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Synthesis of a Conjugated Donor/Acceptor/Passivator (DAP) Polymer

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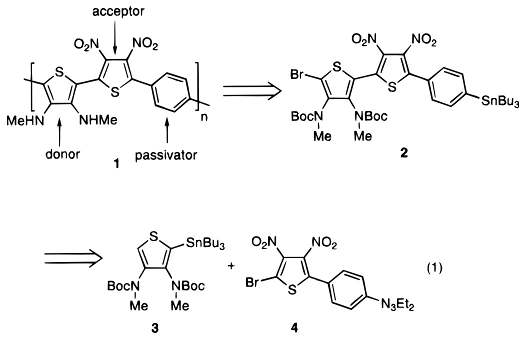
ABSTRACT: A conjugated polymer is described here that possesses main-chain donor/acceptor repeat units separated by aryl passivating units. This donor/acceptor/passivator (DAP) polymer was constructed of sequential electron-rich *N,N′*-dimethyl-3,4-diaminothiophene, electron-deficient 3,4-dinitrothiophene, and passivating phenylene repeat units via Stille coupling reactions. Several new transformations were conducted on thiophene cores in order to construct the monomer units: *tert*-butoxycarbonyl (Boc) amine protections, selective monostannylations, selective monodebrominations, lithium tetramethylpiperidide (LTMP) induced lithiation on nitrothiophenes, and selective stannylations using $Bu_3SnSnBu_3$/Pd on phenylene iodides over thienyl bromides. The Stille polymerization afforded the Boc-protected DAP polymer that was characterized at this stage. $ZnCl_2$-catalyzed Boc removal afforded the desired DAP polymer; however, its insolubility curtailed detailed investigations of the properties.

Introduction

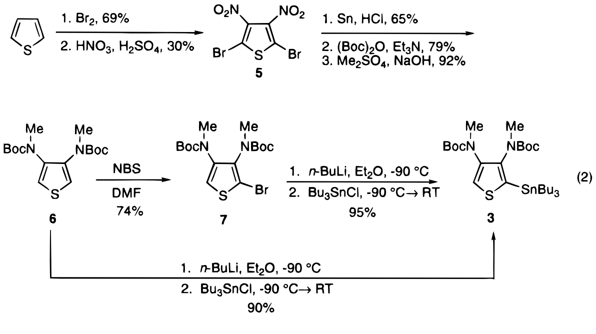
Conjugated polymers are presently regarded as promising materials for the development of optoelectronic devices such as light-emitting diodes, photovoltaic cells, sensors, and nonlinear optical systems.[1,2] The optoelectronic properties of conjugated polymers vary significantly based upon the degree of extended conjugation between the consecutive repeat units; hence, there have been numerous syntheses of ladder-conjugated polymers for the maximization of extended π-conjugation.[3] Other efforts to modify the optoelectronic properties of conjugated polymers have involved the construction of alternating donor/acceptor (DA) repeat units. These are step-growth [AB] polymers where the A-units are electron rich and the B-units are electron-deficient, thereby inducing intramolecular charge transfer (ICT) within the chain with a concomitant decrease in the optical band gaps.[4] In those DA systems, each acceptor unit is fed with electron density from the two adjacent donor units; thus, there is no net dipole on the overall polymer chain (Figure 1). In reality, because of conformation changes, the final net dipole will likely be a nonzero value, but diminutive nonetheless. We thought that the introduction of a rigid passivating unit between each DA subunit in the polymer would increase the overall ICT along one direction of the polymer backbone (Figure 2). Conformational flexibility might cause folding to occur that would ultimately diminish the overall net dipole; however, by using rigid structural elements, retention of the net dipole may be possible. Therefore, we embarked on the synthesis of this donor/acceptor/passivator (DAP) polymer.[4q] The initial results of the synthetic work are described here to establish this unusual constitutional arrangement in a polymer backbone.

