Synthesis of Imine-Bridged Phenylenepyridine Ladder Polymers. Optical Band Gap Widening through Intramolecular Charge Transfer in Planar Polymers

Yuxing Yao and James M. Tour*

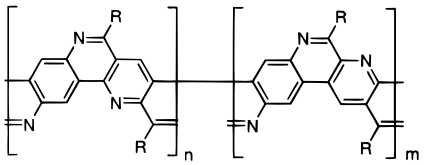
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Received October 16, 1998; Revised Manuscript Received January 12, 1999

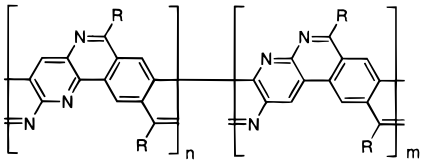
ABSTRACT: The syntheses of planar (ladder) poly(phenylenepyridine)s [(PPhPy)s] are described using Pd-catalyzed cross couplings of aryldistannanes and aryl dihalides. Imine bridges are utilized to effect the planarization of the rigid-rod polymer. In one set of (PPhPy)s, the phenyl rings bear the nitrogen portion of the bridging imines while the pyridine bears the carbon portion of the bridging imine. A second type of (PPhPy)s has the reverse imine-bridging mode. Surprisingly, the study here indicates that construction of alternating donor/acceptor repeat units for inducement of intramolecular charge-transfer resulted in an optical band widening; a result opposite to that obtained in nonplanar polymers possessing alternating donor/acceptor repeat units.

Introduction

Conjugated polymers are presently regarded as promising materials for the development of organic-based electronic devices such as light-emitting diodes, photovoltaic devices, and optoelectronic sensors.[1,2] The optoelectronic properties of conjugated polymers are directly affected by the degree of extended conjugation between the consecutive repeat units and the inherent electron densities in the polymer repeat moieties.[3,4] We and others have shown that an increase of π-conjugation can be attained by forming covalent linkages between the consecutive repeat units for polymer backbone planarization, as reflected by the dramatic decreases in optical band gaps observed in planar polymers.[5,6] Another general approach to lower optical band gaps in conjugated polymers is to construct a regular alternation of electron-donating and electron-accepting moieties to induce intramolecular charge transfer (ICT) within a polymer chain.[7,8] However, the combination of both strategies, planarization and ICT, through the synthesis of planar poly(pyridinethiophene)s, showed an optical band gap widening over that of planar polymers with less pronounced ICT.[9] The unexpected result from the combination of planarization and ICT was intriguing enough to warrant the synthesis of another class of planar conjugated polymers that possess ICT from alternating donor and accepting moieties, namely poly(phenylenepyridine)s (PPhPy)s (**1** and **2**). Though polymers **1** and **2** have similar polymer backbones, **1** should possess greater ICT character than polymer **2**, because the bridging imine nitrogens in **1** will make the inherently electron deficient pyridyl ring even more electron deficient, thereby inducing a larger ICT. Conversely, in polymer **2**, the bridging imine nitrogens would decrease the electron density of the inherently electron richer phenyl ring and result in a smaller ICT effect. In acid-containing solvents, protonation of the bridging imine and main backbone nitrogens would increase the ICT difference between **1** and **2**. Remarkably, the study here indicates that construction of alternating donor/acceptor repeat units for inducement of ICT results in an optical band widening; a result contrary to that obtained in nonplanar polymers possessing alternating donor/acceptor repeat units.



1



2

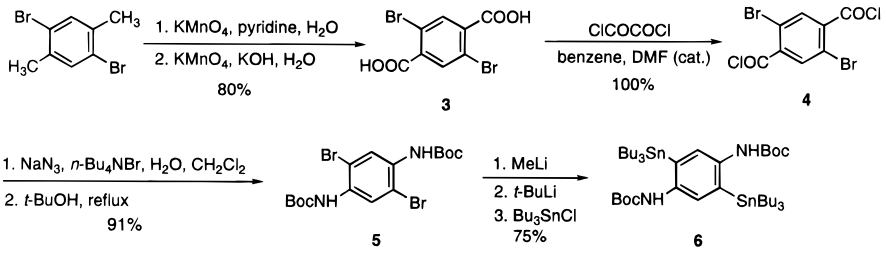
Results and Discussion

The synthesis of the phenyl monomer for **1** is shown in Scheme 1. A two-step oxidation of 1,4-dibromo-*p*-xylene to 1,4-dibromo-2,5-benzenedicarboxylic acid (**3**) has been reported,[5d] but the procedure required 6 days for each step. The use of the condition shown in Scheme 1 greatly reduced the reaction times, and the product was obtained in higher yield. After conversion of **3** to the di(acyl chloride) (**4**), treatment with aqueous sodium azide afforded the di(acyl azide) intermediate[5d] that was directly converted to the bis(*tert*-butoxycarbonyl) (Boc)-protected diaminobenzene **5** by bis-Curtius rearrangement and *tert*-butyl alcohol capture of the isocyanates.[5d,9,10] Deprotonation of the NH protons on **5** followed by lithium−halogen exchange and quenching with tributyltin chloride gave the distannyl monomer **6** in 75% yield.[5l] Unlike its analogue, the bis(pinacol borate),[5d] which had to be purified by a time-consuming charcoal/Celite column due to its extreme instability on silica gel or alumina column, **6** can be easily purified by flashchromatography on an amine treated silica gel column.

The 2,5-dibromophenyl-3,6-diones **7a**−**d** were synthesized as described previously[5l,9] and subjected to

