Synthesis and characterization of novel asymmetrically substituted bisphenazines and their self assembling properties

Kelly Kathleen McGrath
University of Nevada, Las Vegas

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SYNTHESIS AND CHARACTERIZATION OF
NOVEL ASYMMETRICALLY SUBSTITUTED
BISPHENAZINES AND THEIR SELF
ASSEMBLING PROPERTIES

by

Kelly Kathleen McGrath

Bachelor of Science
Ohio University, Athens
2002

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
College of Sciences

Graduate College
University of Nevada, Las Vegas
May 2008
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The Graduate College
University of Nevada, Las Vegas

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Kelly K. McGrath

Entitled
Synthesis and Characterization of Novel Asymmetrically Substituted
Bisphenazines and Their Self-assembling Properties

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Master of Science

Examination Committee Chair

Dean of the Graduate College

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative
ABSTRACT

Synthesis and Characterization of Novel Asymmetrically Substituted Bisphenazines and Their Self-Assembling Properties

by

Kelly Kathleen McGrath

Dr. Dong-Chan Lee, Examination Committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas

The self-assembly of π-conjugated materials into one-dimensional (1-D) nanostructures via intermolecular π-electron overlap is of particular interest for optoelectronic device miniaturization. There have been a number of π-conjugated organic semiconductors reported with the ability to self-assemble to produce nanofibers, nanobelts, and nanotubes. However, the majority of these molecules are electron-rich (p-type) and thus the demand for electron-deficient (n-type) semiconductors is high since the availability of useful n-type semiconductors is limited.

The design strategy and synthetic routes for novel n-type organic semiconductors based on bisphenazine are reported. The thermal, optical, and electrochemical properties studied by DSC, UV-visible and fluorescence spectroscopy, and cyclic voltammetry (CV) are presented. Electronic properties from theoretical calculations are also compared with the experimental results. The assembling properties, organogelation and 1-D assembly, of these new n-type molecules will be discussed with extensive investigations by scanning
electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-Transform infrared (FT-IR) spectroscopy.
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<tr>
<td>I-D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>SA</td>
<td>Self-assembly</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid crystal</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>LMOG</td>
<td>Low molecular weight organogelator</td>
</tr>
<tr>
<td>T&lt;sub&gt;gel&lt;/sub&gt;</td>
<td>Gelling temperature</td>
</tr>
<tr>
<td>CGC</td>
<td>Critical gelling concentration</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier-Transform infrared spectroscopy</td>
</tr>
<tr>
<td>TCE</td>
<td>1,1,1-Trichloroethane</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>TCTFE</td>
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CHAPTER 1

SYTHESES AND PHYSICAL PROPERTIES OF
ASYMMETRIC BISPENAZINES

1.1. General Introduction

Increased interest in miniaturizing organic electro-optical devices has led to extensive research in the area of organic nanomaterials. Of particular interest is the creation of these nanomaterials through the self-assembly of π-conjugated organic semiconductors. π-Conjugated molecules are known to have interesting electro-optical properties which makes them valuable in optoelectronic device applications such as solar cells and field effect transistors. One-dimensional (1-D) nanoclusters of π-conjugated molecules assembled through intermolecular \( \pi-\pi \) interactions are especially important for effective 1-D charge transport and device miniaturization as exemplified in single nanofiber and nanowire field effect transistors\(^1\).

An important issue is the successful and facile generation of 1-D structures via self-assembly. Self-assembly (SA) is the spontaneous thermodynamic organization of molecules into well-defined superstructures generally through weak noncovalent interactions such as hydrogen bonding, \( \pi-\pi \) stacking, van der Waals interactions, and hydrophobic effects. Among them, assembly through \( \pi-\pi \) stacking is our major concern due to the possible utility of the resultant nanostructures in electro-optical
applications. Intermolecular π-π interactions are generally weak, therefore successful assembly requires supporting interactions such as van der Waals or hydrogen bonding. To make these interactions work cooperatively, strategic molecular engineering is critical.

A number of π-conjugated organic semiconductors with the ability to self-assemble to form nanofibers, nanobelts, and nanotubes have already been reported. A general approach to design π-based molecules for 1-D assembly is to employ a symmetric π-core substituted with identical side groups. The morphology of 1-D nanoclusters have often been manipulated by using nonidentical side groups with opposite polarities. Despite these advances, the majority of the self-assembling π-molecules are electron-rich (p-type). Electron-deficient (n-type) organic semiconductors are as equally important as their counterpart in many optoelectronic applications, e.g., donor acceptor type solar cells and complementary circuits. The demand for n-type π-conjugated semiconductors is high due to the availability of only a limited number of useful molecules including perylene bisimide derivatives, C$_{60}$, and poly(benzobisimidazobenzophenanthroline) or BBL. Therefore, the main objective for this thesis is the development of new n-type semiconductors which have 1-D self-assembling abilities through intermolecular π-π interactions as a major driving force.

One approach to create organic n-type semiconductors is by the introduction of electron-withdrawing substituents to the p-type analogue. For example, the addition of cyano groups to poly(p-phenylenevinylene), a well-known p-type polymer, has been shown to successfully create n-type character in that compound. Although this method may successfully introduce electron-deficiency, the self-assembly of the resulting
molecules may be hindered by the new substituents. Another approach is through the introduction of pyridine, pyrizine, or triazine containing fused heterocyclic moieties which will not only enhance 1-D self-assembly due to the flat large π-area\textsuperscript{20-23} but can also impart n-type character owing to the electron-withdrawing imine nitrogens\textsuperscript{24}. A number of imine containing heterocycles such as quinoline, quinoxaline, and anthrazoline have already demonstrated electron transporting abilities in organic light-emitting diodes (OLEDs)\textsuperscript{25}. The introduction of heteroaromatics may be a more sensible approach to achieve dual goals simultaneously; electron-deficiency and self-assembly.

Therefore, this thesis will focus on the design and synthesis of new n-type molecules based on asymmetric bisphenazine. A total of six molecules will be presented and their thermal, optical, and electrochemical characteristics and assembling abilities will be discussed. These molecules are designed based on a heteroaromatic π-core that can easily be substituted peripherally to further tune its assembling ability and electron-deficiency.

1.2. Molecular Design

For this research, bisphenazine was chosen as a platform for both its assembling ability and electron-deficiency. It has been reported that the symmetrically substituted tetraalkoxy bisphenazine exhibits efficient self-assembling properties due to its large flat geometry and shows potential as an electron transporting material\textsuperscript{26}. Further utilization of this attractive heteroaromatic moiety requires the development of a facile synthetic route for its structural modification. However, the chemistries involving bisphenazine have not been extensively studied. Six bisphenazine derivatives were designed and synthesized to study their electronic character and 1-D self-assembly (Figure 1.1). Three major
structural features are of importance in this design. First, bisphenazine is a large, heteroaromatic molecule that may promote self-assembly through its large flat π-core. In addition, the presence of four imine nitrogens makes the ring electron-deficient\textsuperscript{24}.

![Diagram](Figure 1.1. Design rationale for asymmetrically substituted bisphenazine.

The π-core is substituted asymmetrically with two different types of substituents. Long alkoxy chains (C\textsubscript{16} and C\textsubscript{12}) are added to one side of the π-core to promote solubility and assembly through cooperative van der Waals interactions. Growth of the nanoclusters in the direction of the alkoxy side group may be inhibited by the local linear hydrocarbon solvent – side chain interactions while the long axis growth will be favored by π-π stacking. The substituents added to the other side vary in size, electron-withdrawing ability, and conjugation length. These substituents will further tune the electronic properties, such as electron-deficiency and HOMO-LUMO energy gap, while modulating the morphology of the assembly. Overall, this design strategy will allow for the 1-D
growth of nanoclusters through π-π stacking of the bisphenazine cores while fine-tuning the electronic property of the molecule by changing the peripheral substituent.

The first chapter will focus on the synthesis and physical properties of the molecules including thermal, optical, and electrochemical character. The subsequent chapters will focus on the assembly of the final compounds through both organogelation and 1-D assembly using a phase transfer method and recrystallization.

1.3. Instrumentation

Nuclear magnetic resonance (NMR) spectra were obtained at 25 °C on a Varian Gemini 400 MHz spectrometer. Deuterated chloroform (CDCl$_3$) with trimethylsilane (TMS) as an internal standard was used as the solvent for all samples. Mass spectrometry (MS) data was collected at the University of North Carolina Chapel Hill on a Micromass Quattro II triple quadrupole mass spectrometer with nano-electrospray ionization. Differential scanning calorimetry (DSC) measurements were obtained on a TA Instrument 2100 DSC under nitrogen atmosphere with heating and cooling rates of 10 °C per minute. UV-visible absorption spectra of the final products were collected on a Shimadzu UV-2450 UV-visible spectrophotometer from 5 x 10$^{-6}$ M solutions in CHCl$_3$. Fluorescence emission spectra were obtained on a Horiba Fluorescence meter using a xenon lamp for excitation. Data was obtained from 1 x 10$^{-8}$ M solutions in CHCl$_3$ with excitation at 422 nm. Cyclic voltammetry (CV) was performed on a CH Instrument 660C potentiostat using a 3-electrode cell with a platinum disc working electrode, a nonaqueous Ag/Ag$^+$ reference electrode (Ag$^+$ as 10 mM AgNO$_3$ solution in acetonitrile), and a platinum plate as the counter electrode. Measurements for all compounds were
obtained from a methylene chloride solution of the compound in 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The electrolyte solution containing the sample was purged with Ar gas for 30 minutes before each experiment and a blanket of Ar gas was used during the measurements. The scan rate was adjusted to 100 mV for all experiments. All potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc⁷) redox couple.

