Imine-Bridged Planar Poly(phenylenethiophene)s and Polythiophenes

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Abstract: Synthetic routes to soluble planar poly(phenylenethiophene)s and polythiophenes are described. The main polymer backbones are synthesized via Pd(0)-catalyzed couplings of the electron-rich *N,N′*-(bis-*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene with electron-deficient aryldibromodiones. The prebridged polymers have bathochromically shifted absorptions due to donor/acceptor interactions between the consecutive repeat units. Upon exposure of the polymers to trifluoroacetic acid or titanium tetrachloride, imine bridges are formed that force the consecutive units into planarity. The bridging units are sp^2-hybridized, thus allowing for greater electron delocalization between the consecutive aryl units. The syntheses of model trimeric systems were conducted to provide further data for assessing the optical properties of the polymers. Protonation of the imine moieties causes bathochromic shifts of >100 nm in several cases. The effect is explained by an intramolecular charge transfer. Thus these arrangements of planar structures with imine bridges serve as optically based proton sensors with spectral shift differences far-exceeding those of nonplanar imine-containing polymers.

Introduction

The optoelectronic properties of conjugated polymers vary significantly based upon the degree of extended conjugation between their consecutive repeat units. We and others have sought to maximize extended π-conjugation in poly(*p*-phenylene)s (PPPs) by forming covalent linkages between the consecutive repeat units.[1] This results in a lowering of the optical bandgaps or an increase of the bandwidths in the polymers. Although polythiophenes have been studied extensively due to the ease with which they can be functionalized, to our knowledge, there are no reports of ladder polymers based on polythiophenes. The overwhelming majority of conjugated ladder polymers are based upon PPP backbones.[1] There have been proposals that ladder polymers with backbones that are thiophene-based would exhibit unusually low optical bandgaps due to the relative stabilities of their quinoidal forms,[1m] but no experimental studies have been conducted. Here we describe syntheses and optical investigations on planar poly(phenylenethiophene)s and a planar polythiophene. Novel optoelectronic properties in polymers with significant charge transfer (CT) character in their backbones,[2] coupled with the growing interest in developing polymer-based sensors,[3] have promoted us to explore the utility of these thiophene-containing planar polymers and their oligomeric analogues for proton-induced intrachain CT-based variations. We found that a unique method to minimize optical bandgaps in conjugated materials is to combine intramolecular CT with the maximization of conjugation via planarization.

Monomer Preparation

The monomers for the desired planar polymers were readily prepared. Thiophene was selectively brominated at the 2,5-positions and then nitrated. Reduction of the nitro moieties with concomitant dehalogenation[4] followed by *tert*-butoxycarbonyl (Boc) protection and stannylation yielded the requisite thiophene monomer **1** (eq 1). Although the LDA treatment followed by
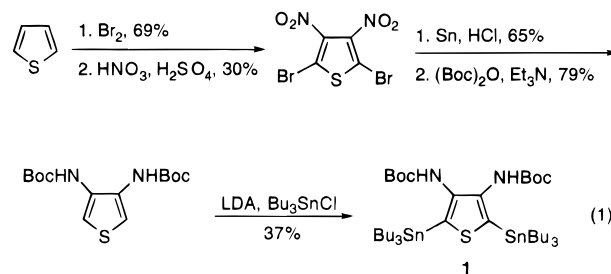
quenching with chlorotrimethylsilane afforded the analogous bis-(silane) in 98% yield, the bis(stannane) **1** was unstable during

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(1) (a) Overberger, C. G.; Moore, J. A. *Adv. Polym. Sci.* **1970**, *7,* 113. (b) Schlüter, A.-D. *Adv. Mater.* **1991**, *3,* 282. (c) Yu, L.; Chen, M. Dalton, L. R. *Chem. Mater.* **1990**, *2,* 649. (d) Hong, S. Y.; Kertesz, M.; Lee, Y. S.; Kim, O.-K. *Chem. Mater.* **1992**, *4,* 378. (e) Godt, A.; Schlüter, A.-D. *Adv. Mater.* **1991**, *3,* 497. (f) Yu. L.; Dalton, L. R. *Macromolecules* **1990**, *23,* 3439. (g) Scherf, U.; Müllen, K. *Synthesis* **1992**, 23. (h) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116,* 11723. (i) Schlüter, A.-D.; Schlicke, B. *Synlett* **1996**, 425. (j) Kertesz, M.; Hong, S. Y. *Macromolecules* **1992**, *25,* 5424. (k) Kintzel, O.; Münch, W.; Schlüter, A.-D.; Godt, A. *J. Org. Chem.* **1996**, *61,* 7304. (l) Scherf, U.; Müllen, K. *Adv. Polym. Sci.* **1995**, *123,* 1. (m) Roncali, J. *Chem. Rev.* **1997**, 1733. (n) Dai, Y.; Katz, T. J.; Nichols, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35,* 2109. (o) Nuckolls, C.; Katz, T. J. Castellanos, L. *J. Am. Chem. Soc.* **1996**, *118,* 3767. (p) Goldfinger, M. B.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116,* 7895. (q) *Handbook of Conducting Polymers*; Skotheim, T. J., Ed.; Dekker: New York, 1986.

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

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

(4) (a) Mozingo, R.; Harris, S. A.; Wolf, D. E.; Hoffhine, C. E., Jr.; Easton, N. R.; Folkers, K. *J. Am. Chem. Soc.* **1945**, *67,* 2092. (b) Galvez, C.; Garcia, F.; Garcia, J.; Soldevila, J. *J. Heterocycl. Chem.* **1986**, *23,* 1103.

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chromatographic purification and even amine-washed silica gel caused significant decomposition of **1**. Hence a low isolated yield of **1** was obtained in our efforts to ensure purities necessary for the subsequent step-growth polymerizations. Diketone **2**[1p] was prepared from 2,4-dibromoterephthaloyl chloride[1h] as described previously, while the complementary compounds **3** (67%) and **4** (63%) were easily prepared by AlCl$_3$-promoted

2, R = C$_{12}$H$_{25}$
3, R = *p*-(C$_6$H$_4$)-C$_4$H$_9$-*n*
4, R = *p*-(C$_6$H$_4$)-C$_8$H$_{17}$-*n*
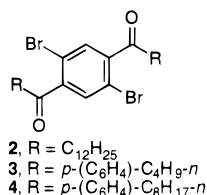
Friedel–Crafts acylation of *n*-butylbenzene or 1-phenyloctane, respectively, with 2,4-dibromoterephthaloyl chloride. Tetrabromination of thiophene followed by selective 2,5-debromination afforded 3,4-dibromothiophene. Cyano-substitution, hydrolysis and bromination at the 2,5-positions afforded the dicarboxylic acid **5**.[5] Bis(acid chloride) formation and treatment with *n*-butylbenzene yielded the diketone monomer **6** (eq 2).

