm}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>$10.669(1) \text{ Å}$</td>
</tr>
<tr>
<td>b</td>
<td>$14.432(2) \text{ Å}$</td>
</tr>
<tr>
<td>c</td>
<td>$19.145(2) \text{ Å}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$70.375(4)^\circ$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$78.215(4)^\circ$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$86.892(4)^\circ$</td>
</tr>
<tr>
<td>$V$</td>
<td>$2717.8(5) \text{ Å}^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P \text{-1} \ (#2)$</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.418 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>1194.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>5.74 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 58453</td>
</tr>
<tr>
<td></td>
<td>Unique: 10121 ($R_{\text{int}} = 0.062$)</td>
</tr>
<tr>
<td>No. Observations ($I&gt;0.00\sigma(I)$)</td>
<td>10121</td>
</tr>
<tr>
<td>No. Variables</td>
<td>704</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>14.38</td>
</tr>
<tr>
<td>Residuals (refined on $F^2$, all data): R1; wR2</td>
<td>0.121; 0.169</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>0.99</td>
</tr>
<tr>
<td>No. Observations ($I&gt;2.00\sigma(I)$)</td>
<td>6424</td>
</tr>
<tr>
<td>Residuals (refined on $F$): R1; wR2</td>
<td>0.061; 0.144</td>
</tr>
<tr>
<td>Bond precision</td>
<td>$\text{C-C} = 0.0080 \text{ Å}$</td>
</tr>
</tbody>
</table>
Table 5.8 X-ray crystal structure details for II-20

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>( \text{C}<em>{58}\text{H}</em>{52}\text{B}<em>{2}\text{N}</em>{8}\text{F}<em>{4}\text{ZnCl}</em>{4} )</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1165.87</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>( 0.05 \times 0.12 \times 0.35 \text{ mm} )</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>( \begin{align*} a &amp;= 10.7063(11) \text{ Å} \ b &amp;= 14.4785(12) \text{ Å} \ c &amp;= 19.1263(18) \text{ Å} \ \alpha &amp;= 70.425(4) ^\circ \ \beta &amp;= 78.184(4) ^\circ \ \gamma &amp;= 86.994(4) ^\circ \ V &amp;= 6037(3) \text{ Å}^3 \end{align*} )</td>
</tr>
<tr>
<td>Space Group</td>
<td>( P - 1 ) (#2)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>( D_{\text{calc}} )</td>
<td>1.416 g/cm(^3)</td>
</tr>
<tr>
<td>( F_{000} )</td>
<td>1200.00</td>
</tr>
<tr>
<td>( \mu(\text{MoK}\alpha) )</td>
<td>7.06 cm(^{-1})</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 21133</td>
</tr>
<tr>
<td></td>
<td>Unique: 18068 (( R_{\text{int}} = 0.046 ))</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00( \sigma )(I))</td>
<td>18068</td>
</tr>
<tr>
<td>No. Variables</td>
<td>703</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>25.70</td>
</tr>
<tr>
<td>Residuals (refined on ( F^2 ), all data): R1; wR2</td>
<td>0.132; 0.175</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>0.96</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00( \sigma )(I))</td>
<td>10208</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.066; 0.148</td>
</tr>
<tr>
<td>Bond precision</td>
<td>( \text{C-C} = 0.0056 \text{ Å} )</td>
</tr>
</tbody>
</table>
Table 5.9 X-ray crystal structure details for II-21

