# Macromolecules

# Sterically Encumbered Bipyridyl-Derivatized Conjugated Polymers and Metallopolymers Incorporating Phenylenevinylene, Phenyleneethynylene, and Fluorenylene Segments

Susan He, Ashley A. Buelt, Jessica M. Hanley, Brad P. Morgan, Andrew G. Tennyson,\* and Rhett C. Smith\*

Department of Chemistry and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, South Carolina 29634, United States

**Supporting Information** 

**ABSTRACT:** This work reports the preparation of a series of 2,2'-bipyridyl (bipy) modified  $\pi$ -conjugated polymers having an average of one or three monomer units (*p*-arylene ethynylene for **PPE1** and **PPE3** or 7,7-dihexylfluorene for **PF1** and **PF3**) between metal-binding sites. Spectroscopic data demonstrate that strategic placement of sterically encumbered mesityl groups about the metal binding sites enforces a 1:1 metal to bipy binding ratio. This steric coordination control ensures that the metalated polymers remain solution processable rather than forming insoluble networks via coordinative cross-linking. The solution photophysical and electrochemical properties of



**Steric Coordination Control** 

metal-free and metalated materials are reported and compared with those of related conjugated polymers and conducting metallopolymers.

# INTRODUCTION

Organic semiconductors such as  $\pi$ -conjugated polymers (CPs, Chart 1A) have been targeted as active components of optoelectronic devices due to their processability, tunability from UV- to IR-range light absorption/emission, and potential for metal-like conductivity in their doped states. These spectacular properties have led to the use of CPs in applications ranging from thin film solar cells and organic light-emitting diodes (OLEDs)<sup>1</sup> to printable circuits and batteries.<sup>2</sup>

Conducting metallopolymers (CMPs) are CPs that have metal ions or atoms incorporated into them.<sup>3</sup> Including metal ions can augment the already impressive property profile of CPs because metals can endow CMPs with a richer range of bonding geometries, magnetic properties, redox chemistry and photochemistry than may be possible from organic CPs alone.<sup>4</sup> CMPs have proven especially successful is in OLEDs. Heavy atoms like transition metals can improve the efficiency of phosphorescence (emission from the triplet excited state) via spin orbit coupling. Because up to 75% of excited states generated in electroluminescent devices are triplets, efficient phosphorescence could lead to up to four times the efficiency of devices that would otherwise rely on fluorescence for light emission. The majority of studies on CMPs for OLEDs to date have focused on iridium<sup>5</sup> and platinum<sup>6</sup> containing CMPs. Because of the added redox tunability and added photophysical nuances endowed by metals, CMPs have also begun to draw interest for use in solar cells.<sup>7</sup>

Although a wide range of ligands have been used to bind metals in CMPs, 2,2'-bipyridyl (bipy) derivatives are among the most common (Chart 1B). This is presumably because of their

relatively facile functionalization, stability and ability to bind a large number of transition and lanthanide elements.<sup>8</sup> The versatility of the bipyridyl scaffold has consequently found extensive use in materials and supramolecular chemistry.9 An early study by Wang and Wasielewski<sup>10</sup> demonstrated the effect of an impressive number of metal ions on the photophysical properties of bipy-modified CPs, including the effect of CP spacer length between bipy units. Bipy-modified CMPs have since found application in conjugated polymetallorotaxanes,<sup>11</sup> electroluminescent devices,<sup>12</sup> organic solar cells,<sup>13</sup> and as chemical sensors.<sup>4f,14</sup> When one attempts to prepare CMPs by metallating a bipy-functionalized CP, multiple bipy units can bind to some metal ions. The result is coordinative cross-link formation (Figure 1, left)<sup>15</sup> and consequent production of a highly insoluble network solid. The loss of solubility leads not only to diminished capacity for processing the materials for devices, but also to a loss of the ability to carry out solution characterization.

The coordination chemistry of bipy derivatives can be controlled by strategic distribution of sterically encumbering units. The strategic distribution of sterically encumbering units have found widespread utility in supramolecular and materials chemistry,<sup>16</sup> and has been exploited in the rational design of elegant bipy-scaffolded supramolecular assemblies.<sup>17</sup> We recently reported that positioning sterically encumbering groups about a bipy binding site can also provide steric

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# **Macromolecules** Chart 1. CPs (A) and Bipy-Derivatized CPs (B) polyfluorene derivatives A) (**PFO**) when R = n-octyl poly (p-phenylene ethynylene) derivatives poly (p-phenylene vinylene) derivatives SPACER SPACER R = OC<sub>6</sub>H<sub>13</sub> **CP1a** -OC<sub>6</sub>H<sub>13</sub> CP2a $-OC_6H_{13}$ OC<sub>6</sub>H<sub>13</sub> CP1b -H C<sub>6</sub>H CP1c -H C<sub>6</sub>H<sub>13</sub> C<sub>6</sub>H<sub>13</sub> 'n Mn+ M

Figure 1. Schematic illustrating how insoluble network formation (left) can be prevented by the steric coordination control strategy (right).

coordination control in a  $\pi$ -conjugated small molecule model compound (**TAB**, Chart 2)<sup>18</sup> and in a bipy modified poly(pphenylenevinylene) derivative (**PPV1**, Chart 2).<sup>19</sup> The sterically enshrouded metal coordination sites enforce a 1:1 metal:bipy binding ratio (Figure 1, right), leading to impressive improvements in the solubility/processability of metalated polymers versus coordinatively cross-linked polymers that are known to form upon metalation of nonsterically encumbered analogues.<sup>15</sup> Furthermore, **PPV1** bound a variety of transition elements with attendant changes in photophysical properties Chart 2. Materials Featuring Sterically Enshrouded 2,2'-Bipyridyl Units



while remaining fully soluble and thus easier to characterize. In the current work, we report statistical copolymers of polyfluorene and poly(*p*-phenylene ethynylene) (PPE) derivatives incorporating different ratios of sterically enshrouded bipy monomer units in their backbones. The photophysical and electrochemical properties of select polymers, metal-free and metalated, are reported.

