

with the oxide species, due to the high synthesis temperatures, in vapors of the Al-O system (e.g., Al<sub>2</sub>O) as well as the reaction of elemental Al and O species.<sup>[6]</sup> Given the simplicity of this process, we believe that it could be easily extended to form BN nanocables filled with other interesting core materials by choosing suitable underlying substrates, thereby offering more nanocomposites for fundamental research and applications.

In summary, we report on the controlled synthesis of BN nanotubes, nanobamboos (nanobells), and nanocables. Our results revealed the dependence of structural characteristics on experimental parameters in producing one-dimensional BN nanomaterials, which advantageously allows a variety of one-dimensional BN nanomaterials to be designed for potential applications based on their morphological and structural features.

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## Conducting Polymers of Tungsten(VI)-Oxo Calixarene: Intercalation of Neutral Organic Guests\*\*

By Arkadi Vigalok and Timothy M. Swager\*

The mechanism of charge transport in conducting polymers is dependent upon many electronic and structural factors. Generally, it is accepted that charge transport involves both

intra-chain delocalization of mobile carriers along the polymer backbone and inter-chain charge hopping.<sup>[1]</sup> In pursuit of novel sensory schemes that modulate charge transport, we were interested in the design of a conducting polymer that would allow for selective intercalation of non-conducting organic molecules between the proximate polymeric strands (Fig. 1). The effect of such binding event should be larger if the electroactive segments are relatively short and the overall conductivity relies heavily on intersegment hopping. Building

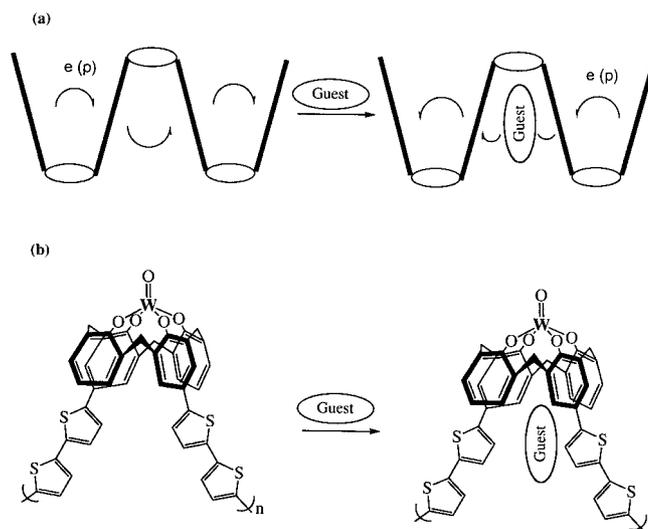


Fig. 1. a) Schematic representation of an organic guest molecule that can be inserted into the charge hopping path in short-chain conducting polymers. b) Conducting polymers incorporating tungsten-oxo calix[4]arenes that can accommodate various organic guests within the calixarene cavity.

upon our interest in conducting sensory polymers incorporating calixarene moieties,<sup>[2]</sup> we designed candidate materials by modification of calixarene molecules at their upper rim with electropolymerizable thiophene groups. The conductivity of the resultant polymer should allow for modification by molecular recognition events inside the calixarene cavity (Fig. 1b). We anticipated that these conjugated polymers would exhibit sensitivity to binding events due to the amplifying nature of conjugated polymers.<sup>[3]</sup> Herein we report novel conducting polymers that use a Lewis acidic calixarene-based cavity to position various neutral guests between polymer chains.<sup>[4]</sup> We further find that the nature of the guest can influence a polymer's conductivity.

The thermodynamic stabilities of the complexation of neutral organic molecules within the calixarene cavities are usually low and do not allow for quantitative complexation.<sup>[5]</sup> We have recently reported a novel class of conducting polymers based upon hexacoordinate tungsten(VI)-capped calixarenes that display xylene-dependent conductivity, however, we were able to produce only circumstantial evidence for host-guest complexation.<sup>[2b]</sup> On the other hand, it has been shown that calixarene complexes of pentacoordinate tungsten(VI) oxide are capable of strong binding of various small Lewis base organic molecules due to penetration of the guest into the Lewis acidic calixarene-based cavity.<sup>[6,7]</sup> We considered that attach-

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ing electropolymerizable groups to the upper rim at the 1 and 3 aromatic rings of the calixarene moiety would provide the desired conducting polymer host–guest complexes (Fig. 1).