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>$\text{C}<em>{81}\text{H}</em>{66}\text{B}<em>{3}\text{N}</em>{12}\text{F}<em>{6}\text{FeCl}</em>{6}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1622.44</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>$0.25 \times 0.25 \times 0.30$ mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>trigonal</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>$a = 26.174(4)$ Å</td>
</tr>
<tr>
<td></td>
<td>$b = 26.174$ Å</td>
</tr>
<tr>
<td></td>
<td>$c = 18.629(3)$ Å</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 90.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 1290.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$V = 11052(2)$ Å$^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$R - 3$ (#148)</td>
</tr>
<tr>
<td>Z value</td>
<td>6</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.463 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>4998.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>4.94 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 66457</td>
</tr>
<tr>
<td></td>
<td>Unique: 6075 (R$_{int} = 0.035$)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00$\sigma$(I))</td>
<td>6075</td>
</tr>
<tr>
<td>No. Variables</td>
<td>349</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>17.41</td>
</tr>
<tr>
<td>Residuals (refined on F$^2$, all data): R1; wR2</td>
<td>0.076; 0.189</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.04</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00$\sigma$(I))</td>
<td>4940</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.065; 0.181</td>
</tr>
<tr>
<td>Bond precision</td>
<td>$\text{C-C} = 0.0047$ Å</td>
</tr>
</tbody>
</table>
Table 5.10 X-ray crystal structure details for II-22

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>$\text{C}<em>{84}\text{H}</em>{78}\text{B}<em>{3}\text{N}</em>{12}\text{O}<em>{3}\text{F}</em>{6}\text{Cl}_{6}\text{Co}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1721.64</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>$0.15 \times 0.20 \times 0.25 \text{ mm}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>trigonal</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>$a = 26.493(1) \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$b = 26.493 \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$c = 18.6511(9) \text{ Å}$</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 90.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 120.0^\circ$</td>
</tr>
<tr>
<td></td>
<td>$V = 11337.0(7) \text{ Å}^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$R - 3$ (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>6</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.513 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>5328.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>5.16 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 46061</td>
</tr>
<tr>
<td></td>
<td>Unique: 4484 ($R_{int} = 0.061$)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00$\sigma$(I))</td>
<td>4484</td>
</tr>
<tr>
<td>No. Variables</td>
<td>361</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>12.42</td>
</tr>
<tr>
<td>Residuals (refined on F$^2$, all data): R1; wR2</td>
<td>0.108; 0.203</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.03</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00$\sigma$(I))</td>
<td>3622</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.075; 0.181</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0033 Å</td>
</tr>
</tbody>
</table>
Table 5.11 X-ray crystal structure details for III-5

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C_{86}H_{74}B_{2}F_{4}N_{12}Cl_{6}Co_{2}</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1703.75</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.05 \times 0.10 \times 0.40 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>a = 13.4104(15) Å</td>
</tr>
<tr>
<td></td>
<td>b = 26.078(2) Å</td>
</tr>
<tr>
<td></td>
<td>c = 12.7437(14) Å</td>
</tr>
<tr>
<td></td>
<td>\alpha = 90.0°</td>
</tr>
<tr>
<td></td>
<td>\beta = 115.666(5)°</td>
</tr>
<tr>
<td></td>
<td>\gamma = 90.0°</td>
</tr>
<tr>
<td></td>
<td>V = 4017.0(7) Å³</td>
</tr>
<tr>
<td>Space Group</td>
<td>P 2₁/c (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>D_{calc}</td>
<td>1.409 g/cm³</td>
</tr>
<tr>
<td>F₀₀₀</td>
<td>1752.00</td>
</tr>
<tr>
<td>\mu(MoK\alpha)</td>
<td>6.76 cm⁻¹</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 30263</td>
</tr>
<tr>
<td></td>
<td>Unique: 7078 (R_{int} = 0.054)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00\sigma(I))</td>
<td>7078</td>
</tr>
<tr>
<td>No. Variables</td>
<td>518</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>13.66</td>
</tr>
<tr>
<td>Residuals (refined on F^2, all data): R1; wR2</td>
<td>0.097; 0.173</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.03</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00\sigma(I))</td>
<td>4797</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.059; 0.150</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0063 Å</td>
</tr>
</tbody>
</table>
Table 5.12 X-ray crystal structure details for III-11

