Synthesis of Imine-Bridged Planar Poly(pyridinethiophene)s. Combination of Planarization and Intramolecular Charge Transfer in Conjugated Polymers

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ABSTRACT: This paper describes an approach to maximize π-conjugation in conjugated polymers by combining two complementary effects: polymer backbone planarization and intense intramolecular charge transfer (ICT). Independently, each of these methods is known to promote a significant lowering of the optical band gap in conjugated polymers. However, as described here, the combination of both strategies, planarization and ICT, only has a marginal effect on reducing the optical band gaps over that of the planarized materials that possess little ICT. The polymers studied here are planar poly(pyridinethiophene)s (PPyThs). The synthesis of the requisite polymers is accomplished by Pd-catalyzed coupling of *N*,*N*′-bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene and 2,5-bis(1′-oxo)-3,6-dibromopyridines to afford PPyThs that are then planarized via Schiff base formation upon protic activation. The planar PPyThs exhibit enormous changes in their optical absorption properties when iodide is present in solution; this dramatic change is not observed with fluoride, chloride, or bromide salts, regardless of the cation. Therefore, these polymers have a propensity to optically distinguish iodide from the other halogens.

Recent developments in nonlinear optics, light-emitting diodes, photovoltaic devices, laser systems utilizing conductive polymer films, and optoelectronic sensors have required the preparation of novel conjugated polymeric frameworks for enhanced performance from these various technologies.[1,2] The ability to control optical or electronic behavior in these systems often depends on the capability to modulate the band gaps and electron densities in the polymeric materials that are at the core of the device functions. The optoelectronic properties of conjugated polymers vary significantly on the basis of the degree of extended conjugation between the consecutive repeat units and the inherent electron densities in the polymer repeat units.[3] We and others have maximized π-conjugation in poly(*p*-phenylene)s (PPPs) by forming covalent linkages between the consecutive repeat units for polymer backbone planarization.[4] Recently, the electron-rich planar polythiophenes (PThs) and electron-deficient planar polypyridines (PPys) have been synthesized in our laboratory.[5] As expected, dramatic decreases in the optical band gaps were observed.[5] Another approach for significantly lowering optical band gaps in conjugated polymers is to construct the backbone with regular alternation of electron-donating and -accepting moieties to induce intramolecular charge transfer (ICT) within a polymer chain.[6,7] In an effort to combine the two methods of band gap lowering, namely planarization by ladder formation and intense ICT by donor/acceptor alternation, we describe here routes to a new class of ladder polymers: planar poly(pyridinethiophene)s (PPyThs) in which the pyridyl system is highly electron-deficient (being a six-membered azaheterocycle bearing imine moieties) and the thienyl systems are electron-rich (being a five-membered thioheterocycle bearing amine units). Moreover, although the majority of polymer-based chemosensory systems are limited to cation detection, it is particularly interesting that these planar PPyThs exhibit dramatic iodide-dependent optical absorption features regardless of the counterion.[2h,8] The intense iodide-induced optical change is opposite to the trend observed when the other halogens are used.

The retrosynthetic strategy for the synthesis of the planar PPyThs (**1**) is outlined in eq 1. The planarization was planned via Schiff base formation between alternating amine and ketone moieties.[4d,5] This approach permits (i) the imine bridges to form in high yields upon proton activation once the polymer backbone is established, (ii) the imine units to be easily substituted with different substituents (R in eq 1) so that the newly

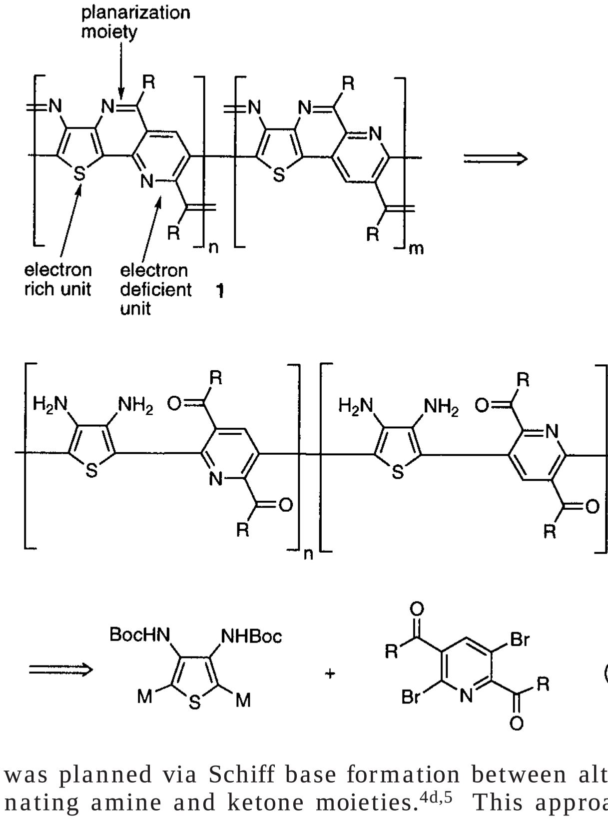

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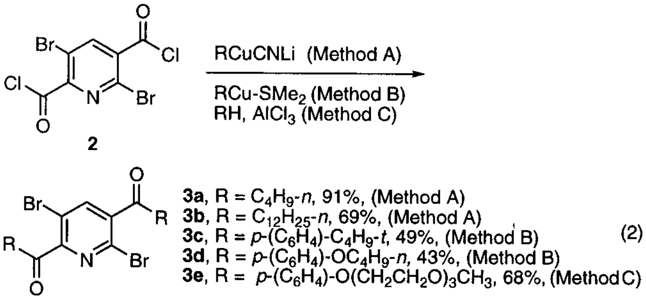
Table 1. Polymerization Optimization Reactions for 3a + 4

reaction	catalyst system	solvent	mole ratio of **4**/**3a**	reaction[a] time (h)	M_n[b]	M_w[b]
1	$PdCl_2(PPh_3)_2/CuI$	NMP/THF	1.02	45	4 400	6 950
2	$Pd(dba)_2/AsPh_3$	THF	0.98	45	10 350	15 100
3	$Pd(dba)_2/AsPh_3$	THF	1.00	45	11 900	17 200
4	$Pd(dba)_2/AsPh_3$	THF	1.00	72	16 650	30 800
5	$Pd(dba)_2/AsPh_3$	THF	1.02	72	21 200	39 250
6	$PdCl_2(AsPh_3)_2$	THF	1.02	45	10 950	16 450

[a] All the reactions were conducted in screw cap tubes under a N_2 atmosphere at 80 °C. [b] All the molecular weights were determined in THF by SEC versus PS standards.