Results and Discussion

Retrosynthetic Analysis. We sought to initiated the synthesis of DAP polymer **1** containing alternating electron-rich and electron-deficient thiophenes with each DA subunit separated by a rigid passivating phenyl group (eq 1). Although the phenyl group is not entirely passivating because of its π-conjugation pathway, as a result of its high degree of resonance stabilization, electron density transfer would be small relative to the thiophenes, and thus, it could serve as a rigid passivator moiety. We envisioned polymer **1** arising from a homopolymerization of the methyl-substituted Boc-protected difunctional monomer **2**. The methyl groups on the amines of **1** would increase the electron density of the donor units increasing the solubility of the final product. We intentionally avoided incorporation of *N,N,N′,N′*-tetramethyl units since steric interactions would limit planarization between the DA moieties. Monomer **2** could arise from Stille coupling of stannylthiophene **3** with **4**.



Monomer Synthesis. Starting from thiophene, bromination and nitration afforded **5,** which would serve as the starting material for both the electron-donating and electron-accepting units (eq 2). The electron-



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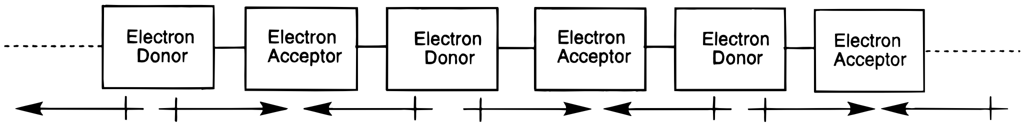


Figure 1. Schematic representation of an alternating donor/acceptor (DA) polymer where the local electronic dipoles give rise to an overall near-zero net dipole along the polymer chain.

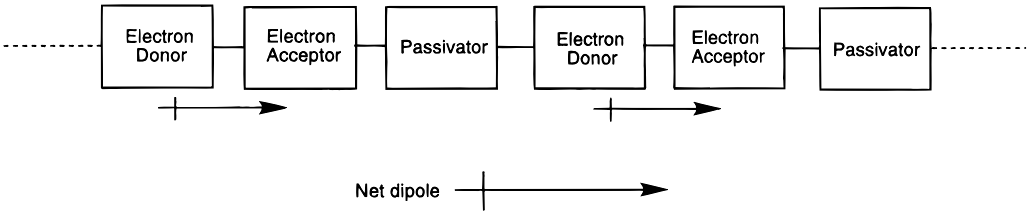
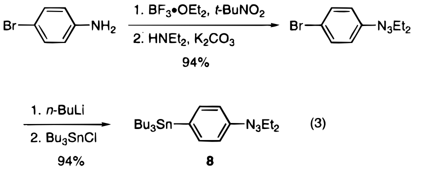


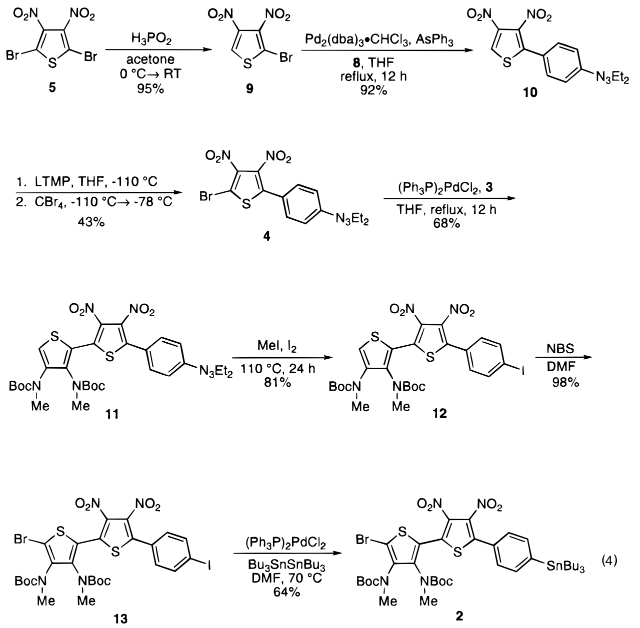
Figure 2. Schematic representation of and alternating donor/acceptor/passivator (DAP) polymer where the local electronic dipoles combine to provide an overall large net dipole.

