ASSEMBLY OF PRUSSIAN BLUE ANALOGUE NANOMATERIALS

by

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BEng, Ecole Polytechnique de Montréal, 2002
MASc, Ecole Polytechnique de Montréal, 2004

A THESISSubmitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

The Faculty of Graduate Studies
(Chemistry)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

April 2011

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ABSTRACT

Coordination polymers have many attractive properties but the development of applications has been hampered by the challenges associated with their processing and the preparation of nanosized analogues. In this thesis, the synthesis and characterization of new coordination polymer nanomaterials with previously inaccessible morphologies and compositions are reported. Prussian blue analogues (PBAs) were investigated as model compounds.

Mesostructured PBAs were fabricated via a ligand-assisted liquid-crystal templating approach. Molecular surfactants having a charged iron cyanide complex as hydrophilic head group and metal-coordinated hydrophobic tails were synthesized. In formamide, the metal-containing template formed liquid-crystalline phases that were crosslinked into PBA mesostructures with the addition of transition metals. PBAs with well-ordered lamellar, hexagonal and cubic structures were obtained with a wide range of compositions. The materials made of iron(II) and iron(III) exhibited mixed-valency and ferromagnetic interactions in the PBA framework.

A synthetic approach to attach a PBA precursor onto polymer-based structure-directing agents was developed. A preformed macromolecular backbone was functionalized with ionic pendant groups that can coordinate iron cyanide complexes. Metal-containing homopolymers and block copolymers were synthesized. In organic solvents, the ionic block copolymers behaved as a block ionomer and self-assembled into stable wormlike and toroidal reverse micelles whose cores were metallated with the iron cyanide complex or used as an ion confinement region for different cyanometallate compounds to be crosslinked into PBA-type frameworks. The soluble PBA nanomaterials are stable in solution, assemble into arrays on surfaces and were used as precursors for metal oxide nanostructures.
Soluble hollow polymer capsules with PBA inner-shells were fabricated via emulsion-induced assembly of the iron cyanide block ionomer. The metal-containing amphiphilic macromolecules stabilized nanosized water droplets dispersed in organic solvent by assembling at the water-oil interface. The hydrophilic iron cyanide inner-shells were crosslinked into PBAs with zinc ions. The hollow capsules have selective permeability, are tunable in size, organize into hexagonal arrays in the solid state and were used as nanocontainers to encapsulate molecular compounds.

A rigid structure-directing ligand was incorporated into the network of a PBA under solvothermal conditions to engineer the connectivity of a coordination polymer. A crystalline triptycene-scaffolded copper PBA was obtained.
In all chapters, Prof. Mark MacLachlan acted in a supervisory role. Chapters 4 and 5 involved collaboration with the research group of Prof. Guojun Liu (Queen’s University).


Chapter 2: A version of this chapter has been published as: Roy, X.; Thompson, L. K.; Coombs, N.; MacLachlan, M. J. "Mesostructured Prussian Blue Analogues,” Angew. Chem. Int. Ed. 2008, 47, 511-514. Portions of the introduction of this chapter have been published in another article: Roy, X.; MacLachlan, M. J. “Coordination Chemistry: New Routes to Mesostructured Materials,” Chem. Eur. J. 2009, 15, 6552-6559. I wrote and edited both papers in collaboration with Prof. MacLachlan. Prof. Laurence K. Thompson (Memorial University) performed superconducting quantum interference device (SQUID) experiments on some of the samples, Dr. Neil Coombs (University of Toronto) performed the transmission electronic microscopy analyses and Dr. Dev Sharma (Simon Fraser University) performed the Mössbauer measurements. I performed all of the other experiments.

Chapter 3: I wrote and edited this chapter with input from Prof. MacLachlan. I collaborated with Dr. Joseph K.-H. Hui for the transmission electronic microscopy analyses. I performed all of the other experiments.

Chapter 4: A version of this chapter has been published as: Roy, X.; Hui, J. K.-H.; Rabnawaz, M.; Liu, G.; MacLachlan, M. J. “Soluble Prussian Blue Nanoworms from the Assembly of Metal-Organic Block Ionomers,” Angew. Chem. Int. Ed. 2011, 50, 1597-1602. I
wrote and edited this paper in collaboration with Prof. MacLachlan. Prof. Guojun Liu and Muhammad Rabnawaz (Queen’s University) synthesized the starting polymer materials; I collaborated with Dr. Joseph K.-H. Hui for the transmission electronic microscopy analyses. I performed all the other experiments.

Chapter 5: A version of this chapter has been submitted for publication as: Roy, X.; Hui, J. K.-H.; Rabnawaz, M.; Liu, G.; MacLachlan, M. J. “Prussian Blue Nanocontainers: Selectively Permeable Hollow Metal-Organic Capsules from Block Ionomer Emulsion-Induced Assembly,” 2011. I wrote and edited this paper in collaboration with Prof. MacLachlan. Prof. Guojun Liu and Muhammad Rabnawaz (Queen’s University) synthesized the starting polymer materials; I collaborated with Dr. Joseph K.-H. Hui for the transmission electronic microscopy analyses. I performed all of the other experiments.

Chapter 6: A version of this chapter will be submitted for publication as: Roy, X.; Chong, J. H.; MacLachlan, M. J. “Molecular Scaffolding of Prussian Blue Analogues Using Phenanthroline-Extended Triptycene Ligands,” 2011. I wrote and edited this paper in collaboration with Prof. MacLachlan. Dr. Jonathan H. Chong synthesized the starting triptycene materials and performed the x-ray diffraction and structure refinement for compounds 14 and 19; Dr. Brian O. Patrick performed the single-crystal x-ray diffraction and structure refinement for compound 20. I performed all of the other experiments.

Chapter 7: I wrote and edited this chapter with input from Prof. MacLachlan. I collaborated with Dr. Joseph K.-H. Hui for the transmission electronic microscopy analyses. I performed all of the other experiments.
TABLE OF CONTENTS

ABSTRACT .................................................................................................................. ii

PREFACE ...................................................................................................................... iv

TABLE OF CONTENTS ................................................................................................. vi

LIST OF TABLES ........................................................................................................... x

LIST OF FIGURES ......................................................................................................... xi

LIST OF SYMBOLS AND ABBREVIATIONS ............................................................ xx

ACKNOWLEDGEMENTS ............................................................................................. xxvi

DEDICATION .................................................................................................................. xxviii

CHAPTER 1 INTRODUCTION ...................................................................................... 1

1.1 Nanomaterials ............................................................................................................. 1
  1.1.1 Overview .............................................................................................................. 1
  1.1.2 General approaches to nanomaterials ................................................................. 2
  1.1.3 Nanoporous materials ......................................................................................... 3

1.2 Coordination polymers ............................................................................................. 3
  1.2.1 Introduction to coordination polymers ............................................................... 3
  1.2.2 Prussian blue and Prussian blue analogues ......................................................... 4
  1.2.3 Metal-organic frameworks ................................................................................. 6
  1.2.4 Nanostructured CFs ......................................................................................... 8

1.3 Mesoporous materials ............................................................................................. 9

1.4 Block copolymers ..................................................................................................... 11
  1.4.1 Phase separation in BCPs .................................................................................... 17
  1.4.2 Micellization of BCPs in solution ....................................................................... 19
  1.4.3 BCPs for the fabrication of inorganic nanomaterials ........................................... 22
    1.4.3.1 BCP nanofabrication .................................................................................. 22
    1.4.3.2 Core-confined nanoreactor ....................................................................... 24
    1.4.3.3 Template assembly .................................................................................... 25
  1.4.4 Block ionomers .................................................................................................. 27
  1.4.5 BIs for the fabrication of inorganic nanomaterials .............................................. 29
  1.4.6 Metal-containing BCPs ...................................................................................... 30
  1.4.7 BCPs with metal atoms in the backbone ............................................................ 32
  1.4.8 BCPs with metals pendent to the backbone or in the side chains ....................... 34
  1.4.9 Supramolecular and metal-terminated BCPs ....................................................... 36

1.5 Goals and scope of the thesis .................................................................................. 40
Conclusions

Results and discussion

CHAPTER 5 PRUSSIAN BLUE NANOCONTAINERS: SELECTIVELY PERMEABLE HOLLOW METAL-ORGANIC CAPSULES FROM BLOCK IONOMER EMULSION-INDUCED ASSEMBLY

5.1 Introduction

5.2 Experimental
5.2.1 Materials
5.2.2 Synthesis of PS270-PHEMAX
5.2.3 Synthesis of the 4,4'-bipyridinium-functionalized bock ionomers (BIX)
5.2.4 Synthesis of sodium amminepentacyanoferriate(II)
5.2.5 Synthesis of [Fe(r)(CN)b]BIX
5.2.6 Synthesis of Zn(b)(Fe(r)(CN)b]MOCX
5.2.7 Synthesis of MB@Zn(b)(Fe(r)(CN)b]MOCX
5.2.8 Equipment

5.3 Results and discussion

5.4 Conclusions

CHAPTER 6 MOLECULAR SCAFFOLDING OF PRUSSIAN BLUE ANALOGUES USING PHENANTHROLINE-EXTENDED TRITYCENE LIGANDS

6.1 Introduction

6.2 Experimental
6.2.1 Materials and methods
6.2.2 Synthesis of triptycencyl phenanthroline (14)
6.2.3 Synthesis of triptycencyl bis(phenanthroline) (16)
6.2.4 Synthesis of triptycencyl tris(phenanthroline) (18)
6.2.5 Synthesis of triptycene-scaffolded PBA
6.2.6 Direct synthesis of d(triptycencyl phenanthroline)copper(I) (22)
6.2.7 Equipment
6.2.8 X-ray diffraction crystallographic analysis
6.2.8.1 X-ray diffraction crystallographic study of 14
6.2.8.2 X-ray diffraction crystallographic study of 19
6.2.8.3 X-ray diffraction crystallographic study of 20

6.3 Results and discussion

6.4 Conclusions
CHAPTER 7    CONCLUSIONS AND FUTURE WORK ........................................ 165

7.1 Conclusions ........................................................................................................ 165

7.2 Future work ......................................................................................................... 169

7.3 Experimental ..................................................................................................... 174
  7.3.1 Starting materials ......................................................................................... 174
  7.3.2 Fe^{III}[Fe^{II}(CN)_5]BI30 nanoworms and Fe^{III}[Fe^{II}(CN)_5]BI75 nanorings (Figure 7.1a-c) ......................................... 174
  7.3.3 Fe^{III}[Fe^{II}(CN)_5]BI30 nanoparticles (Figure 7.1d) .................................. 174
  7.3.4 Zn^{II}[Fe^{II}(CN)_5]MOC30 and Zn^{II}[Fe^{II}(CN)_5]MOC75 (Figure 7.1e and 7.1f) ......................................................... 175
  7.3.5 Block ionomer (BI75) capsules with a PB core (Figure 7.2a) ...................... 175
  7.3.6 Equipment .................................................................................................. 175

REFERENCES ......................................................................................................... 176

APPENDICES .......................................................................................................... 193

Appendix A    Additional characterization for Chapter 2 ........................................ 193
Appendix B    Additional characterization for Chapter 3 ........................................ 194
Appendix C    Additional characterization for Chapter 4 ........................................ 195
Appendix D    Additional characterization for Chapter 5 ........................................ 206
Appendix E    Additional characterization for Chapter 6 ........................................ 209
LIST OF TABLES

Table 2.1. Elemental composition and structural properties of a series of mesostructured PBA. .................................................................60
Table 5.1. Characterization of the starting polymer materials.................................................125
Table 6.1. Selected crystallographic data for compounds 14, 19 and 20. .........................148
LIST OF FIGURES

Figure 1.1. Schematic representation of dimensionality in CPs........................................4
Figure 1.2. Schematic representation of the PB cubic network structure..........................5
Figure 1.3. Structure of MOF-5. a) is the building block Zn₄O(BDC)₃ that assembles into b) a cubic lattice. c) is the porous framework. Zn, purple; O, red; C, grey. Reproduced in part with the permission of the American Chemical Society. 42 ........................................7
Figure 1.4. LC templating approach to mesoporous metal oxides.....................................10
Figure 1.5. Types of copolymers obtained from monomers A and B. .............................13
Figure 1.6. Glossary of polymer structures.................................................................15
Figure 1.7. Phase separation of a diblock copolymer.......................................................16
Figure 1.8. Effect of varying the composition f of a given BCP on the ordered-phase nanostructure. Reproduced in part with the permission of the American Association for the Advancement of Science. 87 ..................................................19
Figure 1.9. Main nanostructures accessible by self-assembly of BCPs. fcc = face-centered cubic; bcc = body-centered cubic; Hex = hexagonal. Reproduced in part with the permission of the American Association for the Advancement of Science. 89 ......................................................20
Figure 1.10. Starlike and crew-cut micelles......................................................................22
Figure 1.11. Nanofabrication processes of nanohole and nanopost arrays using BCPs........23
Figure 1.12. Synthesis of inorganic nanoparticles inside phase separated BCPs............24
Figure 1.13. a) shows the schematic assembly of metal nanoparticles using a BCP template. b), c) and d) describe the preparation of ordered mesoporous materials from Pt nanoparticle-block copolymer self-assembly. b) and c) present the schematic structures of the mesostructured Pt nanoparticle-block copolymer hybrid and of the resulting mesoporous materials, respectively. d) is a transmission electronic microscopy (TEM) micrograph of the mesoporous materials. b), c) and d) were reproduced in part with the permission of the American Association for the Advancement of Science. 100 .................................................................26
Figure 1.14. Examples of metal-containing polymers.......................................................31
Figure 1.15. Structure of dimethylsila[1]ferrocenophane (1) and phenylphospha[1]ferrocenophane (2) and illustrative synthesis of PS-b-PFS by sequential anionic polymerization of styrene and 1.............................................33
Figure 1.16. a) shows the schematic assembly of a co-micelle made of PFS-containing BCPs and b) is a dark-field TEM micrograph of the co-micelles. In the TEM micrograph, the PFS$_{53}$-b-PI$_{320}$ assembly is observed as the thin cylindrical section and the PFS$_{40}$-b-PI$_{310}$ assembly appears thicker because PDMS has more electron density. b) was reproduced in part with the permission of the American Association for the Advancement of Science.\textsuperscript{126}

Figure 1.17. Examples of metal-containing BCPs. ........................................................................................................... 36

Figure 1.18. Modular design of supramolecular metal-containing BCPs................................................................. 38

Figure 1.19. BCP nanofabrication using PS-[Ru]-PEO.......................................................................................... 39

Figure 1.20. a) shows the structure of the iron cyanide-terminated BCP 7 and b) its use in the preparation of PBA nanoshells. c) is a TEM micrograph of the PBA nanoshells. b) and c) were reproduced in part with the permission of the American Chemical Society.\textsuperscript{57}

Figure 2.1. Synthesis of $[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$. ........................................................................................................... 52

Figure 2.2. $^1$H NMR (400 MHz, MeOH-$d_4$) spectrum for unlinked $[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$. The NMR spectrum shows a trace of ethanol impurity (3.6 and 1.2 ppm). The aromatic resonances of the pyrazinium rings are labeled for reference........52

Figure 2.3. ESI mass spectrum of $[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$ (negative mode). The structures of the main aggregates are included.................................................. 53

Figure 2.4. One-pot synthetic approach to $\text{M}^\text{II}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_n$ ................................................................. 54

Figure 2.5. Wide-angle PXRD patterns of a) microcrystalline PB, b) $\text{Fe}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{22}$ and c) $\text{Er}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$. The intensities were normalized to facilitate comparison between the patterns. The microcrystalline PB was prepared using the same experimental conditions as for the mesostructured PBAs but without the addition of the N-alkylpyrazinium bromide surfactant........................................ 55

Figure 2.6. a) shows the low-angle PXRD patterns of (A) 2D hexagonal $\text{Er}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{12}$, (B) 2D hexagonal $\text{Fe}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{20}$, (C) cubic $\text{Cu}^I[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$ and (D) lamellar $\text{Er}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{22}$. b) shows the evolution of the PXRD patterns for $\text{Fe}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_n$ as the alkyl chain length is increased from $\text{C}_{12}$ to $\text{C}_{22}$. The intensities were normalized to facilitate comparison between the patterns.............................. 56

Figure 2.7. a) and b) are TEM micrographs of $\text{Er}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{12}$ perpendicular and parallel to the channels, respectively. c) and d) are TEM micrographs of 2D hexagonal $\text{Fe}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{20}$ and lamellar $\text{Er}^\text{III}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{22}$, respectively. a), b) and c) were obtained in high angle annular dark field (HAADF) mode and d) was taken in bright field mode........................................... 57

Figure 2.8. UV-vis absorption spectra of a) unlinked $[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$, b) $\text{Zn}^\text{II}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$, c) $\text{Fe}^\text{II}[\text{Fe}^\text{II}(\text{CN})_5]\text{C}_{18}$, and d) bulk PB. FWHM was
measured for the band observed in the range 500-1500 nm. FWHM = 210 nm for \([\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\); FWHM = 224 nm for \(\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\); FWHM = 486 nm for \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\); FWHM = 410 nm for bulk PB. The absorbances were normalized to facilitate comparison between the spectra.

**Figure 2.9.** Mössbauer spectrum for \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\) at 300 K fitted as arising from two quadrupole doublets (○ = data; solid line = fit). Site 1 (dotted lines) is assigned to high-spin \(\text{Fe}^{III}\) – isomer shift (\(\delta\)) = 0.57 mm s\(^{-1}\); \(\Delta E_Q = 0.23 \text{ mm s}^{-1}\); Area = 8% – and site 2 (dashed lines) is assigned to low-spin \(\text{Fe}^{II}\) – \(\delta = -0.28 \text{ mm s}^{-1}\); \(\Delta E_Q = 0.58 \text{ mm s}^{-1}\); Area = 42%.

**Figure 2.10.** Temperature dependence of \(\chi_{\delta}T\) at 0.1 Tesla for \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\) (○) and for \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{22}\) (△) \((T = \text{temperature})\). Because the exact molecular structures are not known, the magnetic susceptibilities are calculated per gram of material \((\chi_{\delta})\). Complex \(\text{Fe}^{II}(\text{CN})_5\text{C}_{18}\) is diamagnetic.

**Figure 2.11.** a) is the synthetic approach and b) the idealized structure of a 2D hexagonal mesostructured PBA.

**Figure 2.12.** TGA thermogram for \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}\) under \(N_2\) with a temperature ramp of 10 °C min\(^{-1}\).

**Figure 2.13.** Idealized structure of the walls in the PBA mesostructures. This framework structure is predicted to be very fragile and collapse upon removal of the N-alkylpyrazinium SDA.

**Figure 3.1.** Schematic representation of the Langmuir and BET models of adsorption onto a material surface.

**Figure 3.2.** Attempted synthesis of polymer 9.

**Figure 3.3.** Synthesis of polymer 10.

**Figure 3.4.** \(^1\text{H} \text{NMR spectra (300 MHz)}\) of a) bromoacetylated PHEMA in CDC\(_3\) and b) polyelectrolyte 10 in DMSO-\(d_6\) (one drop of dichloromethane was added to the sample to help solubilize the backbone).

**Figure 3.5.** Complexation of polyelectrolyte 10 and synthesis of the PBA materials \(M^{II}[\text{Fe}^{II}(\text{CN})_5]\text{PE}\).

**Figure 3.6.** UV-vis spectra of \(\text{[Fe}^{II}(\text{CN})_5]\text{PE}, \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{PE}, \text{and Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{PE}\).

**Figure 3.7.** Proposed outer-sphere mechanism for the crosslinking of 10 upon complexation. Complex \(\text{Fe}^{II}(\text{CN})_5\text{C}_n\) is included as an illustrative example. The synthesis and characterization details of this compound can be found in Chapter 2.

**Figure 3.8.** TEM micrographs of the sponge-like morphology of a) \(\text{Fe}^{II}(\text{CN})_5\text{PE}\) and b) \(\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{PE}\).
Figure 3.9. N₂ adsorption isotherm for Fe³⁺[FeII(CN)₅]PE at 77 K. This material exhibits a type IV isotherm and has a BET surface area of 114 m² g⁻¹. ..........92

Figure 4.1. ¹H NMR spectrum (300 MHz, 1:1 v/v DMSO-d₆:CDCl₃; the DMSO-d₅ resonance was used as reference at 2.5 ppm) of PS270-b-PHEMA30. ..........97

Figure 4.2. ¹H NMR spectrum (300 MHz, DMSO-d₆) of BI30*. ..................................101

Figure 4.3. Synthesis of the metal-organic block ionomer [FeII(CN)₅]BI30 and its crosslinking into the PBA framework M⁺[FeII(CN)₅]BI30 (DTBP = 2,6-di-tert-butylpyridine). ..................................103

Figure 4.4. ¹H NMR spectroscopy characterization of the materials. a) and b) are the ¹H NMR spectrum (300 MHz) of BI30 in DMSO-d₆ and THF-d₈, respectively. c) and d) are the ¹H NMR spectra (300 MHz, THF-d₈ (4% v/v D₂O)) of [FeII(CN)₅]BI30 and of the diamagnetic ZnII[FeII(CN)₅]BI30, respectively. In THF-d₈ and THF-d₈/D₂O, only the resonances for the PS block are observed. ..................................104

Figure 4.5. UV-vis absorption spectra in THF with 4% v/v H₂O (~ 10⁻⁶ M [Fe(CN)₅]³⁻) of a) the model compound (18-crown-6)sodium (N-methyl-4,4'-bipyridinium)pentacyanoferrate(II) (shown), b) [FeII(CN)₅]BI30, c) FeIII[FeII(CN)₅]BI30 and d) ZnII[FeII(CN)₅]BI30. The absorbances were normalized to facilitate comparison between the spectra. Photographs of the [FeII(CN)₅]BI30, FeIII[FeII(CN)₅]BI30 and ZnII[FeII(CN)₅]BI30 solutions are also included as a visual reference for the color change. ..........106

Figure 4.6. TEM analysis of the polymeric materials dropcasts. a) and b) are TEM micrographs of [FeII(CN)₅]BI30 and FeIII[FeII(CN)₅]BI30, respectively. c) is a high magnification TEM image of a single FeIII[FeII(CN)₅]BI30 nanoworm and d) is a TEM micrograph of the nanostructure obtained with ZnII[FeII(CN)₅]BI30. .........................................................109

Figure 4.7. a) is the synthetic scheme for the block ionomer-mediated self-assembly of PBA nanoworms. b) shows the schematic cross-sectional view of a typical M⁺[FeII(CN)₅]BI30 nanoworm. As a control experiment, [FeII(CN)₅]BI30 and M⁺[FeII(CN)₅]BI solutions in 1,4-dioxane (4% v/v H₂O), were rapidly frozen in liquid nitrogen and freeze-dried at -10 °C (melting temperature for 1,4-dioxane is 11.8 °C). c) and d) are TEM micrographs of the [FeII(CN)₅]BI30 and M⁺[FeII(CN)₅]BI30 freeze-dried structures, respectively. .................................................................111

Figure 4.8. UV-vis absorption spectra of [FeII(CN)₅]BI30 and FeIII[FeII(CN)₅]BI30 (concentration of BI30 is 0.5 mg mL⁻¹ in THF with 4% v/v H₂O). ...........................................112

Figure 4.9. a) and b) are TEM micrographs of FeIII[FeII(CN)₅]BI30 and CuII[CoIII(CN)₆]BI30, respectively. c) shows the chemical structure of the triethylammonium-functionalized block ionomer labeled BI30* and d) is a TEM micrograph when BI30* is used instead of BI30 in the synthesis of PB nanoworms; seen here is a PB nanocrystal surrounded by PB-free BI30* nanoworms. e) and f) are respectively high magnification and low
magnification TEM micrographs of a mesoporous Fe$_2$O$_3$ film obtained by calcination of Fe$^{III/II}$[Fe$^{II}$](CN)$_6$BI30. ........................................................................................................... 114

Figure 4.10. PXRD pattern of the mesoporous iron oxide nanomaterials obtained by calcination of Fe$^{III/II}$[Fe$^{II}$](CN)$_6$BI30 at 450 °C for 1 h in air. The pattern was indexed as a mixture of α- Fe$_2$O$_3$ (hematite) and γ- Fe$_2$O$_3$ (maghemite). ................................................................................................................... 115

Figure 5.1. Basic structure of a block copolymer capsule................................................................. 118

Figure 5.2. Synthesis of the metal-organic block ionomers [Fe$^{II}$](CN)$_5$BIX and their crosslinking into hybrid polymer-PBA framework capsules Zn$^{II}$[Fe$^{II}$](CN)$_6$MOCX (DTBP = 2,6-di-tert-butylpyridine). ...................................................... 120

Figure 5.3. $^1$H NMR spectra (300 MHz, DMSO-d$_6$) of a) BI30 and b) of BI75. ................. 122

Figure 5.4. Synthetic approach to soluble block ionomer-PBA capsules through emulsion-induced assembly. Photographs of [Fe$^{II}$](CN)$_5$BI75 and Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75 are included as a visual reference for the color change............................................................................................................................................. 126

Figure 5.5. Electronic microscopy characterization of the polymer aggregates. a) is a TEM micrograph of the Zn-crosslinked [Fe$^{II}$](CN)$_5$BI75 nanoring structures observed before the emulsion-induced assembly. b) and c) are TEM micrographs of the soft and deformable [Fe$^{II}$](CN)$_5$MOC75 and the rigid crosslinked Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75 hollow aggregates, respectively. d) is a SEM micrograph showing a mixture of intact and collapsed hollow capsules for Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75. e) and f) are respectively low and high magnification TEM micrographs of Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC30. Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC30 assembles into a 2D hexagonal array upon evaporation as illustrated in f). ...................................................................................................................... 129

Figure 5.6. Histograms showing the inner diameter size distributions for a) Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75 (137 ± 43 nm) and b) Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC30 (53 ± 5 nm). For each sample, the inner diameter of 150 hollow capsules were measured from a number of TEM micrographs using the image analysis software Macnification. The averages and standard deviations were calculated from these data.................................................................................................................. 130

Figure 5.7. TEM micrograph of [Fe$^{II}$](CN)$_5$MOC75 hollow structures prepared at the solution cloud point (ca. 78% v/v THF, 15% v/v chlorobenzene, 7% v/v H$_2$O). ............................................................................................................................................. 131

Figure 5.8. UV-vis absorption spectra in chlorobenzene (~ 10$^{-6}$ M [Fe(CN)$_5$]$^{3-}$) of a) [Fe$^{II}$](CN)$_5$MOC75 and Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75, and b) [Fe$^{II}$](CN)$_5$MOC30 and Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC30. The absorbances were normalized to facilitate comparison between the spectra................................................. 132

Figure 5.9. Encapsulation inside block ionomer-PBA capsules. a) shows the synthetic approach to encapsulating the model compound MB inside the PBA capsules. b) and c) are photographs of Zn$^{II}$[Fe$^{II}$](CN)$_6$MOC75 and
MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 after stirring with water for 24 hours, respectively.

Figure 5.10. UV-vis absorption spectra of MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 in chlorobenzene and MB in water. The absorbances were normalized to facilitate comparison between the spectra.

Figure 5.11. a) is a TEM micrograph of the Zn^{II}[Fe^{II}(CN)_{5}]Bi75 nanorings. An aqueous solution of MB was added to [Fe^{II}(CN)_{5}]Bi75 in THF (10% v/v H_{2}O) and stirred for 5 minutes. Zn(NO_{3})_{2} was then added to crosslink the nanorings into PBA-type frameworks. Chlorobenzene was added dropwise to induce the emulsion and MB was extracted by washing the organic phase with water. The solution was finally dried over activated molecular sieves. b) shows the UV-vis absorption spectra for the MB-free Zn^{II}[Fe^{II}(CN)_{5}]Bi75 nanorings in chlorobenzene and for MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 in chlorobenzene after stirring with water for 24 hours. The absorbances were normalized to facilitate comparison between the spectra.

Figure 5.12. a) is a TEM micrograph of methanol-infiltrated MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 after extraction of the methanol with water and standing over activated sieves. Seen here are mostly intact hollow capsules and one large ruptured nanocontainer. b) shows the UV-vis absorption spectra for the methanol-infiltrated MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 in chlorobenzene with ca. 25% v/v methanol and for the methanol-infiltrated MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 after extraction of the methanol with water and standing over activated sieves. The original MB@Zn^{II}[Fe^{II}(CN)_{5}]MOC75 broad solid absorption spectrum is obtained yet again. The absorbances were normalized to facilitate comparison between the spectra.

Figure 6.1. Synthesis of phenanthroline-extended triptycenes 14, 16 and 18.

Figure 6.2. Solid-state crystal structure of 14 (C_{32.5}H_{20}N_{4}O_{0.5}). Hydrogens have been omitted for clarity. Carbon, grey; nitrogen, blue; oxygen, red. a) is the ORTEP of a single molecule. Ellipsoids are shown at the 50% probability level. b) is a view showing the stacking of molecules. c) is a side view of a pair of stacked molecules. d) is a view down the c-axis showing stacks extending along the a-axis. Guest solvent molecules have been omitted for clarity in a-d). e) is a view down the a-axis showing solvent-filled channels (the methanol molecules are shown in this case).

Figure 6.3. Solid-state crystal structure of 19 (C_{128}H_{72}N_{16}Cl_{4}Cu_{4}O). Hydrogens and solvent molecules have been omitted for clarity. Carbon, grey; nitrogen, blue; copper, green; chlorine, pink. a) is the ORTEP of a single metal complex. The [CuCl_{2}]^{–} counterions and the carbon atom labels on the triptycene ligands have been omitted for clarity. Ellipsoids are shown at the 50% probability level. b) and c) are views showing the stacking of the complexes, along with the [CuCl_{2}]^{–} counterions. b) is a view down the b-axis showing the void channels and the interdigitation of the triptycenes and c) is a view down the c-axis showing the Cu^{+} atom columns.
Figure 6.4. PXRD patterns of the black needles synthesized using two different approaches. a) is the calculated PXRD pattern of 19 (calculated from the single crystal data). b) is the experimental PXRD pattern of 22. The variations between the patterns can be explained by the different amounts of solvent molecules trapped in the structures and a partial collapse of the structure upon drying of 22. .................................................................159

Figure 6.5. Solid-state crystal structure of 20 (C_{69.5}H_{40}N_{10.5}Cu_{2.5}O_{3.3}). Hydrogens, guest solvent molecules and the carbon atom labels on the triptycene ligands have been omitted for clarity. Carbon, grey; nitrogen, blue; oxygen, red; copper, green. a) is the ORTEP for the repeating unit of the triptycene-scaffolded Cu^I PBA chain, along with the triptycene-coordinated guest complex. b) is the ORTEP of the T-shaped Cu1 complex. Ellipsoids for a) and b) are shown at the 50% probability level. c) shows a single Cu^{I} PBA chain and d) is a view down the a-axis showing the arrangement of the PBA chains. The Cu1 metal center has a T-shaped geometry with two N-coordinated cyanide ligands and one aqua ligand that is equally distributed between two orientations. The O1* coordination site on Cu1 is shown as partially transparent to denote a site-occupancy of 0.5. e) is a view down the c-axis showing the stacking of the triptycene moieties and the isolated Cu^{I} PBA chains. The aqua ligands on Cu1 have been omitted for clarity in this case. .................................................................162

Figure 7.1. TEM survey of the morphologies accessible using the iron cyanide block ionomers SDA. a) is a TEM micrograph of Fe^{III}[Fe^{II}(CN)]_{5}BI30 nanoworms. b) and c) are TEM micrographs of a single toroidal Fe^{III}[Fe^{II}(CN)]_{5}BI75 micelle and Fe^{III}[Fe^{II}(CN)]_{5}BI75 multiring assemblies, respectively. d) is a TEM micrograph of Fe^{III}[Fe^{II}(CN)]_{5}BI30 nanoparticles prepared in a mixture of 1,2-dichloroethane and methanol. e) and f) are TEM micrographs of small Zn^{II}[Fe^{II}(CN)]_{5}MOC30 and large Zn^{II}[Fe^{II}(CN)]_{5}MOC75 hollow capsules, respectively. .........................................................171

Figure 7.2. a) is a TEM micrograph of block ionomer (BI75) capsules that appear to have solid cores made of PB. A mixture of BI75, K_{4}[Fe(CN)_{6}] and 18-crown-6 in THF (10% v/v H_{2}O) was sonicated, emulsified with chlorobenzene and centrifuged to remove the excess salt. The resulting assemblies are solvent-filled BI75 capsules with the iron cyanide complex encapsulated in the core. Fe(NO_{3})_{3} was added to crosslink the cores into PB. This micrograph is consistent with the darker core of the capsules being filled with PB. b) is the schematic representation of a soluble core-shell PBA nanoparticle prepared by emulsion-induced assembly of metal-containing block ionomers. .................................................................173

Figure A.1. IR spectra of a) Na_{3}[Fe(CN)_{2}NH_{3}] (\tilde{\nu}_{CN} = 2047 cm^{-1}), b) [Fe^{II}(CN)]_{5}C_{18} (\tilde{\nu}_{CN} = 2069 cm^{-1}), c) Fe^{III}[Fe^{II}(CN)]_{5}C_{18} (\tilde{\nu}_{CN} = 2079 cm^{-1}) and d) Zn^{II}[Fe^{II}(CN)]_{5}C_{18} (\tilde{\nu}_{CN} = 2077 cm^{-1}). .........................................................193

Figure B.1. IR spectra of a) Na_{3}[Fe(CN)_{2}NH_{3}] (\tilde{\nu}_{CN} = 2030 cm^{-1}), b) [Fe^{II}(CN)]_{5}PE (\tilde{\nu}_{CN} = 2046 cm^{-1}), c) Fe^{III}[Fe^{II}(CN)]_{5}PE (\tilde{\nu}_{CN} = 2057 cm^{-1}) and d) Zn^{II}[Fe^{II}(CN)]_{5}PE (\tilde{\nu}_{CN} = 2077 cm^{-1}). .........................................................194

xvii
Figure C.1. Size exclusion chromatography (SEC) analysis of PS-b-PHEMA. The system was calibrated by monodisperse polystyrene standards and DMF was used as eluant, at a flow rate of 0.9 mL min⁻¹. .................................195

Figure C.2. Time-resolved UV-vis spectra for the complexation of B130 into [Fe⁺(CN)₆]B130. The spectra were recorded at the complexation concentration (1 mg mL⁻¹ in THF (8% v/v H₂O)) every 10 minutes. The red dashed curve was obtained at 100 minutes and overlaps perfectly with the spectrum obtained at 90 minutes.................................................................196

Figure C.3. ¹H NMR spectrum (300 MHz, THF-d₈ (4% v/v D₂O)) of Cu⁺[Co II(CN)₆]B130 .............................................................................................................197

Figure C.4. IR spectra of a) Na₃[Fe(CN)₆NH₃] (v CN = 2030 cm⁻¹), b) [Fe⁺(CN)₆]B130 (v CN = 2050 cm⁻¹), c) Fe⁺⁺[Fe⁺(CN)₆]B130 (v CN = 2060 cm⁻¹), d) Zn⁺⁺[Fe⁺(CN)₆]B130 (v CN = 2082 cm⁻¹) and e) Co⁺⁺[Fe⁺(CN)₆]B130 (v CN = 2064 cm⁻¹)........................................................................................................198

Figure C.5. IR spectra of a) Fe⁺⁺[Fe⁺(CN)₆]B130 (v CN = 2056 cm⁻¹), b) Cu⁺⁺[Co II(CN)₆]B130 (v CN = 2185 cm⁻¹) and c) Co⁺⁺[Fe⁺⁺(CN)₆]B130 (v CN = 2069 cm⁻¹). As a reference, the strongest CN stretching band is at v CN = 2039 cm⁻¹, v CN = 2127 cm⁻¹ and v CN = 2116 cm⁻¹ for K₄[Fe(CN)₆], K₃[Co(CN)₆] and K₃[Fe(CN)₆], respectively.................................................................199

Figure C.6. Energy dispersive x-ray (EDX) spectra of a) Fe⁺⁺[Fe⁺(CN)₆]B130, b) Zn⁺⁺[Fe⁺(CN)₆]B130 and c) Co⁺⁺[Fe⁺(CN)₆]B130.................................................................200

Figure C.7. EDX spectra of a) Fe⁺⁺[Fe⁺(CN)₆]B130, b) Cu⁺⁺[Co II(CN)₆]B130 and c) Co⁺⁺[Fe⁺⁺(CN)₆]B130. The low levels of Br are from the inclusion of counterions and the aluminum peaks are contributions from the sample holder........................................................................................................201