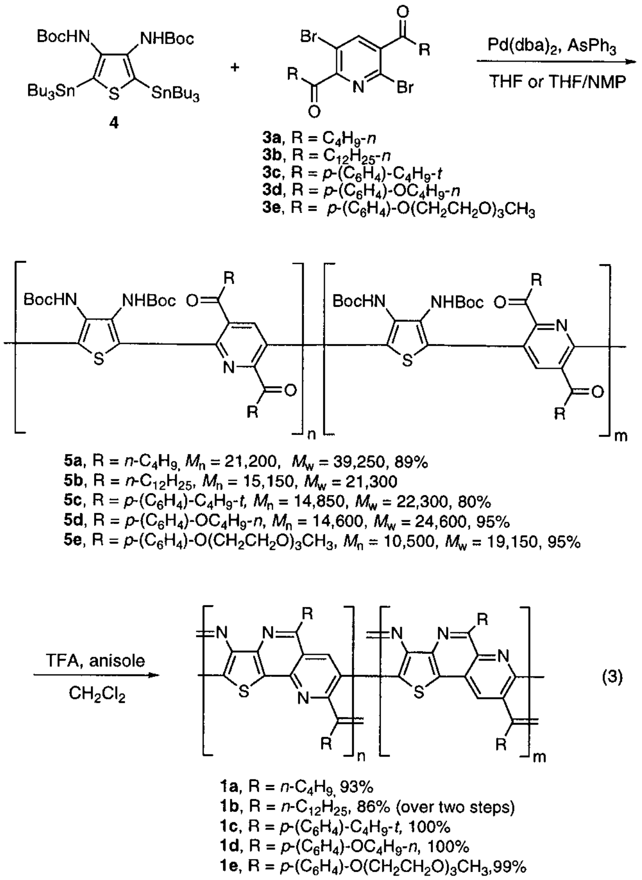
formed polymers are soluble and the substituent/property relationships could be investigated, (iii) the imine bridges to contain double-bonded ladder units to keep the consecutive aryl moieties planar while maximizing π-conjugation through the polymer backbones, thereby increasing the bandwidths and lowering the band gaps, and (iv) the alternation of electron-deficient (pyridine) and electron-rich (thiophene) units for the introduction of ICT along the polymer backbone.[3] We chose the use of diaminothiophenes and diketopyridines over diaminopyridines and diketothiophenes as the monomer units because the former combination would induce larger ICT character in the planar polymer backbone by increasing the electron density of the electron-rich thiophene heterocycle and decreasing the electron density on the electron-deficient pyridine heterocycle. Additionally, we choose the dimetalodiaminothiophene and dihalodiketopyridine as the coupling monomers (rather than the complementary pair of dihalodiaminothiophene and dimetalodiketopyridine) because subsequent oxidative addition reactions with the inherently electron-rich late transition-metal coupling catalysts are facilitated with electron-deficient aryl halides.[2i,2l,9]

The syntheses of diketone monomers are shown in eq 2, starting from the diacid chloride **2** that we prepared previously.[5b] Monomers **3a** and **3b** were prepared by lower order cyanocuprate additions to the acyl moieties. The neutral copper reagent worked more efficiently for the aryl additions to form **3c** and **3d**. Use of ArZnCl/Pd(0) or Friedel–Crafts acylation did not improve the yields for **3c** and **3d**. Copper reagent additions to prepare the oligo(ethylene glycol)-containing diketone **3e** were unsuccessful. However, **3e** was synthesized by Friedel–Crafts acylation using 8 equiv of $AlCl_3$. The use of 3 equiv of the Lewis acid simply gave a clear solution with the recovered starting material after several days, presumably because of complexation of the $AlCl_3$ by the oligo(ethylene glycol) groups which left the carbonyl moieties unactivated. The electron-rich *N*,*N'*-bis(*tert*-butoxycarbonyl)-3,4-diamino-2,5-bis(tri-*n*-butylstannyl)thiophene (**4**) was prepared in five steps from thiophene as described previously.[5a]



2

3a, R = C_4H_9-*n*, 91%, (Method A)
3b, R = $C_{12}H_{25}$-*n*, 69%, (Method A)
3c, R = *p*-(C_6H_4)-C_4H_9-*t*, 49%, (Method B)
3d, R = *p*-(C_6H_4)-OC_4H_9-*n*, 43%, (Method B)
3e, R = *p*-(C_6H_4)-$O(CH_2CH_2O)_3CH_3$, 68%, (Method C)



4

3a, R = C_4H_9-*n*
3b, R = $C_{12}H_{25}$-*n*
3c, R = *p*-(C_6H_4)-C_4H_9-*t*
3d, R = *p*-(C_6H_4)-OC_4H_9-*n*
3e, R = *p*-(C_6H_4)-$O(CH_2CH_2O)_3CH_3$

5a, R = *n*-C_4H_9, M_n = 21,200, M_w = 39,250, 89%
5b, R = *n*-$C_{12}H_{25}$, M_n = 15,150, M_w = 21,300
5c, R = *p*-(C_6H_4)-C_4H_9-*t*, M_n = 14,850, M_w = 22,300, 80%
5d, R = *p*-(C_6H_4)-OC_4H_9-*n*, M_n = 14,600, M_w = 24,600, 95%
5e, R = *p*-(C_6H_4)-$O(CH_2CH_2O)_3CH_3$, M_n = 10,500, M_w = 19,150, 95%

1a, R = *n*-C_4H_9, 93%
1b, R = *n*-$C_{12}H_{25}$, 86% (over two steps)
1c, R = *p*-(C_6H_4)-C_4H_9-*t*, 100%
1d, R = *p*-(C_6H_4)-OC_4H_9-*n*, 100%
1e, R = *p*-(C_6H_4)-$O(CH_2CH_2O)_3CH_3$, 99%

Modified Stille cross-couplings were utilized for the polymerizations (eq 3).[2i,2l,9] To find the optimal conditions, various catalyst and solvent systems were screened using the monomer **3a** (Table 1), and we observed the following: (1) In contrast to the polymerizations involving dihalodiketopyridines (such as **3a**) and *N*,*N'*-bis(*tert*-butoxycarbonyl)-3,6-bis(tri-*n*-butylstannyl)-2,5-diaminopyridine in which the optimal system was $PdCl_2(PPh_3)_2/CuI$ in *N*-methylpyrrolidinone (NMP)/THF,[5b] $AsPh_3$ was the preferred ligand here, and the use of CuI and the polar solvent additive NMP did not improve the outcome of the polymerization. (2) $Pd(dba)_2/AsPh_3$ was a more convenient and slightly better catalyst system than $PdCl_2(AsPh_3)_2$. (3) Slight changes in the monomer ratio dramatically affected the molecular weights of the polymers, and a 1.02 ratio of **4**/**3a** was preferred. (4) Finally, longer reaction times (72 h) were necessary to obtain higher molecular weights. On the basis of the above observations, $Pd(dba)_2/AsPh_3$/THF/72 h (Table 1, reaction 5) gave the best results, and a series of polymerizations of **4** with **3b**–**e** followed. The molecular weights for polymers **5a**–**e** are shown in eq 3. Surprisingly, these conditions were not optimal for the preparation of **5b**. The palladium catalyst precipitated shortly after the reaction initiated, and the highest M_n of the isolated product was 7900. The reason for the difference between the dodecyl monomer **3b** and butyl

