Synthesis of Highly Functionalized Pyridines for Planar Polymers. Maximized π-Conjugation in Electron Deficient Macromolecules

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Abstract: Synthetic routes to planar polypyridines are described. Two pyridine monomers for the step growth polymerization are prepared starting from 2,5-lutidine via 2,5-dibromopyridine-3,6-dicarboxylic acid as the common intermediate. The dicarboxylic acid serves as the key intermediate for the preparation of both the A and B components for the step-growth polymerization. Several novel transformations on sensitive pyridine cores are disclosed while preparing the monomers for the condensation polymerizations. A bis(Curtius) rearrangement followed by *tert*-butyl alcohol capture of the bis(isocyanate) effects the high-yielding conversion of carbonyl moieties to the *tert*-butoxycarbonyl-protected aryldiamine. Lithium−halogen exchange on the protected diaminopyridine followed by stannylation affords the required dimetalated diamine monomer. Treatment of the pyridine(dibromodiacid chloride) with mild cuprates or organocopper reagents affords the pyridine(dibromodiketones). Pd/Cu-catalyzed couplings of dibromopyridines with distannylpyridines are utilized for the polymerization schemes. This approach permits the ladder linkages of the planar polymers to (i) form in high yields upon proton activation once the polymer backbone is intact, (ii) be substituted so that the newly formed polypyridines are soluble, unlike many other aromatic ladder polymers, and (iii) contain double-bonded ladder units to keep the consecutive aryl moieties planar which maximizes extended π-conjugation through the polymer backbones, thereby increasing the bandwidths and lowering the optical band gaps. The planar polypyridines here have optical band gaps of 1.5−2.0 eV which represent 1.3−1.8 eV smaller gaps than nonplanarized polypyridines in similar solvents, demonstrating the efficacy of planarization for band gap shortening.

Recent studies in nonlinear optics, light emitting diodes, photovoltaic devices, laser systems utilizing conductive polymer films, and optoelectronic sensors have required the preparation of novel conjugated polymeric frameworks for enhanced performance.[1,2] The ability to control optical or electronic behavior in these emerging technologies depends, in large part, on the capability to modulate the band gaps and electron densities in the polymeric materials at the core of the devices' functionalities. The optoelectronic properties of conjugated polymers vary significantly based upon the degree of extended conjugation between the consecutive repeat units and the inherent electron densities in the polymer backbones.[3] By forming bridging linkages between the repeat units of conjugated polymers, the extended π-conjugation can be maximized.[4] The majority of conjugated ladder polymers are based upon poly(*p*-phenylene)s,[4] and there are no reports of ladder polymers, to our knowledge, based on electron deficient heterocycles.[5] We describe here routes to soluble planar electron deficient heterocyclic polymers based on pyridines.[6] A convergent approach is utilized wherein both the A and B components for the condensation polymerizations arise from a common pyridine intermediate. Functionalizations of the heterocyclic cores are achieved using bis(Curtius) rearrangements, and dilithiation reactions, via a lithium−halogen exchange process. The planar polypyridines here have dramatically smaller optical band gaps than nonplanarized polypyridines thereby demonstrating the effectiveness of planarization for band gap shortening. Moreover, highly functionalized pyridines are of importance in a broad range of chemistries ranging from materials science to natural products; therefore, the new synthetic reactions described here will likely have applications far beyond the scope of this study.

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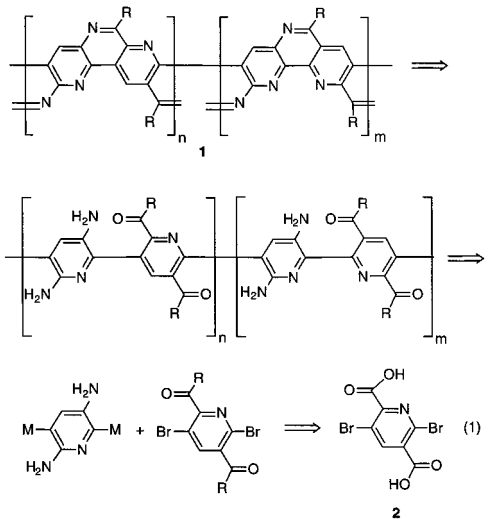
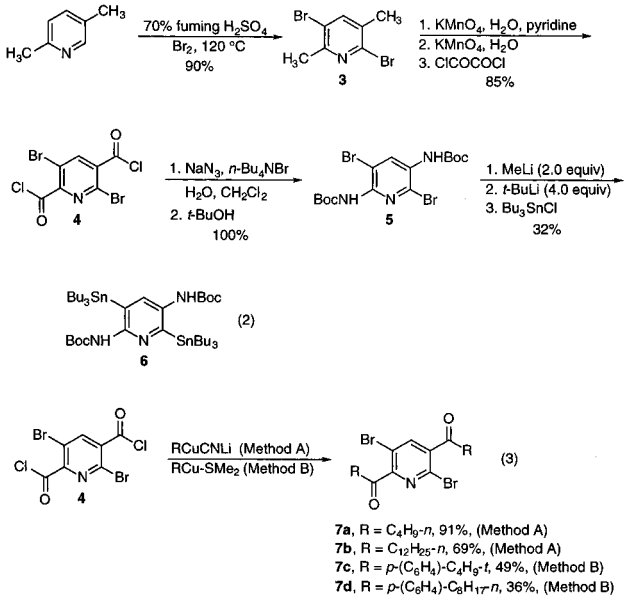


The retrosynthetic strategy for the synthesis of the planar polypyridines (**1**) is outlined in eq 1. The planarization was planned via Schiff base formation between alternating amine and ketone moieties.[4h] This approach permits the imine bridges to (i) form in high yields upon proton activation once the polypyridine backbone is established, (ii) be substituted so that the newly formed polymers are soluble, and (iii) contain double-bonded ladder units to keep the consecutive aryl moieties planar which maximize extended π-conjugation through the polypyridine backbones, thereby increasing the bandwidths and lowering the band gaps.[3] We chose to utilize dimetalodiamines and dihalodiketones as the monomer units (rather than the complementary usage of dimetalodiketones and dihalodiamines) because subsequent oxidative addition reactions of the inherently electron rich late transition metal coupling catalysts are facilitated by electron deficient aryl halides.[2h,i,7] Finally, the two monomers can be prepared from the common dibromopyridinedicarboxylic acid **2**.