10.1021/ma981618k CCC: $18.00
Published on Web 03/16/1999

Scheme 1



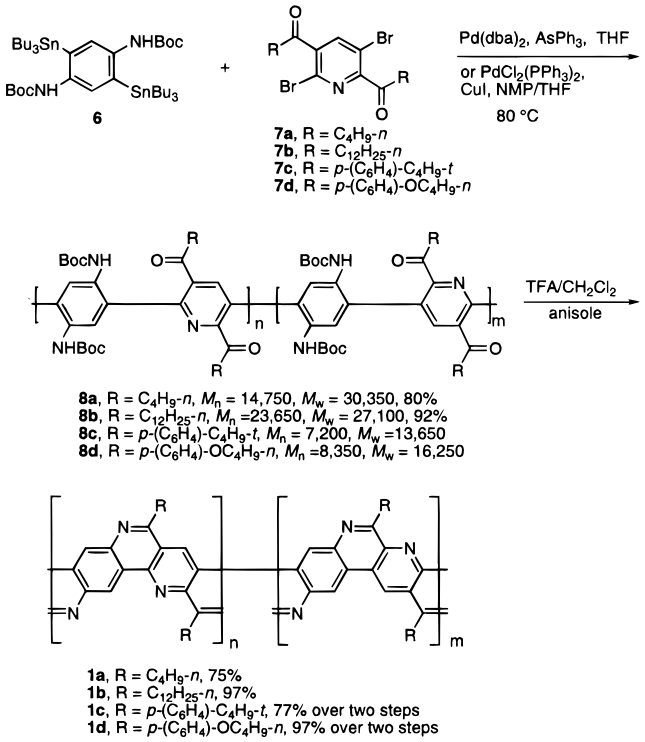
modified Stille cross-coupling conditions with **6**.[2i,m,9,11] $Pd(dba)_2/AsPh_3$ was found to be the optimal catalyst system for polymerizations involving **7a,b**. However, when these condition were applied to the aryl ketones **7c,d**, the Pd catalyst rapidly precipitated and low molecular weight oligomers were obtained. Instead, $PdCl_2(PPh_3)_2$/CuI/NMP/THF proved to be more effective, and the catalyst remained in solution over 6 days. It has been suggested that CuI reacts with organostannanes to produce organocopper intermediates that are presumably more reactive than organostannanes toward transmetalation with the palladium species.[2i,12] Additionally, NMP is known to enhance the stability of the homogeneous Pd intermediates through ligation.[2i,11b]

Polymers **8a**−**d** were purified by precipitation from CH_2Cl_2 into hexane or methanol. All these polymers were soluble in many common organic solvents such as THF and halogenated solvents and thus able to be characterized at this stage. The molecular weights were determined 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; thus, the values provided here (Schemes 2 and 3) serve simply as a reference.[13]

The steric bulkiness of the aryl ketones in **7c,d** could account for the lower molecular weights of **8c,d** when compared to monomers **7a,b** and their corresponding polymers **8a,b**, since both the oxidative addition and the transmetalation steps in Stille couplings are sensitive to the steric bulkiness of the reactants.[2i] The polymers obtained from $Pd(dba)_2/AsPh_3$/THF system (**8a,b**) generally had a good agreement between the actual elemental analysis data and the theoretical values; however, the use of the polar solvent NMP for the synthesis of **8c,d** likely induced some premature Boc removal and thus higher than expected actual carbon content values.[5l,9] This effect has been observed previously in some earlier studies.[5l,13]

Polymers **8a**−**d** were treated with TFA/CH_2Cl_2 and then precipitated into triethylamine/acetone to give planarized polymers **1a**−**d** as a light brown to brown/black solids. The intense IR carbonyl absorption bands in the nonplanar polymers **8a**−**d** disappeared after planarization, though in some cases, trace amounts of the carbonyl absorption were observed, likely from the ketone end groups. Accordingly, weaker carbonyl stretches generally resulted for the planar polymers with higher molecular weights. The ^{1}H NMR signal for CH_2CO in **8b** was not detected in **1b**, consistent with loss of the carbonyl groups upon planarization. Likewise, the protons on the pyridyl and phenyl rings were shifted

Scheme 2



6

7a, R = C_4H_9-*n*
7b, R = $C_{12}H_{25}$-*n*
7c, R = *p*-(C_6H_4)-C_4H_9-*t*
7d, R = *p*-(C_6H_4)-OC_4H_9-*n*

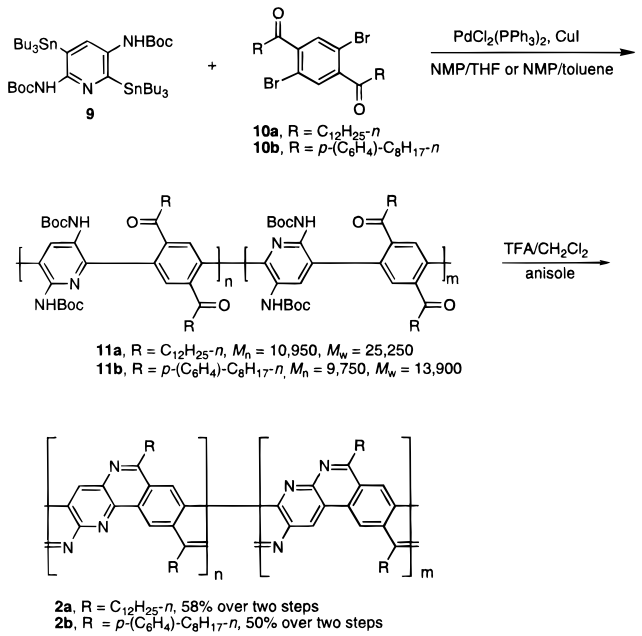
8a, R = C_4H_9-*n*, M_n = 14,750, M_w = 30,350, 80%
8b, R = $C_{12}H_{25}$-*n*, M_n =23,650, M_w = 27,100, 92%
8c, R = *p*-(C_6H_4)-C_4H_9-*t*, M_n = 7,200, M_w =13,650
8d, R = *p*-(C_6H_4)-OC_4H_9-*n*, M_n =8,350, M_w = 16,250

1a, R = C_4H_9-*n*, 75%
1b, R = $C_{12}H_{25}$-*n*, 97%
1c, R = *p*-(C_6H_4)-C_4H_9-*t*, 77% over two steps
1d, R = *p*-(C_6H_4)-OC_4H_9-*n*, 97% over two steps

from 9.0 and 7.6−8.6 ppm to 10.9 and 10.6 ppm, respectively; an observation consistent with the spectral features of other planarized imine-nitrogen containing polymers.[5k,9] The signals for C(CH_3)$_3$ in **1c** and OCH_2 in **1d** also shifted downfield by 0.15−0.35 ppm upon planarization. Polymer **1a** was insufficiently soluble to be clearly examined by NMR.

