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Alternating Donor/Acceptor Repeat Units in Polythiophenes. Intramolecular Charge Transfer for Reducing Band Gaps in Fully Substituted Conjugated Polymers

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Abstract: This paper describes a method to limit the band gap widening that occurs in fully substituted conjugated polymers. This is done by constructing step growth [AB] polymers where the A-units are electron rich and the B-units are electron deficient. The thiophene-based polymers were prepared by modified Stille polymerizations using Pd(0)/CuI catalyst systems in which aryldibromides were coupled with aryldistannanes. The donor units were *N*,*N*′-(bis-*tert*-butoxycarbonyl)-3,4-diaminothiophene, *N*,*N*′-(bis-*tert*-butoxycarbonyl)-*N*,*N*′-(dimethyl)-3,4-diaminothiophene, 3,4-diaminothiophene, or 3,4-dialkoxythiophenes while the acceptor units were 3,4-dinitrothiophene, 3,4-(*N*-*n*-butylimido)thiophene, or 3,4-diketone-containing thiophenes. The optical spectra showed λ_{max} values ranging from 400 to 676 nm (solution) and 400−768 (film) for these fully substituted polythiophenes, consistent with significant decreases in the band gaps. Intramolecular charge transfer character between the consecutive units explained the lowering of the band gaps. Two polymer systems based solely on electron deficient thiophenes were prepared via an Ullmann coupling which had optical absorption maxima that were in the range of 300−340 nm; considerably smaller than the λ_{max} values for the donor/acceptor systems. Several model trimers were prepared which had significantly shorter wavelength optical absorptions than their corresponding polymers, thus confirming the need for the extended polymeric backbones.

The optoelectronic properties of conjugated polymers vary significantly based upon the degree of extended conjugation between their consecutive repeat units. Low band gap polymers can be prepared by maximizing the extended π-conjugation within the conjugated polymer backbones. Generally, ladder-type bonds have been used to afford the coplanar arrangements between the polymer's consecutive repeat units; the twist-inhibition being achieved using irreversible covalent linkages,[1] reversible covalent linkages involving alternating π-bonds[2] or H-bonding[3] moieties. However, without ladder linkages, highly substituted conjugated polymers generally exhibit a plummet in their extended conjugation due to severe steric interactions which retard coplanar approach of the consecutive repeat units.[1l] A strategy to induce minimally twisted arrangements in conjugated polymers involves constructing [AB] polymers where the A-units have strong electron-donating moieties and the B-units have strong electron-withdrawing moieties.[4] This results

(1) (a) Schlüter, A.-D. *Adv. Mater*. **1991**, *3*, 282. (b) Yu, L.; Chen, M.; Dalton, L. R. *Chem. Mater*. **1990**, *2*, 649. (c) Hong, S. Y.; Kertesz, M.; Lee, Y. S.; Kim, O.-K. *Chem. Mater*. **1992**, *4*, 378. (d) Godt, A.; Schlüter, A.-D. *Adv. Mater*. **1991**, *3*, 497. (e) Yu. L.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3439. (f) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (g) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723. (h) Schlüter, A.-D.; Schlicke, B. *Synlett*. **1996**, 425. (i) Kertesz, M.; Hong, S. Y. *Macromolecules* **1992**, *25*, 5424. (j) Kintzel, O.; Münch, W.; Schlüter, A.-D.; Godt, A. *J. Org. Chem.* **1996**, *61*, 7304. (k) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc*. **1997**, *119*, 9624. For a recent review in the area, see: (l) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

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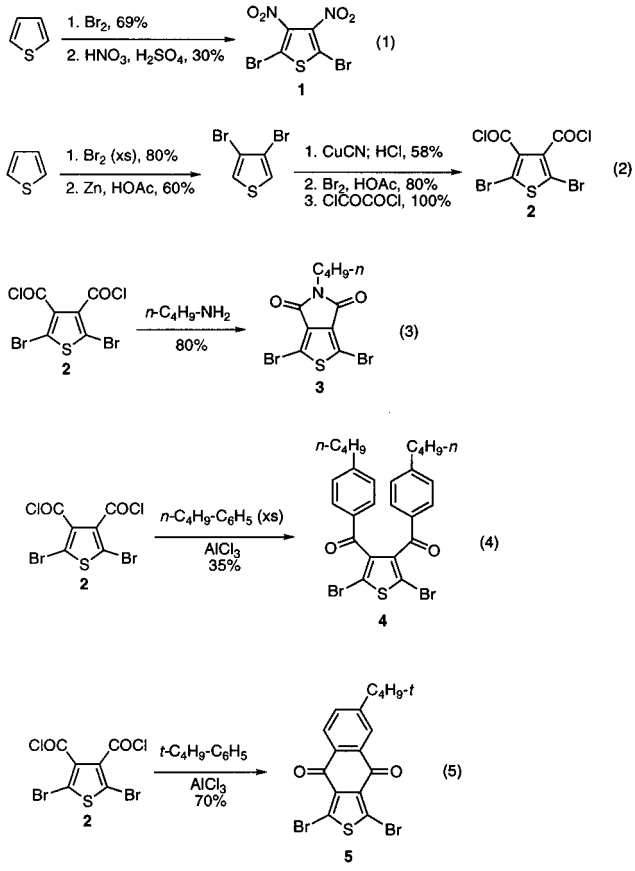
in a consecutive zwitterion-like interaction with high double bond character between the repeat units, stabilizing the low band gap quinoidal-like forms within the polymer backbones.[5] Although [AB] polymers in electrochemically generated systems have received some attention,[4d−m] little work has been done on the synthesis of these polymers using chemically grown [AB] polymers which are soluble and processable.[4a−c] Moreover, there are no previous studies on fully substituted conjugated polyarylenes which demonstrate the efficacy of this approach for band gap shortening. We describe here a series of processable polythiophenes prepared by step-growth polymerization routes which possess consecutive donor/acceptor (D/A) arrangements that permit a high degree of intramolecular charge transfer (ICT)[4a] within the conjugated framework of the polymers, thereby significantly reducing the band gaps.[6] All of the polythiophenes here are fully substituted yet they maintained relatively small optical band gaps due to the intense ICT arrangements.

The preparation of the polymers was planned using step-growth polymerizations via Pd-catalyzed coupling methodologies. Therefore, we sought to keep the halogen-bearing monomers electron deficient to facilitate the oxidative addition reaction with the inherently electron-rich late transition metal catalyst. The syntheses of the electron deficient 2,5-dibromothiophenes (acceptors) were conducted starting from thiophene as shown in Scheme 1. These monomers include a 3,4-dinitro-containing thiophene (**1**), an imido-containing thiophene (**3**), and two 3,4-diketone-containing thiophenes (**4** and **5**). The latter three compounds were conveniently prepared from the common intermediate diacid chloride **2**.

The syntheses of the electron rich thiophenes (donors) are outlined in Scheme 2. The electron deficient monomer **1** was

Scheme 1



reduced and stannylated to afford the electron rich protected diamines **7** and **8** to serve as the nucleophilic partners in the subsequent Pd-catalyzed polymerization reactions (eqs 6 and 7). Three other donor 2,5-distannylthiophenes (**9**, **15**, and **16**) were prepared from the 3,4-dialkoxythiophenes (eqs 8 and 9).