Figure C.8. EDX spectrum of the mesoporous iron oxide nanomaterials obtained by calcination of Fe⁺⁺[Fe⁺(CN)₆]B130 at 450 °C for 1 h in air. The low level of Si present in the sample is most likely contamination from the crucible. ......201

Figure C.9. TGA thermograms of a) [Fe⁺(CN)₆]B130, b) Fe⁺⁺[Fe⁺(CN)₆]B130, c) Zn⁺⁺[Fe⁺(CN)₆]B130 and d) Co⁺⁺[Fe⁺⁺(CN)₆]B130 under N₂.................................................202

Figure C.10. Transmission electronic microscopy (TEM) micrograph of Co⁺⁺[Fe⁺⁺(CN)₆]B130 dropcast onto a TEM grid (polymer solution concentration: 0.5 mg mL⁻¹ in THF (4% v/v H₂O)). B130 was reacted with Na₃[Fe(CN)₆NH₃] to generate [Fe⁺⁺(CN)₆]B130. After dilution and filtration, [Fe⁺⁺(CN)₆]B130 was reacted with Co(NO₃)₂ to crosslink the core of the aggregates into PBA-type networks. See Sections 4.2.5 and 4.2.6 for more details. .................................................................203

Figure C.11. TEM micrograph of Co⁺⁺[Fe⁺⁺(CN)₆]B130 dropcast onto a TEM grid (polymer solution concentration: 0.5 mg mL⁻¹ in THF (4% v/v H₂O)). B130 was sonicated with K₃[Fe(CN)₆] to obtain [Fe⁺⁺(CN)₆]B130. After filtration to remove the excess K₃[Fe(CN)₆], [Fe⁺⁺(CN)₆]B130 was reacted
with Co(NO₃)₂ to crosslink the core of the aggregates into PBA-type networks. See Sections 4.2.8 and 4.2.9 for more details.................................203

**Figure C12.** Thermogravimetric analysis (TGA) thermogram of Fe³⁺[Fe²⁺(CN)₆]BI30 in air. The sample was first quickly heated to 450 °C, kept at that temperature for 1 hour, then ramped to 900 °C at 10 °C min⁻¹. ..........................204

**Figure C.13.** TEM micrograph of the mesoporous iron oxide film.........................................................205

**Figure C.14.** High magnification TEM micrograph of the mesoporous iron oxide film..............205

**Figure D.1.** IR spectra of a) Na₃[Fe(CN)₆]NH₃ (νCN = 2030 cm⁻¹), b) [Fe²⁺(CN)₆]MOC30 (νCN = 2050 cm⁻¹), c) Zn²⁺[Fe²⁺(CN)₆]MOC30 (νCN = 2082 cm⁻¹), d) [Fe²⁺(CN)₆]MOC75 (νCN = 2050 cm⁻¹) and e) Zn²⁺[Fe²⁺(CN)₆]MOC75 (νCN = 2078 cm⁻¹).............................................................206

**Figure D.2.** EDX spectrum of Zn²⁺[Fe²⁺(CN)₆]MOC30. The aluminum peak comes from the sample holder and the silicon peak is most likely contamination from the glass slide. ........................................................................................................................................207

**Figure D.3.** EDX spectrum of Zn²⁺[Fe²⁺(CN)₆]MOC75. The aluminum peak comes from the sample holder and the silicon peak is most likely contamination from the glass slide. ........................................................................................................................................208

**Figure E.1.** IR spectra of a) K₃[Fe(CN)₆] (νCN = 2116 cm⁻¹), b) the black needles 22, c) the red crystals 20 (νCN = 2110 cm⁻¹) and d) the brown cubes 21 (νCN = 2065 cm⁻¹)........................................................................................................................................209
### LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>angstrom</td>
</tr>
<tr>
<td>@</td>
<td>encapsulated in</td>
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<tr>
<td>δ</td>
<td>chemical shift (NMR); isomer shift (Mössbauer)</td>
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<tr>
<td>ν̅</td>
<td>wavenumber</td>
</tr>
<tr>
<td>ΔE_Q</td>
<td>quadrupole splitting</td>
</tr>
<tr>
<td>ΔG_mix</td>
<td>free energy of mixing</td>
</tr>
<tr>
<td>ΔH_mix</td>
<td>enthalpy of mixing</td>
</tr>
<tr>
<td>ΔS_mix</td>
<td>entropy of mixing</td>
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<tr>
<td>χ</td>
<td>Flory-Huggins interaction parameter</td>
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<tr>
<td>χₘ</td>
<td>magnetic susceptibility per gram of material</td>
</tr>
<tr>
<td>a. u.</td>
<td>arbitrary units</td>
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<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerization</td>
</tr>
<tr>
<td>bcc</td>
<td>body-centered cubic</td>
</tr>
<tr>
<td>BCP</td>
<td>block copolymer</td>
</tr>
<tr>
<td>BDC</td>
<td>benzene dicarboxylate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
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<tr>
<td>BI</td>
<td>block ionomer</td>
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<tr>
<td>2,2'-bipy</td>
<td>2,2'-bipyridine</td>
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<tr>
<td>CF</td>
<td>coordination framework</td>
</tr>
<tr>
<td>C3M</td>
<td>complex coacervate core micelles</td>
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<tr>
<td>CMC</td>
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<tr>
<td>CP</td>
<td>coordination polymer</td>
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<tr>
<td>CTA</td>
<td>cetyltrimethylammonium</td>
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<tr>
<td>Cu K$_\alpha$</td>
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<td>d</td>
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<tr>
<td>DCM</td>
<td>dichloromethane</td>
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<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
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<tr>
<td>dmbipy</td>
<td>4,4$'$-dimethyl-2,2$'$-bipyridine</td>
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<tr>
<td>DMF</td>
<td>$N,N$-dimethylformamide</td>
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<tr>
<td>DMSO</td>
<td>dimethylsulfoxide</td>
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<tr>
<td>DTP</td>
<td>2,6-di-tert-butylpyridine</td>
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<tr>
<td>EDX</td>
<td>energy dispersive x-ray</td>
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<tr>
<td>EI</td>
<td>electron impact ionization</td>
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<td>equiv.</td>
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<tr>
<td>ESI</td>
<td>electrospray ionization</td>
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<tr>
<td>EtOH</td>
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<td>f</td>
<td>composition (block copolymer)</td>
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<tr>
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<td>FWHM</td>
<td>full-width at half maximum</td>
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<td>GOF</td>
<td>goodness of fit indicator</td>
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<tr>
<td>HAADF</td>
<td>high angle annular dark field</td>
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<td>HEMA</td>
<td>2-hydroxyethyl methacrylate</td>
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<td>HEMA-TMS</td>
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<td>Hex</td>
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<tr>
<td>HR</td>
<td>high resolution</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
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<td>internal molecular free volume</td>
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<td>IR</td>
<td>infrared</td>
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<td>IVCT</td>
<td>intervalence charge transfer</td>
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<td>J</td>
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<td>$N$</td>
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<td>PYA</td>
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ACKNOWLEDGEMENTS

I would like to thank my supervisor Prof. Mark MacLachlan for all his help over the years. His enthusiasm, dedication and scientific rigor have been very influential. Mark has provided me with the right balance of freedom and supervision. He was always available to discuss new results, and to provide useful feedback and insights. I also appreciate his prompt editing of this thesis.

I am indebted to Prof. Michael Wolf for reading this thesis in record time and offering useful comments. Throughout my PhD, Mike has been very generous with his time and equipment and he has been a valuable resource.

I would like to acknowledge the MacLachlan group members who have helped me throughout this work. I especially want to thank my fellow group member and good friend Pete Frischmann for all the discussions (chemistry and non-chemistry related) and good times we have had. I also would like to thank the graduate students who contributed directly to this thesis: Joseph ‘Ho-Jo’ Hui for all the time spent in the TEM room and Jonathan Chong for the triptycene chemistry.

Thanks also to the Wolf and Fryzuk groups for all the help.

I would like to acknowledge all our contributors: Prof. Guojun Liu and Muhammad Rabnawaz from Queen’s University, Dr. Neil Coombs from the University of Toronto, Prof. Laurence Thompson from Memorial University and Dr. Dev Sharma from Simon Fraser University.
I would like to thank the UBC Chemistry Department staff, the UBC Bioimaging personnel and especially Dr. Brian Patrick and Anita Lam of the UBC Chemistry Department x-ray facility for their patience and assistance.

The financial support of the Fonds de Recherche sur la Nature et les Technologies du Québec, the Natural Sciences and Engineering Research Council of Canada and the University of British Columbia is gratefully acknowledged.

I would like to acknowledge the members of the “chemistry ski crew”: Bryan, Marek, Matty, JM, Pete, Austin, Tara, Kevin and Nick. You guys made these last five years very enjoyable, both on and off the slopes.

I would like to express my gratitude to Bryan (again), Angie, Matty and Pete for letting me sleep on their couch while I wrote parts of this thesis.

Lastly, and most importantly, I would like to thank my parents, Manon and Christian, Alain and my sister Delphine for their unconditional love and support, and Caroline for allowing me into your heart.
To Caroline
CHAPTER 1

INTRODUCTION†

1.1 Nanomaterials

1.1.1 Overview

Nanomaterials are defined as having one or more of their properties arising from domains or features smaller than 100 nm.¹ The idea of controlling matter atom by atom is not a new one; in his 1959 presentation to the American Physical Society entitled “There’s plenty of room at the bottom”, Nobel prize winning physicist Richard P. Feynman foresaw the potential advantages of this approach.² He pointed out that using a cluster made of 100 atoms as a bit of information, one could store all the books ever written on a cube with sides 0.5 mm long.

Today, many of the new materials being developed can be classified as nanomaterials. These include the well-known metal nanoparticles and nanowires, quantum dots, nanoporous materials, fullerenes and carbon nanotubes. Lying midway between the atomic or molecular scale and the bulk scale, nanomaterials are made of a relatively small number of atoms and a large proportion of them are situated at the surface or interface. As a result, the laws of atomic physics that are irrelevant in the bulk suddenly come into play at the nanoscale. This can lead to unexpected and exciting behaviour.

For example, quantum confinement effects in semiconductor nanoparticles generate quantized electronic levels in their valence and conduction bands, which in turn give rise to their fluorescence. In view of that, quantum dots are being investigated for applications as qubits (a quantum bit or qubit is a unit of quantum information, the quantum equivalent of the classical bit) for quantum information processing,\(^3\) as fluorescent dyes for medical imaging\(^4\) and in photovoltaic cells.\(^5\) Many other fascinating properties emerge as materials are miniaturized. For instance, the intense colours observed in some metal nanoparticles come from localized surface plasmon resonance, a phenomenon that only appears at the nanoscale.\(^6\) Because of their very high surface area, many metal nanoparticles and nanoporous materials exhibit catalytic activities that are orders of magnitude higher than their bulk analogues.\(^7\)

### 1.1.2 General approaches to nanomaterials

Nanomaterials have been synthesized using top-down or bottom-up approaches with varying degrees of success. The top-down approach usually relies on lithographic techniques and has been extensively used in the field of microelectronics to generate patterns on surfaces. It is, however, rapidly reaching its maximum resolution and is generally restricted to surfaces. The bottom-up approach, on the other hand, uses the molecule and other nanoscale precursors as building block and therefore does not suffer from these limitations. However, numerous challenges remain, including generating homogenous long-range order, minimizing defects, and controlling the directionality of the structure.

Self-assembly, defined as spontaneous assembly of molecules into structured, stable, non-covalently joined aggregates or patterns representing lowest energy configurations,\(^8\) is seen as a middle ground approach. By using carefully designed building components, nanoscale or mesoscale structures with long-range order in three dimensions can be produced by taking advantage of van der Waals and Coulombic interactions, hydrophobic effects, hydrogen bonds,
and weak, reversible coordination bonds. Moreover, top-down fabrication techniques can be used to pattern self-assembled nanostructures.

### 1.1.3 Nanoporous materials

Nanoporous materials, a subset of nanomaterials, are of scientific and technological interest because of their ability to interact with atoms, ions and molecules, not only at their external surface, but throughout the bulk of the materials by means of their internal surface.\(^9\) They are classified according to their pore size: microporous, mesoporous, and macroporous materials have pores smaller than 2 nm, ranging from 2 to 50 nm, and larger than 50 nm, respectively.\(^10\) Traditionally used as adsorbents and catalysts, nanoporous materials can now be prepared with an ever-expanding range of chemical compositions, pore structures, and morphologies; surface, mechanical, optical, electronic and magnetic properties; and are consequently investigated for more exotic applications such as waveguides,\(^11\) enantioselective separation materials,\(^12\) magnetic chemical sensors,\(^13\) or drug delivery devices.\(^14\)

### 1.2 Coordination polymers

#### 1.2.1 Introduction to coordination polymers

Coordination polymers (CPs) are hybrid structures made of metal cations or clusters linked by bridging organic ligands. As shown in Figure 1.1, depending on the coordination number of the metal center and the geometry of the ligand, one-, two- or three-dimensional networks can be obtained.
Following landmark reports by Robson and Hoskins,\textsuperscript{15,16} 3D CPs began receiving a lot of attention because they can combine many interesting properties such as microporosity, high surface area, electronic and magnetic communication between the metal centers, and structure tunability through judicious selection of the building blocks. They are now being investigated for a number of applications, including gas storage,\textsuperscript{17-21} exchange and sensing,\textsuperscript{13,22-25} as nanoscale laboratories for asymmetric catalysis,\textsuperscript{9,12,19,26} and as luminescent materials.\textsuperscript{22,24,27,28} Numerous appellations are used interchangeably to designate 3D CPs: coordination frameworks (CFs),\textsuperscript{29} metal-organic frameworks (MOFs),\textsuperscript{30} soft porous crystals (SPCs),\textsuperscript{31} porous coordination polymers (PCPs).\textsuperscript{32} The name CF is employed throughout this thesis to describe generic 3D CPs while the labels CP and MOF are reserved for 1D and 2D CPs, and materials based on multicarboxylate ligands, respectively. Two CFs will be discussed in the next sections: Prussian blue analogues and MOFs.

1.2.2 Prussian blue and Prussian blue analogues

Prussian blue (PB) is the first synthetic coordination compound and was initially synthesized by Diesbach and Dippel in 1704 using ox blood as starting material. Throughout history, PB has...
been used as a blue dye for garments and blueprints, in paints by great artists such as Picasso, Monet and van Gogh, and more recently, in the treatment of radioactive $^{137}\text{Cs}$ and Tl poisoning.\textsuperscript{33} Today, PB is generally prepared by reacting $\text{K}_4[\text{Fe(CN)}_6]$ with $\text{Fe}^{\text{III}}$ ions in water. As shown in Figure 1.2, PB is a cubic network of $\text{Fe}_4[\text{Fe(CN)}_6]_3\cdot n\text{H}_2\text{O}$ in which the Fe lie at the lattice points and the cyanide groups are bridging. Significantly, to achieve charge neutrality, the structure exhibits a vacancy of 25% of the $[\text{Fe(CN)}_6]^{4-}$ units randomly distributed throughout the network.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic representation of the PB cubic network structure.}
\end{figure}

Based on the Robin and Day classification,\textsuperscript{34} PB is a class II mixed valence compound, with the charge mainly localized on the $\text{Fe}^{\text{II}}$ center. It readily absorbs light and undergoes an intervalence charge transfer (IVCT) between $\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}$, giving rise to its blue colour. This IVCT transition can be eliminated by oxidizing PB to Berlin green ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{III}}$) or reducing it to Prussian white ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) and a number of electrochromic applications have been developed.
around this property.\(^{35}\) The high reversibility of the redox couple for PB makes it an excellent candidate for electrocatalytic and electrosensing applications.\(^{25}\)

PB is part of a much larger class of CFs called Prussian blue analogues (PBAs) that has the general formula \(M'_a[M''(CN)_x]_b\) and a similar network structure. A wide range of properties and functions can be accessed by carefully selecting the pair of metal ions composing the materials. For example, it was discovered that \(\text{Cu}_3[\text{Co(CN)}_6]_2\) has vacancies at one third of the \([\text{Co(CN)}_6]^{3-}\) sites, creating a highly porous and interconnected network that can store large quantities of hydrogen gas (1.8 wt% \(\text{H}_2\) at 1.2 bar and 77 K).\(^{20}\) PBAs are especially exciting in the preparation of molecule-based magnetic materials because cyanide ligands promote strong spin coupling between the bridged metal ions through superexchange interactions. Ferromagnetic, antiferromagnetic and ferrimagnetic behaviour are all well known, along with the more exotic photoinduced ferrimagnetism\(^{36}\) and room temperature ferrimagnetism.\(^{37}\)

Given the historical and scientific importance of PB and PBAs, it is not surprising that review articles discussing in detail new compounds, structures, synthetic methods or exciting properties are published on a regular basis.\(^{33,38-40}\) For this reason, this section on PB and PBAs was deliberately kept brief.

1.2.3  **Metal-organic frameworks**

CFs built from metal ions or clusters (dubbed secondary building units) bridged by multicarboxylate ligands such as 1,4-benzene dicarboxylate (BDC) or 1,3,5-benzene tricarboxylate (BTC) are often referred to as MOFs. Materials of this type have been popularized by Yaghi in the second half of the 1990s.\(^{41,42}\)

MOF-5 is the archetype metal-organic framework with its thermally stable cubic network made of zinc-oxo clusters bridged by chelating BDCs (see Figure 1.3).\(^{43}\) MOF-5 and its cousins
are generally synthesized under solvothermal conditions where metal ions and organic linkers are reacted together at high temperature and then crystallized into microporous or mesoporous frameworks upon cooling.

**Figure 1.3.** Structure of MOF-5. a) is the building block $\text{Zn}_4\text{O}(\text{BDC})_3$ that assembles into b) a cubic lattice. c) is the porous framework. Zn, purple; O, red; C, grey. Reproduced in part with the permission of the American Chemical Society.$^{42}$

MOFs are predominantly investigated for gas storage because they possess very high surface areas. In fact, of all the materials known, MOFs have the highest surface areas. UMCM-2 is one of the best in that respect with a surface area of 5200 m$^2$ g$^{-1}$.\textsuperscript{44} This is 30% more than MOF-177, one of its closest competitors and roughly 70% more than the best zeolites. However, with respect to its hydrogen storage capacity, UMCM-2 does significantly worse than the benchmark
MOF-177 (6.9 wt% at 46 bar and 77 K for UMCM-2 compared with 7.1 wt% at 40 bar and 77 K for MOF-177), confirming that surface area alone is not the key to hydrogen uptake.

Other applications of MOFs include gas separation and heterogeneous catalysis. For example, Mg-MOF-74 can effectively extract CO\textsubscript{2} from a flowing mixture of CO\textsubscript{2} and CH\textsubscript{4} and then release the trapped gas upon heating to 80 °C.\textsuperscript{18} MOFs have uniform and tunable pore structures that make them especially well suited for many industrial catalytic applications where shape and size selectivity is a vital consideration. They have been investigated as catalytically active species or as porous supports for classic metal catalysts in a number of reactions such as transesterification, hydrogenation, epoxidation and oxidation.\textsuperscript{19}

1.2.4 Nanostructured CFs

By and large, CFs form thermodynamically stable crystalline phases. This makes characterization of the bulk CFs by x-ray diffraction effective and straightforward.\textsuperscript{32} However, this propensity to crystallization makes isolation of nano-CFs all the more challenging. In recent years, the opportunity to discover new properties and integrate new functions into these nanoscale CFs has been the main driving force in overcoming the challenges associated with their synthesis. A few reviews highlighting the main breakthroughs in that direction have been published recently.\textsuperscript{45,46}

The nanosize effects for CFs are wide-ranging both scientifically and in terms of applications. For instance, soluble nano-CFs should help understand the chemistry of formation for these materials and their solution behaviours. New solution-based applications such as homogeneous catalysts or platforms for drug delivery and imaging have already emerged.\textsuperscript{47} Nanoconfinement also generates unique electronic and spin states in nano-CFs and should lead to new quantum, size-dependent and surface effects. For instance, superparamagnetic behaviour
has been reported in some PBA nanoparticles.\textsuperscript{48-51} Finally, nanoscale CFs could lead to the development of patterning techniques for CF-based higher-order structures. Surface arrays are especially important for applications as sensors.

Nano-CFs are usually synthesized inside surfactant-stabilized microemulsions,\textsuperscript{46} but they have also been prepared inside nanoporous templates\textsuperscript{52} and polymer coils,\textsuperscript{53} and using ultrasound\textsuperscript{54} and microwaves.\textsuperscript{55} Of all the CFs that could potentially be nanostructured, PBAs are by far the most studied because of their historical significance, their ease of synthesis, the variety of compositions achievable and their wide range of functions and applications. PBA nanocrystals,\textsuperscript{56} nanowires,\textsuperscript{52} nanoshells,\textsuperscript{57} nanoboxes,\textsuperscript{58} and Langmuir-Blodgett monolayers\textsuperscript{59} are known.

1.3 Mesoporous materials

MCM-41, the first mesoporous silica with an ordered mesoporosity, was discovered in 1992 by Kresge et al.,\textsuperscript{60,61} then at the Strategic Research Center for the Mobil Technology Company. MCM-41 is synthesized via a liquid-crystal (LC) templating approach making use of surfactants as structure-directing agent (SDA). LC templating is usually employed in combination with sol-gel chemistry.\textsuperscript{62} As shown in Figure 1.4, cooperative assembly of the inorganic precursors in solution – the sol, e.g., tetraethyl orthosilicate in water – with the SDA LC forms a gel that is condensed into a mesostructured hybrid material. Calcination fully condenses the walls and removes the organic template to yield the mesoporous materials. This technique has since been generalized for wide ranges of non-siliceous oxides,\textsuperscript{63} pore sizes,\textsuperscript{64} pore network structures\textsuperscript{65} and macroscopic morphologies.\textsuperscript{66}
Figure 1.4. LC templating approach to mesoporous metal oxides.

Mesoporous materials have high surface areas (up to 1500 m$^2$ g$^{-1}$) and are typically investigated for catalysis, adsorption and separation. However, novel applications that could greatly benefit from materials with well-ordered and controlled mesopore networks, narrow pore size distributions and biocompatibility are now being developed. These applications include chiral catalysis and separation$^{67}$ and drug delivery.$^{68}$
There are many incentives to discover synthetic approaches to nonoxidic mesoporous materials, since they should have a broader set of properties than their oxidic cousins. The reports of mesoporous metal chalcogenides were a major advance in that direction.\textsuperscript{69,70} They are typically prepared in formamide by linking metal clusters such as the adamantanoid $[\text{M}_4\text{Q}_{10}]^{4-}$ or the tetrahedral $[\text{MQ}_4]^4^+$ ions ($\text{M} = \text{Ge, Sn}; \text{Q} = \text{S, Se, Te}$) with different metal salts in the presence of a cationic SDA. Materials with a well-defined bandgap and photoluminescence have been synthesized using this method. Mesoporous metallic films have been synthesized by reducing a metal salt around a neutral LC template in aqueous conditions. First developed for Pt,\textsuperscript{71} this method has since then been generalized to other metals.\textsuperscript{72} Mesoporous semiconductors based on elemental germanium have recently been synthesized by two different approaches.\textsuperscript{73,74} Remarkably, these materials show wider bandgaps than bulk Ge due to quantum confinement effects in the 1 nm thick walls. In parallel to the above-mentioned work, tremendous efforts have been devoted to incorporating bridging organic and organometallic species in the preparation of mesoporous silica. Periodic mesoporous organosilicas (PMOs) based on ethane and ethylene bridging groups were the first to be reported.\textsuperscript{75} Inagaki et al. have shown that using a benzene bridge yields hybrid materials with crystalline walls.\textsuperscript{76} The greatest appeal of the PMOs comes from the connection they establish with the vast field of organic chemistry.

### 1.4 Block copolymers

A polymer is defined as a large molecule (macromolecule), natural or synthetic, composed of repeating units called monomers, typically connected by covalent chemical bonds.\textsuperscript{77} To qualify as monomer, a molecule has to possess at least two bonding sites through which it can be linked to other monomers in the polymerization process. While bifunctional monomers generate linear polymer chains, branched polymers and other 3D architectures such as star polymers, dendronized polymers and dendrimers can be obtained using polyfunctional monomers.
Contrary to small molecules, which have discrete sizes, synthetic polymers always come as statistical distributions of molecular weights. The number average molecular weight ($M_n$) and the weight average molecular weight ($M_w$) are respectively defined as:

$$M_n = \frac{\sum n_i \times MW_i}{\sum n_i}$$  \hspace{1cm} (1)  

$$M_w = \frac{\sum n_i \times MW_i^2}{\sum n_i \times MW_i}$$  \hspace{1cm} (2)  

where $n_i$ is the number of species of molecular weight $MW_i$. $M_n$ is obtained from colligative property measurements (e.g., osmotic pressure), by gel permeation chromatography, viscometry or end-group quantification, while $M_w$ is typically determined by light, neutron or x-ray scattering experiments. The polydispersity index (PDI) is used to describe the distribution of molecular weights in a sample. PDI is defined as:

$$PDI = \frac{M_w}{M_n}$$ \hspace{1cm} (3)  

The minimum value for PDI is 1 and is obtained for a monodisperse sample. An increasing PDI indicates a broadening distribution of molecular weights in the sample.

A homopolymer is composed of one type of monomer. When two or more different types of monomers are incorporated into a polymer chain, it is called a copolymer. For the simplest case of a copolymer made of two monomers, A and B, four common situations exist depending on the arrangement of units A and B (see Figure 1.5). A random copolymer has a linear backbone made of randomly distributed monomers A and B. When a regular sequential pattern exists within the chain, the resulting copolymer is classified as alternate copolymer. In a block copolymer (BCP), the chain is exclusively made of large sequences (blocks) of monomer A linked to blocks of
monomer B. If the BCP has only two blocks (one is A and the other one B), it is called a diblock copolymer. Needless to say, triblock and polyblock copolymers also exist. A graft copolymer has a backbone exclusively made of A, with B-type side chains. Although BCPs with elaborate architectures (e.g., star block copolymers) are well known and widely studied, only linear BCPs are discussed in this work.

![Diagram of copolymer types](image)

**Figure 1.5.** Types of copolymers obtained from monomers A and B.

Interest in BCPs originated with the discovery of termination-free (or living) anionic polymerization by Szwarc et al. in 1956,78,79 which made possible the sequential addition of different monomers to a variety of carbanion-terminated polymer chains. This reaction has many advantages: 1) in the absence of impurities, the polymerization proceeds until the monomer is completely consumed and the carbanion stays active indefinitely which allows for the addition of another type of monomer to resume the polymerization; 2) there is a known and constant number of propagating centers, all initiated at the same time – this allows for a precise control of the molecular weight and the polydispersity; 3) chain-end functionalization can be carried out
quantitatively. Since the initial breakthrough, a number of other living polymerization reactions have been developed to synthesize BCPs: living cationic polymerization, atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer polymerization (RAFT), ring-opening metathesis polymerization (ROMP) and chain shuttling polymerization.

In order to facilitate the understanding of this work, a list of all the polymers discussed in this chapter along with their chemical structures is included as Figure 1.6. These compounds are shown as homopolymers for simplicity, but most of them can also be copolymerized. The structures shown in Figure 1.6 should therefore be regarded as a catalog of building blocks that can be linked together to form different BCPs. It is important to note that 1,3-butadiene and isoprene each possess two double bonds and consequently can undergo two types of addition reactions – 1,2-addition and 1,4-addition. When synthesized via free radical polymerization, polybutadiene and polyisoprene are primarily composed of the 1,4-addition product with a small portion of the 1,2-addition product. However, when prepared under living polymerization conditions, 1,3-butadiene and isoprene undergo the 1,4-addition reaction exclusively (the resulting polymer structures are shown in Figure 1.6).
Figure 1.6. Glossary of polymer structures.
BCPs are often called macromolecular surfactants because their versatility and wide range of functions and properties resemble those of molecular surfactants. Like surfactants, BCPs are composed of two (or more) chemically different blocks and they tend to migrate towards interfaces. BCPs are frequently used as stabilizers for colloidal suspensions and also as compatibilizing agents for polymer blends. When no interface exists, BCPs will create some of their own under the right conditions by self-assembling into phase (or block) separated nanoscale domains (see Figure 1.7). This ability to phase separate into well-defined, uniform and organized nanostructures is generating a lot of excitement amongst materials scientists and has been systematically investigated in the past 25 years. BCPs have been employed in the fabrication of many types of materials, including car bumpers, tissue engineering scaffolds, cosmetic products and industrial lubricants. In the next sections, the concepts of BCP phase separation and micellization are introduced, along with a number of BCP families relevant to my research work. I also discuss the use of BCPs in the fabrication of inorganic nanomaterials.

Figure 1.7. Phase separation of a diblock copolymer.
1.4.1.1 Phase separation in BCPs

As for any chemical or physical process, the thermodynamics of phase separation can be described in terms of the change of free energy, $\Delta G$, which is calculated from the entropic and enthalpic contributions.\(^{85}\) In the simplest case – the mixing of two undiluted homopolymers – the free energy of mixing $\Delta G_{\text{mix}}$ is defined as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

(4)

where $\Delta H_{\text{mix}}$ and $\Delta S_{\text{mix}}$ are the enthalpy and entropy of mixing, respectively, and $T$ is the temperature. Two polymers are miscible on a molecular level when $\Delta G_{\text{mix}}$ is negative. For the mixing of high molecular weight polymers, $\Delta S_{\text{mix}}$ is always very small and $\Delta G_{\text{mix}}$ is dominated by the enthalpic contributions, which are generally positive ($\Delta H_{\text{mix}} > 0$).\(^{86}\) Most homopolymer blends are therefore immiscible unless polymer chains having complementary favorable interactions (e.g., ionic interactions or hydrogen bonds) are employed. The phase separation of two homopolymers is a macroscopic process driven to minimize the contact surface area between the two components and the size of the domains depends on the amount of materials available.

A BCP can be regarded as two homopolymers linked together by a covalent bond. In this case, however, the two components cannot diffuse away from each other to form large domains and the phase separation is restricted to nanoscopic dimensions comparable to the chain lengths. The phase behaviour of an undiluted BCP is controlled by three experimental parameters: the overall degree of polymerization $N$, the composition $f$ and the Flory-Huggins interaction parameter $\chi$, which describes the interaction of the blocks ($\chi$ is generally positive and increases for blocks that ‘dislike’ each other).\(^{86}\) At equilibrium, a given assortment of diblock copolymer molecules will adopt a configuration that minimizes the free energy of the system. When $\chi$
increases, the separation of the segments becomes enthalpically favoured. As \( N \) increases, the loss of translational and configurational entropy resulting from the local compositional ordering becomes less important compared to the enthalpy gain. In effect, three situations can arise.\(^{85,87}\)

When \( \chi N < 10 \), the two blocks are miscible, no phase separation is observed and the system stays disordered. For \( \chi N \sim 10 \), the system exists in the weak segregation limit (WSL) and the interfacial boundaries are poorly defined. The strong segregation limit (SSL) is the most relevant for this work. It is reached when \( \chi N >> 10 \) and is characterized by well-defined interfacial boundaries.

The phase behaviour of a BCP in the SSL regime is once again driven by the minimization of the interfacial surface area between the different blocks, which promotes the growth of the domains. However, this tendency is counterbalanced by two other contributions: the entropy losses from the chain extension within the microdomains and the confinement of the BCP joints at the interface. In the solid state, the morphology of the phase-separated BCP nanostructure is therefore the result of a subtle balance between these three competing thermodynamic factors. For a given BCP – that is where \( \chi \) and \( N \) are kept constant (i.e. invariable chemical composition and molecular weight) – this balance can be modified by varying \( f \) and the effect on the resulting morphology is illustrated in Figure 1.8.
1.4.2 Micellization of BCPs in solution

In solution, the phase behaviour of a BCP is mainly controlled by the interactions of the blocks with the solvent molecules and only to a lesser degree by the interaction of the blocks together. When a BCP is dissolved in a good solvent for all the blocks, no phase separation occurs. Interesting phase separation behaviour arises when the BCP is dissolved in a selective solvent. For a diblock copolymer AB, a selective solvent is one in which A is soluble and B is insoluble. Above a certain concentration called the critical micelle concentration (CMC), the macromolecules come together and self-assemble to minimize the contact of block B with the solvent. Micelles formed by BCPs are analogous to the ones formed by surfactants in their general construction: a core of insoluble material is surrounded and protected by a soluble corona. Both types of micelles can also adopt a wide variety of morphologies. Figure 1.9 shows an overview of the main nanostructures accessible with BCPs.
Figure 1.9. Main nanostructures accessible by self-assembly of BCPs. fcc = face-centered cubic; bcc = body-centered cubic; Hex = hexagonal. Reproduced in part with the permission of the American Association for the Advancement of Science.\textsuperscript{89}

Surfactants and BCPs micelles differ in a number of ways. First, BCP micelles are generally much bigger in size. More significantly, their micellization processes and the equilibrium states are completely different.\textsuperscript{90} The micellization of surfactants in non-polar solvents occurs through an open association mechanism involving a number of equilibria:

\[
U + U \leftrightarrow \text{Mic}_2 \quad (5)
\]
\[
U + \text{Mic}_2 \leftrightarrow \text{Mic}_3 \quad (6)
\]
\[
U + \text{Mic}_3 \leftrightarrow \text{Mic}_4 \quad (7)
\]
\[
U + \text{Mic}_n \leftrightarrow \text{Mic}_{n+1} \quad (8)
\]

where U is a unimer and Mic is a micelle made of n molecules.
BCP micelles on the other hand are made up of entangled polymer chains. This entanglement greatly reduces the possibility of a single chain coming in or out of the aggregate. A closed association mechanism involving a single equilibrium is usually invoked to explain the aggregation behaviour:

\[ \text{ZU} \rightleftharpoons \text{Mic}_Z \]  

(9)

where Z is the number of macromolecules that make up the micelle (Z is usually called the aggregation number). For this reason, BCPs tend to form micelles with much narrower size distributions, compared to surfactants. Kinetically, the association and dissociation reactions are much slower for BCPs because of the chain entanglement. In some cases, BCP micelles can be described as ‘frozen’ (especially at temperatures below the glass temperature of the core component).

The vocabulary employed to describe surfactant and block copolymer micelles differs as well. Surfactant molecules are said to ‘associate’ into micelles, suggesting a completely reversible process. On the other hand, the term ‘aggregation’ often employed for BCPs implies irreversibility to a certain extent.

Based on the relative length of the soluble and the insoluble segments, two categories of spherical micelles can exist: crew-cut\(^9\) and starlike micelles (see Figure 1.10).\(^9\) In a crew-cut micelle, the insoluble block is longer than the soluble block, such that the micelle has a large core and thin corona. Conversely, starlike micelles have small insoluble cores surrounded by long soluble coronal ‘hairs’.
1.4.3 BCPs for the fabrication of inorganic nanomaterials

BCPs possess a unique combination of properties that makes them especially attractive for the fabrication of inorganic nanomaterials. They are varied, relatively easy to synthesize and fairly inexpensive; they can be processed into thin films, bulk solids, gels and other forms via a number of approaches; they are stable and tunable; and, most importantly, they can self-assemble into well-understood and controllable nanostructures. Countless inorganic nanomaterials have been prepared using BCPs but, for the most part, the fabrication processes employed can be classified into three general categories: BCP nanofabrication, core-confined nanoreactor and template assembly.

1.4.3.1 BCP nanofabrication

BCPs are being investigated as substitutes for the traditional microfabrication and nanofabrication techniques, which are respectively quickly reaching their maximum resolution, and are prohibitively time-consuming and expensive. Surface polymer masks have been built from phase-separated BCP films without the need for the traditional photoresist and photomask.
combination. Figure 1.11 shows the general concept of BCP nanofabrication. Patterned polymer masks are fabricated by selectively degrading one block of specifically engineered BCPs using UV irradiation or ozone plasma. For example, the PBu block of PS-b-PBu can be selectively removed by ozonation. The masks are then used as sacrificial etching layers to fabricate nanohole arrays or as molds to be filled with another inorganic species to create nanopost arrays. This general approach was employed to fabricate nanostructures out of different materials such as silicon nitride nanoholes and nanoposts, and silica and Co nanoposts. The dimensions and the organization of the features were controlled by the architecture of the BCP employed.