1.4. Synthesis

All chemicals and solvents were purchased from commercial sources and used as received. The intermediates 2,7-di-t-butylpyrene-4,5,9,10-tetraone²⁷, 1,2-diamino-4,5-dihexadecoxybenzene²⁸-²⁹, 1,2-diamino-4,5-diodobenzene³⁰, 1,2-diamino-4,5-dinitrobenzene³¹ were synthesized according to the literature and all ¹H-NMR results were as expected. Compound 4 was prepared according to an unpublished work³².

**Compound A**

2,7-Di-t-butylpyrene-4,5,9,10-tetraone (0.891 g, 2.38 mmol) was suspended in 60 mL absolute ethanol and 20 mL glacial acetic acid. To that mixture, 1,2-diamino-4,5-diodobenzene (0.857 g, 2.38 mmol) was added at once. The reaction mixture was refluxed overnight under a positive N₂ flow. The mixture was cooled in the refrigerator, filtered with hot absolute ethanol, and dried under vacuum. The product was obtained as an orange solid (74% impure).

**Compound B**

2,7-Di-t-butylpyrene-4,5,9,10-tetraone (0.981 g, 2.62 mmol) was dissolved in 132 mL of chloroform and 33 mL of glacial acetic acid. 1,2-Diamino-4,5-dihexadecoxybenzene
(0.883 g, 1.50 mmol) was added at once and the mixture was refluxed for 2 hrs under a positive N₂ flow. The reaction mixture was cooled to room temperature and washed with H₂O and 10% NaOH(aq). The organic layer was collected and dried over Na₂SO₄. The Na₂SO₄ was filtered out and rinsed with hot methylene chloride. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (CH₂Cl₂/hexane 1/1 v/v). The pure product was obtained as a yellow solid (72%).

¹H-NMR: (CDCl₃) δ [ppm]: 9.52 (d, J = 2.0, 2H, Ar-H), 8.51 (d, J = 2.0, 2H, Ar-H), 7.41 (s, 2H, Ar-H), 4.25 (t, J = 6.6, 4H, -CH₂), 2.04 – 1.97 (m, 4H, -CH₂), 1.58 (s, 18H, -CH₃), 1.49 – 1.26 (m, 52H, -CH₂), 0.87 (t, J = 6.8, 6H, -CH₃)

¹³C-NMR: (CDCl₃) δ [ppm]: 180.55, 153.97, 152.02, 140.21, 138.85, 130.66, 129.89, 129.44, 129.13, 127.63, 106.62, 69.34, 35.58, 31.93, 31.28, 29.73, 29.67, 29.66, 29.42, 29.37, 28.89, 26.09, 22.69, 14.13 (5 alkyl peaks not seen due to overlapping signals)

[M+H]⁺: Calcd 927.69, Found 927.7

Compound 1

Compound B (0.200 g, 0.216 mmol) was dissolved in 52 mL chloroform and 17 mL glacial acetic acid. To that solution, 1,2-diaminobenzene (0.025 g, 0.231 mmol) in acetic acid/chloroform was added at once. The mixture was refluxed for 3 hrs under a positive N₂ flow. The mixture was cooled to room temperature and washed with H₂O, 10% NaOH(aq), and saturated NaCl(aq). The organic layer was collected, dried over Na₂SO₄, and filtered with hot chloroform. The solvent was removed under vacuum to yield the crude product as an orange/yellow solid which was purified by silica gel column
chromatography (CH$_2$Cl$_2$/hexane 2/3 v/v). The pure product was obtained as a yellow solid (80%).

$^1$H-NMR: (CDCl$_3$) $\delta$ [ppm]: 9.76 (d, $J = 2.0$, 2H, Ar-H), 9.75 (d, $J = 2.0$, 2H, Ar-H), 8.44 – 8.41 (m, 2H, Ar-H), 7.90 – 7.87 (m, 2H, Ar-H), 7.61 (s, 2H, Ar-H), 4.32 (t, $J = 6.6$, 4H, -CH$_2$), 2.05 – 1.98 (m, 4H, -CH$_2$), 1.76 (s, 18H, -CH$_3$), 1.64 – 1.56 (m, 4H, -CH$_2$), 1.50 – 1.26 (m, 48H, -CH$_2$), 0.87 (t, $J = 6.8$, 6H, -CH$_3$)

$^{13}$C-NMR: (CDCl$_3$) $\delta$ [ppm]: 153.37, 150.55, 143.23, 142.23, 140.43, 139.99, 129.70, 129.55, 129.26, 125.21, 123.76, 123.69, 106.93, 69.25, 35.89, 31.93, 31.90, 29.75, 29.68, 29.46, 29.38, 28.96, 26.12, 22.71, 14.13 (6 alkyl peaks and 1 aromatic peak not seen due to overlapping signals)

[M+H]$^+$: Calcd 999.74, Found 999.8

**Compound 2**

**Route 1** (Figure 1.2): 2,7-Di-\textit{t}-butylpyrene-4,5,9,10-tetraone (0.505 g, 1.35 mmol) was dissolved in 340 mL chloroform and 115 mL glacial acetic acid. 1,2-Diamino-4,5-dihexadecyloxybenzene (0.722 g, 1.23 mmol) was added at once and the mixture was refluxed for 2 hours under a positive N$_2$ flow. The reaction mixture was cooled slightly and 1,2-diamino-4,5-diiodobenzene (0.583 g, 1.62 mmol) was added at once and the reaction was refluxed for an additional 2 hours under a positive N$_2$ flow. The reaction was filtered using hot chloroform and the filtrate was collected and washed with H$_2$O and saturated NaHCO$_3$(aq). The organic layer was collected, dried over Na$_2$SO$_4$, and filtered. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (CHCl$_3$/hexane 1/1 v/v). The pure product was obtained as a yellow solid (35%).
Route 2 (Figure 1.2): Compound A was suspended in 370 mL chloroform and 108 mL glacial acetic acid and heated to 60°C. 1,2-Diamino-4,5-dihexadecoxybenzene (1.03 g, 1.77 mmol) was added at once and refluxed overnight under a positive N₂ flow. The reaction mixture was filtered with boiling chloroform and the organic layer was collected and washed with H₂O, 10% NaOH(aq), and saturated NaCl(aq). The organic layer was collected, dried over Na₂SO₄, and filtered. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (CHCl₃/hexane 1/1 v/v). The pure product was obtained as a yellow solid (16%).

Route 3 (Figure 1.2): Compound B (0.900 g, 0.97 mmol) was dissolved in 200 mL chloroform and 62 mL glacial acetic acid. To that solution, 1,2-diamino-4,5-diiodobenzene (0.028 g, 0.078 mmol) was added at once and the mixture was refluxed overnight under a positive N₂ flow. The mixture was cooled to room temperature and washed with H₂O and 10% NaOH(aq). The organic layer was collected, dried over Na₂SO₄, and filtered. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (CH₂Cl₂/hexane 2/3 v/v). The pure product was obtained as a yellow solid (71%).

¹H-NMR: (CDCl₃) δ [ppm]: 9.70 (d, J = 2.0, 2H, Ar-H), 9.59 (d, J = 2.0, 2H, Ar-H), 8.86 (s, 2H, Ar-H), 7.53 (s, 2H, Ar-H), 4.29 (t, J = 6.6, 4H, -CH₂), 2.04 – 1.97 (m, 4H, -CH₂), 1.76 (s, 18H, -CH₃), 1.63 – 1.58 (m, 4H, -CH₂), 1.49 – 1.26 (m, 48H, -CH₂), 0.87 (t, J = 7.0, 6H, -CH₃)

¹³C-NMR: (CDCl₃) δ [ppm]: Significant ¹³C-NMR results were not obtained due to limited solubility.

[M+H]⁺: Calcd 1251.53, Found 1251.5
Compound 3

Compound B (0.487 g, 0.525 mmol) was dissolved in 128 mL chloroform and 40 mL glacial acetic acid. To that mixture, 1,2-diamino-4,5-difluorobenzene (0.075 g, 0.525 mmol) was added at once and the reaction was refluxed for 2 hrs under a positive N₂ flow. The reaction mixture was cooled to room temperature and washed with H₂O and 10% NaOH(aq). The organic layer was collected and dried over Na₂SO₄ and filtered. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (CH₂Cl₂/hexane 1/3 v/v). The pure product was obtained as a yellow solid (77%).