deficient **5** was reduced to the diamine with concomitant dehalogenation, *tert*-butoxycarbonyl (Boc)-protection, and dimethylation to afford **6**.[4m] Our initial efforts at direct lithiation/stannylation of Boc-protected diaminothiophene **6** in tetrahydrofuran (THF) repeatedly gave low yields of **3**, causing us to pursue lithium−halogen exchange from bromothiophene **7** that was synthesized in good yield by monobromination of **6** with *N*-bromosuccinimide in dimethylformamide (DMF) (eq 2). Lithium−halogen exchange on **7** using *n*-butyllithium in ether followed by quenching with tributyltin chloride afforded **3** in excellent yield. It is crucial that ether be used as the reaction medium in order to obtain high yields of the desired monostannyl adduct. Use of THF as a solvent, under a variety of conditions, afforded mixtures of mono- and distannylated products. We subsequently discovered that **3** could indeed be prepared in high yield by direct lithiation/stannylation of **6** by using ether as the reaction medium (eq 2).

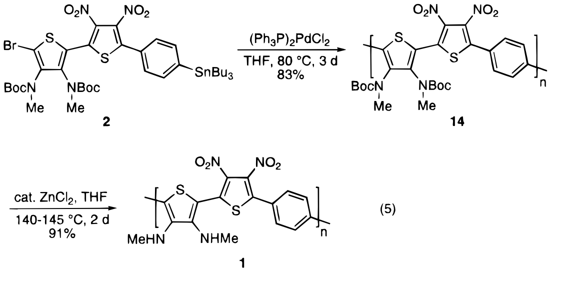
Synthesis of the passivator unit was accomplished using 4-bromoaniline via conversion to the corresponding diethyltriazene. Lithiation and stannylation afforded desired **8** where the triazene served as a masked iodide moiety (eq 3).[5]



Initially, we hoped that Pd-catalyzed coupling[6] of **8** with 2,5-dibromo-3,4-dinitrothiophene (**5**) would directly lead to **4**. Unfortunately, because of the extremely high reactivity of the highly electron-deficient **5**, inseparable mixtures of products repeatedly resulted from these attempts. Therefore, treatment of **5** with hypophosphorous acid in acetone gave monobromide **9** in excellent yield (eq 4).[7] Stille coupling of stannane **8** with the monobromide **9** using $Pd(0)/AsPh_3$ afforded **10** in high yield.[6] Whereas lithiation of **10** with lithium diisopropylamide (LDA) resulted in decomposition of the starting material, use of lithium tetramethylpiperidide (LTMP) followed by quenching with carbon tetrabromide gave electron-deficient bromothiophene **4** in 43% yield. Stille coupling of electron-rich monostannane **3** with electron-deficient monobromide **4** afforded the DAP assembly **11,** which needed only to be end-functionalized appropriately for the Stille polymerization.[6,8] Conversion of the triazene moiety to the iodide[5] followed by bromination of the electron-rich thiophene ring afforded bromoiodide **13**. The desired monomer **2** was obtained upon selective coupling at the iodide position on **13** with hexabutyldistannane using $(Ph_3P)_2PdCl_2$; the bromide on **13** was on the electron-rich thiophene unit, which conveniently retarded its reactivity relative to the passivator-bearing iodide (eq 4).



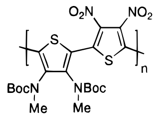
Polymer Synthesis and Deprotection. With the desired DAP monomer in hand, Boc-protected polymer **14** was prepared in 83% yield by polymerization of monomer **2** using $(Ph_3P)_2PdCl_2$ (eq 5). As we have previously observed, these Pd(0)-catalyzed polymerizations are extremely sensitive to the precise choice of ligands, cocatalysts, and solvents. For example, treat-



ment of **2** with $Pd_2(dba)_3$/CuI/$AsPh_3$ in THF afforded no polymer. Experience with numerous Stille polymerizations have shown us that the ultimate choice of catalyst and solvent is empirical; there is no obvious trend in predicting polymerization conditions for these thiophene-containing polymers.[3o,3p,3t,4g,4m] The molecular weight of **14** ($M_n = 14\,500$, $M_w = 24\,700$) was determined by size exclusion chromatography (SEC) in THF relative to polystyrene (PS) standards.[9] The optical spectra were consistent with the fact that **14** (λ_{abs} 341 nm with tailing edge ~500 nm, λ_{emis} 554 nm, THF) has a significant degree of distortion from planarity because of the steric bulkiness of the amine substituents.[4m]