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{38}$H$</em>{38}$N$_4$O$_4$Zn$_2$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>745.46</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.05 × 0.07 × 0.40 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>a = 6.7984(2) Å</td>
</tr>
<tr>
<td></td>
<td>b = 24.1679(10) Å</td>
</tr>
<tr>
<td></td>
<td>c = 11.1714(5) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90 °</td>
</tr>
<tr>
<td></td>
<td>β = 100.323(1) °</td>
</tr>
<tr>
<td></td>
<td>γ = 90 °</td>
</tr>
<tr>
<td></td>
<td>V = 1805.78(12) Å</td>
</tr>
<tr>
<td>Space Group</td>
<td>P 2$_1$/c (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>D$_{calc}$</td>
<td>1.371 g/cm$^3$</td>
</tr>
<tr>
<td>F$_{000}$</td>
<td>772.00</td>
</tr>
<tr>
<td>μ(MoKα)</td>
<td>13.71 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 13826</td>
</tr>
<tr>
<td></td>
<td>Unique: 3615(R$_{int}$ = 0.058)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00σ(I))</td>
<td>3615</td>
</tr>
<tr>
<td>No. Variables</td>
<td>220</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>16.43</td>
</tr>
<tr>
<td>Residuals (refined on F$^2$, all data): R1; wR2</td>
<td>0.088; 0.088</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.00</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00σ(I))</td>
<td>2325</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.039; 0.073</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0051 Å</td>
</tr>
</tbody>
</table>
Table 5.13 X-ray crystal structure details for III-31

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical Formula</strong></td>
<td>$\text{C}<em>{69}\text{H}</em>{69}\text{B}<em>{3}\text{N}</em>{6}\text{F}_{6}$</td>
</tr>
<tr>
<td><strong>Formula Weight</strong></td>
<td>1128.73</td>
</tr>
<tr>
<td><strong>Crystal Dimensions</strong></td>
<td>$0.14 \times 0.14 \times 0.50$ mm</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>173 K</td>
</tr>
<tr>
<td><strong>Crystal System</strong></td>
<td>triclinic</td>
</tr>
<tr>
<td><strong>Lattice Parameters</strong></td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>12.3770(7) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>12.5566(7) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>21.9994(12) Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>73.555(3)°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>81.242(3)°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>63.362(3)°</td>
</tr>
<tr>
<td>$V$</td>
<td>2929.8(3) Å³</td>
</tr>
<tr>
<td><strong>Space Group</strong></td>
<td>$P-1$ (#2)</td>
</tr>
<tr>
<td><strong>Z value</strong></td>
<td>2</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.279 g/cm³</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>1188.00</td>
</tr>
<tr>
<td>$\mu$ (MoKα)</td>
<td>0.88 cm⁻¹</td>
</tr>
<tr>
<td><strong>No. of Reflections Measured</strong></td>
<td>Total: 51318</td>
</tr>
<tr>
<td></td>
<td>Unique: 14001 ($R_{\text{int}} = 0.032$)</td>
</tr>
<tr>
<td><strong>No. Observations (I&gt;0.00σ(I))</strong></td>
<td>14001</td>
</tr>
<tr>
<td><strong>No. Variables</strong></td>
<td>867</td>
</tr>
<tr>
<td><strong>Reflection/Parameter Ratio</strong></td>
<td>16.15</td>
</tr>
<tr>
<td><strong>Residuals (refined on $F^2$, all data): R1; wR2</strong></td>
<td>0.103; 0.185</td>
</tr>
<tr>
<td><strong>Goodness of Fit Indicator</strong></td>
<td>1.01</td>
</tr>
<tr>
<td><strong>No. Observations (I&gt;2.00σ(I))</strong></td>
<td>8553</td>
</tr>
<tr>
<td><strong>Residuals (refined on F): R1; wR2</strong></td>
<td>0.058; 0.151</td>
</tr>
<tr>
<td><strong>Bond precision</strong></td>
<td>C-C = 0.0032 Å</td>
</tr>
</tbody>
</table>
Table 5.14 X-ray crystal structure details for IV-26

