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Conducting Bipyridine-Bithiophene Copolymers

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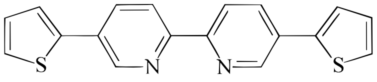
The synthesis and electrochemical polymerization of 6,6′-bis(2″-thienyl)-3,3′-bipyridine (**2**) and 6,6′-bis(2″-thienyl)-2,2′-bipyridine (**3**) are reported. Cyclic voltammetry shows that the resulting polymers have high bandgaps (3.0 and 3.2 eV, respectively) and are unstable in their p-doped (oxidized) states. Both polymers are stable when n-doped, but electronic conductivities determined by impedance spectroscopy were only ca. 3 × 10^{-8} S cm^{-2}. Surprisingly, the greater conjugation in poly-**2**, which is demonstrated by its lower bandgap, does not lead to enhanced conductivity.

1. Introduction

Pyridine-based conducting polymers have been attracting increasing interest in recent years because of their facile n-doping (reduction)[1−4] and their ability to bind metal ions.[4−7] Poly(pyridine-2,5-diyl)s and poly(2,2′-bipyridine-5,5′diyl)s are prepared by the Ni(0)-catalyzed dehalogenation polycondensation of dibromopyridines and 2,2′-bipyridines.[4] Electrochemical generation of the Ni(0) catalyst affords a valuable method for preparing thin films of the polymer on electrodes.[8,9] Copolymers containing pyridine and thiophene,[10−12] *N*-methylpyrrole,[13] or selenophene[13] have been prepared by the electrochemical polymerization of 2,5- and 2,6-bis(2′-thienyl)pyridine, 2,5-bis(1′-methyl-2′-pyrrolyl)-pyridine, and 2,5-bis(2′-selenienyl)pyridine. Similarly, block copolymers of 2,2′-bipyridine and tetrathiophene have been prepared from 5,5′-bis(2″-bithienyl)-2,2′-bipyridine.[6] The monothienyl analogue, 5,5′-bis(2″-thienyl)-2,2′-bipyridine (**1**), was reported not to polymerize.[6]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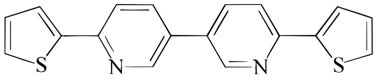
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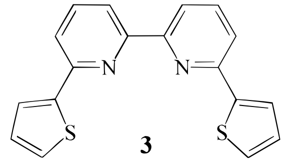
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We report here on two new bithiophene-bipyridine copolymers prepared by electrochemical polymerization of 6,6′-bis(2″-thienyl)-3,3′-bipyridine (**2**) and 6,6′-bis(2″-thienyl)-2,2′-bipyridine (**3**).

Experimental Section

Reagents and Instruments. Tetrakis(triphenylphosphine)-palladium(0), 2,6-bromopyridine, 2,5-dibromopyridine, and 2-thienyllithium were all obtained from Aldrich and used without further purification. Zinc chloride (Anachemia) was dried at 120 °C under vacuum for at least 4 h prior to use. THF (Anachemia) was dried by refluxing over calcium hydride (Fisher) prior to use.

Melting points were obtained using a Fisher-John's hot stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz with TMS as a standard.

Synthesis. *6,6′-Dibromo-3,3′-bipyridine.* The following procedure is based on the method for 6,6′-dibromo-2,2′-bipyridine.[14,15]

n-Butyllithium in hexanes (2.5 M, 7.5 mmol) was added over 1 h to 2,5-dibromopyridine (2.0 g, 8.4 mmol) in diethyl ether (50 mL) at −80 °C. The mixture was then allowed to warm to −65 to −70 °C for 2 h. $CuCl_2$ (0.57 g, 4.2 mmol) was added at −90 °C, and again the temperature was allowed to rise to ca. −65 °C. After 30 min, dry air was bubbled through the reaction mixture for 30 min. The crude product, isolated by filtration following quenching with water at room temperature, was washed with dilute HCl(aq) and dried. Recrystallization from benzene gave a white crystalline solid in 15% yield (mp = 249−251 °C).