¹H-NMR: (CDCl₃) δ [ppm]: 9.74 (d, J = 1.6, 2H, Ar-H), 9.67 (d, J = 2.0, 2H, Ar-H), 8.13 (t, J = 9.4, 2H, Ar-H), 7.60 (s, 2H, Ar-H), 4.32 (t, J = 6.6, 4H, -CH₂), 2.05 – 1.98 (m, 4H, -CH₂), 1.75 (s, 18H, -CH₃), 1.64 – 1.56 (m, 4H, -CH₂), 1.50 – 1.26 (m, 48H, -CH₂), 0.87 (t, J = 7.0, 6H, -CH₃)

¹³C-NMR: (CDCl₃) δ [ppm]: Significant ¹³C-NMR results were not obtained due to limited solubility.

[M+H]^+: Calcd 1034.72, Found 1035.6

Compound 5

2,7-Di-t-butylpyrene-4,5,9,10-tetraone (0.325 g, 0.868 mmol) was dissolved in 105 mL of chloroform and 40 mL of glacial acetic acid. 1,2-Diamino-4,5-didodecyloxybenzene (0.413 g, 0.868 mmol) was added at once and the mixture was refluxed for 17 hrs under a positive N₂ flow. 1,2-Diamino-4,5-dinitrobenzene was dissolved in 5 mL glacial acetic acid and 10 mL CHCl₃ and added to the reaction via pipette. The mixture was refluxed for an additional 3 hours under a positive N₂ flow. The reaction mixture was cooled to
room temperature and filtered with hot chloroform. The filtrate was collected and washed with \( \text{H}_2\text{O} \) and 10\% \( \text{NaOH}_{(aq)} \). The organic layer was collected, dried over \( \text{Na}_2\text{SO}_4 \), and filtered. The solvent was removed under vacuum to yield the crude product which was purified by silica gel column chromatography (\( \text{CH}_2\text{Cl}_2/\text{hexane} \) 2/3 v/v). The pure product was obtained as a yellow solid (35\%).

\[ ^1\text{H-NMR: (CDCl}_3) \delta \text{ [ppm]}: 9.75 (d, J = 2.0, 2H, Ar-H), 9.60 (d, J = 2.0, 2H, Ar-H), 8.90 (s, 2H, Ar-H), 7.54 (s, 2H, Ar-H), 4.31 (t, J = 6.6, 4H, -CH\text{2}), 2.05 – 1.98 (m, 4H, -CH\text{2}), 1.75 (s, 18H, -C\text{H}_3), 1.64 – 1.57 (m, 4H, -CH\text{2}), 1.50 – 1.25 (m, 48H, -CH\text{2}), 0.89 (t, J = 6.6, 6H, -CH\text{3}) \]

\[ ^{13}\text{C-NMR: (CDCl}_3) \delta \text{ [ppm]}: \text{Significant} \]^{13}\text{C-NMR results were not obtained due to limited solubility.} \]

\[ [\text{M+H}]^+: \text{Calcd 976.58, Found 977.6} \]

**Compound C**

\( \text{Pd(PPh}_3)_2\text{Cl}_2 \) (11.4 mg, 0.016 mmol) and compound 2 (0.202 g, 0.162 mmol) were suspended in 32 mL of degassed anhydrous THF. To that mixture CuI (1.5 mg, mol), 4.5 mL of degassed TEA, and 0.07 mL of trimethylsilylacetylene were added. The mixture was heated to 70° overnight under a positive \( \text{N}_2 \) flow. The mixture was filtered through a bed of Celite® using hot methylene chloride. The filtrate was concentrated under vacuum to yield the crude product as a brown oil which was purified by silica gel column chromatography (\( \text{CHCl}_3/\text{hexane} \) 2/3 v/v). The pure product was obtained as a yellow solid (87\%).

\[ ^1\text{H-NMR: (CDCl}_3) \delta \text{ [ppm]}: 9.61 (d, J = 2.0, 2H, Ar-H), 9.58 (d, J = 2.4, 2H, Ar-H), 8.44 (s, 2H, Ar-H), 7.34 (s, 2H, Ar-H), 4.21 (t, J = 6.6, 4H, -CH\text{2}), 1.99 – 1.92 (m, 4H, -CH\text{2}), \]
1.76 (s, 18H, -CH₃), 1.61 – 1.54 (m, 4H, -CH₂), 1.50 – 1.26 (m, 48H, -CH₂), 0.87 (t, J = 6.8, 6H, -CH₃)

¹³C-NMR: (CDCl₃) δ [ppm]: 153.33, 150.59, 144.01, 141.38, 140.22, 139.93, 133.60, 129.69, 128.85, 125.98, 125.21, 124.13, 123.88, 106.82, 102.63, 100.84, 69.22, 35.86, 31.93, 31.84, 29.75, 29.74, 29.68, 29.46, 29.38, 28.95, 28.96, 26.12, 22.70, 14.13, 0.03 (5 alkyl peaks not seen due to overlapping signals)

[M+H]⁺: Calcd 1191.82, Found 1192.9

**Compound 6**

Compound C (0.122 g, 0.113 mmol) was dissolved in 56 mL of CH₂Cl₂. KOH (0.020 g, 0.356 mmol) in 5 mL methanol was added to the solution. The mixture was heated to 45° for 6 hrs, cooled to room temperature, and filtered through a bed of silica with hot chloroform. The solvent was removed under vacuum to yield the crude product as an orange/brown oil which was purified by silica gel column chromatography (CHCl₃). The pure product was obtained as a yellow solid (57%).

¹H-NMR: (CDCl₃) δ [ppm]: 9.66 (d, J = 2.0, 2H, Ar-H), 9.60 (d, J = 2.4, 2H, Ar-H), 8.51 (s, 2H, Ar-H), 7.50 (s, 2H, Ar-H), 4.29 (t, J = 6.6, 4H, -CH₂), 3.51 (s, 2H, acetylenic H), 2.03 – 1.96 (m, 4H, -CH₂), 1.75 (s, 18H, -CH₃), 1.63 – 1.96 (m, 4H, -CH₂), 1.49 – 1.26 (m, 48H, -CH₂), 0.87 (t, J = 6.8, 6H, -CH₃)

¹³C-NMR: (CDCl₃) δ [ppm]: 153.37, 150.62, 144.26, 141.34, 140.13, 139.96, 134.14, 129.68, 128.66, 125.23, 124.95, 124.30, 123.94, 106.82, 82.93, 81.38, 69.23, 35.87, 31.93, 31.86, 29.75, 29.74, 29.69, 29.48, 29.38, 28.96, 26.12, 22.70, 14.13 (5 alkyl peaks not seen due to overlapping signals)

[M+Na]⁺: Calcd 1069.74, Found: 1069.8
1.5. Results and Discussion

1.5.1. Synthesis

The key synthetic step established in this work was the cyclization of 2,7-di-tert-butylnaphthalene-4,5,9,10-tetraone with two different o-diaminoarenes to generate asymmetric bisphenazine. As shown in Figure 1.2, there are 3 available routes to obtain compounds 1 – 5. Route 1 shows the simple sequential addition of 1,2-diamino-4,5-dihexadecylbenzene and the appropriate o-diaminobenzene derivative to 2,7-di-tert-butylnaphthalene-4,5,9,10-tetraone without the purification of intermediates. Although this procedure involves the least number of steps, the yields are statistically low (~33%) due to the formation of two symmetric byproducts in addition to the desired asymmetric bisphenazine. Routes 2 and 3 show the alternative stepwise cyclization. In Route 2, the insolvability of intermediate A hampered its purification thus resulting in a low yield in the second cyclization. On the other hand, Route 3 produced the soluble intermediate B which could successfully be purified with silica gel column chromatography. As a result, route 3 was used for the synthesis of final compounds 1 – 4. Interestingly with compound 5, which has a shorter alkyl chain length, the yield was comparable when route 1 or 3 was used. Therefore, compound 5 was synthesized using route 1 (sequential addition) because there are fewer steps necessary to purify the final product.
Figure 1.2. Three possible synthetic routes to compounds 1 – 5.

Figure 1.3. Sonogashira coupling of 2 and deprotection to afford compound 6.
As shown in Figure 1.3, further chemistry involving the bisphenazine ring was successful. The Sonogashira coupling\(^{33}\) of \(2\) with trimethylsilylacetylene followed by deprotection of the trimethylsilyl groups with KOH gave the final product 6. Sonogashira coupling is a simple and efficient Pd-catalyzed reaction used to form C(sp\(^2\))-C(sp) bonds by replacing an aryl halide by an acetylene group. In addition to compound 2, the brominated version was also used for Sonogashira coupling. However, the coupling of the bromobisphenazine had a consistently lower yield under these Sonogashira conditions due to the lower reactivity of bromine than iodine.