With several donor and acceptor monomers in hand, we proceeded to carry out eight of the possible polymerization reactions to explore the effect of generating polymers with high levels of ICT by constructing step growth [AB] polymers where the A-units were electron rich and the B-units were electron deficient (Scheme 3). After various coupling conditions were screened, the optimal molecular weights, by size exclusion chromatography (SEC) relative to polystyrene (PS) standards, were obtained using a mixed Pd(0)/CuI precatalyst system with triphenylarsine as the supporting ligand for the soluble catalyst.[7] Triphenylphosphine has been reported to undergo aryl transfer reactions acting as a chain terminator, thereby explaining the lower molecular weights obtained with the more traditional ligand.[7c,d] Since SEC is a measure of the hydrodynamic volume and not the actual 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 errors in this M_n range are generally off by a factor of 1.5−2 for polymers of this type.[8] Therefore, the values recorded here are given simply as a reference. After the step-growth polymerization reactions, the polymers were usually purified by dissolution in acetone or dichloromethane and fractional precipitation from

(2) (a) Marsella, M. J.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 12214. (b) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608. (c) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437. (d) McCullough, R. D.; Williams, S. P. *Chem. Mater.* **1995**, *7*, 2001.

(3) (a) Jenekhe, S. A.; Osaheni, J. A. *Macromolecules* **1992**, *25*, 5828. (b) Tarkka, R. M.; Zhang, X.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1996**, *118*, 9438. (c) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer E. W. *Chem. Commun.* **1996**, 2163. (d) Delnoye, D. A. P.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W. *J. Am. Chem. Soc.* **1996**, *118*, 8717.

(4) Although there have been a few reported examples of this alternating D/A strategy for chemically prepared processable polymers, none, to our knowledge, have employed multiple intensely donating and withdrawing groups as described here, and the reported corresponding band gap decreases have usually been considerably less intense. For chemical polymerization routes to D/A polyarylenes that had substitution on the acceptor moieties only, see: (a) 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. (b) Yamamoto, T.; Kanbara, T.; Ooba, N.; Tomaru, S. *Chem. Lett.* **1994**, 1709. For a chemical route to a D/A arylene−vinylene system, see: (c) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. For some excellent electrochemical routes to D/A polymers (several of which afforded insoluble systems and none of which were fully substituted), see: (d) Demanze, F.; Yassar, A.; Garnier, F. *Macromolecules* **1996**, *29*, 4267. (e) Zhou, Z.-h.; Maruyama, T.; Kanbara, T.; Ikeda, T.; Ichimura, K.; Yamamoto, T.; Tokuda, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1210. (f) Havinga, E. E.; ten Hoeve, W.; Wynberg, H. *Polym. Bull.* **1992**, *29*, 119. (g) Lambert, T. L.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 752. (h) Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc., Chem. Commun.* **1991**, 1268. (i) Tamao, K.; Yamaguchi, S.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1994**, 229. (j) Ho, H. A.; Brisset, H.; Frére, P.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1995**, 2309. (k) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791. (l) Tanaka, S.; Yamashita, Y. *Synth. Met.* **1993**, *55*−*57*, 1251. (m) Pagani, G.; Berlin, A.; Canavesi, A.; Schiavon, G.; Zecchin, S.; Zotti, G. *Adv. Mater.* **1996**, *8*, 819.

(5) (a) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986. (b) Zollinger, H. *Color Chemistry*; VCH: New York, 1991.

(6) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

(7) (a) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426. (b) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (c) Farina, V. *Pure Appl. Chem.* **1996**, *68*, 73. (d) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (e) Saá, J. M.; Martorell, G. *J. Org. Chem.* **1993**, *58*, 1963. (f) Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359.

(8) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

Table 1. Molecular Weight and Optical Data for the Donor/Acceptor Polymers and Trimers

compd	M_n[a]	M_w[a]	λ_{max} (nm, THF)[b]	λ_{max} (nm, film)[b]	emissn_{max} (nm, THF)
17	7000	10 200	407[c]	400	550
18	7700	11 000	400	400	579
19	*d*	*d*	676[e]	768	*f*
20	5900	16 800	526[g]	519	602
21	8300	11 500	464	455	572
22	6100	8 500	450	445	555
23	5800	14 400	475	495	608
24	9900	30 800	464	487	590
25	17000	37 900	466	506	590
26	6800	9 700	360 sh	365	515
27	5800	13 500	340, 410 sh	300, 415 sh	549
29			<350[h]		
30			447[h]		
31			375[h]		
32			420[h]		

[a] Recorded by SEC in THF relative to PS standards. [b] No absorptions <300 nm are reported. The underlined value is the more intense of the two recorded values. sh = shoulder. [c] λ_{max} = 395 nm in MeOH. [d] SEC data was recorded in the Boc-protected form **17**. [e] λ_{max} = 662 nm in MeOH. [f] No emission signal was observed in MeOH or THF. [g] λ_{max} = 548 nm in MeOH. [h] Recorded in MeOH.

hexane or methanol. The molecular weight data for all the polymers are listed in Table 1.

The most intense effect of ICT was realized with the strongest electron donor and strongest electron acceptor units, namely 3,4-diaminothiophene and 3,4-dinitrothiophene, respectively (eqs 10 and 11). Thus, coupling **7** or **8** with **1** afforded the organic soluble **17** and **18**, respectively. Boc-removal from **17** with trifluoroacetic acid (TFA) yielded **19** which, due to its solubility in water, required purification by dialysis. There were no residual Boc moieties in **19** as determined by FTIR analysis. There were several pieces of evidence which suggested that **19** had a high degree of zwitterionic character and ICT as depicted by the latter resonance forms in eq 11 (the middle resonance form in eq 11 is more likely to be a major contributor since the last form would lead to electrostatic instabilities between the vicinal pendent moieties). First, unlike **17**, polymer **19** was not soluble in CH_2Cl_2; more polar solvents were required. Second, the optical band gap decreases, evidenced by the strong bathochromic shifts of 269 nm (THF) and 368 nm (film) upon the conversion of **17** to **19**, were profound (Table 1, Figure 1). The solution and solid state optical band gaps for **19** are ca. 1.4 and 1.1 eV, respectively, unusually small values for undoped polythiophenes.[5] The small band gap for **19** was striking in view of the fact that highly regiochemically pure 3-alkyl-substituted polythiophenes have λ_{max} values of 450−460 nm in solution[9] while 3,4-dialkyl-substituted polythiophenes generally have λ_{max} <300 nm due to the unavoidable 4−3′ (head-to-head) interactions.[1i,10] Here we have a fully substituted polythiophenes with an unusually low band gap by exploitation of the D/A ICT repeat unit strategy. A third observation consistent with significant zwitterionic character in **19** is that no fluorescence signal (excitation at λ_{max}) was observed. We have observed this lack of emission in all of our highly delocalized ladder conjugated polymers which bear nitrogen-containing bridges.[1k] Therefore, **19** is especially delocalized due to the D/A arrangement which induces significant ICT character along the backbone. Unfortunately, unlike **17**, upon deprotection of **18** with TFA, only insoluble material was obtained regardless of the solvent polarity.