Although other isomers could be formed by this procedure, only 6,6′-dibromo-3,3′-bipyridine was isolated. The ^{1}H NMR spectrum indicates a symmetrical structure and the melting point is substantially higher than that of 5,5′-dibromo-2,2′-

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Table 1. Formal Potentials or Peak Potentials from Cyclic Voltammetry of Compounds 2 and 3 and Their Polymers in CH_3CN Containing 0.05 M Bu_4NPF_6, and Electrochemical and Spectroscopic HOMO–LUMO Gaps

	potential (V vs SSCE)			
monomer	oxidation	reduction	electrochemical gap (V)	optical gap (eV)
6,6′-bis(2″-thienyl)–3,3′-bipyridine (**2**)	+1.42[a]	−1.90	3.32	3.58[b] (3.23)[c]
poly-**2**	+1.25	−1.77	3.02	
6,6′-bis(2″-thienyl)–2,2′-bipyridine (**3**)	+1.53[a]	−2.09	3.62	3.85[b] (3.52)[c]
poly-**3**	+1.4	−1.85	3.25	

[a] Peak potentials. [b] Peak of the π–π* transition. [c] Onset of the π–π* transition.

bipyridine (222–224 °C).[16] The assigned structure is supported by the ^{1}H NMR spectrum of the bis-thienyl compound derived from it (6,6′-bis(2″-thienyl)-3,3′-bipyridine; see below). ^{1}H NMR (CD_3SOCD_3) σ (ppm) 8.80 (2H,d, $J_{2,4}$ = 2.4 Hz, H-2), 8.15 (2H, dd, $J_{4,5}$ = 8.3 Hz, H-4), 7.81 (2H, d, H-5). Ms *m/z* 314 (100% M^+), 235 (55), 233 (55), 153 (75), 126 (35).

*6,6′-Bis(2″-thienyl)-3,3′-bipyridine (**2**).* 6,6′-Dibromo-3,3′-bipyridine (0.2 g, 0.64 mmol), 2-thienylboronic acid (0.6 g, 4.7 mmol),[17] sodium hydrogen carbonate (0.4 g, 4.8 mmol), and $Pd(PPh_3)_4$ (0.08 g, 0.07 mmol) were heated at reflux in THF (36 mL) and water (4 mL) for 48 h. The reaction mixture was worked up by the addition of water (20 mL) and ether (50 mL). The organic layer was dried with $MgSO_4$ and concentrated. Chromatography on a silica/$CHCl_3$ column yielded a white crystalline solid in 54% yield, mp 211–215 °C.

Calculated for $C_{18}H_{12}N_2S_2$: M^+ = 320.0442. Found: M^+ = 320.0440. ^{1}H NMR (CD_3SOCD_3) σ (ppm) 8.99 (2H,dd, $J_{2,5}$ = 0.4 Hz, $J_{2,4}$ = 2.4 Hz, H-2), 8.26 (2H, dd, $J_{4,5}$ = 8.3 Hz, H-4), 8.06 (2H, dd, H-5), 7.90 (2H, dd, $J_{3'',5''}$ = 0.9 Hz, $J_{3'',4''}$ = 3.6 Hz, H-3″), 7.69 (2H, dd, $J_{4'',5''}$ = 5.1, H-5″), 7.21 (2H, dd, H-4″). Ms *m/z* 320 (100% M^+), 262 (3), 160 (10), 108 (8).

The NMR spectrum of **2** is significantly different from that reported for 5,5′-bis(2″-thienyl)-2,2′-bipyridine (**1**).[6] The key feature supporting our assignment as a 6,6′-substituted bipyridine is the significant separation of the thiophene H-3″ and H-5″ resonances. In **1** these resonances are separated by only 0.05 ppm, while in **2** and **3** they are 0.21 and 0.23 ppm apart, respectively. In 2,5-bis(2′-thienyl)pyridine the separations are 0.23 ppm for the thiophene in the 2-position and 0.05 ppm for the thiophene in the 5-position.[10]

*6,6′-Bis(2″-thienyl-2,2′-bipyridine) (**3**).* The synthesis of **3** has been previously reported, but the overall yield from 2,6-dichloropyridine in two steps was less than 2%[18] The following procedure produced a 10% overall yield from 2,6-dibromopyridine in two steps.