Table 2. Optical Data for the Polymers

compd	λ_{abs} (THF), (nm)[a]	λ_{abs} (CH_2Cl_2/TFA, 2/1), (nm)[a]	λ_{emis} (THF), (nm)[b]	λ_{emis} (CH_2Cl_2/TFA, 2/1), (nm)
5a	$\underline{381}$	[c]	506	[c]
5b	$\underline{379}$[d] ($\epsilon = 1.7 \times 10^4$), $\underline{389}$[e]	[c]	511	[c]
5c	$\underline{293}$, 395	[c]	495	[c]
5d	$\underline{300}$ ($\epsilon = 3.4 \times 10^4$), 390 ($\epsilon = 1.6 \times 10^4$)	[c]	492	[c]
5e	$\underline{300}$, 395	[c]	489	[c]
1a	[f]	274, $\underline{420}$	[f]	NE[g]
1b	[f]	275, $\underline{424}$ ($\epsilon = 4.4 \times 10^4$)	[f]	NE[g]
1c	[f]	272, $\underline{450}$	[f]	NE[g]
1d	[f]	284, $\underline{311}$, $\underline{483}$ ($\epsilon = 3.8 \times 10^4$), 630 (sh)	[f]	NE[g]
1e	271, $\underline{423}$, 529 (sh) ($CHCl_3$)	273, $\underline{468}$	$\underline{580}$ ($CHCl_3$)	NE[g]
	273, $\underline{420}$, 540 (sh) (film)	291, $\underline{444}$ (formic acid)		

[a] The underlined value is λ_{max}, sh = shoulder, and the extinction coefficients are per repeat group. [b] Excitation wavelength was 350 nm, except 400 nm for **1e**. [c] Addition of TFA would have resulted in the loss of the Boc group. [d] Material obtained in THF as the reaction solvent. [e] Material obtained in NMP/THF as the reaction solvent. [f] The polymers were not soluble in THF. [g] NE means no emission signal was observed.

monomer **3a** is unclear. Since a polar solvent can stabilize the homogeneous catalyst, we then used a mixture of NMP/THF (2/1) as the reaction solvent without changing the catalyst or monomer ratios, and the number-average molecular weight nearly doubled.

Polymers **5a**−**e** were purified by fractional precipitation. These polymers had a green/yellow color and were very soluble in common organic solvents such as ether, ethyl acetate, THF, and halogenated solvents. 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 rather than the molecular weight, significant yet consistent errors in M_n and M_w usually result when comparing rigid rod polymers to the flexible coils of PS standards. The M_n data in this range are generally larger than the actual molecular weights by a factor of 1.5−2; thus, the values provided here serve simply as a reference.[10] The FTIR spectra showed the N−H stretches and the strong carbonyl absorptions for compounds **5a**−**e** while the ^1H NMR and ^{13}C NMR spectra further confirmed the identity of the polymers. The structures and purity of **5a** and **5c**−**e** were also supported by close agreement of the combustion analysis data to the theoretical values while the carbon content for **5b** prepared in NMP/THF was higher than the theoretical value, a finding likely due to hot NMP-induced loss of some of the Boc moieties and imine formation under the polymerization conditions.[11] However, when **5b** was formed in THF (M_n = 7900; M_w = 12 350), its elemental analysis data corroborated well with the theoretical value. These solvent-induced differences in Boc-stability were also observed in our previous polypyridine syntheses.[5b]

Treatment of the preplanar polymers **5a**−**e** with trifluoroacetic acid (TFA) at 50 °C induced Boc-removal and Schiff base formation in high yields (eq 3); the elevated temperature was required for complete reaction. Precipitation of the products by addition into a mixed solvent of acetone/triethylamine afforded the planarized polymers **1a**−**e**. Though the imine formation is reversible under acidic conditions, the more stable six-membered imine ring is thermodynamically preferred. It is unlikely that intermolecular Schiff bases remain in the final polymers since that would have resulted in an insoluble cross-linked network. Thus, the imine formation strategy provided an efficient method for the planarization between the consecutive repeat units since we avoided the difficult task of introducing new atoms along a rigid rod backbone from exogenous reagents; all the needed atoms were present in the monomers. There were only trace amounts of ketone-derived stretches in the FTIR spectra, but no Boc-signatures were present in most cases. The small carbonyl absorptions were likely from the end groups. There were no remaining CH_2CO resonances in the ^1H NMR spectrum of **1b** (**1a** was insufficiently soluble to be clearly examined by NMR). No Boc-residues in the planarized polymers were detected by NMR. By ^1H NMR, the proton resonances on the pyridine rings shifted from δ = 7.7−7.9 for **5b**−**e** to δ = 9.8−10.2 for **1b**−**e** after planarization, an observation consistent with the spectral features of other planarized polymers.[4e,5a] Polymers **1a**−**c** were brown while **1d** and **1e** were brown-red. **1e** could readily form a reddish flexible free-standing thin film. All the planar polymers were soluble in acidic solvents such as CH_2Cl_2/TFA (2/1) while **1e** was also soluble in formic acid or $CHCl_3$.

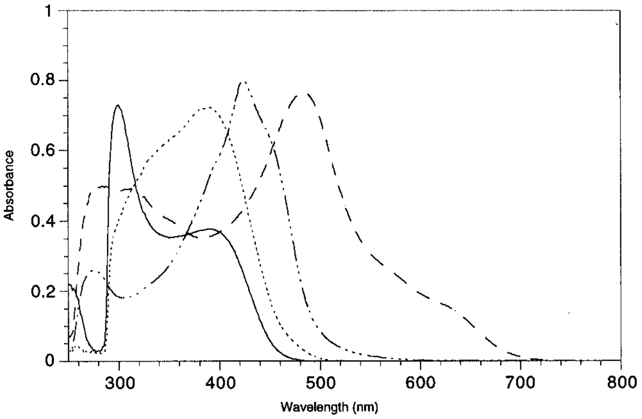


Figure 1. Optical absorption spectra of **5b** (THF) (···), **1b** (CH_2Cl_2/TFA, 2/1) (—···—), **5d** (THF) (—), and **1d** (CH_2Cl_2/TFA, 2/1) (— — —).