The complementary polymers **2a,b** were prepared in a manner analogous to the preparation of **1c,d**, starting from the distannylpyridine **9**, which was synthesized as reported previously,[5l] and the diones **10a,b** (Scheme 3). The bis(dodecyl ketone) **10a**[5d] and aryl ketone **10b** were prepared by a lower order cuprate and Friedel−Crafts acylation, respectively. The use of $Pd(dba)_2/AsPh_3$ resulted in recovery of the ketones **10a,b**. Without CuI or the polar solvent additive NMP, no polymer could be isolated. Significant loss of Boc groups and imine-bridge formation took place in the polymerization processes here, as evidenced by the small carbonyl stretches in the IR spectra and the higher than expected carbon contents by elemental analyses. It is not surprising that the Boc groups in **11a,b** are more prone to be cleaved than in **8a**−**d**, since the pyridyl ring is more electron deficient than the phenyl ring. Additionally, a brown solid precipitated from the reaction solution during the polymerization of **11a,b**, an event not observed in the syntheses of **8a**−**d**, further suggesting much premature Boc loss and planarization. **11a,b** were converted to the

Scheme 3



planar polymers **2a,b**, respectively, upon TFA/CH_2Cl_2 treatment. FTIR and ^{1}H NMR showed the imine formation. The weak carbonyl absorption in **2a** and the small yet observable CH_2CO resonance in **2a** are due to the less efficient polymerization than that obtained for **8b** and its corresponding planar polymer **1b**.

The optical data for nonplanar polymers were recorded in THF (Table 1, Figures 1and 2). The optical absorption maxima for **8a**−**d** are ca. 300−330 nm. Polymers **11a,b** have two major absorption bands at 326 and 327 nm followed by 442 and 458 nm, respectively. The low-energy absorption bands observed for **11a,b** are likely due to the extended conjugation resulting from the large amounts of premature NMP-induced planarization, as described above.

As expected, in all cases, there were large bathochromic shifts upon planarization (**8a**−**d** to **1a**−**d**, respectively, and **11a,b** to **2a,b**, respectively). However, the optical spectral data for planar polymers were recorded in CH_2Cl_2/TFA (2/1) (Table 1). Since the planar polymers were only soluble in acid-containing solvents such as CH_2Cl_2/TFA and the use of any acid for recording the spectra of nonplanar polymers would have caused the loss of Boc groups and imine-bridge formation, a precise comparison of the optical properties between the nonplanar and planar polymers is difficult due to the vastly different solvents used. Therefore, the observed large bathochromic shifts in the planarized polymers **1** and **2** relative to their nonplanar precursors could be an effect of the enhanced π-conjugation upon planarization, changes in ICT, and a solvent-induced difference (Figures 1 and 2). Interestingly, in the planar polymers, the aryl-substituted polymers showed intense low-energy bands beyond their alkyl-substituted counterparts (Table 1). Planar polymers with electron-donating side groups resulted in lower energy bands (**1c** at 520 nm versus **1d** at 560), as we observed in our previous poly(pyridinethiophene) studies.[9] Most importantly, polymer **2** showed intense low-energy bands over polymer **1** having the same or similar side groups (**1b** at λ 397 nm versus **2a** at λ 511 nm, and **1c** at λ 520 nm versus **2b** at λ 556 nm, comparison in Figure 3). Therefore, ICT between the consecutive repeat units does not aid in reducing the optical band gaps in these planar polymers. In fact, contrary to our observations in several nonplanar polymer cases,[7l] the system with the lower ICT (**2**) possessed the lower energy bands.

It is also useful to compare the optical properties of **1b** and **2a** with other planar heterocyclic polymers that we have previously prepared possessing the same side groups, namely dodecyl-substituted planar polypyridines (**12**),[5l] planar poly(phenylenethiophene)s (**13**),[5k] and planar poly(pyridinethiophene)s (**14**) (Figure 4).[9] Again, consistent with the findings observed for **1** and **2** with the same substituents, the absorption bands of **12** and **2a**, polymers with the lowest expected ICT characters, showed the lowest band gaps. This same trend was seen in **13** and **14** where increased ICT resulted in band gap widening. Therefore, in the planarized polymers where maximization of extended π-conjugation occurs through planarization, enhanced ICT results in an increase in the absorption energy, a finding that is in direct contrast to the other nonplanar polymers that have been prepared.[7l] However, by comparing the optical spectra of **1** and **2** series polymers in Figure 3, we do note that the shape of the low-energy bands of **2a,b**, with their steep absorption edges and well-resolved vibronic sidebands, are not characteristic of charge transfer bands. Unfortunately, we currently have no unifying explanation for these result, but they are interesting and consistent nonetheless.

Emission signals with large Stokes shifts were observed for nonplanar polymers **8a**−**d** and **11a,b** (Table 1). There was no emission signal detectable for the planar polymers **1a**−**d** and **2a,b**, a trend we have observed in other imine-bridged planar aromatic polymers.[5k,l,9] Therefore, protonation of the imine nitrogens may have led to exciton quenching, or long-range conjugation may have resulted in exciton−exciton annihilation.

In summary, imine-bridged planar (PPhPy)s have been synthesized. The results indicate that construction of alternating donor/acceptor repeat units for inducement of ICT results in an optical band widening, a result opposite that obtained in nonplanar polymers possessing alternating donor/acceptor repeat units.[7l]

Experimental Section

General. 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 μm and 500 Å 5 μm) eluted with THF at 60 °C and a flow rate of 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. 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 F254 with a layer thickness of 0.25 mm purchased from EM Science. The absorption and emission spectral data are listed in Table 1 while the molecular weight data are listed in the Schemes 2 and 3. The synthesis of compounds **7a**−**c**,[5l] **7d**[9], **9**,[5l] and **10a**[5d] have been described previously. The ^{1}H NMR of the planar polymers were recorded in $CDCl_3$/TFA-*d*, which often results

Table 1. Optical Data for the Polymers

	λ_{abs}, nm[a] (ϵ)		λ_{emis}, nm[a,b]	
compd	THF	CH_2Cl_2/TFA 2/1	THF	CH_2Cl_2/ TFA 2/1
8a	*332* (2.2×10^4)	[c]	*530*	[c]
8b	*331* (1.8×10^4)	[c]	*524*	[c]
8c	*332* (2.8×10^4)	[c]	*505*	[c]
8d	*299* (4.4×10^4)	[c]	*511*	[c]
1a	[d]	373, *393*[f]	[d]	NE[e]
1b	[d]	374, *397* (5.5×10^4)	[d]	NE[e]
1c	[d]	*364* (3.3×10^4), 405, 520 (1.6×10^4)	[d]	NE[e]
1d	[d]	*353* (2.5×10^4), 370, 424 (sh), 560 (1.4×10^4)	[d]	NE[e]
11a	*327* (4.4×10^4), 442 (3.9×10^4)	[c]	450 (sh), *514*	[c]
11b	*326* (4.2×10^4), 458 (2.5×10^4)	[c]	466, *525*	[c]
2a	[d]	*360* (2.5×10^4), 480, *511* (2.0×10^4)	[d]	NE[e]
2b	[d]	*330*, 407 (sh), 522, *556* (2.5×10^4)	[d]	NE[e]

[a] The italic value is λ_{max}. sh = shoulder. The extinction coefficients are per repeat group and determined over three dilution points. [b] Excitation wavelength was 300 nm. [c] Addition of TFA would have resulted in loss of the Boc group. [d] The polymers were not soluble in THF. [e] NE means no emission signal was observed. [f] The extinction coefficient was not attainable due to the limited solubility.