The monomers for the polymerization reactions can be prepared rapidly as shown in eqs 2 and 3. Due to the electrophilicity of the pyridyl ring system, 2,5-lutidine can only undergo electrophilic bromination to afford **3** under extremely vigorous conditions.[8] The two-step permanganate oxidation process provides far better yields of the diacid **2** than either of



the two oxidation reactions alone. Conversion of **2** to the di(carboxylic acid chloride) **4** permits divergence to the two needed monomers. Remarkably, conversion of **4** to the bis(acyl azide) under phase transfer conditions followed by a bis(Curtius) rearrangement and *tert*-butyl alcohol capture of the isocyanates affords the bis(Boc-protected)diamine **5** in quantitative yield.[4h,9] Removal of the NH protons with MeLi is followed by lithium−halogen exchange with *tert*-BuLi affording the tetralithio-intermediate that is quenched with chlorotri-*n*-butylstannane to yield the desired distannyldiamine **6** (eq 2). Use of excess *tert*-BuLi, without MeLi treatment, could be problematic because lithium−halogen exchange with *tert*-BuLi is faster than deprotonation of the Boc-protected amine and could result in subsequent proton transfer and overall reduction of **5**.[4h] Stannane **6** undergoes severe decomposition during column chromatography, and some decomposition is unavoidable even when amine-washed silica gel is used. After workup, rapid flash chromatography of the crude product on an amine-washed silica gel column followed by standing in air for several days gives colorless crystals of **6**. To ensure the high purity of monomers required for the step-growth polymerizations, **6** is further recrystallized from methanol, thereby resulting in its low isolated yield.

The dibromodiketone-containing pyridine monomers **7a**−**d** are prepared by lower order cyanocuprate or organocopper additions to the acyl moieties. The latter neutral copper reagent works more efficiently for the aryl additions to form **7c** and **7d**. Use of ArZnCl/Pd(0) results in multiple products, presumably from addition to the 2-position of **4** due to that center's activation by an α-nitrogen and a β-carbonyl moiety. Use of **4** in a Friedel−Crafts reaction to prepare **7c** and **7d** is unsuccessful.

The polymerization reactions between **6** and **7a**−**d** are shown in eq 4. The optimal catalyst system for the polymerization of the pyridine monomers is $PdCl_2(PPh_3)_2$/CuI in mixed solvents of THF/NMP or toluene/NMP.[2h,2i,7] In the reactions, no polypyridines are isolated without the addition of CuI, even if the mixture is heated for 7 days. Moreover, PPh_3 is the preferred

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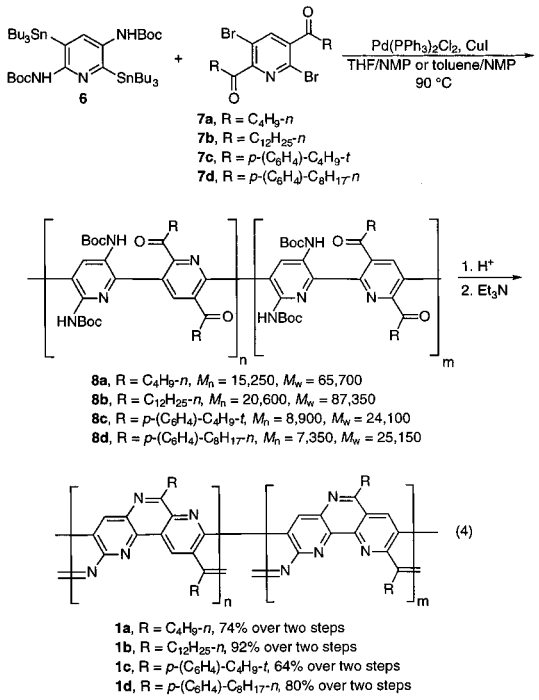

ligand since $PdCl_2(AsPh_3)_2$/CuI gives no polypyridine products. The polar solvent additive NMP can stabilize the homogeneous catalyst; deletion of the additive results in no polypyridines. If only THF is used as the solvent, starting material remains after 7 days. However, some THF or toluene is needed to maintain the solubility of these polymers. In contrast, with thiophene-based polymerizations involving thienylstannanes and thienyl halides, we find that $Pd(dba)_2$/CuI/$AsPh_3$ is the optimal system.[5] For poly(phenylene thiophene)s, $Pd(dba)_2$/$AsPh_3$ is the optimal system; addition of CuI retards the coupling reaction.[5] Therefore, we observe no general catalyst system for this range of arylstannane-aryl halide polymerizations; several catalyst mixtures need to be investigated for each particular monomer combination. The lower molecular weights obtained for the polymers with the aryl pendant groups, **8c** and **8d**, are presumably due to greater steric interactions inhibiting the oxidative addition, the typical slow step in the cross-coupling reaction sequence. All the polymers are analyzed prior to planarization by size exclusion chromatography (SEC) in THF relative to polystyrene (PS) standards. Since SEC is a measure of the hydrodynamic volume rather than the molecular weight, significant yet consistent errors in M_n and M_w usually result when comparing rigid rod polymers to the flexible coils of PS standards. The M_n data in this range are generally larger than the actual molecular weights by a factor of 1.5−2.[10]