We also prepared an analogous D/A system that had an imide rather than a dinitro acceptor unit. Remarkably, even in its sterically encumbered *N*,*N*′-di-Boc-protected form, **20** had an intensely bathochromically shifted optical absorbance maximum (Table 1). Attempts to remove the Boc group yielded insoluble polymer. This may be due to ensuing amide formation and concomitant loss of *n*-butylamine, though we were successful in accomplishing the efficient deprotection in a small oligomeric systems that was later studied (vide infra). Likewise, the Boc-protecting groups could not be removed from **21** without significant intramolecular Schiff base formation between the consecutive repeat units. Efforts to generate an imine-bridged polythiophene from **21** (by complete intramolecular imine formation between the amine and ketone moieties) failed to cleanly produce the desired planar system due likely to the severe bond deformations needed to make the helical polythiophene with these particular six-membered bridging rings.[1k] Several other alkoxy donors were used to produce D/A polymers **22**−**25** which all showed significant decreases in their band gaps relative to fully substituted poly(dialkylthiophene)s. Unlike **19**, the polymers **17**, **18**, and **20**−**25** all exhibited fluorescence signals with large Stokes shifts. Thus, **19**, having the most intense D/A arrangement, gave the understandably smallest optical band gap of all the polymers studied. Generally, less intense donors or acceptors gave commensurately large optical band gaps while the steric bulk of the substituents also affected the optical band gaps. For example, while the strength of the D/A groups in **22** and **23** was approximately the same, the larger steric bulk of the diketone acceptor in **22** caused more interunit interactions and a corresponding hypsochromic shift of the absorption maximum ($\Delta\lambda_{max}$ = 25 nm (THF) and 50 nm (film)).

To confirm the need for the polymers' repeating D/A structure for these unusually large wavelength absorptions, we prepared homopolymers of **4** and **5** using Ullmann coupling methods (Scheme 4). Indeed, both **26** and **27** possessed larger band gaps than the D/A polymers (Table 1).[11]

As a further confirmation of the need for the D/A structure in an extended polymer array for maximization of the ICT effects, trimers **29**−**32** were prepared (Scheme 5) that had one electron-donating group per electron-withdrawing group, as in the D/A polymers. In each case, the superiority of the extended polymeric systems was verified since the polymers had much smaller optical band gaps than their corresponding trimeric models (in MeOH, **17** and **29** > 45 nm shift difference; **19** and **30** = 215 nm shift difference; **20** and **31** = 173 nm shift difference). Remarkably, **20** was 128 nm bathochromically shifted relative to **32** (both spectra recorded in MeOH), even though **20** had sterically larger and electronically poorer donor units than those present in **32**. Therefore, the ICT effect was greatly enhanced when a conjugated polymeric arrangement was present rather than simply shorter oligomeric analogues. However, related studies on ladder oligomers and polymers have shown that ICT can be extremely intense in small model systems if the consecutive units are covalently fixed in a planar conformation.[1k]

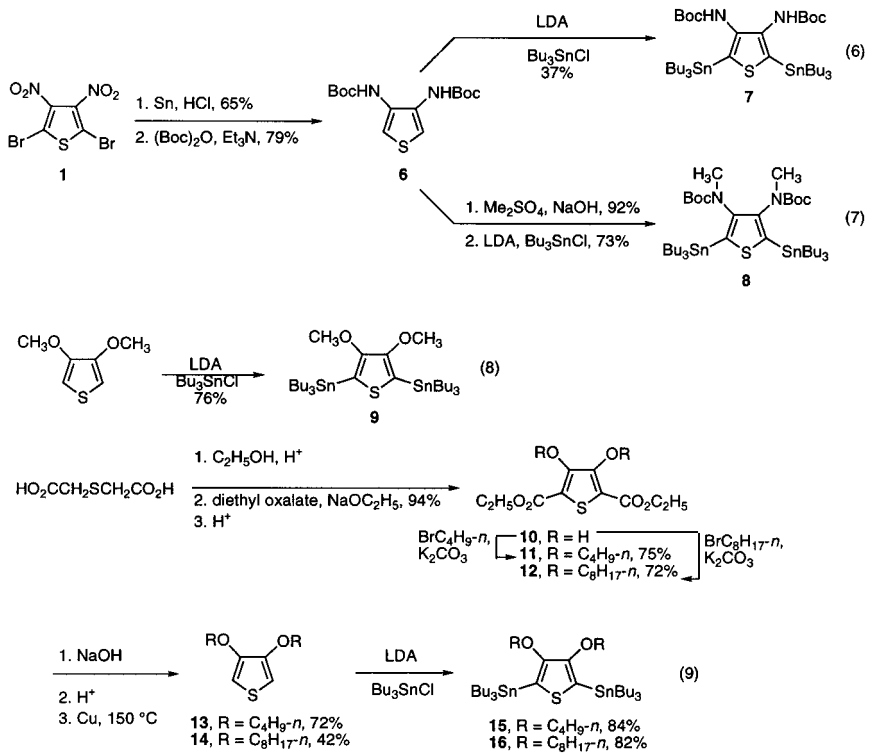
In conclusion, we have prepared low optical band gap chemically polymerized thiophenes based on [AB] systems using

(9) (a) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904. (b) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(10) Kankre, J.; Lukkari, J.; Pasanen, P.; Sillapää, R.; Laine, H.; Harmaa, K. *Macromolecules* **1994**, *27*, 4327.

(11) The sterically less encumbered poly(3,4-dibutoxythiophene), prepared by oxidation of 3,4-dibutoxythiophene, has been reported to have λ_{max} = 460−480 nm. See: (a) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455. (b) Leclerc, M.; Daoust, G. *J. Chem. Soc. Chem. Commun.* **1990**, 273.

Scheme 2



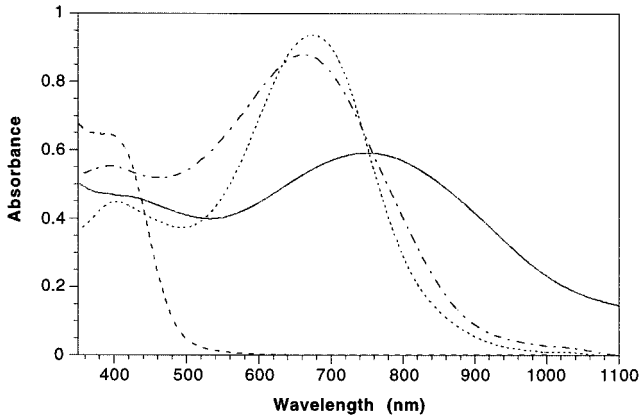


Figure 1. Optical absorption spectra of **17** in THF (− − −), **19** in MeOH (−•−), **19** in THF (•••), and **19** as a film (—).

alternating donor and acceptor moieties within the repeat units to maximize the extended π-conjugations. This arrangement induced backbone ICT and significant zwitterionic character in the polymers as evidenced by their optical absorption maxima and solubility properties. All of the polymers were soluble and processable. Furthermore, we demonstrated that appropriately constructed fully substituted polymers can have small optical band gaps, therefore attenuating the typical effects of interunit twisting due to steric interactions.