$$(2)$$

5

6
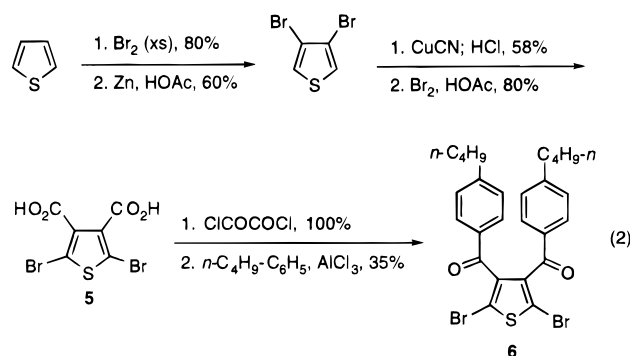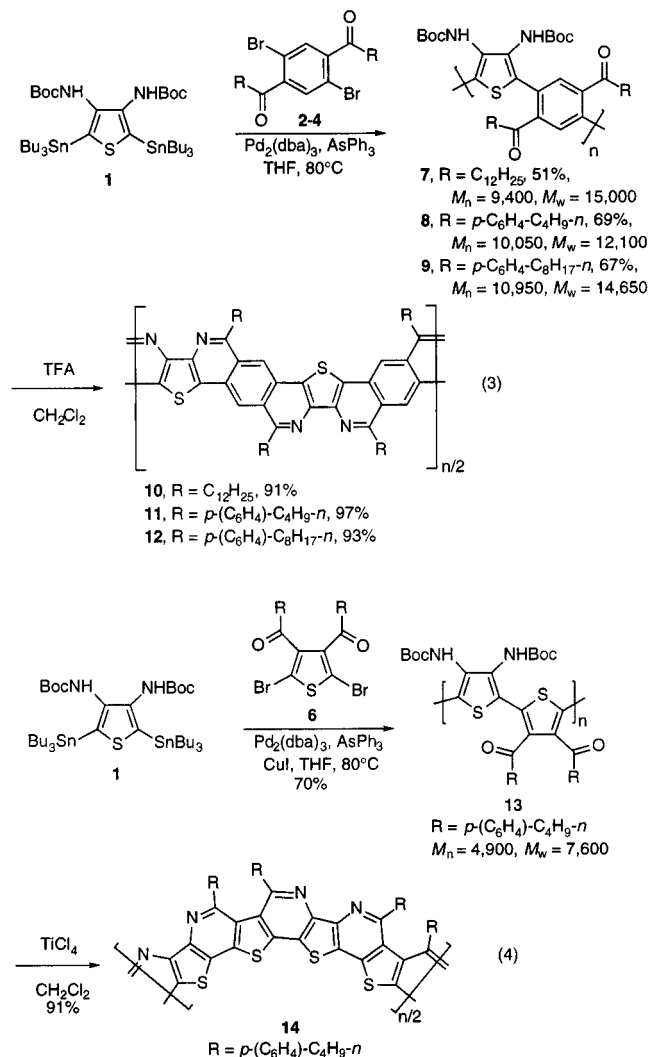
Polymerization Reactions

The modified Stille polymerizations[6] were carried out with a Pd(0) catalyst and triphenylarsine as the supporting ligand. Triphenylphosphine gave lower molecular weight polymers, probably due to phosphine aryl transfer reactions.[6] Addition of CuI as a cocatalyst lowered the molecular weights for the poly(phenylenethiophene)s while CuI addition increased the molecular weights for the polythiophenes. The reason for the catalysis differences in the two polymer systems is unclear. Use of higher polymerization temperatures resulted in the loss of some of the Boc residues and darkening of the material. The polymerizations are shown in Scheme 1. All the polymers were 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 and not 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.[7] The errors in this M_n range are generally off by a factor of 1.5–2. Therefore, the values recorded here are given simply as a reference. The trifluoro-

(5) (a) Gronowitz, S. *Acta Chem. Scand.* **1959**, *13*, 1045. (b) MacDowell, D. W. H.; Wisowaty, J. C. *J. Org. Chem.* **1972**, *37*, 1712. (c) Pomerantz, M.; Yang, H.; Cheng, Y. *Macromolecules* **1995**, *28*, 5706.

(6) (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.

(7) This effect in molecular weight differences was determined using rigid rod oligomers of precisely known length and constitution to generate a calibration curve versus polystyrene in THF by SEC. See: (a) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

Scheme 1

7, R = C$_{12}$H$_{25}$, 51%,
    M_n = 9,400, M_w = 15,000
8, R = *p*-C$_6$H$_4$-C$_4$H$_9$-*n*, 69%,
    M_n = 10,050, M_w = 12,100
9, R = *p*-C$_6$H$_4$-C$_8$H$_{17}$-*n*, 67%,
    M_n = 10,950, M_w = 14,650

$$(3)$$

10, R = C$_{12}$H$_{25}$, 91%
11, R = *p*-(C$_6$H$_4$)-C$_4$H$_9$-*n*, 97%
12, R = *p*-(C$_6$H$_4$)-C$_8$H$_{17}$-*n*, 93%

13
R = *p*-(C$_6$H$_4$)-C$_4$H$_9$-*n*
M_n = 4,900, M_w = 7,600

$$(4)$$

14
R = *p*-(C$_6$H$_4$)-C$_4$H$_9$-*n*

acetic acid (TFA) or TiCl$_4$-induced[8] Boc removal and Schiff base formation products are also shown in Scheme 1. Notice that the imine formation strategy provides an efficient method for the planarization between the consecutive repeat units, since we can avoid the arduous task of introducing new atoms along a rigid rod backbone from exogenous reagents; all the needed atoms are present in the monomers.

Analyses of the Polymers

The protons on the backbone benzenoid moieties shifted from ca. 7.3 ppm in **7–9** to ca. 9.8 ppm in **10–12** upon planarization; a trend consistent with earlier studies on ladder PPPs.[1p] There were only trace amounts of remaining ketone signatures present in the FTIR spectra, likely due to the end groups, and remaining Boc residues were often undetected by NMR and FTIR analyses. Since the imine formation was reversible under the acidic conditions, any intermolecular Schiff base formation could have equilibrated back to the more stable six-membered imine ring. Furthermore, intermolecular Schiff base formation is unlikely to have been obtained in the final polymers since that would have resulted in a cross-linked insoluble network.

The optical spectra for the poly(phenylenethiophene)s **7–9** were recorded in CH$_2$Cl$_2$ (Figure 1). See Table 1 for a complete listing of the optical data. Compounds **7–9** had larger than

(8) (a) Boone, H. W.; Hall, H. K., Jr. *Macromolecules* **1996**, *29*, 5835. (b) Weingarten, H.; Chupp, J. P.; Whiye, W. A. *J. Org. Chem.* **1967**, *32*, 3246.
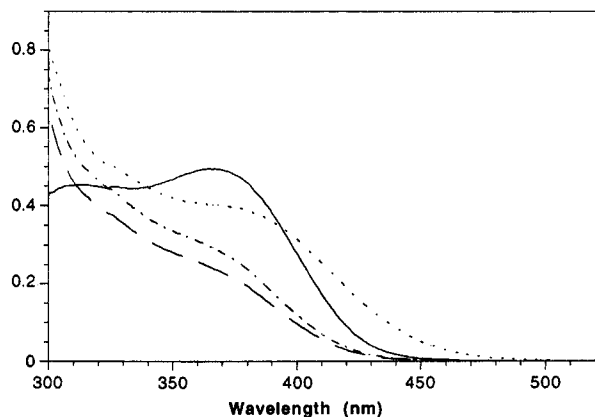
Figure 1. Optical spectra of **7** (—), **8** (- · -), **9** (— — —), and **13** (···) in CH$_2$Cl$_2$.

**Table 1.** Optical Data for the Polymers and Their Corresponding Trimers

compd	λ_{max} (CH$_2$Cl$_2$), (nm)[a]	λ_{max} (TFA/CH$_2$Cl$_2$, 1:2), (nm)[a]	emiss$_{max}$ (CH$_2$Cl$_2$), (nm)	emiss$_{max}$ (TFA/CH$_2$Cl$_2$, 1:2), (nm)
7	372	*c*	479	*c*
8	375 (sh)	*c*	503	*c*
9	375 (sh)	*c*	509	*c*
10	*b*	463	*b*	no emission
11	*b*	477	*b*	no emission
12	*b*	477	*b*	no emission
13	378 (sh)	*c*	523	*c*
14	*412*, 439	450	no emission	no emission
19	*332*, 352	393	413	431
20	356	416	487	457
21	436	495, *526*	514	558
22	425, *449*	515, *551*	475	588
23	*325*, 345 (sh)	380 (sh)	476	*435*, 464
25	358	423	470	451

[a] No absorptions of <310 nm are listed here. The italic values are the more intense of the two listed. [b] The polymers were not soluble in CH$_2$Cl$_2$. [c] Addition of TFA would result in loss of the Boc group.

expected values of λ_{max} when compared to less sterically encumbered poly[(dialkylphenylene)thiophene]s which have λ_{max} values of ca. 340 nm.[6a] In **7−9**, the thiophene moieties are electron rich and the phenylene units are electron deficient, thus inducing an alternating donor/acceptor repeat unit configuration which establishes significant intramolecular charge transfer (CT) character between the consecutive polymer repeat units, resulting in an increase in the absorbance maxima (Figure 1).[2,9] Though a direct comparison was sought of the optical spectral properties of **7−9** versus **10−12** in identical solvents, the planar polymers **10−12** required TFA/CH$_2$Cl$_2$ (1:2) mixtures for their dissolution. Any use of acid for recording the optical spectra of **7−9** would have caused loss of the Boc moieties and planarization. Attempts to cast films of **10−12** from TFA/CH$_2$Cl$_2$ (1:2) followed by removal of the solvent in vacuo did not permit salt removal as indicated by FTIR studies.[2a] Interestingly, the planar polymers **10−12** had significantly longer wavelength absorptions (Figure 2) by ca. 100 nm relative to their nonplanar precursors **7−9**. This could be a function of the enhanced π-conjugation upon planarization, or simply a solvent-induced difference (aprotic for **7−9** and strongly acidic for **10−12**). Due to the solubility differences of the planarized and nonplanarized forms of the poly(phenylenethiophene)s, a more precise explanation awaits an oligomeric study in which common solvents can be used (vide infra).