The synthetic approach toward this monomer is shown in Scheme 1. Refluxing calixarene **1**<sup>[8]</sup> with the equimolar amount of  $\text{WOCl}_4$  in toluene produced the corresponding dibromocalixarene tungsten-oxo derivative **2**. However, attempts to functionalize the bromine atoms via palladium catalyzed cross-coupling reactions have been unsuccessful. Therefore, the  $\text{W}=\text{O}$  group was masked and pure **3** was isolated in high yield upon treatment of **2** with ethylene glycol in the presence of trimethylsilyl chloride ( $\text{TMS-Cl}$ ).<sup>[9]</sup> Complex **3** exists in two isomeric forms due to two possible orientations of the ethylene glycol ligand with regard to the phenolic rings of the calixarene. Stille coupling of **3** with 2-tributylstannyl bithiophene ( $\text{Bu}_3\text{Sn-Bith}$ ) afforded the corresponding bithienyl derivative **4**. Again two isomeric forms were observed. The final step, hydrolysis of the protecting glycol ligand was quantitative in dimethylsulfoxide ( $\text{DMSO}$ )/ $\text{H}_2\text{O}$ , giving the desired monomer **5** as a yellow  $\text{DMSO}$  adduct.

Single crystals of complex **5**– $\text{DMSO}$  were obtained by slow evaporation of its  $\text{CH}_2\text{Cl}_2$ /hexane solution at room temperature. Interestingly, this complex appears to be the first crystallographically characterized tungsten complex containing a sulfoxide molecule.<sup>[10]</sup> The crystal structure of this complex (Fig. 2) revealed that the tungsten atom is located in a distorted octahedral environment with the oxo-ligand and the  $\text{DMSO}$  molecule occupying mutual trans-positions. The  $\text{W}(1)\text{--O}(4)$  and  $\text{S}(3)\text{--O}(4)$  bond lengths of 2.319(7) Å and 1.497(7) Å, respectively, suggest a very weak interaction between the metal and the guest molecule.<sup>[10]</sup> For comparison, the sulfur–oxygen bond lengths of  $\approx 1.520$  Å were reported for iso-electronic  $\text{Mo}^{\text{VI}}$  complexes.<sup>[11]</sup> The  $\text{W}(1)=\text{O}(3)$  distance of 1.696(7) Å is comparable to what was reported for other tungsten-oxo complexes in similar systems.<sup>[6,12]</sup> The torsion angles

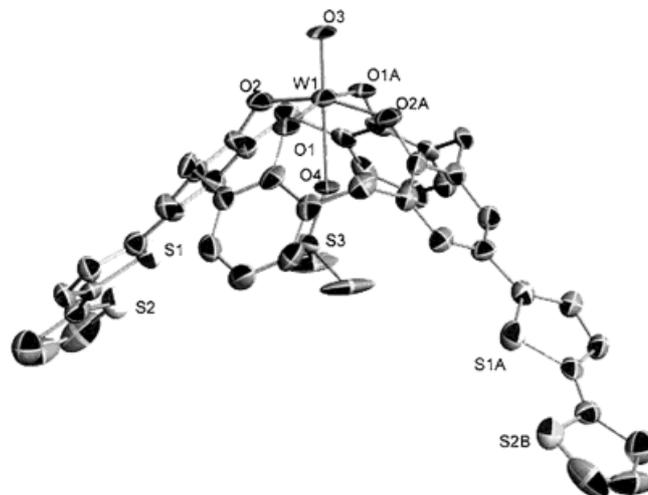
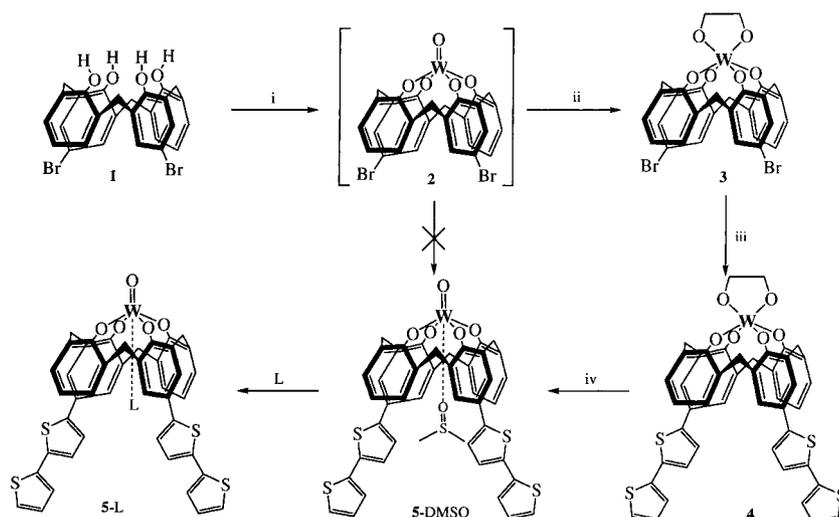