### EXPERIMENTAL SECTION

**General Considerations.** All air-sensitive manipulations were carried out under a N<sub>2</sub> atmosphere employing either an MBraun Unilab glovebox or standard Schlenk techniques. Tetrahydrofuran was made anhydrous/anaerobic by utilizing an MBraun solvent purification system, in which the solvent was passed through alumina columns under a N<sub>2</sub> atmosphere. NMR spectra were obtained using either a Bruker Avance 300 or Joel ECX-300, both operating at 300 MHz for proton and 75 MHz for carbon. Carbon-13 and <sup>1</sup>H NMR Chemical shifts were reported in parts per million ( $\delta$  ppm). Reagents were obtained from Aldrich Chemical Co., TCI America, Alfa Aesar, or Acros and used without further purification.

General Spectroscopic Methods. All solvents were HPLC grade or better and were degassed using nitrogen. The tetrahydrofuran was purified by MBraun solvent purification system which was set up under nitrogen and employed alumina columns. All UV–vis data was collected using a Varian Cary-50 Bio spectrophotometer and the fluorescence data was collected using a Varian Eclipse spectrophotometer. Initial solutions for PL analysis were filtered through 0.2  $\mu$ m PTFE syringe filters prior to analysis.

**General Considerations for Cyclic Voltammetry.** Polymer was dissolved in anhydrous  $CH_2Cl_2$  containing 0.1 M (TBA)PF<sub>6</sub> as supporting electrolyte and 3-mm-diameter glassy carbon disk was used as the working electrode, with Pt as counter electrode and Ag as quasireference electrode. Ferrocene was added at the end of the experiment as internal reference for the potential. Calculation of ionization energies (IE) and electron affinities (EA) were carried out according to the established convention.<sup>28</sup>

**Metal Ion Selectivity Methods.** A 3.0 mL aliquot of each polymer in tetrahydrofuran solution was measured and added to an optical path length of 1 cm quartz cell. Excess metal ions (10 or more equiv) were added to the polymer solution. Absorbance changes were measured. The experiment was repeated and followed by PL spectroscopy.

Absorption and Photoluminescence Titrations of Polymers with Metal lons. A 3.0 mL aliquot of each polymer in tetrahydrofuran solution was added to a quartz cell having an optical path length of 1 cm. Aliquots, each containing 0.1 equiv of each metal ion with respect to bipyridyl ligating units, were added to the polymer solution and an absorption or photoluminescence spectrum was collected after each addition.

**Synthesis of (BrTABBr).** To a mixture of 1 (0.82 g, 1.95 mmol) and 4 (0.40 g, 0.884 mmol) in 100 mL of THF was added KO<sup>t</sup>Bu (0.218 g, 1.95 mmol) in 20 mL of THF dropwise and stirred for 40 h. Upon reaction completion the solution was poured into saturated aqueous sodium bicarbonate (400 mL) to wash any excess KO<sup>t</sup>Bu. The resulting mixture was extracted with dichloromethane and water. Volatiles were removed by rotary evaporation. The product was dissolved in dichloromethane/pentane and cooled to -10 °C. The precipitate was collected by filtration and dried in vacuo to give 0.42 g (47%) of the product as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 2.01 (s, 24H;  $-CH_3$ ), 2.36 (s, 12H;  $-CH_3$ ), 5.80 (d, 2H;  $-CH_2$ ), 6.55 (d, 2H;  $-CH_2$ ), 6.97 (s, 10H), 7.09 (d, 2H), 7.99 (m, 4H). HRMS (*m/z*): calcd for C<sub>62</sub>H<sub>59</sub>Br<sub>2</sub>N<sub>2</sub> (M + H)<sup>+</sup>, 989.3045; found, 989.3045. Mp: 228–229 °C.

Synthesis of 2. A Dean-Stark distillation apparatus was set up containing 1 (2.10 g, 4.98 mmol), ethylene glycol (1.55 g, 24.7 mmol), and tosic acid (0.068 g, 0.399 mmol) dissolved in 180 mL of toluene. The solution was heated at 135 °C until 10 mL of the solution was left in the starting flask, at which point the heat was stopped and the flask was left to cool to room temperature. Dichloromethane (25 mL), saturated sodium bicarbonate (25 mL), and saturated brine solution (25 mL) were added to the solution and the organic layer was collected. The organic layer was rinsed with water  $(5 \times 25 \text{ mL})$  and volatiles were removed by rotary evaporation to yield a yellow solid. The final product was obtained by washing the solid with methanol (6 mL) followed by pentane (10 mL) and drying in vacuo to yield a white solid (2.0 g, 87%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 2.03 (s, 12H;  $-CH_3$ ), 2.33 (s, 6H;  $-CH_3$ ), 2.85 (t, 2H), 3.38 (t, 2H), 5.31 (s, 1H), 6.91 (s, 4H), 7.21 (s, 2H).<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ: 20.8, 21.1, 64.9, 101.9, 123.3, 127.5, 132.0, 132.7, 136.4, 136.6, 136.7, 144.1. HRMS (m/z): calcd for C<sub>27</sub>H<sub>30</sub>O<sub>2</sub>Br (M + H)<sup>+</sup>, 465.1429; found, 465.1425. Mp: 189-190 °C.