1.5.2. UV-visible absorption spectroscopy

The UV-visible absorption spectra for the final compounds are shown in Figure 1.4. The spectra have been normalized at 422 nm for comparison. All of the final compounds showed absorption maxima near 418 and 422 nm arising from the bisphenazine core. The spectra of 2 and 6 have shoulders near 450 nm due to increased conjugation with the halogen and triple bond. The absorption maxima of compounds 4 and 5 are slightly blue-shifted to 396 (\(\Delta\lambda = 22\) nm) and 418 nm (\(\Delta\lambda = 4\) nm) in comparison to the other compounds, however the shoulder is broadened and red-shifted to 468 nm (\(\Delta\lambda = 18\) nm). The greater shift of the shoulder in 4 and 5 is due to more extensive conjugation with the NO\(_2\) groups. The absorption spectra of compounds 4 and 5 are nearly identical. This was expected because changing the alkyl chain length of the side groups does not affect the molecules chromophore.
Figure 1.4. Normalized UV-visible spectra for final compounds 1 – 6.

The absorption edge is gradually shifted to longer wavelengths as the substituent is changed from H (1) to F (3) to I (2) to acetylene (6) to NO₂ (4 and 5). As a result, the HOMO-LUMO energy gap calculated from the tangent of the absorption edge decreases in the same order (Table 1.1). The UV-visible absorption results show that the electronic properties of bisphenazine can be modulated with the type of peripheral substituent introduced.
1.5.3. Fluorescence spectroscopy

The fluorescence emission spectra for compounds 1 – 6 are shown in Figure 1.5. The fluorescence spectra have been normalized at the emission maxima for comparison. The reduction of the optical energy gap seen in the UV-visible spectra also manifests itself in fluorescence. As the HOMO-LUMO gap becomes smaller, the fluorescence wavelength becomes longer which is clearly seen in these molecules.
1.5.4. Differential scanning calorimetry (DSC)

The thermal properties of the final products were investigated by DSC. Three heating and cooling scans were performed to test the reproducibility of the thermal behaviors. Compounds 1 – 3 (Figure 1.6 (A), (B), and (C)) had similar patterns showing one endothermic (melting) and one exothermic (crystallization) peak. Both transitions were reproducible through three heating / cooling scans.

![DSC thermograms](image)

**Figure 1.6.** DSC thermograms for (A) 1, (B) 2, (C) 3, (D) 4, (E) 5, and (F) 6. All thermograms show the 2nd heating and cooling curves.

It is interesting to note that there is a gradual increase in the melting temperature from 83.13 °C to 105.43 °C to 121.94 °C from 1 to 3. These results indicate that the intermolecular interactions become stronger in the series 1 < 2 < 3.

Compound 4 exhibited one exotherm at 114.98 °C and one endotherm at 140.47 °C with an additional small exotherm and endotherm at 157.49 °C and 168.86 °C that may
indicate a liquid crystalline (LC) state. The thermogram of compound 5 exhibits an exotherm at 117.51 °C and an endotherm at 144.22 °C similar to compound 4 with the absence of the exotherm / endotherm at higher temperatures. However, there was an additional exotherm at 65.52 °C. The heat of melting was equal to the sum of the heats of crystallization for the two exotherms. One possible explanation is that two different crystallites are being formed upon cooling and both melt at the same temperature. The higher melting points of compounds 4 and 5 at 140.47 °C and 144.22 °C, respectively, could be attributed to the additional intermolecular interaction present between the NO₂ groups.

The DSC scan of compound 6 showed one exotherm at 90.12 °C and the corresponding endotherm at 102.37 °C in a similar manner to compounds 1 – 3. In addition, there was a second higher temperature endotherm at 124.84 °C. All of the transitions were reproducible over three heating / cooling curves. The second endotherm indicates the possible presence of an LC state. The presence of a side group, such as acetylene or NO₂, which can participate in an additional intermolecular interaction may lead to the molecules arranging in such a way as to create a larger mesogen which could introduce an LC state.

1.5.5. Cyclic voltammetry (CV)

The electrochemical properties of 1 – 6 were studied with cyclic voltammetry (Figure 1.7). Generally, for a system to be considered reversible, the peak splitting should be Nernstian which is defined by the equation: \( \Delta E_p = E_{pc} - E_{pa} = 59 \text{ mV/n} \), where \( n \) is the number of electrons transferred in the process. In the case of a quasi-reversible system, the peak splitting will be larger with values of \( \Delta E_p \geq 90 \text{ mV/n} \). All of the compounds
studied show quasi-reversible first reduction waves with peak splitting of 125 mV (1), 102 mV (3), 79 mV (4), 86 mV (5), and 140 mV (6).

Figure 1.7. Cyclic voltammograms for the reduction of (A) 1, (B) 3, (C) 4, (D) 5, and (E) 6. Scan rate: 100 mV/s.

The peak splitting in compound 2 could not be calculated because the peak potentials are not clearly resolved. Although the reductions of 4 and 5 appear to be quasi-reversible processes, compound 5 exhibits a more reversible reduction in that the cathodic and anodic peak currents are similar. A second reduction wave was observed in the voltammograms of both 4 and 5. The presence of electron-withdrawing NO₂ groups increases the electron affinity of the molecules allowing the second wave to be easily seen. Compounds 1 – 3 may also have second reduction waves, nevertheless they are not clearly observed due to overlap with the solvent background.
The onset of the reduction potential can be directly related to the electron affinity, or LUMO energy, of the molecule. Thus the onset of the first reduction wave is used to approximate the LUMO level\textsuperscript{36} (Table 1.1). The LUMO level was consistently lowered as the electron-withdrawing ability of the peripheral substituent increased from $1 < 3 < 6 < 4 = 5$. One of the objectives of this work, to further increase the electron-affinity of the whole system with a peripheral substituent, was successfully accomplished. To be a useful electron transporting material in OLED and organic photovoltaic (OPV) devices, the electron-affinity of the molecule should be in the range of 2.7 - 3.4 eV and 3.8 - 4.5 eV, respectively\textsuperscript{37}. The CV results imply that compounds 1, 3, and 6 could potentially be applicable for OLEDs, while 4 and 5 could be used in donor/acceptor type OPVs. The onset of the first oxidation wave can similarly be used to approximate the HOMO level of the molecule; however oxidation potentials were not resolved with these compounds due to irreproducibility and overlap with the solvent background. Thus HOMO levels could not be directly estimated from CV. Instead, the HOMO values were calculated using the LUMO energies from CV and the optical energy gap ($E_{\text{gap}}$) values obtained from UV-visible spectroscopy (Table 1.1). Theoretical calculations were performed to further corroborate the experimental HOMO and LUMO energies and energy band gap results obtained from cyclic voltammetry and UV-visible spectroscopy. Optimum geometries were calculated with the density functional theory (DFT) at the B3LYP/6-31G* level and HOMO and LUMO energies and energy gaps were predicted by single point B3LYP/6-31+G*/B3LYP/6-31G*. These values are summarized and compared with experimental values in Table 1.1. Although discrepancies between the experimental and theoretical energy levels were observed, it is important to note that the theoretical calculations
predicted that the LUMO levels would be lowered in the order of \(1 < 3 < 6 < 4 = 5\) which corresponded to the order seen experimentally. In addition, the lowering of the energy gap predicted from theoretical calculations was in the order of \(1 < 3 < 6 < 4 = 5\). This order was observed from UV-Vis experiments \((1 = 3 < 6 < 4 = 5)\) with the exception of 3.

### Table 1.1. Experimental and theoretical electronic properties of final compounds 1 – 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{\text{red}}^\text{peak}) (V)</th>
<th>(E_{\text{red}}^\text{onset}) (V)</th>
<th>(E_{\text{LUMO}}^c) (eV)</th>
<th>(E_{\text{HOMO}}^b) (eV)</th>
<th>(E_{\text{gap}}^c) (eV)</th>
<th>(E_{\text{LUMO}}^d) (eV)</th>
<th>(E_{\text{HOMO}}^d) (eV)</th>
<th>(E_{\text{gap}}^d) (eV)</th>
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</tr>
<tr>
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<td>-1.03</td>
<td>-3.77</td>
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<td>-6.10</td>
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</tr>
<tr>
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<td>-1.03</td>
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<td>2.34</td>
<td>-3.39</td>
<td>-6.10</td>
<td>2.71</td>
</tr>
<tr>
<td>6</td>
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<td>-3.27</td>
<td>-5.85</td>
<td>2.58</td>
<td>-2.66</td>
<td>-5.75</td>
<td>3.09</td>
</tr>
</tbody>
</table>

\[ a \ E_{\text{LUMO}} = (E_{\text{red}}^\text{onset} + 4.8 \text{ eV}), \ b \ E_{\text{HOMO}} = E_{\text{gap}} - E_{\text{LUMO}}, \ c \ \text{optical HOMO-LUMO gap}, \ d \ \text{Theoretical calculation}. \]

#### 1.6. Conclusions

The detailed synthetic route to asymmetrically substituted bisphenazine molecules 1 – 6 was successfully established. The sequential addition and stepwise cyclization to produce asymmetric bisphenazine was completed for the first time. In addition, the reaction of the bisphenazine ring under Sonogashira coupling conditions was conducted producing compound 6 from 2 in high yield. \(^1\)H and \(^13\)C NMR and mass spectral analyses confirmed that the correct molecules were obtained. The thermal behavior of the final compounds, investigated using DSC, showed that by changing the peripheral substituent the melting and crystallization behaviors of the molecule were altered due to differences
in the degree of intermolecular interactions caused by the substituents. It was shown from UV-visible and fluorescence spectroscopy that as the conjugation with the substituent is increased, the absorption edge is pushed to longer wavelengths, which results in a decrease in the energy gap. This decrease in the energy gap is further manifested in the fluorescence emission which is shifted to longer wavelengths. Cyclic voltammetry and theoretical calculations further corroborated that by changing the peripheral substituent the electronic properties of the molecule, the electron affinity and HOMO-LUMO energy gap, could be modulated.