Exposure of **8a**−**d** to trifluoroacetic acid (TFA) induces Boc-removal and Schiff base formation to afford the planarized polymers **1a**−**d**, respectively. There are only trace amounts of carbonyl groups, and no Boc absorptions, in the FTIR spectra of **1a**−**d**. There are no remaining CH_2CO resonances in the ^{1}H NMR spectrum of **1b** (**1a** is insufficiently soluble to be clearly examined by NMR). The weak carbonyl absorptions are probably derived from the end groups. Further heating in an amine solvent at high temperature is required for the clean cyclization/planarization of **8a** and **8c**. As with other ladder polymers that we have prepared, the planar polypyridines are only soluble in acidic media such as CH_2Cl_2/TFA (3/2).[4h,5] It is apparent from the spectral and elemental analysis data that partial loss of the Boc groups and cyclization occurs in **8a**−**d** under the polymerization conditions. Boc-protected amines are known to be thermally labile.[11] Hence it is more accurate to record the yields for the two-step sequences **7a**−**d** to **1a**−**d**, respectively, as shown in eq 4. Thus the imine formation strategy provides an efficient method for planarization because all the requisite atoms are present in the monomers; we can avoid the difficult problem of introducing new atoms along a rigid rod backbone from exogenous reagents. Intermolecular Schiff bases unlikely remain in the final polymers since that would have resulted in a cross-linked insoluble network; the more stable six-membered imine ring is thermodynamically preferred.

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Table 1. Optical Data for the Polypyridines

compd	λ_{abs} (THF),[a] (nm)	λ_{abs} (CH_2Cl_2/TFA, 3/2),[a] (nm)	λ_{emis} (THF),[b] (nm)	λ_{emis} (CH_2Cl_2/TFA, 3/2), (nm)
8a	355, 438	*c*	529	*c*
8b	352, 437	*c*	534	*c*
8c	364, 451	*c*	540	*c*
8d	363, 453	*c*	530	*c*
1a	*d*	351, 559	*d*	NE[e]
1b	*d*	355, 566	*d*	NE[e]
1c	*d*	350, 512	*d*	NE[e]
1d	*d*	348, 505	*d*	NE[e]

[a] No absorptions <310 nm are listed here. The underlined values are the more intense of the two listed. [b] Excitation wavelength was 350 nm. [c] Addition of TFA would result in loss of the Boc group. [d] The polymers were not soluble in THF. [e] No emission signal was observed.

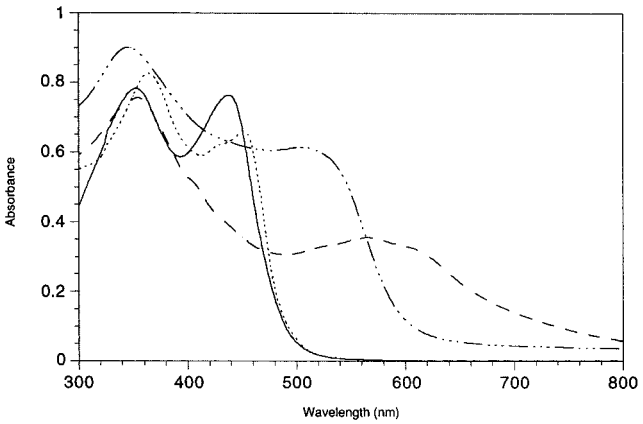

Figure 1. Optical Spectra of **8b** (THF) (−), **1b** (CH_2Cl_2/TFA, 3/2) (− − −), **8c** (THF) (···), and **1c** (CH_2Cl_2/TFA, 3/2) (−···−).

The optical absorption data were recorded in THF for **8a**−**d** and CH_2Cl_2/TFA (3/2) for **1a**−**d** (Table 1, Figure 1). Compounds **8a**−**d** have two major absorption bands. The lower wavelength bands are at 352−364 nm, which are close to the absorptions of the less sterically encumbered poly(pyridine-2,5-diyl)s (ca. 370 nm in formic acid) and poly(6-hexylpyridine-2,5-diyl) (ca. 340 nm in formic acid; ca. 320 nm in benzene).[6a] However the higher wavelength absorptions at 437−453 nm in **8a**−**d** are unique. Several factors could account for this observation. First, **8a**−**d** are partially planarized as discussed above, thereby generating units that are further conjugated and bathochromically shifted. Second, the amine-bearing pyridyl units are more electron rich than the ketone-bearing pyridyl rings. This establishes an alternating electron donor/acceptor arrangement which generates intramolecular charge-transfer character along the polymer backbone that can result in large

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bathochromic shifts.[5,6i,12] Third, intramolecular hydrogen bonding between the protons of Boc-protected amines and the adjacent pyridine nitrogens may induce planarity in the polymer backbones and further extend the π-conjugations with concomitant bathochromic shifts.[2e−h] These factors notwithstanding, there are enormous bathochromic shifts upon Schiff base formation (**8a**−**d** to **1a**−**d**, respectively) indicative of greater electron delocalizations through the polymer backbones once planarizations are achieved (Table 1, Figure 1). Since Boc-removal and planarization would have accompanied the study of **8a**−**d** in acidic solvents, and the different solvent systems (neutral versus acidic) can have influences on the degree of intramolecular charge transfer in the planar systems,[5] further comparisons between the optical spectra of **8a**−**d** and **1a**−**d** would not be conclusive. However, the best analogy comes from comparison of **1a**−**d** with the reported poly(pyridine-2,5-diyl) and poly(6-hexylpyridine-2,5-diyl)[6a] wherein all the spectra were recorded in an acidic environment. There are ca. 200 nm bathochromic shifts in the planarized polypyridines versus the nonplanar polypyridines. Poly(pyridine-2,5-diyl) and poly(6-hexylpyridine-2,5-diyl) have optical band gaps of 3.3 eV,[6a] while the planar polymers here have 1.3−1.8 eV smaller optical band gaps (**1a** = 1.5 eV, **1b** = 1.5 eV, **1c** = 2.0 eV, **1d** = 2.0 eV as determined from the tailing edge of the optical spectra). This demonstrates the efficacy of the planarization strategy for obtaining dramatic decreases in the optical band gaps of conjugated polymers. Attempts to cast films of **1a**−**d** from CH_2Cl_2/TFA followed by removal of the solvent in vacuo does not permit salt removal as judged by FTIR analysis.[6i]

Emission signals with large Stokes shifts are apparent for the preplanar polymers **8a**−**d** in THF. Polymers **1a**−**d** showed no emission signals; a trend we have observed in other nitrogen-containing planar aromatic polymers (Table 1).[5] Therefore, the nitrogen atoms play a key role in exciton quenching.