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>$C_{112} H_{94} N_{15} Co_3 Cl_{21}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>2571.26 g/mol</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>$0.12 \times 0.26 \times 0.40 \text{ mm}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>12.4491(15) Å</td>
</tr>
<tr>
<td>$b$</td>
<td>25.874(3) Å</td>
</tr>
<tr>
<td>$c$</td>
<td>18.994(2) Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>90.0°</td>
</tr>
<tr>
<td>$\beta$</td>
<td>94.322(7)°</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>90.0°</td>
</tr>
<tr>
<td>$V$</td>
<td>6100.8(12) Å $^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P 2/c$ (#13)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>$D_{calc}$</td>
<td>1.400 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>2618.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>9.15 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td></td>
</tr>
<tr>
<td>Total:</td>
<td>45124</td>
</tr>
<tr>
<td>Unique:</td>
<td>10894 (R$_{int}$ = 0.040)</td>
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<tr>
<td>No. Observations (I$&gt;0.00 \sigma$(I))</td>
<td>10894</td>
</tr>
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<td>No. Variables</td>
<td>744</td>
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<td>Reflection/Parameter Ratio</td>
<td>14.64</td>
</tr>
<tr>
<td>Residuals (refined on $F^2$, all data):</td>
<td>R1; wR2</td>
</tr>
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<td></td>
<td>0.107; 0.224</td>
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<tr>
<td>Goodness of Fit Indicator</td>
<td>1.10</td>
</tr>
<tr>
<td>No. Observations (I$&gt;2.00 \sigma$(I))</td>
<td>6756</td>
</tr>
<tr>
<td>Residuals (refined on $F$): R1; wR2</td>
<td>0.069; 0.203</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0067 Å</td>
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</table>
Table 5.15 X-ray crystal structure details for IV-28

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C_{175}H_{145}N_{25}Co_{5}</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>2892.81</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.15 × 0.26 × 0.45 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>a = 45.955(3) Å</td>
</tr>
<tr>
<td></td>
<td>b = 10.1669(6) Å</td>
</tr>
<tr>
<td></td>
<td>c = 48.223(3) Å</td>
</tr>
<tr>
<td></td>
<td>α = 90.0°</td>
</tr>
<tr>
<td></td>
<td>β = 106.055(2)°</td>
</tr>
<tr>
<td></td>
<td>γ = 90.0°</td>
</tr>
<tr>
<td></td>
<td>V = 21652(2) Å</td>
</tr>
<tr>
<td>Space Group</td>
<td>P 2_1/c (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>4</td>
</tr>
<tr>
<td>D_{calc}</td>
<td>0.887 g/cm(^3)</td>
</tr>
<tr>
<td>F_{000}</td>
<td>6020.00</td>
</tr>
<tr>
<td>µ(MoKα)</td>
<td>4.16 cm(^{-1})</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 125774</td>
</tr>
<tr>
<td></td>
<td>Unique: 28076 (R_{int} = 0.172)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00σ(I))</td>
<td>28076</td>
</tr>
<tr>
<td>No. Variables</td>
<td>1752</td>
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<td>Reflection/Parameter Ratio</td>
<td>16.03</td>
</tr>
<tr>
<td>Residuals (refined on F(^2), all data): R1; wR2</td>
<td>0.202; 0.226</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>0.85</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00σ(I))</td>
<td>9475</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.087; 0.199</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0147 Å</td>
</tr>
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</table>
Table 5.16 X-ray crystal structure details for IV-34

<table>
<thead>
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<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>C$<em>{76}$H$</em>{66}$N$_{10}$Co$<em>2$Cl$</em>{12}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1662.65</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>0.10 $\times$ 0.15 $\times$ 0.45 mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>173 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>$a = 10.467(2)$ Å</td>
</tr>
<tr>
<td></td>
<td>$b = 12.376(2)$ Å</td>
</tr>
<tr>
<td></td>
<td>$c = 15.364(3)$ Å</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 85.567(6)^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 72.546(7)^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 83.501(6)^{\circ}$</td>
</tr>
<tr>
<td></td>
<td>$V = 1884.4(6)$ Å$^3$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P - 1$ (#2)</td>
</tr>
<tr>
<td>Z value</td>
<td>1</td>
</tr>
<tr>
<td>$D_{calc}$</td>
<td>1.465 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>850.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>9.16 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 14821</td>
</tr>
<tr>
<td></td>
<td>Unique: 4700 ($R_{int} = 0.055$)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00$\sigma$(I))</td>
<td>4700</td>
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<tr>
<td>No. Variables</td>
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<td>Reflection/Parameter Ratio</td>
<td>9.63</td>
</tr>
<tr>
<td>Residuals (refined on $F^2$, all data): R1; wR2</td>
<td>0.111; 0.158</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.13</td>
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<td>No. Observations (I&gt;2.00$\sigma$(I))</td>
<td>3351</td>
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<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.077; 0.142</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0102 Å</td>
</tr>
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</table>
Table 5.17 X-ray crystal structure details for IV-35