![Diagram of BCP nanofabrication process](image)

**Figure 1.11.** Nanofabrication processes of nanohole and nanopost arrays using BCPs.

Although several BCP nanofabrication protocols have been developed over the last few years, the structure and the chemistry of the surface patterns accessible using this approach remain limited and uncomplicated. In fact, the bulk of the work in this area has focused on the spherical and cylindrical phases. Additionally, the lingering issues of long-range order, alignment and defects will have to be addressed before any real-world applications can be developed.
1.4.3.2 Core-confined nanoreactor

The core of phase-separated BCPs offers a very suitable environment for the synthesis of inorganic spherical or cylindrical nanoparticles. This is typically accomplished by loading dissolved preformed BCP micelles with inorganic precursors that are subsequently converted into the desired materials (see Figure 1.12). Sequestration of the inorganic precursors is generally achieved by loading organic solvent-soluble water-swelled reverse micelles with water-soluble species or by using coordinating BCPs such as PS-\textit{b}-P4VP to assemble micelles with binding sites for the precursors in the core. Employing this approach, BCP-sequestered metal salts were converted to metal nanoparticles using reducing agents such as hydrazine, hydrogen or NaBH$_4$ and to semiconductor nanoparticles with H$_2$S or hydrogen fluoride-pyridine. Silica and several metal oxide nanoparticles were also prepared by sol-gel techniques.

![Figure 1.12. Synthesis of inorganic nanoparticles inside phase separated BCPs.](image)

In a related approach, metal nanowires were fabricated on surfaces using preassembled solid-state nanoconfinement reactors. The hydrophilic domains of a phase-separated BCP film were selectively loaded with metal salts. Once again, PVP BCPs were used to sequester and retain the metals inside the films. The metal salts were then reduced and the polymer removed by plasma treatment to access the metal nanowires. Interestingly, by using topologically designed silicon substrates, aligned nanowire patterns were assembled inside 30-35 nm deep trenches.
1.4.3.3 Template assembly

Rather than employing the core of phase-separated BCPs to synthesize nanomaterials, one can exploit the corona and/or the periodicity of the BCP assemblies to template the formation of organic-inorganic hybrid nanomaterials that can be subsequently converted into fully inorganic nanomaterials by removing the polymer.\textsuperscript{99} Once again, specific interactions between the inorganic precursor and one block of the template macromolecules – coordination or hydrogen bonds, hydrophobic and hydrophilic effects or electrostatic interactions – are employed to sequester the inorganic species inside one BCP domain. This can also be achieved by capping nanoparticles with functional ligands that can be selectively recognized by one block.\textsuperscript{100} After assembly, the polymer template can be dissolved, calcined, degraded using UV or ozone treatment, crosslinked or converted to carbon by calcination under a hydrogen atmosphere.

BCPs have been used to direct the spatial distribution of nanoparticles and thereby tailor the properties of the composite (see Figure 1.13a).\textsuperscript{99} The spherical, cylindrical, lamellar and cubic BCP phases have all been investigated. One striking success of this approach is the fabrication of mesoporous materials made from Pt nanoparticles.\textsuperscript{100} A specifically engineered BCP was used to assemble Pt nanoparticles capped with ionic liquid ligands into a mesostructured Pt nanoparticle-BCP hybrid (Figure 1.13b). The materials were subsequently annealed to fully develop the mesostructure and calcined under Ar to convert them into Pt-carbon mesoporous materials. The carbon was finally removed by ozone treatment (see Figure 1.13c and 1.13d).
Figure 1.13. a) shows the schematic assembly of metal nanoparticles using a BCP template. b), c) and d) describe the preparation of ordered mesoporous materials from Pt nanoparticle-block copolymer self-assembly. b) and c) present the schematic structures of the mesostructured Pt nanoparticle-block copolymer hybrid and of the resulting mesoporous materials, respectively. d) is a transmission electronic microscopy (TEM) micrograph of the mesoporous materials. b), c) and d) were reproduced in part with the permission of the American Association for the Advancement of Science.\textsuperscript{100}

Metal nanowire patterns can be fabricated by metal vapour-deposition onto thin spin-coated phase-separated BCP films.\textsuperscript{101} After annealing, the metals were shown to preferentially grow on the BCP domains with the highest wetting properties. Using a PS-\textit{b}-PMMA film, Au and Ag nanostructures were grown onto the PS domains while Pb and In were selectively deposited onto the PMMA domains.
BCPs can also be used in combination with sol-gel chemistry to template the formation of mesoporous silica and metal oxides.\textsuperscript{64,102} The approach, analogous to the surfactant-based LC templating described in Section 1.3, typically employs PEO-\textit{b}-PPO-\textit{b}-PEO triblock copolymers – commercially available under the tradename Pluronics – as SDAs. The materials fabricated via this technique have significantly bigger pores (5-30 nm) as well as thicker microporous walls, when compared with MCM-41. In addition to being investigated for well-established applications such as catalysis and separation, these materials have been used to template the formation of mesoporous carbons\textsuperscript{103} and metal nanowires.\textsuperscript{104}

### 1.4.4  Block ionomers

Ionic diblock copolymers are composed of one non-ionic (typically hydrophobic) block and one ionic block.\textsuperscript{105} The most common ionic blocks include quaternized PVPs such as poly(\textit{N}-methyl-4-vinylpyridinium) halide and poly(\textit{N}-methyl-2-vinylpyridinium) halide, poly(metal methacrylates), poly(metal acrylates) and poly(metal styrene sulfonate) (see Figure 1.6). Ionic BCPs have a large interaction parameter $\chi$, reflecting the very different chemical nature of their component blocks. This extreme incompatibility creates a strong driving force for phase separation and micellization, which is reflected in the unusually low CMC and high aggregate stability, compared with non-ionic BCPs. The cores of the ionic BCP aggregates are generally free of solvent and in a glassy state, which add to the overall stability of the micelles, even at high temperature.\textsuperscript{105} Ionic BCP micelles are generally regarded as ‘frozen’ or with no kinetic exchange between unimers and micelles\textsuperscript{106,107} and a wide range of shapes and sizes are known for these aggregates.\textsuperscript{108}

Ionic diblock copolymers are divided into two main categories: block polyelectrolytes and block ionomers (BIs). This classification is based on the effect of the ionic block on the properties of the materials and it typically reflects the solvent employed to dissolve the
Block polyelectrolytes have properties that are governed by long-range electrostatic interactions within the coronae and between the aggregates. These can be observed in aqueous solutions where they form regular micelles with non-ionic cores and ionic coronae. BIs, in contrast, have properties governed by strong, short-range electrostatic interactions within the microdomains. They are obtained in low dielectric constant solvents and they assemble into reverse micelles with the ionic block in the cores and hydrophobic coronae. Based on this classification system, a given ionic BCP can therefore be a block polyelectrolyte and a BI, depending on the solvent employed. Since I exclusively used BIs in my research, only their properties will be discussed in details in the rest of this section.

BI aggregates were first described in the early 1990s by Eisenberg. BIs are generally composed of a long hydrophobic block (e.g., PS) and a short ionic block, and they assemble into *starlike* reverse micelles. Using size exclusion chromatography (SEC), viscometry and dynamic light scattering (DLS), it was established that for a given hydrophobic segment length, both the aggregation number and the hydrodynamic radii \( R_h \) increase with an increasing ionic segment length. A longer hydrophobic block improves the solubility of the unimer and decreases the aggregation number. At the same time, \( R_h \) increases because of a thicker corona. BIs assemble into aggregates with very narrow core size dispersities. For instance, the radius polydispersity index for the ionic core of PS-\( b \)-PCsA micelles was measured to be approximately 1.03, as measured by small-angle x-ray scattering (SAXS).

With their high inter-block incompatibility, BIs are well within the strong segregation limit (SSL). In order to minimize the interfacial energy between the ionic and non-ionic components, well-defined interfaces are formed and the ionic chains stretch to a maximum within the cores of the micelles (in some cases, an extension of more than 100% of the contour length has been calculated). It was established by relaxation time measurement NMR experiments that the
hydrophobic chain mobility within the corona is restricted close to the ionic core and increases moving away from the center.\textsuperscript{111} When water is added to BI aggregates, it tends to migrate towards the core of the micelles and solvate the ionic chains. However, the water is not restricted to the ionic cores and is known to exchange freely between the micelles and the solvent. The partition coefficient of water between the inside of the micelles and the organic solvent primarily depends on the solubility of water in the solvent. The following order was determined: cyclohexane $>$ benzene $\sim$ toluene $>>$ THF $\sim$ DMF.$^{112}$

1.4.5 BIs for the fabrication of inorganic nanomaterials

BIs have been extensively employed as fully organic nanocontainers for a wide variety of biomedical compounds.$^{113}$ However, considering their many attractive aggregative properties – namely low CMC, aggregate stability and uniformity, and the possibility to partition water inside the core – it is rather surprising that BIs have not been more thoroughly investigated for the fabrication of inorganic nanomaterials. Their challenging synthesis and relative scarcity when compared with non-ionic BCPs might be contributing factors.

Nevertheless, BIs have been used as core-confining nanoreactors to assemble metal, semiconductor and one-dimensional coordination polymer nanoparticles. Gold nanoparticles were synthesized by first reacting PS-$b$-P2VP with HAuCl$_4$, generating the BI PS-$b$-P2VPH$^+$AuCl$_4^-$ that assembles into spherical inverse micelles with the Au anions segregated in the cores. Au$^{III}$ was then reduced to Au nanoparticles using NaBH$_4$.$^{114}$ Dissolved PS-$b$-PCdA micelles were converted to polymer-protected CdS nanoparticles by bubbling H$_2$S in the mixture.$^{115}$ More often than not, spherical nanoparticles are obtained, but other shapes have been reported. For instance, complex coacervate core micelles (C3Ms) were employed to prepare wormlike aggregates with one-dimensional coordination polymers in the cores.$^{116}$ C3Ms are formed by co-assembling a BI and an oppositely charged species in water. In this case,
poly(ethylene oxide)-b-poly(N-methyl-2-vinylpyridinium) iodide and a negatively charged cyclic di-zinc complex were used. In water, this BI does not phase separate because both blocks are soluble. It did however aggregate into wormlike micelles upon addition of the di-zinc complex, which undergoes a metathesis reaction with the iodide anion on the BI. Once in the micelle cores, the cyclic complexes were ring-open polymerized into one-dimensional zinc coordination polymers.

1.4.6 Metal-containing BCPs

Transition metal-containing polymers or metallopolymers were first reported in 1955 but progress was slow until the development of new synthetic methods in the mid 1990s that gave access to soluble and characterizable polymers. Metallopolymers can be separated into two general categories depending on the bonding of the metal atoms to the polymer chain. The first class is for polymers that have the metals in their backbones, either incorporated directly through metal-carbon σ-bonds or metal-metal bonds, or part of a π-coordinated backbone. The second class includes the polymers that have metal-containing pendent groups or side chains. The metal atoms can once again either be σ- or π-coordinated to the polymer. Figure 1.14 shows a few examples of both types of metallopolymers. Transition metal-containing polymers are part of a larger family of materials called inorganic polymers, which also include PDMS, polymethyleneephosphine and polyphosphazene. Here, only transition metal-containing polymers (simply called metal-containing polymers from here onward) are discussed as they are most relevant to this work.
I. Metal in the polymer backbone

![Metal complex](image)

Figure 1.14. Examples of metal-containing polymers.

II. Metal pendent to the polymer backbone or in the side chains

![Polymer structures](image)

Metal-containing polymers can combine the magnetic, electronic, optical and catalytic properties afforded by metal complexes with the mechanical strength and processability of polymer materials. A number of applications can profit from this unique combination of properties. For instance, polymers containing photoactive metal complexes have been made into thin films and incorporated into microfabricated electroluminescent and photovoltaic devices.\textsuperscript{119} Other metal-containing polymers have been used as stimuli responsive materials in actuators,\textsuperscript{120} and also as precursor for ceramic materials.\textsuperscript{121}

Metal-containing BCPs having low polydispersities are especially attractive for the fabrication of self-assembled inorganic nanostructures but their synthesis presents additional challenges associated with the reactivity or instability of the metal atoms or complexes under
living polymerization conditions. Nevertheless, these difficulties have been, in part, overcome through the development of new synthetic approaches. Metal-containing BCPs can also be classified based on the bonding position of the metal atoms in the polymer chain but unlike to metal-containing homopolymers, more than two configurations can exist. In the next subsections, each family of metal-containing BCPs is described, along with a few examples of applications.

1.4.7 BCPs with metal atoms in the backbone

Discovered in 1996 by Manners, polyferrocene-containing BCPs are the first and, to this day, still the only true examples of low polydispersity BCPs with skeletal transition metal atoms. They are synthesized by living anionic ring-opening polymerization of strained ferrocenophane cyclic monomers using initiators such as BuLi. Compound 1 and to a lesser degree compound 2 (shown in Figure 1.15) are the most prevalent monomers for this approach. Polymerization of 1 and 2 gives polyferrocenylsilane (PFS) and polyferrocenylphosphine (PFP), respectively. A wide variety of BCPs based on these two building blocks have been reported, including PS-b-PFS (shown in Figure 1.15), PI-b-PFS, PFS-b-PDMS and PFP-b-PFS-b-PDMS. BCPs with narrow polydispersities (PDI < 1.2) and wide ranges of molecular weights and compositions can be prepared this way. Polyferrocene-containing BCPs were also synthesized via sequential ring opening metathesis polymerization of ansa-vinylene-ferrocene and norborne using the Schrock molybdenum catalyst. However, this system is poorly behaved as the polymerization reaction is not entirely living and it yields polymers with limited solubility and wide polydispersities.
PFS-containing BCPs are typically made of very dissimilar and incompatible blocks and they therefore experience a strong driving force to phase separate. Interestingly, the PFS segments have a propensity to organize into semi-crystalline domains upon phase separation. Spherical, cylindrical, tubular and lamellar structures with semi-crystalline PFS cores have been reported.\textsuperscript{124} One of the most exciting applications for these materials is in BCP nanolithography (see section 1.4.3.1 for more details on this technique). Films of phase-separated PS-\textit{b}-PFS have shown very high etching contrasts, with the PS phase being etched much faster than the PFS phase. These films were used as lithographic masks to fabricate simple sub-100 nm Co and W nanopost arrays.\textsuperscript{125} Other applications for these BCPs include the fabrication of electrochemically active nanomaterials, the synthesis of patterned single-walled carbon nanotubes and as precursors for nanostructured magnetic ceramics.\textsuperscript{124} In one particularly
interesting study, PFS-containing BCPs were used to assemble a new type of co-micelles. These co-micelles were prepared in solution by epitaxially growing semi-crystalline PFS$_{40}$-b-PDMS$_{330}$ micelles onto pre-assembled semi-crystalline PFS$_{53}$-b-PI$_{320}$ micelles (see Figure 1.16).$^{126}$ These nanomaterials are now being investigated for BCP nanolithography.

![Figure 1.16](image)

**Figure 1.16.** a) shows the schematic assembly of a co-micelle made of PFS-containing BCPs and b) is a dark-field TEM micrograph of the co-micelles. In the TEM micrograph, the PFS$_{53}$-b-PI$_{320}$ assembly is observed as the thin cylindrical section and the PFS$_{40}$-b-PI$_{330}$ assembly appears thicker because PDMS has more electron density. b) was reproduced in part with the permission of the American Association for the Advancement of Science.$^{126}$

### 1.4.8 BCPs with metals pendent to the backbone or in the side chains

BCPs with metals pendent to the backbones or in the side chains are much more common because their synthesis is less restrictive; the metals can be conveniently attached post-polymerization to the preformed functional organic backbone. As discussed in section 1.4.3, PVP-containing BCPs have been used to fabricate metallic nanopatterns on surfaces by selectively loading the PVP domains of a phase-separated film with different metals. In a related approach, metal nanoparticles were synthesized using metal-loaded PVP-containing BCP micelles. Systems like these do not technically qualify as metal-containing polymers because they are not composed of discrete metal-coordinated macromolecules. Genuine metal-
coordinated PVP-containing BCPs have been prepared by tethering a number of complexes to
the organic backbone, including \([\text{Ru(terpy)(dmbipy)Cl}]^+\) and \([\text{Re(2,2'\text{-bipy})(CO)}_3]^+\) (terpy = 2,2';6',2''-terpyridine; dmbipy = 4,4'-dimethyl-2,2'-bipyridine; 2,2'-bipy = 2,2'-bipyridine).\(^{127,128}\)

Other examples of BCPs with metals pendent to the backbone or in the side chains have
been prepared using an array of functional groups that can anchor metal complexes. Some of the
most prevalent ligand classes include terpyridine, 2,2'-bipyridine, S-C-S pincer ligand, aniline
and porphyrin. Figure 1.17 shows a few recent examples of BCPs with metals pendent to the
backbone or in the side chains. Polymer 3 was obtained by amidation of a PS-\(b\)-PAA with an
amine-terminated \([\text{Ru(terpy)}_2]^{2+}\) complex.\(^{129}\) Polymers 4 and 5 were both synthesized by
sequential ring-opening metathesis polymerization (ROMP) of the metal-containing monomer
followed by the organic monomer using Grubbs’ first generation catalyst.\(^{130,131}\) The organic
backbone of the rod-coil 6 was synthesized by coupling an azide-terminated phthalic anhydride-
protected poly(3,5-dimethyl-4-aminostyrene) with an ethynyl-terminated poly(phenylene
vinylene) via click chemistry. The molybdenum oxide cluster \([\text{Mo}_6\text{O}_{18}]^{2-}\) was then coordinated to
the deprotected aminostyrene pendent groups.\(^{132}\)

Metal-containing BCPs are made of chemically dissimilar and highly incompatible blocks,
which lead to large driving forces for phase separation and self-assembly. For instance, 3 was
shown to form a luminescent hexagonal lyotropic liquid-crystalline phase in chloroform.\(^{129}\)
Luminescent vesicles and tubules were obtained by assembling 4 in a solvent mixture of
acetonitrile and chloroform.\(^{130}\) Microporous photovoltaic polymer films showing very efficient
interpolymer electron transfer properties were obtained from 6.\(^{132}\) Finally, 5 was investigated for
multi-molecular recognition applications.\(^{131}\)
1.4.9 Supramolecular and metal-terminated BCPs

BCPs in this class do not have metals incorporated in one of the blocks but instead the metal atoms are located at the block junctions or at the chain-end. Developed by Schubert, supramolecular BCPs are built around the concept of using coordination chemistry to link two or more homopolymer chains together (see Figure 1.18). A number of terpyridine-terminated macromolecules such as PEO and PS have been combined to create diblock and triblock copolymers using a single metal atom as connector. Although a wide variety of metals have been
used as connector, ruthenium is by far the most common because it is essentially inert to substitution reactions with terpyridines coordinated. Interestingly, ruthenium-linked PS-\(b\)-PEO BCPs, labeled PS-[Ru]-PEO, were used in the nanofabrication process of porous polymer films (see Figure 1.19).\(^{135}\) The process involved first spincoating a thin film of PS-[Ru]-PEO onto a Si wafer. The BCP self-assembled into a cylindrical phase with the PEO cylinders perpendicular to the surface upon evaporation of the solvent. These PEO domains were then ‘etched’ away by soaking the film in an aqueous solution of Ce(SO\(_4\))\(_2\), which oxidized the Ru metal centers and released the PEO chains.
Figure 1.18. Modular design of supramolecular metal-containing BCPs.
Metal-terminated BCPs can either have a metal atom attached at one end of the chain or at both ends. Hydroxyl-terminated PEO-\textit{b}-PPO-\textit{b}-PEO BCPs have been end-functionalized with different ligands to tether a number of metal complexes. One recent report describes the functionalization of one such Pluronics copolymer with the metal complex (dimethylaminopyridine)pentacyanoferrate(II). The assembly of this novel metal-terminated BCP into Prussian blue analogue (PBA) nanoshells via an approach called miniemulsion periphery polymerization was also investigated (see Figure 1.20). These nanomaterials could potentially be used to encapsulate guest compounds for various applications such as sensors, bioactive compounds carriers and catalysis although removal of the organic core to access the hollow capsules has not yet been achieved.

\textbf{Figure 1.19.} BCP nanofabrication using PS-[Ru]-PEO.
**Figure 1.20.** a) shows the structure of the iron cyanide-terminated BCP 7 and b) its use in the preparation of PBA nanoshells. c) is a TEM micrograph of the PBA nanoshells. b) and c) were reproduced in part with the permission of the American Chemical Society.\(^{57}\)

1.5 **Goals and scope of the thesis**

The premise of this thesis is the preparation and characterization of nanostructured coordination polymers. Specifically, I selected PBAs as model compounds because their chemistry is varied and well established, and their characterization is straightforward using the CN stretching frequency in the IR and the different metal-to-ligand and intervalence charge transfer transitions in the UV-vis. PBAs exhibit exciting optical, electronic and magnetic properties, and can store large quantities of small gas molecules such as hydrogen. In addition, PB itself is biocompatible. The nanostructuring of these materials is an attractive goal because it could lead to the discovery of new properties and functions such as patternable low-dimensional
magnetism or PBA ferrofluids, and nanosized PBAs could be incorporated into nano- and biodevices.

The unifying theme of my thesis is molecular assembly. I used a number of organic structure-directing agents – surfactants, block copolymers and rigid templates – to build nanostructured PBAs. The preparation of mesostructured PBAs via a ligand-assisted liquid-crystal templating approach and the attempted removal of the template to access the mesoporosity are described in Chapter 2. Several mesostructures are investigated and the magnetic properties of the materials are also explored. The use of ionic polymers and block copolymers to assemble PBA nanomaterials is examined in Chapters 3, 4 and 5. In Chapter 3, I focus on the synthetic efforts to synthesize a polymer capable of tethering an iron cyanide complex. A number of systems are considered and the preparation of a polyelectrolyte model compound is reported. The synthesis of metal-containing ionic block copolymers and their use in the fabrication of soluble PBA nanoworms are described in Chapter 4. The assembly process is studied and the conversion of the materials into nanostructured metal oxide is explored. Chapter 5 focuses on the fabrication of soluble hollow polymer capsules with PBA inner-shells via the emulsion-induced assembly of block ionomers. The effect of the block ionomer architecture on the aggregate morphologies is examined and the materials are investigated as functional nanocontainers to encapsulate a molecular compound. Finally, the incorporation of triptycene-based ligands into the molecular structure of a PBA under solvothermal conditions is examined in Chapter 6.
CHAPTER 2

MESOSTRUCTURED PRUSSIAN BLUE ANALOGUES†

2.1 Introduction

Mesoporous silica, a form of SiO$_2$ with periodic organization of channels on the nanometer length scale, is formed by an aqueous liquid-crystal (LC) templating route.$^{60,61}$ In addition to silica, this approach has been used to prepare a wide range of mesoporous metal oxides$^{64,75,76,136-140}$ and heavier chalcogenides,$^{69,141,142}$ and these materials are now investigated for catalytic$^{143}$ and separation$^{144}$ applications. Non-chalcogenide mesoporous materials should have a broader set of properties and functions and could lead to new and unexpected applications. However, the synthesis of these novel materials remains a significant challenge for a number of reasons, including the stability and solubility of the precursor species in the liquid-crystalline phase and a challenging polymerization chemistry.$^{70,71,73,74,145}$

Coordination frameworks (CFs) are another type of materials that has received a lot of attention in recent years.$^{13,32,41-44,47,54,55}$ They are microporous crystalline solids composed of metal ions linked into a three-dimensional network by bridging ligands. By and large, CFs

possess exciting properties conferred by their high surface areas and the possibility to functionalize, modify, or exchange the organic linkers depending on the applications targeted. They are promising candidates for asymmetric catalysis and separations,\textsuperscript{12,26} molecular sensing\textsuperscript{22} and gas storage\textsuperscript{17-19} but their use is limited to small molecules because their internal surface area is mostly inaccessible to larger species due to their small pore sizes (typically 0.5-1.5 nm).

One way to remedy this limitation is to incorporate a series of large holes – mesopores, i.e. pores in the range 2-50 nm – inside the microporous solid. If dense enough, this network of mesopores should make possible the diffusion of big molecules inside the materials. With the exceptional reactivity of their internal surface area accessible to a myriad of chemicals, these new materials should prove valuable for new chemistry, storage, and sensing applications.

This concept of synthesizing a material with bimodal porosities has already been reported by Holland et al.,\textsuperscript{146} but on a bigger length scale. By introducing monodisperse latex spheres as macroscale porogen in the synthesis of mesoporous metal oxides, the researchers were able to prepare macro-mesoporous materials. Unfortunately, this approach cannot be easily adapted for the preparation of the meso-microporous analogues because the availability of incorporable mesoscale porogens is limited. An alternative approach is therefore needed.

LC templating, which uses surfactant assemblies as a structure-directing agent (SDA), does not suffer from these limitations. It has already been used to prepare mesoporous aluminosilicates from preformed microporous zeolite seeds.\textsuperscript{147,148} These materials show very good hydrothermal stability and strong acidity, and are now being investigated as catalysts for diverse industrial reactions. Based on this precedent and on the fact that mesoporous materials and microporous coordination frameworks have separately been receiving a lot of attention in the past years, it is rather surprising that little work has been done in combining LC templating with
coordination chemistry to prepare mesostructured CFs, especially considering the abundance of coordination solids available.

This chapter details a strategy to synthesize mesostructured CFs based on Prussian Blue analogues (PBAs) using a variation of the LC templating approach coined ligand-assisted LC templating in which the SDA is chemically linked to the precursor species. This approach has already been successfully used to synthesize mesoporous niobium, tantalum and titanium oxides.\textsuperscript{149,150} The diversity of these new materials is illustrated with representative monometallic and bimetallic solids that form lamellar, hexagonal, and cubic phases. The electronic and magnetic properties of these materials are also studied.

PBAs were selected as the prototype for CF mesostructures. Prussian blue (PB) is the first synthetic coordination compound. It was first prepared accidentally by Diesbach and Dippel in 1704, and has endured a rich history.\textsuperscript{33,151,152} Owing to its intense blue color, PB has long been used as a dye, and in paints by artists including Picasso, Monet, and van Gogh. The archetypical PB is a cubic network of $\text{Fe}_4[\text{Fe}($CN$)_6]_3\cdot n(\text{H}_2\text{O})$ with Fe at the lattice points and cyanide bridging groups, and the PBA family now includes diverse cyanometallates with similar formulae and network structures. Recently, the use of these generic PBAs as coatings,\textsuperscript{25,153} photomagnetic switches,\textsuperscript{36,38} electrocatalysts,\textsuperscript{153} and sensors\textsuperscript{23,39} has been explored. Even though bulk crystallites of PBA can be adequate for these applications, the development of mesotstructured PBA could provide materials with high surface area, porosity, and low-dimensional magnetism, properties that may be desirable for other applications. PBA nanocrystals,\textsuperscript{48,53,56,154} nanoshells,\textsuperscript{57,58} nanowires\textsuperscript{52} and Langmuir monolayers\textsuperscript{59} have been reported, but the challenges in fabricating mesostructured PBAs have remained without a solution.
2.2 Experimental

2.2.1 Synthesis of the starting materials

The $N$-alkylpyrazinium bromides (8) were synthesized using a modified literature preparation previously used to prepare analogues with shorter chains.\textsuperscript{155} A four-fold excess of pyrazine was added to the $n$-bromoalkane in DMF. The mixture was stirred at 60 °C for 2-3 days and the product was precipitated with diethyl ether, filtered and recrystallized from cold ethanol and diethyl ether. Typical yield: 30%.

2.2.1.1 $N$-dodecylpyrazinium bromide

$^1$H NMR (400 MHz, MeOH-$d_4$): $\delta = 9.50$ ppm (d; 2H; CH), 9.14 (d; 2H; CH), 4.73 (t; $^3$$\gamma$(H,H) = 7.8 Hz; 2H; CH$_2$), 2.09 (m; 2H; CH$_2$), 1.43 (m; 2H; CH$_2$), 1.30 (m; 16H; CH$_2$), 0.91 (t; $^3$$\gamma$(H,H) = 7.0 Hz; 3H; CH$_3$). Elemental Analysis (EA): calculated (%) for C$_{16}$H$_{29}$N$_2$Br: C 58.35, H 8.88, N 8.51; found: C 58.70, H 9.15, N 8.56.

2.2.1.2 $N$-tetradecylpyrazinium bromide

$^1$H NMR (400 MHz, MeOH-$d_4$): $\delta = 9.50$ ppm (d; 2H; CH), 9.14 (d; 2H; CH), 4.72 (t; $^3$$\gamma$(H,H) = 7.8 Hz; 2H; CH$_2$), 2.08 (m; 2H; CH$_2$), 1.43 (m; 2H; CH$_2$), 1.30 (m; 20H; CH$_2$), 0.91 (t; $^3$$\gamma$(H,H) = 6.8 Hz; 3H; CH$_3$). EA: calculated (%) for C$_{18}$H$_{33}$N$_2$Br: C 60.50, H 9.31, N 7.84; found: C 60.86, H 9.63, N 8.00.

2.2.1.3 $N$-hexadecylpyrazinium bromide

$^1$H NMR (400 MHz, MeOH-$d_4$): $\delta = 9.50$ ppm (d; 2H; CH), 9.14 (d; 2H; CH), 4.73 (t; $^3$$\gamma$(H,H) = 7.8 Hz; 2H; CH$_2$), 2.09 (m; 2H; CH$_2$), 1.43 (m; 2H; CH$_2$), 1.30 (m; 24H; CH$_2$), 0.91 (t; $^3$$\gamma$(H,H) = 7.0 Hz; 3H; CH$_3$).
\( ^3J(H,H) = 6.8 \text{ Hz; } 3H; \text{ CH}_3 \). EA: calculated (%) for \( C_{20}H_{37}N_2\text{Br} \): C 62.32, H 9.68, N 7.27; found: C 62.46, H 9.76, N 7.5.

### 2.2.1.4 \textit{N-octadecylpyrazinium bromide}

\(^1\text{H} \) NMR (400 MHz, MeOH-\( d_4 \)): \( \delta = 9.50 \) ppm (d; 2H; CH), 9.13 (d; 2H; CH), 4.72 (t; 3J(H,H) = 7.8 Hz; 2H; CH\(_2\)), 2.08 (m; 2H; CH\(_2\)), 1.43 (m; 2H; CH\(_2\)), 1.30 (m; 28H; CH\(_2\)), 0.91 (t; 3J(H,H) = 6.8 Hz; 3H; CH\(_3\)). EA: calculated (%) for \( C_{22}H_{41}N_2\text{Br} \): C 63.91, H 9.99, N 6.78; found: C 64.18, H 10.30, N 6.64.

### 2.2.1.5 \textit{N-icosylpyrazinium bromide}

\(^1\text{H} \) NMR (400 MHz, MeOH-\( d_4 \)): \( \delta = 9.50 \) ppm (d; 2H; CH), 9.12 (d; 2H; CH), 4.71 (t; 3J(H,H) = 7.8 Hz; 2H; CH\(_2\)), 2.08 (m; 2H; CH\(_2\)), 1.43 (m; 2H; CH\(_2\)), 1.29 (m; 32H; CH\(_2\)), 0.91 (t; 3J(H,H) = 7.0 Hz; 3H; CH\(_3\)). EA: calculated (%) for \( C_{24}H_{45}N_2\text{Br} \): C 65.29, H 10.27, N 6.34; found: C 65.46, H 10.40, N 6.62.

### 2.2.1.6 \textit{N-docosylpyrazinium bromide}

\(^1\text{H} \) NMR (400 MHz, MeOH-\( d_4 \)): \( \delta = 9.50 \) ppm (d; 2H; CH), 9.12 (d; 2H; CH), 4.71 (t; 3J(H,H) = 7.8 Hz; 2H; CH\(_2\)), 2.08 (m; 2H; CH\(_2\)), 1.43 (m; 2H; CH\(_2\)), 1.29 (m; 36H; CH\(_2\)), 0.91 (t; 3J(H,H) = 7.0 Hz; 3H; CH\(_3\)). EA: calculated (%) for \( C_{26}H_{49}N_2\text{Br} \): C 66.50, H 10.52, N 5.97; found: C 66.72, H 10.90, N 6.06.

### 2.2.1.7 \textit{Sodium amminepentacyanoferrate(II)}

\( \text{Na}_3[\text{Fe(CN)}_5\text{NH}_3]\)•\( 3\text{H}_2\text{O} \) was prepared from sodium nitroprusside according to the procedure by Kenney et al.\(^{156} \) The yellow solid was recrystallized from a solution of ammonium hydroxide and methanol.
2.2.1.8 Cetyltrimethylammonium ferrocyanide and cetyltrimethylammonium ferricyanide

Cetyltrimethylammonium ferrocyanide (CTA₄[Fe(CN)₆]) was synthesized by a cation metathesis reaction between K₄[Fe(CN)₆]•3H₂O and CTABr in water, according to a modified published procedure.¹⁵⁷ CTABr (2.50 g; 6.9 mmol) was dissolved in 25 mL of deionized water at 50 °C. The ionic compound K₄[Fe(CN)₆] (0.72 g; 1.7 mmol), was dissolved in 5 mL of deionized water and added dropwise to the stirred CTABr solution. A yellow precipitate instantly formed. The reaction was stirred for 1 h at 50 °C and then for 12 h at room temperature. The solid was filtered, washed sequentially with water, cold ethanol and diethyl ether, and then dried under vacuum at 50 °C. Yields 2.3 g of yellowish powder (99%). CTA₄[Fe(CN)₆] was used without further purification for step 2.2.2. The same procedure was employed to prepare cetyltrimethylammonium ferricyanide (CTA₃[Fe(CN)₆]) using K₃[Fe(CN)₆] and CTABr as starting materials.

NMR spectroscopy was only performed on the diamagnetic compound CTA₄[Fe(CN)₆]. ¹H NMR (300 MHz, MeOH-d₄): δ = 3.05 ppm (m; 2H; CH₂), 2.68 (s; 9H; CH₃), 1.68 (m; 2H; CH₂), 1.29 (m; 26H; CH₂), 0.90 (t, ³J(H,H) = 6.5 Hz; 3H; CH₃).

2.2.2 Attempted fabrication of mesostructured PB using CTA₄[Fe(CN)₆] or CTA₃[Fe(CN)₆] as precursor

The precursor CTA₄[Fe(CN)₆] (500 mg, 370 µmol) was dissolved in 15 mL of formamide at 80 °C. Fe(NO₃)₃•6H₂O (300 g; 740 µmol) in 5 mL of formamide was added dropwise to the stirred solution. A blue precipitate instantly formed. The solution was stirred for 10 min at 80 °C and then aged without stirring at room temperature for 12 h. The product was isolated by centrifugation, washed with methanol and hot water (80 °C), then dried under vacuum at 50 °C,
yielding 95 mg of a blue powder. The same procedure was employed for the CTA₃[Fe(CN)₆] precursor using FeCl₂•4H₂O as the crosslinking metal.

2.2.3 Synthesis of [Feᴵᴵ(CN)₅]C₁₈

N-Octadecylpyrazinium bromide (350 mg, 846 µmol) was dissolved in 15 mL of water at 70 °C. An aqueous solution of Na₃[Fe(CN)₅NH₃]•3H₂O (69 mg in 5 mL of water; 212 µmol) was added dropwise to the stirred solution. A blue precipitate formed instantly. The slurry was stirred at 70 °C for 10 min and then hot filtered and washed with hot water (70 °C). A blue solid was obtained. The solid was redissolved in EtOH, filtered to remove insoluble material, and dried under vacuum at 50 °C. Yield: 238 mg of blue solid (95%).

The ¹H NMR spectrum of [FeᴵІ(CN)₅]C₁₈ is shown in Figure 2.2. ¹H NMR (400 MHz, MeOH-d₄): δ = 9.91 ppm (d; 2H; CH), 9.57 (d; 4H; CH), 9.26 (d; 4H; CH), 7.97 (d; 2H; CH), 4.88 (4H; overlapping with the residual H₂O peak), 4.00 (t; ³J(H,H) = 7.4 Hz; 2H; CH₂), 2.14 (m; 4H; CH₂), 1.99 (m; 2H; CH₂), 1.32 (m; 90H; CH₂), 0.93 (t; ³J(H,H) = 6.8 Hz; 9H; CH₃).