In the case of the polythiophenes **13** and **14**, CH$_2$Cl$_2$ could be used to dissolve both the preplanar (**13**) and planar (**14**) forms. Upon the conversion of **13** to **14** (Scheme 1, eq 4), an
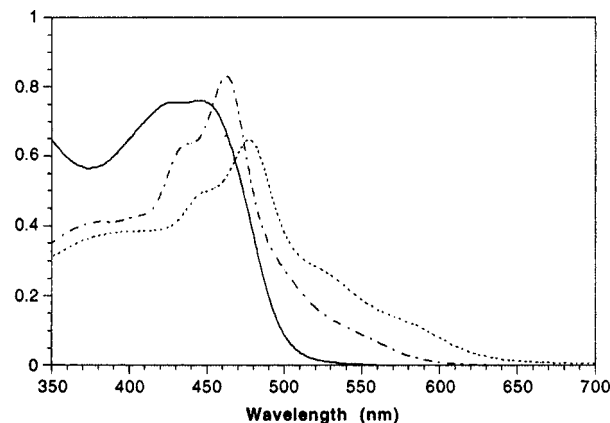
Figure 2. Optical spectra of **10** (- · -), **11** (···), and **14** (—) in TFA/CH$_2$Cl$_2$ (1:2). The spectrum for **12** is nearly identical to the spectrum of **11**.

increase in λ_{max} (Figures 1 and 2, and Table 1) was noticed which could be indicative of the greater electron delocalization in the planar form. However, there are two factors that must be considered. First, **13** has an unusually large λ_{max} value when compared to typical fully substituted polythiophenes. Highly regiochemically pure 3-substituted polythiophenes have λ_{max} values of 450−460 nm in solution,[10] while 3,4-disubstituted polythiophenes generally have λ_{max} < 300 nm due to the unavoidable 3−3′ (head-to-head) interactions.[11] In the case of **13**, the large λ_{max} value is likely due to the donor/acceptor alternating arrangement which induces intramolecular CT as described above.[2,9] Second, in **14**, molecular modeling[12] confirms that there is severe buttressing of the two aryl moieties at the adjacent imine-carbon positions which causes a twisting of the planar backbone. Recording of the optical spectra of **14** in TFA/CH$_2$Cl$_2$ (1:2) resulted in a bathochromic shift over that recorded in CH$_2$Cl$_2$ albeit smaller than the shifts observed in the poly(phenylenethiophene)s (Table 1). This could be the result of a proton-induced enhancement of the intramolecular CT.[2a]

With all of the ladder polymers, the nitrogen lone pair remains orthogonal to the polymer backbone, hence it is no longer able to add electron density to the polymer backbone by a resonance effect. Thus the donor portion is not as strong a donor in the planar polymer as it is in the nonplanar polymer. Though the carbonyl portion of the acceptor moiety is lost upon planarization, the imine remains an electron-withdrawing group in the cyclized material. The imine units in the ladder polymer are fixed in near planarity with the conjugated polymer backbone, thereby increasing their electron-accepting ability. Hence planarization has a dual effect on the donor/acceptor properties. Interestingly, even though **10−12** had thiophene units that were forced into a nearly 180° relationship between the 2,5-bonds (148° being the optimal bond angle in an unperturbed thiophene),[13] the linear arrangements permitted a greater degree

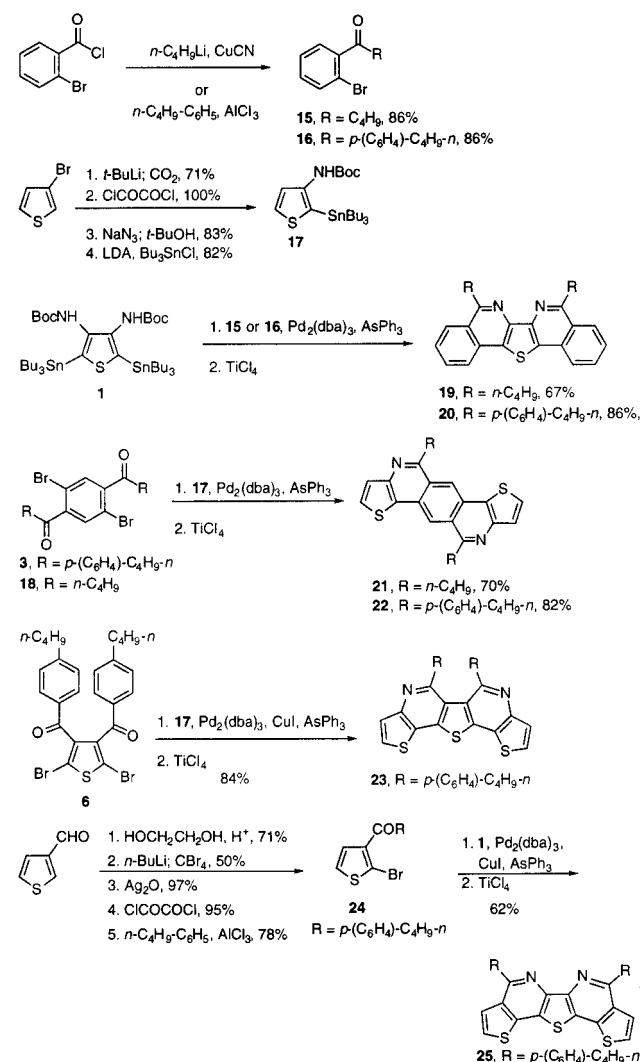(9) (e) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 5065.

(10) (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.

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

(12) Molecular modeling was performed using a Silicon Graphics Power Indigo2 employing MacroModel 4.5 for both structure drawing and minimization. Minimization was done on a tetramer containing four thiophene units and three imine brides using a MM2* force field. The energy calculation was minimized over a large number of iterations to convergence at a local minimum nearest in energy to the drawn starting compound's initial energy.

(13) Phillips, R. W.; Sheares, V. V.; Samuliski, E. T.; DeSimone, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 367.
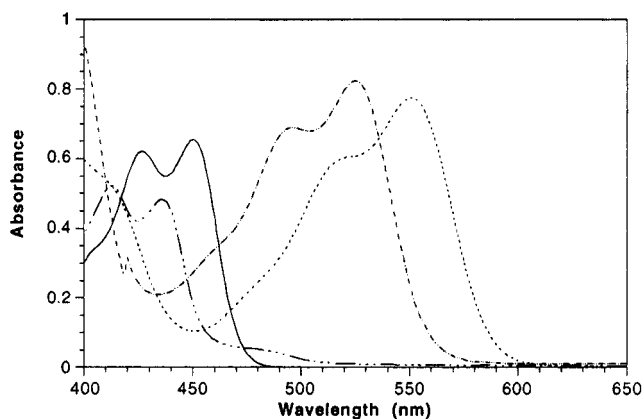
Scheme 2

Figure 3. Optical spectra of **21** in CH_2Cl_2 (−···), **21** in TFA/CH_2Cl_2 (1:2) (- · -), **22** in CH_2Cl_2 (−), and **22** (···) in TFA/CH_2Cl_2 (1:2).

Aqueous workup afforded the aldehyde which was oxidized to the carboxylic acid,[15] converted to the acid chloride, and subjected to Friedel−Crafts acylation conditions to afford **24**. The couplings were achieved using the same conditions that afforded the corresponding polymers.