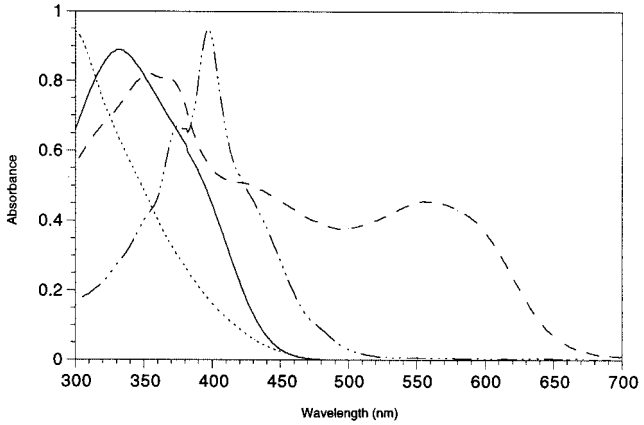


Figure 1. Optical absorption spectra of **8b** (THF) (—), **1b** (CH_2Cl_2/TFA, 2/1) (—··· —), **8d** (THF) (···), and **1d** (CH_2Cl_2/TFA, 2/1) (— — —).

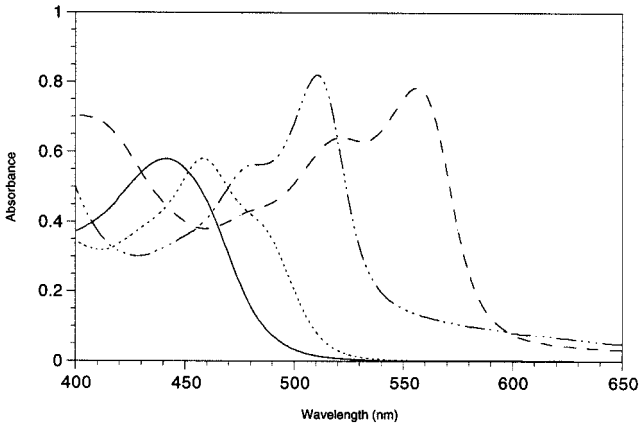


Figure 2. Optical absorption spectra of **11a** (THF) (—), **2a** (CH_2Cl_2/TFA, 2/1) (—··· —), **11b** (THF) (···), and **2b** (CH_2Cl_2/ TFA, 2/1) (— — —).

in broadening of the aromatic signals that are near to the protonated nitrogen atoms, thereby making aromatic/aliphatic proton integration ratios inaccurate.

2,5-Dibromoterephthalic Acid (3).[5d] To a solution of 2,5-dibromo-*p*-xylene (27.1 g, 103 mmol) in pyridine (300 mL) under reflux was added over 1 h a hot aqueous solution of potassium permanganate (73.1 g, 463 mmol) in water (200 mL). After the addition, the mixture was stirred until the purple color disappeared. The reaction mixture was cooled to room temperature 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 2,5-dibromo-*p*-xylene (8.6 g). The aqueous

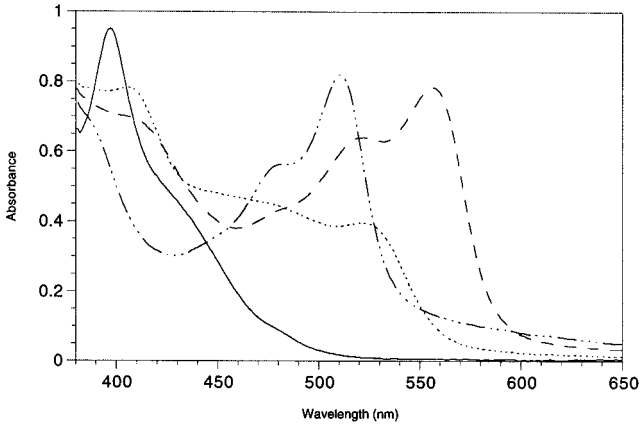


Figure 3. Optical absorption spectra of **1b** (CH_2Cl_2/TFA, 2/1) (—), **1c** (CH_2Cl_2/TFA, 2/1) (···), **2a** (CH_2Cl_2/TFA, 2/1) (—··· —), and **2b** (CH_2Cl_2/TFA, 2/1) (— — —).

solvent was acidified with 3 N HCl to pH ~1 and the resulting white suspension was extracted with ethyl acetate (3×). Removal of the solvent gave a white solid. This solid was suspended in water (100 mL), and potassium hydroxide (7.0 g, 130 mmol) was added. The resulting solution was heated to 90 °C. To this solution was added over 40 min an aqueous solution of potassium permanganate (22.0 g, 139 mmol) in water (300 mL). The solution was further stirred for 1 h. The reaction mixture was cooled to room temperature, methanol (10 mL) was added, and the reaction was stirred until the purple color disappeared. The mixture was filtered. Removal of the filtrate afforded a white solid which was treated with 3 N HCl to pH ~1. The resulting slurry was extracted with ethyl acetate (3×). The extracts were washed with brine and dried over magnesium sulfate. Removal of solvents in vacuo afforded **3** as a white solid (18.2 g, 80% based on reacted 2,5-dibromo-*p*-xylene). This represents a yield improvement over our previous report on this synthesis. Spectra data were identical to those reported earlier.[5d]

3,6-Dibromo-2,5-phenylenendi(carboxylic acid chloride) (4).[5d] To **3** (6.70 g, 20.7 mmol) in benzene (80 mL) was added one drop of DMF and oxalyl chloride (5.4 mL, 62 mmol). The mixture was heated to reflux for 2 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 (7.58 g, 100%). Spectra data were identical to those reported earlier.[5d]

***N,N′*-Bis(*t*-butoxycarbonyl)-1,4-diamino-2,5-dibromobenzene (5).**[5d] To a mixture of saturated sodium azide solution (100 mL, ca. 640 mmol, ca. 6.4 M), tetrabutylammonium bromide (60 mg), and dichloromethane (50 mL) at −5 to 0 °C was added a solution of **4** (40.85 g, 113.2 mmol) in dichloromethane (200 mL) over 1.5 h. After the addition, the mixture was further stirred for 10 min. The organic phase was