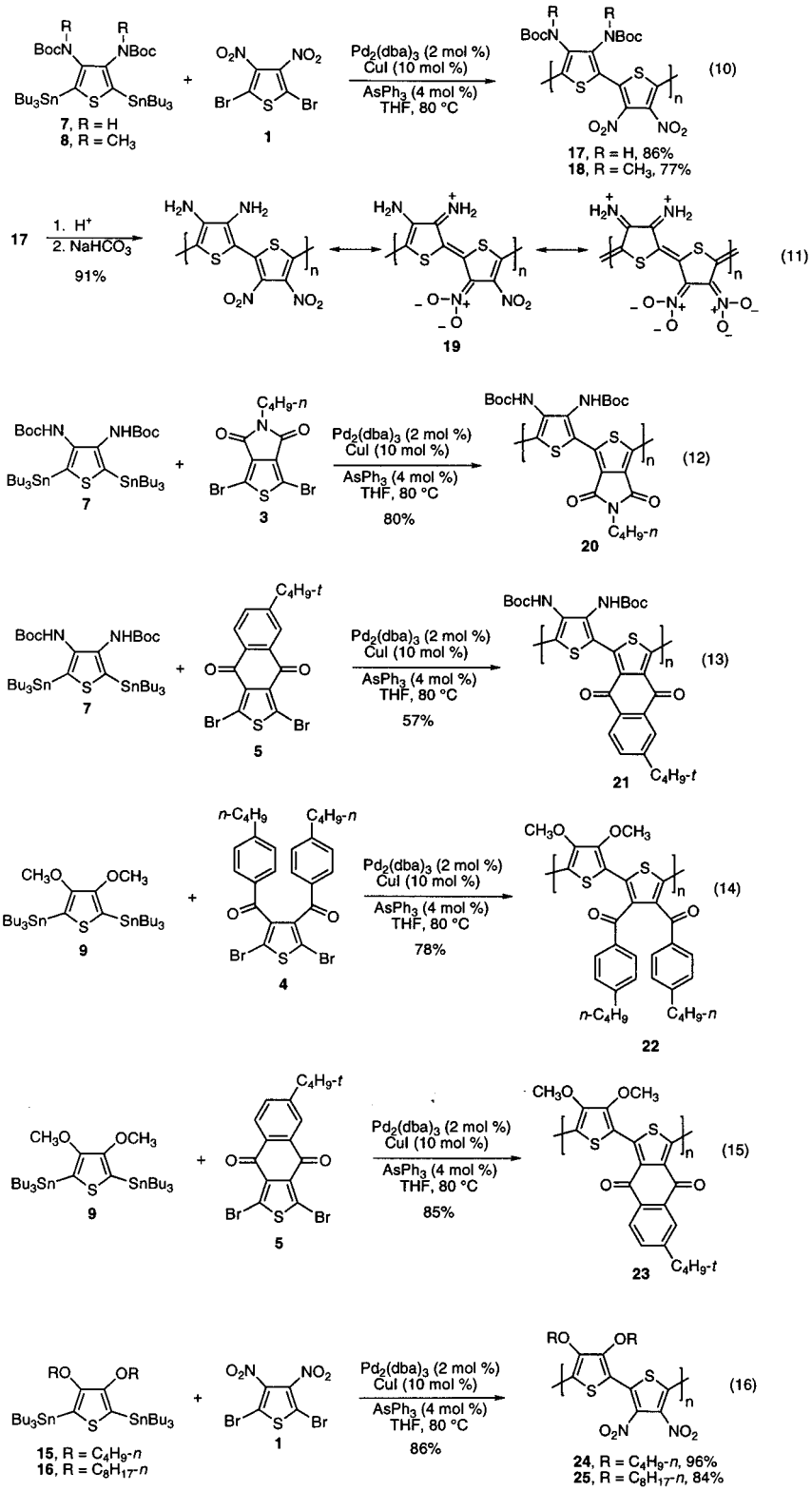
Experimental Section

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 (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 Aldrich Chemical Co. Inc. or 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 polymer molecular weight data, and absorption and emission spectral data are listed in Table 1.

3,4-(*N*-*n*-Butylimido)-2,5-dibromothiophene (3). A mixture of *n*-butylamine (0.619 g, 7.78 mmol) and 2,5-dibromothiophene-3,4-dicarboxylic acid chloride (**2**)[1k] (2.83 g, 8.26 mmol) was heated to 140 °C for 30 min. The mixture was cooled to room temperature and washed with a saturated sodium bicarbonate solution. The solid was then filtered, and the product was purified by flash chromatography on silica gel with hexane/ethyl acetate (10:1) to afford 2.26 g (80%) of the title compound: IR (KBr) 3129, 2935, 2871, 1764, 1695, 1533, 1385, 1321, 1146, 1048, 953, 748, 680 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.58 (t, J = 7.8 Hz, 2 H), 1.60 (p, J = 7.3 Hz, 2 H), 1.32 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 134.8, 112.9, 38.5, 30.3, 20.0, 13.6; HRMS calcd for $C_{10}H_9Br_2NO_2S$ 364.8721, found 364.8710.

Diketone Monomer 5. A solution of 2,5-dibromothiophene-3,4-dicarboxylic acid chloride (**2**)[1k] (2.50 g, 6.87 mmol) in dichloromethane was slowly added to a suspension of aluminum chloride (3.98 g, 29.87 mmol) in dichloromethane (10 mL) maintained at 0 °C. The mixture was allowed to stir at 0 °C for 10 min. *tert*-Butylbenzene (1.27 mL, 8.21 mmol) was slowly added. The mixture was stirred for 30 min and then poured onto ice. Dichloromethane (50 mL) was added, and the mixture was shaken vigorously. The layers were separated, and the aqueous layer was extracted with dichloromethane (3×). The combined organic portions were washed with a saturated sodium bicarbonate solution and water and then dried over magnesium sulfate.

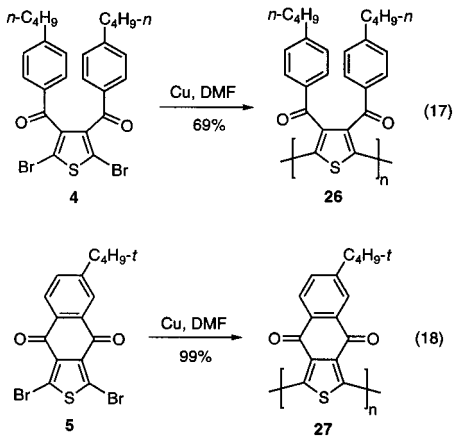
Scheme 3



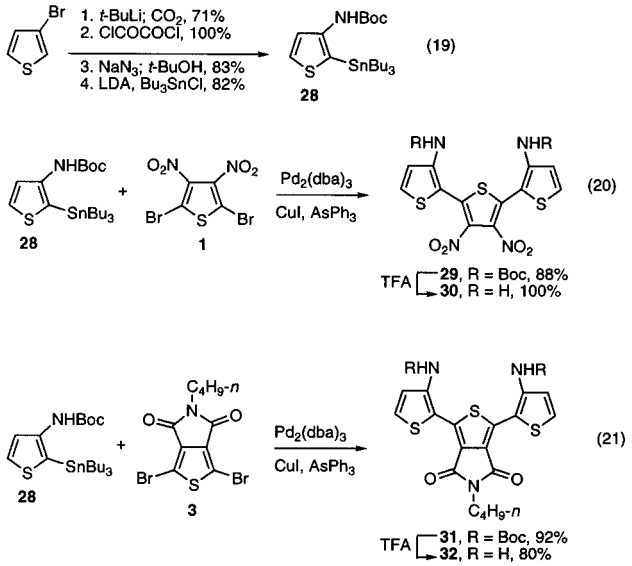
The residue, which remained after the solvent was evaporated, was purified by flash chromatography on silica gel with ethyl acetate/hexane (1:10) to give 2.05 g (70%) of the title compound: IR (KBr) 3139, 2950, 1677, 1595, 1436, 1385, 1359, 1231, 1210, 1031, 739, 703, 615; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, $J = 2.0$ Hz, 1 H), 8.20 (d, $J =$ 8.2 Hz, 1 H), 7.80 (dd, $J = 8.2$, 2.0 Hz, 1 H), 1.38 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 177.4, 158.6, 134.2, 133.0, 132.9, 132.1, 131.7, 127.7, 124.4, 120.9, 120.6, 35.6, 30.9; HRMS calcd for $C_{16}H_{12}Br_2O_2S$ 425.8925, found 425.8930. Anal. Calcd for $C_{16}H_{12}Br_2O_2S$: C, 44.89; H, 2.83. Found: C, 44.77; H, 2.83.