Removal of the Boc groups from polymer **14** was attempted under a variety of conditions that we have used successfully on other conjugated polymers bearing Boc-protected amines including neat CF_3CO_2H, CF_3CO_2H/CH_2Cl_2/anisole, CF_3CO_2H/THF/anisole, and 3 N HCl/THF.[3g,3h,3o,3p,3t,4g,4m] All of these methods gave only partially deprotected material, possibly because of the decreasing solubility of the polymer as Boc groups were removed, a finding that would ultimately prove deleterious for the use of this particular polymer system. Finally, we discovered that treatment of **14** with a catalytic amount of $ZnCl_2$ in THF yielded the desired DAP polymer **1** in 91% yield. Complete removal of the protecting groups was confirmed by the absence of Boc carbonyl stretches in the infrared spectrum of the resulting polymer. UV−vis spectroscopy of the solid polymer showed λ_{abs} 453 (max) and 500 (br) nm, and this bathochromic shift was consistent with the expected increased conjugation in the deprotected polymer.[4g,4m] Interestingly, the tailing extended edge extends to ~900 nm. Unfortunately, because of the low solubility of polymer **1** in numerous solvents including dimethyl sulfoxide, THF, dichloromethane, and mixtures thereof, investigation of its properties was inhibited. The high degree of DAP polymer insolubility in this zigzag backbone was surprising on the basis of our earlier work on thiophene-based DA polymers.[4g,4m] This may allude to some unforeseen interchain stacking property that would make these DAP polymers particularly difficult to solublize. We even tried solublizing **1** in nitromethane with the addition of $AlCl_3$ (up to two equiv per repeat unit) with no success. To make these compounds more soluble, we attempted to construct related DAP polymers bearing phenylene-ring substituents or longer chain alkyl-substituted amines on the donor units. Our initial attempts at preparing these modified monomers have been frustrating since the precise conditions found to yield the monomers here were not amenable to use on the more substituted monomers; low-yield transformations have been repeatedly obtained. Hence, major modification of the route must be attempted.

Optical Comparisons to Related Polymers. In previous studies, we prepared DA polymers that contained structural units similar to those in the DAP polymers described here.[4m] For example, Boc-protected **14** was 60 nm hypsochromically shifted relative to the Boc-protected **15** (λ_{abs} 400 nm in THF) that contained no passivator unit. Although we would like a direct comparison based on the relative DA properties between these two systems, the *o*-hydrogens in the phenyl ring on **14** project toward the adjacent thiophene units, skewing them further from planarity and causing a retardation in the extended π-overlap.[3] However, that the phenyl ring is skewed relative to the thiophene units is beneficial for the DAP properties since it would serve as a more efficient passivator. Thus, we cannot easily segregate the steric and electronic components in the comparison between **14** and **15**, complicating a unifying explanation of any optical observations at this point.



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Summary

We synthesized a unique polymer (**1**) possessing sequential electron-rich (donor) and electron-deficient (acceptor) thiophene rings and a passivating phenylene group that separates each donor/acceptor subunit. Several new functionalization schemes on thiophene cores have been developed. The final DAP polymer was prepared by Stille coupling of a difunctional monomer. Polymer **1** was insoluble in a variety of organic solvents; therefore, characterization of its properties could not sufficiently be conducted. Although comparisons of these DAP polymers were made to similar DA polymers, direct comparison could not be reached because of our failed efforts at preparing more soluble DAP systems. The results described here serve primarily to illustrate a new strategy to prepare intense dipole-containing polymers and to outline novel avenues to unique electron-rich and electron-deficient thiophene-based monomers that will likely show utility in other conjugated polymer syntheses involving electron-rich and/or electron-deficient monomers.