The optical absorption data for **5a**−**e** were recorded in THF (Table 2, Figure 1) and they showed broad peaks with large absorption maxima at approximately 380−390 nm. Polymer **5b** shows a 10-nm longer λ_{max} value for the material isolated from NMP/THF, consistent with partial NMP-induced Boc-loss and -planarization. The 380−390-nm peaks could be assigned to an ICT band because 3,4-disubstituted polythiophenes (λ_{max} < 300 nm)[12] and monoalkyl-substituted polypyridines (λ_{max} = 310−340 nm)[13] have far smaller absorption wavelengths. The ICT arises from electron donation of the electron-rich thiophene units into the electron-deficient pyridine moieties. Therefore, even prior to

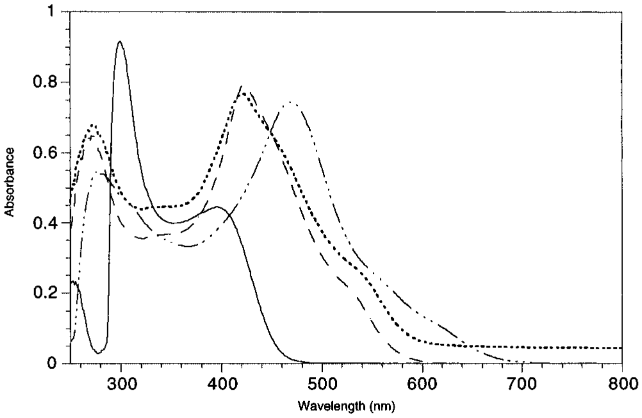


Figure 2. Optical absorption spectra of **5e** (THF) (—) and **1e** ($CHCl_3$) (— — —), (CH_2Cl_2/TFA, 2/1) (—···—), (film) (···).

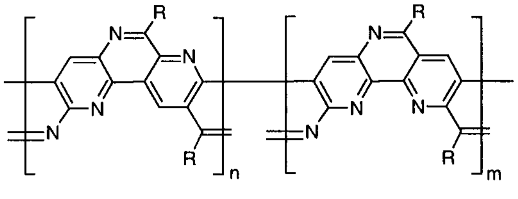
Schiff base formation, the ICT is exerting a pronounced effect despite the repeat units being highly substituted and thereby forced out of planarity.

The optical spectra for planarized polymers **1a**−**e** were recorded in CH_2Cl_2/TFA (2/1) (Table 2, Figures 1 and 2). **1a**−**d** were only soluble in acidic media; thus, a direct comparison of their optical absorption properties to those of **5a**−**d** is difficult because any use of acidic solvents for optical measurements of **5a**−**d** would have resulted in the loss of the Boc protecting groups and imine-bridge formations. However, **1e** could be solublized in nonacid solvents and it showed a λ_{max} at 423 nm with a shoulder at 529 nm in $CHCl_3$, very similar to the optical properties of the film. Thus, a bathochromic shift of approximately 30 nm was observed for the ICT band upon the conversion of the nonplanar **5e** to the planar **1e** with a concomitant decrease in the optical band gap of 0.6 eV as determined from the tailing edge of the optical spectrum. The Boc-protected amines in **5e** are less electron-donating than unprotected amines. However, upon planarization, the lone pairs of the imine-bridged nitrogens become orthogonal to the polymer backbone; hence, they are no longer able to add electron density to the thiophene ring by a resonance effect, causing the thiophene moiety to be less electron-rich and weakening the ICT character of the polymer repeat units. Thus, the net bathochromic shift upon the conversion of **5e** to **1e** is a combination of several effects.

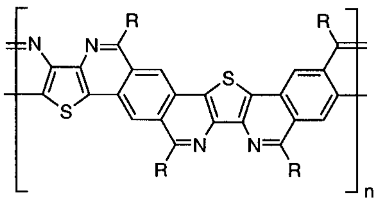
Protic solvents showed considerable optical effects on the imine-bridged planar polymers (Table 2, Figures 1 and 2). **1e** had a longer wavelength absorption maximum in formic acid and CH_2Cl_2/TFA than in $CHCl_3$ likely because of stronger ICT character in protic solvents. Protonation of the imine nitrogen makes the pyridyl ring more electron-deficient and thus a better electron acceptor. We have noticed this trend in other imine-containing planar polymers that we have prepared.[5] Again, since the newly formed imine-bridged lone pairs are orthogonal to the conjugated backbone of the thiophene rings, protonation has little effect on the electron-donating ability of the thienyl ring. Moreover, substituents played important roles in affecting the optical properties of **1a**−**e**. The aryl-substituted polymers **1c**−**e** had absorptions at longer wavelengths than alkyl-substituted **1a**−**b**, and the *p*-alkoxyphenyl-substituted **1d** shifted the most bathochromically.

A most informative comparison is between the optical band gaps of **1e** in formic acid (2.1 eV) and the nonplanar and unsubstituted poly(pyridinethiophene) (2.3 eV)[6d] in the same solvent. Hence, the decrease in the optical band gap for the planarized system is only slight. A rationale may be that the planarized structure causes the thiophene ring system to be less electron-donating because of the orthogonality of the nitrogen lone pair (vide supra). Thus, although planarization increases the overall π-delocalization, the planarization may decrease the donor capability of the thiophene units.

Another useful correlation for the planar PPyThs here is to compare them to the planar polypyridines (**6**),[5b] and planar poly(phenylenethiophene)s (**7**)[5a] that we prepared previously. The planar PPy (**6**) had a more bathochromically shifted ICT band than **1b**. Interestingly, the absorption maxima for the planar PPyThs (**1a**−**e**) were quite similar to the optical data of **7**, although **1a**−**e** have more intense electron-withdrawing moieties (pyridine units) than the phenylenes present in **7**.



6, R = $C_{12}H_{25}$-*n*
λ_{max} (CH_2Cl_2/TFA, 3/2) = 355, 566



7, R = $C_{12}H_{25}$
λ_{max} (CH_2Cl_2/TFA, 2/1) = 463

The response of these planar PPyThs to halogen-based salts is quite interesting. Despite having the oligo(ethylene glycol) pendants, the optical spectra of **1e** changed little upon varying cations in solution (Table 3). Conversely, the optical spectra were greatly affected by different anions. As shown in Figure 3, remarkable features were observed when halogen anions were present in a CH_2Cl_2/TFA (2/1) solution of **1e**.