**Synthesis of 3.** In the glovebox 2 (2.19 g, 4.71 mmol) was dissolved in THF (50 mL). The reaction flask was sealed, brought out of the glovebox and cooled to -78 °C under nitrogen. Once cooled, an aliquot of *n*-butyl lithium (2.5 M in hexanes, 2.2 mL, 5.65 mmol) was added via syringe followed by stirring for 1 h. Iodine (2.4 g, 9.42 mmol) was then added to quench the reaction. The reaction contents were allowed to warm to room temperature and stirred for a further 12 h. Excess iodine was quenched with saturated aqueous sodium sulfite (30 mL). The organic layer was collected and HCl(aq) (9 M, 30 mL) was added and the mixture was refluxed for 12 h. A yellow, semicrystalline solid formed upon cooling. The solid was collected, washed with pentane (2 × 10 mL) and dried in vacuo to afford the target as a white solid (1.44 g, 65.6%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 2.00 (s, 12H;  $-CH_3$ ), 2.34 (s, 6H;  $-CH_3$ ),  $\delta$ : 20.6, 21.1, 101.2,

128.2, 132.0, 132.8, 134.8, 135.1, 137.5, 138.8, 145.2, 191.8.2768; HRMS (m/z): calcd for C<sub>25</sub>H<sub>25</sub>OI (M +,H)<sup>+</sup>, 468.0963; found, 468.0951. Mp: 160–161 °C.

Synthesis of ITABI. To a mixture of 3 (1.0 g, 2.14 mmol) and 4 (0.487 g, 0.107 mmol) in THF (20 mL), was added dropwise potassium tert-butoxide (0.35 g, 3.12 mmol) in THF (20 mL). The resultant dark brown solution was stirred for 40 h. An aliquot of HCl(aq) (3.6 M, 4 mL) was then added dropwise to quench excess potassium tert-butoxide. Volatiles were removed under reduced pressure to yield a sticky yellow residue. Reprecipitation by addition of a concentrated dichloromethane solution to pentane produced a yellow powder that was ~90% by <sup>1</sup>H NMR spectroscopy. The final product was obtained by washing the initial solid sequentially with methanol and pentane  $(3 \times 10 \text{ mL})$  and drying in vacuo to afford a yellow powder, 0.75 g (65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 2.01 (s, 24H; -CH<sub>3</sub>), 2.36 (s, 12H; -CH<sub>3</sub>), 5.81 (d, 2H; -CH<sub>2</sub>), 6.56 (d, 2H;  $-CH_2$ ), 6.96 (s, 4H), 7.08 (d, 2H), 7.48 (s, 8H), 8.00 (d, 2H).<sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>), δ: 20.5, 21.1, 93.5, 120.4, 126.7, 128.2, 128.4, 132.9, 133.3, 133.4, 135.5, 136.8, 137.3, 137.8, 142.7, 147.6, 154.2. HRMS (m/z): calcd for C<sub>62</sub>H<sub>59</sub>I<sub>2</sub>N<sub>2</sub>  $(M + H)^+$ , 1085.2768; found, 1085.2788. Mp: 226-227 °C.

Synthesis of 1,4–Bis(hexyloxy)-2,5-diiodobenzene. Synthesis of this compound followed the reported procedure.<sup>20</sup> A mixture of 1,4-bis(hexyloxy)benzene (1.11 g, 4.0 mmol), iodine (0.91 g, 3.6 mmol), and potassium iodate (0.42 g, 2.4 mmol) was dissolved in sulfuric acid (30%, 1.2 mL), CCl<sub>4</sub> (1.6 mL) and acetic acid (7 mL) and refluxed for 3 h at 75 °C. The reaction was then placed on ice for 30 min to afford pink crystals. The crystals were washed with methanol (20 mL × 4) and dried *in vacuo* for 4 h to yield the final product (1.19 g, 56.1%) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 0.93 (t, 6H; -CH<sub>3</sub>), 1.36 (m, 8H; -CH<sub>2</sub>), 1.54 (m, 4H; -CH<sub>2</sub>), 1.82 (m, 4H; -CH<sub>2</sub>), 3.94 (t, 4H, OCH<sub>2</sub>), 7.19 (s, 2H, aromatic H).

Synthesis of 2,7-Diiodo-9,9-dihexylfluorene. Synthesis of this compound followed the reported procedure.<sup>20</sup> Iodine (0.585 g, 2.30 mmol), and potassium iodate (0.330 g, 1.54 mmol) were added to a mixture of 9,9-dioctyl-9H-fluorene (1.0 g, 2.56 mmol) in sulfuric acid (30%, 1.2 mL), carbon tetrachloride (1.6 mL) and acetic acid (7.0 mL). The reaction mixture was refluxed at 80 °C for 48 h then allowed to cool to room temperature for 1 h. Upon cooling two layers were observed, one light yellow and one dense orange. The yellow layer (aqueous acid) was decanted away and then the dense orange layer was added to a 5-fold volume of MeOH (10 mL), leading to formation of a precipitate. Solvent was decanted away and the crude product was dissolved in 4 mL of pentane. Slow evaporation of the pentane at -10°C yielded pale yellow crystals that were dried in vacuo to provide the final product (1.0 g, 60%).  $^1\mathrm{H}$  NMR (300 MHz, CDCl3),  $\delta:$  0.59 (virtual triplet, 6H; -CH<sub>3</sub>), 0.85 (m, 6H; -CH<sub>2</sub>), 1.21 (m, 18H; -CH<sub>2</sub>), 1.92 (m, 4H; -CH<sub>2</sub>), 7.41 (d, 2H, aromatic H), 7.68 (t, 4H, aromatic H).