In summary, synthetic routes to planar polypyridines are described which represent the first examples of planar conjugated polymers based on electron deficient heterocycles. Several novel transformations of the pyridine intermediates are used to attain the desired monomers. These include bis(Curtius) rearrangements and bis(metalation) reactions by lithium−halogen exchange to afford highly functionalized pyridines. Pd/Cu-couplings yield the polymerized products that can be easily planarized via the formation of imine bridges by proton activation. Thus the effective formation of electron deficient ladder polymers is achieved which demonstrates the efficacy of ladder formation for intense optical band gap shortening. Further optoelectronic studies may reveal unique properties of these planar polymers which could also act as proton acceptors and metal binders.

Experimental Section

General Methods. Unless otherwise noted, all operations were carried out under a dry, oxygen-free nitrogen atmosphere. Molecular weight analyses were performed using two 30 × 75 cm Burdick and Jackson GPC columns (10^5 Å 10 μ and 500 Å 5 μ) eluted with THF at 60 °C (flow rate 1.0 mL/min). Molecular weight results were based on five polystyrene standards (M_w = 435 500, 96 000, 22 000, 5050, and 580 with a correlation coefficient >0.9998) purchased from Polymer Laboratories Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using an Alltech model 932525 (25 m × 0.25 mm, 0.2 μm film of AT-1 stationary phase) capillary GC column. Alkyllithium reagents were obtained from FMC. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade benzene and dichloromethane were distilled over calcium hydride. Bulk grade hexane was distilled prior to use. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out using 230−400 mesh silica gel from EM Science. Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. Unless otherwise noted, all monomers for the polymerizations were >99.5% pure, and all other nonpolymeric materials were >96% pure as judged by NMR, GC, or combustion analyses. The absorption and emission spectral data are listed in Table 1, while the molecular weight data are listed in the equations.

2,5-Dibromo-3,6-dimethylpyridine (3).[8] The procedure by Abblard was modified as follows. A stock solution of 70% fuming sulfuric acid was prepared by slowly adding molten SO_3 (40 g) to commercially available 30% fuming sulfuric acid (15.7 mL) and storing it in a Teflon-capped bottle. To 70% fuming sulfuric acid (30 mL) in a screw cap tube cooled to −78 °C was slowly added 2,5-lutidine (11.6 mL, 100 mmol) and bromine (7.2 mL, 140 mmol). The tube was capped, and the mixture was warmed to room temperature and then heated to 100 °C. After 41 h, the temperature was raised to 120 °C and held there for an additional 9 h. The solution was allowed to cool to room temperature and poured onto ice. The precipitate was collected by filtration. The solid was washed with water and dissolved in ether and filtered. The ether solution was washed with water (3×) and dried over magnesium sulfate. Removal of solvent in vacuo gave 23.0 g (87%; 90% based on the 96% purity of commercially available 2,5-lutidine) of **3** as a white solid. Mp 87−88 °C (lit.[8a] 92 °C). FTIR (KBr) 3415, 3138, 3015, 1574, 1523, 1420, 1384, 1333, 1128, 1077, 969, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1 H), 2.58 (s, 3 H), 2.31 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.49, 141.92, 141.83, 133.97, 120.08, 23.98, 21.18.

2,5-Dibromo-3,6-pyridinedicarboxylic Acid (2). To **3** (21.76 g, 82.1 mmol) in pyridine (120 mL) at 100 °C was added aqueous potassium permanganate (58.4 g/750 mL of H_2O) over 4 h through a dropping funnel. After the addition, the mixture was stirred until the purple color disappeared. The reaction mixture was cooled to ca. 60 °C and filtered. The residue was washed with hot water and ethyl acetate. The aqueous layer was extracted with ethyl acetate (2×). The combined organics gave unreacted starting material **3** (4.23 g). The aqueous solvent was removed to give a white solid which was a mixture of potassium salts of the diacid and monoacid. This solid was redissolved in water (150 mL). The solution was heated to reflux, aqueous potassium permanganate (19 g/250 mL water) was added over 40 min, and the solution was further stirred for 1 h. The reaction mixture was cooled to room temperature, and methanol (10 mL) was added. Filtration and removal of solvent afforded a white solid. The solid was acidified to ca. pH = 1 with 3 N HCl. The resultant slurry was extracted with ethyl acetate (3×). The extracts were washed with brine and dried over magnesium sulfate. Removal of solvents in vacuo afforded **2** as a white solid (18.21 g, 85% on reacted **3**). Mp 171−173 °C. FTIR (KBr) 3500−2100, 1707, 1569, 1446, 1379, 1328, 1272, 1226, 1066, 923, 785 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 8.5 (s, 1 H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.36, 165.07, 153.10, 144.06, 137.30, 133.77, 116.14.

3,6-Dibromo-2,5-pyridinedi(carboxylic acid chloride) (4). To **2** (13.17 g, 40.5 mmol) in benzene (100 mL) was added one drop of DMF and oxalyl chloride (10.8 mL, 122 mmol). The mixture was heated to reflux for 6 h. The resulting golden yellow clear solution was cooled to room temperature. The solvent was removed in vacuo to give **4** as a crystalline yellow solid (14.72 g, 100%). Mp 62−67 °C. FTIR (KBr) 3073, 1749, 1560, 1389, 1323, 1200, 1089, 922, 850, 713 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.14, 163.51, 151.11, 145.79, 136.73, 136.14, 116.86.