Experimental Procedures

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 SEC columns (10^5 Å (10 μm) and 500 Å (5 μm)) eluted with THF at 60 °C and a flow rate of 1.0 mL/min. Molecular weight results were based on five polystyrene standards ($M_w = 435\,500$, 96 000, 22 000, 5050, and 580 with a correlation coefficient >0.9998) purchased from Polymer Laboratories, Ltd. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Alkyllithium reagents were obtained from FMC. Reagent grade diethyl ether and THF were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade benzene and dichloromethane were distilled over calcium hydride. Bulk grade hexane was distilled prior to use. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out using 230−400 mesh silica gel from EM Science. Thin-layer chromatography was performed using glass plates precoated with silica gel 60 F254 with a layer thickness of 0.25 mm purchased from EM Science. The synthesis of **6** was described previously.[4m]

***N*,*N*′-(Bis-*tert*-butoxycarbonyl)-*N*,*N*′-(dimethyl)-2-bromo-3,4-diaminothiophene (7).** To a solution of **6**[4m] (3.4 g, 10 mmol) in DMF (15 mL) was added dropwise *N*-bromosuccinimide (1.9 g, 11 mmol) in DMF (10 mL) over a 2 h period. The mixture was stirred for 12 h at room temperature, then diluted with ether (200 mL), and successively washed with $Na_2S_2O_3$ (20% aq), water, and brine. After it was dried over $MgSO_4$, the mixture was concentrated and purified by flash chromatography on silica gel (2% EtOAc in hexane) to afford **7** (3.12 g, 74%), the 2,5-dibromide (500 mg, 10%), and starting material (170 mg, 5%). Mp: 58−59 °C. IR (KBr): 3082 (m), 2976 (s), 1698 (vs), 1546 (m), 1442 (s), 1361 (vs), 1157 (s), 860 (m), 770 (m), 607 (s) cm^{-1}. (Mixture of stereoisomers around the carbamates) ^1H NMR (300 MHz, $CDCl_3$): δ 7.00 (s, 1 H), 2.99 (br s, 6 H), 1.40 (br s, 9 H), 1.35 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.6, 154.5, 154.2, 138.6, 138.3, 138.1, 119.7, 109.4, 80.6, 80.3, 37.1, 36.1, 35.0, 28.2, 28.1. HRMS calcd for $C_{16}H_{25}N_2O_4SBr$: 420.0718. Found: 420.0713.

***N,N′*-(Bis-*tert*-butoxycarbonyl)-*N,N′*-(dimethyl)-3,4-diamino-2-(tri-*n*-butylstannyl)thiophene (3).** Starting from **7**, to a solution of **7** (2.1 g, 5.0 mmol) in ether (30 mL) was added dropwise *n*-BuLi (1.80 M, 2.78 mL, 5.0 mmol) under nitrogen at −90 °C (liq. N_2/acetone). The mixture was stirred at −90 °C for 2 h, and Bu_3SnCl (1.35 mL, 5.00 mmol) was added. The resulting mixture was stirred for 1 h at −78 °C and allowed to warm gradually over 3 h to ambient temperature. The resulting mixture was diluted with ether (100 mL), washed with water (2 × 30 mL) and brine (2 × 30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuo to give **3** (3.0 g, 95%, >90% purity by ^1H NMR), which was used without further purification. Attempted purification using silica gel or silica gel pretreated with triethylamine led to complete decomposition. Starting from **6**,[4m] to a solution of **6** (2.7 g, 5.8 mmol) in ether (30 mL) was added dropwise *n*-BuLi (1.65 M, 4.0 mL, 6.8 mmol) under nitrogen at −90 °C (liq. N_2/acetone). The mixture was stirred at −90 °C for 2 h, and Bu_3SnCl (1.60 mL, 5.8 mmol) was added. The resulting mixture was stirred for 1 h at −78 °C and allowed to warm over 3 h to ambient temperature. The resulting mixture was diluted with ether (100 mL), washed with water (2 × 30 mL) and brine (2 × 30 mL), dried, and filtered. The filtrate was concentrated in vacuo to give **3** (3.3 g, 90%, >90% purity by ^1H NMR), which was used without further purification. Attempted purification using silica gel or silica gel pretreated with triethylamine led to complete decomposition (loss of the stannyl moiety).