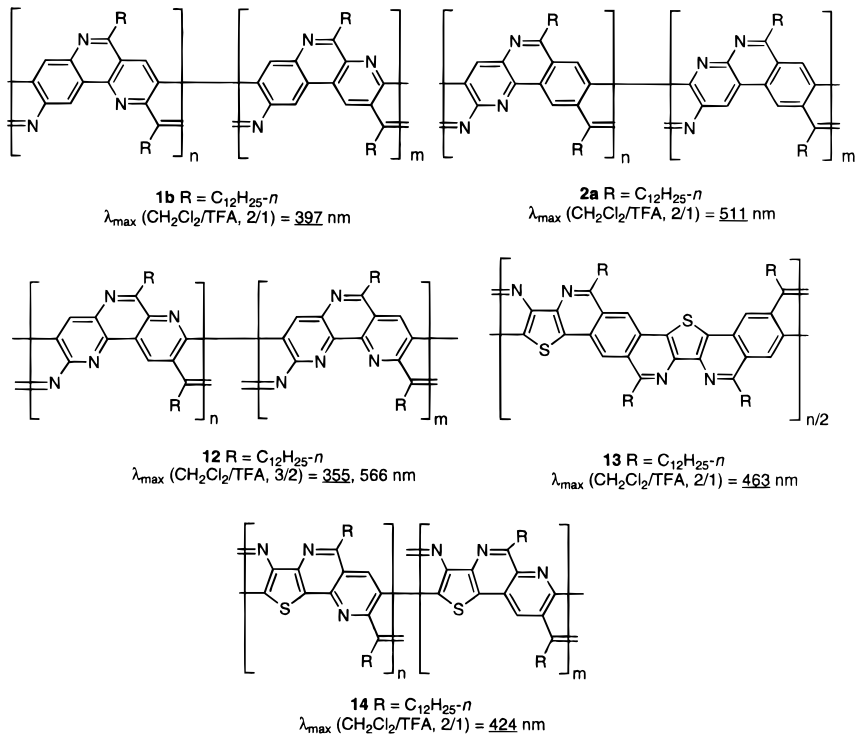


Figure 4. Several planar heterocyclic polymers that have been prepared.

then separated. The aqueous phase was extracted with cold dichloromethane (2×). The combined organic fractions were washed with cold water (2×) and dried over magnesium sulfate at 0 °C. The solution was filtered through a pad of magnesium sulfate/Celite. The filtrate was further dried over calcium hydride at 0 °C for 40 min. The mixture was filtered through another pad of magnesium sulfate/Celite. The light yellow filtrate (ca. 400 mL) was mixed with *tert*-butyl alcohol (250 mL, 2.6 mol) and heated to reflux for 9 h. The mixture was cooled to room temperature. Removal of the solvent in vacuo gave a white solid that was redissolved in $CHCl_3$ (150 mL) and filtered through a silica gel plug. The filtrate was concentrated in vacuo and the resulting residue was crystallized from ethyl acetate to give **5a** as colorless flakelike crystals (48.06 g, 91%). This represents a yield improvement over our previous report on this synthesis. Spectra data were identical to those reported earlier.[5d]

***N,N′*-Bis(*t*-butoxycarbonyl)-1,4-diamino-2,5-bis(tri-*n*-butylstannyl)benzene (6).** To **5** (4.66 g, 10.0 mmol) in ether (60 mL) at −78 °C was added methyllithium (12.7 mL, 21.0 mmol, 1.65 M). The slurry was stirred for 10 min at −78 °C and allowed to warm to 0 °C. This light yellow slurry was then added to *tert*-butyllithium (27.3 mL, 45.0 mmol, 1.65 M) in ether (20 mL) at −78 °C via cannula. The mixture was stirred for 4 h and then slowly warmed to 0 °C. The light brown slurry was recooled to −78 °C and tributyltin chloride (7.4 mL, 26 mmol) was added. The clear light brown solution was warmed to 0 °C and water (50 mL) was added. The two layers were separated. The aqueous phase was extracted with ether (2×). The combined organic fractions were washed with water (2×) and brine (1×) and then dried over sodium sulfate. After filtration, the solvent was removed in vacuo. The residue was purified by flash chromatography [silica gel treated with hexane/Et_3N (9/1) and washed with hexane, hexane as eluant] to give **6** as a white solid (6.67 g, 75%). FTIR (KBr) 3436, 3333, 2964, 2923, 2851, 1708, 1549, 1523, 1467, 1354, 1287, 1241, 1220, 1159, 1087, 1051, 1026, 867, 769, 667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (br s, 2 H), 6.12 (br s, 2 H), 1.57−1.48 (m, 12 H), 1.48 (s, 18 H), 1.33 (sext, J = 7.3 Hz, 12 H), 1.08 (t, J = 8.3 Hz, 12 H), 0.89 (t, J = 7.3 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.61, 139.59, 136.10, 130.70, 79.85, 29.08, 28.37, 27.38, 13.63, 10.03. Anal. Calcd for $C_{40}H_{76}N_2O_4Sn_2$: C, 54.20; H, 8.64; N, 3.16. Found: C, 54.30; H, 8.59; N, 3.18.

General Procedure for Polymerization Reactions. To an oven-dried screw-cap tube were added the dibromodiketone monomer (1.0 equiv), distannyl monomer (1.02 equiv), and the catalyst(s). The tube was transferred to a nitrogen-filled drybox. To the tube was added the solvent(s). The tube was capped and heated to 90 °C for 3 days (unless otherwise noted). 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. 5 mL that was then added to methanol, hexane, or acetone. The precipitate was collected by filtration, and further washing with methanol, hexane, or acetone gave the nonplanar polymer.

Polymer 8a. The compounds used were **6** (0.452 g, 0.510 mmol), **7a** (0.203 g, 0.500 mmol), $Pd(dba)_2$ (0.0057 g, 0.010 mmol), $AsPh_3$ (0.0061 g, 0.020 mmol), and THF (5 mL). The polymer was obtained by precipitation from dichloromethane into hexane (150 mL). **8a** was obtained as a yellow/green solid (0.22 g, 80%). FTIR (film) 3436, 3344, 2964, 2933, 2872, 1728, 1703, 1677, 1574, 1533, 1456, 1369, 1333, 1246, 1154, 1051, 1026, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.7−8.7 (m, 1 H), 8.6−7.4 (m, 2 H), 6.5−6.1 (br s, 2 H), 3.6−2.3 (m, 4 H), 1.48 (br s, 26 H), 0.88 (br s, 6 H); ^{13}C NMR (125 MHz $CDCl_3$) δ 204, 156, 153, 147, 142, 138, 134, 127, 122, 90, 84, 81, 43, 40, 36, 31, 29−22, 14. Anal. Calcd for $(C_{31}H_{41}N_3O_6)_n$: C, 67.49; H, 7.49; N, 7.62. Found: C, 67.41; H, 7.43; N, 7.69.