**Synthesis of [PdCl<sub>2</sub>(BrTABBr)].** To a solution of **BrTABBr** (50 mg, 0.0505 mmol) in 5 mL of THF was added PdCl<sub>2</sub> (9.0 mg, 0.0507 mmol) in 2 mL of methanol and 3 mL of dichloromethane. The solution mixture was refluxed at 70 °C for 15 h then the solution was filtered through a 0.2  $\mu$ m pore size PTFE membrane to remove palladium particles. Hexane diffusion into the filtrate gave analytically pure gold-yellow crystals (59 mg, 60%) that were also suitable for X-ray diffraction. <sup>1</sup>H NMR (300 MHz, THF- $d_8$ ),  $\delta$ : 2.02 (s, 24H; –CH<sub>3</sub>), 2.38 (s, 12H; –CH<sub>3</sub>), 5.78 (d, 2H; –CH<sub>2</sub>), 6.77 (d, 2H; –CH<sub>2</sub>), 7.02 (s, 8H), 7.37 (d, 6H), 7.82 (d, 2H), 8.78 (S, 2H). <sup>13</sup>C NMR (75.4 MHz, THF- $d_8$ ),  $\delta$ : 17.8, 18.6, 120.0, 120.6, 124.3, 126.6, 127.9, 129.7, 130.2, 132.5, 133.1, 134.2, 134.6, 135.9, 141.7, 146.9, 152.0. Anal. Calcd for C<sub>62</sub>H<sub>58</sub>Br<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd·2H<sub>2</sub>O: C, 61.83; H, 5.19; N, 2.33; Found: C, 61.79; H: 5.12; N: 2.35. Mp: 178–179 °C.

**Synthesis of PF1.** Dimethylformamide (15.0 mL) was added to **ITABI** (50.0 mg, 0.0461 mmol), 9,9-dihexylfluorene-2,7-bis-(trimethyleneborate) (23.1 mg, 0.0461 mmol), cesium carbonate (90.0 mg, 0.277 mmol) and *tetrakis*(triphenylphosphine)palladium (2 mg, 0.002 mmol). The reaction mixture was heated at 100 °C for 20 h, and then allowed to cool to room temperature for 1 h. The organics were extracted with dichloromethane, EDTA(aq) and brine (50 mL

each). The dichloromethane layer was collected and concentrated via rotary evaporation to ~3 mL. The concentrated solution was then added dropwise to 20 mL of methanol to yield a fine green-yellow precipitate that was subsequently dried *in vacuo* to give **PF1** (30 mg, 55%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 0.69–2.38 (26H), 2.12 (s, 24H; -CH<sub>3</sub>), 2.42 (s, 12H; -CH<sub>3</sub>), 5.85 (d, 2H, -CH<sub>2</sub>), 6.74 (d, 2H, -CH<sub>2</sub>), 6.98 (s, 2H), 7.05 (8H), 7.10–7.21 (4H), 7.54 (4H), 7.65–7.76 (4 H), 8.06 (s, 2H). GPC:  $M_w/M_n = 14519/8026 = 1.8$ .

**Synthesis of PF3.** Dimethylformamide (18 mL) was added to **ITABI** (50.0 mg, 0.0461 mmol), 9,9-dihexylfluorene-2,7-bis-(trimethyleneborate) (51.5 mg, 0.0922 mmol), 2,7diiodo-9,9-dioctyl-9H-fluorene (29.6 mg, 0.0461 mmol), cesium carbonate (90.0 mg, 0.277 mmol) and tetrakis(triphenylphosphine)palladium (2.1 mg, 0.002 mmol). The reaction mixture was heated at 95 °C for 18 h and then allowed to cool to room temperature for 2 h. The organics were extracted with dichloromethane (2 × 15 mL) and washed with EDTA (2 × 25 mL) and a brine solution (2 × 25 mL). The dichloromethane layer was collected and concentrated to ~3 mL by reduced pressure and then added dropwise to 20 mL of methanol, which afforded a fine green-yellow precipitate, subsequently dried *in vacuo* for 18 h to yield **PF3** (51 mg, 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$ : 0.65–1.11, 1.98–2.39, 5.81 (d, 2H,  $-CH_2$ ), 6.71 (d, 2H,  $-CH_2$ ), 6.94–7.12, 7.50–7.81, 8.02. GPC:  $M_w/M_n = 24714/7536 = 3.28$ .

Synthesis of PPE1. A mixture of 1,4-diethynyl-2,5-bis(hexyloxy)benzene (13.0 mg, 0.0433 mmol) in 4.0 mL of diisopropylamine was added dropwise to a separate solution containing BrTABBr (50.0 mg, 0.0433 mmol), copper iodide (0.33 mg, 0.002 mmol) and tetrakis-(triphenylphosphine)palladium (2.0 mg, 0.002 mmol) in 5.0 mL of toluene. The reaction mixture was stirred at room temperature for 25 h then refluxed at 50 °C for 24 h. The contents were allowed to cool to room temperature, and then concentrated by rotary evaporation which gave a polymer film. Dichloromethane (3 mL) was added to dissolve the film and the resultant solution was added dropwise to 20 mL of methanol to afford a fine orange-yellow precipitate. The crude product was subsequently dried in vacuo to yield PPE1 (29 mg, 60%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.79–1.61 (22H), 2.02 (s, 24H;  $-CH_3$ ), 2.36 (s, 12H;  $-CH_3$ ), 4.01 (t, 4H;  $-OCHH_2$ ), 5.82 (d, 2H; -CH<sub>2</sub>), 6.66 (t, 2H), 6.93 (s, 4H), 6.98-7.14 (6H), 7.30 (2H), 7.48 (s, 8H), 8.01 (s, 2H). GPC:  $M_w/M_n = 38716/9369 = 4.1$ .

Synthesis of PPE3. To a mixture of BrTABBr (50.0 mg, 0.0433 mmol), copper iodide (0.35 mg, 0.002 mmol) and tetrakis-(triphenylphosphine)palladium (2.0 mg, 0.002 mmol) toluene (10 mL) was added 1,4-diethynyl-2,5-bis(hexyloxy)benzene (27.8 mg, 0.092 mmol) and 1,4-bis(hexyloxyl)-2,5-diiodobenzene (24.4 mg, 0.046 mmol) in 5.0 mL of diisopropylamine. The reaction was stirred at room temperature for 25 h then refluxed at 80 °C for 24 h. Once the reaction contents cooled to room temperature the volatiles were removed by rotary evaporation and a polymer film remained. Dichloromethane (3.0 mL) was added to dissolve the film and then was added dropwise to 20 mL of MeOH which gave an orange-yellow precipitate. The organics were decanted and the resulting solid was dried in vacuo to yield PPE3 (48 mg, 65%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>2</sub>),  $\delta$ : 0.81–1.86 (66H), 2.02 (s, 24H; -CH<sub>3</sub>), 2.38 (s, 12H; -CH<sub>3</sub>), 4.03 (t, 12H; -OCHH<sub>2</sub>), 5.83 (d, 2H; -CH<sub>2</sub>), 6.77 (d, 2H), 6.93 (s, 4H), 6.98-7.14 (6H), 7.30 (6H), 7.48 (6H), 8.03 (s, 2H). GPC:  $M_{\rm w}/M_{\rm n} = 9757/3471 = 2.81$ .