6,6-Dibromo-2,2-bipyridine[14,15] (3.1 g, 10 mmol), 2-thienylzinc chloride (6.8 g, 50 mmol),[19] and $Pd(PPh_3)_4$ (0.3 g, 0.25 mmol) were stirred for 16 h at room temperature in THF (50 mL). HCl(aq) (10 mL, 1.5 M) was then added, and the precipitate was collected by filtration. Sublimation gave white crystals with mp = 202–206 °C (lit. 206–208 °C[18]).

^{1}H NMR (CD_3SOCD_3/CD_3COCD_3) σ (ppm) 8.49 (2H, dd, $J_{3,5}$ = 1.2 Hz, $J_{3,4}$ = 7.8 Hz, H-3), 8.04 (2H, t, $J_{4,5}$ = 8.0 Hz, H-4), 8.02 (2H, dd, H-5), 7.92 (2H, dd, $J_{3'',5''}$ = 0.9 Hz, $J_{3'',4''}$ = 3.6 Hz, H-3″), 7.69 (2H, dd, $J_{4'',5''}$ = 5.1 Hz, H-5″), 7.23 (2H, dd, H-4′). Ms *m/z* 320 (100%, M^+), 287 (8), 210 (8), 159 (10), 138 (10), 39 (7).

Electrochemistry. Electrochemical experiments were performed in conventional three-compartment glass cells at room temperature. The working electrode was a 0.0052 cm^2 Pt disk sealed in glass, and the reference electrode was a saturated sodium chloride calomel electrode (SSCE). Tetrabutylammonium hexafluorophosphate (Fluka, 98%) and acetonitrile (Fisher, HPLC grade) were used as received.

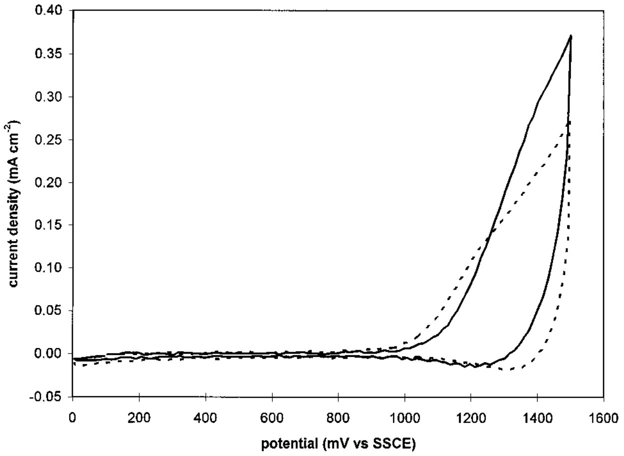

Figure 1. Cyclic voltammograms (100 mV s^{-1}; first (—) and second (– – –) scans) of a poly-**2** coated Pt electrode in acetonitrile containing 0.05 M Bu_4NPF_6. The polymer film was prepared using a charge density (Q_{prep}) of 10 mC cm^{-2}.

Impedance measurements were carried out with a Solartron frequency response analyzer (Model 1250) and a Solartron electrochemical interface (Model 1286). All data were collected and analyzed using an IBM compatible microcomputer and ZPLOT software (Scribner Associates Inc.).

Results and Discussion

Electrochemical and spectroscopic data for the monomers **2** and **3** are presented in Table 1. Electrochemical oxidation was irreversible for both compounds and resulted in film formation on the electrode. Reduction was reversible in both cases. The difference between the peak potential for the irreversible oxidation and the formal potential for the reversible reduction provides an estimate of the HOMO–LUMO gap of the compound. These electrochemically determined energy gaps are consistent with UV–vis data, falling between the onset and peak of the π–π* transition (Table 1). The smaller HOMO–LUMO gap for compound **2** reflects the greater degree of conjugation resulting from 2,5-linkages at the pyridines.[13]

Polymer films were prepared on Pt at a constant current density of 0.19 mA cm^{-2} from ca. 3 mM solutions in acetonitrile containing 0.05 M Bu_4NPF_6. In both cases, the potential decreased during the first ca. 20–100 s of polymerization and then began to increase. The minimum potential during polymerization was typically ca. +1.36 V for **2** and +1.44 V for **3**. The minimum occurred at shorter times for poly-**3**, and the subsequent increase in potential, which is due to oxidative degradation of the polymer (overoxidation),[13] was more rapid.