Fig. 2. Single crystal ORTEP (thermal ellipsoids drawn at 30 % probability) structure of complex **5**– $\text{DMSO}$ .

between the thiophene moieties and phenyl rings are 2.2(13)° and 6.9(13)°, respectively, which shows a high degree of conjugation between the aromatic rings.

Subjecting complex **5**– $\text{DMSO}$  complex to high vacuum for 24 h results in removal of  $\text{DMSO}$  and the formation of a poorly soluble yellow solid. The poor solubility is probably the result of a head-to-tail stacking arrangement, with  $\text{O}\cdots\text{W}=\text{O}$  interactions.<sup>[7]</sup> The **5**– $\text{DMSO}$  complex readily reacts with various substituted formamides giving the corresponding host–guest adducts. The complexation of these new guests inside the calixarene cavity is indicated by  $^1\text{H}$  nuclear magnetic resonance (NMR) spectral data of the adducts that reveal the formyl protons in the 3–4 ppm range (Table 1), or about 5 ppm upfield from the resonances of the free ligands.<sup>[13]</sup> The infrared (IR) band due to the amide carbonyl group also shifts 10–40  $\text{cm}^{-1}$  to lower energies upon complexation to the tungsten center. Complex **5** reacts similarly with water to give an  $\text{H}_2\text{O}$  adduct (Scheme 1). While the monosubstituted formamides bind strongly to the tungsten center, the bulkier disubstituted ones show weaker interactions and can be replaced by a water molecule. Complex **5f** was only observed with excess of di-*n*-butyl formamide.

Oxidative electrodeposition of complexes **5** was performed under nitrogen in  $\text{CH}_2\text{Cl}_2$ /0.1 M  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  using 5  $\mu\text{m}$  interdigitated microelectrodes. The potentials were referenced to external  $\text{Fc}/\text{Fc}^+$ . The guest's nature generally had no effect on the oxidation potential of monomeric **5**. Repeated cycling between  $-0.2$  V and 0.65 V at 50 mV/s resulted in the anodic deposition of polymeric films of **5**.<sup>[12]</sup> Cyclic voltammetry (CV) of poly**5** exhibits broad redox signals similar to other segmented thienyl phenylene complexes studied by this group.<sup>[14]</sup>



Scheme 1. i)  $\text{WOCl}_4$ , toluene, reflux, 12 h, 95 %; ii) ethylene glycol, 2 equiv.  $\text{TMS-Cl}$ , toluene, reflux, 20 h, 90 %; iii)  $\text{Bu}_3\text{Sn-bithiophene}$ ,  $\text{Pd}(\text{Ph}_3\text{P})_3$ , 5 mol-%, toluene, reflux, 6 h, 65 %; iv)  $\text{DMSO}$ , 5  $\mu\text{L}$   $\text{H}_2\text{O}$ , 130 °C, 18 h, 95 %. Ligands (L):  $\text{H}_2\text{O}$  (**5a**),  $\text{PhNHCHO}$  (**5b**),  $\text{PhCH}_2\text{NHCHO}$  (**5c**),  $\text{NH}_2\text{CHO}$  (**5d**),  $\text{Me}_2\text{NCHO}$  (**5e**),  $\text{N-Bu}_2\text{NCHO}$  (**5f**).

Both the electrodeposition and the polymer properties (see below) were independent of the concentration of the guest. Polymers obtained using a large excess of the guest showed features nearly identical to polymers deposited from pure 1:1 complexes. These results are indicative of the large binding constant of the guest molecules in the monomer and the polymer throughout the electropolymerization.<sup>[15]</sup> Guest incorporation in the films was further confirmed by the IR spectrum of poly**5b** deposited on an ITO (indium tin oxide) modified SrF<sub>2</sub> window, which showed a band at 1654 cm<sup>-1</sup> due to the coordinated formamide carbonyl group.