While there was practically no change in the optical absorption features upon the addition of fluoride salts, chloride or bromide salts caused a bathochromic shift of the absorption maximum to ensue, regardless of the cation. Conversely, the addition of the iodide salts resulted in intense hyperchromicity of a band at approximately 300 nm, again, regardless of the cation. Polymer **1d** showed a similar optical response in CH_2Cl_2/TFA (2/1) toward the addition of LiCl and LiBr; however, when LiI was used, precipitation of the polymer resulted. **1c** also showed significant optical responses with different anions, although with less intensity than **1d** and **1e**. **1b** showed the least sensitivity and **1a** was not investigated due to its limited solubility. Presently, we have no reasonably encompassing explanation for these interesting optical properties, although iodide can serve as a reducing agent which is the basis behind its detection using numerous other analytical methods.

Emission signals with large Stokes shifts were observed for the preplanar polymers **5a**−**e** in THF and

Table 3. Effect of Salt Additives on the Optical Spectra of 1e

entry	additive[a]	λ_{abs} (CH_2Cl_2/TFA, 2/1), (nm)[b]
1	none	273, $\underline{468}$
2	LiF	275, $\underline{468}$
3	LiCl	276, 310, $\underline{487}$, 600 (sh)
4	LiBr	270, 311, $\underline{491}$, 596
5	LiI	$\underline{300}$, 380 (sh)
6	LiOAc	274, $\underline{468}$
7	NaF	275, $\underline{474}$
8	NaCl	273, $\underline{472}$
9	NaBr	273, 310, $\underline{488}$, 610 (sh)
10	NaI	$\underline{300}$, 390 (sh), 510 (sh)
11	NaOAc	274, $\underline{473}$
12	KF	$\underline{268}$, 472[c]
13	KCl	276, 308, $\underline{483}$, 605 (sh)
14	KBr	273, 313, $\underline{492}$, 610 (sh)
15	KI	$\underline{308}$, 400 (sh), 510 (sh)
16	KOAc	275, $\underline{467}$
17	NH_4Cl	276, 307, $\underline{483}$, 610 (sh)
18	NH_4I	$\underline{276}$, 390 (sh), 500 (sh)
19	n-Bu_4NF	275, $\underline{471}$
20	n-Bu_4NCl	289, $\underline{480}$, 610 (sh)[c]
21	n-Bu_4NBr	272, 313, $\underline{489}$, 600 (sh)
22	n-Bu_4NI	$\underline{288}$, 344, 520 (sh)

[a] To 4 mL of the polymer solution in CH_2Cl_2/TFA (prepared from 6 mg of **1e** in 450 mL of CH_2Cl_2/TFA (2/1)) was added 5 mg of the salt. [b] The underlined value is λ_{max} and sh = shoulder. [c] The λ_{max} absorption intensity change was only slightly in favor of the lower wavelength absorption band.

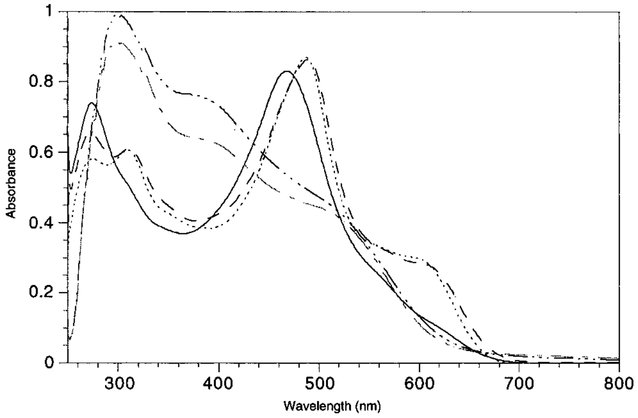


Figure 3. Optical absorption spectra of **1e** in CH_2Cl_2/TFA (2/1): without salts (—); with added LiCl (···); with added LiI (—···—); with added NaBr (— — —); with added NaI (—·—).

planar polymer **1e** in $CHCl_3$ (Table 2). In contrast, planar polymers **1a**−**e** showed no emission signals in CH_2Cl_2/TFA (2/1), a trend we have observed in other imine-bridged planar aromatic polymers.[4d,5] Therefore, protonation of the imine nitrogens led to exciton quenching. Conductivity studies were carried out on a thin film of **1e**. Four-point probe measurements indicate that the undoped polymer had a conductance value $< 10^{-7}\ \Omega^{-1}\ cm^{-1}$, and an iodine vapor doped thin film had a conductance of $5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$, close to the unsubstituted PPyTh of 10^{-4}−$10^{-2}\ \Omega^{-1}\ cm^{-1}$.[6d] The doped blackened material was stable in air and showed no significant loss of conductivity over a period of 3 weeks. Longer duration tests were not performed.

In summary, imine-bridged planar PPyThs have been synthesized. Pd-couplings produced the polymerized products that could be easily planarized in high yields via the formation of imine bridges by proton activation. Maximized π-conjugation and ICT accounted for the shortening of the optical band gaps; however, the shortening for the combination of the two effects was less dramatic than expected. The planar polymers showed remarkable optical response changes to specific anions, regardless of the cations. Protonation of the polymers led to exciton quenching, and the iodine-doped polymers were resilient semiconductors.

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, respectively) eluted with THF at 60 °C and a flow rate of 1.0 mL/min. Molecular weight results were based on five polystyrene standards (M_w = 435 500, 96 000, 22 000, 5050, and 580 with a correlation coefficient > 0.9998) purchased from Polymer Laboratories Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using an Alltech model 932525 (25-m × 0.25-mm, 0.2-μm film of AT-1 stationary phase) capillary GC column. Alkyllithium reagents were obtained from FMC. Reagent-grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent-grade benzene and dichloromethane were distilled over calcium hydride. Bulk-grade hexane was distilled prior to use. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out using 230−400-mesh silica gel from EM Science. Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F254 with a layer thickness of 0.25 mm purchased from EM Science. 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 Tables 2 and 3 while the molecular weight data are listed in eq 3 and Table 1. The synthesis of compounds **2**,[5b] **3a**−**c**,[5b] and **4**[5a] have been described previously.