***N,N′*-(Bis(*tert*-butoxycarbonyl)-*N,N′*-dimethyl-3,4-diaminothiophene.** To a stirred mixture of *N,N′*-bis(*tert*-butoxycarbonyl)-3,4-diaminothiophene (**6**)[1k] (4.72 g, 15.0 mmol) and sodium hydroxide (5.29 g, 132.3 mmol) in acetonitrile (20 mL) was added dimethyl sulfate (6.26 mL, 66.2 mmol). The reaction mixture was stirred overnight. Water (50 mL) was added, and the solution was allowed to stirred overnight before being extracted with dichloromethane (20 mL) (3×). The combined organic layer was dried over magnesium sulfate. Filtration and removal of the solvent *in vacuo* afford 4.72 g (92%) of the title compound: FTIR (KBr) 3077, 2974, 1692, 1482, 1359, 1144,

Scheme 4



Scheme 5



928, 851, 764; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (br s, 2 H), 3.08 (s, 6 H), 1.39 (br s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 138.5, 119.0, 80.0, 37.0, 28.2; HRMS calcd for $C_{16}H_{26}N_2O_4S$ 342.1613, found 342.1603. Anal. Calcd for $C_{16}H_{26}N_2O_4S$: C, 56.12; H, 7.65; N 8.18. Found: C, 56.17; H, 7.68; N, 8.22.

***N,N′*-(Bis(*tert*-butoxycarbonyl)-*N,N′*-dimethyl-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (8).** A solution of *n*-butyllithium (19.49 mL, 28.26 mmol, 1.45 M in hexane) was slowly added to diisopropylamine (3.70 mL, 28.26 mmol) in ether (15 mL) at −78 °C. The solution was warmed to room temperature then cooled to 0 °C with an ice bath. A solution of *N,N′*-bis(*tert*-butoxycarbonyl)-*N,N′*-dimethyl-3,4-diaminothiophene (3.23 g, 9.42 mmol) in THF (8 mL) was added, and the mixture warmed to room temperature for 10 min. After re-cooling to 0 °C, chloro(tri-*n*-butyl)stannane (6.15 mL, 20.72 mmol) was added. The mixture was stirred for 1 h. A saturated sodium chloride solution (50 mL) was added, the organic layer was separated, and the aqueous layer was extracted with dichloromethane (3×). The combined organic layers were dried over anhydrous sodium sulfate and filtered. Triethylamine (30 mL) was added to the filtrate, and the resulting solution was stirred overnight. The solvent was evaporated in vacuo, and the residue was purified by flash chromatography with hexane on treated silica gel (washed the silica gel with neat triethylamine, then hexane). The solvent was removed in vacuo to give 6.31 g (73%) of the title compound: FTIR (KBr) 2958, 2927, 2872, 2854, 1705, 1437, 1366, 1147, 688 cm^{-1}; rotomers were present at room temperature and partially resolved by NMR, ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (m, 6 H), 1.55−1.45 (m, 21 H), 1.33−1.26 (m, 21 H), 1.00−1.24 (m, 12 H), 0.89−0.87 (m, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 155.1, 154.9, 146.2, 145.9, 139.1, 79.8, 79.6, 79.3, 37.8, 37.5, 37.1, 29.0, 29.0, 28.9, 28.8, 28.4, 28.4, 28.3, 27.5, 27.3, 27.1, 26.9, 13.6, 12.1, 10.3, 10.3, 8.6; LRMS maximum isotopic intensity calcd for $C_{40}H_{78}N_2O_4SSn_2$ 921.6, found 921.6. Anal. Calcd for $C_{40}H_{78}N_2O_4SSn_2$: C, 52.19; H, 8.54; N, 3.04. Found: C, 52.29; H, 8.60; N, 3.05.

2,5-Bis(tri-*n*-butylstannyl)-3,4-dimethoxythiophene (9). See the preparation of **8** for details. Compounds used were *n*-butyllithium (2.06 mL, 3.0 mmol, 1.45 M in hexane), diisopropylamine (0.39 mL, 3.0 mmol), ether (5 mL), 3,4-dimethoxythiophene[12] (0.144 g, 1.00 mmol) in ether (1.0 mL), chloro(tri-*n*-butyl)stannane (0.65 mL, 2.2 mmol), saturated sodium chloride solution (50 mL), dichloromethane (3×), and triethylamine (3.0 mL). Flash chromatography with hexane on treated silica gel (washed the silica gel with neat triethylamine, then hexane) gave 0.547 g (76%) of the title compound: FTIR (KBr) 2957, 2931, 2872, 2852, 1456, 1355, 1133, 1042, 668, 599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 6 H), 1.54 (p, J = 7.6 Hz, 12 H), 1.32 (sext, J = 7.2 Hz, 12 H), 1.08 (t, J = 7.5 Hz, 12 H), 0.87 (t, J = 7.3 Hz, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 125.0, 60.4, 29.0, 27.2, 13.7, 10.7. Anal. Calcd for $C_{30}H_{60}O_2SSn_2$: C, 49.89; H, 8.37. Found: C, 50.03; H, 8.44.

3,4-Dioctoxythiophene (14). Starting from **10**,[13] the procedure for 3,4-diethoxythiophene[13] was followed, except 1-bromooctane was substituted for bromoethane to afford the title compound in 30% yield from **10**: FTIR (KBr) 3118, 2923, 2851, 1559, 1497, 1467, 1374, 1200, 1144, 1021, 964, 862, 739; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (s, 2 H), 3.95 (t, J = 6.8 Hz, 4 H), 1.80 (p, J = 7.4 Hz, 4 H), 1.53−1.26 (m, 20 H), 0.87 (t, J = 7.6 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.6, 96.8, 70.6, 31.8, 29.4, 29.3, 29.0, 26.0, 22.7, 14.1; HRMS calcd for $C_{20}H_{36}O_2S$ 340.2436, found 340.2431.