Polymer 8b. The compounds used were **6** (0.452 g, 0.510 mmol), **7b** (0.315 g, 0.500 mmol), $Pd(dba)_2$ (0.0057 g, 0.010 mmol), $AsPh_3$ (0.0061 g, 0.020 mmol), and THF (5 mL). The polymer was obtained by precipitation from dichloromethane into methanol (150 mL). **8b** was obtained as a yellow/green solid (0.36 g, 92%). FTIR (film) 3436, 2923, 2850, 1731, 1674, 1529, 1457, 1363, 1327, 1249, 1156, 1047 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.7−8.7 (m, 1 H), 8.6−7.4 (m, 2 H), 6.5−6.1 (br s, 2 H), 3.9−2.2 (m, 4 H), 2.2−1.0 (br m, 58 H), 0.9 (br s, 6 H); ^{13}C NMR (125 MHz $CDCl_3$) δ 203, 155, 153, 146, 141−121, 90, 83, 81, 43, 40, 32, 30−27, 24−23, 14. Anal. Calcd for $(C_{47}H_{73}N_3O_6)_n$: C, 72.74; H, 9.48; N, 5.41. Found: C, 72.78; H, 9.40; N, 5.50.

Polymer 8c. The compounds used were **6** (0.452 g, 0.510 mmol), **7c** (0.278 g, 0.500 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol), THF (3 mL), and NMP (3 mL). The mixture was stirred for 6 days at 80 °C. The polymer

was obtained by precipitation from dichloromethane into methanol (150 mL). **8c** was obtained as a light brown solid (0.23 g). The yield was determined after the next step due to the partial loss of the Boc moieties and imine formation at this stage. FTIR (film) 3426, 2964, 2904, 2872, 1728, 1672, 1605, 1569, 1523, 1462, 1267, 1236, 1154, 1108, 929, 841, 667 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.7−7.3 (m), 1.34 (br m); ^{13}C NMR (125 MHz $CDCl_3$) δ 194−192, 158, 153, 147, 143−140, 135, 132−128, 126, 120, 80, 35, 31, 28. Anal. Calcd for $(C_{43}H_{49}N_3O_6)_n$: C, 73.38; H, 7.02; N, 5.97. Found: C, 74.49; H, 6.79; N, 6.55. The discrepancies in the theoretical and found analytical values are due to partial loss of the Boc moieties, as described in the main text.

Polymer 8d. The compounds used were **6** (0.452 g, 0.510 mmol), **7d** (0.295 g, 0.500 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol), THF (3 mL), and NMP (3 mL). The mixture was stirred for 6 days at 80 °C. The polymer was obtained by precipitation from dichloromethane into methanol (150 mL). **8d** was obtained as a light brown solid (0.32 g). The yield was determined after the next step due to the partial loss of Boc moieties and imine formation at this stage. FTIR (film) 3426, 2964, 2933, 2872, 1728, 1662, 1600, 1569, 1508, 1472, 1369, 1308, 1251, 1154, 1051, 1026, 923, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.0−8.4 (m), 8.2−7.4 (m), 7.1−6.2 (m), 4.0 (br m), 1.8 (br m,), 1.6−1.0 (m), 0.97 (br m); ^{13}C NMR (125 MHz $CDCl_3$) δ 193, 192, 164, 160, 153, 133, 132, 131, 130−127, 115, 114, 81−80, 68, 31, 28, 19, 14. Anal. Calcd for $(C_{43}H_{49}N_3O_8)_n$: C, 70.19; H, 6.71; N, 5.71. Found: C, 70.96; H, 6.38; N, 6.13. The discrepancies in the theoretical and found analytical values are due to partial loss of the Boc moieties, as described in the main text.

Ketone 10b. To a slurry of aluminum chloride (3.2 g, 24 mmol) in dichloromethane (50 mL) at 0 °C was added a solution of **4** (3.61 g, 10.0 mmol) in the same solvent (15 mL). The mixture was stirred for 20 min and *n*-octylbenzene (4.5 mL, 20 mmol) in dichloromethane (10 mL) was added. The mixture was allowed to warm to room temperature and stir overnight. The mixture was poured onto ice. HCl (3 N) was added until the solution became clear. The aqueous layer was extracted with dichloromethane (1×). The combined organic fractions were washed with saturated sodium bicarbonate solution (1×) and water (1×) and then dried over magnesium sulfate. Removal of solvent in vacuo gave a white solid that was crystallized from hexane to afford **10b**. Spectra data were identical to those reported earlier.[5d]

Polymer 11a. The compounds used were **9** (0.453 g, 0.510 mmol), **10a** (0.314 g, 0.500 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol), THF (3 mL), and NMP (3 mL). The mixture was stirred for 52 h at 85−95 °C. The polymer was obtained by precipitation from dichloromethane into acetone (150 mL × 2). **11a** was obtained as a light red solid (0.212 g). The yield was determined after the next step due to partial loss of Boc moieties and imine formation at this stage. FTIR (film) 2923, 2851, 1718, 1692, 1585, 1518, 1462, 1369, 1236, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.8−2.8 (m), 2.2−1.0 (m), 0.9 (br s); ^{13}C NMR (125 MHz $CDCl_3$) δ 204, 169−164, 156−146, 144−115, 82−80, 43−41, 36, 31−27, 24, 23, 14. Anal. Calcd for $(C_{47}H_{73}N_3O_6)_n$: C, 72.74; H, 9.48; N, 5.41. Found: C, 76.29; H, 9.48; N, 6.91. The discrepancies in the theoretical and found analytical values are due to partial loss of the Boc moieties, as described in the main text.