2.2.4 Synthesis of M⁺[Feᴵᴵ(CN)₅]Cₙ

The preparation of Feᴵᴵ⁺[Feᴵᴵ(CN)₅]C₁₈ is as follows: Na₃[Fe(CN)₅NH₃]•3H₂O (1.25 g) dissolved in 25 mL of formamide was added dropwise to a stirred solution of N-octadecylpyrazinium bromide (14.8 g) in formamide (150 mL) at 80 °C. The solution immediately turned dark blue. After stirring for 10 min, 12.4 g of Fe(NO₃)₃•6H₂O in 25 mL of hot formamide (80 °C) were added dropwise to the solution. The mixture was stirred at 80 °C for 10 min and then aged without stirring at room temperature for 12 h. The precipitate was collected on a Büchner funnel, and washed with formamide (80 °C), boiling ethanol, and water (80 °C), then dried under vacuum. Yield: 3.1 g of blue powder. The same procedure was used for
the other materials, varying the N-alkylpyrazinium bromide and the linking metal. Fe(NO$_3$)$_3$, Cu(NO$_3$)$_2$, CuCl, Ni(NO$_3$)$_2$, Mn(O$_2$CCH$_3$)$_2$, Zn(NO$_3$)$_2$, Gd(NO$_3$)$_3$, Er(NO$_3$)$_3$, and other metal complexes were used and in every case a mesostructured product was obtained. When an unreactive (inert) metal salt (e.g., Cr$^{III}$) was used, no precipitate formed.

### 2.2.5 Equipment

The 300 MHz and 400 MHz $^1$H NMR spectra were recorded on Bruker AV-300 and AV-400dir spectrometers, respectively. The powder x-ray diffraction (PXRD) patterns were obtained using a Bruker D8 Discover equipped with a Cu K$_{a}$ sealed tube x-ray source. A Hitachi-2000 transmission electronic microscope operating at 200 kV was used to image the materials. Some pictures were obtained in high angle annular dark field (HAADF) mode. IR spectra were obtained using a Thermo Scientific Nicolet 4700 FTIR spectrophotometer. The samples were dispersed in a potassium bromide matrix and transmission was measured in the range 400-4000 cm$^{-1}$. The UV-vis spectra were recorded on a Varian Cary 5000 spectrophotometer. The samples were dispersed in a potassium bromide matrix and absorbance was measured in the range 200-2000 nm. The spectra were fitted using the software PeakFit to calculate the peak positions and the full width at half maximum (FWHM). Mössbauer spectroscopy was performed on a WEB Mössbauer spectroscopy system equipped with a Janis Research variable temperature SH1-850 cryostat, closed cycle refrigerator and a $^{57}$Co in Rh matrix source (~ 40 mCi). The powder was loaded into a custom-made Teflon holder. The Mössbauer spectrum of the sample was taken at 300 K. The velocity was scanned between 8 and -8 mm s$^{-1}$ using a constant acceleration triangular waveform. Magnetic measurements were collected over the range of 2-300 K using a Quantum Design MPMS5S SQUID magnetometer operating at 0.1 T and corrected for diamagnetic contributions of the sample holder. The C, H and N elemental analyses were obtained at the UBC Microanalytical Services Laboratory and the metal analyses were performed.
by Canadian Microanalytical Service Ltd. using ICP-MS of digested (boiling H$_2$SO$_4$/HNO$_3$) samples. The ESI-MS spectra were also obtained at the UBC Microanalytical Services Laboratory using a Waters ZQ mass spectrometer coupled with a Waters Alliance 2695 delivery system. Energy-dispersive x-ray (EDX) spectroscopy was performed using a Hitachi S-3000N scanning electron microscope equipped with a Quartz Xone EDX system. The N$_2$ adsorption isotherm and the BET surface area were measured on a Micromeritics ASAP 2010 physisorption analyzer and software.

2.3 Results and discussion

Preparation of mesostructured PB using the classic LC templating approach was first attempted. SDA-containing PB precursors such as CTA$_x$[Fe(CN)$_6$] (CTA = cetyltrimethylammonium; x = 3 or 4) were synthesized by a cation metathesis reaction between K$_x$[Fe(CN)$_6$] and CTABr in water. The surfactant-containing iron cyanide compounds were then dissolved in formamide and crosslinked into PB-type frameworks with FeCl$_2$ (for x = 3) and Fe(NO$_3$)$_3$ (for x = 4). The materials obtained after addition of the linking metal showed no low-angle diffraction peaks that could be associated with a mesostructure. Instead, a broad pattern that could be assigned to microcrystalline PB was observed. IR spectroscopy confirmed that the surfactant was excluded from the product. I also tried similar approaches using different ionic and nonionic surfactants, all with the same, unsuccessful outcome.

Recognizing that it would be difficult to circumvent the formation of the thermodynamically stable PBA lattice, a means to attach the SDA to the precursor was explored. Based on a number of reports describing the outstanding stability of the complex $N$-methylpyrazinium pentacyanoferrate(II), a family of $N$-alkylpyrazinium surfactants (8) that could tether to the PBA precursors was synthesized to enable the isolation of a kinetically controlled mesostructure.
Addition of \( N \)-octadecylpyrazinium bromide (8; \( n = 18 \)) in hot water to an aqueous solution of \( \text{Na}_3[\text{Fe(CN)}_5\text{NH}_3] \) caused rapid precipitation of \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) (Figure 2.1). Deep blue \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) has a coordination complex as its large polar head group bearing a \(-2\) charge, and derives its color from a metal-to-ligand charge transfer (MLCT) band. It was anticipated that amphiphilic \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) would behave as a surfactant in solvents such as water or formamide. Unfortunately, once isolated, \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) proved impossible to redissolve in water or formamide without partial decomposition (similar results were obtained using the other \( N \)-alkylpyrazinium bromide). Instead, the \( ^1\text{H} \) NMR spectrum of \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) was obtained in methanol (Figure 2.2), a solvent that readily dissolves the compound but does not produce liquid-crystalline phases. It shows that \( [\text{Fe}^{\text{II}}(\text{CN})_5]C_{18} \) precipitates with two \( N \)-octadecylpyrazinium counterions. The upfield shift observed for the b’ protons on the coordinated ligand, when compared with the uncoordinated ligand (b protons), is the result of the metal-to-ligand backbonding. The downfield shift of the a’ protons arises from the paramagnetic anisotropy of the adjacent Fe\(^{\text{II}}\) center and the electric field effects coming from the dipole moments of the cyanide ligands.\(^{162}\)
Figure 2.1. Synthesis of $[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}$.

Figure 2.2. $^1\text{H}$ NMR (400 MHz, MeOH-$d_4$) spectrum for unlinked $[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}$. The NMR spectrum shows a trace of ethanol impurity (3.6 and 1.2 ppm). The aromatic resonances of the pyrazinium rings are labeled for reference.

Figure 2.3 shows the electrospray ionization (ESI) mass spectrum for $[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}$. A number of aggregates are observed, all including the intact $[\text{Fe}^{II}(\text{CN})_5]\text{C}_{18}$ complex. All but one
peak contain the unlinked $N$-octadecylpyrazinium cation. No peaks due to partial hydrolysis of the metal complex are observed.

In order to prevent decomposition of the amphiphilic precursor complex, $\text{[Fe}^\text{II}(\text{CN})_5\text{]}\text{C}_n$ was used in situ in a one-pot synthesis of coordination mesostructures (Figure 2.4). First, $\text{Na}_3[\text{Fe(CN)}_5\text{NH}_3]$ was slowly added to a solution of 8 in hot formamide, giving a blue solution characteristic of amphiphilic iron complex $\text{[Fe}^\text{II}(\text{CN})_5\text{]}\text{C}_n$. Next, a transition metal salt (e.g., Fe(NO$_3$)$_3$, Cu(NO$_3$)$_2$, CuCl, Mn(O$_2$CCH$_3$)$_2$, Ni(NO$_3$)$_2$, Zn(NO$_3$)$_2$, Gd(NO$_3$)$_3$, Er(NO$_3$)$_3$) in

Figure 2.3. ESI mass spectrum of $\text{[Fe}^\text{II}(\text{CN})_5\text{]}\text{C}_{18}$ (negative mode). The structures of the main aggregates are included.
formamide was added, precipitating a richly coloured solid. Water can also be used as a solvent for 8 with the shorter alkyl chains (n = 12 and 14), but formamide yields better ordered materials in all cases. The materials are designated using the general formula: \( \text{M}^x[\text{Fe}^{II}(\text{CN})_5]C_n \), where \( \text{M} \) represents the linking metal with its oxidation state as a superscript, \( \text{Fe}^{II} \) designates the cyanometallate headgroup, and \( C_n \) specifies the number of carbon atoms for the alkyl chain \((C_nH_{2n+1})\) of the tethered \( N \)-alkylpyrazinium. For example, a material prepared using \( N \)-octadecylpyrazinium bromide \((n = 18)\), \( \text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3] \) and \( \text{Zn(NO}_3)_2 \) as linking agent is referred to as \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]C_{18} \).

Figure 2.4. One-pot synthetic approach to \( \text{M}^x[\text{Fe}^{II}(\text{CN})_5]C_n \).

Figure 2.5 shows the powder x-ray diffraction (PXRD) patterns for microcrystalline PB and two representative materials, \( \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{22} \) and \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{18} \). Low-angle peaks \((2\theta < 5^\circ)\) for \( \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{22} \) and \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{18} \) that correspond to neither 8 nor \( [\text{Fe}^{II}(\text{CN})_5]C_n \) confirm the existence of a mesostructured product. The higher angle peaks are in the same region as those in bulk PB, and suggest some order in the cyanometallate wall structure. PXRD patterns indicative of mesostructures were observed for all metal combinations used. In addition, a given metal combination reproducibly yields a given mesostructure (i.e., phase and
order from PXRD) with the structural variability presumably arising from the different coordination numbers and geometries of the linking metals.

Figure 2.5. Wide-angle PXRD patterns of a) microcrystalline PB, b) Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]C\textsubscript{22} and c) Er\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]C\textsubscript{18}. The intensities were normalized to facilitate comparison between the patterns. The microcrystalline PB was prepared using the same experimental conditions as for the mesostructured PBAs but without the addition of the N-alkylpyrazinium bromide surfactant.

Figure 2.6 shows the low-angle regions of PXRD patterns of four representative samples. Er\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]C\textsubscript{12} and Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]C\textsubscript{20} both exhibit an intense low-angle peak at 37 Å and 40 Å, respectively, and a weak unresolved feature at 2θ ~ 4-5° which, according to the transmission electron microscopy (TEM) micrographs, can be assigned to the overlapping (11) and (20) reflections of a hexagonal \textit{p6mm} symmetry mesostructure. Interestingly, when Cu\textsuperscript{I} is used as linking metal, a material is obtained that has a diffraction pattern with five diffraction peaks that index to a cubic phase. Disorder present in the structure, however, prevented us from obtaining satisfactory TEM images of this product. Figure 2.6a, trace D, shows the lamellar order for Er\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]C\textsubscript{22}. Although a mesostructured product was obtained for all the metal and alkyl chain combinations tested, the chain length used in these preparations still affects the
dimensions of the mesostructures and the extent of order in the materials, as illustrated for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_n$ (Figure 2.6b). Upon extending the chain length from 12 to 22 carbons, the first diffraction peak shifts to lower angle and all low angle peaks increase in intensity, characteristic of improved order. Table 2.1 lists the structures observed for all the materials fabricated.

**Figure 2.6.** a) shows the low-angle PXRD patterns of (A) 2D hexagonal Er$^{III}$[Fe$^{II}$(CN)$_5$]C$_{12}$, (B) 2D hexagonal Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_{20}$, (C) cubic Cu$^{II}$[Fe$^{II}$(CN)$_5$]C$_{18}$ and (D) lamellar Er$^{III}$[Fe$^{II}$(CN)$_5$]C$_{22}$. b) shows the evolution of the PXRD patterns for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_n$ as the alkyl chain length is increased from C$_{12}$ to C$_{22}$. The intensities were normalized to facilitate comparison between the patterns.
Figure 2.7 presents representative TEM micrographs of the mesostructured PBA materials. \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{12} \) was successfully imaged both perpendicular and parallel to the channels (Figures 2.7a and 2.7b, respectively). Both views show a hexagonally packed structure of cylindrical channels with an average diameter of 30-35 Å. Figure 2.7c confirms the 2D hexagonal structure for \( \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{20} \), and Figure 2.7d shows the lamellar structure of \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{22} \) with an interplane distance of approximately 40 Å (46 Å by PXRD).

**Figure 2.7.** a) and b) are TEM micrographs of \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{12} \) perpendicular and parallel to the channels, respectively. c) and d) are TEM micrographs of 2D hexagonal \( \text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{20} \) and lamellar \( \text{Er}^{III}[\text{Fe}^{II}(\text{CN})_5]C_{22} \), respectively. a), b) and c) were obtained in high angle annular dark field (HAADF) mode and d) was taken in bright field mode.
The composition and connectivity of the structures were established using elemental analysis (EA), energy dispersive x-ray (EDX) analysis, thermogravimetric analysis (TGA), IR spectroscopy, and UV-vis spectroscopy. EA of the materials (Table 2.1) confirms the incorporation of ca. 5-25 wt.% iron and the second metal in the structure. As expected, lengthening the alkyl chain generally increases the carbon content and decreases the fraction of metal and nitrogen. Atomic metal ratios (M³/FeⅡ) ranging from 0.7 to 3 are typically measured. EDX also showed low levels of halides and alkali metals in the samples; the remainder of the mass balance is likely oxygen from included or coordinated solvent, water, and counterions (e.g., NO₃⁻). TGA of the materials showed 5-8% weight loss below 200 °C, mainly attributed to the release of the solvent molecules or water trapped in the mesostructure (see Figure 2.12 for an example of a typical TGA thermogram obtained for the PBA mesostructures). The main weight loss resulting from the decomposition of the N-alkylpyrazinium ligand combined with the breakdown of the PBA network occurs between 200 and 600 °C.

IR spectra of the mesostructured materials show peaks attributable to the N-alkylpyrazinium moiety and to the [Fe(CN)₅]³⁻ unit. IR also confirmed that the walls of the mesostructures contain metal centers linked by bridging cyanide ligands. The three $\nu_{CN}$ stretching modes of the approximately $C_{4v}$ symmetrical [Fe(CN)₅NH₃]³⁻ are in the range 2000-2150 cm⁻¹, with the strongest band at 2047 cm⁻¹. Replacing the amine ligand with the π-accepting N-alkylpyrazinium results in increased $\nu_{CN}$ stretching frequencies,¹⁶¹ with the most intense band observed at 2069 cm⁻¹ for unlinked [FeⅡ(CN)₅]Cₙ. Upon formation of the mesostructured material, the product shows a significantly broader $\nu_{CN}$ stretching band that is always at higher frequency (2075-2105 cm⁻¹). It is well established that $\nu_{CN}$ modes for bridging cyanides appear at higher wavenumber than for terminal cyanides.¹⁶³
Further evidence for the connectivity in the structures emerged from stability studies. The insoluble mesostructured materials retain their order (as confirmed by PXRD spectroscopy) after washing with formamide, hot water, hot alcohols, chlorinated solvents, and DMSO, or sonication in methanol and drying under vacuum for extended periods. For metal analysis, it was necessary to degrade samples in boiling $\text{H}_2\text{SO}_4/\text{HNO}_3$. 
<table>
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<th>% H</th>
<th>% N</th>
<th>% Fe</th>
<th>% M</th>
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<td>40</td>
<td>Cubic</td>
</tr>
<tr>
<td>Gd&lt;sup&gt;III&lt;/sup&gt;[Fe&lt;sup&gt;II&lt;/sup&gt;(CN)&lt;sub&gt;5&lt;/sub&gt;]C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>48.54</td>
<td>7.41</td>
<td>13.86</td>
<td></td>
<td></td>
<td>42</td>
<td>Lamellar</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;II&lt;/sup&gt;[Fe&lt;sup&gt;II&lt;/sup&gt;(CN)&lt;sub&gt;5&lt;/sub&gt;]C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>46.69</td>
<td>7.09</td>
<td>10.77</td>
<td>5.82</td>
<td>10.80</td>
<td>43</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;II&lt;/sup&gt;[Fe&lt;sup&gt;II&lt;/sup&gt;(CN)&lt;sub&gt;5&lt;/sub&gt;]C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>55.64</td>
<td>8.03</td>
<td>13.25</td>
<td>4.77</td>
<td>7.17</td>
<td>37</td>
<td>Lamellar</td>
</tr>
<tr>
<td>Zn&lt;sup&gt;II&lt;/sup&gt;[Fe&lt;sup&gt;II&lt;/sup&gt;(CN)&lt;sub&gt;5&lt;/sub&gt;]C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>50.53</td>
<td>7.26</td>
<td>11.48</td>
<td></td>
<td></td>
<td>34</td>
<td>**</td>
</tr>
</tbody>
</table>

* obtained by EDX analysis by measuring the atomic ratio relative to Fe. ** Phase could not be accurately determined as only 1 peak was observed in the PXRD pattern.
The intense color of PB arises from an intervalence charge transfer (IVCT) band at ca. 720 nm (Figure 2.8d; full width at half maximum (FWHM) = 410 nm). The mesostructured materials have brilliant colors akin to PB, and their colors are dependent on the metal combination utilized. UV-vis spectroscopy verified mixed valency in the mesostructured materials (Figure 2.8). The UV-vis spectrum of unlinked [Fe(II)(CN)5]C18 shows high-energy bands in the UV – most likely arising from free Fe(II) and electron transfer between the cyanide ligands and Fe(II) – as well as a broad MLCT absorption band centered at 681 nm (Figure 2.8a; FWHM = 210 nm). Zn(II)[Fe(II)(CN)5]C18, which is not expected to exhibit any mixed valency since Zn(II) has a d10 electronic configuration, displays a slightly blue-shifted, but otherwise unchanged, MLCT band centered at 616 nm (Figure 2.8b; FWHM = 224 nm). On the other hand, mesostructured Fe(III)[Fe(II)(CN)5]C18 shows a significantly broader absorption band (Figure 2.8c; FWHM = 486 nm) centered at 690 nm resulting from the overlap of the MLCT and the IVCT bands. These data support the conversion of the iron cyanide complexes into PBA-type frameworks while remaining coordinated to the SDA. All of the Fe(III)[Fe(II)(CN)5]Cn materials exhibit this broad IVCT band, characteristic of Robin and Day Class II delocalization between the cyanide-bridged metal centers. None of the mixed metal mesostructures show significant valence delocalization.
Figure 2.8. UV-vis absorption spectra of a) unlinked [Fe$^\text{II}$](CN)$_3$C$_{18}$, b) Zn$^\text{II}$[Fe$^\text{II}$](CN)$_3$C$_{18}$, c) Fe$^\text{III}$[Fe$^\text{II}$](CN)$_3$C$_{18}$, and d) bulk PB. FWHM was measured for the band observed in the range 500-1500 nm. FWHM = 210 nm for [Fe$^\text{II}$](CN)$_3$C$_{18}$; FWHM = 224 nm for Zn$^\text{II}$[Fe$^\text{II}$](CN)$_3$C$_{18}$; FWHM = 486 nm for Fe$^\text{III}$[Fe$^\text{II}$](CN)$_3$C$_{18}$; FWHM = 410 nm for bulk PB. The absorbances were normalized to facilitate comparison between the spectra.
The room-temperature $^{57}$Fe Mössbauer spectrum for Fe$^{III}$[Fe$^{II}$(CN)$_3$]C$_{18}$ (Figure 2.9) shows two quadrupole doublets assigned to high-spin Fe$^{III}$ and low-spin Fe$^{II}$. The large quadrupole splitting ($\Delta E_Q$) for Fe$^{II}$ indicates significant distortion from octahedral geometry, as expected for an intact complex [Fe$^{II}$(CN)$_3$]C$_{18}$. The quadrupole splitting for Fe$^{III}$ arises from its unsymmetrical coordination sphere composed of N-bonded cyanides and solvent molecules.

![Mössbauer spectrum](image)

**Figure 2.9.** Mössbauer spectrum for Fe$^{III}$[Fe$^{II}$(CN)$_3$]C$_{18}$ at 300 K fitted as arising from two quadrupole doublets (○ = data; solid line = fit). Site 1 (dotted lines) is assigned to high-spin Fe$^{III}$ – isomer shift ($\delta$) = 0.57 mm s$^{-1}$; $\Delta E_Q$ = 0.23 mm s$^{-1}$; Area = 8% – and site 2 (dashed lines) is assigned to low-spin Fe$^{II}$ – $\delta$ = -0.28 mm s$^{-1}$; $\Delta E_Q$ = 0.58 mm s$^{-1}$; Area = 42%.

The magnetic properties of the mesostructured materials were investigated using superconducting quantum interference device (SQUID) magnetometry. In PB, the Fe$^{III}$ spin centers, which are separated by low spin Fe$^{II}$, couple ferromagnetically at low temperature (Curie temperature ($T_C$) = 5.6 K). Magnetometry measurements of Fe$^{III}$[Fe$^{II}$(CN)$_3$]C$_{18}$ and Fe$^{III}$[Fe$^{II}$(CN)$_3$]C$_{22}$ (Figure 2.10) show ferromagnetic interactions below 10 K indicating that the magnetic order is preserved in the mesostructured PBAs despite defects and wall curvature.
Ni$^{II}$[Fe$^{II}$(CN)$_5$]C$_{18}$ and Cu$^{II}$[Fe$^{II}$(CN)$_5$]C$_{18}$ did not show significant spin interaction at low temperatures.

![Graph of temperature dependence of $\chi g T$ at 0.1 Tesla for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_{18}$ (●) and for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_{22}$ (△) (T = temperature). Because the exact molecular structures are not known, the magnetic susceptibilities are calculated per gram of material ($\chi g$). Complex [Fe$^{II}$(CN)$_5$]C$_{18}$ is diamagnetic.]

**Figure 2.10.** Temperature dependence of $\chi g T$ at 0.1 Tesla for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_{18}$ (●) and for Fe$^{III}$[Fe$^{II}$(CN)$_5$]C$_{22}$ (△) (T = temperature). Because the exact molecular structures are not known, the magnetic susceptibilities are calculated per gram of material ($\chi g$). Complex [Fe$^{II}$(CN)$_5$]C$_{18}$ is diamagnetic.

Based on the results presented here, reaction of 8 and Na$_3$[Fe(CN)$_5$NH$_3$] in formamide gives an amphiphilic intermediate, [Fe$^{II}$(CN)$_5$]C$_n$, that templates the formation of a mesostructured material upon addition of a second metal salt. From PXRD and TEM, the materials exhibit long-range periodic order on the nanometer scale, and can exhibit lamellar, hexagonal, or cubic phases. IR and UV-vis spectroscopy indicate that, analogous to PB, the metal centers of the mesostructured materials are connected by cyanide bridges. Figure 2.11 illustrates the idealized supramolecular assembly and resulting mesostructure.
The materials fabricated in this work are mesostructured but they do not possess a porous structure, as confirmed by N$_2$ adsorption experiments. Non-porous mesostructures have been investigated as laboratory model compounds as well as for a number of applications, including fast response photochromic materials\textsuperscript{165} and photonic crystals.\textsuperscript{166} Still, the removal of the organic template is necessary to access the mesoporosity and unlock the full potential of these materials.
Mesoporous metal oxides and chalcogenides are generally accessed by calcining the organics at high temperature in air or by solvent extraction of the SDA. Unfortunately, neither of these approaches can be used for the removal of the coordinated $N$-alkylpyrazinium SDA from the PBA mesostructures.

Selective pyrolysis, where the materials are heated to a precise temperature at which the organic SDA decomposes but the coordination framework stays intact, was attempted. No such critical temperature was found. Instead, TGA suggests that the PBA coordination framework decomposes in the same temperature range as the organic template. Figure 2.12 presents a typical TGA thermogram for $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{C}_{18}$ performed under N$_2$. Although the curve does not show a plateau that would suggest a two-step thermal degradation process, an upward inflection is observed around 300 °C. However, when heated to that temperature under N$_2$ in a tube furnace, the materials lost their mesostructures as confirmed by PXRD. IR spectroscopy verified that the PBA framework was destroyed. Similar results were obtained when the experiments were performed in air or at other temperatures.
Figure 2.12. TGA thermogram for $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]C_{18}$ under $\text{N}_2$ with a temperature ramp of 10 °C min$^{-1}$.

Because the $N$-alkylpyrazinium structure-directing agent is firmly coordinated to the $[\text{Fe(CN)}_3]^{3-}$ complex inside the PBA mesostructures, it cannot be extracted in hot solvents. I attempted to exchange the template ligand with a number of smaller incoming ligands such as pyridine, $N$-methylpyrazinium and diethylamine. When needed, a small organic salt (e.g., tetramethylammonium bromide) was added to the mixture to balance the charges inside the pores for the leaving $N$-alkylpyrazinium. After a period of several hours of stirring the mesostructured materials with the incoming ligands, the reaction mixture was filtered, the solvent was evaporated, and the residue was analyzed by NMR spectroscopy to detect extracted $N$-alkylpyrazinium. In all cases, no exchanged $N$-alkylpyrazinium was observed by NMR spectroscopy and IR spectroscopy of the PBA mesostructures confirmed that the SDA was still
inside the materials. In addition, no porosity was measured by N₂ adsorption in the resulting materials.

DMSO is known to displace N-methylpyrazinium complexed to pentacyanoferrate(II). The mesostructured PBAs were stirred in DMSO in the presence of tetramethylammonium bromide with the expectation that DMSO would displace the N-alkylpyrazinium template. No exchange was observed at room temperature. However, when the mixture was heated to 60 °C, free N-alkylpyrazinium was observed in the reaction mixture by NMR spectroscopy, suggesting exchange (DMSO-d₆ was employed for this experiment). Unfortunately, the materials collapsed upon removal of the SDA as indicated by the loss of the low-angle mesostructure peaks in the PXRD of the resulting materials.

Figure 2.13 presents a rationalization for these results. Based on the idealized structure described in Figure 2.11, the PBA walls are very thin – at most, the walls are 3 metal ions and 2 bridging cyanides thick. The coordination framework is predicted to be substantially distorted because of the curvature imposed by the SDA. It is also expected to contain some defects throughout – these defects are anticipated to come from an incomplete crosslinking reaction and should help accommodate the wall curvature strain. The structure described here is obviously extremely fragile and the removal of the N-alkylpyrazinium template will certainly result in the collapse of the structure.
Figure 2.13. Idealized structure of the walls in the PBA mesostructures. This framework structure is predicted to be very fragile and collapse upon removal of the N-alkylpyrazinium SDA.

Based on this model, thicker PBA walls may be built by adding [Fe(CN)$_6$]$^{4-}$ units to the mesostructured PBAs. Materials fabricated using a small fraction of K$_4$[Fe(CN)$_6$] in the preparation (< 25 mol.% of the precursor species) remained mesostructured but did not show improved stability in hot DMSO. Interestingly, the mesostructure vanished when more than ca. 25 mol.% of K$_4$[Fe(CN)$_6$] was used in the protocol. These results once again highlight the need for a strongly tethered SDA.

2.4 Conclusions

The object of this chapter was the preparation of mesostructured materials made of PBA. Fabrication of these materials was first attempted employing the classic liquid-crystal templating approach and novel iron cyanide compounds that contain the precursor and the SDA species. It
was recognized that the SDA ought to be tethered to the PBA precursor in order to circumvent the thermodynamic stability of the PBA framework that leads to the formation of the bulk phase. A series of stable tailor-made amphiphilic compounds built from a pentacyanoferroate(II) hydrophilic precursor headgroup and a variety of metal-coordinated hydrophobic $N$-alkylpyrazinium SDAs were used in a one-pot synthesis to prepare PBAs with order on the nanometer scale. In formamide, these iron cyanide surfactants formed liquid-crystalline phases that were crosslinked into PBA-type frameworks with the addition of transition metals. Significantly, the $N$-alkylpyrazinium SDA remained coordinated to the $[\text{Fe(CN)}_5]^3-$ complex in the PBA materials. Well-ordered PBAs with lamellar, hexagonal and cubic structures and a wide range of metal compositions were fabricated using this technique. Interestingly, the materials made of $\text{Fe}^{\text{III}}$ and $\text{Fe}^{\text{II}}$ exhibit valence delocalization and magnetic interactions in the framework.

Removal of the organic template was attempted in order to create mesoporous PBAs. However, because the SDA is coordinated to the PBA, it cannot be washed away as with the mesoporous silicas formed with molecular surfactants. Several techniques were nonetheless investigated, including selective calcinations and ligand exchange-extraction. It was discovered that the PBA framework is too fragile to form free-standing mesoporous materials; the materials collapsed upon exchange-extraction of the $N$-alkylpyrazinium template.

The approach developed in this chapter demonstrates that previously inaccessible PBA nanomaterials can be built by tethering the SDA to the metal cyanide precursor. In the next chapters, this concept is generalized for the fabrication of a wide range of novel PBA nanomaterials using different coordinating templates. Furthermore, as the $[\text{Fe(CN)}_5]^3-$ building block is part of the much larger cyanometallate family, it is anticipated that this route to PBAs will provide an array of mesostructures with tuneable magnetic, optical and electronic properties.
CHAPTER 3

POLYMER PRECURSOR TO PRUSSIAN BLUE

3.1 Introduction

Although Prussian blue (PB) was discovered as early as 1704 by Diesbach and Dippel, it took more than 270 years to confirm its structure.\(^{152}\) One of the early identification challenges was to recognize that the compound originally coined Turnbull’s blue – obtained by reacting \(\text{K}_3[\text{Fe(CN)}_6]\) and \(\text{FeCl}_2\) – is actually PB – obtained by reacting \(\text{K}_4[\text{Fe(CN)}_6]\) and \(\text{FeCl}_3\). Theoretical investigations of the electronic configuration of PB based on ligand field theory suggested that \(\text{Fe}^{\text{III}}\) and \([\text{Fe(CN)}_6]^{4-}\) are the stable species in PB,\(^{34,168}\) and x-ray diffraction,\(^{151,152}\) Mössbauer spectroscopy\(^{169}\) and calorimetric analysis\(^{170}\) confirmed those predictions. These findings indicate that when \(\text{K}_3[\text{Fe(CN)}_6]\) is reacted with \(\text{FeCl}_2\) to prepare Turnbull’s blue, \(\text{Fe}^{\text{II}}\) transfers an electron through the cyanide bridge to the \([\text{Fe(CN)}_6]^{3-}\) complex and PB is obtained. This electron then becomes localized on the \([\text{Fe(CN)}_6]^{4+}\) but it will undergo intervalence charge transfer (thermal or photoinduced) between the two metal sites.\(^{168,34}\)

The kinetics of formation of PB proved to be equally problematic for rigorous characterization of the structure. PB forms at once upon mixing the two reagents and this makes the production of single crystals big enough for x-ray diffraction analysis extremely difficult. Early on, powder x-ray diffraction (PXRD) of the nanocrystalline materials revealed the basic cubic structure of PB\(^{151}\) but single crystal x-ray diffraction data were required to obtain a complete representation of the network. PB single crystals of x-ray quality were finally obtained by slow water vapour diffusion into a solution of PB in concentrated HCl.\(^{152}\)
This last report also highlighted another difficulty in establishing the crystal structure of PB: the network has a high concentration of vacancies. These vacancies – one in every four $[\text{Fe(CN)}_6]^{4-}$ sites – are randomly distributed throughout the materials and maintain the charge neutrality of the network. Unfortunately, they also introduce a lot of disorder in the structure, and make characterizing the materials by x-ray diffraction all the more challenging.

Nanomaterials are transforming and revolutionizing many areas of science and engineering.\textsuperscript{171,172} Interestingly, PB nanomaterials were discovered and employed for many applications well before the concept of nanotechnology was proposed. Reacting FeCl$_3$ with an excess of K$_4[\text{Fe(CN)}_6]$ yields ‘soluble’ PB, a colloidal suspension of KFe[Fe(CN)$_6$]. Because it is stable in aqueous solution for hours, soluble PB has been used in paints and inks.\textsuperscript{33} Unfortunately the size of the nanocrystals cannot be controlled using this approach and polydisperse samples are always obtained. Also, because the nanocrystals are not protected with capping agents, they tend to aggregate and eventually precipitate.

Several methods to fabricate PB and Prussian blue analogue (PBA) nanomaterials have been developed in recent years. PB and PBA nanocrystals with well-controlled dimensions have been synthesized inside reverse surfactant micelles and inside polymer coils.\textsuperscript{28,40,48,50,51,53,56,154,173-176} PB nanowires were electrodeposited inside a porous anodic alumina template that was subsequently removed to release the nanomaterials.\textsuperscript{52,177-179} These PB nanowires are stable and crystalline but they cannot be dissolved for solution processing. Langmuir-Blodgett PBA monolayers were synthesized at a water-oil interface using different interfacial agents.\textsuperscript{59,180,181} PBA nanoshells and nanoboxes were fabricated by Wang via a technique called miniemulsion periphery polymerization (see Section 1.4.9 for more details).\textsuperscript{57,58} Triblock copolymers with iron cyanide complexes at both ends of the chains were used to stabilize an oil-in-water emulsion.
The periphery of the assembly was crosslinked into PBA nanoshells with the addition of Fe$^{III}$ ions. Unfortunately, removal of the organic core to access the hollow capsules was not reported.

This last report is especially interesting because it introduces the first polymer-based PBA precursor. Compounds of this type are attractive because they could be employed in the making of processable PBAs, in the preparation of layer-by-layer electrostatic self-assembled PBA films$^{182}$ or in the fabrication and patterning of novel PBA nanomaterials. The polymer reported by Wang has only two iron cyanide complexes per molecular chain and its use is intrinsically restricted to the fabrication of very thin and delicate PBA structures. A more adaptable metal cyanide-containing polymer system is therefore needed for many applications.

In this chapter, I describe my synthetic efforts towards the preparation of a polymer containing an appreciable number of metal cyanide complexes. This homopolymer is used as a model compound and testing ground for the synthesis of metal cyanide-containing block copolymers that I describe in Chapters 4 and 5.

The materials fabricated in this chapter are characterized using a technique that is unusual for most chemists but is used routinely by materials scientists: $N_2$ adsorption. Adsorption is the adhesion of adsorbates – in this case the adsorbates are $N_2$ molecules, but those can also be atoms, ions or biomolecules – to a surface – the adsorbent. This process produces films of surface-adsorbed species and can be used to estimate the surface area of materials.$^{183}$ By enclosing a degassed sample inside a chamber of known volume and then injecting a known amount of $N_2$, one can measure the quantity of $N_2$ that is adsorbed on the sample at a given temperature – i.e., the difference in chamber pressure with and without the sample inside the chamber. A number of models have been developed to calculate the surface area of the adsorbent from these data, including the Langmuir$^{184}$ and BET$^{185}$ models (Figure 3.1). In the Langmuir model, the adsorbates are postulated to not interact and can therefore only adhere to the
adsorbent. At maximum adsorption, a monolayer is formed. The Langmuir model best describes chemisorption processes as well as physical adsorption inside microporous solids where the pores are too small to allow the deposition of multilayers. In a lot of cases, however, molecules do form multilayers. The BET model – the name BET is for the model’s authors: Brunauer, Emmett and Teller – assumes a random distribution of adsorbate species on the material surface and allows multilayer deposition. This model works best for the physical adsorption of gas molecules onto non-microporous materials.

\[ \text{○} = \text{Adsorbate} \]

\[ \text{Langmuir model} \quad \text{BET model} \]

**Figure 3.1.** Schematic representation of the Langmuir and BET models of adsorption onto a material surface.

### 3.2 Polymer design

Three design requirements were considered in the synthesis of the metal cyanide-containing polymer.

1. The metal cyanide-containing polymer should be built by functionalizing a preformed macromolecular backbone, ideally one that is commercially available. Importantly, block copolymers integrating this backbone should be accessible.

2. The metal cyanide complexes should be strongly tethered to the polymer chain. This implies selecting a complex that is kinetically inert once coordinated to the backbone.
Although many PBA nanomaterials have been fabricated using weakly or non-interacting precursors and structure-directing agents (SDAs),\textsuperscript{53,56} many other nanostructures are inaccessible because the thermodynamic stability of the PBA network precludes their formation. Having the precursors species strongly coordinated to the SDA should provide better control over the nanomaterial formation process. This requirement is partly based on my attempts at making mesostructured PBAs (described in Chapter 2) but also on reports that employed coordinating SDAs or hard templates.\textsuperscript{52,57,58}

3. The functionalization should be high yielding. By this, I mean that modification of just about every monomer unit on a polymer chain should be achievable and that there should be no substantial loss of starting materials in the process.