The optical spectra of the trimeric (phenylenethiophene)s **19**−**22** showed unexpected and remarkable features. The optical absorption maxima underwent enormous bathochromic shifts when recorded in TFA/CH_2Cl_2 (1:2) versus CH_2Cl_2 (Table 1). The protic system is likely increasing the intramolecular CT by making the iminium-bearing units more electron deficient. Moreover, these spectra were recorded at varying concentrations to confirm that the charge transfer is likely intramolecular (or inter-repeat unit)[2a] and not intermolecular; there was no change in λ_{max} upon dilution. The high degree of conjugation in the planar systems is further suggested since the affect of CT separation between the protonated and nonprotonated forms is far greater than the differences noted in nonplanarized polymers.[2a] Using these simple trimeric models, it is obvious that a direct comparison of the optical data for **7**−**9** in CH_2Cl_2 versus **10**−**12** in TFA/CH_2Cl_2 is not be possible since the charge separation in the protonated cases greatly lowers the optical bandgaps. A common solvent must be utilized.

While the optical absorption maxima of the trimers **19** and **20** were considerably smaller than the absorption maxima of polymers **10**−**12**, the absorption maxima of **21** and **22** are large relative to the corresponding absorptions of the polymers (all using TFA/CH_2Cl_2 (1:2), Table 1, Figures 2 and 3). The optical absorption maximum of the polymers **10**−**12** reside between the values for the complementary trimers **19/20** and **21/22**. It is unclear why the complementary pairs **19/20** and **21/22** exhibit such large (ca. 100−130 nm) optical absorption differences regardless of their protonated or unprotonated states. In **21/22**, the acceptor units are polarized in opposite directions while they are pointing in the same direction in **19/20**. Thus greater CT separation is likely in **21/22** with a concomitant bathochromic shift. In polymers **10**−**12**, the intramolecular CT separation can follow both opposing and similar directions, resulting in optical absorptions that reside between the values for the complementary trimer pairs.

The problem of comparing polymer **14** to trimers **23** and **25** is exacerbated since **14** and **23** have the aryl buttressing problem (leading to backbone twisting) while **25** does not. Nevertheless, polymer **14** has a longer wavelength maximum than either of the complementary trimeric forms.

To further explore this protonation effect on planar oligomers, we reinvestigated two planar trimeric phenylenes that were

of π-conjugation, as evidenced by the optical absorption maxima, than the curved and distorted backbone configuration (due to aryl buttressing) in **14**.

Emission signals with very large Stokes shifts (ca. 100−130 nm) were apparent for the preplanar polymers **7**−**9** and **13** in CH_2Cl_2. Since highly delocalized systems can undergo exciton−exciton annihilation, it is not surprising that the corresponding planar polymers **10**−**12** and **14** showed no emission signals (Table 1). Conversely, this could be an effect of the azine functionality.

Synthesis of Model Trimers and Their Optical Analyses

To more precisely assess the degree of extended conjugation or intrachain CT interactions in the in the polymers, it was necessary to prepare systems that could be dissolved in a common solvent system. Using reactions similar to those described above, the syntheses of model trimers were conducted as shown in Scheme 2. **17** was prepared by lithium−halogen exchange of 3-bromothiophene followed by carboxylation. Acid chloride formation, conversion to the acyl azide, and Curtius rearrangement with *tert*-butyl alcohol capture yielded the Boc-protected amine. Finally, Boc-directed 2-position lithiation and quenching with the chlorostannane afforded the desired **17**.[14] Thiophene-3-carbaldehyde was protected as its acetal which directed 2-position lithiation and subsequent bromination.

(14) Björk, P.; Aakermann, T.; Hornfeldt, A.-B.; Gronowitz, S. *J. Heterocycl. Chem.* **1995**, *32*, 751.

(15) (a) Fournari, P.; Guilard, R.; Person, M. *Bull. Soc. Chim. Fr.* **1967**, 4115. (b) Campaigne, E.; LeSuer, W. M. *J. Am. Chem. Soc.* **1949**, *71*, 333.

models for the planar PPPs (**26**−**28**) that we synthesized previously.[1h] The planar PPPs were not soluble without TFA being present, however, the oligomeric versions were previously studied only in CH_2Cl_2. The CT bands in **26**−**28** are assigned to 514, 516, and 549 nm bands, respectively, since these bands are not present in typical nonheteroatom-containing ladder PPPs.[1,2a] In this case, polymers **26**−**28** have longer absorption maxima than either of the two complementary trimers **29/30**. Notice, as with the previous planar trimers, there is an enormous optical difference when **29** or **30** are subjected to acidic versus neutral conditions. Thus planarization greatly affects the amount
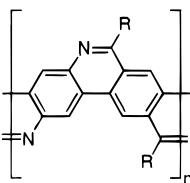
26, R = *n*-C$_4$H$_9$, λ_{max} (TFA/CH$_2$Cl$_2$)= <u>396</u>, 514 nm
27, R = *n*-C$_{12}$H$_{25}$, λ_{max} (TFA/CH$_2$Cl$_2$)= <u>400</u>, 516 nm
28, R = *p*-(C$_6$H$_4$)-C$_8$H$_{17}$-*n*, λ_{max} (TFA/CH$_2$Cl$_2$)= <u>402</u>, 549 nm
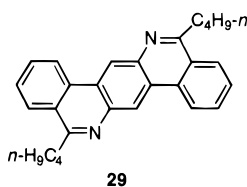
29
λ_{max} (CH$_2$Cl$_2$) = 295 nm
λ_{max} (TFA/CH$_2$Cl$_2$) = 418 nm
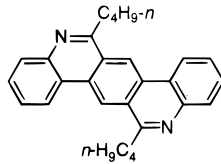
30
λ_{max} (CH$_2$Cl$_2$) = 303 nm
λ_{max} (TFA/CH$_2$Cl$_2$) = <u>376</u>, 472 nm

of CT possible when we compare these to nonplanarized imine-containing CT polymers,[2a] thereby indicating that the propensity for extended conjugation in the ladder systems permits an optimization of intramolecular CT.

Conductivity Studies

As a test case, we studied the conductivity characteristics on pressed pellets of polymer **11** in their neutral and HCl-protonated forms. Four-point probe measurements indicated that both forms had conductivity values of $<10^{-7}$ $\Omega \cdot cm^{-1}$, thus making these insulators. Iodine doping of the neutral material gave no enhancement of the conductivity. Due to the presence of the electron deficient pyridyl system in the ladder polymers, p-doping becomes more difficult than in typical polythiophenes, a phenomenon that we have observed previously in the planar PPPs such as **27**.[1h]

Conclusion

We have described routes to soluble planar poly(phenylene-thiophene)s and polythiophenes by using Pd-catalyzed coupling routes followed by Schiff base formations to force the consecutive repeat units into near planarity. Bond deformations that are caused by pendant group interactions can adversely affect the conjugation. Intramolecular CT profoundly decreases the optical bandgap in the planarized systems, especially when the CT effect is enhanced by protonation of the imine units; shifts in the optical absorption maxima of 100 nm can be observed upon protonation. The effect of intramolecular CT can even be observed with small oligomeric ladder systems which provides a further motivation to study these simple small conjugated structures. Therefore, coupling of intramolecular CT with maximization of conjugation via planarization is a unique method to minimize optical bandgaps in conjugated materials.

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) eluting 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 absorption and emission spectral data are listed in Table 1, while the molecular weight data are listed in Scheme 1.

***N,N′*-Bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butyl-stannyl)thiophene (1).** A solution of *n*-butyllithium (44.30 mL, 70.0 mmol, 1.58 M in hexane) was slowly added to diisopropylamine (8.46 mL, 60.0 mmol) in ether (50 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)-3,4-diaminothiophene[4b] (3.14 g, 10 mmol) in THF (10.0 mL) was added, and the mixture was warmed to room temperature for 10 min. After the mixture was recooled to 0 °C, chlorotributylstannane (6.52 mL, 22.0 mmol) was added. The yellow mixture was stirred for 3 h. A saturated sodium chloride solution (50 mL) was added, the organic layer was separated off, 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 with triethylamine, then hexane). The product was collected as the first fraction. The solvent was removed in vacuo to give 2.94 g (37%) of the title compound. FTIR (KBr): 3278, 2957, 2926, 2872, 1717, 1506, 1392, 1376, 1246, 1162, 1065, 1018, 876, 771 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.37 (s, 2 H), 1.51 (m, 12 H), 1.47 (s, 18 H), 1.33 (sext, *J* = 7.4 Hz, 12 H), 1.10 (m, 12 H), 0.88 (t, *J* = 7.3 Hz, 18 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.0, 138.6, 136.2, 82.4, 29.4, 28.7, 27.7, 14.0, 11.2. LRMS (positive ion APCI) calcd relative isotopic intensities for C$_{38}$H$_{74}$N$_2$O$_4$SSn$_2$ (M$^+$): 888.4 (13%), 890.4 (41%), 891.3 (82%), 893.3 (100%), 895.4 (80%), 896.4 (49%), 899.4 (19%). Found: 887.6 (12%), 889.5 (41%), 891.5 (76%), 893.5 (100%), 895.5 (81%), 896.5 (42%), 897.5 (25%). Anal. Calcd for C$_{38}$H$_{74}$N$_2$O$_4$SSn$_2$: C, 51.14; H, 8.35; N, 3.14. Found: C, 51.20; H, 8.37; N, 3.07.