Polymer 11b. The compounds used were **9** (0.453 g, 0.510 mmol), **10b** (0.334 g, 0.500 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol), PPh_3 (0.0026 g, 0.01 mmol), toluene (3 mL), and NMP (3 mL). The mixture was stirred for 3 days at 95−105 °C. The polymer was obtained by precipitation from dichloromethane into acetone/methanol (50/100 mL). **11b** was obtained as a light red solid (0.19 g). The yield was determined after the next step due to the partial loss of Boc moieties and imine formation at this stage. FTIR (film) 2954, 2923, 2851, 1723, 1667, 1605, 1456, 1410, 1364, 1313, 1272, 1241, 1180, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.6−6.2 (m), 3.3−2.3 (m), 2.2−0.6 (m); ^{13}C NMR (125 MHz $CDCl_3$) δ 196, 166−160, 152−148, 146−141, 138−133, 131−122, 81, 36, 32−28, 23, 14. Anal. Calcd for $(C_{51}H_{65}N_3O_6)_n$: C, 75.06; H, 8.03; N, 5.15. Found: C, 80.53; H, 7.78; N, 6.73. The discrepancies in the theoretical and found analytical values are due to partial loss of the Boc moieties, as described in the main text.

General Procedure for Imine-Bridge Formation. To a solution of the polymer in dichloromethane were added trifluoroacetic acid (TFA) and anisole. 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 acetone (10/100 mL). The precipitate was collected by filtration. The solid was suspended in triethylamine (5 mL) and heated in a screw-cap tube at 80 °C overnight. After cooling to room temperature, the suspension was filtered and further washed with acetone to give the planarized polymer.[15]

Polymer 1a. The compounds used were **8a** (0.098 g), dichloromethane (8 mL), TFA (4 mL), and anisole (0.5 mL). **1a** was obtained as a light green solid (0.042 g, 75%). FTIR (KBr) 2954, 2923, 2862, 1574, 1462, 1410, 1297, 1267, 1200, 1144, 908, 882, 621 cm^{-1}; no NMR data could be obtained due to the minimal solubility. Anal. Calcd for $(C_{21}H_{21}N_3)_n$: C, 79.97; H, 6.71; N, 13.32. Found: C, 77.04; H, 6.45; N, 12.60.[15]

Polymer 1b. The compounds used were **8b** (0.11 g), dichloromethane (8 mL), TFA (1 mL), and anisole (0.5 mL). **1b** was obtained as a brown solid (0.074 g, 97%). FTIR (KBr) 2923, 2850, 1576, 1467, 1410, 1312, 902, 882, 721, 618 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/TFA-*d* 1/1) δ 10.9 (s, 1 H), 10.6 (s, 2 H), 2.3 (br s, 4 H), 1.7 (br m, 4 H), 1.5−1.2 (m, 36 H), 0.9 (br s, 6 H). Anal. Calcd for $(C_{37}H_{53}N_3)_n$: C, 82.32; H, 9.90; N, 7.78. Found: C, 80.82; H, 9.77; N, 7.66.[15]

Polymer 1c. The compounds used were **8c** (0.10 g), dichloromethane (6 mL), TFA (3 mL), and anisole (0.5 mL). **1c** was obtained as a dark brown solid (0.079 g, 77% over two steps). FTIR (KBr) 2954, 2903, 2872, 1605, 1569, 1544, 1477, 1405, 1385, 1364, 1313, 1267, 1195, 1108, 1015, 959, 913, 882, 836, 805 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/TFA-*d* 1/1) δ 10.6 (s, 1 H), 10.3−10.1 (m, 2 H), 8.4 (br s, 2 H), 8.1−7.9 (m, 6 H), 1.5 (br s, 18 H). Anal. Calcd for $(C_{33}H_{29}N_3)_n$: C, 84.76; H, 6.25; N, 8.99. Found: C, 82.43; H, 6.28; N, 8.99.[15]

Polymer 1d. The compounds used were **8d** (0.10 g), dichloromethane (8 mL), TFA (1 mL), and anisole (0.5 mL). **1d** was obtained as a brown solid (0.076 g, 97% over two steps). FTIR (KBr) 2954, 2871, 1659, 1602, 1571, 1508, 1472, 1384, 1306, 1249, 1167, 1027, 949, 840, 799 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/TFA-*d* 1/1) δ 10.5 (s, 1 H), 10.2−10.0 (m, 2 H), 8.5 (br s, 2 H), 8.1 (br s, 2 H), 7.4 (br s, 4 H), 4.3 (br s, 4 H), 2.0 (br s, 4 H), 1.6 (br s, 4 H), 1.1 (br s, 6 H). Anal. Calcd for $(C_{33}H_{29}N_3O_2)_n$: C, 79.33; H, 5.85; N, 8.41. Found: C, 75.60; H, 5.92; N, 7.89.[15]

Polymer 2a. The compounds used were **11a** (0.095 g), dichloromethane (6 mL), TFA (3 mL), and anisole (0.5 mL). **2a** was obtained as a brown/black solid (0.070 g, 58% over two steps). FTIR (KBr) 2923, 2851, 1697, 1585, 1462, 1385, 1364, 1297 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/TFA-*d* 1/1) δ 11.8−10.8 (m, 1 H), 10.7−10.5 (m, 2 H), 2.3 (m, 4 H), 1.7 (br s, 4 H), 1.3 (m, 36 H), 0.88 (br s, 6 H). Anal. Calcd for $(C_{37}H_{53}N_3)_n$: C, 82.32; H, 9.90; N, 7.78. Found: C, 77.10; H, 9.18; N, 7.63.[15]

Polymer 2b. The compounds used were **11b** (0.077 g), dichloromethane (6 mL), TFA (3 mL), and anisole (0.5 mL). **2b** was obtained as a deep red solid (0.060 g, 50% over two steps). FTIR (KBr) 2923, 2851, 1662, 1605, 1456, 1364, 1313, 1272, 1185 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$/TFA-*d* 1/1) δ 10.8 (br s, 1 H), 10.5−10.3 (m, 2 H), 8.2−7.7 (m, 8 H), 3.0 (br s, 4 H), 1.8 (br s, 4 H), 1.4 (br m, 20 H), 0.9 (br s, 6 H). Anal. Calcd for $(C_{41}H_{45}N_3)_n$: C, 84.93; H, 7.82; N, 7.25. Found: C, 80.34; H, 7.52; N, 7.01.[15]

Acknowledgment. Support came from the Office of Naval Research. The NMR instrumentation was purchased, in part, with a grant from the National Science Foundation (CHE-9601723). We thank FMC for a gift of alkyllithium reagents.