2,5-Bis(tri-*n*-butylstannyl)-3,4-dibutoxythiophene (15). See the preparation of **8** for details. Compounds used were *n*-butyllithium (20 mL, 30.0 mmol, 1.52 M in hexane), diisopropylamine (3.93 mL, 30.0 mmol), ether (50 mL), 3,4-dibutoxythiophene[11,13] (2.28 g, 10.0 mmol), and chloro(tri-*n*-butyl)stannane (5.97 mL, 22.0 mmol). Flash chromatography with hexane on treated silica gel (washed the silica gel with neat triethylamine, then hexane) afforded 6.76 g (84%): FTIR (KBr) 2958, 2918, 2857, 1459, 1423, 1347, 1159, 1068, 1022, 966, 920, 870, 662; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (t, J = 6.8 Hz, 4 H), 1.70 (p, J = 7.5 Hz, 4 H), 1.60−1.20 (m, 16 H), 1.33 (sext, J = 7.4 Hz, 12 H), 1.08 (t, J = 8.2 Hz, 12 H), 0.96 (t, J = 7.3 Hz, 6 H), 0.88 (t, J = 7.3 Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 124.7, 72.9, 32.4, 29.1, 27.3, 19.4, 14.1, 13.7, 10.7. Anal. Calcd for $C_{36}H_{72}O_2SSn_2$: C, 53.62; H, 9.00. Found: C, 53.66; H, 9.03.

2,5-Bis(tri-*n*-butylstannyl)-3,4-dioctoxythiophene (16). See the preparation of **8** for details. Compounds used were *n*-butyllithium (20 mL, 30.0 mmol, 1.52 M in hexane), diisopropylamine (3.9 mL, 30.0 mmol), ether (50 mL), 3,4-dioctoxythiophene (**14**) (3.40 g, 10.0 mmol), and chloro(tri-*n*-butyl)stannane (5.97 mL, 22.0 mmol). Flash chromatography with hexane on treated silica gel (washed the silica gel with neat triethylamine, then hexane) afforded 7.53 g (82%): FTIR (KBr) 2928, 2857, 1504, 1459, 1423, 1347, 1154, 1063, 1072, 870, 667; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (t, J = 6.8 Hz, 4 H), 1.70 (p, J = 7.7 Hz, 4 H), 1.54 (m, 12 H), 1.40−1.27 (m, 32 H), 1.10 (t, J = 8.0 Hz, 12 H), 0.88 (t, J = 7.3 Hz, 24 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 124.7, 73.2, 31.9, 30.3, 29.2, 29.6, 28.9, 27.7, 27.3, 26.9, 26.2. Anal. Calcd for $C_{44}H_{88}O_2SSn_2$: C, 57.53; H, 9.66. Found: C, 57.60; H, 9.62.

Polymer 17. In a drybox under nitrogen, *N,N′*-bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (**7**)[1k] (1.8392 g, 2.0603 mmol) and 2,5-dibromo-3,4-dinitrothiophene (**1**)[1k] (0.6978 g, 2.1023 mmol) were dissolved in THF (5.0 mL) in a screw cap tube. $Pd_2(dba)_3$ (0.0377 g, 0.0412 mmol), CuI (0.0393 g, 0.2063 mmol), and $AsPh_3$ (0.0252 g, 0.0824 mmol) were added to the solution. The tube was capped, removed from the drybox, and heated to 80 °C for 72 h. After cooling, the black mixture was poured into a solution of aqueous KF (10 mL, 1.00 M) and stirred for 30 min. The insoluble white solid was removed by filtration. The filtrate was extracted with dichlo-

(12) Keegstra, M. A.; Peters, T. H. A.; Brandsma, L. *Tetrahedron* **1992**, *48*, 3633.

(13) (a) Overberger, C. G.; Lal, J. *J. Am. Chem. Soc.* **1951**, *73*, 2956. (b) Sankaran, B.; Reynolds, J. R. *Am. Chem. Soc. (Div. Polym. Mater. Sci. Eng.)* **1995**, *72*, 319.

romethane (3×). The combined organic layers were dried over sodium sulfate and evaporated to dryness. Acetone (5.0 mL) was added to dissolve the residue. The solution was added slowly to hexane (200 mL). The precipitate was collected by filtration, redissolved in acetone, and precipitated with hexane again. The polymer was collected by filtration and then dried in vacuo to afford 0.86 g (86%) of the title compound: FTIR (KBr) 3405, 2985, 1728, 1544, 1385, 1323, 1241, 1159, 1010, 867, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (br s, 2 H), 1.46 (br s, 18 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.14, 138.74, 133.98, 133.07, 119.94, 83.02, 28.59. Anal. Calcd for $(C_{18}H_{20}N_4O_8S_2)_n$: C, 44.62; H, 4.16; N, 11.56. Found: C, 44.56; H, 4.18; N, 11.46.

Polymer 18. See the preparation of **17** for details. Compounds used were *N*,*N*′-bis(*tert*-butoxycarbonyl)-*N*,*N*′-dimethyl-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (**8**) (0.451 g, 0.49 mmol), 2,5-dibromo-3,4-dinitrothiophene (**1**)[1k] (0.1650 g, 0.50 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0092 g, 0.01 mmol), CuI (0.0095 g, 0.05 mmol), and $AsPh_3$ (0.0061 g, 0.02 mmol). The dissolution/precipitation solvents were dichloromethane/hexane to afford 0.1980 g (77%) the title compound: FTIR (KBr) 3128, 2974, 2923, 1713, 1544, 1477, 1436, 1333, 1149, 851, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.28−2.90 (br m, 6 H), 1.60−1.20 (br m, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 139.5, 137.9, 130.6, 124.2, 82.5, 35.9, 28.1. Anal. Calcd for $(C_{20}H_{24}N_4O_8S_2)_n$: C, 46.87; H, 4.72; N, 10.93. Found: C, 46.93; H, 4.73; N, 10.82.

Polymer 19. Trifluoroacetic acid (TFA) (1.5 mL) was added to polymer **17** (0.2183 g, 0.4505 mmol) in dichloromethane (1.5 mL) and anisole (1.0 mL) at room temperature. The brown solution was stirred for 12 h at room temperature. The solution was poured slowly into a solution of aqueous sodium bicarbonate (10 mL, saturated). The mixture was stirred at room temperature for 1 h. The solvent and water were removed in vacuo. Water (10 mL) was added to the resulting solid. The mixture was poured into molecularporous dialysis tubing (Spectra/Por 3 with a MWCO of 3500). The tubing was place in deionized water (500 mL), and the water was changed 3× per day for 7 days whereupon the resistivity of water remained constant. The tubing was opened up, and the mixture was poured into a flask. The water was removed in vacuo to give 0.1168 g (91%) of the title compound: FTIR (KBr) 3426, 3139, 1523, 1380, 1308, 1159, 1128, 1000, 744 cm^{-1}. Anal. Calcd for $(C_8H_4N_4O_4S_2)_n$: C, 33.80; H, 1.42; N, 19.71. Found: C, 35.24; H, 1.85; N, 14.64. The high C and H, and low N content is presumably due to traces of TFA that were not removed. No ^{13}C NMR (due to quadrupolar broadening effects of N) resonances could be detected for **19** in DMSO-d_6 or methanol-d_4.