## RESULTS AND DISCUSSION

**Design and Synthesis.** Because the steric capsule about the bipy unit in **TAB** (Chart 2)<sup>18</sup> enforces a 1:1 metal:bipy ratio in **PPV1**,<sup>19</sup> we have chosen to incorporate this same motif into the polyfluorene (PF) and poly(*p*-phenylene ethynylene) (PPE) derivatives (Chart 2) for the current study. The goal was to explore how the photophysical and electrochemical properties of metal-free and metalated materials are related to the identity and length of the  $\pi$ -conjugated spacer between ligand monomer units. Another goal was to compare the properties of the sterically encumbered materials to those of previously reported materials lacking such bulk.

Preparation of **TAB**-modified PF and PPE derivatives required a bipy-modified monomer capable of participating in Sonogashira-Hagihara or Suzuki-Miyaura type coupling, respectively. The initial monomer targeted was **BrTABBr**. This monomer was readily prepared in 47% yield by Horner-Wittig condensation of the *m*-terphenyl aldehyde 1 with bis(phosphonate ester)-modified bipy derivative 4 as shown in Scheme 1. Unfortunately, the degrees of polymerization for





polymers produced using **BrTABBr** were unsatisfactory. To solve this problem, we prepared **ITABI**, whose aryl iodide units make it more active in Pd-catalyzed coupling compared to **BrTABBr**. Preparation of **ITABI** required a more involved synthetic approach than did **BrTABBr** (Scheme 1). The first step was protection of the aldehyde functionality in 1 as an acetal to give 2 (87%). This was followed by lithium–bromine exchange of 2 with *n*-butyl lithium, subsequent quenching with molecular iodine, and finally an acid work-up to deprotect the aldehyde, giving 3 (66%). Compound 3 was then employed in a Horner-Wittig condensation with 4 to give **ITABI** (65%).

Although spectroscopic studies had verified the 1:1 metal to ligand ratio for TAB derivatives,<sup>18,19</sup> it was of interest to isolate and structurally characterize metal complexes in order to unequivocally demonstrate the geometry of metal binding sites available from the sterically encumbered ligand. In this vein,  $[PdCl_2(BrTABBr)]$  was prepared and characterized by single crystal X-ray diffraction (Figure 2). Despite the global steric protection about the bipy unit, the distribution of bulky groups provides a pocket of free space about the Pd center such that a standard pseudosquare planar geometry is observed, with no apparent distortions. The average Pd–N (2.03 Å) and Pd–Cl (2.27 Å) bond lengths in  $[PdCl_2(BrTABBr)]$  compare well to the Pd–N (2.02 Å) and Pd–Cl (2.29 Å) lengths in unencumbered  $[PdCl_2(2,2'-bipyridine)]$ .<sup>21</sup> The N–Pd–N (80.95(17)°) and Cl–Pd–Cl (90.15(7)°) angles in  $[PdCl_2(BrTABBr)]$  are also similar to analogous N–Pd–N (80.6(1)°) and Cl–Pd–Cl (89.94(5)°) for  $[PdCl_2(2,2'-bipyridine)]$ .<sup>21</sup>

Whereas **BrTABBr** had performed poorly in Pd-catalyzed coupling polymerization attempts, polymerization reactions



Figure 2. ORTEP drawing (50% probability ellipsoids) of [PdCl<sub>2</sub>(BrTABBr)]. H atoms are excluded for clarity. Refinement details are provided in the Supporting Information.

#### Scheme 2. Preparation of Bulky Bipy Polymers



employing ITABI (Scheme 2) produced polymers with reasonable molecular weights. A 1:1 ratio of ligand to spacer monomer was used to produce alternating copolymers **PF1** and **PPE1**. A 1:3 ratio of ligand to spacer monomer was used to produce statistical copolymers **PF3** and **PPE3**. It is worth noting that, although **ITABI** features steric hindrance about the bipy binding site, it is not encumbered at the iodo substituent, and thus no detrimental influence of reaction rate was anticipated, an assumption supported by the reasonable polymer masses attained. These particular polymers were selected so that a comparison of copolymers **PF3** and **PPE3** to **PF1** and **PPE1** (as well as to previously reported **PPV1**) could be undertaken to reveal how properties change with (1) spacer identity selected from common CP components and (2) the average spacer length between ligating sites.

All of the polymers are readily soluble in common polar organic solvents such as chlorobenzene, dichloromethane, chloroform, acetone, and tetrahydrofuran (THF). Visually, **PF1** and **PF3** were yellow to yellow-green solids, while **PPE1** and **PPE3** were isolated as bright yellow solids. All of the polymers are also brightly photoluminescent in solution upon irradiation with a hand-held UV light ( $\lambda_{\text{excit}} = 365$  nm).