While poly**5a–d** showed two distinct redox waves poly**5e** showed a broader single redox wave at a potential intermediate between the two waves in poly**5a–d**. Upon oxidation poly**5** became conductive; the conductivity was, however, noticeably dependent on the bound guest molecule. Figure 3 shows representative CVs and in-situ conductivity profiles for

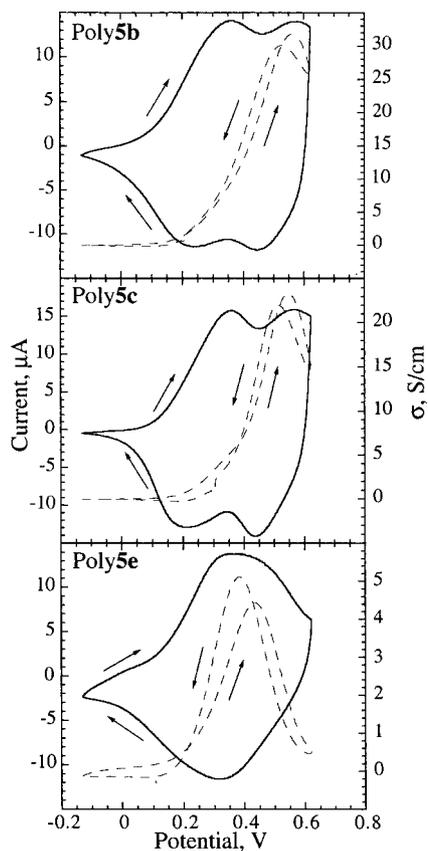


Fig. 3. CV and in-situ conductivity measurements in 0.1 M *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>-</sup>/CH<sub>2</sub>Cl<sub>2</sub> using microelectrodes with 5 µm interdigitated spacing. Sweep rates are 50 mV/s for CV and 10 mV/s with 40 mV offset potential for conductivity measurements.

poly**5b,c,e**. While the polymers containing monosubstituted formamide guests displayed comparable or slightly lower conductivity values relative to the H<sub>2</sub>O adduct ( $\sigma \approx 40$  S/cm), the disubstituted formamide guests yielded the far less conductive polymeric films.<sup>[16]</sup> The guest effect was observed only with poly**5** and not with poly**4**, which yielded conducting polymers upon electropolymerization. Due to coordinative saturation

of the tungsten center poly**4** lacks the ability to coordinate formamide. Interestingly, while the conductivity of poly**5a** did not change upon one-time exposure to a methylene chloride solution of dimethyl- or di-*n*-butyl formamide for several hours, it dropped dramatically when poly**5a** was subjected to repeated electrooxidation in the presence of these disubstituted formamides.<sup>[17]</sup> A plausible mechanism for the observed effect may involve conformational changes upon oxidation of the thiophene-based polymeric backbone that promote the guest diffusion into the film and the inclusion into the calixarene cavity. Consistent with our results for the polymerization of the monosubstituted formamide complexes, no significant conductivity drop was observed when poly**5a** was repeatedly scanned in the presence of these species.

In summary, we have prepared and characterized, including X-ray crystallography, a series of host-guest complexes of tungsten(vi)-oxo calixarenes substituted with two bithiophene groups at the upper rim. These complexes undergo electropolymerization resulting in the first conducting polymers that contain guest molecules inside the calixarene cavity. The conductivities of the obtained polymers are dependent on the nature of the guest, being significantly lower for the disubstituted formamide complexes. Studies regarding the applicability of the reported system to sensing of neutral organic molecules are currently underway.

## Experimental

**Spectroscopic Data:** Selected spectroscopic data (<sup>1</sup>H NMR, IR) for complexes **5a–e** (Scheme 1) are given below.

H<sub>2</sub>O (**5a**): 7.36 (s, 4H, Ar-H), 7.23 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.22 (br d, *J* = 5.1 Hz, 2H, Ar-H), 7.21 (br d, *J* = 3.5 Hz, 2H, Ar-H), 7.12 (ABd, *J* = 3.8 Hz, 2H, Ar-H), 7.05 (m, 6H, Ar-H), 6.79 (t, *J* = 7.5 Hz, 2H, Ar-H), 4.72 (d, *J* = 12.5 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 3.86 (s, 2H, H<sub>2</sub>O), 3.41 (d, *J* = 12.5 Hz, 4H, Ar-CH<sub>2</sub>-Ar).