Compound 3. A solution of dibromoterephthaloyl chloride[1h] (2.00 g, 5.97 mmol) in dichloromethane was added slowly to a suspension of aluminum chloride (3.18 g, 23.90 mmol) in dry dichloromethane (15 mL) maintained at 0 °C. The mixture was allowed to stir at 0 °C for 10 min. *n*-Butylbenzene (4.01 g, 29.85 mmol) was slowly added. The mixture was stirred for 30 min and was 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 (50 mL) and water, then dried over magnesium sulfate. 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 2.2 g (67%) of the title compound. FTIR (KBr): 2926, 2857, 1669, 1604, 1460, 1416, 1384, 1344, 1248, 1184, 1152, 1060, 934, 881, 841, 752, 666. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.74 (d, *J* = 8.20 Hz, 4 H),

7.56 (s, 2 H), 7.26 (d, J = 8.20 Hz, 4 H), 2.68 (t, J = 7.80 Hz, 4 H), 1.62 (p, J = 7.40 Hz, 4 H), 1.35 (sext, J = 7.40 Hz, 4 H), 0.92 (t, J = 7.40 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 193.33, 150.53, 143.35, 132.90, 130.48, 129.00, 118.43, 35.87, 33.11, 22.11, 13.89. Anal. Calcd for C$_{28}$H$_{28}$Br$_2$O$_2$: C, 60.45; H, 5.07. Found: C, 60.32; H, 5.14. HRMS calcd for C$_{28}$H$_{28}$Br$_2$O$_2$: 554.0456. Found: 554.0461.

Compound 4.[1h] This compound was synthesized in the same manner as described for compound **3**. Used were 2,5-dibromoterephthaloyl chloride[1h] (3.00 g, 8.31 mmol) and 1-phenyloctane (3.95 g, 20.78 mmol). The yield was 3.50 g (63%). Spectral properties were identical to those reported earlier[1h] though the synthesis was different.

2,5-Dibromothiophene-3,4-dicarboxylic Acid (5). Thiophene-3,4-dicarboxylic acid[5b] (0.50 g, 2.91 mmol) and glacial acetic acid (5 mL) were added to a 10 mL flask with a stirring bar. Bromine (0.90 mL, 17.4 mmol) was added dropwise. The mixture was stirred overnight. Aqueous sodium bisulfate solution was added until the reddish color disappeared. The mixture was filtered, and a gray solid was obtained. The crude product was recrystallized from water to give 0.96 g (80%) of the title compound. IR (KBr): 3300−2600, 1697, 1465, 1377, 1247, 912, 687 cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ 13.6 (br s). ^{13}C NMR (100 MHz, CDCl$_3$) δ 163.0, 135.6, 114.9.

2,5-Dibromothiophene-3,4-dicarboxylic Acid Chloride. Oxalyl chloride (1.06 mL, 12.1 mmol) was slowly added to 2,5-dibromothiophene-3,4-dicarboxylic acid (1.00 g, 3.03 mmol) and DMF (1 drop) in benzene (50 mL). The mixture was heated to reflux for 1 h, then cooled to room temperature. The volatiles were removed in vacuo, affording 1.19 g (100%) of the title compound. IR (KBr): 1755, 1414, 1356, 1145, 992, 949, 716, 673 cm^{-1}. ^{13}C NMR (100 MHz, CDCl$_3$): δ 160.2, 136.4, 118.8. HRMS calcd for C$_6$Br$_2$Cl$_2$O$_2$S: 363.7363. Found: 363.7361. No MS peak for the cyclic anhydride (C$_6$Br$_2$O$_2$S) at 311.9 amu was observed.

Compound 6. This compound was synthesized in the same manner as described for compound **3**. Used were 2,5-dibromothiophene 3,4-diacid chloride (0.50 g, 1.49 mmol) and n-butylbenzene (1.15 mL, 7.45 mmol). The yield was 0.23 g (35%). IR (KBr): 2954, 2862, 1662, 1600, 1436, 1380, 1251, 1174, 995, 841, 769, 626. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, J = 8.3 Hz, 4 H), 7.19 (d, J = 8.3 Hz, 4 H), 2.61 (t, J = 7.8 Hz, 4 H), 1.57 (p, J = 7.3 Hz, 4 H), 1.31 (sext, J = 7.3 Hz, 4 H), 0.91 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.2, 149.8, 142.0, 134.0, 130.0, 128.6, 113.7, 35.8, 33.1, 22.3, 13.9. Anal. Calcd for C$_{26}$H$_{26}$Br$_2$O$_2$S: C, 55.54; H, 4.66. Found: C, 55.61; H, 4.67. HRMS calcd for C$_{26}$H$_{26}$Br$_2$O$_2$S: 560.0020. Found: 560.0005.

General Polymerization Procedure for Polymers 7, 8, 9, and 13. In a drybox, the diketone monomer (0.50 mmol) and N,N'-bis($tert$-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-n-butylstannyl)thiophene (0.49 mmol) were dissolved in dry THF (5.0 mL) in a screw cap tube. Pd$_2$-(dba)$_3$ (2 mol %) and AsPh$_3$ (4 mol %) were added to the solution. The tube was capped and heated to 80 °C for 72 h. The dark mixture was cooled, poured into a solution of KF (10 mL, 1.00 M), and stirred for 30 min. The insoluble white solid was removed by filtration. The organic layer was separated, 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 under vacuum.

Polymer 7. N,N'-Bis($tert$-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-n-butylstannyl)thiophene (0.4374 g, 0.4900 mmol), **2** (0.314 g, 0.5000 mmol), dry THF (5.0 mL), Pd$_2$(dba)$_3$ (0.0092 g, 0.0100 mmol), and AsPh$_3$ (0.0061 g, 0.0200 mmol) were used. The yield was 0.20 g (51%). FTIR (KBr): 3415, 3374, 3149, 2923, 2851, 1723, 1697, 1497, 1456, 1385, 1246, 1164, 1077, 1005, 872, 769, 605. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.61−7.52 (br s, 2 H), 6.91−6.70 (br s, 2 H), 2.70 (br s, 4 H), 1.70−1.50 (m, 4 H), 1.38 (m, 18 H), 1.30 (br s, 36 H), 0.89 (t, J = 7.0 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 204.91, 153.27, 142.54, 130.97, 130.12, 129.20, 124.82, 124.60, 80.82, 42.07, 31.92, 29.71, 29.68, 29.61, 29.55, 29.37, 29.30, 28.31, 28.12, 24.47, 22.69, 14.12. Anal. Calcd for (C$_{46}$H$_{72}$N$_2$O$_6$S)$_n$: C, 70.73; H, 9.29; N, 3.59. Found: C, 70.84; H, 9.36; N, 3.52.

Polymer 8. N,N'-Bis($tert$-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-n-butylstannyl)thiophene (0.4374 g, 0.4900 mmol), **3** (0.278 g, 0.5000 mmol), dry THF (5.0 mL), Pd$_2$(dba)$_3$ (0.0092 g, 0.0100 mmol), and AsPh$_3$ (0.0061 g, 0.02 mmol) were used. The yield was 0.29 g (69%). FTIR (KBr): 3423, 3359, 2959, 2931, 2871, 2860, 1730, 1665, 1605, 1506, 1455, 1384, 1368, 1280, 1244, 1171, 943, 854, 771. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62∠7.50 (br d, J = 8.35 4 H), 7.40−7.22 (br s, 2 H), 7.20−6.90 (br s, 4 H), 2.80−2.30 (br s, 4 H), 1.60−1.02 (m, 26 H), 1.00−0.80 (br t, J = 7.90 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.96, 153.09, 149.21, 140.95, 133.95, 132.00, 130.54, 129.47, 128.32, 80.15, 35.69, 33.04, 28.10, 22.29, 13.83. Anal. Calcd for (C$_{42}$H$_{48}$N$_2$O$_6$S)$_n$: C, 71.16; H, 6.82; N, 3.95. Found: C, 71.23; H, 6.80; N, 3.89.