Photophysical Properties of Metal-Free Polymers. Select photophysical data for PF1, PF3, PPE1, PPE3, PPV1 and some related bipy-modified CPs from the literature (Chart 1B) are provided in Table 1. The  $\pi$ -conjugated backbone of PF1 is identical to that in CP1c,<sup>4f</sup> with the only structural

difference being the presence of flanking mesityl groups as steric shields in PF1.

|                       | $\lambda_{abs} (nm)$    | $\lambda_{\text{emit}}^{a}$ (nr | n) Stokes shift (nm)      | Φ       | $I_{\rm o}/I_{\rm Cu(II)}$ |
|-----------------------|-------------------------|---------------------------------|---------------------------|---------|----------------------------|
| PF1                   | 400                     | 452                             | 52                        | 0.49    | 239                        |
| CPlc                  | 402                     | 485                             | 83                        | 0.44    | 310                        |
| PF3                   | 390                     | 448                             | 58                        | 0.62    | 154                        |
| PPE1                  | 410                     | 461                             | 51                        | 0.32    | 57                         |
| CPlb                  | 380                     | 430                             | 50                        | 0.41    | 58                         |
| PPE3                  | 416                     | 468                             | 52                        | 0.32    | 37                         |
| PPV1                  | 437                     | 505                             | 68                        | 0.37    | 31                         |
| CPla                  | 462                     | 540                             | 78                        | 0.30    | 6.2                        |
| CP2a                  | 449                     | 515                             | 66                        | 0.34    | NA                         |
| <sup>a</sup> Photolui | ninescent of $\pm 0.05$ | quantum                         | efficiencies $(\Phi)$ are | repored | with an                    |
| accuracy              | $1 \pm 0.05$ .          |                                 |                           |         |                            |

Predictably, the absorption maxima  $(\lambda_{max})$  for the two polymers are nearly identical. A significant difference between the materials is that the Stokes shift of **CP1c** (83 nm) is significantly greater than that of **PF1** (52 nm) so the emission maxima  $(\lambda_{em})$  of **CP1c** (485 nm) and **PF1** (452 nm) differ by 33 nm. The magnitude of a Stokes shift is related to the difference in geometry of the ground versus excited state,<sup>22</sup> so a smaller Stokes shift can reflect a more rigid CP backbone and its greater resistance to geometric distortion.<sup>23</sup> The sterically

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|      | no M <sup>n+</sup>  |                | Zn <sup>2+</sup>    |                    | Cd <sup>2+</sup> |                  | Hg <sup>2+</sup>   |               |                     | Co <sup>2+</sup>   |               |                  | Cu <sup>2+</sup>   |                   |                     |                |               |
|------|---------------------|----------------|---------------------|--------------------|------------------|------------------|--------------------|---------------|---------------------|--------------------|---------------|------------------|--------------------|-------------------|---------------------|----------------|---------------|
|      | $\lambda_{\rm max}$ | $\lambda_{em}$ | $\lambda_{\rm max}$ | $\lambda_{\rm em}$ | $I_{\rm o}/I$    | $\lambda_{\max}$ | $\lambda_{\rm em}$ | $I_{\rm o}/I$ | $\lambda_{\rm max}$ | $\lambda_{\rm em}$ | $I_{\rm o}/I$ | $\lambda_{\max}$ | $\lambda_{\rm em}$ | I <sub>o</sub> /I | $\lambda_{\rm max}$ | $\lambda_{em}$ | $I_{\rm o}/I$ |
| PF1  | 408                 | 452            | 408                 | 452                | 1.3              | 408              | 453                | 1.0           | 408                 | 453                | 1.1           | 408              | 453                | 17                | 408                 | 453            | 239           |
| PF3  | 400                 | 450            | 400                 | 452                | 1.1              | 400              | 452                | 3.1           | 400                 | 452                | 1.3           | 400              | 452                | 51                | 400                 | 452            | 162           |
| PPE1 | 410                 | 461            | 410                 | 460                | 1.3              | 410              | 460                | 1.3           | 410                 | 460                | 1.2           | 410              | 460                | 32                | 410                 | 460            | 57            |
| PPE3 | 416                 | 468            | 416                 | 468                | 3.6              | 416              | 468                | 1.2           | 416                 | 468                | 1.1           | 416              | 468                | 201               | 416                 | 468            | 37            |
| PPV1 | 437                 | 505            | 437                 | 502                | 1.8              | 437              | 504                | 4.5           | 437                 | 505                | 1.7           | 437              | 505                | 7.6               | 473                 | 500            | 31            |





Figure 3. Absorption (left) and photoluminescence (right) responses of PPE1 (A) and PF1 (B) to addition of metal ions. The band at 535 nm in the PPE1 +  $Co^{2+}$  absorption spectrum is due to the excess cobalt salt used in the titration.

encumbering groups in **PF1** are likely to diminish the conformational flexibility of **PF1** and may thus be the origin of the smaller Stokes shift. A similar Stokes shift is observed in the other sterically encumbered derivative **PF3** (58 nm), although its  $\lambda_{max}$  is shifted to the blue by ~10 nm versus **CP1c** or **PF1** because fluorenylene units comprise a higher percentage of the polymer chain in **PF3**. The photoluminescence quantum efficiency ( $\Phi$ ) of **PF1** (0.49) and **CP1c** (0.44) are identical within error, whereas that of **PF3** (0.62) is significantly higher, suggesting that incorporation of bipy units into the backbone is what leads to the diminished photoluminescence efficiency.

The  $\pi$ -conjugated backbone of **PPE1** is identical to that in **CP1b**, again with the only structural difference being the mesityl groups in **PPE1**. The absorption maxima ( $\lambda_{max}$ ) for the two polymers differ by about 20 nm, while the Stokes shift for sterically encumbered **PPE1** (51 nm) and **PPE2** (52 nm) are nearly identical to unencumbered **CP1b** (50 nm), and  $\Phi$  is slightly higher for **CP1b** (0.41) versus **PPE1** (0.32) and **PPE3** (0.32). As noted previously,<sup>4f</sup> the difference in how

incorporating bipy units influences the properties of PF versus PPE derivatives stems from the difference in energy matching between the spacer (2,7-fluorenylene of phenylene ethynylene, respectively) and the bipy unit. Energy matching is an important characteristic when determining delocalization of  $\pi$ electrons, where the better the energy match (smaller band gap) the more delocalization is enhanced. The 2,5-dialkoxyphenyleneethynylene units in the PPE derivatives PPE1 and PPE3 are significantly more electron rich than are the 7,7dialkylfluorenylene units in PF derivatives PF1 and PF2, leading to a poorer energy match between the spacer and the metal-binding subunits of the polymer. Such considerations regarding energy matching between the conjugated system and the embedded metal complex<sup>3</sup> are another motivation for determining relative orbital energies by electrochemical measurements, as will be discussed further in the following sections.