1.7. References


CHAPTER 2

ORGANOGELS

2.1 Introduction

Organogels, a rapidly growing research topic, are the result of solvent being trapped in a 3-D network of 1-D nanofibers of low molecular weight organogelator (LMOG) molecules. LMOGs can assemble through a variety of interactions including hydrogen bonding, π-π interactions, solvophobic effects, metal-ligand interactions, etc. In most instances, there is a collaborative interplay of more than one type of intermolecular interaction involved in the assembly of the LMOG molecules. Such multiple interactions are necessary because the nanofibers formed must be strong enough to hold a significant volume of solvent thus forming the organogel.

A number of LMOG molecules have been reported with the ability to form organogels through a variety of interactions\textsuperscript{1,2}. Among the reported gelators, π-conjugated LMOGs are of particular interest because of their unique electro-optical properties. Most of the reported π-conjugated LMOGs form 1-D nanofibers in the gel state in which chromophores are linked by cofacial intermolecular π-electron overlap. These systems have already demonstrated their utility in electro-optical applications such as energy transfer\textsuperscript{3-5} and photoluminescence switching\textsuperscript{6}. 

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Although π-conjugated LMOGs present a number of benefits, there are only a handful of examples present in the literature including acene, oligo(p-phenylenevinylene) (OPV), oligo(p-phenyleneethynylene) (OPE), phthalocyanine, phenazine, and perylenebisimide derivatives. Moreover, there have been no examples of organogelators based on bisphenazine.

The design principle of the asymmetric bisphenazines presented in this chapter aims to induce 1-D assembly, with the molecules potentially also acting as organogelators. Indeed, compound 6 was found to gel select organic solvents by forming 1-D nanofibers. Thus, this chapter will be dedicated to the extensive investigation of the gelation of compound 6 in a variety of solvents. The gelling temperature (T_gel) and critical gelling concentration (CGC) were determined and the gel structure was examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-Transform infrared (FT-IR) spectroscopy. In addition, the colorimetric response of the dried gel to the vapor of acid will be discussed in detail with UV-visible and FT-IR spectroscopy.

2.2. Experimental

2.2.1. Organogel formation

A measured amount of compound and solvent was added to a 4 mL screw-cap vial and heated in a hot oil bath at the boiling point of the solvent until a homogeneous solution was obtained. The vial was then left undisturbed to cool to room temperature and if no flow was observed upon inverting the vial then the mixture was considered gelled.
2.2.2. $T_{gel}$

The gelation temperature ($T_{gel}$) of gels of 6 formed in decane (1.3 mM), hexadecane (1.0 mM), and 1,1,1-trichloroethane (TCE) (10 mM) were determined using the 'inverse flow'\textsuperscript{12} method. Gels were formed as previously described and placed upside down in a temperature regulated H$_2$O bath (decane and TCE) or a silicon oil bath (hexadecane). The $T_{gel}$ of the hexadecane gel was well above the temperature range of the H$_2$O bath thus a silicon oil bath was used. The temperature at which the gel fell from the bottom of the vial was taken as $T_{gel}$ for that sample.

2.2.3. Scanning electron microscopy (SEM)

Samples were prepared by dropping a solution of 6 in decane (1.3 mM) or TCE (10 mM) onto a silicon wafer and allowing the solvent to evaporate under ambient conditions. SEM imaging of the xerogels was performed at the University of North Carolina Chapel Hill on a Hitachik S-4700 scanning electron microscope with an accelerating voltage of 2 kV. The samples were sputter-coated with a 2.3 nm layer of gold before imaging to prevent charging.

2.2.4. UV-visible spectroscopy

The UV-visible absorption solution spectrum was obtained from a $5 \times 10^{-6}$ M solution of 6 in CHCl$_3$. The organogel spectrum was obtained with the gel of 6 from decane. The gel was prepared as described above and sandwiched between two glass cover slips for analysis. The UV-visible spectra were collected on a Shimadzu UV-2450 UV-visible spectrophotometer.
2.2.5. X-ray diffraction (XRD)

The organogel of 6 from decane was placed on a glass slide and the solvent was allowed to evaporate under ambient conditions. The xerogel was carefully scraped off of the slide with a new razor blade and broken into small pieces with a spatula. The sample was then placed on a zero background plate for analysis. X-ray diffractograms were obtained on an X’Pert PRO PANalytical diffractometer at 25 °C using Cu-Kα radiation (λ = 1.54 Å, 40 kV, 40 mA).

2.2.6. ¹H-NMR concentration study

Solutions of 6 in CDCl₃ were prepared at concentrations of 1, 2, 5, 10, and 15 mM. The solutions were analyzed at 25 °C on a Varian Gemini 400 MHz spectrometer with trimethylsilane (TMS) as an internal standard.

2.2.7. Fourier-Transform infrared (FT-IR) spectroscopy

Solution IR was obtained from a 0.32 mM solution of 6 in CCl₄. A KBr cell with a 1 mm Teflon spacer was utilized to obtain solution IR data. The spectrum of the organogel was obtained by sandwiching a 1.3 mM decane gel of 6 between two NaCl plates. FT-IR spectra were recorded at 25 °C with a spectral resolution of 2 cm⁻¹ on a Shimadzu IRPrestige-21 FTIR spectrometer.

2.2.8. UV-visible spectroscopy on the acid responsiveness of the xerogel of 6

Solution spectra were obtained from a 5 x 10⁻⁶ M solution of 6 in CHCl₃. Increasing amounts of trifluoroacetic acid (TFA) were added to the solution until the spectral change was saturated. Spectra were obtained 30 minutes after the addition of TFA. The absorbance of the exposed xerogel from TCE exceeded the instrument limits thus the xerogel film from decane was used because it has a lower gel concentration. The xerogel
was obtained by placing the decane gel of 6 on a glass slide and evaporating the solvent under ambient conditions. The xerogel was placed in a Petri dish with one drop of TFA for 3 seconds and the exposed film was immediately analyzed. The film was left under ambient conditions to allow the TFA to evaporate until the original spectrum (before exposure) was obtained. All of the spectra were collected on a Shimadzu UV-2450 UV-visible spectrophotometer.

2.2.9. Colorimetric response upon exposure to acid

The xerogel films were prepared by placing the gel of 6 from TCE on a glass slide and drying under ambient conditions. As a control, a cast film was prepared by dropping a homogeneous solution of 6 in TCE onto a hot glass slide and rapidly evaporating the solvent. The sample was placed in a Petri dish with one drop of TFA, hydrochloric acid (HCl), or sulfuric acid (H₂SO₄) and quickly covered. Color changes were verified by visual inspection.

2.2.10. FT-IR study on the acid responsiveness of the xerogel of 6

The xerogel film was prepared by placing the gel of 6 from TCE on a NaCl plate and evaporating the solvent under ambient conditions. The FT-IR spectrum of the unexposed xerogel was taken as a control. The xerogel was placed in a Petri dish with one drop of TFA for 3 minutes. The exposed xerogel was immediately analyzed. The xerogel was left under ambient conditions to allow the TFA to evaporate. The FT-IR spectrum of the evaporated film was taken after 24 hours and 3 days. All FT-IR spectra were recorded at 25 °C with a spectral resolution of 2 cm⁻¹ on a Shimadzu IRPrestige-21 FTIR spectrometer.
2.3. Results and Discussion

2.3.1. Gelation

A compound is considered gelled if, upon cooling a warm homogeneous solution, no flow is observed when the vial is inverted. The process of gelation is dependent on 1) the interaction between LMOG molecules and 2) the local interaction of the LMOG with the solvent. The LMOG should not be completely soluble nor insoluble to form a gel in a particular solvent. The presence of a solubilizing moiety on the LMOG is necessary so that there is some extent of solvent – LMOG interaction.

![Figure 2.1. Compound 6 in (a) CHCl₃ solution and (b) a decane gel (1.3 mM).](image)

The key to forming an organogel is to find an appropriate solvent that 1) the LMOG has fair solubility in at room temperature but under gentle heating will be soluble and 2) will not interact with the LMOG strongly enough to disrupt the assembly. The gelling ability of compounds 1, 2, and 6 were examined in a variety of solvents of varying polarity.
(Table 2.1). All of the compounds showed good solubility in chloroform, carbon tetrachloride, and methylene chloride, and thus an organogel was not formed in these solvents. The compounds formed precipitates in toluene upon cooling due to their poor solubility in the solvent. The long chain hydrocarbon solvents, decane and hexadecane, were chosen due to the high structural similarity with the long hexadecoxy side chains of the bisphenazine compounds. It would be reasonable to expect that all of the final compounds would gel in the long hydrocarbon chain solvents due to the presence of long alkoxy side groups. However, as seen in Table 2.1, only compound 6 formed a gel in decane (Figure 2.1 b) and hexadecane due to the presence of an additional intermolecular interaction between the LMOGs. This phenomenon will be explained in greater detail in a later section with FT-IR results. The high solubility of 6 in chlorinated solvents and its gelling ability in long alkyl chain solvents led to the discovery of gelation in TCE.