4-Diethyltriazenyl-1-bromobenzene. See Jones et al. for use of this protocol.[5] To a solution of BF_3-OEt_2 (8.46 g, 60 mmol) was added 4-bromoaniline (6.88 g, 40 mmol) in dichloromethane (40 mL) under nitrogen through a double-end needle at 0 °C. *tert*-Butylnitrite (6 mL, 50 mmol) was then added, and the resulting mixture was stirred at that temperature for 40 min. K_2CO_3 (20 g, 145 mmol) was added, followed by diethylamine (20 mL, 194 mmol). After being stirred for 1 h, water (60 mL) was added, and the organic layer was separated. The aqueous layer was extracted with ether (2 × 60 mL). The combined organic layer was washed successively with water (2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried ($MgSO_4$) and filtered, and the filtrate was concentrated in vacuo. The residue was separated by a flash column chromatography on a silica gel column by eluting with 10% ethyl acetate in hexane to afford the title compound (9.1 g, 94%) as yellow oil. IR (neat): 2976 (s), 1392 (s), 1237 (s), 1105 (s), 1003 (m), 830 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 9.0 Hz, 2 H), 7.28 (d, J = 8.9 Hz, 2 H), 3.75 (q, J = 7.2 Hz, 4 H), 1.26 (br t, J = 7 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 131.6, 122.0, 117.9, 49 (br), 14 (br). HRMS calculated for $C_{16}H_{14}N_3Br$: 255.0371. Found: 255.0378.

4-(Diethyltriazenyl)-1-(tri-*n*-butylstannyl)benzene (8). To a solution of 4-diethyltriazenyl-1-bromobenzene (9.08 g, 37.5 mmol) in THF (50 mL) was added dropwise *n*-BuLi (1.6 M, 23.5 mL, 37.5 mmol) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 2 h, and Bu_3SnCl (10.29 mL, 38 mmol) was added. The resulting mixture was allowed to warm gradually to ambient temperature over 4 h and then was diluted with ether (200 mL). The organic layer was washed successively with water (2 × 30 mL) and brine (2 × 30 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column, pretreated with 10% triethylamine in hexane, and washed with hexane (2 × 300 mL). By eluting with hexane, **8** (16.4 g, 94%) was obtained as yellow oil. IR (neat): 2926 (s), 1582 (w), 1461 (m), 1235 (s), 1101 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2 H), 7.38 (d, J = 7.2 Hz, 2 H), 3.75 (q, J = 8.1 Hz, 4 H), 1.61 (m, 6 H), 1.49 (q, J = 7 Hz, 6 H), 1.30 (t, J = 7.3 Hz, 6 H) 1.06 (t, J = 8.1 Hz, 6 H), 0.89 (t, J = 7.3 Hz, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.1, 138.0, 137.0, 120.1, 29.2, 27.4, 13.7, 9.6. HRMS calcd for $C_{22}H_{41}N_3Sn$: 467.2326. Found: 467.2325.×

2-Bromo-3,4-dinitrothiophene (9).[7] To a solution of **5**[4m] (5.0 g, 15.1 mmol) in acetone (50 mL) was added hypophosphorous acid (9 mL, 50% solution in water) at 0 °C, and the solution was stirred for 20 min. The ice bath was removed, and the mixture was stirred for 3 h at room temperature and poured into ice (300 g). The white solid was filtered, washed with water (3 × 30 mL) and dried in vacuo to give **9** (3.4 g, 95%, >98% purity by ^1H NMR). The compound was used without further purification. However, an analytical sample was recrystallized from chloroform to give a white crystalline solid. Mp: 87−88 °C (lit. 88−89 °C).[7] IR (KBr): 3108 (m), 1544 (s), 1333 (s), 873 (m), 732 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 139.9, 128.9, 113.1.

2-(4′-Diethyltriazenylphenyl)-3,4-dinitrothiophene (10). To a solution of $Pd_2(dba)_3-CHCl_3$ (1.36 g, 1.31 mmol) in THF (20 mL) was added $AsPh_3$ (3.33 g, 10.9 mmol) under nitrogen, and the mixture was stirred for 30 min at room temperature. **8** (20.4 g, 43.8 mmol) in THF (40 mL) and **9** (11.13 g, 44 mmol) were added successively, and the mixture was heated to reflux for 12 h. The resulting mixture was cooled to ambient temperature and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column by eluting with 10% ethyl acetate in hexane. **10** (14.0 g, 92%) was obtained as red-orange solid. Mp: 115−116 °C. IR (KBr): 3113 (s), 2990 (m), 1597 (s), 1522 (s), 1329 (s), 1161 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (s, 1 H), 7.46 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.9 Hz, 2 H), 3.78 (q, J = 7.2 Hz, 4 H), 1.35−1.27 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 141.2, 140.1, 128.8, 128.5, 126.0, 123.7, 121.2, 49 (br), 41 (br), 14 (br), 11 (br). HRMS calcd for $C_{14}H_{15}N_5O_4S$: 349.0845. Found: 349.0841.