The three PPV derivatives listed in Table 1 all feature the same  $\pi$ -conjugated backbone, but each has a different number of hexyloxy side chains, and **PPV1** additionally features bulky

Table 3. Electrochemical and Band Gap Data<sup>c</sup>

|      | ion                | ization energy | (eV)              | e                  | lectron affinity (       | eV)               | bandgap E <sub>g</sub> (eV) <sup>b</sup> |                   |                   |  |
|------|--------------------|----------------|-------------------|--------------------|--------------------------|-------------------|--|-------------------|-------------------|--|
|      | no M <sup>n+</sup> | $+Zn^{2+}$     | +Cu <sup>2+</sup> | no M <sup>n+</sup> | $+Zn^{2+}$               | +Cu <sup>2+</sup> | no M <sup>n+</sup>                       | +Zn <sup>2+</sup> | +Cu <sup>2+</sup> |  |
| PF1  | 5.35               | _              | _                 | 2.71 <sup>a</sup>  | _                        | _                 | (2.64)                                   | (2.25)            | (2.38)            |  |
| PF3  | 5.42               | 5.16           | 5.10              | 2.86               | 2.70 <sup><i>a</i></sup> | 2.72 <sup>a</sup> | 2.56 (2.70)                              | (2.46)            | (2.38)            |  |
| PFO  | 5.80               | NA             | NA                | 2.90               | NA                       | NA                | 2.90                                     | NA                | NA                |  |
| PPE1 | 4.55               | 4.57           | 4.56              | 2.76               | 3.26                     | 3.20              | 1.79                                     | 1.31              | 1.36              |  |
| PPE3 | 5.12               | -              | -                 | 2.54 <sup>a</sup>  | -                        | -                 | (2.58)                                   | (2.41)            | (2.38)            |  |
| PPE  | 5.90               | NA             | NA                | 2.50               | NA                       | NA                | 3.40                                     | NA                | NA                |  |
|      |                    |                |                   | 1.                 |                          |                   |  |                   |                   |  |

<sup>a</sup>These data are estimated using the optical bandgap. <sup>b</sup>Numbers in parentheses are bandgaps estimated from onset of absorption. <sup>c</sup>Values for ionization energies and electron affinities are quoted as values below vacuum level.

mesityl substituents (structures are provided in Chart 1). Alkoxy-substituted PPV derivatives exhibit bathochromically shifted absorption and emission versus derivatives lacking such electron donating substituents.<sup>24</sup> Similarly, the  $\lambda_{max}$  values for PPV derivatives in Table 2 predictably increase as the number of electron-releasing hexyloxy substituents increases from **PPV1** (437 nm) to **CP2a** (449 nm)<sup>25</sup> to **CP1a** (462 nm). The  $\Phi$ values for PPV derivatives (0.30–0.37) are similar to one another and to those of the PPE derivatives discussed above (0.32–0.42). The Stokes shift of PPV derivatives are also similar to one another (66–78 nm) and only slightly higher than those of PPE derivatives (50–52 nm), reflecting the additional conformational flexibility afforded by the double bonds in PPV derivatives versus triple bonds in PPE derivatives.

The influence of the spacer on photophysical properties is apparent upon comparison of absorption and emission maxima. The general trend that emerges is that the absorption and emission maxima are progressively red-shifted upon changing from PF to PPE to PPV-based spacers. This is not surprising because the same trend is observed for photophysical parameters of the bipy-free parent polymers comprised of 7,7-dialky-2,7-fluorenylene, 2,5-dialkoxyphenyleneethynylene, or 2,5-dialkoxyphenylenevinylene repeat units.

Photophysical Response of Polymers to Metal Ion Coordination. Previous work with TAB and PPV1 confirmed that the dissociation constants of these sterically encumbered ligands for metals such as Cu<sup>2+</sup>, Fe<sup>3+</sup>, and Zn<sup>2+</sup> are essentially the same as they are for simple, unencumbred 2,2'-bipyridyl.<sup>18</sup> Job analysis derived from titrations followed by absorption and photoluminescence spectroscopy confirmed the 1:1 metal:bipy binding mode, and the results of a single crystal X-ray diffraction structure determination of [PdCl<sub>2</sub>(BrTABBr)] (Figure 2) demonstrate the ability of the core to shield the metal-bound  $\pi$ -conjugated construct from external  $\pi$ - $\pi$ interactions or coordinative cross-links. In the current study, the photophysical response of the polymers to select metal ion coordination was examined by absorption and photoluminescence spectroscopy. The spectroscopic changes observed upon excess metal ion (10-20 equiv) addition to PF1 and PPE1 are provided in Figure 3. Corresponding data for PF3 and PPE3 were similar, and their spectra are thus provided in the Supporting Information. Titrations of each polymer with each metal ion were also carried out and followed by both absorption and photoluminescence spectroscopy in order to observe the gradual change of the spectra as up to one equiv of each metal ion was added. The effects of excess metal ion addition on absorption and emission properties are summarized in Table 2, while spectra for all titrations are provided in the Supporting Information.