<table>
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<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>( \text{C}<em>{76}\text{H}</em>{66}\text{N}<em>{10}\text{Zn}</em>{2} )</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>1675.53</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>(0.10 \times 0.13 \times 0.45 \text{ mm})</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>triclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>(a = 10.4630(9) \text{ Å} )</td>
</tr>
<tr>
<td></td>
<td>(b = 12.3228(10) \text{ Å} )</td>
</tr>
<tr>
<td></td>
<td>(c = 15.318(1) \text{ Å} )</td>
</tr>
<tr>
<td></td>
<td>(\alpha = 85.573(5)^\circ )</td>
</tr>
<tr>
<td></td>
<td>(\beta = 72.448(4)^\circ )</td>
</tr>
<tr>
<td></td>
<td>(\gamma = 83.460(4)^\circ )</td>
</tr>
<tr>
<td></td>
<td>(V = 1868.9(3) \text{ Å}^3 )</td>
</tr>
<tr>
<td>Space Group</td>
<td>(P\ -1\ (#2) )</td>
</tr>
<tr>
<td>Z value</td>
<td>1</td>
</tr>
<tr>
<td>(D_{\text{calc}})</td>
<td>1.489 g/cm(^3)</td>
</tr>
<tr>
<td>(F_{000})</td>
<td>856.00</td>
</tr>
<tr>
<td>(\mu(\text{MoK}\alpha))</td>
<td>11.22 cm(^{-1})</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 146685</td>
</tr>
<tr>
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<td>Unique: 9313 (R(_{int}) = 0.040)</td>
</tr>
<tr>
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<td>9313</td>
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<tr>
<td>No. Variables</td>
<td>591</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>15.76</td>
</tr>
<tr>
<td>Residuals (refined on (F^2), all data): R1; wR2</td>
<td>0.056; 0.106</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.02</td>
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<td>No. Observations (I&gt;2.00(\sigma(I)))</td>
<td>7573</td>
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<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.040; 0.096</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0030 Å</td>
</tr>
</tbody>
</table>
Table 5.18 X-ray crystal structure details for IV-36

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical Formula</td>
<td>$C_{134}H_{116}N_{18}Zn_{4}Cl_{18}$</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>2878.03</td>
</tr>
<tr>
<td>Crystal Dimensions</td>
<td>$0.08 \times 0.25 \times 0.35$ mm</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 K</td>
</tr>
<tr>
<td>Crystal System</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Lattice Parameters</td>
<td>$a = 26.431(1)$ Å, $b = 19.1050(9)$ Å, $c = 13.3295(6)$ Å, $\alpha = 90^\circ$, $\beta = 97.864(1)^\circ$, $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P2_1/c$ (#14)</td>
</tr>
<tr>
<td>Z value</td>
<td>2</td>
</tr>
<tr>
<td>$D_{\text{calc}}$</td>
<td>1.434 g/cm$^3$</td>
</tr>
<tr>
<td>$F_{000}$</td>
<td>2944.00</td>
</tr>
<tr>
<td>$\mu$(MoK$\alpha$)</td>
<td>11.28 cm$^{-1}$</td>
</tr>
<tr>
<td>No. of Reflections Measured</td>
<td>Total: 92591, Unique: 16118 ($R_{\text{int}} = 0.062$)</td>
</tr>
<tr>
<td>No. Observations (I&gt;0.00$\sigma$(I))</td>
<td>16118</td>
</tr>
<tr>
<td>No. Variables</td>
<td>820</td>
</tr>
<tr>
<td>Reflection/Parameter Ratio</td>
<td>19.66</td>
</tr>
<tr>
<td>Residuals (refined on $F^2$, all data): R1; wR2</td>
<td>0.122; 0.207</td>
</tr>
<tr>
<td>Goodness of Fit Indicator</td>
<td>1.10</td>
</tr>
<tr>
<td>No. Observations (I&gt;2.00$\sigma$(I))</td>
<td>10933</td>
</tr>
<tr>
<td>Residuals (refined on F): R1; wR2</td>
<td>0.072; 0.169</td>
</tr>
<tr>
<td>Bond precision</td>
<td>C-C = 0.0064 Å</td>
</tr>
</tbody>
</table>
CHAPTER 6