Polymer 20. See the preparation of **17** for details. Compounds used were *N*,*N*′-bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (**7**)[1k] (1.7496 g, 1.9599 mmol), 3,4-(*N*-*n*-butylimido)-2,5-dibromothiophene (**3**) (0.7340 g, 2.000 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0366 g, 0.0400 mmol), CuI (0.0380 g, 0.2000 mmol), and $AsPh_3$ (0.0245 g, 0.0800 mmol. The dissolution/precipitation solvents were dichloromethane/hexane followed by dichloromethane/methanol to afford 0.5891 g (80%) of the title compound: FTIR (KBr) 3303, 2964, 2934, 2872, 1728, 1679, 1528, 1497, 1451, 1385, 1364, 1333, 1246, 1159, 1077, 872, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (br s, 2 H), 3.71 (br s, 2 H), 1.66 (m, 2 H) 1.53 (br s,18 H), 1.39 (m, 2 H), 0.96 (br t, J = 7.0 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.90, 153.55, 135.67, 133.00, 129.50, 125.00, 81.49, 38.75, 30.52, 28.31, 20.15, 13.76. Anal. Calcd for $(C_{24}H_{29}N_3O_6S_2)_n$: C, 55.47; H, 5.63; N, 8.09. Found: C, 55.20; H, 5.66; N, 7.81.

Polymer 21. See the preparation of **17** for details. Compounds used were *N*,*N*′-bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (**7**)[1k] (0.4374 g, 0.4900 mmol), **5** (0.2129 g, 0.5000 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0092 g, 0.0100 mmol), and $AsPh_3$ (0.0061 g, 0.0200 mmol). The dissolution/precipitation solvents were dichloromethane/hexane to afford 0.1633 g (57%): FTIR (KBr) 3333, 2964, 2862, 1723, 1667, 1595, 1477, 1369, 1236, 1159, 1026, 856, 754, 641; ^1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 7.79 (d, J = 8.2 Hz, 1 H), 7.80 (d, J = 8.2 Hz, 1 H), 7.42 (br s, 2 H), 1.42 (br s, 9 H), 1.38 (br s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180, 158, 152, 141, 134, 132.4, 132.2, 131, 127, 124, 123, 80, 35, 31, 28. Anal. Calcd for $(C_{30}H_{32}N_2O_6S_2)_n$: C, 62.05; H, 5.55; N, 4.82. Found: C, 60.94; H, 5.74; N, 4.57.

Polymer 22. See the preparation of **17** for details. Compounds used were 2,5-bis(tri-*n*-butylstannyl)-3,4-dimethoxythiophene (**9**) (1.7694 g, 2.450 mmol), **4**[1k] (1.4050 g, 2.500 mmol), THF (8.0 mL), $Pd_2(dba)_3$ (0.0458 g, 0.050 mmol), and $AsPh_3$ (0.0306 g, 0.10 mmol). The dissolution/precipitation solvents were dichloromethane/hexane followed by dichloromethane/methanol to afford 1.03 g (78%): FTIR (KBr) 3118, 2923, 2851, 1662, 1600, 1461, 1385, 1308, 1221, 1169, 1051, 974, 836, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.29 Hz, 4 H), 6.96 (d, J = 8.2 Hz, 4 H), 3.46 (br s, 6 H), 2.53 (br t, J = 7.2 Hz, 4 H), 1.50 (p, J = 7.2 Hz, 4 H), 1.27 (sext, J = 7.2 Hz, 4 H), 0.88 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.4, 148.6, 147.2, 138.8, 134.9, 133.3, 129.6, 128.1, 116.7, 60.1, 35.7, 33.2, 22.3, 13.9. Anal. Calcd for $(C_{32}H_{32}O_4S_2)_n$: C, 67.20; H, 6.49. Found: C, 69.09; H, 6.02.

Polymer 23. See the preparation of **17** for details. Compounds used were 2,5-bis(tri-*n*-butylstannyl)-3,4-dimethoxythiophene (**9**) (1.0618 g, 1.47 mmol), **5** (0.6388 g, 1.50 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0275 g, 0.030 mmol), and $AsPh_3$ (0.0184 g, 0.060 mmol). The dissolution/precipitation solvents were dichloromethane/hexane to afford 0.52 g (85%) the title compound: FTIR (KBr) 3128, 2944, 2862, 1662, 1590, 1472, 1374, 1267, 1231, 1056, 969, 846, 744, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (br s, 1 H), 8.26 (d, J = 8.2 Hz, 1 H), 7.79 (d, J = 8.2 Hz, 1 H), 4.07 (br s, 3 H), 4.06 (br s, 3 H), 1.39 (br s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.0, 179.5, 158.0, 149.4, 141.7, 134.4, 132.4, 131.8, 131.5, 131.2, 127.6, 124.4, 117.7, 60.49, 60.42, 35.7, 31.1. Anal. Calcd for $(C_{22}H_{18}O_4S_2)_n$: C, 64.37; H, 4.42. Found: C, 64.29; H, 4.39.

Polymer 24. See the preparation of **17** for details. Compounds used were 2,5-bis(tri-*n*-butylstannyl)-3,4-dibutoxythiophene (**15**) (0.7903 g, 0.98 mmol), 2,5-dibromo-3,4-dinitrothiophene (**1**)[1k] (0.3319 g, 1.00 mmol), $Pd_2(dba)_3$ (0.0183 g, 0.02 mmol), CuI (0.0190 g, 0.10 mmol), and $AsPh_3$ (0.0122 g, 0.04 mmol). The dissolution/precipitation solvents were dichloromethane/hexane to afford 0.3757 (96%): FTIR (KBr) 3108, 2954, 2872, 1539, 1456, 1385, 1318, 1277, 1041, 933, 759 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.15 (t, J = 6.5 Hz, 4 H), 1.70 (p, J = 7.1 Hz, 4 H), 1.42 (sext, J = 7.5 Hz, 4 H), 0.97 (t, J = 7.4 Hz s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 136.9, 130.1, 114.5, 74.3, 31.9, 19.0, 13.8. Anal. Calcd for $(C_{16}H_{18}N_2O_6S_2)_n$ C, 48.23; H, 4.55; N, 7.03. Found: C, 48.15; H, 4.50; N, 6.92.

Polymer 25. See the preparation of **17** for details. Compounds used were 2,5-bis(tri-*n*-butylstannyl)-3,4-dioctoxythiophene (**16**) (0.4502 g, 0.4900 mmol), 2,5-dibromo-3,4-dinitrothiophene (**1**)[1k] (0.1660 g, 0.5000 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0092 g, 0.01 mmol), CuI (0.0095 g, 0.05 mmol), and $AsPh_3$ (0.0061 g, 0.02 mmol). The dissolution/precipitation solvents were dichloromethane/hexane followed by dichloromethane/methanol to afford 0.21 g (84%) the title compound: FTIR (KBr) 3120, 2922, 2849, 1539, 1455, 1382, 1314, 1278, 1044, 939, 872, 752, 663, 616 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.10 (br s, 4 H), 1.71 (br s, 4 H), 1.44−1.20 (br s, 20 H), 1.00−0.80 (br s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.3, 137.0, 130.1, 114.5, 74.6, 31.8, 29.9, 29.4, 29.2, 25.8, 22.6, 14.1. Anal. Calcd for $(C_{24}H_{34}N_2O_6S_2)_n$: C, 56.45; H, 6.71; N, 5.49. Found: C, 56.07; H, 6.86; N, 5.10.