Polymer 9. N,N'-Bis($tert$-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-n-butylstannyl)thiophene (0.4374 g, 0.4900 mmol), **4** (0.3340 g, 0.5000 mmol), dry THF (5.0 mL), Pd$_2$(dba)$_3$ (0.0092 g, 0.0100 mmol), and AsPh$_3$ (0.0061 g, 0.0200 mmol) were used. The yield was 0.276 g (67%). FTIR (KBr): 3356, 2928, 2856, 1728, 1664, 1605, 1493, 1385, 1245, 1161, 933, 767. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70-7.50 (br d, J = 8.35 Hz, 4 H), 7.40−7.22 (br s, 2 H), 7.20−6.80 (br s, 4 H), 2.80−2.30 (br s, 4 H), 1.70−1.02 (m, 42 H), 0.90−0.80 (br t, J = 7.40 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.78, 153.03, 149.25, 140.90, 133.96, 130.55, 129.46, 128.26, 80.12, 36.03, 31.87, 30.97, 29.37, 29.21, 28.11, 22.66, 14.09. Anal. Calcd for (C$_{50}$H$_{64}$N$_2$O$_6$S)$_n$: C, 73.14; H, 7.86. N, 3.41. Found: C, 73.13; H, 7.89; N, 3.34.

General Schiff Base Formation Procedure for Polymers 10, 11, and 12. Under nitrogen, trifluoroacetic acid (1.5 mL) was added to the Boc-protected polymer in methylene chloride (1.5 mL) at room temperature. The brown solution was stirred at room temperature for 12 h, then poured into a solution of aqueous sodium hydroxide (10 mL, 3 M). The mixture was stirred at room temperature for 2 h, then heated to evaporate the methylene chloride. The resulting solid was collected by filtration and was washed with water, methylene chloride, and ether. To this solid in a screw cap tube was added triethylamine, and the mixture was heated 80 °C for 12 h. The mixture was allowed to cool to room temperature, then the solid was collected by filtration and washed with water, ether, and methylene chloride. The solid was dried in vacuo to give the title compound.

Polymer 10. This compound was synthesized as described in the general procedures. Polymer **7** (0.1302 g, 0.1666 mmol) was used as the starting material. The yield was 0.0874 g (91%). FTIR (KBr): 3149, 2923, 2851, 1569, 1451, 1385, 1205, 1154, 872, 662. ^{1}H NMR (300 MHz, TFA-d/CDCl$_3$ (1:1)): δ 9.9 (br s, 2 H), 4.19 (br s, 4 H), 2.22 (br, 4 H), 1.80 (br, 4 H), 1.62−1.10 (br, 32 H), 0.90 (br, 6 H). Anal. Calcd for (C$_{36}$H$_{52}$N$_2$S)$_n$: C, 79.36; H, 9.62; N, 5.14. Found: C, 76.81; H, 9.43; N, 5.02.[16]

Polymer 11. This compound was synthesized as described in the general procedures. Polymer **8** (0.6190 g, 0.8731 mmol) was used as the starting material. The yield was 0.3983 g (97%). FTIR (KBr): 3139, 2913, 2851, 1610, 1554, 1451, 1385, 1236, 841, 651. ^{1}H NMR (300 MHz, TFA-d/CDCl$_3$ (1:1)): δ 9.78 (br s, 2 H), 8.10 (br m, 4 H), 7.78 (br m, 4 H), 3.05−2.80 (br, 4 H), 1.68−1.40 (br, 4 H), 1.20−0.90 (br, 6 H). Anal. Calcd for (C$_{32}$H$_{28}$N$_2$S)$_n$: C, 81.32; H, 5.97; N, 5.93. Found: C, 78.33; H, 5.79; N, 5.60.[16]

Polymer 12. This compound was synthesized as described in general procedures. Polymer **9** (0.2547 g, 0.3101 mmol) was used as the starting material. The yield was 0.1687 g (93%). FTIR (KBr): 3139, 2913, 2841, 1549, 1456, 1380, 1236, 887, 836, 646. ^{1}H NMR (300 MHz, TFA-d/CDCl$_3$ (1:1)): δ 9.78 (br s, 2 H), 8.10 (br, 4 H), 7.82 (br, 4 H), 3.10 (br, 4 H), 1.94 (br, 4 H), 1.80−1.30 (br, 20 H), 0.98 (br, 6 H). Anal. Calcd for (C$_{40}$H$_{44}$N$_2$S)$_n$: C, 82.15; H, 7.58; N, 4.79. Found: C, 80.43; H, 7.61; N, 4.53.[16]

Polymer 13. N,N'-Bis($tert$-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-n-butylstannyl)thiophene (0.4374 g, 0.4900 mmol), **6** (0.2810 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) were used. The yield was 0.2810 g (70%). FTIR (KBr): 3426, 3159, 2964, 2923, 2862, 1723, 1656, 1605, 1497, 1385, 1241, 1164, 1000, 872, 841, 764, 615. ^{1}H NMR (400 MHz,

(16) 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 1h 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.

CDCl$_3$): δ 8.00−7.02 (br d, J = 8.3 Hz, 4 H), 7.02−6.80 (m, 4 H), 2.60−2.30 (m, 4 H), 1.70−1.10 (m, 26 H), 1.00−0.80 (m, 6 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ 192.00, 153.07, 148.86, 140.00, 134.81, 132.15, 131.51, 129.78, 128.43, 128.08, 80.63, 35.59, 33.06, 28.28, 22.16, 13.87. Anal. Calcd for (C$_{40}$H$_{46}$N$_2$O$_6$S$_2$)$_n$: C, 67.20; H, 6.49; N, 3.92. Found: C, 65.94; H, 6.41; N, 3.75.

Polymer 14. Under nitrogen, titanium tetrachloride (1.0 mL, 1.0 M in methylene chloride) was added slowly to a solution of polymer **13** (0.0376 g, 0.051 mmol) in methylene chloride (1.0 mL). The mixture was stirred at room temperature for 12 h, then poured into water (10 mL). The mixture was extracted with methylene chloride (3×). The combined organic layers were dried over magnesium sulfate and filtered. The solvent was removed in vacuo. The crude material was added to triethylamine (2.0 mL) in a screw cap tube and was heated 80 °C for 12 h. The mixture was allowed to cool to room temperature, then the solid was collected by filtration and washed with water. The product was dried in vacuo to give 0.0224 g (91%) of the title compound. FTIR (KBr): 2933, 2864, 1663, 1607, 1485, 1396, 1220, 838, 760, 624. ^{1}H NMR (300 MHz, TFA-d/CDCl$_3$ (1:1)): δ 7.30−7.00 (br, 8 H), 2.80−2.50 (br, 4 H), 1.70 (br, 4 H), 1.50 (br, 4 H), 1.10 (br, 6 H). Anal. Calcd for (C$_{32}$H$_{28}$N$_2$S)$_n$: C, 75.28; H, 5.47; N, 5.85. Found: C, 71.79; H, 5.57; N, 5.33.[16]

2-Bromo-4′-(*n*-butyl)benzophenone (16). This compound was synthesized in the same manner as described for compound **3**. Used were 2-bromobenzoic acid chloride[1h] (2.18 g, 9.95 mmol), aluminum chloride (1.99 g, 14.93 mmol), and *n*-butylbenzene (1.86 mL, 11.94 mmol) to afford 2.70 g (86%). IR (KBr): 3046, 2949, 2862, 1667, 1595, 1467, 1426, 1302, 1282, 928, 749. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (d, J = 8.0 Hz, 2 H), 7.62 (d, J = 7.9 Hz, 1 H), 7.39−7.30 (m , 3 H), 7.24 (d, J = 8.0 Hz, 2 H), 2.66 (t, J = 7.3 Hz, 2 H), 1.60 (p, J = 7.3 Hz, 2 H), 1.35 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 195.7, 149.7, 141.0, 133.8, 133.1, 131.0, 130.4, 128.9, 128.7, 127.1, 119.5, 85.8, 33.2, 22.4, 13.9. HRMS calcd for C$_{17}$H$_{17}$BrO: 316.0463. Found: 316.0465.