Table 2.1. Gelling abilities of 1, 2, and 6 at room temperature.

<table>
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<th>6a</th>
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<td>NS</td>
<td>NS</td>
</tr>
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<td>Decane</td>
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<td>PG</td>
<td>1.3b, TR</td>
</tr>
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<td>1.0b, TR</td>
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<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DCE</td>
<td>PPT</td>
<td>NS</td>
<td>PPT</td>
</tr>
<tr>
<td>TCE</td>
<td>PG</td>
<td>S</td>
<td>10.0b, OP</td>
</tr>
<tr>
<td>TCTFE</td>
<td>NS</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>THF</td>
<td>PPT</td>
<td>PPT</td>
<td>S</td>
</tr>
</tbody>
</table>

a OP – opaque gel  TR – transparent gel  PG – partial gel  PPT – precipitate  NS – not soluble  S – solution at room temperature  
b CGC in millimolar (mM)
TCE was chosen as a solvent because it was thought that the introduction of alkyl character to a polar chlorinated solvent would 1) decrease the solubility of the compound and 2) the addition of an alkyl moiety would lead to increased interaction with the long hexadecoxy side groups thus allowing for gel formation.

2.3.2. Gelation temperature (T\text{gel}) and critical gelling concentration (CGC)

The gelation temperature, or T\text{gel}, of the organogel of 6 formed from decane, hexadecane, and TCE were obtained using the 'inverse flow' method (Table 2.2). T\text{gel} can be directly related to the stability of the organogel. The T\text{gel} increased significantly from 44 °C (TCE) to 77 °C (decane) to 116 °C (hexadecane). These results indicate that the hexadecane gel is the most robust which was further substantiated by the gels high stability under ambient conditions to > 1 month. The stability of the hexadecane gel can be attributed to the low volatility of the solvent and the low solubility of 6 in hexadecane which prevents it from going into solution. At the same time, the long hexadecoxy side groups can have local interactions with hexadecane due to their structural similarity. As expected, the decane gel was also stable to >1 month. A reasonable estimate of the stability of the TCE gel was not obtained due to the high volatility of the solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CGC</th>
<th>T\text{gel}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>10.0 mM</td>
<td>44 °C</td>
</tr>
<tr>
<td>Decane</td>
<td>1.3 mM</td>
<td>77 °C</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>1.0 mM</td>
<td>116 °C</td>
</tr>
</tbody>
</table>

The critical gelling concentration (CGC) is the minimum amount of an LMOG necessary to gel a particular solvent. As shown in Table 2.2, the CGC increased from 1.0
mM (hexadecane) to 1.3 mM (decane) to 10.0 mM (TCE). The CGC is inversely related to the strength of the gel. The higher CGC in TCE implies that compound 6 has a higher solubility in TCE than in decane or hexadecane. These results, in addition to the $T_{gel}$ values, confirm that the hexadecane gel of 6 is the most robust.

2.3.3. Scanning electron microscopy (SEM)

Figure 2.2. SEM images of xerogel of 6 from decane gel. Scale bars: a) 4.00 µm b) 1.00 µm c) 1.00 µm d) 200 nm e) 300 nm.
SEM images of the xerogel (dried gel) of 6 showed similar morphologies when prepared from decane (Figure 2.2) or TCE (Figure 2.3). SEM images of the gel from hexadecane were not obtained due to the low volatility of the solvent which made the xerogel difficult to acquire under ambient conditions. In the case of decane (Figure 2.2), the fibers are flat and have a fairly homogeneous size distribution. The large width fibers are actually composed of bundles of smaller fibers (Figure 2.2 e) and are also flat and interwoven throughout the sample. The small bundles vary slightly in width from ca. 50 nm.

The TCE gel is composed of fibers of a similar shape in addition to the presence of large globules of dense fibers. The fibers formed from the TCE gel are smaller in width of ca. 15 nm (Figure 2.3). It is reasonable to assess that the higher gel concentration in TCE leads to increased aggregation as the solvent evaporates and that the rapid evaporation of the solvent prevents lateral growth of the fibers thus leading to smaller widths than the fibers from the decane gel.
Figure 2.3. SEM images of xerogel of 6 from TCE gel. Scale bars: a) 10.00 μm b) 2.00 μm c) 1.00 μm d) 500 nm e) 500 nm.
2.3.4. UV-visible absorption spectroscopy

![Normalized UV-visible spectra of 6 in CHCl₃ solution (solid line) and in the decane gel (dashed line).](image)

The UV-visible spectra of 6 in CHCl₃ solution and in the gel state were compared to assess the intermolecular interactions involved in the assembly. The spectra are normalized at 422 nm for comparison. The spectrum of compound 6 in CHCl₃ solution has absorption maxima at 402 nm and 422 nm arising from the bisphenazine core. The decane gel shows a red-shift in these absorption maxima to 410 nm and 433 nm. In addition, a more resolved peak at 462 nm appears which was seen as a shoulder in the CHCl₃ solution at 447 nm. These features suggest the formation of a $J$-aggregate in the gel (assembled) state$^{13}$. 
2.3.5. X-ray diffraction (XRD)

XRD analysis of the xerogel of 6 was used to examine the existence of π-π stacking in the fibers. The XRD pattern of the xerogel of 6 is shown in Figure 2.5. The peak of interest is at 23.8° (2θ) corresponding to a d-spacing of 3.73 Å which is similar to the typical π-π stacking distance of 3.5 Å. This verifies, together with the UV-Vis results, that the major driving force for assembly of 6 in the organogel is through π-π interactions.
2.3.6. $^1$H-NMR concentration study

A concentration study was conducted with compound 6 to see if increasing the number of molecules in solution would lead to a change in the chemical shifts of the aromatic protons which would be indicative of interactions between the $\pi$-cores. The concentration of compound 6 in CDCl$_3$ was increased from 1 mM to 15 mM. As the concentration of 6 increases the molecules will be forced closer together and interactions between the aromatic rings will occur. As shown in Figure 2.6, all of the aromatic peaks were shifted upfield as the concentration of 6 was increased. The changes in the chemical shift ($\Delta\delta$) as the concentration was increased from 1 mM to 15 mM are 0.23 ppm, 0.18 ppm, 0.18 ppm, and 0.19 ppm for protons a – d, respectively. The upfield shift in the aromatic resonances can be attributed to the close proximity of the bisphenazine cores.
resulting in shielding from the ring current of the neighboring bisphenazine π-systems\textsuperscript{15}. Although nanofibers are not actually formed from these samples, it does corroborate with the findings from XRD and UV-visible spectroscopy that these molecules interact through π-π interactions.

2.3.7. FT-IR of the xerogel and CHCl\textsubscript{3} solution of 6

The most crucial evidence for only compound 6 forming an organogel was obtained from FT-IR spectroscopy. The FT-IR spectrum of a CCl\textsubscript{4} solution (0.32 mM) of 6 was compared to that of the xerogel to study the interactions between molecules upon assembly. In solution, one characteristic ‘free’ acetylene C-H stretching peak is seen at 3311 cm\textsuperscript{-1} (Figure 2.7 (A)) while two C-H stretching peaks are observed in the xerogel, one with a stronger intensity at 3247 cm\textsuperscript{-1} and the other at 3318 cm\textsuperscript{-1} (Figure 2.7 (B)).

![FT-IR spectra of 6 in (A) CCl\textsubscript{4} solution and (B) the xerogel.](image)

Figure 2.7. FT-IR spectra of 6 in (A) CCl\textsubscript{4} solution and (B) the xerogel.
The extensive low frequency shift to 3247 cm\(^{-1}\) is indicative of the acetylenic proton hydrogen-bonding to an electronegative atom\(^{16}\). From these results, we can infer that there is significant hydrogen bonding between the acetylenic proton and the imine nitrogen of a neighboring molecule. The presence of two C-H stretching peaks in the xerogel indicates that not all of the acetylenic protons are involved in hydrogen bonding. Hence, the second C-H stretching peak in the xerogel (3318 cm\(^{-1}\)) is assigned to the C-H stretching of the free acetylenic proton. It is logical to believe that the proton not involved in H-bonding will experience an electron-withdrawing substituent effect\(^{17}\) due to the o-disubstitution of the ring thus shifting it to a slightly higher wavenumber. These results demonstrate that all three intermolecular interactions, π-π, hydrogen bonding, and van der Waals, are necessary to induce gelation and only compound 6 possesses all of these necessary components.