Polymer 26. In a drybox, **4**[1k] (0.281 g, 0.50 mmol) and copper powder (0.254 g, 4.00 mmol) were added to DMF (1.5 mL) in a screw cap tube.[2c] The tube was capped, removed from the drybox, and heated to 150 °C for 48 h. After cooling, the mixture was poured into hydrochloric acid (10 mL, 3 M) and extracted with dichloromethane (10 mL) (3×). The combined organic layers were washed with hydrochloric acid (10 mL, 3 M) (2×), water (10 mL) (2×), and then dried over sodium sulfate. The solvent was removed in vacuo. Dichloromethane (2 mL) was added to dissolve the residue. The solution was slowly added to methanol (100 mL). The precipitate was collected by filtration to afford 0.14 g (69%) of the title compound: FTIR (KBr) 3015, 2933, 2862, 1662, 1600, 1569, 1462, 1410, 1380, 1267, 1226, 1169, 974, 841, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 7.4 Hz, 4 H), 6.87 (d, J = 7.4 Hz, 4 H), 2.46 (br s, 4 H), 1.49 (br s, 4 H), 1.27 (sext, J = 7.2 Hz, 4 H), 0.89 (t, J = 7.2 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 148.8, 141.9, 134.6, 129.7,

128.4, 128.1, 35.6, 33.1, 22.3, 13.9. Anal. Calcd for $(C_{26}H_{26}O_2S)_n$: C, 77.56; H, 6.52. Found: C, 77.47; H, 6.54.

Polymer 27. See the procedure for **26** for details. Compounds used were **5** (0.511 g, 1.20 mmol), copper power (0.61 g, 9.6 mmol) and DMF (5.0 mL). The yield was 0.32 g (99%): FTIR (KBr) 3149, 2954, 2872, 1667, 1595, 1462, 1380, 1231, 1015, 851, 744, 703, 631 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (br s, 1 H), 8.17 (br d, $J = 7.7$ Hz, 1 H), 7.78 (d, $J = 7.7$ Hz, 1 H), 1.36 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7, 179.2, 158.4, 140.5, 134.8, 134.5, 132.5, 131.5, 127.8, 124.6, 35.7, 31.0. Anal. Calcd for $(C_{16}H_{12}O_2S)_n$: C, 71.62; H, 4.51. Found: C, 71.01; H, 4.76.

Trimer 29. See the preparation of **17** for detilas. Compounds used were 2,5-dibromo-3,4-dinitrothiophene (**1**)[1k] (0.3319 g, 1.00 mmol), *N*-(*tert*-butoxycarbonyl)-3-amino-2-(tri-*n*-butylstannyl)thiophene (**28**)[1k] (0.9571 g, 1.96 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0183 g, 0.02 mmol), CuI (0.0.019 g, 0.10 mmol), and $AsPh_3$ (0.0122 g, 0.04 mmol) at 80 °C for 12 h. The dark mixture was cooled, poured into a solution of KF (10 mL, 1.00 M), and stirred for 30 min. The precipitate was filtered and redissolved in acetone. The insoluble white solid was removed by filtration. The acetone solution was dried over sodium sulfate and evaporated to dryness. The product was purified by a flash chromatograph on silica gel with ethyl acetate/hexane (1:10) to give 0.492 g (88%) of the title compound: IR (KBr) 3241, 3118, 2974, 1728, 1687, 1580, 1549, 1523, 1497, 1385, 1256, 1159, 877, 749; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (br d, $J = 5.5$ Hz, 2 H), 7.50 (d, $J = 5.5$ Hz, 2 H), 6.99 (br s, 2 H), 1.51 (s, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 139.0, 138.9, 134.9, 129.7, 124.1, 108.5, 81.8, 28.4; HRMS calcd for $C_{22}H_{24}N_4O_8S_3$ 568.0756, found 568.0756.

Trimer 30. TFA (1.0 mL) was slowly added to trimer **29** (0.20 g, 0.35 mmol), in dichloromethane (2.0 mL), and the mixture was stirred for 3 h before pouring it into aqueous sodium bicarbonate. The precipitate was collected by filtration, and the solid was washed with hexane to afford 0.13 g (100%) of the title compound: IR (KBr) 3415, 3344, 3231, 3108, 1626, 1533, 1405, 1380, 1313, 1251, 872, 739, 636; ^1H NMR (300 MHz, DMSO-d_6) δ 7.60 (d, $J = 5.4$ Hz, 2 H), 6.66 (d, $J = 5.4$ Hz, 2 H), 5.91 (s, 4 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 150.1, 135.3, 134.4, 130.1, 121.5, 95.6; HRMS calcd for $C_{12}H_8N_4O_4S_3$ 367.9708, found 367.9697.

Trimer 31. See the preparations of **17** and **29** for details. Compounds used were 3,4-bis(*N*-*n*-butylimido)-2,5-dibromothiophene (**3**) (0.2931 g, 0.80 mmol), *N*-*(tert*-butoxycarbonyl)-3-amino-2-(tri-*n*-butylstannyl)thiophene (**28**)[1k] (0.7643 g, 1.57 mmol), THF (5.0 mL), $Pd_2(dba)_3$ (0.0146 g, 0.016 mmol), CuI (0.0152 g, 0.08 mmol), and $AsPh_3$ (0.0098 g, 0.032 mmol). The product was purified by a flash chromatograph on silica gel with ethyl acetate/hexane (1:10) to give 0.435 (92%) of the title compound: IR (KBr) 3292, 3200, 3097, 2974, 2923, 1728, 1677, 1554, 1385, 1241, 1159, 1067, 759, 677; ^1H NMR (300 MHz, $CDCl_3$) δ 8.67 (br s, 2 H), 7.53 (br s, 2 H), 7.38 (d, $J = 5.5$ Hz, 2 H), 3.71 (t, $J = 7.0$ Hz, 2 H), 1.65 (p, $J = 7.2$ Hz, 2 H), 1.48 (s, 18 H), 1. 34 (sext, $J = 7.2$ Hz, 2 H), 0.92 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 153.3, 137.4 (2), 128.1, 127.0, 126.3, 116.0, 80.6, 38.8, 30.5, 28.3, 20.1, 13.8; HRMS calcd for $C_{28}H_{33}N_3O_6S_3$ 603.1532, found 603.1530.

Trimer 32. TFA (1.0 mL) was slowly added to **31** (0.21 g, 0.35 mmol) in dichloromethane (2.0 mL), and the mixture was stirred for 3 h before pouring it into aqueous sodium bicarbonate. The aqueous phase was extracted with dichloromethane (10 mL) (3×). The combined organic layer was washed water, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo, and the residue was dissolved in dichloromethane and poured into hexane. The solid was collected by filtration to afford 0.112 g (80%) of the title compound: IR (KBr) 3446, 3354, 3210, 2933, 2862, 1713, 1677, 1521, 1539, 1415, 1385, 1354, 1256, 1056, 939, 739, 662; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, $J = 5.3$ Hz, 2 H), 6.61 (d, $J = 5.3$ Hz, 2 H), 5.20 (s, 4 H), 3.63 (t, $J = 7.23$ Hz, 2 H), 1.63 (p, $J = 7.4$ Hz, 2 H), 1.34 (sext, $J = 7.4$ Hz, 2 H), 0.92 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 146.7, 137.8, 128.5, 125.3, 123.1, 106.6, 38.5, 30.6, 20.2, 13.7; HRMS calcd for $C_{18}H_{17}N_3O_2S_3$ 403.0483, found 403.0485.

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Supporting Information Available: Solution and film optical absorption spectra for **18** and **20**−**25** (14 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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