Supporting Information Available: NMR, IR, and elemental analysis data for the compounds discussed. This

material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Hauschel, B.; Stihler, P.; Hanack, M. *Trends Polym. Sci.* **1996**, *4*, 348. (b) Wang, C.-S. *Trends Polym. Sci.* **1997**, *5*, 138. (c) Conwell, E. *Trends Polym. Sci.* **1997**, *5*, 218.

(2) (a) Osaheni, J. A.; Jenekhe, S. A.; Burns, A.; Du, G.; Joo, J.; Wang, Z.; Epstein, A, J.; Wang, C.-S. *Macromolecules* **1992**, *25*, 5828. (b) Grem, G.; Leising, G. *Synth. Met.* **1993**, *55*−*57*, 4105. (c) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (d) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214. (e) Tian, J.; Wu, C.-C.; Thompson, M. E.; Sturm, J. C.; Register, R. A. *Chem. Mater.* **1995**, *7*, 2190. (f) Onoda, M. *J. Appl. Phys.* **1995**, *78*, 1327. (g) McCullough, R. D.; Williams, S. P. *Chem. Mater.* **1995**, *7*, 2001. (h) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437. (i) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426. (j) Wang, H. L.; MacDiarmid, A. G.; Wang, Y. Z.; Gebler, D. D.; Epstein, A. J. *Synth. Met.* **1996**, *78*, 33. (k) Epstein, A. J.; Blatchford, J. W.; Wang, Y. Z.; Jessen, S. W.; Gebler, D. D.; Lin, L. B.; Gustafson, T. L.; Wang, H.-L.; Park, Y. W.; Swager, T. M.; MacDiarmid, A. G. *Synth. Met.* **1996**, *78*, 253. (l) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer E. W. *Chem. Commun.* **1996**, 2163. (m) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717. (n) Tarkka, R. M.; Zhang, X.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 9438. (o) Dai, Y.; Katz, T.; Nochols, D. A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 18. (p) Bolognesi, A.; Bajo, G.; Paloheimo, J.; Östergård, T.; Stubb, H. *Adv. Mater.* **1997**, *9*, 121. (q) Dai, Y.; Katz, T. *J. Org. Chem.* **1997**, *62*, 1274. (r) Wang, Y. Z.; Gebler, D. D.; Fu, D. K.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1179. (s) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, G. M.; Feld, W. A. *J. Am. Chem. Soc.* **1998**, *120*, 231.

(3) (a) Scherf, U. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. J., Elsenbaumer, R. L., Reynolds, J. R., Ed.; Marcel Dekker, New York, 1998. (b) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986.

(4) Kertesz, M. *Macromolecules* **1995**, *28*, 1475. (b) Kertesz, M.; Ashertehrani, A. *Macromolecules* **1996**, *29*, 940.

(5) (a) Scherf, U.; Müllen, K. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 489. (b) Chmil, K.; Scherf, U. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 217. (c) Tour, J. M.; Lamba, J. S. S. *J. Am. Chem. Soc.* **1993**, *115*, 4935. (d) Lamba, J. S. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723. (e) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 7895. (f) Schlüter, A.-D.; Löffler, M.; Enkelmann, V. *Nature* **1994**, *368*, 831. (g) Löffler, M.; Schlüter, A.-D.; Katrin, G.; Saenger, W.; Toussaint, J.-M.; Brédas, J.-L. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2209. (h) Schlicke, B.; Schirmer, H.; Schlüter, A.-D. *Adv. Mater.* **1995**, *7*, 544. (i) Fiesel, R.; Huber, J.; Scherf, U. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2111. (j) Schlicke, B.; Frahn, J.; Schlüter, A.-D. *Synth. Met.* **1996**, *83*, 173. (k) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 9624. (l) Yao, Y.; Lamba, J. S. S.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 2805. (m) Schlicke, B.; Schlüter, A.-D.; Hauser, P.; Heinze, J. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1996.

(6) (a) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (b) Scherf, U.; Müllen, K. *Adv. Polym. Sci.* **1995**, *123*, 1.

(7) Zhou, Z.-H.; Maruyama, T.; Kanbara, T.; Ikeda, T.; Ichimura, K.; Yamamoto, T.; Tokuda, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1210. (b) Havinga, E. E.; Hoeve, W. ten; Wynberg, H. *Synth. Met.* **1993**, *55*−*57*, 299. (c) Stanaka, S.; Yamashita, Y. *Synth. Met.* **1993**, *55*−*57*, 1251. (d) Yamamoto, T.; Zhou, Z.-H.; Maruyama, T.; Kanbara, T. *Synth. Met.* **1993**, *55*−*57*, 1209. (e) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Lett.* **1996**, 63. (f) Yamamoto, T.; Zhou, Z.-h.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B.-L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389. (g) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065. (h) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (i) Goodson, F. E.; Hartwig, F. *Macromolecules* **1998**, *31*, 1700. (j) Chenthamarakshan, C. R.; Ajayagohosh, A. *Chem. Mater.* **1998**, *10*, 1657. (k) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem. Eur. J.* **1998**, *4*, 1237. (l) Zhang, Q.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355. (m) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (n) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806.

(8) Bakhshi, A. K.; Yamaguchi, Y.; Ago, H.; Yamabe, T. *Synth. Met.* **1996**, *79*, 115.

(9) Yao, Y.; Zhang, Q. T.; Tour, J. M. *Macromolecules* In press.

(10) (a) Smith, P. A. S. *Org. React.* **1946**, *3*, 337. (b) Baumgarten, H. E.; Smith, H. L.; Staklis, A. *J. Org. Chem.* **1975**, *40*, 3554. (c) Binder, D.; Habison, G.; Noe, C. R. *Synthesis* **1977**, 255. (d) Pfister, J. R.; Wymann, W. E.; *Synthesis* **1983**, 38. (e) Ruediger, E. H.; Gandhi, S. S; Gibson, M. S.; Farcasiu, D.; Uncuta, C. *Can. J. Chem.* **1986**, *64*, 577.

(11) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (c) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (d) Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73.

(12) (a) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359. (b) Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. S. *J. Org. Chem.* **1994**, *59*, 5905. (c) Hodgson, D. M.; Witherington, J.; Moloney, B. A.; Richards, I. C.; Brayer, J. L. *Synlett* **1995**, 32. (d) Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73.

(13) (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (b) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376. (c) Jones, L.; Schumm, J. S. Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388.

(14) Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 2nd ed.; Wiley: New York, 1991.

(15) 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 refs 5b,d,h,k,l and 9 and (a) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411, (b) Stephens, E. B.; Tour, J. M. *Macromolecules* **1993**, *26*, 2420.

MA981618K