5-Bromo-2-(4-diethyltriazenylphenyl)-3,4-dinitrothiophene (4). A solution of 2,2,6,6-tetramethylpiperidine (2.36 mL, 14 mmol) was cooled to −78 °C. *n*-BuLi (8.82 mL, 1.60 M in hexane, 14 mmol) was added dropwise, and the mixture was stirred for 5 min. The cooling bath was removed, and the mixture was brought to room temperature and stirred for 5 min. The mixture was cooled back to 0 °C and diluted with THF (15 mL).

The resulting lithium 2,2,6,6-tetramethylpiperidide in dry THF was added dropwise to a solution of **10** (3.49 g, 10 mmol) in dry THF/ether (40 mL, 1/1) at −110 °C (THF−ether/liq. N_2 bath). The mixture was stirred for 45 min, and CBr_4 (3.93 g, 30 mmol) in THF (10 mL) was added dropwise. The cooling bath was replaced with a dry ice−acetone bath (−78 °C) and stirred for 2 h. The mixture was brought to ambient temperature, quenched with water, and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 × 50 mL). The combined organic layer was washed with water (2 × 30 mL) and brine (2 × 30 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column by eluting with 20% ethyl acetate in hexane. **4** (1.82 g, 43%) was obtained as orange-red solid. Mp: 135−136 °C. IR (KBr): 2981 (w), 1594 (m), 1539 (vs), 1387 (s), 1231 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, $J = 8.5$ Hz, 2 H), 7.37 (d, $J = 8.5$ Hz, 2 H), 3.77 (q, $J = 7.2$ Hz, 4 H), 1.27 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 142.4, 140.1, 135.9, 129.3, 122.9, 121.1, 112.2, 49 (br), 41 (br), 14 (br), 11 (br). HRMS calcd for $C_{14}H_{14}BrN_5O_4S$: 426.9950. Found: 426.9941.

11. To a solution of $(Ph_3P)_2PdCl_2$ (0.50 g, 0.71 mmol) in THF (40 mL) was added **4** (4.28 g, 10.0 mmol) and **3** (9.45 g, 15.0 mmol) in THF (20 mL), and the mixture was heated to reflux for 12 h. The resulting mixture was cooled to ambient temperature and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column by eluting with 10% ethyl acetate in hexane to afford **11** (6.0 g, 88%). Mp: 74−75 °C. IR (KBr): 2977 (s), 1712 (vs), 1392 (s), 1154 (s), 767 (s) cm^{-1}. (Stereoisomers around the carbamate plus quadrupolar distortions) ^1H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, $J = 8.5$ Hz, 2 H), 7.40 (d, $J = 8.5$ Hz, 2 H), 7.25 (m, 1 H), 3.77 (q, $J = 7.2$ Hz, 4 H), 3.09−2.97 (3 peak m, 6 H), 1.42−1.29 (m, 24 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.4, 153.9, 153.7, 153.6, 153.4, 142.5, 138.9, 137.6, 135.9, 130.1, 129.7, 129.6, 129.0, 123.8, 123.5, 123.0, 121.1, 121.0, 81.5, 81.1, 80.8, 50.2, 41.4, 36.6, 36.1, 28.3, 28.1, 14.5, 11.3. HRMS calcd for $C_{30}H_{39}O_8N_7S_2$: 689.2302. Found: 689.2322.