***N,N′*-Di(*tert*-butoxycarbonyl)-2,5-diamino-3,6-dibromopyridine (5).** A solution of **4** (7.6 g, 21.0 mmol) in dichloromethane (40 mL)

(12) (a) Ferraris, J. P.; Bravo, A.; Kim, W.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1994**, 991. (b) Karikomi, M.; Kitamura, C.; Tanak, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791. (c) Havinga, E. E.; Ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119. (d) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

was added to a mixture of tetra-*n*-butylammonium bromide (12 mg), saturated aqueous sodium azide (20 mL, 130 mmol, ca. 6.4 M), and dichloromethane (20 mL) at −5 to 0 °C over 20 min. The mixture was further stirred for 10 min at −5 to 0 °C. The organic layer was separated. The aqueous layer was extracted with cold dichloromethane (2×). Combined organic fractions were washed with cold water (2×) and cold brine (1×). The solution was dried over magnesium sulfate at 0 °C for 10 min and filtered. The filtrate was stirred with calcium hydride at 0 °C for 45 min. The mixture was filtered through a pad of Celite. To the filtrate (ca. 200 mL) was added *tert*-butyl alcohol (44 mL, 460 mmol), and the mixture was heated to reflux for 12 h. The colorless solution was cooled to room temperature. Removal of solvents in vacuo gave **5** as a white solid (9.81 g, 100%). Mp 164 °C (dec). FTIR (KBr) 3303, 2985, 2933, 1703, 1564, 1528, 1513, 1364, 1354, 1272, 1256, 1231, 1149, 1103, 1046, 1026, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (br s, 1 H), 6.98 (br s, 1 H), 6.88 (br s, 1 H), 1.51 (s, 9 H), 1.50 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.91, 150.82, 142.31, 131.58, 130.91, 127.74, 110.22, 82.17, 81.67, 28.21, 28.19. HRMS calcd for $C_{15}H_{21}Br_2N_3O_4$: 464.9899. Found: 464.9883.

***N,N′*-Di(*tert*-butoxycarbonyl)-2,5-bis(tri-*n*-butylstannyl)-3,6-diaminopyridine (6).** Methyllithium (1.3 mL, 2.2 mmol, 1.67 M in ether) was added dropwise to a suspension of **5** (0.467 g, 1.00 mmol) in ether (10 mL) at 0 °C. After 30 min, the pale yellow slurry was cooled to −78 °C, and *tert*-butyllithium (2.9 mL, 4.5 mmol, 1.57 M in pentane) was added. The mixture was stirred at −78 °C for 40 min and another 30 min at room temperature. The resultant brown slurry was recooled to −78 °C. Chlorotri-*n*-butylstannane (1.4 mL, 5 mmol) was added, followed by THF (10 mL). The solution was allowed to warm to room temperature and was stirred for 50 min before pouring into water. The aqueous phase was extracted with ether. The combined organic fractions were washed with water and brine. The solution was dried over sodium sulfate, and the solvent was removed in vacuo. Flash chromatography (silica gel, treated with 10% triethylamine in hexane, then rinsing with hexane, and using hexane as eluent) gave a yellow oil. The oil was left standing in air for 5 days and crystals formed. The crystals were washed with methanol and recrystallized from methanol to afford **6** as colorless cubic crystals (0.281 g, 32%). Mp 86−87 °C. FTIR (KBr) 3223, 3169, 3116, 2957, 2913, 2860, 1698, 1560, 1501, 1458, 1384, 1362, 1245, 1154, 1064 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (br s, 1 H), 6.87 (s, 1 H), 6.12 (br s, 1 H), 1.57−1.50 (m, 12 H), 1.48 (s, 9 H), 1.47 (s, 9 H), 1.35−1.26 (m, 12 H), 1.09 (t, J = 8.2 Hz, 6 H), 1.02 (t, J = 8.3 Hz, 6 H), 0.87 (t, J = 7.3 Hz, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.33, 153.52, 137.79, 128.10, 80.33, 29.14, 29.07, 28.34, 28.31, 27.48, 27.34, 13.66, 13.63, 11.64, 10.32. Anal. Calcd for $C_{39}H_{75}N_3O_4Sn_2$: C, 52.78; H, 8.52; N, 4.73. Found: C, 52.84; H, 8.52, N, 4.67. HRMS calcd for $^{12}C_{35}H_{66}{}^{14}N_3{}^{16}O_4{}^{120}Sn_2$ (M−C_4H_9): 832.3079. Found: 832.3076.

2,5-Bis(1′-oxo-*n*-pentyl)-3,6-dibromopyridine (7a). To a suspension of copper(I) cyanide (2.26 g, 25 mmol) in THF (50 mL) at −78 °C was added dropwise *n*-butyllithium (14.5 mL, 22 mmol, 1.52 M in hexane). The slurry was warmed to −20 °C and then recooled to −78 °C. A precooled THF (10 mL) solution of **4** (3.62 g, 10 mmol) at −78 °C was transferred via cannula to the above green/black cuprate slurry. The slurry was stirred for 15 min at −78 °C. A saturated solution of NH_4Cl/NH_4OH (9/1, 50 mL) was added. The mixture was warmed to room temperature and filtered. The aqueous phase was separated and extracted with ether (2×). The combined organic fractions were washed with water (2×) and brine (1×). The solution was dried over magnesium sulfate and filtered. Removal of the solvent in vacuo followed by flash chromatography [silica gel, hexane/ether (15:1)] gave **7a** as a pale yellow solid (3.7 g, 91%). Mp 45−46 °C. FTIR (KBr) 2964, 2933, 2872, 1713, 1564, 1462, 1405, 1328, 1256, 1195, 1123, 1092, 1015, 974, 769 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1 H), 3.04 (t, J = 7.3 Hz, 2 H), 2.92 (t, J = 7.3 Hz, 2 H), 1.69 (p, J = 7.4 Hz, 2 H), 1.67 (p, J = 7.5 Hz, 2 H), 1.39 (sext, J = 7.6 Hz, 4 H), 0.933 (t, J = 7.3 Hz, 3 H), 0.930 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz $CDCl_3$) δ 200.88, 199.90, 154.05, 142.25, 141.07, 134.78, 116.44, 42.42, 39.74, 25.84, 25.59, 22.22, 22.18, 13.88, 13.81. Anal. Calcd for $C_{15}H_{19}Br_2NO_2$: C, 44.47; H, 4.73; N, 3.46. Found: C, 44.47; H, 4.67; N, 3.48. HRMS calcd for $C_{15}H_{19}Br_2NO_2$: 402.9782. Found: 402.9763.