4-*n*-Butoxy-1-bromobenzene. A mixture of *p*-bromophenol (35 g, 200 mmol), *n*-bromobutane (27.7 g, 200 mmol), and potassium carbonate (34.6 g, 250 mmol) in acetone (500 mL) was heated to reflux for 44 h. The mixture was cooled to room temperature and water was added. The organic layer was separated. The aqueous phase was extracted with ether (1×). The combined organic solution was concentrated in vacuo and then diluted with ether. The mixture was washed with water (1×) and brine (1×), and dried over magnesium sulfate. Removal of the solvent in vacuo followed by Kugelrohr distillation gave **4** as a colorless oil (43.67 g, 95%). FTIR (neat): 2964, 2933, 2872, 1590, 1580, 1487, 1472, 1390, 1287, 1246, 1169, 1072, 1026, 1005, 974, 821, 641 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 7.34 (d, J = 8.6 Hz, 2 H), 6.75 (d, J = 8.6 Hz, 2 H), 3.90 (t, J = 6.5 Hz, 2 H), 1.74 (p, J = 7.0 Hz, 2 H), 1.46 (sext, J = 7.4 Hz, 2 H), 0.95 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 158.74, 132.61, 116.73, 112.98, 68.33, 31.71, 19.70, 14.32. HRMS calcd for $C_{10}H_{13}BrO$: 228.0150. Found: 228.0158.

2,5-Bis[*p*-(*n*-butoxy)benzoyl]-3,6-dibromopyridine (3d). To a solution of *tert*-butyllithium (29 mL, 50 mmol, 1.73 M in pentane) in ether (10 mL) at −78 °C was added 4-(*n*-butoxy)-1-bromobenzene (5.73 g, 25 mmol) in ether (4 mL). The mixture was stirred for 5 min at −78 °C and warmed to 0 °C. The yellow solution was transferred via cannula to a suspension of a copper(I) bromide/dimethyl sulfide complex (5.6 g, 27 mmol) in THF (50 mL) at −78 °C. The mixture was stirred for 20 min at −78 °C and warmed to approximately −20 °C. The resultant green/black solution was recooled to −78 °C. To this mixture was added via cannula a precooled THF (14 mL) solution of **2** (3.62 g, 10 mmol) at −78 °C. The slurry was stirred for 10 min at −78 °C. A solution of saturated NH_4Cl/NH_4OH (9/1, 10 mL) was added. The mixture was warmed to room temperature and filtered. The aqueous phase was separated and extracted with ether (2×). Combined organic fractions were washed with 1 N HCl (1×), water (2×), and brine (1×). The solution was dried over magnesium sulfate and filtered. Removal of solvents followed by flash chromatography [silica gel, hexane/CH_2Cl_2 (1/1), then CH_2Cl_2 as the eluent] and recrystallization from hexane/CH_2Cl_2 gave **3d** as colorless crystals (2.51 g, 43%). mp: 152−153 °C. FTIR (KBr): 2954, 2933, 2872, 1667, 1595, 1508, 1426, 1385, 1328, 1251, 1164, 1087, 933, 903, 846, 662 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86 (s, 1 H), 7.81 (d, J = 8.3 Hz, 2 H), 7.79 (d, J = 8.4 Hz, 2 H), 6.97 (d, J = 8.6 Hz, 2 H), 6.95 (d, J = 8.6 Hz, 2 H), 4.05 (t, J = 6.3 Hz, 2 H), 4.04 (t, J = 6.4 Hz, 2 H), 1.81−1.79 (m, 4 H), 1.53−1.47 (m, 4 H), 0.98 (t, J = 7.4 Hz, 3 H), 0.97 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (125 MHz, CDCl3) δ: 190.60, 190.02, 165.00, 164.84, 157.90, 141.59, 140.10, 136.78, 133.25, 133.18, 127.96, 127.33, 117.00, 115.23, 115.07, 68.65, 68.55, 31.43, 19.55, 14.20. HRMS calcd for $C_{27}H_{27}Br_2NO_4$: 587.0295. Found: 587.0307. Anal. Calcd for $C_{27}H_{27}Br_2NO_4$: C, 55.03; H, 4.62; N, 2.38. Found: C, 55.04; H, 4.58; N, 2.37.

Methoxytris(ethoxy)benzene. See the procedure for the preparation 4-*n*-butoxy-1-bromobenzene. Used were phenol (7.53 g, 80 mmol), 1-bromo-2-(methoxy-bis(ethoxy))ethane[2h] (18.17 g, 80 mmol), potassium carbonate (16.6 g, 120 mmol), sodium iodide (0.75 g, 5 mmol), and acetone (100 mL). The mixture was heated to reflux for 34 h. Kugelrohr distillation gave the title compound as a colorless oil (12.57 g, 65%). FTIR (neat): 2924, 2882, 1598, 1587, 1497, 1454, 1354, 1295, 1248, 1131, 1110, 1062, 945, 924, 850, 754, 691 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.25 (dd, J = 8.6, 7.4 Hz, 2 H), 6.95−6.88 (m, 3 H), 4.11 (t, J = 4.9 Hz, 2 H), 3.84 (t, J = 4.9 Hz, 2 H), 3.74−3.71 (m, 2 H), 3.68−3.62 (m, 4 H), 3.55−3.51 (m, 2 H), 3.36 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.78, 129.40, 120.82, 114.61, 71.92, 70.81, 70.65, 70.54, 69.75, 67.29, 58.99. HRMS calcd for $C_{13}H_{20}O_4$: 240.1362. Found: 240.1361.

2,5-Bis[*p*-(methoxytris(ethoxy)benzoyl]-3,6-dibromopyridine (3e). To a slurry of **2** (3.62 g, 10 mmol) and alumina chloride (10.67 g, 80 mmol) in methylene chloride (50 mL) at 0 °C was added methoxytris(ethoxy)benzene (4.81 g, 20 mmol). The mixture was warmed to room temperature and stirred for 40 h. The mixture was carefully poured into dilute aqueous HCl. The solution was extracted with ethyl acetate (4×). The combined extracts were dried over magnesium sulfate and filtered. Removal of the solvent in vacuo gave a yellow oil, which was purified by flash chromatography (silica gel, hexane/ethyl acetate/methanol (9/9/2)) to give **3e** (5.24 g, 68%) as light yellow crystals. mp: 85−87 °C. FTIR (cast): 2882, 1667, 1600, 1574, 1508, 1456, 1426, 1328, 1256, 1164, 1118, 1087, 1056, 933, 846 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.86 (s, 1 H), 7.81 (d, J = 8.7 Hz, 2 H), 7.79 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 4.21 (m, 4 H), 3.88 (m, 4 H), 3.73−3.71 (m, 4 H), 3.68−3.62 (m, 8 H), 3.54−3.51 (m, 4 H), 3.36 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 190.17, 189.60, 164.19, 164.04, 157.40, 141.19, 139.62, 136.33, 132.77, 132.70, 127.80, 127.16, 116.56, 114.95, 114.80, 71.85, 70.82, 70.57, 70.50, 69.35, 67.88, 67.80, 58.96. HRMS calcd for $C_{33}H_{39}{}^{79}Br_2NO_{10}$: 767.0941. Found: 767.0938. Anal. Calcd for $C_{33}H_{39}Br_2NO_{10}$: C, 51.51; H, 5.11; N, 1.82. Found: C, 51.60; H, 5.02; N, 1.82.