I selected poly(2-hydroxyethyl methacrylate) (PHEMA) as the macromolecular backbone for the metal cyanide-containing polymer. PHEMA is a commercially available polymer that is employed in the fabrication of contact lenses. It is stable under most conditions and is soluble in DMSO, DMF, short chain alcohols, and hot THF and 1,4-dioxane in some cases. Significantly, it possesses a hydroxyl group that can be functionalized using standard chemical techniques. This hydroxyl group is far enough away from the backbone that it should reduce the steric and electrostatic repulsions that are expected upon complexation of the polymer. HEMA is routinely polymerized by living anionic polymerization and a number of PHEMA block copolymers are known, including PS-\textit{b}-PHEMA, PI-\textit{b}-PHEMA and PMMA-\textit{b}-PHEMA (PS = polystyrene; PI = polyisoprene and PMMA = poly(methyl methacrylate); see Figure 1.6 for the chemical structures).\textsuperscript{186-188}
A few kinetically inert metal cyanide complexes are known, including \([\text{Cr}(\text{CN})_4(2,2'\text{-bipy})]^+\) and \([\text{Fe}(\text{CN})_6(2,2'\text{-bipy})]^{2-}\) \((2,2'\text{-bipy} = 2,2'\text{-bipyridine})\). However, most of these complexes require multistep syntheses or conditions that cannot be incorporated into the preparation protocol of the polymer. One metal cyanide complex, pentacyanoferrate(II), forms stable and kinetically inert compounds with strong π-accepting ligands such as N-methylpyrazinium, N-methyl-4,4′-bipyridinium and \(N,N,N\text{-trimethylammonium-4-pyridine}\). These stable complexes are conveniently prepared by reacting Na₃[Fe(CN)₅NH₃] with the ligand in solution. A complex of this type was employed in Chapter 2 to prepare mesostructured PBAs ([Fe(II)(CN)₅]Cₙ is shown below). Using this complex, the target metal cyanide-containing polymer should be accessible in two steps. First, monoquaternized \(N,N'\text{-heterocycle groups}\) are appended onto the PHEMA backbone. Second, the functionalized ionic polymer is complexed with Na₃[Fe(CN)₅NH₃].
Appending the monoquaternized \(N,N'\)-heterocycle groups onto the PHEMA proved to be the most challenging task. Based on previous successes using complex \([\text{Fe}^{II}(\text{CN})_5]\text{C}_n\), it was decided that the PHEMA backbone ought to be functionalized with pyrazinium pendent groups (polymer 9 in Figure 3.2). A number of synthetic routes and conditions were attempted (see Figure 3.2 for an overview). PHEMA was functionalized with bromoacetyl bromide (Figure 3.2a) and 4-toluenesulfonyl chloride (Figure 3.2e) to introduce leaving groups onto the backbone. However, because of its poor nucleophilicity, pyrazine could not be appended onto the polymer chains in good enough yields (conversion < 15%). Coupling of functional pyrazinium compounds onto the macromolecular backbone was also unsuccessful. PHEMA was converted to a polyazide macromolecular backbone (Figure 3.2b) and reacted with alkyne-terminated pyrazinium bromide species under Cu\(^{I}\)-catalyzed “click chemistry” conditions. Direct \(N,N'\)-dicyclohexylcarbodiimide-mediated coupling of carboxylic acid-terminated pyrazinium bromides onto PHEMA was also attempted (Figure 3.2d). Both of these experiments resulted in complete degradation of the pyrazinium substrates and highlight the susceptibility of such organic salt compounds to coupling agents. A slightly different approach was attempted in Figure 3.2c. Pyrazine pendent groups were first attached to the backbone and then converted to \(N\)-methylpyrazinium iodides. However, because iodomethane selectively reacts at the 4-nitrogen, complexation of the resulting pyrazinium-functionalized polymer was unsuccessful. Steric crowding at the non-quaternized nitrogen due to the adjacent ester linkage most likely prevented coordination of the iron cyanide complex onto the polymer.
Based on these results, I elected to replace pyrazine with the more nucleophilic 4,4'-bipyridine. Although pKₐ does not provide a quantitative description of the nucleophilic character of a heterocyclic compound, it is usually a respectable comparative parameter between chemically similar nucleophiles ¹⁹¹ the pKₐ’s of pyrazine and 4,4'-bipyridine in H₂O are 0.65 and 4.87, respectively.¹⁹² The remainder of Chapter 3 describes the synthesis of polymer 10 along with its complexation with iron cyanide complexes and its crosslinking into PBAs. Characterization of these PBA materials is also discussed.

Figure 3.2. Attempted synthesis of polymer 9.
3.3 Experimental

3.3.1 Materials

Two PHEMAs were used in this chapter: a low molecular weight PHEMA ($M_v = 20,000$ g mol$^{-1}$) and a high molecular weight PHEMA ($M_v = 300,000$ g mol$^{-1}$). Both polymers are commercially available materials (Sigma Aldrich). 1,4-Dioxane and DMF were dried over activated molecular sieves for at least 24 h.

3.3.2 Synthesis of polymer 10

3.3.2.1 Bromoacetylation of PHEMA

Low molecular weight PHEMA (0.50 g) was heated to reflux in 200 mL of 1,4-dioxane in a Schlenk flask under N$_2$ until complete dissolution of the polymer occurred. The solution was cooled down to room temperature and a cloudy gel-like mixture was obtained. Potassium carbonate (K$_2$CO$_3$; 2.57 g; 18.6 mmol) was added as a solid to the mixture. Bromoacetyl bromide (3.76 g, 18.6 mmol, 5 equiv. based on the HEMA unit) was added dropwise to the stirred suspension. The reaction mixture was stirred at room temperature under N$_2$ for 12 h. The
polymer solution was concentrated by rotary evaporation and a white solid was precipitated with water, centrifuged, washed with water three times, then dried under vacuum at 60 °C. Yield: 0.85 g (89%).

Bromoacetylation of the high molecular weight PHEMA using the same procedure was not successful because of the poor solubility of the starting material and the product in 1,4-dioxane or THF. The reaction was attempted in DMF, using 2,6-di-tert-butylpyridine as a base but an insoluble material was obtained.

3.3.2.2 Attachment of the 4,4’-bipyridinium groups

The bromoacetylated low molecular weight PHEMA (0.30 g) was dissolved in 10 mL DMF and added dropwise to a large excess of 4,4’-bipyridine (1.85 g, 11.8 mmol, 10 equiv. based on the HEMA unit) dissolved in 10 mL DMF at room temperature. The solution was stirred at 65 °C under N₂ for 18 h. Polymer 10 was then precipitated with acetone, centrifuged, and washed with acetone three times. Yield: 0.42 g (86%). ¹H NMR spectroscopy showed 100% conversion of the bromoacetyl groups to the bipyridinium bromide.

3.3.3 Synthesis of sodium amminepentacyanoferrate(II)

Na₃[Fe(CN)₅NH₃]•3H₂O was prepared from sodium nitroprusside according to the procedure by Kenney et al.¹⁵⁶ The yellow solid was recrystallized from a solution of ammonium hydroxide and methanol.

3.3.4 Synthesis of [Fe⁹⁺(CN)₅]PE – complexation of 10

Polymer 10 (30 mg) was dissolved in 30 mL of deionized water. In a separate vial, 24 mg (72 µmol) of Na₃[Fe(CN)₅NH₃]•3H₂O was dissolved in 10 mL of deionized water and added dropwise to the vigorously stirred solution of 10. A blue precipitate formed instantly. The
suspension was stirred for 30 min at room temperature. $[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ was centrifuged at 4500 rpm and washed with water and dried under vacuum at 50 °C to isolate the solid material. Yield: 15 mg.

3.3.5 Synthesis of $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ and $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$

An aqueous solution of $\text{Fe(NO}_3)_3\cdot6\text{H}_2\text{O}$ (15 mg in 5 mL of $\text{H}_2\text{O}$) was added dropwise to an aqueous suspension of $[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ (15 mg in 20 mL of $\text{H}_2\text{O}$). The suspension was stirred for 60 min at room temperature. $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ was centrifuged at 4500 rpm and washed with water to isolate the solid material for characterization. Yield: 17 mg. The procedure was repeated with $\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O}$ to get $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$.

3.3.6 Characterization of the materials

3.3.6.1 UV-vis spectroscopy

An aliquot of the $[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ suspension (ca. 0.3 mL) obtained in section 3.4.4 was diluted in 4 mL of deionized water. The UV-vis spectrum was recorded on a Varian Cary 5000 spectrophotometer in the range 200-1300 nm. The same procedure was employed for $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$ and $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_5]\text{PE}$.

3.3.6.2 Transmission electronic microscopy

The materials (2-3 mg) were suspended in methanol (ca. 2 mL) and dropcast onto transmission electronic microscopy (TEM) grids. The samples were imaged using a Hitachi H7600 transmission electronic microscope operating at 80 kV.
3.3.6.3 Other equipment

The 300 MHz $^1$H NMR spectra were recorded on a Bruker AV-300 spectrometer. IR spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR spectrophotometer equipped with a Smart Orbit attenuated total reflectance (ATR) accessory. The N$_2$ adsorption isotherm and the BET surface area were measured on a Micromeritics ASAP 2010 physisorption analyzer and software. The powder x-ray diffraction (PXRD) patterns were obtained using a Bruker Advance diffractometer equipped with a Cu K$_\alpha$ sealed tube x-ray source.

3.4 Results and discussion

Figure 3.3 shows the synthetic approach to polymer 10.

![Synthesis of polymer 10](image)

Figure 3.3. Synthesis of polymer 10.

Two PHEMAs with different molecular weights were tested for this preliminary study: a low molecular weight PHEMA ($M_v = 20,000$ g mol$^{-1}$) and a high molecular weight PHEMA ($M_v = 300,000$ g mol$^{-1}$). The viscosity average molecular weight ($M_v$) is calculated from the viscosity of a polymer solution measured at different concentrations. It is employed as a fast and inexpensive method to determine the molecular weight of polymers. Although different from the number average ($M_n$) or the weight average ($M_w$) molecular weight, $M_v$ is closer to $M_w$. 
PHEMAs of all molecular weights are soluble in DMF, DMSO and short chain alcohols. Unfortunately, these solvents proved unsuitable for the bromoacetylation reaction. Low molecular weight bromoacetylated PHEMA was synthesized by reacting the polymer with an excess of bromoacetyl bromide in 1,4-dioxane with potassium carbonate as a base. The low molecular weight PHEMA was dissolved in 1,4-dioxane heated to reflux and then cooled down to room temperature to obtain a cloudy gel-like mixture. Upon addition of the bromoacetyl bromide, the solution became clear again. This suggests an effective conversion of the hydroxyl to bromoacetylate groups (the resulting bromoacetylated polymer is much more soluble in 1,4-dioxane). $^1$H NMR spectroscopy confirms a high conversion rate of the hydroxyl to bromoacetate (Figure 3.4a). High molecular weight bromoacetylated PHEMA could not be synthesized because the starting material does not dissolve in 1,4-dioxane or THF. The qualifier “low molecular weight” is therefore omitted for PHEMA and its derivatives from here onward.

Polymer 10 was synthesized by adding dropwise a DMF solution of the bromoacetylated PHEMA to an excess of 4,4′-bipyridine in DMF at room temperature and then stirring the reaction at 65 °C for 24 hours. Interestingly, a precipitate formed when the 4,4′-bipyridine solution was added to the polymer solution or when the solutions were mixed while hot. This insoluble solid is most likely a crosslinked network of polymer chains that forms when 4,4′-bipyridine acts as a crosslinking agent by reacting at both nitrogen atoms to form viologen-type compounds. Maintaining a large excess of 4,4′-bipyridine around the polymer completely eliminated this side reaction. Polymer 10 is soluble in water, methanol and DMSO, and $^1$H NMR spectroscopy confirms a high conversion rate of the bromoacetylate groups into monoquaternized 4,4′-bipyridinium groups (see Figure 3.4b). Polymer 10 can also be called a polyelectrolyte (PE) because it bears an electrolyte group at each repeating unit. The terms polymer and polyelectrolyte will be used interchangeably to describe 10 in this chapter.
Polyelectrolytes are useful for a number of applications such as stabilizers for colloidal suspensions, flocculation agents and in the fabrication of polyelectrolyte monolayers by layer-by-layer electrostatic assembly.\textsuperscript{182} Polyelectrolyte 10 is especially interesting because it can coordinate transition metals and could be employed to introduce the rich chemistry of inorganic compounds in some of these applications. Although potentially useful and deserving further investigation, these ideas were not pursued in this work.
Figure 3.4. ^1^H NMR spectra (300 MHz) of a) bromoacetylated PHEMA in CDCl\textsubscript{3} and b) polyelectrolyte 10 in DMSO-\textit{d}_6 (one drop of dichloromethane was added to the sample to help solubilize the backbone).

The top reaction in Figure 3.5 shows the expected complexation and product. Adding Na\textsubscript{3}[Fe(CN)\textsubscript{5}NH\textsubscript{3}] to an aqueous solution of 10 should exchange the labile amine ligand for the \pi-accepting monoquaternized 4,4'-bipyridinium and attach the iron cyanide complex onto the
polymer chain. The anticipated iron cyanide-containing polymer is still ionic and should be soluble in water. Surprisingly, a blue precipitate ([Fe$^{II}$(CN)$_5$]PE) formed instantly when an aqueous solution of Na$_5$[Fe(CN)$_5$NH$_3$] was added to a solution of polyelectrolyte 10 in water. The same blue solid was also obtained when 10 was added to Na$_5$[Fe(CN)$_5$NH$_3$] in water. UV-vis spectroscopy of the [Fe$^{II}$(CN)$_5$]PE suspension in water shows the typical metal-to-ligand charge transfer (MLCT) transition centered around 580 nm expected for a 4,4'-bipyridinium-coordinated [Fe(CN)$_5$]$^{3-}$ complex (Figure 3.6). This suggests attachment of the iron cyanide complex onto the 4,4'-bipyridinium-modified polymer. The higher energy bands (200-400 nm) observed in all of the spectra in Figure 3.6 probably come from the free monoquaternized 4,4'-bipyridinium ligand and charge transfer transitions between the cyanide ligands and the Fe$^{II}$ center.$^{160}$ A [Fe$^{II}$(CN)$_5$]PE suspension in water was reacted with Fe$^{III}$ and Zn$^{II}$ ions to crosslink the iron cyanide-containing polymer into PBA-type frameworks. A very broad absorption band, akin to the intervalence charge transfer (IVCT) transition displayed by PB, is observed for Fe$^{III}$[Fe$^{II}$(CN)$_5$]PE in the UV-vis spectrum. This band, centered around 780 nm, extends well into the near-IR region and overlaps with the MLCT transition. The UV-vis spectrum for Zn$^{II}$[Fe$^{II}$(CN)$_5$]PE, which is not expected to display an IVCT since Zn$^{II}$ has d$^{10}$ electronic configuration, only shows a slightly blue-shifted, but otherwise unchanged, MLCT transition centered around 520 nm. These data support the conversion of the iron cyanide complexes into a PBA-type framework while remaining coordinated to the polymer.
Figure 3.5. Complexation of polyelectrolyte 10 and synthesis of the PBA materials $M^x[Fe^{II}(CN)_3]PE$. 
Further evidence for the connectivity of the PBA network was obtained by IR spectroscopy of the dry purified materials. IR spectra of the different materials consistently show peaks that are attributable to the organic backbone and to the pentacyanoferrate(II) complex. As mentioned in Chapter 2, the energy of the $\tilde{\nu}_{CN}$ stretching band is of particular interest because it is diagnostic of the coordination environment for the iron cyanide complex. The approximately $C_4v$-symmetric precursor $\text{Na}_3[\text{Fe(CN)}_5\text{NH}_3]$ displays three $\tilde{\nu}_{CN}$ stretching modes, with the most intense band at 2030 cm$^{-1}$. A blue shift of 16 cm$^{-1}$ was observed for this band to 2046 cm$^{-1}$ upon exchange of the labile amine ligand with the $\pi$-accepting polymer-tethered 4,4'-bipyridinium. The metal-crosslinked $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{PE}$ and $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{PE}$ show a single broad $\tilde{\nu}_{CN}$ stretching band at 2057 cm$^{-1}$ and 2077 cm$^{-1}$, respectively. This broadening and blue shift is a well-established trend for cyanide ligands switching from a terminal mode to a bridging one as expected for the formation of PBA-type frameworks.$^{163}$

Figure 3.6. UV-vis spectra of [Fe$^{II}$(CN)$_5$]PE, Fe$^{III}$[Fe$^{II}$(CN)$_5$]PE, and Zn$^{II}$[Fe$^{II}$(CN)$_5$]PE.
Powder x-ray diffraction (PXRD) experiments were attempted to probe the crystallinity of the PBA framework. Fe^{III}[Fe^{II}(CN)_5]PE was weakly diffracting and gave a broad and non-descript powder pattern that overlaps with the broad amorphous diffraction of 10. These results suggest that Fe^{III}[Fe^{II}(CN)_5]PE is made of nanoscale and partially condensed PBA frameworks.

The precipitation of [Fe^{II}(CN)_5]PE upon complexation of 10 is not fully understood. Figure 3.7 presents a proposed mechanism to explain these observations. It is postulated that the blue solid is a cosslinked network of polymer chains. Complexes of the type [Fe(CN)_5L]^2- (L are cationic ligands such as N-methylpyrazinium or N-methyl-4,4'-bipyridinium) are well known to form outer-sphere complexes with monoquaternized N,N'-heterocycle cations such as 4,4'-bipyridinium. Compounds of this kind were also observed in Chapter 2: reacting Na_3[Fe(CN)_5NH_3] with N-octadecylpyrazinium bromide in water yields the substituted complex [Fe^{II}(CN)_5]C_n that precipitates with two N-alkylpyrazinium cations, as suggested by NMR spectroscopy and electrospray ionization mass spectroscopy (see Figure 3.7 for the structure). In the polymer case, the crosslinking mechanism involves the formation of an outer-sphere complex between a polymer-tethered iron cyanide complex and a 4,4'-bipyridinium cation on another polymer chain. Outer-sphere complexes are generally highly reversible but the simultaneous formation of several crosslinks is likely enough to cause precipitation of the polymer network.
Figure 3.7. Proposed outer-sphere mechanism for the crosslinking of 10 upon complexation. Complex $[\text{Fe}^{II}(\text{CN})_5]C_n$ is included as an illustrative example. The synthesis and characterization details of this compound can be found in Chapter 2.

The material $[\text{Fe}^{II}(\text{CN})_5]\text{PE}$ was isolated by centrifugation and washed with water to remove the byproducts and remaining reagents. It was deposited on a transmission electron microscopy (TEM) grid from a methanol suspension and imaged by TEM. Figure 3.8a shows the macroporous sponge-like morphology of $[\text{Fe}^{II}(\text{CN})_5]\text{PE}$. This image is consistent with the material being made of metal-containing polymer chains crosslinked into a network. TEM of $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{PE}$ confirmed that the macroporous sponge-like morphology is preserved in the PBA materials (Figure 3.8b).
Interestingly, these images suggest a sizeable surface area for these nanomaterials. N\textsubscript{2} adsorption was employed to further investigate this question. The BET model was used here because it adequately describes physical adsorption onto non-microporous materials\textsuperscript{183,185}. Figure 3.9 shows a type IV N\textsubscript{2} adsorption isotherm for Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]PE at 77 K. Type IV isotherms have hysteresis loops, which are typically associated with capillary condensation taking place inside mesopores\textsuperscript{194}. For Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]PE, the hysteresis loop is narrow and observed at high relative pressure. This is an indication that the capillary condensation is taking place in large mesopores. These data are consistent with the TEM micrographs and suggest that the materials are mostly macroporous with a fraction of large mesopores. A BET surface area of 114 m\textsuperscript{2} g\textsuperscript{-1} is measured for this material.

Figure 3.8. TEM micrographs of the sponge-like morphology of a) [Fe\textsuperscript{II}(CN)\textsubscript{5}]PE and b) Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]PE.
Figure 3.9. N$_2$ adsorption isotherm for Fe$^{III}$[Fe$^{II}$(CN)$_3$]PE at 77 K. This material exhibits a type IV isotherm and has a BET surface area of 114 m$^2$ g$^{-1}$.

3.5 Conclusions

The purpose of this investigation was the design, synthesis and characterization of a polymer precursor to PBAs. This polymer is to be used as a model compound for the synthesis of metal cyanide-containing block copolymers. Three conditions have been considered in the design of the metal cyanide-containing polymer: 1. it should be built from a preformed macromolecular backbone that can be integrated in the preparation of block copolymers; 2. the metal cyanide complexes should be strongly tethered to the polymer chains; and 3. the functionalization should be high yielding. Based on these design requirements, the commercially available poly(2-hydroxyethyl methacrylate) (PHEMA) was selected as the macromolecular backbone. PHEMA was functionalized with pendent monoquaternized 4,4$'$-bipyridinium groups that were
then used to anchor iron cyanide complexes. The complexation reaction yielded a blue precipitate instead of the expected water-soluble compound. UV-vis and IR spectroscopy nonetheless confirmed coordination of the iron cyanide complex with the polymer-tethered bipyridinium ligand. The blue solid is believed to form by outer-sphere crosslinking of the polymer chains upon complexation. These materials can still be converted into PBA frameworks with metal ions such as Fe$^{III}$ and Zn$^{II}$. Significantly, the iron cyanide complex stays coordinated to the polymer after condensation of the PBA framework. TEM showed sponge-like structures in the macroporous range and BET N$_2$ adsorption experiments suggested that the materials contain a fraction of large mesopores. A surface area of 114 m$^2$ g$^{-1}$ was measured. The materials developed in this chapter could potentially be employed in the fabrication of PBA-containing hydrogels and in the production of porous PBA-modified electrodes for electrocatalytic and sensor applications.

Although the synthesis of a soluble polymer precursor to PBA could not be achieved, the synthetic approach developed here is simple, high yielding and general enough to be used for the preparation of a soluble block copolymer precursor to PBA. The next chapter describes the synthesis of this novel iron cyanide-containing block copolymer and its self-assembly into soluble and patternable PBA nanomaterials.
CHAPTER 4

SOLUBLE PRUSSIAN BLUE NANOWORMS FROM METAL-ORGANIC BLOCK IONOMER ASSEMBLY†

4.1 Introduction

Progress in metal-organic coordination frameworks is thriving owing to the high degree of control over their properties afforded by judicious selection of their building blocks. The thermodynamic stability of the crystalline framework for these materials has made the investigation of their bulk phase convenient and successful, but is now the main obstacle associated with preparing nanosized forms of these materials. Forming discrete, nanosized coordination frameworks may offer the opportunity to integrate new functions into their nanoscale analogues, and enable incorporation of these materials into new devices.

Prussian blue (PB) is a coordination framework of Fe$_4$[Fe(CN)$_6$]$_3$•n(H$_2$O) constructed from iron (Fe$^{II}$ or Fe$^{III}$) vertices bridged by cyanide ligands. PB and its analogues (PBAs) of the general chemical formula M$'_a$[M$''$(CN)$_b$] can exhibit electronic delocalization and magnetic communication between the metal centers, leading to fascinating optical, electronic, and magnetic properties. Nanostructured PBAs, primarily nanoparticles, have been prepared by several approaches and are now being explored for applications including...

† A version of this chapter has been published as: Roy, X.; Hui, J. K.-H.; Rabnawaz, M.; Liu, G.; MacLachlan, M. J. “Soluble Prussian Blue Nanoworms from the Assembly of Metal-Organic Block Ionomers,” Angew. Chem. Int. Ed. 2011, 50, 1597-1602.
electrochromic materials,\textsuperscript{174,201} molecule-based magnets,\textsuperscript{28,176} electrocatalysts\textsuperscript{202,203} and photoswitches.\textsuperscript{28,204}

Phase-separated block copolymers offer unique reaction environments for assembling\textsuperscript{96} and patterning\textsuperscript{205,206} organic,\textsuperscript{108,207,208} organic-inorganic hybrid\textsuperscript{116,126,209} and fully inorganic\textsuperscript{64,100} nanomaterials. Polymers containing an ionic block are especially remarkable because of their exceptionally low critical micelle concentration (CMC) and their ability to assemble into ‘frozen’ aggregates that could potentially be used to create and pattern nanomaterials.\textsuperscript{105,108,210,211} Ionic block copolymers are generally classified according to their solution behaviours: they are either block polyelectrolytes or block ionomers, depending on the nature of the solvent.\textsuperscript{105} When dissolved in water, ionic block copolymers are block polyelectrolytes. They form micelles with nonionic cores and coronae composed of the soluble ionic segments. In organic solvents, ionic block copolymers are called block ionomers and they assemble into reverse micelles with ionic cores surrounded by the nonionic soluble blocks. Eisenberg has extensively studied the assembly of block polyelectrolytes and used them in the fabrication of a variety of materials.\textsuperscript{108,110,210} Block ionomers on the other hand have seldom been employed for the assembly of nanomaterials. They have been used for the preparation of quantum dots and metal nanoparticles\textsuperscript{115} but, to the best of my knowledge, they have never been employed in the fabrication of nanostructured coordination frameworks.

In Chapter 3, I described the synthesis of a polymer precursor to PBAs. In this chapter, I expand this approach to block copolymers. Specifically, the synthesis and characterization of a novel comb-type metal-organic block ionomer is reported and its assembly into soluble worm-like PBA nanostructures that can form organized two-dimensional arrays upon evaporation is demonstrated. The nanomaterial formed from Fe\textsuperscript{III}/Fe\textsuperscript{II} can be further calcined in air to form mesoporous iron oxide films. Interestingly, PBA nanostructures are known to exhibit
superparamagnetism and other types of magnetic ordering. The materials described in this chapter could find application as soluble and patternable magnetic materials and as precursors for multimetallic oxide catalysts.

4.2 Experimental

4.2.1 Materials

A sequential distillation of 1,1-diphenylethylene was performed over calcium hydride and n-butyllithium. Styrene was distilled twice, first over calcium hydride and subsequently over dibutylmagnesium. 2-Trimethylsiloxyethyl methacrylate (HEMA-TMS) was synthesized from 2-hydroxyethyl methacrylate (HEMA) according to a literature method and distilled over calcium hydride and triethylaluminum (1 M in hexane). sec-Butyllithium (1.4 M in hexane) was used as received. THF was dried over sodium and benzophenone, and distilled immediately before the reaction. Dichloromethane was dried by passage through a column of activated alumina and DMF was dried over activated sieves.

4.2.2 Synthesis of PS270-PHEMA30

The diblock copolymer PS270-b-PHEMA30 (PS = polystyrene and PHEMA = poly(2-hydroxyethyl methacrylate)) was synthesized by anionic polymerization in a 500 mL 2-necked round bottom flask using vacuum-line techniques. Lithium chloride (85 mg, 2 mmol) was first added to the flask, followed by 250 mL of freshly distilled THF. The flask was cooled to -78 °C in a dry ice / acetone bath. sec-Butyllithium (0.14 mL, 0.2 mmol) was added, followed by the addition of 5.62 g of styrene (54 mmol) and the reaction was prolonged for 2 h. 1,1-Diphenylethylene (72 mg, 0.4 mmol) was added and the reaction was stirred for another 20 min, followed by the addition of HEMA-TMS (1.20 g, 6 mmol). The reaction was prolonged for 2.5 h, and was then terminated by adding degassed methanol. PS270-b-P(HEMA-TMS)30 was
converted into \textbf{PS270-}b-PHEMA30 by adding 40 mL of methanol and 8 mL of water to the THF solution and stirring the reaction at room temperature for 1 h. The solution was concentrated by rotary evaporation and the addition of a methanol/water mixture (1:1 v/v) precipitated the block copolymer \textbf{PS270-}b-PHEMA30 in quantitative yield.

The block copolymer \textbf{PS270-}b-PHEMA30 was characterized by size-exclusion chromatography (SEC) to measure the number average molecular weight ($M_n = 34,800$ g mol$^{-1}$), the weight average molecular weight ($M_w = 36,100$ g mol$^{-1}$) and the polydispersity index (PDI = 1.04). Figure 4.1 shows the $^1$H NMR spectrum of \textbf{PS270-}b-PHEMA30.

4.2.3 \textit{Synthesis of the 4,4′-bipyridinium-functionalized block ionomer (BI30)}

\textbf{PS270-}b-PHEMA30 (300 mg) and 2,6-di-\textit{ tert-}butylpyridine (235 mg, 1.2 mmol, 5 equiv. based on the HEMA unit) were dissolved in 60 mL of dry dichloromethane under N$_2$ and cooled
to 0 °C in an ice bath. Bromoacetyl bromide (250 mg, 1.2 mmol, 5 equiv. based on the HEMA unit) was added dropwise to the stirred solution. The reaction mixture was warmed to room temperature and stirred for 4 h. The polymer solution was concentrated by rotary evaporation and a white powder was precipitated with acetonitrile, centrifuged, washed with acetonitrile three times, then dried under vacuum at 60 °C. Yield: 312 mg (95%).

The bromoacetylated block copolymer (300 mg) was dissolved in 5 mL of DMF and added dropwise to 5 mL of a solution of 4,4′-bipyridine (385 mg, 2.5 mmol, 10 equiv. based on the HEMA unit) in DMF. The solution was stirred at 65 °C under N₂ for 18 h. The block ionomer BI30 was then precipitated with acetone, centrifuged, and washed sequentially with acetone and acetonitrile (three times each). Yield: 305 mg (91%). ¹H NMR spectroscopy showed 100% conversion of the bromoacetyl groups to the monoquaternized 4,4′-bipyridinium bromide.

4.2.4 Synthesis of sodium amminepentacyanoferrate(II)

Na₃[Fe(CN)₅NH₃]•3H₂O was prepared from sodium nitroprusside according to the procedure by Kenney et al.¹⁵⁶ The yellow solid was recrystallized from a solution of ammonium hydroxide and methanol.

4.2.5 Synthesis of [FeⅡ(CN)₅]BI30

BI30 (60 mg) was dissolved in 60 mL of THF. In a separate vial, 17 mg (51 µmol) of Na₃[Fe(CN)₅NH₃]•3H₂O and 41 mg (155 µmol) of 18-crown-6 were dissolved in 4.8 mL of deionized water and added dropwise to the vigorously stirred BI30 solution. The solution was stirred for 90 min at room temperature, then diluted with 60 mL of THF and finally filtered to afford a clear blue solution. [FeⅡ(CN)₅]BI30 can be precipitated in water, centrifuged and washed with water to isolate the solid material, or the solution can be used directly in the next step.
Synthesis of $\text{M}^\circ\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$

Fe(NO$_3$)$_2$•6H$_2$O (21 mg, 52 µmol) dissolved in a minimum (ca. 1 mL) of THF was added dropwise to the $\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$ solution (125 mL). The $\text{Fe}^\text{III}\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$ solution was stirred at room temperature for 30 min, then centrifuged at 4500 rpm and filtered to remove any trace of insoluble bulk PBA. $\text{M}^\circ\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$ can be precipitated in water, centrifuged, washed with water and dried under vacuum at 50 °C for 24 h to isolate the solid materials (yield: 70 mg), or the solution can be dropcast to generate PBA nanoworm surface assemblies. The procedure was repeated with Zn(NO$_3$)$_2$•6H$_2$O and Co(NO$_3$)$_2$•6H$_2$O to get $\text{Zn}^\text{II}\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$, and $\text{Co}^\text{II}\text{[Fe}^\text{II}(\text{CN})_3]\text{BI30}$, respectively.

Synthesis of (18-crown-6)sodium $(N$-methyl-$4',4''$-bipyridinium)pentacyanoferrate(II)

$\text{Na}_3\text{[Fe(CN)}_5\text{NH}_3]\text{•3H}_2\text{O}$ (24 mg, 74 µmol) and 59 mg (224 µmol) of 18-crown-6 dissolved in 2.5 mL of deionized water were added to 24 mg (81 µmol) of $N$-methyl-$4',4''$-bipyridinium iodide$^{214}$ in 2.5 mL of deionized water. The solution was stirred for 30 min and diluted with 125 mL of THF. (18-crown-6)sodium $(N$-methyl-$4',4''$-bipyridinium)pentacyanoferrate(II) is very poorly soluble in THF (4% v/v H$_2$O) and the suspension had to be filtered a few times to remove all of the precipitate. A light blue solution was obtained and used for the UV-vis experiment.

Synthesis of $\text{[Fe}^\text{II}(\text{CN})_6]\text{BI30}$, $\text{[Fe}^\text{III}(\text{CN})_6]\text{BI30}$ and $\text{[Co}^\text{III}(\text{CN})_6]\text{BI30}$

A solution of $\text{BI30}$ (60 mg) in 120 mL of THF was prepared. $\text{K}_4\text{[Fe(CN)}_6]\text{)}$ (60 mg, 142 µmol) and 150 mg (568 µmol) of 18-crown-6 were dissolved in 4.8 mL of deionized water and added dropwise to the vigorously stirred $\text{BI30}$ solution. The resulting suspension was sonicated for 1 h and filtered to remove the excess salt. $\text{[Fe}^\text{II}(\text{CN})_6]\text{BI30}$ was obtained as a clear beige
THF (4% v/v H₂O) solution and used directly in the next step. The procedure was repeated with K₃[Fe(CN)₆] and K₃[Co(CN)₆] to prepare [Fe⁢III(CN)₆]BI₃₀ and [Co⁢III(CN)₆]BI₃₀, respectively.

### 4.2.9 Synthesis of Fe⁢III[Fe⁡II(CN)₆]BI₃₀, Cu⁢II[Co⁢III(CN)₆]BI₃₀ and Co⁢II[Fe⁢II(CN)₆]BI₃₀

Fe(NO₃)₃•6H₂O (21 mg, 52 mmol) dissolved in a minimum (ca. 1 mL) of THF was added dropwise to the [Fe⁡II(CN)₆]BI₃₀ solution (125 mL). The solution was stirred at room temperature for 30 min, centrifuged at 4500 rpm and filtered to remove any trace of insoluble bulk PB. Fe⁢III[Fe⁡II(CN)₆]BI₃₀ can be precipitated in water, centrifuged, washed with water and dried under vacuum at 50 °C for 24 h to isolate the solid materials (yield: 64 mg), or the solution can be dropcast to generate PBA nanoworm surface assemblies. The procedure was repeated with Cu(NO₃)₂•6H₂O and Co(NO₃)₂•6H₂O to yield Cu⁢II[Co⁢III(CN)₆]BI₃₀, Co⁢II[Fe⁢II(CN)₆]BI₃₀, respectively.

### 4.2.10 Synthesis of the triethylammonium-functionalized block ionomer (BI₃₀*)

BI₃₀* was synthesized using the same approach as for BI₃₀ and replacing 4,4'-bipyridine with triethylamine. Figure 4.2 shows the ¹H NMR spectrum of BI₃₀*. 
Figure 4.2. $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of BI30$^*$. 

4.2.11 Fabrication of the mesoporous iron oxide film

Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 was deposited on a Si TEM grid with a Si$_3$N$_4$ membrane. The grid was placed on a holder and heated in a furnace to 450 °C in air for 1 h.

In order to get PXRD data, the iron oxide nanomaterials were prepared on a larger scale. The blue Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 powder purified by precipitation in water and dried under vacuum was placed in a ceramic crucible and subjected to the same heat treatment as the sample deposited on the TEM grid. A brownish powder was obtained.

4.2.12 Equipment

300 MHz $^1$H NMR spectra were recorded on a Bruker AV-300 spectrometer. Powder x-ray diffraction (PXRD) patterns were obtained using a Bruker D8 Advance diffractometer equipped with a Cu K$_\alpha$ sealed tube x-ray source. A Hitachi H7600 transmission electronic microscope operating at 80 kV was used to image the PBA nanoworms. The calcined iron oxide mesoporous films were imaged using a FEI Tecnai G2 transmission electronic microscope operated at 200 kV. IR spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR spectrophotometer.
equipped with a Smart Orbit attenuated total reflectance (ATR) accessory. A Perkin Elmer Pyris 6 TGA was used to perform the thermogravimetric analysis (TGA). The UV-vis absorption spectra were recorded on a Varian Cary 5000 spectrophotometer. The energy-dispersive x-ray (EDX) spectroscopy analyses were performed using Hitachi S3000N and Hitachi S2600N scanning electron microscopes. Both microscopes were equipped with Quartz Imaging Systems Xone EDX apparatus. Size exclusion chromatography (SEC) measurements for the copolymer were performed on a Waters 515 system equipped with three columns (one µ-Styrage 500 Å and two Styrage HR 5E columns) and a Waters 2410 refractive index detector equilibrated at 70 °C. The system was calibrated with monodisperse polystyrene standards and DMF was used as eluant, at a flow rate of 0.9 mL min⁻¹. A Wyatt DyanPro dynamic light scattering (DLS) apparatus was employed to study the aggregation of the polymers in solution. The diameter of the core and the thickness of the corona were measured at different points along isolated nanoworms on a number of transmission electronic microscopy micrographs (55 measurements for the core diameter and 80 measurements for corona thickness) using the image analysis software Macnification. The averages and standard deviations were calculated from these data.