Figure 1 shows cyclic voltammograms for oxidation (p-doping) of a poly-**2** film. The oxidation wave exhibits a shoulder at ca. 1.2–1.3 V, and a small reduction wave appears in the same potential range. The formal

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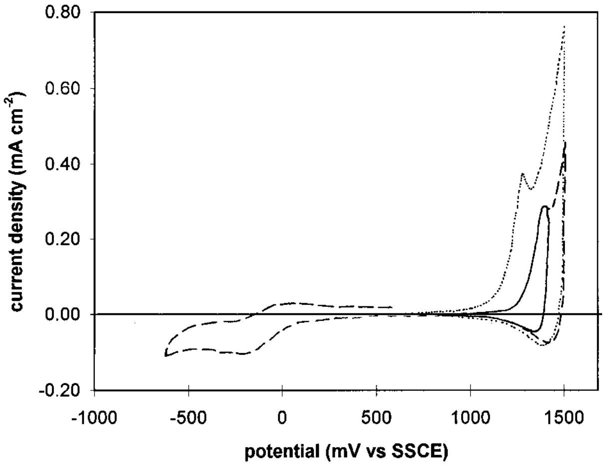

Figure 2. Cyclic voltammograms (100 mV s^{-1}; first (—), second (— — —), and third (···) scans) of a poly-**3**-coated Pt electrode (Q_{prep} = 20 mC cm^{-2}) in acetonitrile containing 0.05 M Bu_4NPF_6.

potential for p-doping can therefore be taken as ca. 1.25 V. The charge passed during the first oxidation to +1.5 V was ca. 7.5% of the polymerization charge. Values of ca. 30% are expected for the polymerization and doping of 4-ring monomers.[13] The low doping/polymerization charge ratio observed here is typical for pyridine containing polymers and appears to result from low polymerization efficiencies.[13] The charges under the reduction waves in Figure 1 are much lower than for the corresponding oxidation waves. This indicates that the p-doped state is unstable. On the basis of the behavior of other p-doped conducting polymers,[20] we assume that it reacts with trace water in the electrolyte solution to produce a material with interrupted conjugation. The observation of a substantial oxidation wave on the second and subsequent (not shown) scans, suggests that the undoped polymer (or a substituted version) is regenerated in some way. Precedent for this has been observed in the reaction between Cl$^-$ and p-doped polythiophenes.[21]

Figure 2 shows cyclic voltammograms for oxidation (p-doping) of a poly-**3** film. This polymer exhibits a distinct oxidation peak at ca. +1.40 V, and a more pronounced reduction peak than was observed for poly-**2** (Figure 1). Thus, although the formal potential of poly-**3** (ca. +1.40 V) is significantly more positive than that of poly-**2** (ca. +1.25 V), its p-doped state is more stable. This is unusual, and contrary to the behavior of poly-bis(2-thienyl)pyridines, where the 2,6-linked isomer forms the least stable p-doped state.[13] Another unusual feature of the p-doping electrochemistry of poly-**3** is the reduction wave at ca. − 0.2 V, and another of similar size at ca. −0.8 V that is not shown in Figure 2. Cycling through one or both of these waves leads to an enhancement of the next oxidation wave, suggesting some type of charge trapping.[22]

Figure 3 shows cyclic voltammograms for reduction (n-doping) of poly-**2**. The reduction and reoxidation waves at a formal potential of ca. −1.77 V initially grew with cycling. This type of break-in phenomenon is commonly observed for n-doping, and appears to be due to slow uptake of countercations from the electrolyte solution.[13,23] When the potential range was limited to −1.0 to −1.9 V, the anodic peak began to decrease while the cathodic peak continued to grow. This suggests there is an accumulation of sites that are trapped in the reduced state.[22] The voltammograms shown in Figure 3 indicate that the reduced state of poly-**2** is quite stable.