General Procedure for the Polymerization Reactions between 3a−e and 4. To an oven-dried screw cap tube were added the dibromodiketone monomer **3** (1.0 equiv), the distannylthiophene **4**[5a] (1.02 equiv), $Pd(dba)_2$ (0.02 equiv), and $AsPh_3$ (0.04 equiv). The tube was transferred to a nitrogen-filled drybox. To the tube was added THF (NMP/THF (2/1) was also used for **3b**). The tube was capped and heated to 80 °C for 72 h (unless otherwise noted). The reaction mixture was cooled to room temperature. Dichloromethane (10 mL) was added and the mixture was filtered through a pad of Celite. The solution was concentrated in vacuo to approximately 3 mL which was then fractionally precipitated into hexane (100 mL). The precipitate was collected and washed with hexane to afford the desired polymers **5a**−**e**.

Polymer 5a. Used were **4** (0.455 g, 0.51 mmol), **3a** (0.203 g, 0.5 mmol), $Pd(dba)_2$ (0.006 g, 0.01 mmol), $AsPh_3$ (0.006 g, 0.02 mmol), and THF (5 mL). **5a** was obtained as a green/yellow solid (0.247 g, 89%). FTIR (film): 3344, 2964, 2933, 2872, 1733, 1708, 1569, 1508, 1456, 1421, 1395, 1369, 1339, 1246, 1164, 1087, 1010, 913, 877, 769, 733 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87−7.83 (br 1 H), 3.15 (br s, 2 H), 2.81 (br s, 2 H), 1.75−1.10 (m, 26 H), 0.95 (br s, 3 H), 0.88 (br s, 3 H). ^{13}C NMR (125 MHz $CDCl_3$) δ: 204.5−202.2, 154.2, 153.6, 147.9, 140.9, 137.3−136.9, 132.5−132.2, 130.4, 125.6, 81.8, 81.0, 42.9−42.3, 40.2−39.9, 28.7−28.2, 26.9, 26.1, 22.7−22.6, 14.4, 14.2. Anal. Calcd for $(C_{29}H_{39}N_3O_6S)_n$: C, 62.46; H, 7.05; N, 7.53. Found: C, 62.29; H, 6.98; N, 7.49.

Polymer 5b. Using THF/NMP: Used were **4** (0.455 g, 0.51 mmol), **3b** (0.315 g, 0.5 mmol), $Pd(dba)_2$ (0.006 g, 0.01 mmol), $AsPh_3$ (0.006 g, 0.02 mmol), THF (2 mL), and NMP (4 mL). The mixture was heated to 80 °C for 2 days. Precipitation was performed from methanol (150 mL). **5b** was obtained as a light brown solid (0.283 g) and the yield was determined after the acid treatment. FTIR (film): 3333, 2923, 2851, 1728, 1708, 1569, 1513, 1456, 1426, 1395, 1369, 1246, 1164, 1087, 1005, 877, 769 cm^{-1}. ^{1}H NMR (300 MHz, CDCl3) δ: 8.80−7.9 (m, 1 H), 3.80−2.80 (m, 4 H), 2.0−1.2 (m, 58 H), 0.85 (br s, 6 H). ^{13}C NMR (125 MHz CDCl3) δ: 203.6 (br), 163.6 (br), 158.1 (br), 153.6 (br), 148.9−145.8, 140.9−137.4, 132.3−121.3, 121.3 (br), 81.8−81.2, 43.2 (br), 40.7−40.3, 36.1−35.6, 32.6−28.5, 24.8−22.7, 14.8−14.1. Anal. Calcd for $(C_{45}H_{71}N_3O_6S)_n$: C, 69.10; H, 9.15; N, 5.37. Found: C, 70.75; H, 9.10; N, 5.80. The discrepancies in the theoretical and found analytical values are due to partial loss of the Boc-moieties as described in the main text. **Using THF only:** The results were the same as above except THF (5 mL) was used as the solvent in the reaction and the reaction time was 3 days. **5b** was obtained as a light brown solid (0.289 g, 74%). Anal. Calcd for $(C_{45}H_{71}N_3O_6S)_n$: C, 69.10; H, 9.15; N, 5.37. Found: C, 69.17; H, 9.15; N, 5.34. $M_n = 7900$; $M_w = 12\,350$.

Polymer 5c. Used were **4** (0.455 g, 0.51 mmol), **3c** (0.279 g, 0.5 mmol), $Pd(dba)_2$ (0.006 g, 0.01 mmol), $AsPh_3$ (0.006 g, 0.02 mmol), and THF (5 mL). **5c** was obtained as a green/yellow solid (0.283 g, 80%). FTIR (film): 3324, 2965, 2903, 2873, 1729, 1672, 1606, 1565, 1508, 1411, 1370, 1267, 1247, 1165, 1108, 913, 847, 775, 734 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (m, 5 H), 7.37 (br 4 H), 1.29−1.25 (m, 36 H). ^{13}C NMR (125 MHz $CDCl_3$) δ: 194.6−192.5, 158.3−157.3, 155.0−153.0, 147.5 (br), 140.7−140.1, 134.6−133.8, 133.0−132.8, 131.1−130.1, 126.9−125.2, 81.4−80.3, 35.5, 31.4, 28.5−28.3. Anal. Calcd for $(C_{41}H_{47}N_3O_6S)_n$: C, 69.37; H, 6.67; N, 5.92. Found: C, 69.13; H, 6.72; N, 5.76.

Polymer 5d. Used were **4** (0.455 g, 0.51 mmol), **3d** (0.295 g, 0.5 mmol), $Pd(dba)_2$ (0.006 g, 0.01 mmol), $AsPh_3$ (0.006 g, 0.02 mmol), and THF (5 mL). **5d** was obtained as a green/yellow solid (0.351 g, 95%). FTIR (film): 3323, 2964, 2933, 2872, 1728, 1662, 1600, 1574, 1508, 1421, 1395, 1369, 1313, 1256, 1164, 1067, 1005, 913, 846, 769 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (m, 5 H), 6.80 (br 4 H), 4.00 (br s, 4 H), 1.75 (br s, 4 H), 1.45−1.42 (m, 4 H), 1.24 (br s, 18 H), 0.96−0.94 (m, 6 H). ^{13}C NMR (125 MHz $CDCl_3$) δ: 193.5−191.6, 166.7−164.5, 161.9−160.8, 154.7−153.1, 148.3 (br), 140.4 (br), 134.6−133.2, 130.1−126.9, 125.8 (br), 122.7−118.0, 115.0−114.8, 81.1−79.5, 31.6, 28.5−28.3, 19.9−19.2, 14.5−13.8. Anal. Calcd for $(C_{41}H_{47}N_3O_8S)_n$: C, 66.38; H, 6.39; N, 5.66. Found: C, 66.23; H, 6.34; N, 5.67.