Confirmation that the metal ions are binding to the bipy sites in the polymers is provided by the observed red-shift in absorption maxima for each of the polymer/metal combinations (Table 2), similar to the trend noted for **TAB**.<sup>18</sup> The specific manner in which different metals impact photoluminescence, however, varies. One observation that applies generally to all of the polymers in Table 2, though, is that they exhibit significantly less photoluminescence quenching upon binding the diamagnetic  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  ions, all of which have a closed-shell  $d^{10}$  electronic configuration, compared to  $Co^{2+}$  and  $Cu^{2+}$ , both of which have only partially filled *d* electron shells. This is similar to the trend observed for small molecule model **TAB**<sup>18</sup> as well as related bipy-modified CPs such as those shown in Chart 1.<sup>4f,10,14b,d</sup>

The trends in photoluminescence quenching efficacy induced by binding are quite different for Cu<sup>2+</sup> versus Co<sup>2+</sup>. First, Cu<sup>2+</sup> induces a greater quenching effect the more electron deficient the polymer host; quenching follows the trend PF > PPE > PPV. The Co<sup>2+</sup> induced quenching follows the opposite trend, with the greatest quenching for the most electron rich polymer host, PPV1. With this trend in mind, it is not surprising that the presence of a greater percentage of electron-withdrawing bipyridyl units in PF1/PPE1 leads to greater Cu2+ induced quenching of either of these versus their less bipy-laden analogues PF3 and PPE3, respectively. Predictably, then, Co<sup>2+</sup> induces greater quenching in PF3 and PPE3 versus more electron deficient PF1 or PPE1, respectively. We hypothesize that the origin of the disparity between the quenching induced by  $Cu^{2+}$  versus  $Co^{2+}$  is that  $Cu^{2+}$  is in its highest readily accessible oxidation state under the experimental conditions employed, while  $Co^{2+}$  can attain a  $Co^{3+}$  oxidation state through release of an electron to the ligand host. Unfortunately, efforts to confirm this hypothesis by observing the metal to ligand charge transfer (MLCT) band in the absorption spectrum of the  $PF1-Co^{2+}$  complex in Figure 2A (left), was complicated by the presence of the band at 535 nm that is attributable to the  $Co^{2+}$  complex used in the titration.

**Electrochemistry of Polymers and Metallopolymers.** The electrochemical properties of the **TAB**-modified CPs along with  $Zn^{2+}$  and  $Cu^{2+}$  metallopolymer derivatives were probed by cyclic voltammetry (CV) with the aim of elucidating the HOMO (ionization energy, IE) and LUMO (electron affinity, EA) levels. Electrochemical data are summarized in Table 3, along with data for **PFO**<sup>26</sup> (Chart1A) and unmodified PPE<sup>27</sup> for comparison. In some cases, either EA, IE or both could not be determined by CV. In these cases the band gap estimated from the onset of absorption spectra were used to fill in data where possible.

Predictably, as more of the bipy-containing monomer units of metal free CPS were replaced by fluorenylene (from **PF1** to PF3 to PFO) or phenyleneethynylene units (from PPE1 to PPE3 to PPE), the EA, IE and band gap all approached those of the bipy-free parent CPs for metal-free materials. Incorporating bipy units had the effect of raising the IE closer to the vacuum level versus the IE in the bipy-free materials which is presumably due to the diminished stability of positive charge on the electron deficient bipy-appended systems. Bipy incorporation had a greater impact on the IEs of the PPE derivatives than on those of the PF derivatives because the fluorenvlene units are already significantly more electron deficient compared to the 2,5-dialkoxyphenyleneethynylene units in the PPE derivatives. The EAs were less effected than the IEs by incorporating bipy units, but this is not altogether surprising given that organic CPs tend to be much more readily oxidatively doped than reductively doped; incorporating bipy units does not seem to significantly alleviate this difficulty.

Because the steric coordination control strategy allows CMP derivatives of our polymers to remain soluble and free of coordinative cross-links, they were amenable to solution cyclic voltammetric studies that are not possible for CMPs prepared by metalation of traditional bipy-CPs. When PF derivatives bind metal ions, which are positively charged and thus electronwithdrawing, the effect is similar to incorporating electronwithdrawing bipy units. First, and consistent with the observed red shift in absorption spectra, the band gap decreases upon metal ion binding. Metal coordination to the polymers additionally leads to raising the IE toward the vacuum level. For the PPE derivatives, the large effect of bipy incorporation remains relatively the same even after metal ions bind. The EA, however, is relatively constant for PF derivatives before and after metal binding, whereas the EA sinks lower below vacuum level in the PPE derivatives. Unfortunately, however, observations pertaining to the EA values must be viewed with caution because the EA values for metal-free and metalated polymers were only electrochemically determinable (without using less-reliable optical band gap estimation) for one polymer (PF1). Nonetheless, the data that were obtainable suggest that the family of soluble and easily metalated materials studied may have potential for independently tuning the EA and IE to desired levels for device applications through judicious selection of polymer host and metal complex guest energy levels.<sup>3</sup>

## CONCLUSIONS

Through judicious monomer design, a motif was accessed that provides a 2,2'-bipyridyl unit that provides steric shielding from undesired cross-linking/network formation, while simultaneously leaving a cleft of free space about the bipy center to allow undistorted metal coordination environment, as confirmed by ligand dissociation constant measurements and, in one case, by X-ray diffraction. Furthermore, the modular nature of the ligand allowed its utility in preparation of polymers with different ligand-to-ligand distances and selection of spacer identities from among commonly studies CP backbones. The steric coordination control afforded by the ligand design allowed the preparation of soluble metalated CPs for solution photophysical and electrochemical characterization. Additional polymer constructs and extension to optoelectronic devices are currently underway in our laboratories.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Proton and <sup>13</sup>C NMR spectra for polymers, monomers and monomer precursors, absorption and photoluminescence

spectra for titrations of polymers with metal ions, refinement details, and .cif files for single crystal X-ray diffraction data for **2** and  $[PdCl_2(BrTABBr)]$ , and an ORTEP drawing for **2**. This material is available free of charge via the Internet at http:// pubs.acs.org.

# AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: rhett@clemson.edu.

#### Notes

The authors declare no competing financial interest.

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