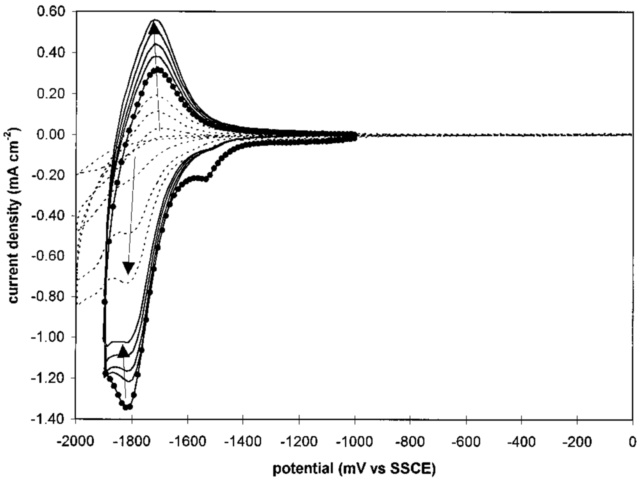

Figure 3. Cyclic voltammograms (100 mV s^{-1}) of a poly-**2**-coated Pt electrode (Q_{prep} = 30 mC cm^{-2}) in acetonitrile containing 0.05 M Bu_4NPF_6. (— — —) first 4 scans (0 ↔ −2.0 V); (●) fifth scan (−1.0 ↔ −1.9 V); (—) scans 6−9. Arrows indicate growth or decay of peaks.

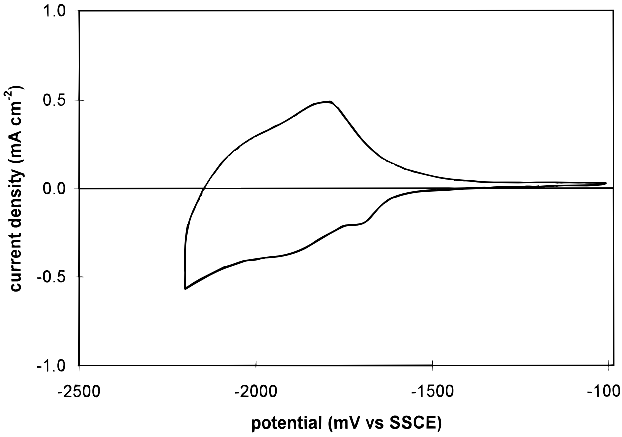

Figure 4. Cyclic voltammogram (100 mV s^{-1}; 10th scan) of a poly-**3** coated Pt electrode (Q_{prep} = 30 mC cm^{-2}) in acetonitrile containing 0.05 M Bu_4NPF_6.

Figure 4 shows a cyclic voltammogram following breakin for reduction (n-doping) of poly-**3**. The formal potential is ca. −1.85 V, and the reduced state is stable on the voltammetric time scale.

Formal potentials for the two polymers are summarized in Table 1 with data for the monomers. The difference between the formal potentials for p- and n-doping can be taken as an estimate of the polymer's bandgap (HOMO−LUMO). For both materials, polymerization leads to a decreased bandgap, which indicates that the mean conjugation length has increased. Shifts in both formal potentials occur during polymerization, indicating that in the polymer the HOMO, LUMO, and p- and n-type charge carriers are delocalized over more

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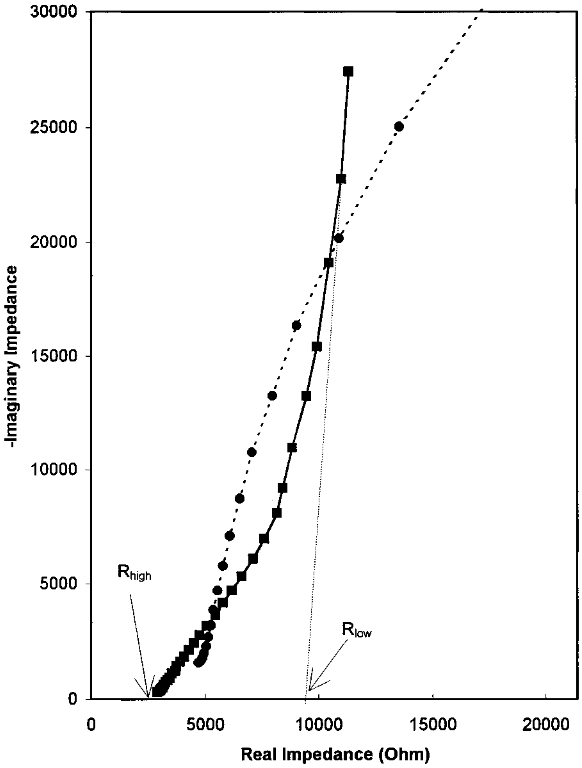

Figure 5. Complex plane impedance plots at 0 V (●) and −1.8 V (■) for the electrode in Figure 4.

than four rings. The lower bandgap and formal potentials of poly-**2** indicate a greater degree of conjugation than in poly-**3**.