Thesis summary and future work
6.1 Thesis summary

Dipyrromethenes are a group of compounds composed of two pyrrole rings fused through a methine group. Past research has shown that dipyrromethenes and their homologs provide a series of interesting self-assembled molecules when coordinated to transition metals. Meso-substituted dipyrrins can be prepared via a two-step procedure: the acid-catalyzed condensation between pyrrole and an aldehyde, followed by the oxidation of the dipyrromethane. In this study, different types of meso-bridged bis(dipyrren)s were prepared to investigate their metal coordination reaction and their application in the self-assembly chemistry.

Difluoroborondipyrromethenes (BODIPY) and dipyrromethene metal complexes have been extensively studied. In this work, a new type of ligand was synthesized. These ligands are combined systems, in which BODIPY was on one side of the linker, while the free-base dipyrromethene was on the other side. The ligands were treated with various metals to form complexes. The crystal structures of the metal complexes were investigated and correlations between the structural features and optical properties were established.

The previous attempts of employing bis(dipyrren)s to obtain the linear dipyrren metal complexes have been generated in a “random” polymerization manner. Here, the BF$_2$ capped dipyrrins have been used to terminate oligomerization in order to form a series of controlled length assemblies. To further investigate the possibility of the synthesis of linear dipyrren oligomers which incorporates different metals in one molecule, the bis(dipyrren) heteroleptic metal complex intermediates were introduced into the system. These heteroleptic metal complexes can act as both the ligand and the metal ion source to generate the controlled length oligomers in a step-wise fashion.
In order to achieve the cyclic complex structure, a series of bis(dipyrrin)s were prepared with two dipyrrin moieties linked at the meso-positions by an angled spacer. By carefully choosing the spacers with different directional angles, the metal complexation of these angled bis(dipyrrin)s generated the cyclic dipyrринato metal complexes with different core sizes. In one example, when two dipyrrin moieties were directed 35° apart by a carbazole unit, the result dimeric complexes are a mixture of stereoisomers, because the dipyrrin planes around the metal center are not perfectly perpendicular. Furthermore, by employing the linear bis(dipyrrin) heteroleptic metal complex intermediates as metal source, a rectangular-shaped metal complex with mixed ligands were formed, with the carbazole units being the shorter edges of the rectangle, and the linear bis(dipyrrin) units being the longer edges.

6.2 Future work

Following the studies described in this thesis, a number of projects could be taken up. Compare to largely explored boron-dipyrromethene complexes, the optical properties of dipyrrin metal complexes are less reported. The dipyrrin metal complexes are highly colored and show strong absorption peaks in UV/Vis spectrum. Introducing of luminescent BODIPY into extended dipyrrin metal complexes have been achieved here, and the study of their photochemical properties and electron/energy transfer applications could be an area of future research. As described at the end of Chapter 3, inspired from the successful removing BF$_2$ from BODIPY by Thompson and her colleague, a possible new synthetic route of liner dipyrрин metal complexes has been designed. The feasibility of this method still needs further investigation.
The coordination cavities have enormous potential application in gas adsorption and host-guest interactions. Through careful design of the linker, dimeric dipyrrin ligands can form stable metallomacrocyclic structures. The recognition ability of these metallomacrocycles with various guest molecules will also be a fascinating future research area.
REFERENCES


220