4.3 Results and discussion

The synthetic approach to construct soluble PBA nanoworms is illustrated in Figure 4.3. A diblock copolymer (PS270-b-PHEMA30) containing 270 styrene and 30 2-hydroxyethyl methacrylate repeat units (PS and PHEMA, respectively), as measured (Mₙ) by size exclusion chromatography (SEC), and having a narrow polydispersity (PDI = 1.04) was first synthesized (see Section 4.2.2 for more details and the characterization details including the ¹H NMR spectrum). The PHEMA block was then functionalized with bromoacetyl bromide and further reacted with an excess of 4,4'-bipyridine to obtain pendant monoquaternized 4,4'-bipyridinium bromide substituents.
The bipyridinium-functionalized block ionomer (BI30) is soluble in DMSO, DMF, halogenated solvents, THF, 1,4-dioxane and toluene. In addition to validating the structure of BI30, NMR spectroscopy provides the first evidence of its assembly in solution (Figure 4.4). BI30 is made of two blocks that are chemically dissimilar and finding a solvent that can dissolve both blocks for NMR spectroscopy characterization was problematic. DMSO-$d_6$ proved to be the best solvent for the measurements but neither of the blocks are particularly soluble and only small amounts of material can be dissolved. All the expected resonances are nonetheless observed as very broad peaks in the NMR (Figure 4.4a). When the block ionomer BI30 is dissolved in a less polar solvent, such as THF-$d_8$, it assembles into reverse micelles with the ionic block in the core (Figure 4.4b). These large aggregates have no dynamic equilibrium between micelles and single chains on the NMR time scale as suggested by the absence of the ionic block signals in the NMR spectrum (the resonances a-e are absent).
Figure 4.4. $^1$H NMR spectroscopic characterization of the materials. a) and b) are the $^1$H NMR spectra (300 MHz) of BI30 in DMSO-$d_6$ and THF-$d_8$, respectively. c) and d) are the $^1$H NMR spectra (300 MHz, THF-$d_8$ (4% v/v D$_2$O)) of [Fe$^{II}$(CN)$_5$]BI30 and of the diamagnetic Zn$^{II}$[Fe$^{II}$(CN)$_5$]BI30, respectively. In THF-$d_8$ and THF-$d_8$/D$_2$O, only the resonances for the PS block are observed.
Metal complexation of the block ionomer was accomplished by slowly adding an aqueous solution of Na$_3$[Fe(CN)$_5$NH$_3$] and 18-crown-6 to a THF solution of BI30. UV-visible spectroscopy was employed to monitor the change in the electronic structure of the polymer at each step of the synthesis (Figure 4.5). After dilution and filtration, the resulting comb-type pentacyanoferrate(II) block ionomer ([Fe$^{II}$CN$_5$]BI30) is blue in THF (4% v/v H$_2$O) as a consequence of a metal-to-ligand charge transfer (MLCT) transition centered around 685 nm (Figure 4.5b) and analogous to the one measured for the model compound (18-crown-6)sodium(N-methyl-4,4′-bipyridinium)pentacyanoferrate(II) (Figure 4.5a). The complexation reaction was monitored by UV-vis spectroscopy; no further increase in the intensity of the MLCT band was observed after 90 minutes for the typical experimental complexation conditions (1 mg mL$^{-1}$ BI30 in THF (8% v/v H$_2$O); see Appendix C). The block ionomer [Fe$^{II}$CN$_5$]BI30 is anticipated to aggregate in solution because of its amphiphilic nature and, as expected, only the PS block is observed in the NMR spectrum of [Fe$^{II}$CN$_5$]BI (resonances f-h in Figure 4.4c).
Figure 4.5. UV-vis absorption spectra in THF with 4% v/v H2O (~ 10⁻⁶ M [Fe(CN)₅]³⁻) of a) the model compound (18-crown-6)sodium (N-methyl-4,4'-bipyridinium)pentacyanoferrate(II) (shown), b) [Fe''(CN)₅]BI30, c) Fe''[Fe''(CN)₅]BI30 and d) Zn''[Fe''(CN)₅]BI30. The absorbances were normalized to facilitate comparison between the spectra. Photographs of the [Fe''(CN)₅]BI30, Fe''[Fe''(CN)₅]BI30 and Zn''[Fe''(CN)₅]BI30 solutions are also included as a visual reference for the color change.

The metal-containing polymer [Fe''(CN)₅]BI30 was reacted with different transition metal salts such as Fe(NO₃)₃, Zn(NO₃)₂ and Co(NO₃)₂ to crosslink the [Fe(CN)₅]³⁻ terminal groups into PBA-type frameworks. The materials were labeled with the general formula Mˣ[Fe''(CN)₅]BI30, where M represents the crosslinking metal with oxidation state +x. In all cases, the resulting
product is soluble in THF (4% v/v H$_2$O) and Figure 4.4d shows the $^1$H NMR spectrum of the diamagnetic Zn$^{II}$[Fe$^{II}$(CN)$_5$]BI30. As with the unlinked polymer, [Fe$^{II}$(CN)$_5$]BI30, only the PS block is observed for Zn$^{II}$[Fe$^{II}$(CN)$_5$]BI30. Predictably, NMR spectroscopy of the paramagnetic materials (Fe$^{III}$[Fe$^{II}$(CN)$_5$]BI30 and Co$^{II}$[Fe$^{II}$(CN)$_5$]BI30) gave broad non-descriptive spectra. The mixed valent compound Fe$^{III}$[Fe$^{II}$(CN)$_5$]BI30 is purple and exhibits a broad transition centered around 875 nm (Figure 4.5c) that was assigned to intervalence charge transfer (IVCT) between the cyanide-bridged iron centers, akin to the one known for bulk PB.$^{168}$ The MLCT band, still present, is blue shifted by 140 nm (relative to [Fe$^{II}$(CN)$_5$]BI30) to around 545 nm and confirms that the [Fe(CN)$_5$]$^{3-}$ complex is still coordinated to the block ionomer. Zn$^{II}$[Fe$^{II}$(CN)$_5$]BI30, which is not expected to have any valence delocalization since Zn$^{II}$ has a d$^{10}$ electronic configuration, shows the same blue shift for the MLCT, but no IVCT band as shown in Figure 4.5d. These data support the conversion of the block ionomer-tethered metal complexes into an extended PBA-type coordination framework.

Further evidence for the connectivity of the PBA network was obtained by IR spectroscopy of the solid materials purified by precipitation in water. IR spectra of the different polymeric materials consistently show peaks attributable to both organic blocks and to the pentacyanoferrate(II) complex. Of particular interest is the energy of the $\tilde{\nu}_{\text{CN}}$ stretching band, which is diagnostic of the coordination environment for the iron cyanide complex. The approximately $C_{4v}$-symmetric precursor complex Na$_3$[Fe(CN)$_5$NH$_3$] exhibits three $\tilde{\nu}_{\text{CN}}$ stretching modes, with the strongest band at 2030 cm$^{-1}$. Exchanging the amine with the strong $\pi$-accepting 4,4′-bipyridinium ligand upon metallation of BI30 results in a 20 cm$^{-1}$ blue shift for the $\tilde{\nu}_{\text{CN}}$ stretching mode of [Fe$^{II}$(CN)$_5$]BI30 to 2050 cm$^{-1}$. Crosslinking [Fe$^{II}$(CN)$_5$]BI30 into the various M$^+$[Fe$^{II}$(CN)$_5$]BI30 shifts this $\tilde{\nu}_{\text{CN}}$ stretching band to even higher energies (2060-2085 cm$^{-1}$).
This blue shift is a well-established trend for cyanide ligands going from a terminal mode to a bridging one as expected for the formation of PBA-type frameworks.\textsuperscript{163}

Energy dispersive x-ray analysis (EDX) and thermogravimetric analysis (TGA) confirmed the incorporation of iron and the other metal in the polymeric materials. Atomic ratios (M\textsuperscript{x}/Fe) ranging from 1.2 to 1.6 are typically measured with no alkali metal observed. TGA of [Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} showed a 95% weight loss between 100 and 500 °C ascribed to the thermal decomposition and removal of the organic portion of the polymer. For M\textsuperscript{x}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30}, 88 to 90 wt.% is typically lost by calcination under N\textsubscript{2}, as measured by TGA.

Transmission electron microscopy (TEM) was used to investigate the assembly of the metal-organic block ionomers dropcast from THF (4% v/v H\textsubscript{2}O) solutions onto TEM grids. The worm-like nanostructures observed for [Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} and Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} are shown in Figures 4.6a and 4.6b. TEM images of these two materials are similar, although Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} had significantly better contrast than [Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30}, which also exhibited some degradation under the electron beam. These observations are consistent with the Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} nanoworms being made of metal-crosslinked PBA cores as crosslinking is well known to improve the stability of polymers under the electron beam.\textsuperscript{215,216} The inner diameter of the cylindrical micelles is monodisperse throughout the materials and reproducible for all of the polymeric compounds. High magnification microscopy shows a 19.9 ± 1.4 nm diameter PBA core and a 24.1 ± 3.1 nm-thick PS corona for isolated Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} worms like the ones shown in Figure 4.6c. Beam-induced sample degradation prevented the acquisition of comparable high magnification images of [Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30}. Similar nanostructures were obtained for the mixed metal PBA analogues Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} and Co\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]BI\textsubscript{30} as exemplified in Figure 4.6d, as well as for materials that were aged in solution for 24 hours before dropcasting on a TEM grid. The UV-vis and IR spectra were also unaffected by the aging
process. A small proportion of toroidal aggregates and spherical micelles was observed in all of the samples, regardless which linking metal was used. This suggests that the shape of the aggregates is not controlled by the coordination geometry of the linking metal. The fabrication of these diversely shaped aggregates is briefly discussed in Chapter 7.

![Figure 4.6](image)

**Figure 4.6.** TEM analysis of the polymeric materials dropcasts. a) and b) are TEM micrographs of $[\text{Fe}^{II}(\text{CN})_3]\text{BI30}$ and $\text{Fe}^{II}[[\text{Fe}^{II}(\text{CN})_3]\text{BI30}$, respectively. c) is a high magnification TEM image of a single $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_3]\text{BI30}$ nanoworm and d) is a TEM micrograph of the nanostructure obtained with $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_3]\text{BI30}$.

It was hypothesized that in solution, the metal-containing block ionomer $[\text{Fe}^{II}(\text{CN})_3]\text{BI30}$ self-assembles into nanoworms in THF with the iron cyanide block in the ionic core. Addition of transition metals then crosslinks the iron cyanide core into a PBA-type framework and slow
evaporation organizes these nanoworms into a tightly packed structure, which can also be described as a thin PS film with ordered embedded monodisperse PBA nanowires. The idealized supramolecular assembly and the schematic cross-sectional view of a micelle are shown in Figures 4.7a and 4.7b, respectively. Dynamic light scattering (DLS) experiments were performed to investigate the aggregation of the polymers in solution. Apparent hydrodynamic radii ($R_{h,app}$) of $51.1 \pm 1.2$ nm and $71.0 \pm 1.6$ nm were measured for BI30 and $[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ (0.5 mg mL$^{-1}$ in THF (4% v/v H$_2$O)), respectively. These DLS data confirm the aggregation of the polymers in solution, but because of the worm-like shape of the micelles, it does not provide accurate dimensions of the aggregates. Therefore, a series of freeze-drying experiments were performed to corroborate the DLS results and verify the existence of the nanoworms in solution. Samples of $[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ and $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ in 1,4-dioxane (4% v/v H$_2$O) deposited on TEM grids were rapidly frozen in liquid nitrogen to immobilize their solution assemblies. (It was verified that the same nanoworm structures are obtained by evaporation self-assembly when THF was replaced with the higher melting 1,4-dioxane.) The structures obtained after removal of the solvent by freeze-drying for $[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ and $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ are shown in Figures 4.7c and 4.7d, respectively. Disordered or isolated cylindrical micelles were observed for both polymeric materials, confirming that the nanoworms are present in solution.
Figure 4.7. a) is the synthetic scheme for the block ionomer-mediated self-assembly of PBA nanoworms. b) shows the schematic cross-sectional view of a typical $M^+[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ nanoworm. As a control experiment, $[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ and $M^+[\text{Fe}^{II}(\text{CN})_6]\text{BI}$ solutions in 1,4-dioxane (4% v/v H$_2$O), were rapidly frozen in liquid nitrogen and freeze-dried at -10 °C (melting temperature for 1,4-dioxane is 11.8 °C). c) and d) are TEM micrographs of the $[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ and $M^+[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ freeze-dried structures, respectively.

In the course of this investigation, it was discovered that the use of Na$_3[\text{Fe(CN)}_3\text{NH}_3]$ is not necessary to obtain the PBA nanoworm assemblies. Adding an excess of K$_4[\text{Fe(CN)}_6]$ and 18-crown-6 (1:4 molar ratio) in water to a THF solution of BI30 (0.5 mg mL$^{-1}$), sonicating the resulting suspension for one hour and filtering the excess salt gave the block ionomer-ferrocyanide hybrid $[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ as a clear beige THF (4% v/v H$_2$O) solution. $[\text{Fe}^{II}(\text{CN})_6]\text{BI30}$ was then crosslinked into a PB framework with an excess of Fe(NO$_3$)$_3$ and, after centrifugation and filtration to remove any trace of insoluble bulk PB, soluble
Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 materials were obtained. Figure 4.8 shows the UV-vis absorption spectra of [Fe$^{II}$(CN)$_6$]BI30 and Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30. The expected IVCT band typical of PB is observed around 700 nm for the metal-crosslinked Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30. IR spectroscopy and EDX also confirm the formation of PB, while TGA suggests a slightly higher metal content for Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 (85.5% wt. loss upon calcination) compared with Fe$^{III}$[Fe$^{II}$(CN)$_5$]BI30.

![UV-vis absorption spectra](image)

**Figure 4.8.** UV-vis absorption spectra of [Fe$^{II}$(CN)$_6$]BI30 and Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 (concentration of BI30 is 0.5 mg mL$^{-1}$ in THF with 4% v/v H$_2$O).

Once again, assemblies made of monodisperse 20 nm PB nanoworms are obtained by dropcasting Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 on a TEM grid (Figure 4.9a). This approach is not limited to Fe$^{III}$[Fe$^{II}$(CN)$_6$], but can be extended to different PBAs known to have a wide range of properties and potential applications. Co$^{II}$[Fe$^{III}$(CN)$_6$]BI30 and Cu$^{II}$[Co$^{III}$(CN)$_6$]BI30 (Figure 4.9b) were selected as representative examples.
To test whether the 4,4’-bipyridinium-modified block ionomer is necessary to generate the PBA nanoworms, a non-coordinating triethylammonium-functionalized block ionomer analogue was synthesized (BI30*, Figure 4.9c) and used in the approach. Microscopy of the unfiltered Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30* dropcast on a TEM grid (Figure 4.9d) shows that in this case, the core of the nanoworms does not contain PB, which is instead observed as crystals outside of the micelles. From this result, it may be inferred that a coordinating ligand is necessary to anchor the PBA inside the ionic core. In the approach beginning with [M\textsuperscript{3+}(CN)\textsubscript{6}]BI30 where the complex is not coordinated to the polymer, the crosslinking metal added becomes coordinated to the BI30.

Interestingly, Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30 can be used as a precursor to iron oxide nanostructures. Calcining Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30 deposited on a Si/Si\textsubscript{3}N\textsubscript{4} TEM grid at 450 °C for one hour in air converted the PB nanoworm assembly into a mesoporous Fe\textsubscript{2}O\textsubscript{3} film made of ca. 10 nm nanofibers (Figures 4.9e and 4.9f). The PB nanoworms aggregated during the high temperature oxidation to form a Fe\textsubscript{2}O\textsubscript{3} nanofiber mesh. TGA confirmed the complete removal of the organic template under the experimental conditions and the powder x-ray diffraction (PXRD) pattern of the resulting material was indexed as a mixture of α- Fe\textsubscript{2}O\textsubscript{3} (hematite) and γ- Fe\textsubscript{2}O\textsubscript{3} (maghemite), the latter oxide being ferrimagnetic and superparamagnetic at the nanoscale (Figure 4.10). This approach could potentially be used to prepare a wide range of magnetically and catalytically active multimetallic oxide nanomaterials.
Figure 4.9. a) and b) are TEM micrographs of Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30 and Cu\textsuperscript{II}[Co\textsuperscript{III}(CN)\textsubscript{6}]BI30, respectively. c) shows the chemical structure of the triethylammonium-functionalized block ionomer labeled BI30\textsuperscript{*} and d) is a TEM micrograph when BI30\textsuperscript{*} is used instead of BI30 in the synthesis of PB nanoworms; seen here is a PB nanocrystal surrounded by PB-free BI30\textsuperscript{*} nanoworms. e) and f) are respectively high magnification and low magnification TEM micrographs of a mesoporous Fe\textsubscript{2}O\textsubscript{3} film obtained by calcination of Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30.
Figure 4.10. PXRD pattern of the mesoporous iron oxide nanomaterials obtained by calcination of Fe$^{III}$[Fe$^{II}$(CN)$_6$]BI30 at 450 °C for 1 h in air. The pattern was indexed as a mixture of α- Fe$_2$O$_3$ (hematite) and γ- Fe$_2$O$_3$ (maghemite).

4.4 Conclusions

This chapter presented an approach to fabricating soluble PBA nanoworms using a novel block copolymer that contains the PBA precursor complexes. This metal-containing block copolymer was built by selectively functionalizing one block of a preformed block copolymer with ionic monoquaternized 4,4'-bipyridinium pendant groups that can tether metal complexes. When dissolved in organic solvents the ionic block copolymer behaved as a block ionomer and self-assembled into stable cylindrical reverse micelles whose ionic cores can be metallated with an iron(II) cyanide complex or used as an ion confinement region for different cyanometallate compounds to be crosslinked into coordination frameworks. It was demonstrated that the nanoworms containing PBA-type coordination frameworks are stable in solution for hours,
organize into fingerprint surface structures upon evaporation, and can be used as precursors for metal oxide nanostructures.

The approach developed in this chapter demonstrates that block copolymers can be employed to assemble previously inaccessible PBA nanomaterials. Interestingly, the use of the block copolymer as SDA could offer the possibility of patterning these nanomaterials into functional structures. Furthermore, based on the size and diversity of the PBA family and the different aggregate morphologies known for block ionomers, it is anticipated that this approach will provide a useful route to soluble and patternable nanomaterials with tunable magnetic, optical and electronic properties. The approach may also be generalized to fabricate nanomaterials that incorporate other types of coordination polymers such as metal-organic frameworks (MOFs).
CHAPTER 5

PRUSSIAN BLUE NANOCONTAINERS: SELECTIVELY PERMEABLE HOLLOW METAL-ORGANIC CAPSULES FROM BLOCK IONOMER EMULSION-INDUCED ASSEMBLY†

5.1 Introduction

Metallopolymers were reported as early as 1955, but progress in this field was slow until the 1990s when improved synthetic methods were developed to access soluble, characterizable and processable macromolecules. Metal-containing block copolymers are especially advantageous because they can be made to assemble into a variety of inorganic nanostructures. In particular, these have been used as precursors for ceramics, for self-assembled nanolithography, and in the synthesis and patterning of nanoparticles and metal clusters.

Organic block copolymers have been investigated extensively as functional nanocontainers to encapsulate, protect, and release active compounds. In particular, amphiphilic block copolymers have been widely employed in the fabrication of drug carrier and delivery systems. Figure 5.1 shows the basic structure of a block copolymer nanocapsule, which is

† A version of this chapter has been submitted for publication as: Roy, X.; Hui, J. K.-H.; Rabnawaz, M.; Liu, G.; MacLachlan, M. J. “Prussian Blue Nanocontainers: Selectively Permeable Hollow Metal-Organic Capsules from Block Ionomer Emulsion-Induced Assembly,” 2011.
comprised of a gel- or liquid-core that is encapsulated by a shell, itself enveloped in a soluble corona. The nature of the core dictates the type of compounds that can be encapsulated inside the capsule (e.g., hydrophobic or hydrophilic guest) and the composition of the corona determines its solubility properties. Yet, the shell is often the most important component of the structure: it confers stability to the aggregate, controls the diffusion in and out of the capsule – acting as a porous membrane or an impermeable layer – and can regulate its degradation process.\textsuperscript{226,227}

![Figure 5.1. Basic structure of a block copolymer capsule.](image)

Crosslinking the shell of nanocapsules is an effective approach to improve the mechanical and thermal stability of the aggregates, and control their permeability.\textsuperscript{226} New properties and functions have also been achieved by incorporating metal and semiconductor nanoparticles inside the shell,\textsuperscript{228} but to the best of my knowledge, hollow polymer aggregates having a shell made of coordination framework have never been reported. Coordination frameworks are particularly attractive because they possess controllable microporosities, high surface areas, good mechanical and thermal stabilities, and exciting electronic and magnetic properties.\textsuperscript{21,24,32,33} Their incorporation into polymer capsules could lead to materials with exciting new properties and
functions such as improved mechanical and thermal stability, selective permeability and magnetic walls.

Prussian blue analogues (PBAs) are a family of coordination frameworks constructed from metal ions bridged by cyanide ligands. Nanomaterials have been constructed from PBAs through a variety of approaches. It has been intercalated into surfactant multibilayer vesicles and core-shell PBA nanoparticles have also been reported, although removal of the organic core was not achieved in the latter case.

In Chapter 4, I reported the synthesis and self-assembly of a novel metal-cyanide block ionomer that can be crosslinked into worm-shaped PBA frameworks. In this chapter, I describe the preparation of soluble metal-organic capsules (MOC) made of a PBA through emulsion-induced assembly and their encapsulation of methylene blue, a dye molecule. Contrary to the self-assembly process by which molecules adopt a defined arrangement without guidance or management from an outside source, emulsion-induced assembly is a directed self-assembly process by which an outside driving force (the emulsification in this case) forces the molecules into a novel ordered nonequilibrium arrangement, free from the constraints of entropy maximization.

5.2 Experimental

Figure 5.2 shows the general synthetic scheme for the fabrication of the MOCs.
Figure 5.2. Synthesis of the metal-organic block ionomers $[\text{Fe}^{II}(\text{CN})_5]\text{BIX}$ and their crosslinking into hybrid polymer-PBA framework capsules $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOCX}$ (DTBP = 2,6-di-tert-butylpyridine).

5.2.1 Materials

A sequential distillation of 1,1-diphenylethylene was performed over calcium hydride and n-butyllithium. Styrene was distilled twice, first over calcium hydride and subsequently over dibutylmagnesium. 2-Trimethylsiloxyethyl methacrylate (HEMA-TMS) was synthesized from 2-hydroxyethyl methacrylate (HEMA) according to a literature method and distilled over calcium hydride and triethylaluminum (1 M in hexane). sec-Butyllithium (1.4 M in hexane) was used as received. THF was dried over sodium and benzophenone, and distilled immediately before the reaction. Dichloromethane was dried by passage through a column of activated alumina and DMF was dried over activated sieves.
5.2.2 Synthesis of PS270-PHEMA

The diblock copolymer PS270-b-PHEMA30 (PS = polystyrene and PHEMA = poly(2-hydroxyethyl methacrylate)) was synthesized using the approach described in Section 4.2.2. The same procedure was also employed for PS270-b-PHEMA75 using monomers in a ratio (HEMA-TMS / styrene) of 0.28.

5.2.3 Synthesis of the 4,4′-bipyridinium-functionalized block ionomers (BIX)

PS270-b-PHEMA30 (300 mg) and 2,6-di-tert-butylpyridine (235 mg, 1.2 mmol, 5 equiv. based on the HEMA unit) were dissolved in 60 mL of dry dichloromethane under N₂ and cooled to 0 °C in an ice bath. Bromoacetyl bromide (250 mg, 1.2 mmol, 5 equiv. based on the HEMA unit) was added dropwise to the stirring solution. The reaction mixture was warmed to room temperature and stirred for 4 h. The polymer solution was concentrated by rotary evaporation and a white powder was precipitated with acetonitrile, centrifuged, washed with acetonitrile three times, then dried under vacuum at 60 °C. Yield: 312 mg (95%).

The bromoacetylated block copolymer (300 mg) was dissolved in 5 mL of DMF and added dropwise to 5 mL of a solution of 4,4′-bipyridine (385 mg, 2.5 mmol, 10 equiv. based on the HEMA unit) in DMF. The solution was stirred at 65 °C under N₂ for 18 h and the block ionomer B130 was then precipitated with acetone, centrifuged, and washed sequentially with acetone and acetonitrile (three times each). Yield: 305 mg (91%). ¹H NMR spectroscopy showed 100% conversion of the bromoacetyl groups to the monoquaternized 4,4′-bipyridinium bromide. The same procedure was employed for B175 (combined yield: 86%). Figure 5.3 shows the ¹H NMR spectra of B130 and B175.
5.2.4 Synthesis of sodium amminepentacyanoferrate(II)

Na$_3$[Fe(CN)$_5$NH$_3$]•3H$_2$O was prepared from sodium nitroprusside according to the procedure by Kenney et al.$^{156}$ The yellow solid was recrystallized from a solution of ammonium hydroxide and methanol.
5.2.5 Synthesis of [Fe$^\text{II}$(CN)$_5$]BI$^\text{IX}$

BI$^\text{130}$ (30 mg) was dissolved in 15 mL of THF. In a separate vial, 7 mg (23 µmol) of Na$_3$[Fe(CN)$_5$NH$_3$]•3H$_2$O and 18 mg (69 µmol) of 18-crown-6 were dissolved in 1.5 mL of deionized water and added dropwise to the vigorously stirred BI$^\text{130}$ solution. The solution was sonicated for 90 min at room temperature to afford a clear blue solution, which was used directly in the next steps. The same procedure was employed for [Fe$^\text{II}$(CN)$_5$]BI$^\text{175}$ using 19 mg (58 µmol) of Na$_3$[Fe(CN)$_5$NH$_3$]•3H$_2$O and 45 mg (173 µmol) of 18-crown-6.

5.2.6 Synthesis of Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{X}$

Chlorobenzene (50 mL) was added dropwise (ca. 1 drop s$^{-1}$) to the vigorously stirred [Fe$^\text{II}$(CN)$_5$]BI$^\text{130}$ solution. The emulsion was stirred for 30 min at room temperature and then sonicated for another 30 min. [Fe$^\text{II}$(CN)$_5$]MOC$^\text{30}$ was obtained as a cloudy purple colloidal solution. Zn(NO$_3$)$_2$•6H$_2$O (10 mg, 34 µmol) dissolved in 4 mL of THF was added dropwise to the stirring solution and the reaction mixture was stirred for 60 min. Using an extraction funnel, the organic phase was washed with 150 mL of water (6 times). Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{30}$ was obtained as a clear burgundy solution upon standing over activated molecular sieves. The solution was centrifuged at 2500 rpm to remove any trace of insoluble bulk PBA. Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{30}$ can be isolated by rotary evaporation and vacuum dried at 50 ºC for 24 h to obtain the solid product or the solution can be dropcast to generate surface assemblies. Yield: 29 mg. The same procedure was employed for Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{75}$ using 25 mg of Zn(NO$_3$)$_2$. Yield: 25 mg. Contrary to Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{30}$, Zn$^\text{II}$[Fe$^\text{II}$(CN)$_5$]MOC$^\text{75}$ was not sonicated.
5.2.7 Synthesis of MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOCX

Methylene blue (MB; 15 mg, 47 µmol) dissolved in 1.5 mL of water was added to the vigorously stirred [Fe$^{II}$(CN)$_5$]BI$_30$ solution (16.5 mL; see section 5.2.5), followed by 50 mL of chlorobenzene (1 drop s$^{-1}$). The emulsion was stirred for 30 min at room temperature and then sonicated for another 30 min. Zn(NO$_3$)$_2$•6H$_2$O (10 mg, 34 µmol) dissolved in 4 mL of THF was added dropwise to the stirred solution and the reaction mixture was stirred for 60 min. Using an extraction funnel, the organic phase was repeatedly washed with 150 mL of water until no blue color was observed in the aqueous phase. MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC$_{30}$ was obtained as a clear deep blue solution upon standing over activated molecular sieves. MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC$_{30}$ was dropcast to generate the surface assemblies. The same procedure was employed for MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC$_{75}$ using 25 mg (84 µmol) of Zn(NO$_3$)$_2$•6H$_2$O. Contrary to MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC$_{30}$, MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC$_{75}$ was not sonicated.

5.2.8 Equipment

300 MHz $^1$H NMR spectra were recorded on a Bruker AV-300 spectrometer. A Hitachi H7600 transmission electronic microscope operating at 80 kV and a Hitachi S4700 scanning electron microscope were used to image the materials. IR spectra were obtained using a Thermo Scientific Nicolet 6700 FTIR spectrophotometer equipped with a Smart Orbit attenuated total reflectance (ATR) accessory. The UV-vis spectra were recorded on a Varian Cary 5000 spectrophotometer. The energy dispersive x-ray (EDX) analyses were performed using a Hitachi S2600N SEM equipped with a Quartz Imaging Systems Xone EDX apparatus. Size exclusion chromatography (SEC) measurements for the copolymer were performed on a Waters 515 system equipped with three columns (one µ-Styragel 500 Å and two Styragel HR 5E columns) and a Waters 2410 refractive index detector equilibrated at 70 °C. The system was calibrated with monodisperse polystyrene standards and DMF was used as eluant, at a flow rate of 0.9 mL
min\(^{-1}\). The inner diameter of the aggregates was calculated by measuring the dimensions of 150 hollow capsules from a number of transmission electronic microscopy micrographs using the image analysis software Macnification.

### 5.3 Results and discussion

Figure 5.4 illustrates the approach to fabricating PBA capsules. The block ionomers BI30 and BI75 employed in the procedure are composed of 30 and 75 4,4'-bipyridinium-functionalized 2-hydroxyethyl methacrylate units, respectively, and 270 styrene units. These were prepared by sequentially reacting two tailor-made block copolymers (PS270-b-PHEMA30 and PS270-b-PHEMA75) with excesses of bromoacetyl bromide and 4,4'-bipyridine (see Figure 5.2 and Sections 5.2.2 and 5.2.3 for the experimental details). Table 5.1 details the molecular weights and polydispersity indices for both starting materials as measured by size-exclusion chromatography (SEC).

**Table 5.1. Characterization of the starting polymer materials.**

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS270-b-PHEMA30</td>
<td>34,800 g mol(^{-1})</td>
<td>36,100 g mol(^{-1})</td>
<td>1.04</td>
</tr>
<tr>
<td>PS270-b-PHEMA75</td>
<td>40,950 g mol(^{-1})</td>
<td>43,100 g mol(^{-1})</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Figure 5.4. Synthetic approach to soluble block ionomer-PBA capsules through emulsion-induced assembly. Photographs of $[\text{Fe}^{II}(\text{CN})_6]\text{BI75}$ and $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_6]\text{MOC75}$ are included as a visual reference for the color change.
**BI30** and **BI75** were reacted with Na$_3$[Fe(CN)$_5$NH$_3$] and 18-crown-6 in THF (10% v/v H$_2$O) to yield [Fe$^{II}$(CN)$_5$]BI30 and [Fe$^{II}$(CN)$_5$]BI75, respectively. The deep blue materials are soluble in THF, benzene, toluene and most halogenated solvents. Addition of chlorobenzene to the stirred THF (10% v/v H$_2$O) mixtures induced a water-in-oil emulsion, which was promptly stabilized by [Fe$^{II}$(CN)$_5$]BI30 or [Fe$^{II}$(CN)$_5$]BI75 present in solution. The amphiphilic macromolecules are expected to assemble at the water-oil interface of nanosized water droplets and prevent the dispersed aqueous phase from coalescing. The metal salt Zn(NO$_3$)$_2$ in THF was added to the emulsion to crosslink the [Fe(CN)$_5$]$^{3-}$-containing shells into PBA-type frameworks. Zinc ferrocyanide was selected as model compound because its porous framework efficiently promotes diffusion of small species and it lacks a charge transfer band that limits spectroscopic investigation of encapsulated dye. THF was finally removed from the organic phase by aqueous extraction. The solvent-filled capsules Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC30 and Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC75 were obtained as clear burgundy chlorobenzene solutions upon standing over activated molecular sieves. A polystyrene corona renders the crosslinked spheres soluble in many organic solvents, including chlorobenzene, benzene, toluene, THF and chlorinated hydrocarbons.

In THF (10% v/v H$_2$O), [Fe$^{II}$(CN)$_5$]BI30 and [Fe$^{II}$(CN)$_5$]BI75 assemble into nanoworms (see Chapter 4) and nanorings, respectively. Figure 5.5a shows the Zn-crosslinked [Fe$^{II}$(CN)$_5$]BI75 nanorings obtained by dropcasting on a transmission electron microscopy (TEM) grid. A small proportion of spherical micelles and short nanoworms is also typically observed. The unlinked hollow capsules [Fe$^{II}$(CN)$_5$]MOC75 formed upon addition of chlorobenzene are very soft and deformable as illustrated in Figure 5.5b. Crosslinking the [Fe(CN)$_5$]$^{3-}$ terminal groups with Zn$^{II}$ visibly strengthens the shell and produces rigid spherical hollow capsules (Figure 5.5c). These structures are stable for days in solution as confirmed by TEM and can even be diluted in THF/water mixtures without any observable morphological
change. Scanning electron microscopy (SEM) also confirmed that the aggregates are round and hollow. A mixture of intact and collapsed spherical capsules (Figure 5.5d) is observed for \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75} \).

The average inner diameter of the spheres for \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75} \) is 137 ± 43 nm (see Figure 5.6 for the inner diameter size distributions). Figures 5.5e and 5.5f show that smaller and nearly monodisperse hollow capsules (53 ± 5 nm) are obtained for \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC30} \) by sonicating \( [\text{Fe}^{II}(\text{CN})_5]\text{MOC30} \) before crosslinking. Strikingly, \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC30} \) spheres assembled into 2D hexagonal arrays in the solid state as observed in Figure 5.5f.
Figure 5.5. Electronic microscopy characterization of the polymer aggregates. a) is a TEM micrograph of the Zn-crosslinked \([\text{Fe}^{II}(\text{CN})_3]\text{BI75}\) nanoring structures observed before the emulsion-induced assembly. b) and c) are TEM micrographs of the soft and deformable \([\text{Fe}^{II}(\text{CN})_3]\text{MOC75}\) and the rigid crosslinked \(\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_3]\text{MOC75}\) hollow aggregates, respectively. d) is a SEM micrograph showing a mixture of intact and collapsed hollow capsules for \(\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_3]\text{MOC75}\). e) and f) are respectively low and high magnification TEM micrographs of \(\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_3]\text{MOC30}\). \(\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_3]\text{MOC30}\) assembles into a 2D hexagonal array upon evaporation as illustrated in f).
Figure 5.6. Histograms showing the inner diameter size distributions for a) Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC75 (137 ± 43 nm) and b) Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC30 (53 ± 5 nm). For each sample, the inner diameter of 150 hollow capsules were measured from a number of TEM micrographs using the image analysis software Macnification. The averages and standard deviations were calculated from these data.

The assembly mechanism was further investigated by performing a series of emulsion experiments around the solution cloud point (ca. 78% v/v THF, 15% v/v chlorobenzene, 7% v/v H$_2$O). Figure 5.7 shows a TEM micrograph of [Fe$^{II}$(CN)$_5$]MOC75 hollow structures dropcast from a solution at the cloud point. Although the composition of the solvent mixture is expected to change to some extent upon evaporation on the TEM grid, this result supports an emulsion-induced mechanism for the formation of the capsules. The image clearly shows a number of dried-up metal-containing block ionomer-stabilized droplets.
In chlorobenzene, $[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ is purple owing to a metal-to-ligand charge transfer (MLCT) transition centered at ca. 600 nm (Figure 5.8a). This band, still present for $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$, is blue shifted by 70 nm (relative to $[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$) to around 530 nm after addition of Zn$^{II}$ metal ions, confirming that the $[\text{Fe}^{II}(\text{CN})_5]^{3-}$ complex is still coordinated to the block ionomer. These data support the conversion of the block ionomer-tethered iron cyanide complexes into an extended PBA-type coordination framework (see Chapters 2-4). Similar transitions were measured for $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC30}$ (Figure 5.8b).