N-(*tert*-Butoxycarbonyl)-3-amino-2-(tri-*n*-butylstannyl)thiophene (17). A solution of *n*-butyllithium (23.74 mL, 36.08 mmol, 1.52 M in hexane) was slowly added to diisopropylamine (4.73 mL, 36.08 mmol) in ether (50 mL) at −78 °C. The solution was warmed to room temperature then cooled to 0 °C with an ice bath. A solution of *N*-(*tert*-butoxycarbonyl)-3-aminothiophene[14] (3.59 g, 18.04 mmol) in ether (10.0 mL) was added, and the mixture was warmed to room temperature for 10 min. After the mixture was recooled to 0 °C, chlorotributylstannane (6.46 mL, 19.84 mmol) was added. The yellow mixture was stirred for 1 h. A saturated sodium chloride solution (50 mL) was added, the organic layer was separated off, 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 with triethylamine, then hexane). The solvent was removed in vacuo to give 7.19 g (82%) of the title compound. FTIR (KBr): 3436, 3333, 2954, 2913, 2851, 1713, 1544, 1513, 1462, 1364, 1246, 1146, 1056, 867, 713. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.49 (d, J = 4.9 Hz, 1 H), 7.36 (br s, 1 H), 6.32 (br s, 1 H), 1.56 (q, J = 8.1 Hz, 6 H), 1.49 (s, 9 H), 1.38 (sext, J = 7.2 Hz, 6 H), 1.12 (t, J = 8.0 Hz, 6 H), 0.89 (t, J = 7.3 Hz, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 153.5, 142.9, 130.7, 124.1, 122.0, 80.1, 29.0, 28.4, 27.3, 13.7, 11.0. Anal. Calcd for C$_{21}$H$_{39}$NO$_2$SSn: C, 51.65; H, 8.05; N, 2.87. Found: C, 51.71; H, 7.99; N, 2.94.

General Procedure for Pd-Catalyzed Couplings to Prepare the Trimers. In a drybox, the diketone and the stannane were dissolved in dry THF in a screw cap tube. Pd$_2$(dba)$_3$ (2 mol %) and AsPh$_3$ (4 mol %) were added to the solution. The tube was capped, removed from the drybox and heated to 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, filtered, and evaporated to dryness. In some cases, the product was purified by a flash chromatograph on silica gel with ethyl acetate:hexane (1:10) to give the desired compounds.

General Procedure for Schiff Base Formation on the Trimers. Under nitrogen, titanium tetrachloride (1.0 M in methylene chloride) was added slowly to a solution of the nonplanar trimer in methylene chloride. The mixture was stirred at room temperature for 3 h, then poured into water. The mixture was extracted with dichloromethane (3×). The combined organic layer was washed with aqueous potassium carbonate (2.0 M) and water, then dried over magnesium sulfate and filtered. The solvent was removed in *vacuo* to give desired the desired products.

Trimer 19. 1 (0.4374 g, 0.49 mmol), **15**[1h] (0.2411 g, 1.0 mmol), Pd$_2$(dba)$_3$ (0.0092 g, 0.0100 mmol), AsPh$_3$ (0.0062 g, 0.0200 mmol), and THF (5 mL) were used to afford the nonplanar trimer which was used directly for the next step with titanium tetrachloride (2.0 mL, 1.0 M in CH$_2$Cl$_2$). The total yield for two steps was 0.1913 g (67%). IR (KBr): 3117, 2953, 2862, 1549, 1380, 749, 672. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.29 (d, J = 8.3 Hz, 2 H), 8.13 (d, J = 7.6 Hz, 2 H), 7.75 (t, J = 8.2 Hz, 2 H), 7.62 (t, J = 8.2 Hz, 2 H), 3.55 (t, J = 7.2 Hz, 4 H), 2.00 (p, J = 7.8 Hz, 4 H), 1.60 (sext, J = 7.4 Hz, 4 H), 1.01 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 162.1, 145.0, 132.2, 130.5, 128.3, 127.2, 127.2, 125.6, 123.7, 36.1, 32.7, 23.3, 14.1. HRMS calcd for C$_{26}$H$_{26}$N$_2$S: 398.1817. Found: 398.1804.

The Nonplanar Trimer Leading to 20. 1 (0.8748 g, 0.98 mmol), **16** (0.6345 g, 2.00 mmol), Pd$_2$(dba)$_3$ (0.0184 g, 0.02 mmol), AsPh$_3$ (0.0124 g, 0.04 mmol), and THF (5 mL) were used to afford 0.80 g (92%). IR (KBr): 3333, 2964, 2923, 2862, 1728, 1708, 1605, 1523, 1487, 1456, 1385, 1287, 1246, 1159, 928, 754, 692. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58 (d, J = 8.2 Hz, 4 H), 7.47−7.39 (m , 6 H), 7.30 (d, J = 7.6 Hz, 2 H), 7.11 (d, J = 7.5 Hz, 4 H), 6.95 (br s, 2 H), 2.59 (t, J = 7.8 Hz, 4 H), 1.56 (p, J = 7.6 Hz, 4 H), 1.45−1.22 (m, 22 H), 0.88 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 197.9, 153.3, 148.7, 139.8, 134.7, 131.6, 130.4, 130.1, 130.0, 128.7, 128.4, 128.2, 127.7, 122.5, 79.9, 35.8, 33.2, 28.1, 22.4, 13.9. HRMS calcd for C$_{48}$H$_{54}$N$_2$O$_6$S: 786.3703. Found: 786.3682.

Trimer 20. The above nonplanar trimer (0.5642 g, 0.7169 mmol) in methylene chloride (2.0 mL) and titanium tetrachloride (4.0 mL, 1.0 M in methylene chloride) were used. The yield was 0.3762 g (93%). IR (KBr): 3159, 3036, 2944, 2913, 2851, 1610, 1539, 1380, 1303, 1010, 841, 774, 754, 677, 656. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.24 (2 overlapping d, app t, J = 8.0 Hz, 4 H), 7.80 (t, J = 7.2 Hz, 2 H), 7.73 (d, J = 7.6 Hz, 4 H), 7.56 (dd, J = 8.0, 7.1 Hz, 2 H), 7.31 (d, J = 7.2 Hz, 4 H), 2.71 (t, J = 7.8 Hz, 4 H), 1.65 (p, J = 7.8 Hz, 4 H), 1.39 (sext, J = 7.2, 4 H), 0.96 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 160.2, 145.2, 143.3, 137.0, 132.4, 130.7, 130.4, 129.4, 128.8, 128.2, 127.0, 125.6, 123.2, 35.6, 33.7, 22.4, 14.1. HRMS calcd for C$_{38}$H$_{37}$N$_2$S: 550.2443. Found: 550.2443.

Trimer 21. 3 (0.1005 g, 0.25 mmol), **17** (0.2393 g, 0.49 mmol), Pd$_2$(dba)$_3$ (0.0046 g, 0.005 mmol), AsPh$_3$ (0.0031 g, 0.01 mmol), and THF (3 mL) were used to form the nonplanar trimer which was used directly for the next step with titanium tetrachloride (1.0 mL, 1.0 M in CH$_2$Cl$_2$). The total yield for two steps was 0.0691 g (70%). IR (KBr): 3118, 3067, 2944, 2862, 1564, 1456, 1380, 1277, 682, 697. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.91 (s, 2 H), 7.71 (d, J = 5.2 Hz, 2 H), 7.64 (d, J = 5.2 Hz, 2 H), 3.51 (t, J = 7.8 Hz, 4 H), 2.00 (p, J = 7.8 Hz, 4 H), 1.39 (sext, J = 7.4, 4 H), 1.05 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 161.4, 129.3, 126.8, 126.0, 124.8, 121.8, 35.6, 31.9, 23.0, 14.1. HRMS calcd for C$_{24}$H$_{24}$N$_2$S$_2$: 404.1381. Found: 404.1384.