PhNHCHO (**5b**): 7.35 (s, 4H, Ar-H), 7.21 (dd, *J* = 5.1 and 1.1 Hz, 2H, Ar-H), 7.18 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.14 (dd, *J* = 3.6 and 1.2 Hz, 2H, Ar-H), 7.05 (ABd, *J* = 3.6 Hz, 2H, Ar-H), 7.02 (dd, *J* = 5.1 and 3.6 Hz, 2H, Ar-H), 6.94 (ABd, *J* = 3.6 Hz, 2H, Ar-H), 6.84 (m, 1H, Ar-H), 6.78 (m, 2H, Ar-H), 6.65 (t, *J* = 7.6 Hz, 2H, Ar-H), 5.74 (m, 2H, Ar-H), 4.75 (d, *J* = 12.6 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 4.36 (ABq, *J* = 12.2 Hz, 2H, -NH-CHO), 3.38 (d, *J* = 12.6 Hz, 4H, Ar-CH<sub>2</sub>-Ar). IR (film): 1650 cm<sup>-1</sup> (s, -C=O-W).

PhCH<sub>2</sub>NHCHO (**5c**): 7.34 (s, 4H, Ar-H), 7.21 (dd, *J* = 5.1 and 1.1 Hz, 2H, Ar-H), 7.16 (dd, *J* = 3.6 and 1.1 Hz, 2H, Ar-H), 7.11 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.09 (m, 3H, Ar-H), 7.07 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 7.02 (dd, *J* = 5.1 and 3.6 Hz, 2H, Ar-H), 6.99 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 6.95 (m, 2H, Ar-H), 6.52 (t, *J* = 7.6 Hz, 2H, Ar-H), 6.16 (m, 2H, Ar-H), 4.71 (d, *J* = 12.6 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 3.89 (d, *J* = 12.6 Hz, 1H, -CHO), 3.33 (d, *J* = 12.6 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 2.98 (br s, 1H, -NH-CHO), 2.81 (d, *J* = 6.1 Hz, 2H, Ar-CH<sub>2</sub>-N). IR (film): 1660 cm<sup>-1</sup> (s, -C=O-W).

NH<sub>2</sub>CHO (**5d**): 7.34 (s, 4H, Ar-H), 7.21 (dd, *J* = 5.1 and 1.1 Hz, 2H, Ar-H), 7.17 (d, *J* = 7.5 Hz, 4H, Ar-H), 7.17 (overlapped, dd, *J* = 3.6 and 1.1 Hz, 2H, Ar-H), 7.09 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 7.05 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 7.02 (dd, *J* = 5.1 and 3.6 Hz, 2H, Ar-H), 6.69 (t, *J* = 7.5 Hz, 2H, Ar-H), 4.72 (d, *J* = 12.7 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 4.17 (br s, 1H, -NH-CHO), 4.03 (dd, *J* = 14.0 and 2.5 Hz, 1H, -CHO), 3.72 (br d, 1H, -NH-CHO), 3.35 (d, *J* = 12.7 Hz, 4H, Ar-CH<sub>2</sub>-Ar). IR (film): 1667 cm<sup>-1</sup> (s, -C=O-W).

Me<sub>2</sub>NCHO (**5e**): 7.28 (s, 4H, Ar-H), 7.20 (dd, *J* = 5.1 and 1.1 Hz, 2H, Ar-H), 7.15 (d, *J* = 7.6 Hz, 4H, Ar-H), 7.14 (dd, *J* = 3.7 and 1.1 Hz, 2H, Ar-H), 7.07 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 7.01 (dd, *J* = 5.1 and 3.6 Hz, 2H, Ar-H), 6.98 (ABd, *J* = 3.7 Hz, 2H, Ar-H), 6.69 (t, *J* = 7.6 Hz, 2H, Ar-H), 4.77 (d, *J* = 12.8 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 3.64 (s, 1H, -CHO), 3.37 (d, *J* = 12.8 Hz, 4H, Ar-CH<sub>2</sub>-Ar), 1.51 (s, 3H, N-CH<sub>3</sub>), 0.53 (s, 3H, N-CH<sub>3</sub>). IR (film): 1644 cm<sup>-1</sup> (s, -C=O-W).