2.3.8. Acid sensing ability of 6

The presence of hydrogen bonding in the gel of 6 was further evidenced by the disruption of the gel upon the addition of an organic acid which can protonate the imine nitrogen, thus hindering hydrogen bonding with the terminal acetylene. One drop of TFA was added to the organogel of 6 in TCE. As a result, the organogel of 6 showed a dramatic color change from yellow to red (Figure 2.8 (b)). Over 4 hours the acid penetrated the remainder of the gel thus further disrupting the gel matrix and forming a red mixture of solution and broken gel. This result implied that the nanofibers of 6 could be a potential colorimetric acid sensor. Therefore, the acid responsiveness of compound 6 was investigated. When TFA was added to a chloroform solution of 6, the UV-visible absorptions at 422 nm and 402 nm decreased while new absorbances at 493 nm and 435
nm increased with increasing amounts of TFA (Figure 2.9 (A)). Although there is a change in absorbance of the solution with TFA, a substantial excess was necessary to saturate the change.

![Figure 2.8. TCE gel before (a) the addition of 1 drop of TFA (i), immediately after the addition of TFA (b), and after >4 hours (c).](image)

Note that no further spectral change was observed even after overnight standing indicating that the process is thermodynamic rather than kinetic. On the other hand, the xerogel of 6 showed a drastic change in absorbance upon exposure to TFA vapors for 3 seconds (Figure 2.9 (B)). This response is fully reversible as seen by the return of the original spectrum after 1 hour standing after exposure. This enhanced response can be attributed to the built-in voids of the fibrous network of the xerogel which provide a massive surface area for the TFA to react. In addition to TFA (Figure 2.10 (b)), the xerogel film was exposed to the vapors of HCl and H\textsubscript{2}SO\textsubscript{4}. There was an immediate color change observed in the film, again from yellow to red, upon exposure to HCl vapors. No instantaneous color change was detected upon exposure to H\textsubscript{2}SO\textsubscript{4}. This can be attributed to the low volatility of the acid (boiling point = 290 °C) which would make it difficult to obtain a saturated atmosphere of acid vapors thus no recognition occurs.

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Figure 2.9. Acid responsiveness of compound 6. A) UV-Vis in CHCl₃ with increasing amount of TFA (0 (red curve), 3, 4, 6, 8, 10, 15, 20, 40, 60 μL). B) UV-Vis of xerogel (a) after 3 sec exposure to the vapor of TFA, (b) 30 min standing after the exposure, (c) 1 hr standing after the exposure (The spectrum is identical to that before exposure to TFA vapor).

Figure 2.10. Cast film (a) and xerogel (b) of 6 from TCE before and after (i) exposure to TFA.
As a control experiment, the cast film (Figure 2.10 (a)) of 6 was prepared by dropping a TCE solution of 6 onto a hot glass substrate to prevent fiber formation. The cast film exhibited a minimal change in color upon exposure to the vapor of TFA. This can be explained by the amorphous nature of the film which only allows interaction with TFA at the surface. These results show the utility of the xerogel film as an acid sensor while other forms of the compound are ineffective.

Figure 2.11. FT-IR spectra of the xerogel of 6 (A) before exposure, (B) after 1 minute exposure to TFA vapors, (C) after 24 hours and (D) 3 days standing after exposure.
FT-IR spectroscopy was used to investigate the mechanism of the color change in the xerogel film upon exposure to TFA. Upon exposure to the vapor of TFA for one minute, two important changes in the spectrum were seen; (1) a new peak at 1655 cm\(^{-1}\) was observed which is thought to be due to the protonation of the imine nitrogen\(^{18-19}\) and (2) the acetylenic C-H stretching at 3247 cm\(^{-1}\) was nearly disappeared. Upon protonation, the alteration of conjugation through resonance can be expected which will cause a change in color. Resonance occurs to delocalize the positive charge on the nitrogen which extends to the acetylene side group resulting in less acetylenic character. The loss of hydrogen bonding and reduction of acetylenic character was supported by the decrease in the acetylenic C-H peak, especially the peak at 3247 cm\(^{-1}\) corresponding to the hydrogen bonded acetylenic C-H. (Figure 2.11 (B) box a). The broad peak at 1778 cm\(^{-1}\) (Figure 2.11 (B) box b) can be attributed to the carboxylate stretching of the deprotonated TFA. It is interesting to note that protonation was reversible which was indicated by the return of the original imine character after 1 day standing at ambient conditions (Figure 2.11 (C) box b). This indicates that the imine and acetylene remained in close proximity upon protonation such that the original hydrogen bonding could be restored after the evaporation of the acid. It is worthwhile to comment that the loss of the acetylenic stretching peaks corroborates with the collapse of the organogel upon the addition of TFA (Figure 2.8 (c)), which further supports that the hydrogen bonding between the imine nitrogen and acetylene moieties is necessary for organogel formation.
2.4. Conclusions

In this chapter, the gelling ability of compounds 1, 2, and 6 were studied in a variety of solvents. It was found that only compound 6 formed an organogel in decane, hexadecane, and TCE. The high \( T_{gel} \) and low CGC of the gel obtained from hexadecane indicated that it was the most robust which was further confirmed by the gels stability to \( >1 \) month. SEM images of the xerogels from TCE and decane confirmed that the formation of 1-D nanofibers indeed drove the organogel formation. The existence of \( \pi-\pi \) interactions was confirmed by (1) the formation of a J-aggregate, (2) a diffraction peak corresponding to a \( d \)-spacing of 3.73 Å which is typical of \( \pi-\pi \) stacking, and (3) an upfield shift in the aromatic \( ^1H \)-NMR resonances with increasing concentrations of 6. FT-IR spectra verified that hydrogen bonding between the acetylenic proton and imine nitrogen is an additional important intermolecular interaction which enabled the gelation of 6. The interesting colorimetric response of 6 with the addition of an organic acid was attributed to the protonation of the imine nitrogens in the bisphenazine ring. Rapid saturation of the spectral change in the UV-visible absorption spectra indicated that the xerogel was more effective at sensing protons than other forms of the compound.

2.5. References


CHAPTER 3

1-D ASSEMBLY

3.1. Introduction

The 1-D SA of \( \pi \)-conjugated organic semiconductors into nanofibers\(^{1-4} \), nanobelts\(^{5-8} \), and nanotubes\(^{9-11} \) with high aspect ratios has been one of the recent exciting research focuses due to their potential application in nanoscale optoelectronic devices\(^{12} \). As mentioned in the introduction of chapter 1, there are a number of approaches to design \( \pi \)-conjugated molecules to create 1-D nanostructures under the appropriate assembly conditions; including the utilization of a symmetric or asymmetric \( \pi \)-core with identical or nonidentical side groups.

The design strategy of the asymmetric bisphenazines in this work was to incorporate the ability to generate 1-D nanostructures through intermolecular \( \pi-\pi \) interaction as the major driving force with other supporting weak intermolecular interactions such as van der Waals. It should be noted that we aim to achieve not only 1-D nanostructures of the new \( n \)-type semiconductors but also the ability to tune the electronic properties of the heteroaromatic moiety without compromising the assembling ability. In the first chapter, we already demonstrated that the small peripheral substituents were effective at modifying the electronic property of the whole system. However, those substituents are expected to influence the morphology of the 1-D nanostructures even with their trivial size. Therefore, in this chapter the 1-D assembly of compounds 1 – 6 will be investigated.
in detail and their structure-morphology relationship will be discussed in conjunction with SEM and XRD.

One important issue to induce 1-D SA is that the assembly methodology must be chosen wisely even with properly designed molecules. Typical methods for SA include injection\(^5\), phase transfer\(^6,13-14\), solvent vapor annealing\(^13\), and recrystallization\(^12\). The most appropriate method is highly dependent on the molecular structure. Moreover, even after determining the proper method, the conditions for assembly still need to be optimized. For example, when a binary solvent system is used, as in the cases of injection and phase transfer, many assembly parameters should be optimized to control the morphology of the resultant 1-D structures. These include solvent polarity, concentration, the ratio of good to poor solvent, the duration of assembly, etc. It was found that the phase transfer method was particularly effective for the 1-D assembly of the asymmetric bisphenazines presented in this work. Thus, a detailed discussion on phase transfer compared with recrystallization will be provided in this chapter.

3.2. Experimental

3.2.1. Phase transfer (PT) assembly

All solvents were filtered through a 0.2 μm PTFE filter before each PT experiment. A homogeneous solution of the compound was prepared in a ‘good’ solvent (CH\(_2\)Cl\(_2\)) and was filtered through a PTFE filter into a clean 20 mL screw-cap vial. The ‘poor’ solvent (hexane or methanol) was slowly added to the CH\(_2\)Cl\(_2\) solution so that two phases could be maintained. The biphasic mixture was then left undisturbed overnight to induce 1-D assembly.
3.2.2. Recrystallization

A concentrated homogeneous solution of the compound was prepared using the least volume of solvent necessary under gentle heating. The solution was then left undisturbed overnight to induce crystallization.

3.2.3. Scanning electron microscopy (SEM)

Assembled samples were prepared as described above. The assembled product was drop cast onto gold mica and the solvent was evaporated under ambient conditions. SEM images of the 1-D assembled samples were obtained on a Jeol JSM-5600 scanning electron microscope. Before imaging, all samples were sputter-coated (50 mA, 60 sec.) with a thin layer of gold to prevent charging. Accelerating voltages and working distances are specified with each image.