Nonplanar Trimer Leading to 22. 18[1h] (0.2000 g, 0.3598 mmol), **17** (0.3443 g, 0.7052 mmol), Pd$_2$(dba)$_3$ (0.0066 g, 0.0072 mmol), AsPh$_3$ (0.0044 g, 0.0144 mmol), and THF (5 mL) were used. The yield was 0.260 g (89%). IR (KBr): 3426, 3109, 2959, 2924, 2857, 1729, 1667, 1600, 1571, 1467, 1421, 1383, 1237, 1154, 945, 879. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, J = 8.1, 4 H), 7.52 (s, 2 H), 7.35 (br s, 2 H), 7.17 (d, J = 8.1 Hz, 4 H), 7.09 (d, J = 5.5 Hz, 2 H), 6.80 (br s, 2 H), 2.61 (t, J = 7.6 Hz, 4 H), 1.56 (p, J = 7.4 Hz, 4 H), 1.47 (s, 18 H), 1.32 (sext, J = 7.4 Hz, 4 H), 0.90 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 196.3, 152.8, 149.8, 142.2, 134.4, 133.8, 132.2, 130.9, 130.2, 129.8, 128.8, 128.6, 125.0, 80.6, 35.8, 33.1, 28.3, 22.3, 13.9. HRMS calcd for C$_{46}$H$_{52}$N$_2$O$_6$S$_2$: 792.3267. Found: 792.3270.

Trimer 22. The above nonplanar trimer (0.0664 g, 0.0837 mmol) in methylene chloride (2.0 mL) and titanium tetrachloride (1.0 mL, 1.0 M in methylene chloride) were used. The yield was 0.0451 g (97%).

IR (KBr): 3108, 2920, 2912, 2851, 1610, 1554, 1380, 1292, 826, 733, 667. ^{1}H NMR (300 MHz, TFA-*d*): δ 9.60 (s, 2 H), 8.18 (br d, 2 H), 7.92 (d, $J = 8.2$ Hz, 6 H), 7.73 (d, $J = 8.2$ Hz, 4 H), 2.92 (t, $J = 7.5$ Hz, 4 H), 1.80 (p, $J = 7.5$ Hz, 4 H), 1.50 (sext, $J = 7.5$ Hz, 4 H), 1.01 (t, $J = 7.2$ Hz, 6 H). HRMS calcd for $C_{36}H_{32}N_2S_2$: 556.2007. Found: 556.1995.

Nonplanar Trimer Leading to 23. 6 (0.5620 g, 1.00 mmol), **17** (0.9571 g, 1.96 mmol), $Pd_2(dba)_3$ (0.0183 g, 0.02 mmol) $AsPh_3$ (0.0122 g, 0.04 mmol), and THF (5 mL) were used. The yield was 0.693 g (88%). IR (KBr): 3313, 3118, 2964, 2923, 2862, 1723, 1656, 1569, 1477, 1385, 1236, 1159, 1067, 759, 636. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.68 (br s, 2 H), 7.41 (br overlapping d, $J = 5.5-8.2$ Hz, 6 H), 7.21 (d, $J = 5.5$ Hz, 2 H), 6.97 (d, $J = 8.32$ Hz, 4 H), 2.52 (t, $J = 7.51$ Hz, 4 H), 1.52−1.43 (m, 22 H), 1.24 (sext, $J = 7.5$ Hz, 4 H), 0.87 (t, $J = 7.3$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 191.7, 152.7, 149.2, 140.5, 136.8, 136.6, 134.6, 129.6, 128.2, 126.6, 123.6, 113.7, 80.7, 35.6, 33.0, 28.4, 22.1, 13.9. HRMS calcd for $C_{44}H_{50}N_2O_6S_3$: 798.2831. Found: 798.2811.

Timer 23. The above nonplanar trimer (0.1801 g, 0.2254 mmol), methylene chloride (2.0 mL) and titanium tetrachloride (1.0 mL, 1.0 M in methylene chloride) were used. The yield was 0.120 g (95%). IR (KBr): 3087, 2923, 2851, 1610, 1544, 1508, 1462, 1354, 1108, 810, 667. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.72 (d, $J = 5.4$ Hz, 2 H), 7.65 (d, $J = 5.4$ Hz, 2 H), 6.99 (d, $J = 8.0$ Hz, 4 H), 6.83 (d, $J = 8.0$ Hz, 4 H), 2.52 (t, $J = 7.5$ Hz, 4 H), 1.60 (p, $J = 7.8$ Hz, 4 H), 1.39 (sext, $J = 7.3$ Hz, 4 H), 0.97 (t, $J = 7.3$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 155.3, 153.2, 142.4, 141.5, 139.5, 129.1, 128.5, 127.9, 126.0, 125.4, 124.6, 35.5, 33.5, 22.5, 14.1. HRMS calcd for $C_{34}H_{30}N_2S_3$: 562.1571. Found: 562.1559.

2-Bromothiophene-3-carboxylic Acid Chloride. Oxalyl chloride (3.1 mL, 35.4 mmol) was slowly added to 2-bromothiophene-3-carboxylic acid[15] (4.88 g, 23.6 mmol) and DMF (1 drop) in benzene (50 mL). The mixture was heated to reflux for 1 h, then cooled to room temperature. The volatiles were removed in vacuo, affording 5.06 g (95%) of the title compound. IR (KBr): 3108, 1759, 1703, 1492, 1390, 1210, 995, 836, 728, 677, 641 cm^{-1}. ^{1}H NMR (400 MHz,

CDCl$_3$): δ 7.52 (d, $J = 5.9$ Hz, 1 H), 7.28 (d, $J = 5.9$ Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 159.7, 133.8, 131.6, 126.3, 123.5.

Compound 24. This compound was synthesized in the same manner as described for compound **3**. Used were 2-bromothiophene-3-carboxylic acid chloride (4.87 g, 21.59 mmol), aluminum chloride (3.60 g, 26.90 mmol), and *n*-butylbenzene (6.8 mL, 43.6 mmol). The yield was 5.46 g (78%). IR (KBr): 3097, 2933, 2862, 1651, 1600, 1508, 1400, 1256, 1169, 990, 882, 841. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.75 (d, $J = 8.3$ Hz, 2 H), 7.27 (m, 3 H), 7.08 (d, $J = 5.7$, 1 H), 2.67 (t, $J = 7.5$ Hz, 2 H), 1.60 (p, $J = 7.3$ Hz, 2 H), 1.38 (sext, $J = 7.3$ Hz, 2 H), 0.91 (t, $J = 7.3$ Hz, 3 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 190.4, 149.2, 139.7, 134.8, 130.2, 129.4, 128.6, 126.2, 116.1, 35.8, 33.2, 22.4, 13.9. HRMS calcd for $C_{15}H_{15}BrOS$: 322.0227. Found: 322.0015.

Trimer 25. *N,N′*-Bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (0.8182 g, 0.92 mmol), **24** (0.6047 g, 1.9 mmol), $Pd_2(dba)_3$ (0.0183 g, 0.02 mmol), AsPh$_3$ (0.0123 g, 0.04 mmol), and THF (5 mL) were used. General procedure for Schiff base formation was directly carried out on the product. The total yield for two steps was 0.32 g (62%). IR (KBr): 3108, 3026, 2913, 2851, 1523, 1456, 1385, 1313, 1159, 1062, 831, 703. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.90 (d, $J = 8.1$ Hz, 4 H), 7.70 (d, $J = 5.4$ Hz, 2 H), 7.47 (d, $J = 5.4$ Hz, 2 H), 7.32 (d, $J = 8.1$ Hz, 4 H), 2.71 (t, $J = 7.5$ Hz, 4 H), 1.40 (p, $J = 7.4$ Hz, 4 H), 1.60 (sext, $J = 7.4$, 4 H), 0.96 (t, $J = 7.3$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 154.5, 145.7, 143.8, 142.4, 137.3, 132.9, 129.8, 128.52, 125.7, 125.5, 125.2, 35.6, 33.6, 22.4, 14.0. HRMS calcd for $C_{34}H_{30}N_2S_3$: 562.1571. Found: 562.1587.

Supporting Information Available: FTIR and ^{1}H NMR spectra for **7−14**, **19−23**, and **25** (28 pages). See any current masthead page for ordering and Internet access instructions.

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