Figure 5.7. TEM micrograph of $[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ hollow structures prepared at the solution cloud point (ca. 78% v/v THF, 15% v/v chlorobenzene, 7% v/v H$_2$O).
Figure 5.8. UV-vis absorption spectra in chlorobenzene (~ $10^{-6}$ M [Fe(CN)$_3$]$^{3-}$) of a) [Fe$^{II}$(CN)$_3$]MOC75 and Zn$^{II}$[Fe$^{II}$(CN)$_3$]MOC75, and b) [Fe$^{II}$(CN)$_3$]MOC30 and Zn$^{II}$[Fe$^{II}$(CN)$_3$]MOC30. The absorbances were normalized to facilitate comparison between the spectra.

Further evidence for the connectivity of the PBA network was obtained by IR spectroscopy and energy dispersive x-ray analysis (EDX) of the solid materials (see Appendix D). IR spectra
of the different polymer aggregates consistently show peaks attributable to both organic blocks and to the pentacyanoferrate(II) complex. As mentioned in previous chapters, the approximately $C_{4v}$-symmetric precursor Na$_3$[Fe(CN)$_5$NH$_3$] exhibits three $\nu_{\text{CN}}$ stretching modes, with the strongest band at 2030 cm$^{-1}$. Exchanging the amine ligand with the $\pi$-accepting 4,4'-bipyridinium ligand results in a 20 cm$^{-1}$ blue shift for the $\nu_{\text{CN}}$ stretching mode of the block ionomer-tethered iron cyanide complex to 2050 cm$^{-1}$. Crosslinking [Fe$^{II}$(CN)$_5$]MOC30 and [Fe$^{II}$(CN)$_5$]MOC75 into zinc-iron cyanide framework shells broadens and shifts the $\nu_{\text{CN}}$ stretching band to even higher energies (2078 and 2082 cm$^{-1}$, respectively). This trend is a well-established one for cyanide ligands switching from a terminal mode to a bridging position as expected for the formation of PBA-type frameworks.$^{163}$ In addition, EDX confirmed the incorporation of both Zn and Fe in the polymer aggregates.

After confirming that the crosslinked metal-organic capsules form reproducibly, they were investigated for the encapsulation of methylene blue (MB), a prototypical water-soluble compound (see Figure 5.8 for the details). The charged organic molecular dye MB was selected because it has an easily recognizable solution absorption band at ca. 650 nm (see Figure 5.10). An aqueous solution of MB was first added to [Fe$^{II}$(CN)$_5$]BI30 or [Fe$^{II}$(CN)$_5$]BI75 in THF (10% v/v H$_2$O), followed by chlorobenzene addition to give the water-in-oil emulsion. Due to its hydrophilicity, some MB is expected to stay in the aqueous phase that will get trapped inside the block ionomer assemblies. The solvent-filled aggregates were then crosslinked with Zn(NO$_3$)$_2$ and the non-encapsulated MB was extracted by washing the organic phase with water until no blue color was observed in the aqueous phase. MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC30 and MB@Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC75 were obtained as clear blue chlorobenzene solutions upon standing over activated molecular sieves.
Figure 5.9. Encapsulation inside block ionomer-PBA capsules. a) shows the synthetic approach to encapsulating the model compound MB inside the PBA capsules. b) and c) are photographs of Zn$^{II}$[Fe$^{II}$ (CN)$_5$]MOC75 and MB@Zn$^{II}$[Fe$^{II}$ (CN)$_5$]MOC75 after stirring with water for 24 hours, respectively.

The UV-vis absorption spectrum for MB@Zn$^{II}$[Fe$^{II}$ (CN)$_5$]MOC75 is shown in Figure 5.10. In this case, the much stronger absorption of MB overwhelms that of Zn$^{II}$[Fe$^{II}$ (CN)$_5$]MOC75 and only absorptions due to MB are observed in the range 500-800 nm. The absorption band for MB@Zn$^{II}$[Fe$^{II}$ (CN)$_5$]MOC75 is much broader and has a different shape when compared with MB in aqueous solution. The absorption spectrum is in fact analogous to the one measured for a MB film deposited on a silica surface.$^{233}$ MB most likely precipitates inside the capsules during the encapsulation process and a broad transition for the dye in the solid-state is recorded.
Figure 5.10. UV-vis absorption spectra of MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 in chlorobenzene and MB in water. The absorbances were normalized to facilitate comparison between the spectra.

The possibility that MB might be trapped inside the PBA network or precipitated within the polystyrene corona and not actually encapsulated inside the capsule was also explored. As a control experiment, [Fe\textsuperscript{II}(CN)\textsubscript{5}]BI75 was first crosslinked with Zn(NO\textsubscript{3})\textsubscript{2} in THF (10% v/v H\textsubscript{2}O) in the presence of MB. The water-in-oil emulsion was then induced with the addition of chlorobenzene and after thorough washing, it was verified by TEM that toroidal structures were obtained (Figure 5.11a). UV-vis absorption spectroscopy confirmed that no MB was present in the aggregates as illustrated in Figure 5.11b, which only shows the MLCT band. (The absorbance of this transition is much weaker than that of MB but it was normalized to facilitate comparison of the spectra.)

MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 and MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC30 can be stirred with water for days with no transfer of the blue color into the aqueous phase (Figure 5.9c). Furthermore, no change in the absorption spectrum was detected (Figure 5.11b), indicating that water does not cross the hydrophobic polystyrene corona to solvate MB.
Figure 5.11. a) is a TEM micrograph of the Zn$^{II}$[Fe$^{II}$(CN)$_3$]BI75 nanorings. An aqueous solution of MB was added to [Fe$^{II}$(CN)$_3$]BI75 in THF (10% v/v H$_2$O) and stirred for 5 minutes. Zn(NO$_3$)$_2$ was then added to crosslink the nanorings into PBA-type frameworks. Chlorobenzene was added dropwise to induce the emulsion and MB was extracted by washing the organic phase with water. The solution was finally dried over activated molecular sieves. b) shows the UV-vis absorption spectra for the MB-free Zn$^{II}$[Fe$^{II}$(CN)$_3$]BI75 nanorings in chlorobenzene and for MB@Zn$^{II}$[Fe$^{II}$(CN)$_3$]MOC75 in chlorobenzene after stirring with water for 24 hours. The absorbances were normalized to facilitate comparison between the spectra.
In contrast, addition of methanol to $\text{MB@Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ and $\text{MB@Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC30}$ rapidly and noticeably changed the color of the solutions. Figure 5.12b shows the UV-vis absorption spectrum for $\text{MB@Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ in chlorobenzene with ca. 25% v/v methanol. This spectrum is nearly identical to the MB solution spectrum (see Figure 5.10). These data confirm that methanol molecules can cross the polystyrene and zinc-iron cyanide framework barriers and solvate MB inside the capsules. TEM confirmed that the majority of the hollow structures remained intact after addition of methanol although some ruptured capsules were also observed, probably due to rapid uptake of methanol into the core (Figure 5.12a). The methanol and free MB (released from the broken aggregates) can be extracted with water and the original broad $\text{MB@Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ UV-vis absorption spectrum is obtained yet again after the MB-infiltrated spheres stand over activated molecular sieves (Figure 5.12b). Thus, the dye remains inside the metal-organic capsules, and the solvent in the interior can be exchanged.
Figure 5.12. a) is a TEM micrograph of methanol-infiltrated MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 after extraction of the methanol with water and standing over activated sieves. Seen here are mostly intact hollow capsules and one large ruptured nanocontainer. b) shows the UV-vis absorption spectra for the methanol-infiltrated MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 in chlorobenzene with ca. 25% v/v methanol and for the methanol-infiltrated MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 after extraction of the methanol with water and standing over activated sieves. The original MB@Zn\textsuperscript{II}[Fe\textsuperscript{II}(CN)\textsubscript{5}]MOC75 broad solid absorption spectrum is obtained yet again. The absorbances were normalized to facilitate comparison between the spectra.
5.4 Conclusions

This chapter described the synthesis of soluble hybrid polymer-PBA capsules and the encapsulation of a water-soluble compound in its hollow core. These nanocontainers were prepared by directed self-assembly of an ionic block copolymer that contains the PBA precursor complex. Emulsification of a solution of the amphiphilic macromolecules induces the iron cyanide-containing block copolymers to assemble at the water-oil interface and stabilize nanoscale water droplets. The hydrophilic iron cyanide blocks were then crosslinked into PBA shells that provide mechanical strength and improved stability to the capsules. The nanosized hollow aggregates are tunable in size, are stable in solution for days, show selective permeability and assemble into 2-D hexagonal arrays in the solid state.

The incorporation of a coordination framework shell into hollow polymer particles is advantageous because coordination frameworks possess a wide range of properties that could lead to materials with exciting new properties and functions such as improved mechanical and thermal stability, selective permeability and magnetic walls. The nanomaterials reported in this chapter could be useful to encapsulate and nanopattern active compounds for applications such as drug delivery, sensor arrays and catalyst immobilization and organization. Based on the diversity of the PBA family, it is envisioned that this approach will provide a convenient route to capsules with tunable magnetic, optical and electronic properties.
CHAPTER 6

MOLECULAR SCAFFOLDING OF PRUSSIAN BLUE ANALOGUES USING PHENANTHROLINE-EXTENDED TRIPTYCENE LIGANDS†

6.1 Introduction

Coordination polymers (CPs) have metal ions linked together into an infinite structure by bridging ligands. CPs are called coordination frameworks (CFs) when their structure is a three-dimensional network. Although the first synthetic CP, Prussian blue (PB), was discovered as early as 1704, these materials received little attention until landmark reports by Robson and Hoskins\(^{15,16}\) that introduced the concept of a net-based approach for the design of CPs. The idea of ‘engineering’ the structure of CPs through rational design in order to achieve desired properties revolutionized the field and led to the discovery of some of the most exciting functional materials of the past fifteen years. For instance, metal-organic frameworks (MOFs) are made of metal ions or clusters (usually copper or zinc-oxo clusters) bridged by multicarboxylate ligands such as benzene dicarboxylate and benzene tricarboxylate. These materials are thermally stable and capable of storing large quantities of gas molecules.\(^{17,41-43}\) Another family of CFs, zeolitic imidazolate frameworks (ZIFs), is composed of metal ions (Zn\(^{II}\), Co\(^{II}\) or Mg\(^{II}\)) bridged by imidazole ligands. The structure of ZIFs can be precisely controlled to

† A version of this chapter will be submitted for publication as: Roy, X.; Chong, J. H.; MacLachlan, M. J. “Molecular Scaffolding of Prussian Blue Analogues Using Phenanthroline-Extended Triptycene Ligands”, 2011.
discriminate between adsorbing species, and these materials have been used to selectively capture CO$_2$ from a mixture of gases.$^{18,234}$

One wide-ranging objective of materials chemistry is the rational design and synthesis of solid-state structures with customized properties. Several approaches are being investigated to achieve this goal. For instance, crystal engineers and supramolecular chemists seek to exploit weak coordination bonds and reversible intermolecular interactions (e.g., hydrogen bonding, van der Waals interaction, $\pi-\pi$ interaction, halogen bonding) to build new materials. In comparison, the field of CPs is more focused since it relies primarily on the coordination chemistry of the building blocks. In spite of this – or maybe because of this – it has been extremely successful.$^9,12,15-19,22,26,27,32,40-47,55,146,234$

Prussian blue (PB) is the archetypical CP. It is a three-dimensional cubic network of Fe$_4$[Fe(CN)$_6$]$_3$•nH$_2$O in which the Fe atoms (Fe$^{II}$ or Fe$^{III}$) lie at the lattice points and the cyanide groups are bridging. The PB framework is thermodynamically stable and is obtained for a wide range of Prussian blue analogues (PBAs). Cyanide ligands are interesting because they promote strong spin coupling between the bridged metal ions through superexchange interactions and PBAs have been investigated extensively for their magnetic properties.$^{36-38}$ On the other hand, the internal surface area of these materials is usually inaccessible to guest molecules because the pores made by bridging cyanides are too small and not interconnected. Recently, a certain degree of control over the structure of the network was achieved by changing the oxidation state of the metal ions in the PBA$^{20}$ and by using metals with different coordination geometries.$^{235,236}$ PBAs with bigger pores made from cyanide-capped metal clusters$^{23}$ and incorporating a third building block$^{237}$ have also been reported.

Another approach to engineering the network of PBAs is to incorporate structure-directing ligands into the molecular structure. To achieve this, one can use PBA precursors that are pre-
coordinated with ligands such as 2,2′-bipyridine\textsuperscript{189,238} or nitrosyl,\textsuperscript{239} or incorporate the organic compounds into the PBA network under hydrothermal conditions.\textsuperscript{240-246} In the latter approach, the cyanide ligands become labile at high temperature and the thermodynamic product is obtained. In addition to introducing new functional units into the materials, one can control the dimensionality of the PBA network using this technique – this is especially important for molecule-based magnets. For instance, the fabrication of mixed-ligand heterometallic Cu\textsuperscript{I}/Fe\textsuperscript{II} and homometallic Cu\textsuperscript{I} PBAs under hydrothermal conditions has been studied extensively and one-dimensional chains,\textsuperscript{242,243} two-dimensional layers,\textsuperscript{241} and three-dimensional frameworks\textsuperscript{240} have been synthesized using 1,10-phenanthroline and 2,2′-bipyridine as chelating ligands. Other structure-modified PBAs such as Ni/Co\textsuperscript{246} and Cr/Mn\textsuperscript{189} have also been reported.

Triptycene (11) is an attractive building block for the fabrication of solid-state nanostructures because it possesses a large internal molecular free volume (IMFV) conferred by its rigid three-dimensional paddlewheel geometry that resists effective packing. Triptycene is the simplest member of the iptycene family of polyaromatic compounds. It was first obtained by Bartlett et al. in 1942 through a six step synthesis beginning from anthracene and \textit{p}-benzoquinone.\textsuperscript{247} Today, triptycene is synthesized through a Diels-Alder cycloaddition reaction and a large number of derivatives are known.\textsuperscript{248} Triptycene has been investigated as a porosity-generating compound in a number of materials\textsuperscript{248-256} and a few derivatives have been used in the fabrication of CPs\textsuperscript{250} and MOFs.\textsuperscript{256} Thus far, triptycene has not been incorporated into PBAs.
Recently, a new family of phenanthroline-extended triptycenes was reported.\textsuperscript{257} These compounds could be used as rigid scaffolding ligands for the fabrication of novel CPs and molecular solid-state assemblies but no coordination complexes were reported in the article. In this chapter, I describe a synthetic strategy to prepare solid-state CPs based on these phenanthroline-extended triptycene. I selected the inorganic compounds CuCl\textsubscript{2} and K\textsubscript{3}[Fe(CN)\textsubscript{6}] as starting materials for the preparation of triptycene-scaffolded PBAs because they are known to form PBAs that incorporate a variety of chelating ligands under hydrothermal conditions. A novel triptycene-coordinated Cu\textsuperscript{I} molecular complex is also discussed en route to the triptycene-scaffolded PBA.

6.2 Experimental

6.2.1 Materials and methods

The polyaminotriptycenes 12, 15 and 17 were prepared according to published procedures (see Figure 6.1 for the structures).\textsuperscript{250,251} 1,10-Phenanthroline-5,6-quinone (13) was obtained from Sigma-Aldrich. The reactions to prepare the phenanthroline-extended triptycene compounds were performed under a nitrogen atmosphere. The solvents were degassed by nitrogen sparging before use.

The solvothermal reactions were performed in 22 mL Parr pressure vessels equipped with Teflon liners. A maximum of 10 mL of solvent was used for the solvothermal reactions. The pressure vessels were placed in a preheated programmable oven for a given time and then cooled down to room temperature using a controlled ramp of 7 °C h\textsuperscript{-1}. 

143
6.2.2 Synthesis of triptycenyl phenanthroline (14)

A solution of 2,3-diaminotriptycene (12) (200 mg, 0.70 mmol) and 13 (171 mg, 0.81 mmol) in ethanol (40 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the precipitate was collected by suction filtration and washed with ethanol. Vacuum drying at 50 °C yielded the desired product as a pale yellow solid (260 mg, 81% yield). Single crystals of 14 were obtained by heating a suspension of 14 (5 mg, 11 µmol) in 10 mL of methanol in a pressure vessel at 180 °C for 24 h and then slowly cooling down the pressure vessel.

1H NMR (400 MHz, CDCl₃) δ = 9.57 ppm (d of d, 3J(H,H) = 2, 8 Hz; 2H; CH), 9.22 (d of d, 3J(H,H) = 2, 4 Hz; 2H; CH), 8.24 (s; 2H; CH), 7.74 (d of d, 3J(H,H) = 4, 8 Hz; 2H; CH), 7.54-7.52 (m; 4H; CH), 7.13-7.10 (m; 4H; CH), 5.74 (s; 2H; bridgehead). 13C NMR (100.6 MHz, CDCl₃) δ = 152.1, 147.9, 147.0, 143.5, 141.6, 140.2, 133.3, 127.4, 126.2, 124.1, 123.8, 122.7, 53.7 ppm. HR-MS (EI, 70 eV) calculated for C₃₂H₁₈N₄: 458.15315; found: 458.15394. IR ν = 3350, 2967, 1574, 1479, 1448, 1430, 1401, 1358, 1336, 1315, 1273, 1150, 1122, 1109, 1071, 1053, 1029, 893, 807, 767, 749, 736, 628, 597, 564, 492, 481 cm⁻¹. Mp. > 300 °C.

6.2.3 Synthesis of triptycenyl bis(phenanthroline) (16)

A solution of 2,3,6,7-tetraaminotriptycene (15) (95 mg, 0.30 mmol) and 13 (142 mg, 0.68 mmol) in ethanol (40 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the precipitate was collected by suction filtration and washed with ethanol. Vacuum drying at 50 °C yielded the desired product as a light brown, shiny solid (186 mg, 93% yield).

1H NMR (400 MHz, CD₂Cl₂) δ = 9.61 ppm (d of d; 3J(H,H) = 2, 8 Hz; 4H; CH), 9.18 (d of d; 3J(H,H) = 2, 5 Hz; 4H; CH), 7.77 (d of d, 3J(H,H) = 4, 8 Hz; 4H; CH), 7.71-7.68 (m; 2H; CH),
7.24-7.22 (m; 2H; CH), 6.13 (s; 2H; bridgehead). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta =$ 152.4, 145.4, 142.1, 141.8, 140.8, 133.6, 127.5, 127.1, 125.6, 124.6, 124.1, 123.7, 53.5 ppm. HR-MS (EI, 70 eV) calculated for C$_{44}$H$_{22}$N$_8$: 662.19674; found: 662.19507. IR $\tilde{\nu} =$ 3360, 1633, 1574, 1478, 1448, 1418, 1358, 1337, 1228, 1197, 1165, 1149, 1128, 1107, 1070, 1030, 890, 808, 760, 738, 629, 608, 593, 564, 490 cm$^{-1}$. Mp. > 300 °C.

6.2.4 Synthesis of triptycenyl tris(phenanthroline) (18)

A solution of 2,3,6,7,14,15-hexaaminotriptycene (17) (100 mg, 0.29 mmol) and 13 (197 mg, 0.94 mmol) in ethanol (30 mL) was heated to reflux under a nitrogen atmosphere for 18 h. After cooling to room temperature, the precipitate was collected by suction filtration and washed with ethanol. Vacuum drying at 50 °C yielded the desired product as a brown solid (137 mg, 54% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta =$ 9.64 ppm (d of d; $^3$$\nu$(H,H) = 2, 8 Hz; 6H; CH), 9.26 (d of d; $^3$$\nu$(H,H) = 2, 4 Hz; 6H; CH), 7.80 (d of d; $^3$$\nu$(H,H) = 4, 8 Hz; 6H; CH), 6.41 (s; 2H; bridgehead). HR-MS (ESI, MeOH) calculated for C$_{56}$H$_{27}$N$_{12}$: 867.2482 ([M•H]$^+$); found: 867.2499. IR $\tilde{\nu} =$ 3390, 1633, 1537, 1478, 1447, 1402, 1357, 1338, 1228, 1198, 1123, 1070, 1030, 889, 807, 740, 616, 597, 564, 491 cm$^{-1}$. Mp. > 300 °C. Too insoluble for $^{13}$C NMR spectroscopy.

6.2.5 Synthesis of triptycene-scaffolded PBA

Triptycenyl phenanthroline (14, 10.0 mg, 22 µmol), CuCl$_2$•2H$_2$O (3.7 mg, 22 µmol), K$_3$[Fe(CN)$_6$] (7.2 mg, 22 µmol) and 10 mL of methanol were loaded in a Parr pressure vessel equipped with a Teflon liner. The pressure vessel was placed in a preheated programmable oven at 180 °C for 48 h. The reaction was then cooled down to room temperature using a controlled ramp of 7 °C h$^{-1}$. A mixture of black needles (19), orange plates (20) and brown cubes (21) were obtained. The black needles and brown cubes were decanted off while the orange plates stuck to
the walls of the Teflon liner. The black needles aggregate into a wool-type material that was easily separated from the brown cube using tweezers. The orange plates were suspended into methanol by sonication. All the materials were kept in methanol until x-ray diffraction crystallographic characterization. Compound 20 was isolated by centrifugation at 4500 rpm, washed with dichloromethane and dried under vacuum for at 60 °C 24 h. Yields 4.0 mg of orange plates (37% based on Cu).

X-ray diffraction analysis of 20 suggests a chemical formula of $C_{66.5}H_{36}N_{10.5}Cu_{2.5}\cdot[0.5H_2O]$ along with three methanol guest molecules in the asymmetric unit. The sample submitted for elemental analysis (EA) was dried under vacuum at 60 °C for 24 h to remove as much guest solvent molecules as possible. The dried structures most likely adsorbed a number of water molecules upon standing in air. Satisfactory EA of 20 was obtained assuming 1.5 $H_2O$ and 1 $CH_3OH$ guest molecules per asymmetric unit in the structure. EA: calculated (%) for $C_{66.5}H_{36}N_{10.5}Cu_{2.5}\cdot[0.5H_2O]\cdot1.5H_2O\cdotCH_3OH$: C 67.06, H 3.67, N 12.16; found: C 66.94, H 3.36, N 12.25.

A similar procedure was attempted using the compounds 16 and 18. Amorphous powders were obtained in both cases. No further characterization was performed on these materials.

6.2.6 Direct synthesis of di(triptycenyl phenanthroline)copper(I) (22)

Triptycenyl phenanthroline (14, 17.1 mg, 37 µmol), CuCl$_2\cdot$2$H_2O$ (6.3 mg, 37 µmol), and 10 mL of methanol were loaded in a Parr pressure vessel equipped with a Teflon liner. The pressure vessel was placed in a preheated programmable oven at 180 °C for 24 h. The reaction mixture was then cooled down to room temperature using a controlled ramp of 7 °C h$^{-1}$. Black needles (22) were obtained as the only product. The needles were centrifuged at 4500 rpm, washed with
dichloromethane and dried under vacuum for 18 h. Yields 18.1 mg of crystalline black solid (88% based on Cu).

EA: calculated (%) for C_{64}H_{36}N_{8}Cu_{2}Cl_{2}: C 68.94, H 3.25, N 10.05; found: C 68.71, H 3.38, N 10.26.

### 6.2.7 Equipment

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV-300 spectrometer. $^{13}$C NMR spectra were recorded using a proton decoupled pulse sequence. $^{13}$C NMR spectra were calibrated to the deuterated solvent at $\delta = 77.00$ ppm in CDCl$_3$. IR spectra were obtained using a Thermo Fisher Nicolet 6700 equipped with a Smart Orbit attenuated total reflectance (ATR) accessory. Electron impact ionization (EI) mass spectra were obtained using a double focusing mass spectrometer (Kratos MS-50) coupled with a MASPEC data system with EI operating conditions of: source temperatures 250-320 °C and ionization energy 70 eV. Melting points were obtained on a Fisher-John’s melting point apparatus. Electrospray ionization (ESI) mass spectra were obtained on a Waters/Micromass LCT time-of-flight mass spectrometer equipped with an electrospray ion source. The C, H and N elemental analyses were obtained at the UBC Microanalytical Services Laboratory. The N$_2$ adsorption isotherm was measured on a Micromeritics ASAP 2010 physisorption analyzer and software. Powder x-ray diffraction (PXRD) patterns were obtained using a Bruker D8 Advance diffractometer equipped with a Cu K$\alpha$ sealed tube x-ray source.

### 6.2.8 X-ray diffraction crystallographic analysis

Suitable crystals of compounds 14, 19 and 20 were mounted on a glass fibre with oil. Structure solutions were refined using the SHELXL software.$^{258}$
Table 6.1. Selected crystallographic data for compounds 14, 19 and 20.

<table>
<thead>
<tr>
<th>Compound</th>
<th>14</th>
<th>19</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{32.5}H_{20}N_{4}O_{0.5}</td>
<td>C_{128}H_{72}N_{16}Cl_{4}Cu_{4}O</td>
<td>C_{69.5}H_{49}N_{10.5}Cu_{2.5}O_{3.5}</td>
</tr>
<tr>
<td>MW</td>
<td>474.53</td>
<td>2245.98</td>
<td>1246.04</td>
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<td>Lattice type</td>
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<td>monoclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2_1/n</td>
<td>C 2/c</td>
<td>P 2_1/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>8.011(2)</td>
<td>88.779(12)</td>
<td>15.577(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>30.610(3)</td>
<td>8.2340(11)</td>
<td>27.390(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>18.451(8)</td>
<td>27.418(4)</td>
<td>13.570(1)</td>
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<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>97.264(4)</td>
<td>102.6170(10)</td>
<td>96.227(3)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>4488.4(7)</td>
<td>19559(5)</td>
<td>5755.3(9)</td>
</tr>
<tr>
<td>Z value</td>
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<td>4</td>
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</tr>
<tr>
<td>D_{calc} (g cm⁻³)</td>
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<td>1.385</td>
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<tr>
<td>T (K)</td>
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<td>150</td>
<td>90</td>
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<tr>
<td>GOF on F²</td>
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<td>0.994</td>
<td>1.13</td>
</tr>
<tr>
<td>R₁ [I &gt; 2σ(I)]</td>
<td>0.0531</td>
<td>0.0526</td>
<td>0.073</td>
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<tr>
<td>wR₂ (all data)</td>
<td>0.1182</td>
<td>0.1390</td>
<td>0.194</td>
</tr>
</tbody>
</table>

6.2.8.1 X-ray diffraction crystallographic study of 14

Crystals of 14 suitable for x-ray diffraction were grown by slowly cooling a methanol solution heated to 180 °C in a sealed Parr pressure vessel. All measurements were made on a
Bruker X8 diffractometer at 173 ± 1 K using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Data was collected to a maximum 2θ value of 51.34° in a series of φ and ω scans in 0.50° oscillations with 60 s exposures. Of the 40914 reflections that were collected, 8505 were unique (Rint = 0.0810); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package.\textsuperscript{259} Data were corrected for absorption effects using a multi-scan technique (SADABS),\textsuperscript{260} with max and min transmission coefficients of 0.996 and 0.858, respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.\textsuperscript{261} All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The final cycle of full-matrix least-squares refinement on F² was based on 8505 reflections and 668 variable parameters and converged (largest parameter shift was 0.000 times its esd).

6.2.8.2 X-ray diffraction crystallographic study of 19

Crystals of 19 suitable for x-ray diffraction were obtained according to the procedure in section 6.2.5 of this thesis. Intensity data were collected at 150 K on a D8 goniostat equipped with a Bruker APEX II CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory)\textsuperscript{262} using synchrotron radiation tuned to λ = 0.7749 Å. The detector-to-crystal distance was 6 cm. A series of 4 s data frames measured at 0.2° increments of ω were collected to calculate a unit cell. For data collection frames were measured for a duration of 4 s at 0.3° intervals of ω with a maximum 2θ value of 60°. The data frames were collected using the program APEX2\textsuperscript{263} and processed using the program SAINT\textsuperscript{264} routine within APEX2. Of the 63492 reflections that were collected, 12459 were unique (Rint = 0.0948); equivalent reflections were merged. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS,\textsuperscript{260} with max and min transmission coefficient of 0.990 and 0.806, respectively. The data were corrected for Lorentz
and polarization effects. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated locations but were not refined. The final cycle of full-matrix least-squares refinement on $F^2$ was based on 12459 reflections, 1369 variable parameters and 2 restraints, and converged (largest parameter shift was 0.001 times its esd).

6.2.8.3 X-ray diffraction crystallographic study of 20

Crystals of 20 suitable for x-ray diffraction were obtained according to the procedure in section 6.2.5 of this thesis. All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Cu K$_\alpha$ radiation ($\lambda = 1.54178$ Å). The data were collected at a temperature of 90 ± 0.1 K to a maximum 2θ value of 131.1°. Data were collected in a series of $\phi$ and $\omega$ scans in 1.0 oscillations using 10 s exposures. The crystal-to-detector distance was 5 cm. Of the 67431 reflections that were collected, 9634 were unique ($R_{int} = 0.046$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The linear absorption coefficient, $\mu$, for Cu K$_\alpha$ radiation is 15.87 cm$^{-1}$. Data were corrected for absorption effects using the multi-scan technique SADABS, with minimum and maximum transmission coefficients of 0.861 and 0.954, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The material crystallized with one cyanide ligand (C66 – N10) disordered between Cu3 atoms related by inversion symmetry. The material also crystallized with methanol molecules in the lattice. Three methanol molecules were located and modeled in the asymmetric unit. Two of these molecules, however, appear to be disordered and were modeled in multiple orientations. Finally, there is a partially occupied water site coordinated to Cu1. The water molecule is present with a site-occupancy-factor of 0.5. All non-
hydrogen atoms except O1 were refined anisotropically. All hydrogen atoms were placed in calculated positions, including the hydroxyl hydrogens in each methanol and the water molecule fragment. The final cycle of full-matrix least-squares refinement on F² was based on 9634 reflections and 849 variable parameters and converged (largest parameter shift was 0.00 times its esd).

6.3 Results and discussion

The phenanthroline-extended triptycenes 14, 16 and 18 were prepared by Schiff-base condensation of the commercially available 1,10-phenanthroline-5,6-quinone (13) with the polyaminotriptycenes 12, 15 and 17, respectively (Figure 6.1). Compound 14 is known but only the n-butyl and tert-butyl derivatives of 18 have been reported because of solubility issues. Satisfactory ¹H NMR and electrospray ionization mass spectra of 18 were nonetheless obtained in this work although ¹³C NMR spectroscopy could not be performed because of the low solubility of 18. Compound 16, which has never been reported, was fully characterized.
Figure 6.1. Synthesis of phenanthroline-extended triptycenes 14, 16 and 18.

Single crystals of 14 were obtained by heating a suspension of the compound in methanol to 180 °C in a Parr pressure vessel for 48 hours. Compound 14 is presumably partially soluble in methanol at that temperature and single crystals were grown by slowly cooling down the pressure vessel. Figure 6.2a shows the solid-state structure for 14. The extended packing arrangement along the \( \alpha \)-axis shows partial overlap of the aromatic rings in the phenanthroline moiety, with the rings separated by approximately 3.4 Å, which is an optimal distance for \( \pi \)-
stacking (Figures 6.2b, 6.2c and 6.2d). While stacking typically improves packing efficiency, the rigid bulky triptycene moieties force the molecules to adopt a staggered conformation within the stacks (staggering angle is ca. 120°) and prevent the stacks from assembling into a close-packed structure. The stacks instead adopt an up-down or undulating arrangement along the $b$-axis (Figure 6.2e). The unfilled space between the stacks contains guest methanol molecules, producing solvent-filled channels that extend along the direction of the $a$-axis (Figure 6.2e).
Figure 6.2. Solid-state crystal structure of 14 (C$_{32.5}$H$_{26}$N$_4$O$_{0.5}$). Hydrogens have been omitted for clarity. Carbon, grey; nitrogen, blue; oxygen, red. a) is the ORTEP of a single molecule. Ellipsoids are shown at the 50% probability level. b) is a view showing the stacking of molecules. c) is a side view of a pair of stacked molecules. d) is a view down the c-axis showing stacks extending along the a-axis. Guest solvent molecules have been omitted for clarity in a-d). e) is a view down the a-axis showing solvent-filled channels (the methanol molecules are shown in this case).
Synthesis of triptycene-scaffolded PBAs under solvothermal conditions was attempted using compounds 14, 16 and 18. It was anticipated that the combination of high temperature and high pressure would help dissolve the starting materials, provide enough thermal energy to labilize the cyanide ligands and assist in the incorporation of the phenanthroline-extended triptycene ligands into the PBA framework. In addition, the slow cooling of the reaction mixture should facilitate the growth of single crystals suitable for x-ray diffraction characterization.

Using a one-pot synthesis approach, 14, CuCl₂ and K₃[Fe(CN)₆] were combined with methanol in a Parr pressure vessel and heated to 180 °C for 48 hours. A mixture of crystalline products was obtained upon cooling of the reaction: thin black needles (19), orange plates (20) and brown cubes (21). Because of the extremely small size of the black needles, x-ray diffraction of 19 was performed using synchrotron radiation. The solid-state structure of 19 shows two ligands 14 chelating one copper atom; the pseudo-tetrahedral geometry at the metal center suggests that it is in the +1 oxidation state (Figure 6.3a). The charge balance of the structure is also consistent with a Cu⁺ species: the +1 charge on the chelated metal is balanced by one [CuCl₂]⁻ counterion in its vicinity. Under the reaction conditions (high temperature and high pressure), the Cu²⁺ ions are most likely reduced to Cu⁺ with methanol molecules, the N-heterocyclic compounds or free cyanides from the dissociation of [Fe(CN)₆]³⁻ (or a combination of these species) acting as reducing agent.²⁴⁰,²⁴¹ Although somewhat unusual, the anion [CuCl₂]⁻ has nonetheless been observed and characterized crystallographically many times.²⁶⁵ Figures 6.3b and 6.3c show the extended structure of 19. The copper atoms assemble into columns along the b-axis, with some interdigitation of the triptycenes along the c-axis. Two types of stacking arrangement are observed for ligand 14: one with no significant overlap along the stacks and one with some amount of overlap between the phenanthrolines although there is a slight deviation from coplanarity (Figure 6.3b). The presence of the triptycenes, combined with the constraints
imposed by the tetragonal metal center hinders packing, resulting in void channels running along the direction of the $b$-axis (Figure 6.3b). The voids are partially filled by the $[\text{CuCl}_2]^{-}$ counterions and a single peak of electronic density that was satisfactorily modeled as an oxygen atom was also detected in the asymmetric unit (not shown in Figure 6.3). This oxygen is probably from a guest water molecule since there is no residual electronic density to suggest that it is a methanol molecule.
Figure 6.3. Solid-state crystal structure of 19 ($C_{128}H_{72}N_{16}Cl_4Cu_4O$). Hydrogens and solvent molecules have been omitted for clarity. Carbon, grey; nitrogen, blue; copper, green; chlorine, pink. a) is the ORTEP of a single metal complex. The $[CuCl_2]^-$ counterions and the carbon atom labels on the triptycene ligands have been omitted for clarity. Ellipsoids are shown at the 50% probability level. b) and c) are views showing the stacking of the complexes, along with the $[CuCl_2]^-$ counterions. b) is a view down the $b$-axis showing the void channels and the interdigitation of the triptycenes and c) is a view down the $c$-axis showing the Cu$^+$ atom columns.
In order to investigate the formation of compound 19, the solvothermal synthesis was performed for 12 hours and for five days. The mixture of products obtained after the five day synthesis is analogous to the one obtained after 48 hours of reaction but the product obtained after only 12 hours contained almost exclusively black needles. Resuming the solvothermal reaction for an additional 36 hours, and reusing the 12 hours synthesis products as starting materials yielded the usual mixture of orange plates (20) and brown cubes (21), along with a small fraction of black needles (19). These results suggest that the copper ions (reduced to CuI or not) first react with 14 to form complex 19 and this compound is then slowly converted to 20 and 21 upon further heating.