3.2.4. X-ray diffraction (XRD)

Assembled samples were prepared as described above. The assembled product was drop cast onto a zero background plate and the solvent was evaporated under ambient conditions. X-ray diffraction analyses were carried out on an X'Pert PRO PANalytical diffractometer at 25 °C using Cu-Kα radiation (λ = 1.54 Å, 40 kV, 40 mA).

3.3. Results and Discussion

3.3.1. 1-D Self-assembly

The 1-D SA of compounds 1 – 5 were studied using recrystallization from CH₂Cl₂ and a phase transfer method using two different binary solvent systems; CH₂Cl₂/ hexane and CH₂Cl₂/ methanol. The 1-D assembly of compound 6 was not examined by these methods because it was already shown in chapter 2 that the molecule forms 1-D
nanostructures very effectively through organogelation. In the case of the recrystallization method, only the nitrobisphenazine compounds (4 and 5) formed nanoclusters which were examined by SEM and XRD. On the other hand, in the recrystallization of compound 1, a partial gel with some precipitation was formed. The recrystallization of 2 and 3 exhibited similar behaviors as 1.

3.3.2. Scanning electron microscopy (SEM)

SEM was used to examine the morphology of the 1-D assembled nanoclusters formed through the PT and recrystallization methods. The morphology of the nanoclusters and their size distribution was compared based on the peripheral substituent (X), the alkyl chain length (C_{12} or C_{16}) and assembly method, and on the solvents used to induce the assemblies.

The effect of the peripheral substituents on the morphology of the 1-D nanoclusters formed through PT

The peripheral substituent effect on the self-assembly of asymmetric bisphenazines 1 – 4 was examined by comparing the morphologies of the nanoclusters obtained. Assembly was studied in two solvent systems, CH_{2}Cl_{2}/ hexane and CH_{2}Cl_{2}/ methanol. Compounds 1 – 3 did not show any assembly in the CH_{2}Cl_{2}/ hexane system which may be attributed to the slight solubility of the compounds in the binary solvent system. However, compound 4 was assembled using both solvent systems and the morphologies of the 1-D nanoclusters were slightly different, which will be discussed in a later section. Compound 1 formed endless, flexible, and flat nanofibers. Fiber bundles varied in size from ca. 300 nm to ca. 2 μm.
On the other hand, iodobisphenazine (2) formed very short inhomogeneous nanofibers. This behavior was expected due to the large size of the iodine substituents which likely
hinders the effective π-π stacking of the molecules. Compound 3 formed fairly homogeneous belt like nanofibers of approximately 600 nm in width. The nanobelts formed are much straighter and shorter than those formed from compound 1. The nitro substituted bisphenazine compound 4 formed straight nanofibers ranging in width from ca. 900 nm to 3 µm. The nanofibers of 4 showed more of a belt-like morphology than the other compounds and were much less flexible than the nanofibers of 1 and 3.

The effect of the alkyl side group length and the assembly method on the morphology of the 1-D nanoclusters

![Diagram of molecules](image)

Figure 3.2. SEM images of 4 (A, B) and 5 (C, D) recrystallized from CH$_2$Cl$_2$. Scale bars: A and C are 50 µm; B and D are 10 µm.

Unlike the other compounds, 4 and 5 produced very homogeneous nanobelts by recrystallization from CH$_2$Cl$_2$. The width of the nanobelts obtained from 5 are much smaller than those of 4. The widths of the nanobelts obtained from 4 varied from ca. 1 µm
to 8 µm while those of 5 varied from ca. 400 nm to 2 µm. The reason why 4 produced wider nanobelts than 5 can be attributed to the higher solubility of 5 in CH₂Cl₂ leading to slower aggregation and thus the more thermodynamic product is formed and additionally lateral growth is hindered.

The effect of the binary solvent system on the morphology of the 1-D nanoclusters

![Image of chemical structures and SEM images](image)

Figure 3.3. SEM images of the phase transfer assemblies of 4 (A and B) and 5 (C and D). Binary solvent system for A and C: CH₂Cl₂ / hexane, for B and D: CH₂Cl₂ / methanol. Scale bars: 10 µm.

In general, similar morphologies to those obtained from recrystallization were seen with the PT assemblies of 4 and 5 from CH₂Cl₂ / hexane and CH₂Cl₂ / methanol. The 1-D nanostructures of 4 obtained from CH₂Cl₂ / hexane ranged in width from ca. 600 nm – 3 µm and those from CH₂Cl₂ / methanol were ca. 900 nm to ca. 3 µm. In the case of
compound 5, the width of the 1-D clusters from CH₂Cl₂/ hexane ranged from ca. 250 nm – 500 nm and those from CH₂Cl₂/ methanol were ca. 600 nm to 900 nm.

Three observations can be made from these results; 1) in the PT method, the nanoclusters formed from compound 4 are again wider than those of 5 as previously described with those from recrystallization, 2) the width of the nanoclusters from the CH₂Cl₂/ hexane binary solvent system are smaller than those from CH₂Cl₂/ methanol, which is indicative of some extent of solubility in the CH₂Cl₂/ hexane system thus forming the more thermodynamic product, and 3) the narrower width in the case of the PT assemblies of both 4 and 5 versus those from recrystallization may be from the forced aggregation of the molecules by the addition of a nonsolvent which can lead to faster precipitation.

3.3.3. X-ray diffraction (XRD)

XRD studies were conducted on the 1-D self-assembled nanobelts of compounds 1 – 5. Although XRD alone is not sufficient to deduce the molecular packing in the 1-D nanoclusters, the major purpose of this study was to determine if significant π-π interactions were present in the assembled clusters. The typical distance for π-π stacking is 3.5 Å.¹⁵

First of all, the XRD patterns of the nanofibers of 1, 2, and 3 obtained from the phase transfer method using CH₂Cl₂/ methanol were compared to determine the effect of the peripheral substituents on the 1-D assembly. Although there are a number of peaks present in the patterns, the peaks of interest are near 23° (2θ) corresponding to the π-π stacking distance along the fiber growth direction. In compound 1 (Figure 3.4 (A)) the diffraction pattern shows sharp, intense peaks indicative of crystallinity in the assembly.
The peaks of interest here correspond to d-spacings of 3.79, 3.73, and 3.61 Å. Compound 3 has a diffraction pattern similar to that of 1 but with a more intense peak at 3.83 Å and a smaller peak at 3.57 Å. Compound 2 exhibits peaks similar to those found in 1 and 3 but they are of lower intensity and are less defined and more broad indicating more amorphous character which was also evidenced in the lack of 1-D assembly shown in SEM.

Figure 3.4. XRD patterns of PT assemblies of (A) 1, (B) 2, and (C) 3 from CH₂Cl₂/methanol.
Figure 3.5. XRD patterns of 4 recrystallized from CH$_2$Cl$_2$ (A), PT from CH$_2$Cl$_2$/hexane (B), and CH$_2$Cl$_2$/methanol (C).

The XRD patterns of the recrystallized samples (compounds 4 and 5) exhibited sharp, well-defined diffraction patterns indicative of high crystallinity in the assembly. The peak of interest is at 22° ($2\theta$) corresponding to $d$- spacings of 3.96 Å for 4 (Figure 3.5 (A)) and 4.02 Å for 5 (Figure 3.6 (A)) which are larger than those of 1 – 3. This may be due to the tilting of the NO$_2$ groups from the plane of the heteroaromatic core which was predicted by theoretical calculations. The small difference in the $d$-spacings in 4 and 5 could be due to slight variations in the tilt angle of the NO$_2$ groups from planarity.
The diffraction patterns of the phase transfer assemblies have less defined peaks and a number of additional peaks are also seen. In the case of phase transfer, the molecules are forced to aggregate by a decrease in solubility due to the addition of a nonsolvent. However, the diffraction pattern of the PT assemblies from CH$_2$Cl$_2$/hexane is more similar to the recrystallized pattern than the methanol PT. This could be due to the lower solubility of the compounds in methanol which forces faster aggregation thus producing the less thermodynamically stable product.
3.4. Conclusions

The 1-D SA abilities of compounds 1 – 5 were examined using recrystallization and a phase transfer method. It was shown with SEM results that the peripheral substituent greatly affects the morphology of the 1-D nanoclusters formed through the PT method. In the case of the nitro compounds (4 and 5), the shorter alkyl chain length imparts increased solubility to the molecule and as a result thinner nanoclusters are obtained due to the more thermodynamic product being formed. The assembly method and the binary solvent system used for PT further influenced the morphology of the nanoclusters. Generally, recrystallization showed the highest crystallinity. In the case of the PT method, the CH₂Cl₂/ hexane solvent system produced nanoclusters with morphologies most similar to those from recrystallization. XRD results indicated that the major driving force for the assembly of compounds 1 – 5 was through π-π stacking and that the nature of the peripheral substituent can greatly affect that distance. These results further verified the molecular design strategy presented in chapter 1 for the 1-D assembly of asymmetric bisphenazine molecules.

3.5. References


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