Polymer 5e. Used were **4** (0.357 g, 0.4 mmol), **3e** (0.302 g, 0.39 mmol), $Pd(dba)_2$ (0.005 g, 0.008 mmol), $AsPh_3$ (0.005 g, 0.016 mmol), and THF (4 mL). The solution was heated to 80 °C for 45 h. **5e** was obtained as a green/yellow solid (0.340 g, 95%). FTIR (film): 3303, 2974, 2933, 2882, 1728, 1662, 1600, 1574, 1508, 1456, 1421, 1390, 1369, 1308, 1262, 1159, 1108, 1056, 918, 846, 769, 733 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.70 (m, 5 H), 6.81 (br 4 H), 4.15 (m, 4 H), 3.82 (m, 4 H), 3.67 (m, 4 H), 3.60 (m, 8 H), 3.49 (m, 4 H), 3.31−3.30 (m, 6 H), 130−1.23 (18 H). ^{13}C NMR (125 MHz $CDCl_3$) δ: 193.0−191.0, 163.6−163.0, 153.8−152.6, 147.7 (br), 139.4 (br), 134.0−132.7, 129.6−128.2, 125.4−121.9, 114.7−114.1, 80.8−79.8, 71.8, 70.8−70.5, 69.4, 67.6, 58.9, 28.1−27.9. Anal. Calcd for $(C_{47}H_{59}N_3O_{14}S)_n$: C, 61.22; H, 6.45; N, 4.56. Found: C, 60.33; H, 6.43; N, 4.56.

General Procedure for the Conversion of 5a−e to 1a−e, Respectively. To a solution of polymer **5** in dichloromethane (8 mL) was added anisole (0.5 mL) and TFA (4 mL). The mixture was stirred at room temperature for 2 h and heated to 50 °C overnight. After the solution cooled to room temperature, it was carefully and slowly added to a vigorously stirred mixture of triethylamine (20 mL) and acetone (100 mL). The precipitate was collected by filtration. Further washing with acetone afforded the planarized polymers **1a**−**e**.[14]

Polymer 1a. Used were **5a** (0.097 g), TFA (4 mL), CH_2Cl_2 (8 mL), and anisole (0.5 mL). **1a** was obtained as a brown solid (0.052 g, 93%). FTIR (KBr): 2954, 2923, 2872, 1574, 1487, 1462, 1380, 1339, 1303, 1205, 1113, 1046, 990, 892, 656 cm^{-1}. No ^{1}H NMR data could be obtained due to the minimal solubility. Anal. Calcd for $(C_{19}H_{19}N_3S)_n$: C, 70.99; H, 5.96; N, 13.07. Found: C, 69.01; H, 5.86; N, 12.46.[14]

Polymer 1b. Used were **5b** (0.132 g), TFA (4 mL), CH_2Cl_2 (8 mL), and anisole (0.5 mL). **1b** was obtained as a brown/red solid (0.11 g, 86% over two steps from **3b** made by the THF/NMP method). FTIR (KBr): 2923, 2851, 1574, 1462, 1385 cm^{-1}. ^{1}H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ: 10.2 (m, 1H), 2.3−1.1 (m, 44 H), 1.29 (br s, 6 H). Anal. Calcd for $(C_{35}H_{51}N_3S)_n$: C, 77.01; H, 9.42; N, 7.70. Found: C, 75.92; H, 9.29; N, 7.54.[14]

Polymer 1c. Used were **5c** (0.093 g), TFA (4 mL), CH_2Cl_2 (8 mL), and anisole (0.5 mL). **1c** was obtained as a brown solid (0.062 g, 100%). FTIR (KBr): 2964, 2903, 2872, 1605, 1569, 1549, 1477, 1385, 1364, 1318, 1267, 1215, 1195, 1108, 1021, 903, 841, 790, 621 cm^{-1}. ^{1}H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ: 10.1 (m, 1 H), 8.4 (m, 2 H), 8.2−7.8 (m, 6 H), 1.57 (br s, 18 H). Anal. Calcd for $(C_{31}H_{27}N_3S)_n$: C, 78.61; H, 5.75; N, 8.87. Found: C, 76.50; H, 5.69; N, 8.44.[14]

Polymer 1d. Used were **5d** (0.1 g), TFA (4 mL), CH_2Cl_2 (8 mL), and anisole (0.5 mL). **1d** was obtained as a red solid (0.068 g, 100%). FTIR (KBr): 2954, 2933, 2872, 1605, 1554, 1508, 1472, 1385, 1369, 1308, 1246, 1221, 1174, 1067, 1026, 897, 836, 790, 646 cm^{-1}. ^{1}H NMR (400 MHz, TFA/$CDCl_3$ 1:1) δ: 10.1−9.9 (m, 1 H), 8.6−8.5 (m, 2 H), 8.2−8.0 (m, 2 H), 7.4 (br m, 2 H), 4.38 (br m, 4 H), 2.03 (br m, 4 H), 1.69 (br m, 4 H), 1.13 (br m, 6 H). Anal. Calcd for $(C_{31}H_{27}N_3O_2S)_n$: C, 73.64; H, 5.38; N, 8.31. Found: C, 71.74; H, 5.43; N, 7.95.[14]

Polymer 1e. Used were **5e** (0.06 g), TFA (2 mL), CH_2Cl_2 (4 mL), and anisole (0.2 mL). **1e** was obtained as a red rubbery thin film (0.044 g, 99%). FTIR (KBr): 2872, 1728, 1600, 1559, 1508, 1477, 1369, 1303, 1251, 1174, 1113, 1062, 949, 908, 836, 641 cm^{-1}. ^{1}H NMR (300 MHz, TFA/$CDCl_3$ 1:1) δ: 10.1−9.8 (m, 1 H), 8.6−8.4 (m, 2 H), 8.2−7.9 (m, 2 H), 8.6−7.2 (m, 4 H), 4.53 (m, 4 H), 4.24 (m, 4 H), 4.07 (m, 4 H), 3.93−3.87 (m, 12 H), 3.56−3.53 (m, 6 H). Anal. Calcd for $(C_{37}H_{39}N_3O_8S)_n$: C, 64.80; H, 5.73; N, 6.13. Found: C, 62.98; H, 5.63; N, 5.89.[14]

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