These changes are typical for the polymerization of oligomers,[24,25] and support our presumption that the films formed in this work are indeed polymers. By analogy with the polymerization of other thiophenes and thiophene-based oligomers, we assume that polymerization occurs at the α-position of the thiophene rings.[26]

The kinetics of the reductive electrochemistry of the two polymers were investigated by impedance spectroscopy. Figure 5 show impedance data for the poly-**3** film and electrolyte solution used for Figure 4. At 0 V, the polymer is in its neutral undoped state and should exhibit no electrochemical response to the ac stimulation. The impedance data at this potential (●) form a large arc, representative of a parallel RC circuit with a resistance of >200 kΩ and a capacitance of 10 μF cm^{-2}. The magnitude of this capacitance indicates that is due to charging of the double-layer of the Pt electrode.[27] The high-frequency real axis intercept of the impedance data (ca. 5 kΩ) therefore represents the sum of the uncompensated ionic resistances of the electrolyte solution (R_{sol}) and the polymer film ($R_{film,ionic}$).[27] Using a bare Pt electrode, R_{sol} was determined to be 1.0 kΩ. $R_{film,ionic}$ was therefore ca. 4 kΩ at 0 V.

At −1.8 V, the polymer film is partially n-doped and exhibits an electrochemical response to the ac stimulation. This redox involves transport of both ions and electrons within the film. In the absence of a significant charge-transfer resistance the film should give a finite Warburg-type (diffusion/migration) impedance response.[28,29] The theoretical complex plane impedance response consists of a 45° region at high frequency and a 90° region at low frequency. The data at −1.80 V in Figure 5 approximate this response quite well. The polymer film's ionic ($R_{film,ionic}$) and electronic ($R_{film,electronic}$) resistances can therefore be estimated from the high and low-frequency limiting resistances (R_{high} and R_{low} in Figure 5), by using eqs 1 and 2.

$$1/(R_{high} - R_{sol}) = 1/R_{film,electronic} + 1/R_{film,ionic} \quad (1)$$

$$3(R_{low} - R_{sol}) = R_{film,ionic} + R_{film,electronic} \quad (2)$$

Film resistances of 1.9 and 23 kΩ were obtained from the data at −1.80 V in Figure 5. Since the ionic resistance should decrease with reduction, due to the incorporation of counterions into the film, the value of 1.9 kΩ can be confidently assigned as $R_{film,ionic}$. The electronic resistance of the film at −1.80 V was therefore ca. 23 kΩ. On the basis of typical densities (~1 g cm^{-3}) and doping levels (~0.25 e/ring) for conducting polymers, the poly-**3** film used here can be estimated to have been ca. 30 nm thick. Its electronic conductivity at −1.80 V was therefore ca. 3×10^{-8} S cm^{-1}. Impedance measurements on a ca. 50 nm poly-**2** film gave an electronic conductivity of ca. 2×10^{-8} S cm^{-1}. Such low conductivities appear to be typical for pyridine containing copolymers in their n-doped state.[13]

Conclusions

Both 6,6′-bis(2″-thienyl)-3,3′-bipyridine (**2**) and 6,6′-bis(2″-thienyl)-2,2′-bipyridine (**3**) have been successfully polymerized electrochemically in acetonitrile. The resulting polymers exhibit high bandgaps and are unstable in their p-doped (oxidized states). They both form stable n-doped materials, but these exhibit only low electronic conductivities. Surprisingly, the greater conjugation in poly-**2**, which is demonstrated by its lower bandgap, does not lead to enhanced conductivity.

The properties of poly-**2** and poly-**3**, are for the most part consistent with those of the polymers formed by 2,6- and 2,5-bis(2-thienyl)pyridine.[13] The formal potentials, bandgaps, and n-type conductivities are all similar. The bipyridine containing polymers are somewhat less stable when p-doped than the corresponding pyridine containing materials. The π-deficient bipyridine units presumably cause greater localization of polarons and/or bipolarons on bithiophene segments of the polymer, making them more susceptible to attack by trace water.

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