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## Electron Transport in Thin-Film Transistors from an n-Type Conjugated Polymer\*\*

By Amit Babel and Samson A. Jenekhe\*

Great strides have been made in developing organic thin-film transistors for applications in low-cost electronic circuits and microelectronic systems.<sup>[1–7]</sup> The field-effect transistor (FET) has also been an excellent platform for investigating the charge transport properties of organic semiconductors. Field-effect mobilities as high as 0.5 to 1  $\text{cm}^2/\text{V s}$  have now been achieved in crystalline organic semiconductors such as

pentacene, oligothiophenes, and oligophenylenes.<sup>[1–4]</sup> In the case of semiconducting polymers, field-effect mobilities of up to 0.05–0.1  $\text{cm}^2/\text{V s}$  have also been achieved with highly ordered regioregular poly(hexylthiophene) (PHT).<sup>[5]</sup> Surprisingly, all the conjugated polymers widely investigated as semiconductors in thin-film transistors have to date been p-type materials giving rise to p-channel transistors with mobile holes.<sup>[1,5,6]</sup> n-Type conjugated polymers with high electron mobility are needed for developing n-channel thin-film transistors and all-polymer complementary integrated circuits. Besides, very little is currently known about electron transport and field-effect mobility of electrons in polymeric semiconductors.

Electron transport in an n-type conjugated polymer was investigated based on FETs made from ladder poly(benzobisimidazobenzophenanthroline) (BBL) thin films. Field-effect mobilities of up to  $5 \times 10^{-4} \text{ cm}^2/\text{V s}$  were observed for unipolar n-channel thin-film transistors fabricated by spin coating. This field-effect mobility of electrons is the highest yet observed for intrinsic electron transport in conjugated polymers. The field-effect mobility of electrons in BBL thin films was found to vary by 2 orders of magnitude depending on the solution thin-film processing method used. Because of the highly efficient  $\pi$ - $\pi$  interchain stacking of this ladder polymer, we expect significantly higher electron mobilities to result from improvement in thin-film processing, control of the thin-film morphology and purity of the material.

We focus our investigation of electron transport in thin-film transistors fabricated from BBL, which is known to be an n-type (electron transport) semiconductor based on electrochemical doping experiments,<sup>[8,9]</sup> photoinduced electron transfer and photoconductivity studies,<sup>[10]</sup> and photovoltaic devices.<sup>[11]</sup> Knowledge of the intrinsic electron transport and mobility in BBL thin films is currently lacking. Very recently, thin-film transistors based on BBL thin films, spin coated from Lewis acid ( $\text{AlCl}_3$ ,  $\text{GaCl}_3$ )/nitromethane solutions,<sup>[12]</sup> were reported to exhibit novel ion-modulated ambipolar charge transport.<sup>[7]</sup> Ion-modulated field-effect mobilities as high as  $6 \times 10^{-2} \text{ cm}^2/\text{V s}$  for n-channel operation and  $3 \times 10^{-2} \text{ cm}^2/\text{V s}$  for p-channel operation along with on/off current ratios of 2 to 50 were observed when mobile ions and moisture were present in the films.<sup>[7]</sup> However, only n-type transistor behavior with a field-effect mobility of  $4 \times 10^{-6} \text{ cm}^2/\text{V s}$  was observed after 24 h drying of the BBL transistors in vacuum.<sup>[7]</sup> This intrinsic field-effect mobility of electrons in BBL thin films,  $4 \times 10^{-6} \text{ cm}^2/\text{V s}$ , is rather low compared to typical hole mobilities of  $10^{-5}$  to  $10^{-3} \text{ cm}^2/\text{V s}$  in p-type conjugated polymers such as poly(alkylthiophene)s.<sup>[1,5,6]</sup> It is thus of interest to explore effects of solution thin-film processing methods on the field-effect mobility of electrons in BBL thin films.

The molecular structure of BBL is shown in Figure 1. The many unusual physical and chemical properties of this rigid-chain ladder polymer,<sup>[8–15]</sup> such as high-temperature resistance, high glass transition temperature ( $T_g > 500^\circ\text{C}$ ), and insolubility in aprotic organic solvents, stem from the very strong intermolecular  $\pi$ - $\pi$  stacking into quasi two-dimensional sheets.<sup>[12–15]</sup> X-ray scattering from BBL thin films, solu-

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