2,5-Bis(1′-oxo-*n*-tridecyl)-3,6-dibromopyridine (7b). To a solution of *tert*-butyllithium (30.3 mL, 50 mmol, 1.65 M in pentane) in ether (20 mL) at −78 °C was added 1-iododododecane (6.3 mL, 25 mmol) dropwise. The solution was warmed to 0 °C and transferred via cannula to a suspension of copper(I) cyanide (2.53 g, 28 mmol) in THF (45 mL) at −78 °C. The slurry was stirred for 25 min before warming to 0 °C. The resultant green/black solution was recooled to −78 °C, and a precooled THF (10 mL) solution of **4** (3.62 g, 10 mmol) at −78 °C was added by cannula. The slurry was stirred for 10 min at −78 °C. A saturated solution of NH_4Cl/NH_4OH (9/1, 50 mL) was added. The mixture was warmed to room temperature and filtered. The aqueous phase was separated and extracted with ether (2×). Combined organic fractions were washed with water (2×) and brine (1×). The solution was dried over magnesium sulfate. The solvent was removed in vacuo. The residues were dissolved in a hexane/CH_2Cl_2 mixture (3/2) and filtered through a plug of silica gel. Removal of the solvents in vacuo followed by recrystallization from hexane gave **7b** as light yellow crystals (4.32 g, 69%). Mp 58−60 °C. FTIR (KBr) 2913, 2854, 1703, 1560, 1466, 1406, 1312, 1099, 955, 901, 777, 717 cm^{-1}. ^1H NMR (400 MHz $CDCl_3$) δ 7.84 (s, 1 H), 3.03 (t, J = 7.3 Hz, 2 H), 2.91 (t, J = 7.3 Hz, 2 H), 1.69 (p, J = 7.2 Hz, 2 H), 1.67 (p, J = 7.5 Hz, 2 H), 1.24 (m, 36 H), 0.86 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.92, 199.95, 154.05, 142.26, 141.06, 134.80, 116.45, 42.72, 40.04, 31.91, 29.69, 29.65, 29.62, 29.57, 29.46, 29.41, 29.34, 29.08, 29.02, 23.80, 23.53, 22.68, 14.11. Anal. Calcd for $C_{31}H_{51}Br_2NO_2$: C, 59.14; H, 8.16; N, 2.22. Found: C, 59.22; H, 8.10; N, 2.23. HRMS calcd for $C_{31}H_{51}Br_2NO_2$: 627.2287. Found: 627.2283.

2,5-Bis(*p*-*tert*-butylbenzoyl)-3,6-dibromopyridine (7c). To *p*-(*tert*-butyl)bromobenzene (3.20 g, 15 mmol) in THF (15 mL) at −78 °C was added *tert*-butyllithium (17.9 mL, 30 mmol, 1.68 M in pentane) dropwise. The solution was stirred for 20 min and transferred via cannula to a suspension of copper(I) bromide dimethyl sulfide complex (3.29 g, 16 mmol) in THF (25 mL) at −78 °C. The mixture was stirred for 35 min. To this mixture was added by cannula a precooled THF (6 mL) solution of **4** (1.81 g, 5 mmol) at −78 °C. The resultant slurry was stirred for 20 min at −78 °C. A saturated solution of NH_4Cl/NH_4OH (9/1, 10 mL) was added. The mixture was warmed to room temperature and filtered. The aqueous phase was separated and extracted with ether (2×). Combined organic fractions were washed with 1 N HCl (1×), water (2×), and brine (1×). The solution was dried over magnesium sulfate and then filtered. Removal of solvents followed by flash chromatography [silica gel, hexane/Et_2O (12/1) and then hexane/CH_2Cl_2 (1/1) as eluent], and recrystallization from ethyl acetate gave **7c** as white crystals (1.37 g, 49%). Mp 204.5−206 °C. FTIR (KBr) 3046, 2964, 2872, 1682, 1600, 1564, 1462, 1415, 1364, 1323, 1262, 1190, 1169, 933, 908, 846, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1 H), 7.80 (d, J = 8.4 Hz, 2 H), 7.78 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.52 (d, J = 8.2 Hz, 2 H), 1.35 (s, 9 H), 1.34 (s, 9 H). ^{13}C NMR (100 MHz $CDCl_3$) δ 191.47, 190.74, 159.06, 158.73, 157.50, 141.23, 139.62, 136.32, 132.25, 131.55, 130.47, 130.33, 126.13, 125.93, 116.58, 35.44, 35.39, 31.02. Anal. Calcd for $C_{27}H_{27}Br_2NO_2$: C, 58.19; H, 4.88; N, 2.51. Found: C, 58.32; H, 4.92; N, 2.41. HRMS calcd for $C_{27}H_{27}Br_2NO_2$: 555.0409. Found: 555.0406.