The direct solvothermal synthesis of 19 (without the addition of K₃[Fe(CN)₆]) was also attempted by reacting one equivalent of 14 with one equivalent of CuCl₂ in methanol at 180 °C for 24 hours. Black crystalline needles (22) akin to 19 were obtained in high yields. Powder x-ray diffraction (PXRD) experiments were performed on 22 (Figure 6.4b) and the experimental data was compared with the PXRD pattern of 19 calculated from the single crystal data (Figure 6.4a). Although not identical, the two patterns are in good agreement, supporting the idea that 22 and 19 are in fact the same compound. The variations between the patterns could be explained by the different amounts of solvent molecules trapped in the structures and a partial collapse of the structure upon drying of 22. Elemental analysis (EA) of 22 provides further evidence for the direct solvothermal synthesis of 19. Compound 22 has the same C, H and N composition as 19 ([([14]₂Cu)[CuCl₂]). Finally, the IR spectrum of 22 shows a number of peaks that belong to 14. No peak that can be assigned to cyanide ligands is observed. All these results suggest that 19 can be synthesized directly without the addition of K₃[Fe(CN)₆]. In this case, methanol or the N-heterocyclic compounds most likely act as the reducing agent. Interestingly, reacting 14 with CuCl under the same conditions did not yield the expected crystalline product.
Figure 6.4. PXRD patterns of the black needles synthesized using two different approaches. a) is the calculated PXRD pattern of 19 (calculated from the single crystal data). b) is the experimental PXRD pattern of 22. The variations between the patterns can be explained by the different amounts of solvent molecules trapped in the structures and a partial collapse of the structure upon drying of 22.

Interestingly, the solid-state crystal structure of 19 suggests a porous structure that may possess a sizeable surface area. N$_2$ adsorption experiments were performed to further investigate this question. Unfortunately, no surface area could be measured for these materials. The porous
structure probably collapses upon removal of the guest solvent molecules under vacuum. These results are consistent with a structure that is composed of weakly interacting metal complexes and also with the partially degraded PXRD pattern for the air-dried compound 22.

The orange plates 20 were first analyzed by IR spectroscopy to confirm the formation of a PBA network and the incorporation of 14 (see Appendix E). The IR spectrum of 20 shows a broad cyanide stretching band at $\tilde{\nu}_{CN} = 2110$ cm$^{-1}$ that does not correspond to $K_3[Fe(CN)_6]$ (narrow; $\tilde{\nu}_{CN} = 2116$ cm$^{-1}$). Peaks attributable to the phenanthroline-extended triptycene are also observed in the IR spectrum. These data suggest the incorporation of 14 into the metal cyanide network.

Single crystals of 20 suitable for x-ray diffraction were isolated from the product mixture. Figure 6.5 shows the solid-state crystal structure of 20. The first noticeable feature of the structure is the nature of the metal centers. Although $K_3[Fe(CN)_6]$ was added to the reaction mixture, Cu is the only metal present in the final structure. Under solvothermal conditions, $K_3[Fe(CN)_6]$ becomes a source of cyanide but the Fe atoms were not incorporated into the PBA in this case. This behaviour is well known for the Fe/Cu system and a number of homometallic Cu$^I$ PBAs have been reported. Three different geometries are observed for the Cu centers: T-shaped Cu1, pseudo-trigonal planar Cu2 and pseudo-tetragonal Cu3 (Figure 6.5a and 6.5b). These geometries (all known for Cu$^I$ complexes), the charge balance of the structure and the oxidation state of the precursor complex 19 strongly suggest that the Cu atoms in compound 20 are in the +1 oxidation state.

The structure of 20 is made of infinite one-dimensional zig-zag Cu$^I$ cyanide chains extending in the direction of the c-axis and separated by interdigitated triptycene ligands coordinated to the chains (Figure 6.5c and 6.5d). Strikingly, the voids between the triptycene pillars are filled with large intercalated guest complexes consisting of a tricoordinate Cu$^I$ center.
(Cu2) chelated by one triptycenyl phenanthroline and also one cyanide ligand. The chain itself is composed of cyanide-bridged pseudo-tetrahedral (Cu3) and T-shaped (Cu1) Cu\textsuperscript{I} centers alternating in a Cu1-Cu3-Cu3-Cu1-Cu3-Cu3 fashion. The two Cu3 atoms next to each other in the chain are related by inversion symmetry and, as expected, the cyanide ligand bridging them (C66-N10) has no preferential orientation and is observed as disordered in the x-ray diffraction (hence the ligand having both C66 and N10 labels for each constituting atom in Figure 6.5). In addition to that disordered cyanide, the coordination sphere of Cu3 is composed of another C-bonded cyanide and a chelated ligand 14. The Cu1 atom with T-shaped geometry has two pseudo-linear N-bonded cyanide ligands and one aqua ligand (O1) (Figure 6.5b). Two partially occupied water sites coordinated to Cu1 were identified (site-occupancy-factor of 0.5). These data suggest that two equivalent orientations exist for O1. Regardless of its orientation, the aqua ligand on Cu1 is perfectly positioned to hydrogen-bond with the nitrogen on the phenazine portion of 14 (N8 in Figure 6.5a). The O1* coordination site on Cu1 is shown as partially transparent in Figure 6.5c and 6.5d to highlight the site-occupancy of 0.5 for the aqua ligand. It is worth noting that several chelated (bidentate or tridentate) T-shaped Cu\textsuperscript{I} complexes have been reported recently.\textsuperscript{266,267} In contrast, T-shaped Cu\textsuperscript{I} complexes containing only monodentate ligands like the one observed in 20 are much more unusual.\textsuperscript{268}

Figure 6.5e shows the stacking of the triptycene moieties in the direction of the c-axis and isolated Cu\textsuperscript{I} PBA chains connecting the stacks along the b-axis. The arrangement of the shape-persistent triptycenes results in void channels between the stacks running along the c-axis. These pores are filled with solvent molecules. Three molecules of methanol were located and modeled in the asymmetric unit (not shown in Figure 6.5).
Figure 6.5. Solid-state crystal structure of 20 ($C_{69.5}H_{49}N_{10.5}Cu_{2.5}O_{3.5}$). Hydrogens, guest solvent molecules and the carbon atom labels on the triptycene ligands have been omitted for clarity. Carbon, grey; nitrogen, blue; oxygen, red; copper, green. a) is the ORTEP for the repeating unit of the triptycene-scaffolded Cu$^+$ PBA chain, along with the triptycene-coordinated guest complex. b) is the ORTEP of the T-shaped Cu1 complex. Ellipsoids for a) and b) are shown at the 50% probability level. c) shows a single Cu$^+$ PBA chain and d) is a view down the a-axis showing the arrangement of the PBA chains. The Cu1 metal center has a T-shaped geometry with two N-coordinated cyanide ligands and one aqua ligand that is equally distributed between two orientations. The O1* coordination site on Cu1 is shown as partially transparent to denote a site-occupancy of 0.5. e) is a view down the c-axis showing the stacking of the triptycene moieties and the isolated Cu$^+$ PBA chains. The aqua ligands on Cu1 have been omitted for clarity in this case.
At first glance, compound 21 appeared to be dark brown cubic crystals big enough for x-ray diffraction. Upon careful inspection, 21 turned out to be cubic particles of aggregated microcrystalline materials. Whereas x-ray diffraction proved useless to unambiguously identify compound 21, IR spectroscopy was employed to probe its nature. The IR spectrum of 21 shows a strong and broad band that can be assigned to the stretching mode of a cyanide species ($\nu_{\text{CN}} = 2065 \text{ cm}^{-1}$). The broadness of the peak is consistent with the cyanides being in a bridging mode. No peaks corresponding to 14 are observed. These limited results suggest that 21 is the triptycene-free PBA by-product left over from the solvothermal decomposition of K$_3$[Fe(CN)$_6$].

The same solvothermal procedure was attempted using compounds 16 and 18 as scaffolding agents. Unfortunately, only amorphous or microcrystalline powders were obtained in all cases and no further characterization was performed on these materials. The added phenanthroline units on compounds 16 and 18, compared with 14, and their increased bulk and internal molecular free volume presumably induces additional restrictions for the building of a metal cyanide framework that in the end does not form under the conditions tested. In addition, poor solubility of the organic molecules in methanol, even at high temperature, might hinder the formation of crystalline materials. Other solvents were also tested but similar amorphous products were always isolated.

6.4 Conclusions

The molecular scaffolding of PBAs is an attractive goal as it could lead to materials with tunable and low-dimensional magnetic and electrochemical properties, and with improved gas storage capacities, among others. In this chapter, the molecular scaffolding of a Cu$^+$ cyanide PBA using a new family of phenanthroline-extended triptycene compounds as structure-directing ligand is investigated. The smallest member of this family, triptycenyl phenanthroline, formed a
coordination complex with Cu\textsuperscript{I} ions when reacted with CuCl\textsubscript{2} and K\textsubscript{3}[Fe(CN)\textsubscript{6}] in methanol under solvothermal conditions. This coordination complex, made of one Cu\textsuperscript{I} center chelated by two triptycenyl phenanthroline ligands, can be directly synthesized by reacting the ligand with CuCl\textsubscript{2} under solvothermal conditions. It was converted into a triptycene-scaffolded Cu\textsuperscript{I} PBA by heating it further in methanol under solvothermal conditions with K\textsubscript{3}[Fe(CN)\textsubscript{6}], which acts as a source of cyanide. This homometallic PBA is composed of one-dimensional zig-zag chains of cyanide-bridged Cu\textsuperscript{I} centers. The chains are separated by interdigitated phenanthroline-extended triptycene pillars, and the voids between the pillars are filled with large intercalated (triptycenyl phenanthroline)copper(I) cyanide guest complexes. Interestingly, three coordination geometries are observed for the Cu\textsuperscript{I} centers in the structure, including an unusual T-shaped complex with three monodentate ligands. The approach to triptycene-scaffolded PBAs developed here could not be generalized for the bigger phenanthroline-extended triptycene ligands such as triptycenyl bis(phenanthroline) and triptycenyl tris(phenanthroline).

Copper(I) cyanide coordination polymers based on N-heterocyclic ligands like the one described in this work are particularly interesting because of their strong fluorescence. The incorporation of porosity-generating triptycene derivatives into their structure and the structure of other PBAs could potentially allow small molecules to penetrate and interact with the bulk of the materials.
Prussian blue (PB), the first coordination polymer (CP), was discovered in 1704 and rapidly became a commercially valuable pigment because of its intense blue colour.\textsuperscript{33} Interest in CPs has always been driven by the discovery of new or unexpected properties. After the initial advances related to the discovery of PB, progress in the field of CPs was slow until the mid 1990s when exciting magnetic properties\textsuperscript{36,37,200} and gas storage capabilities\textsuperscript{17,41-43} were reported for Prussian blue analogues (PBAs) and metal-organic frameworks (MOFs), respectively. In recent years, it was recognized that processable and patternable nanoscale coordination polymers could offer the opportunity to discover new properties and integrate novel functions into these materials. However, many challenges associated with the synthesis of these nanomaterials, including the propensity of CPs to crystallize into the bulk phase, still remain.

This thesis aims at developing new synthetic techniques for the fabrication of processable CP nanomaterials. Specifically, it reports the assembly of PBA nanostructures with previously inaccessible morphologies and compositions using a variety of organic structure-directing agents (SDA). Significantly, this work clearly demonstrates that the tethering of a precursor to PBA onto the SDA is an effective method to circumvent the formation of the thermodynamically stable bulk materials. Three categories of coordinating SDA were studied: molecular surfactants, block copolymers and a rigid scaffolding ligand.
Chapter 2 describes the synthesis of the first mesostructured PBAs. Mesomaterials have features in the range 2-50 nm and are typically synthesized via a liquid-crystal templating approach using surfactants as SDA.\textsuperscript{60,61} Mesomaterials are currently being investigated for applications as fast response photochromic materials\textsuperscript{165} and as photonic crystals\textsuperscript{166} and their mesoporous cousins have proved to be effective for catalysis and separation.\textsuperscript{67} A series of stable molecular surfactants having a charged iron cyanide complex as hydrophilic head group and metal-coordinated hydrophobic $N$-alkylpyrazinium tails of various length were prepared and used in a one-pot synthesis to fabricate PBAs with order on the nanometer scale. In formamide, these metal-containing surfactants formed liquid-crystalline phases that were crosslinked into PBA frameworks with the addition of transition metals. Significantly, the $N$-alkylpyrazinium template remained coordinated to the iron cyanide complex in the materials. PBAs with well-ordered lamellar, hexagonal and cubic structures and a wide range of metal compositions can be fabricated using this approach. Interestingly, the materials made of Fe$^{\text{III}}$ and Fe$^{\text{II}}$ exhibited mixed-valency and magnetic interactions in the framework. Unfortunately, removal of the organic template to access the mesoporosity proved impossible without collapse of the structure.

Chapters 3, 4 and 5 examine the use of metal-containing macromolecular SDAs to assemble PBA nanomaterials. Chapter 3 focuses on the synthesis of a homopolymer capable of tethering a precursor to PBA. This homopolymer was used as a model compound and testing ground for the preparation of the metal-containing block copolymers employed in Chapters 4 and 5. A number of systems were considered and the final design for the metal-containing polymer is built from 2-hydroxyethyl methacrylate units functionalized with pendent monoquaternized 4,4$'$-bipyridinium groups that can anchor iron cyanide complexes. Complexation of the polyelectrolyte crosslinked the polymer and porous sponge-like PBA materials with a surface area of 114 m$^2$ g$^{-1}$ were obtained.
In Chapter 4, the synthetic approach developed in Chapter 3 was adapted for the preparation of a novel ionic block copolymer that contains the precursor to PBA. This metal-containing block copolymer was built by selectively functionalizing the poly(2-hydroxyethyl methacrylate) block of a preformed polystyrene-\textit{b}-poly(2-hydroxyethyl methacrylate) backbone with monoquaternized 4,4′-bipyridinium pendent groups that can tether the iron cyanide complexes. When dissolved in organic solvents, the ionic block copolymer behaved as a block ionomer and self-assembled into stable wormlike reverse micelles with the 4,4′-bipyridinium groups in the ionic cores. The core of the micelles can be metallated with the iron cyanide complex or it can be used as an ion confinement region for different cyanometallate compounds to be crosslinked into PBA-type frameworks. The PBA nanoworms are soluble in a variety of organic solvents, are stable in solution for hours, organize into fingerprint surface structures upon evaporation and can be converted into metal oxide nanostructures. Toroidal PBA nanomaterials were prepared using block ionomers with a longer ionic segment.

Chapter 5 reports the block ionomer directed-assembly of soluble hollow polymer capsules with PBA inner-shells. Emulsification of a solution of the metal-containing macromolecules induced the amphiphilic compounds to assemble at the water-oil interface and stabilize nanosized spherical water droplets. The water-filled hollow aggregates have a hydrophilic iron cyanide inner-shell that can be crosslinked into PBA with zinc ions and a polystyrene corona that renders them soluble in many organic solvents. Crosslinking the capsules improved their mechanical strength and stability when compared with the non-crosslinked ones. The hollow capsules can be used as nanocontainers to encapsulate molecular compounds, have selective permeability, are tunable in size and organize into hexagonal arrays in the solid state.

Chapters 2, 3, 4 and 5 describe molecular and macromolecular assembly processes that rely on weak interactions. It should be noted that although the forces (electrostatic interactions and
hydrophobic effects) ‘felt’ by each individual repeating unit on the block ionomers are rather weak, the overall driving force for the assembly of the macromolecules can still be very large. The techniques developed in this thesis offer unprecedented control over the fabrication of nanosized PBAs. The connectivity of the PBA network in the nanomaterials is essentially the same as in the bulk phase. By design, these preparation techniques are ineffective at controlling the molecular structure of the PBA network.

In contrast, in Chapter 6, a SDA that can alter the molecular structure of a copper homometallic PBA is examined. The ligand is based on triptycene, a paddlewheel-shaped compound with a large internal molecular free volume. Phenanthroline units capable of chelating metal atoms were added to the triptycenes. Under solvothermal conditions, the structure-directing ligands first reacted with copper ions to form a new coordination complex made of one Cu\(^{1}\) center chelated by two triptycenyl phenanthroline ligands. This complex was then converted to a triptycene-scaffolded Cu\(^{1}\) PBA under solvothermal conditions with K\(_3\)[Fe(CN)\(_6\)] acting as a source of cyanide. The new homometallic PBA is composed of one-dimensional zig-zag chains of cyanide-bridged Cu\(^{1}\) centers separated by interdigitated triptycene pillars. The incorporation of the scaffolding ligand generates large void spaces, some of which are filled with bulky intercalated (triptycenyl phenanthroline)copper(I) cyanide guest complexes. The other voids are filled with solvent molecules.

The new synthetic methods developed in this work should provide useful routes to nanomaterials with tunable magnetic, optical, electrochemical and electronic properties. Significantly, the PBA materials detailed in Chapters 4 and 5 are soluble and processable and the use of the block copolymers as SDA offers the possibility of patterning these nanomaterials into functional structures. The incorporation of porosity-generating compounds such as triptycene derivatives into the structure of PBAs could allow small molecules to penetrate and interact with
the bulk of the network. Materials with tunable and low-dimensional magnetic and electrochemical properties and, with improved molecular storage capabilities could be prepared in this fashion. The techniques described in this thesis could also be used for the fabrication of other types of CPs and inorganic nanomaterials and I anticipate that they will become part of the common toolbox for the fabrication of functional materials.

7.2 Future work

This thesis is mainly focused on addressing the synthetic challenges posed by the fabrication of processable CPs nanomaterials. Standard characterization techniques were employed to study the nanostructures, probe the assembly processes, and confirm the chemical nature and connectivity of the CPs. However, except for Chapter 2, which briefly studies the magnetic interactions in the mesostructured PBAs using superconducting quantum interference device (SQUID) measurements and Mössbauer spectroscopy, the magnetic, electronic, electrochemical and optical properties of the nanomaterials were not investigated. An extensive survey of the physical and chemical properties of the materials reported in this work would therefore be beneficial to researchers in this field and in other fields, and for the development of new applications. In addition, improved materials could be synthesized based on the findings. The magnetic properties of the PBA nanomaterials should receive special attention as some compounds may exhibit low-dimensional or photo-induced magnetism, or superparamagnetism.

The variety of morphologies accessible using the coordinating block ionomers described in Chapters 4 and 5 as structure-directing agent is one of the most exciting results reported in this thesis. Figure 7.1 is a transmission electronic microscopy (TEM) survey of the different nanostructures observed in this research work. These include worms, toroids, multirings, nanoparticles and hollow spheres (big and small). A number of these morphologies could not be
thoroughly investigated and even for those that were studied in-depth, the assembly mechanism and the conditions under which they form are not completely understood. The toroidal PBA structures (Figures 7.1b and 7.1c) are especially intriguing and certainly deserve further investigation considering the level of interest that these types of aggregates have received recently.\textsuperscript{207,269,270} Determining the conditions necessary to form isolated toroids is a critical first step and this should be followed by a study of their magnetic properties.

Interestingly, the shape of the micelles is also dependent on the solvents employed. Small mostly spherical PBA nanoparticles can be synthesized in a mixture of 1,2-dichloroethane and methanol (Figure 7.1d). Similarly, experimental conditions are critical in controlling the size of the hollow spheres. When \([\text{Fe}^{II}(\text{CN})_5]\text{BI30}\) was used, small, mostly monodisperse \(\text{Zn}^{II}\text{[Fe}^{II}(\text{CN})_5]\text{MOC30}\) capsules were obtained regardless of the rate of addition of chlorobenzene (Figure 7.1e). However, \(\text{Zn}^{II}\text{[Fe}^{II}(\text{CN})_5]\text{MOC75}\) capsules significantly bigger than the ones discussed in Chapter 5 were observed when chlorobenzene was added rapidly (Figure 7.1f). This increase in capsule diameter was accompanied by a wider distribution of sizes. This idea of controlling the diameter of the PBA capsules with the rate of addition of chlorobenzene is worth pursuing.
Figure 7.1. TEM survey of the morphologies accessible using the iron cyanide block ionomers SDA. a) is a TEM micrograph of $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{BI30}$ nanoworms. b) and c) are TEM micrographs of a single toroidal $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{BI75}$ micelle and $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{BI75}$ multiring assemblies, respectively. d) is a TEM micrograph of $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{BI30}$ nanoparticles prepared in a mixture of 1,2-dichloroethane and methanol. e) and f) are TEM micrographs of small $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{MOC30}$ and large $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_3]\text{MOC75}$ hollow capsules, respectively.
The $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ nanoworms reported in Chapter 4 can be calcined in air to generate iron oxide nanostructures. This approach could be investigated to prepare multimetallic oxide nanomaterials for catalysis applications.

Chapter 5 describes the encapsulation of an ionic molecular compound inside the hollow capsules. Sure enough, other compounds can also be encapsulated within the core of the aggregates. Preliminary experiments suggest that polymer capsules with solid PB cores can be prepared by encapsulating $\text{K}_4[\text{Fe(CN)}_6]$ inside solvent-filled $\text{BI75}$ capsules (the metal-free block ionomer was employed in this experiment) and crosslinking the iron cyanide-containing cores into PB with $\text{Fe}^{III}$ ions. The TEM micrograph of the material dropcast shows spherical particles with darker cores (Figure 7.2a). In contrast, hollow capsules have lighter interiors by TEM analysis (see Figures 7.1e and 7.1f for examples). These results are consistent with the idea that PB is in the core of the capsules. More interestingly, soluble core-shell nanoparticles could be accessible. As shown in Figure 7.2b, these nanoparticles would have a core made of one type of PBA and a shell composed of another type of PBA. They may be fabricated by encapsulating a cyanometallate complex ($[\text{M(CN)}_6]^{\text{x}^-}$) inside solvent-filled $[\text{Fe}^{II}(\text{CN})_5]\text{MOC30}$ or $[\text{Fe}^{II}(\text{CN})_5]\text{MOC75}$ capsules and crosslinking at once the shell and the core with a metal ion ($\text{M'}$). These soluble core-shell nanoparticles could exhibit exciting tunable magnetic and electrochemical properties. In addition, the block ionomer SDA offers the possibility of patterning these nanomaterials into functional arrays.
Figure 7.2. a) is a TEM micrograph of block ionomer (Bi75) capsules that appear to have solid cores made of PB. A mixture of Bi75, K₄[Fe(CN)₆] and 18-crown-6 in THF (10% v/v H₂O) was sonicated, emulsified with chlorobenzene and centrifuged to remove the excess salt. The resulting assemblies are solvent-filled Bi75 capsules with the iron cyanide complex encapsulated in the core. Fe(NO₃)₃ was added to crosslink the cores into PB. This micrograph is consistent with the darker core of the capsules being filled with PB. b) is the schematic representation of a soluble core-shell PBA nanoparticle prepared by emulsion-induced assembly of metal-containing block ionomers.

Finally, PBA mesomaterials could be fabricated using an iron cyanide block copolymer analogous to the ones developed in this thesis. A block polyelectrolyte, as opposed to a block ionomer, would be needed for this application. It should have a short nonionic block and a longer metal-containing ionic segment. When dissolved in water, it should form micelles with nonionic cores surrounded by soluble iron cyanide-rich coronae. The aggregates could be deposited and assembled onto a surface, and then crosslinked into a mesostructured PBA film by dipping the substrate into a non-aqueous solution of a metal salt. They could also be crosslinked in solution to form bulk PBA mesostructures. The block copolymer-templated meso-PBAs are expected to possess walls significantly thicker than the mesomaterials assembled using the iron cyanide molecular surfactants described in Chapter 2. They should therefore have improved stability and
mesoporous PBAs could become accessible by extracting the coordinated block copolymer template in hot DMSO.

7.3 Experimental

7.3.1 Starting materials

The block ionomers BI30 and BI75 were synthesized according to the procedure described in Sections 5.2.2 and 5.2.3. The metal-containing block ionomers [Fe^{II}(CN)₅]BI30 and [Fe^{II}(CN)₅]BI75 were prepared according to the procedure outlined in Sections 5.2.5. Na₃[Fe(CN)₅NH₃]•3H₂O was prepared from sodium nitroprusside according to the procedure by Kenney et al. The yellow solid was recrystallized from a solution of ammonium hydroxide and methanol.

7.3.2 Fe^{III}[Fe^{II}(CN)₅]BI30 nanoworms and Fe^{III}[Fe^{II}(CN)₅]BI75 nanorings (Figure 7.1a-c)

The Fe^{III}[Fe^{II}(CN)₅]BI30 nanoworms and Fe^{III}[Fe^{II}(CN)₅]BI75 nanorings were fabricated according to the procedure outlined in Sections 4.2.6.

7.3.3 Fe^{III}[Fe^{II}(CN)₅]BI30 nanoparticles (Figure 7.1d)

The block ionomer BI30 (9 mg) was dissolved in 18 mL of 1,2-dichloroethane. In a separate vial, 2 mg (6 µmol) of Na₃[Fe(CN)₅NH₃]•3H₂O and 6 mg (23 µmol) of 18-crown-6 were dissolved in 1 mL of methanol and added dropwise to the vigorously stirred BI30 solution. The solution was stirred for 90 min at room temperature to afford a clear blue solution. Fe(NO₃)₃•6H₂O (5 mg, 12 µmol) dissolved in 1 mL of methanol was added to the stirred [Fe^{II}(CN)₅]BI30 solution. The reaction was stirred at room temperature for 60 min and then filtered to remove any trace of insoluble bulk PBA or insoluble Fe(NO₃)₃. The solution was
dropcast onto a TEM grid that was kept under a watch glass to prevent moisture from condensing on the sample.

7.3.4 **Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC30 and Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC75 (Figure 7.1e and 7.1f)**

The hollow capsules Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC30 were prepared according to the procedure outlined in Section 5.2.6. The large Zn$^{II}$[Fe$^{II}$(CN)$_5$]MOC75 hollow capsules were prepared according to the same procedure but chlorobenzene was added at once to generate the emulsion instantly.

7.3.5 **Block ionomer (BI75) capsules with a PB core (Figure 7.2a)**

A solution of BI75 (10 mg) in 10 mL of THF was prepared. K$_4$[Fe(CN)$_6$] (20 mg, 47 µmol) and 50 mg (189 µmol) of 18-crown-6 were dissolved in 1 mL of deionized water and added dropwise to the vigorously stirred BI75 solution. The resulting suspension was sonicated for 1 h. Chlorobenzene (25 mL) was added dropwise (1 drop s$^{-1}$) to the vigorously stirred mixture. The emulsion was stirred for 30 min at room temperature, sonicated for another 30 min and centrifuged at 500 rpm to remove most of the excess salt. Fe(NO$_3$)$_3$•6H$_2$O (20 mg, 50 µmol) dissolved in 4 mL of THF was added dropwise to the stirred solution and the reaction was stirred for 60 min. The suspension was centrifuged at 4500 rpm to remove any trace of insoluble PB. Using an extraction funnel, the organic phase was repeatedly washed with water to extract the THF and any remaining Fe(NO$_3$)$_3$. A clear blue solution was obtained upon standing over activated molecular sieves. It was dropcast onto a TEM grid for analysis.

7.3.6 **Equipment**

A Hitachi H7600 transmission electronic microscope operating at 80 kV was used to image the materials.
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260. *SADABS - Bruker Nonius area detector scaling and absorption correction*, v. 2.05;
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343-350.

262. Crystallographic data were collected through the SCrALS (Service Crystallography at
Advanced Light Source) program at the Small-Crystal Crystallography Beamline 11.3.1
(developed by the Experimental Systems Group) at the Advanced Light Source (ALS).
The ALS is supported by the U.S. Department of Energy, Office of Energy Sciences
Materials Sciences Division, under contract DE-AC02-05CH11231 at Lawrence
Berkeley National Laboratory.


264. *SAINT*, v. 7.56A; Bruker AXS: Madison.


Appendix A  Additional characterization for Chapter 2

Figure A.1. IR spectra of a) $\text{Na}_3[\text{Fe(CN)}_6\text{NH}_3] \ (\bar{\nu}_{\text{CN}} = 2047 \ \text{cm}^{-1})$, b) $[\text{Fe}^{\text{II}}(\text{CN})_3]C_{18} \ (\bar{\nu}_{\text{CN}} = 2069 \ \text{cm}^{-1})$, c) $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_3]C_{18} \ (\bar{\nu}_{\text{CN}} = 2079 \ \text{cm}^{-1})$ and d) $\text{Zn}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_3]C_{18} \ (\bar{\nu}_{\text{CN}} = 2077 \ \text{cm}^{-1})$. 
Figure B.1. IR spectra of a) Na₃[Fe(CN)₅NH₃] (\(\nu_{CN} = 2030 \text{ cm}^{-1}\)), b) [Fe⁰(CN)₅]PE (\(\nu_{CN} = 2046 \text{ cm}^{-1}\)), c) Fe³⁺[Fe⁰(CN)₅]PE (\(\nu_{CN} = 2057 \text{ cm}^{-1}\)) and d) Zn⁰[Fe⁰(CN)₅]PE (\(\nu_{CN} = 2077 \text{ cm}^{-1}\)).
Figure C.1. Size exclusion chromatography (SEC) analysis of PS-\textit{b}-PHEMA. The system was calibrated by monodisperse polystyrene standards and DMF was used as eluant, at a flow rate of 0.9 mL min$^{-1}$. 
Figure C.2. Time-resolved UV-vis spectra for the complexation of Bi30 into [Fe$^{III}$(CN)$_3$]Bi30. The spectra were recorded at the complexation concentration (1 mg mL$^{-1}$ in THF (8% v/v H$_2$O)) every 10 minutes. The red dashed curve was obtained at 100 minutes and overlaps perfectly with the spectrum obtained at 90 minutes.
NMR spectroscopy of the paramagnetic materials - Fe$^{III}$Fe$^{II}$(CN)$_5$BI30, Co$^{II}$Fe$^{II}$(CN)$_5$BI30, Fe$^{III}$Fe$^{II}$(CN)$_6$BI30, Cu$^{II}$Co$^{III}$(CN)$_6$BI30 and Co$^{II}$Fe$^{III}$(CN)$_6$BI30 – gave broad non-descriptive spectra. Figure C.3 shows a typical spectrum for the paramagnetic Cu$^{II}$Co$^{III}$(CN)$_6$BI30.

Figure C.3. $^1$H NMR spectrum (300 MHz, THF-$d_8$ (4% v/v D$_2$O)) of Cu$^{II}$Co$^{III}$(CN)$_6$BI30.
Figure C.4. IR spectra of a) Na₃[Fe(CN)₅NH₃] (ν₀ = 2030 cm⁻¹), b) [Fe⁰(CN)₅]BI30 (ν₀ = 2050 cm⁻¹), c) Fe³⁺[Fe⁰(CN)₅]BI30 (ν₀ = 2060 cm⁻¹), d) Zn⁰[Fe⁰(CN)₅]BI30 (ν₀ = 2082 cm⁻¹) and e) Co⁰[Fe⁰(CN)₅]BI30 (ν₀ = 2064 cm⁻¹).
Figure C.5. IR spectra of a) Fe$^{III}$[Fe$^{II}$,(CN)$_6$]BI30 (\(\bar{\nu}_{CN} = 2056 \text{ cm}^{-1}\)), b) Cu$^{II}$[Co$^{III}$,(CN)$_6$]BI30 (\(\bar{\nu}_{CN} = 2185 \text{ cm}^{-1}\)) and c) Co$^{II}$[Fe$^{III}$,(CN)$_6$]BI30 (\(\bar{\nu}_{CN} = 2069 \text{ cm}^{-1}\)). As a reference, the strongest CN stretching band is at \(\bar{\nu}_{CN} = 2039 \text{ cm}^{-1}\), \(\bar{\nu}_{CN} = 2127 \text{ cm}^{-1}\) and \(\bar{\nu}_{CN} = 2116 \text{ cm}^{-1}\) for K$_4$[Fe(CN)$_6$], K$_3$[Co(CN)$_6$] and K$_3$[Fe(CN)$_6$], respectively.
Figure C.6. Energy dispersive x-ray (EDX) spectra of a) $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$, b) $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ and c) $\text{Co}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$. 
Figure C.7. EDX spectra of a) $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\text{BI30}$, b) $\text{Cu}^{\text{II}}[\text{Co}^{\text{III}}(\text{CN})_6]\text{BI30}$ and c) $\text{Co}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]\text{BI30}$. The low levels of Br are from the inclusion of counterions and the aluminum peaks are contributions from the sample holder.

Figure C.8. EDX spectrum of the mesoporous iron oxide nanomaterials obtained by calcination of $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]\text{BI30}$ at 450 °C for 1 h in air. The low level of Si present in the sample is most likely contamination from the crucible.
Figure C.9. TGA thermograms of a) $[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$, b) $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$, c) $\text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ and d) $\text{Co}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{BI30}$ under N$_2$. 
**Figure C.10.** Transmission electronic microscopy (TEM) micrograph of \( \text{Co}^{II}[\text{Fe}^{II}(\text{CN})_6]\text{BI30} \) dropcast onto a TEM grid (polymer solution concentration: 0.5 mg mL\(^{-1}\) in THF (4% v/v \(\text{H}_2\text{O}\)). \text{BI30} was reacted with \( \text{Na}_3[\text{Fe}([\text{CN}]_6)\text{NH}_3] \) to generate \( [\text{Fe}^{II}(\text{CN})_6]\text{BI30} \). After dilution and filtration, \( [\text{Fe}^{II}(\text{CN})_6]\text{BI30} \) was reacted with \( \text{Co(NO}_3)_2 \) to crosslink the core of the aggregates into PBA-type networks. See Sections 4.2.5 and 4.2.6 for more details.

**Figure C.11.** TEM micrograph of \( \text{Co}^{II}[\text{Fe}^{III}(\text{CN})_6]\text{BI30} \) dropcast onto a TEM grid (polymer solution concentration: 0.5 mg mL\(^{-1}\) in THF (4% v/v \(\text{H}_2\text{O}\)). \text{BI30} was sonicated with \( \text{K}_3[\text{Fe}([\text{CN}]_6)] \) to obtain \( [\text{Fe}^{III}(\text{CN})_6]\text{BI30} \). After filtration to remove the excess \( \text{K}_3[\text{Fe}([\text{CN}]_6)] \), \( [\text{Fe}^{III}(\text{CN})_6]\text{BI30} \) was reacted with \( \text{Co(NO}_3)_2 \) to crosslink the core of the aggregates into PBA-type networks. See Sections 4.2.8 and 4.2.9 for more details.
To confirm that all the organic matter is removed under the conditions used to prepare the mesoporous iron oxide nanomaterials (1 hour at 450 °C in air), a modified TGA experiment was performed on Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30. The first heating stage of the TGA experiment is analogous to the calcination conditions. The sample was quickly heated to 450 °C in air and kept at that temperature for 1 hour. Afterward, the temperature was ramped to 900 °C at 10 °C min\textsuperscript{-1} in air. No change in weight was observed in the second heating stage confirming that all the organic was removed under our calcination conditions.

**Figure C12.** Thermogravimetric analysis (TGA) thermogram of Fe\textsuperscript{III}[Fe\textsuperscript{II}(CN)\textsubscript{6}]BI30 in air. The sample was first quickly heated to 450 °C, kept at that temperature for 1 hour, then ramped to 900 °C at 10 °C min\textsuperscript{-1}. 
Figure C.13. TEM micrograph of the mesoporous iron oxide film.

Figure C.14. High magnification TEM micrograph of the mesoporous iron oxide film.
Appendix D  Additional characterization for Chapter 5

Figure D.1. IR spectra of a) Na₃[Fe(CN)₆NH₃] (ν CN = 2030 cm⁻¹), b) [Fe(II)(CN)₆]MOC30 (ν CN = 2050 cm⁻¹), c) Zn(II)[Fe(II)(CN)₅]MOC30 (ν CN = 2082 cm⁻¹), d) [Fe(II)(CN)₆]MOC75 (ν CN = 2050 cm⁻¹) and e) Zn(II)[Fe(II)(CN)₅]MOC75 (ν CN = 2078 cm⁻¹).
The samples were dropcast onto glass slides, air-dried for 12 hours and then vacuum-dried for another 12 hours. The thin burgundy films were scrapped onto scanning electronic microscopy aluminum sample holders covered with carbon double-sided tape.

Figure D.2. EDX spectrum of \( \text{Zn}^{II}[\text{Fe}^{II}(\text{CN})_5]\text{MOC30} \). The aluminum peak comes from the sample holder and the silicon peak is most likely contamination from the glass slide.
Figure D.3. EDX spectrum of Zn$^{	ext{II}}$[Fe$^{	ext{II}}$(CN)$_5$]MOC75. The aluminum peak comes from the sample holder and the silicon peak is most likely contamination from the glass slide.
Appendix E  Additional characterization for Chapter 6

**Figure E.1.** IR spectra of a) $\text{K}_3\text{[Fe(CN)]}_6$ ($\nu_{\text{CN}} = 2116$ cm$^{-1}$), b) the black needles 22, c) the red crystals 20 ($\nu_{\text{CN}} = 2110$ cm$^{-1}$) and d) the brown cubes 21 ($\nu_{\text{CN}} = 2065$ cm$^{-1}$).