2,5-Bis(*p*-*n*-octylbenzoyl)-3,6-dibromopyridine (7d). To *p*-(*n*-octyl)bromobenzene[4h] (5.65 g, 21 mmol) in THF (20 mL) at −78 °C was added *tert*-butyllithium (25 mL, 42 mmol, 1.68 M in pentane) dropwise. The solution was stirred for 15 min and added by cannula to a suspension of copper(I) bromide dimethyl sulfide complex (4.52 g, 22 mmol) in THF (30 mL) at −78 °C. The mixture was stirred for 20 min. To the mixture was added by cannula a precooled THF (6 mL) solution of **6** (3.62 g, 10 mmol) at −78 °C. The resultant slurry was stirred for 20 min at −78 °C. A saturated solution of NH_4Cl/NH_4OH (9/1, 10 mL) was added. The mixture was warmed to room temperature and filtered. The aqueous phase was separated and extracted with ether (2×). Combined organic fractions were washed with 1 N HCl (1×), water (2×), and brine (1×). The solution was dried over magnesium sulfate and then filtered. Removal of solvents followed by flash chromatography [silica gel, hexane/ethyl acetate (20/1) and then CH_2Cl_2 as eluent], and recrystallization from hexane gave **7d** as white cotton-like crystals (2.41 g, 36%). Mp 101.5−102.5 °C. FTIR (KBr) 3056, 2954, 2923, 2851, 1677, 1662, 1605, 1333, 1251,

1164, 1082, 939, 908 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1 H), 7.77 (d, $J = 7.9$ Hz, 2 H), 7.75 (d, $J = 7.9$, 2 H), 7.33 (d, $J = 8.6$ Hz, 2 H), 7.30 (d, $J = 8.5$, 2 H), 2.69 (t, $J = 6.2$ Hz, 2 H), 2.67 (t, $J = 7.3$ Hz, 2 H), 1.64 (m, 4 H), 1.30−1.25 (m, 20 H), 0.86 (t, $J = 6.8$ Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.50, 190.79, 157.45, 151.13, 150.84, 141.24, 139.63, 136.37, 132.54, 131.83, 130.61, 130.48, 129.18, 128.99, 116.58, 36.22, 31.84, 30.98, 29.39, 29.28, 29.20, 22.65, 14.10. Anal. Calcd for $C_{35}H_{43}Br_2NO_2$: C, 62.79; H, 6.47; N, 2.09. Found: C, 62.68; H, 6.50; N, 2.09. HRMS calcd for $C_{35}H_{43}Br_2NO_2$: 667.1661. Found: 667.1636.

General Procedure for Polymerization Reactions of Pyridine-Derived Monomers. To an oven dried screw cap tube was added the dibromodiketone monomer (1.0 equiv), **6** (1.02 equiv), $PdCl_2(PPh_3)_2$ (0.02 equiv), and CuI (0.02 equiv). The tube was transferred to a nitrogen-filled drybox. To the tube was added THF (toluene was used for **8c**) and NMP. The tube was capped and heated to 90 °C for 2 days (unless otherwise stated). The reaction mixture was cooled to room temperature. Dichloromethane (10 mL) was added, and the mixture was filtered through a pad of Celite. The solution was concentrated in vacuo to ca. 10 mL which was then added to acetone (methanol was used for **8d**) (150 mL) dropwise. The precipitate was collected by filtration. The solid was dissolved in a minimal amount of chloroform, and the fractional precipitation procedure was repeated. As stated previously, the analytical analysis data suggested that partial cyclization had occurred; therefore, the yield was calculated after the planarization step.

Polymer 8a. Used were **6** (1.810 g, 2.04 mmol), **7a** (0.810 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol), CuI (0.008 g, 0.04 mmol), THF (20 mL), and NMP (10 mL). **8a** was obtained as a brown solid (0.695 g). FTIR (cast) 3210, 2954, 2933, 2872, 1728, 1574, 1503, 1467, 1369, 1236, 1154, 1082, 1051, 764 cm^{-1}. ^1H NMR (400 MHz) δ 8.0−7.4 (br m), 4.0−3.0 (br m), 2.3−0.9 (br m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 166.6, 153.6−121.4, 81.8, 44.3, 39.5, 35.0, 31.6−13.6. Anal. Calcd for $(C_{30}H_{40}N_4O_6)_n$: C, 65.20; H, 7.29; N, 10.14. Found: C, 67.83; H, 6.85; N, 13.07.

Polymer 8b. Used were **6** (0.869 g, 0.98 mmol), **7b** (0.604 g, 0.96 mmol), $PdCl_2(PPh_3)_2$ (0.014 g, 0.019 mmol), CuI (0.004 g, 0.019 mmol), THF (12 mL), and NMP (5 mL). The solution was heated to 80 °C for 3.5 days. **8b** was obtained as a brown solid (0.572 g). FTIR (cast) 3210, 2923, 2851, 1728, 1703, 1574, 1503, 1467, 1369, 1236, 1154, 1082, 1051, 764, 718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.8−7.1 (br m), 3.7−3.1 (br m), 2.13 (br m), 1.7−1.5 (br m), 1.2 (br m), 0.8 (br m). ^{13}C NMR (125 MHz $CDCl_3$) δ 204.1, 169.1−165.7, 153.5−121.3, 87.4, 54.1−53.4, 32.3−28.8, 23.0, 14.4. Anal. Calcd for $(C_{46}H_{72}N_4O_6)_n$: C, 71.10; H, 9.34; N, 7.21. Found: C, 74.11; H, 9.23; N, 8.60.

Polymer 8c. Used were **6** (0.453 g, 0.51 mmol), **7c** (0.279 g, 0.5 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol), toluene (3 mL), and NMP (3 mL). The solution was heated to 100 °C for 21 h. Another portion of **6** (0.013 g, 0.015 mmol) and toluene (1 mL) was added. The solution was further stirred at 100 °C for 2 days. **8c** was obtained as a dark brown solid (0.155 g). FTIR (cast) 3313, 3067, 2964, 2903, 2872, 1728, 1672, 1605, 1569, 1508, 1477, 1395, 1364, 1267, 1236, 1154, 1108, 1077, 1015, 944, 908, 846, 764, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.7−7.4 (br m), 1.8−1.0 (br m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.9−153.5, 149.9−139.5, 135.4−121.3, 81.2, 35.4, 31.9, 31.5, 28.6. Anal. Calcd for $(C_{42}H_{48}N_4O_6)_n$: C, 71.57; H, 6.86; N, 7.95. Found: C, 74.41; H, 6.47; N, 9.76.

Polymer 8d. Used were **6** (1.810 g, 2.04 mmol), **7d** (1.339 g, 2.00 mmol), $PdCl_2(PPh_3)_2$ (0.028 g, 0.04 mmol), CuI (0.008 g, 0.04 mmol), THF (10 mL), and NMP (10 mL). The solution was heated to 100 °C for 3 days. **8d** was obtained as a brown solid (1.252 g). FTIR (cast) 3292, 2954, 2923, 2851, 1728, 1667, 1605, 1569, 1549, 1503, 1462, 1410, 1364, 1308, 1267, 1236, 1154, 1076, 1046, 1015, 939, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.6−7.2 (br m), 2.8 (br m), 1.7−0.8 (br m). ^{13}C NMR (125 MHz $CDCl_3$) δ 198.0−193.0, 159.5−120.8, 82.5−81.1, 36.5, 32.6−28.6, 23.1, 14.6, 14.5. Anal. Calcd for $(C_{50}H_{64}N_4O_6)_n$: C, 73.50; H, 7.89; N, 6.86. Found: C, 77.36; H, 7.56; N, 8.40.

General Procedure for Imine-Bridge Formation. To a solution of the polymer in dichloromethane was added trifluoroacetic acid (TFA). The mixture was heated to reflux overnight. After cooling to room temperature, the solution was carefully and slowly added to a mixed solvent of triethylamine and dichloromethane. The precipitate was collected by filtration. The solid was suspended in triethylamine and heated in a screw cap tube. The solution was filtered. The residue was further washed with dichloromethane and ether.

Polymer 1a. Used were **8a** (0.565 g), dichloromethane (20 mL), and TFA (10 mL), and the polymer precipitated from the solution. Further precipitation was performed from triethylamine (35 mL) and dichloromethane (35 mL). The solid and triethylamine (15 mL) were heated to 100 °C for 10 h and 180 °C for 1 day. **1a** was obtained as a dark brown solid (0.380 g, 74% over two steps). FTIR (KBr) 3395, 2954, 2923, 2862, 1697 (w), 1574, 1503, 1462, 1395, 1369, 1292−1108, 903, 821 cm^{-1}. No ^1H NMR data could be obtained due to the minimal solubility. Anal. Calcd for $(C_{20}H_{20}N_4)_n$: C, 75.92; H, 6.37; N, 17.71. Found: C, 69.26; H, 6.00; N, 15.27. The precipitation from the dichloromethane/TFA mixture, hence the low degree of solubility, likely contributed to the poor elemental analysis data obtained.[13]

Polymer 1b. Used were **8b** (0.481 g), dichloromethane (20 mL), and TFA (10 mL). Precipitation was performed from triethylamine (30 mL) and dichloromethane (20 mL). The solid in triethylamine (15 mL) was heated to 90 °C for 6 h. **1b** was obtained as a black solid (0.40 g, 92% over two steps) that had a solubility of ca. 6 mg/mL in CH_2Cl_2/TFA (2:1). FTIR (KBr) 2925, 2848, 1707 (w), 1576, 1465, 1397, 1387, 1363, 1295, 1101, 908, 820. ^1H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ 1.30 (br s, 44 H), 0.88 (br s, 6 H). Anal. Calcd for $(C_{36}H_{52}N_4)_n$: C, 79.95; H, 9.69; N, 10.36. Found: C, 75.28; H, 9.24; N, 10.05.[13]

Polymer 1c. Used were **8c** (0.892 g), dichloromethane (30 mL), and TFA (15 mL). Precipitation was performed from triethylamine (50 mL) and dichloromethane (30 mL). The solid in triethylamine (20 mL) was heated at 100 °C for 13 h and 180 °C for 24 h. **1c** was obtained as a brown solid (0.868 g, 64% over two steps) that had a solubility of ca. 38 mg/mL in CH_2Cl_2/TFA (2:1). FTIR (KBr) 3385, 3056, 2964, 2903, 2872, 1667 (w), 1605, 1492, 1456, 1395, 1364, 1267, 1195, 1103, 1021, 949, 836 cm^{-1}. ^1H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ 8.8−7.6 (m, 8 H), 1.8−1.2 (m, 18 H). Anal. Calcd for $(C_{32}H_{28}N_4)_n$: C, 82.02; H, 6.02; N, 11.96. Found: C, 77.16; H, 6.26; N, 11.32.[13]

Polymer 1d. Used were **8d** (0.196 g), dichloromethane (15 mL), and TFA (5 mL). Precipitation was performed from triethylamine (30 mL) and dichloromethane (10 mL). The solid in triethylamine (10 mL) was heated to 80 °C for 1 day. **1d** was obtained as a brown solid (0.144 g, 80% over two steps) that had a solubility of ca. 30 mg/mL in CH_2Cl_2/TFA (2:1). FTIR (KBr) 2925, 2857, 1666 (w), 1610, 1579, 1553, 1461, 1383, 1301, 1183, 1121, 1018, 951, 838, 807 cm^{-1}. ^1H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ 8.9−7.6 (m, 8 H), 3.0 (m, 4 H), 1.9 (m, 4 H), 1.4 (m, 20 H), 0.97 (m, 6 H). Anal. Calcd. for $(C_{40}H_{44}N_4)_n$: C, 82.72; H, 7.64; N, 9.65. Found: C, 80.08; H, 7.65; N, 9.40.[13]

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(13) It is common to obtain low carbon values in combustion analyses of highly unsaturated polymers based on arene structures. This is due to incomplete combustion with remaining carbon residues. In most cases, the H and N values remain reasonably accurate. See ref 4h and (a) Chimil, K.; Scherf, U. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 217. (b) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411. (c) Stephens, E. B.; Tour, J. M. *Macromolecules* **1993**, *26*, 2420.