12. To a solution of **11** (1.9 g, 2.76 mmol) in iodomethane (20 mL) in a pressure tube was added I_2 (0.14 g, 0.55 mmol), and the solution was sparged with N_2 before capping. The pressure tube was kept at 110 °C for 24 h. The mixture was cooled to ambient temperature, and the excess iodomethane was removed in vacuo. The residue was dissolved in ethyl acetate (100 mL) and successively washed with 20% aq $Na_2S_2O_3$ (2 × 30 mL), water (2 × 30 mL), and brine (2 × 30 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column by eluting with 10% ethyl acetate in hexane. **12** (1.1 g, 81%) was obtained as red-yellow crystals. Mp: 78−79 °C. IR (KBr): 2977 (s), 1702 (vs), 1545 (s), 1354 (s), 1152 (vs), 736 (s) cm^{-1}. (Stereoisomers around the carbamate) ^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, $J = 7.07$ Hz, 2 H), 7.30 (m, 1 H), 7.18 (d, $J = 8.3$ Hz, 2 H), 3.08−2.95 (3 peak m, 6 H), 1.40−1.27 (2 peak m, 18 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 153.7, 153.5, 140.6, 139.2, 139.0, 138.53, 138.49, 137.4, 130.5, 130.4, 127.4, 127.1, 123.5, 123.3, 120.5, 97.9, 97.8, 81.5, 81.3, 80.8, 36.0, 28.3, 28.1. HRMS calcd for $C_{26}H_{29}IO_8N_4S_2$: 716.0472. Found: 716.0492.

13. To a solution of **12** (1.0 g, 1.4 mmol) in DMF (5 mL) was added *N*-bromosuccinimide (0.32 g, 1.8 mmol), and the mixture was stirred at room temperature for 4 h. The resulting mixture was dissolved in ether (100 mL), washed with water (3 × 20 mL) and brine (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column by eluting with 20% ethyl acetate in hexane to afford **13** (1.09 g, 98%) as a yellow oil. IR (neat): 2975 (w), 1717 (vs), 1541 (s), 1357 (s), 1143 (vs), 764 (m) cm^{-1}. (Stereoisomers around the carbamate) ^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, $J = 8.0$ Hz, 2 H), 7.16 (d, $J = 8.4$ Hz, 2 H), 3.14−2.93 (4 peak m, 6 H), 1.49−1.28 (m, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 153.7, 153.6, 153.4, 153.2, 140.8, 140.5, 139.5, 139.0, 138.8, 138.6, 137.6, 137.4, 136.4, 130.8, 130.4, 130.3, 130.1, 130.0, 127.1, 126.8, 121.0, 120.6, 115.6, 115.0, 114.7, 98.1, 98.0, 97.9, 82.1, 81.9, 81.6, 81.5, 81.3, 81.1, 36.2, 36.1, 36.0, 35.7, 35.0, 34.6, 28.2, 28.1, 28.0, 27.9. HRMS calcd for $C_{26}H_{28}BrIO_8N_4S_2$: 793.9576. Found: 793.9554. Anal. calcd for $C_{26}H_{28}BrIO_8N_4S_2$: C, 39.26; H, 3.55; N, 7.04. Found: C, 38.99; H, 3.51; N, 7.01.

Monomer 2. To a solution of **13** (1.34 g, 1.69 mmol) in DMF (8 mL) was added $Bu_3SnSnBu_3$ (1.10 g, 1.9 mmol) and $(Ph_3P)_2PdCl_2$ (0.06 g, 0.08 mmol), and the mixture was stirred at 80 °C for 2 h. The resulting mixture was dissolved in ether (200 mL), washed with water (3 × 20 mL) and brine (2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was separated by flash column chromatography on a silica gel column, pretreated with 10% triethylamine in hexane and washed with hexane (2 × 500 mL), by eluting with 2% ethyl acetate in hexane to afford **2** (1.04 g, 64%) as a yellow oil. If THF was used instead of DMF, the yield was 54%. IR (neat): 2927 (m), 1715 (vs), 1548 (m), 1367 (m), 1147 (s) cm^{-1}. (Stereoisomers around the carbamate) ^1H NMR (300 MHz, $CDCl_3$): δ 7.56 (d, $J = 7.2$ Hz, 2 H), 7.36 (d, $J = 7.1$ Hz, 2 H), 3.15−3.00 (m, 6 H), 1.6−1.3 (m, 30 H), 1.07 (t, $J = 8.4$ Hz, 6 H), 0.88 (t, $J = 7.3$ Hz, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 153.5, 153.1, 147.5, 147.3, 141.9, 139.2, 138.8, 138.7, 137.4, 137.2, 137.1, 136.1, 129.6, 127.6, 126.9, 126.6, 121.3, 114.5, 82.0, 81.8, 81.6, 81.2, 81.0, 36.3, 36.1, 35.9, 35.1, 34.7, 29.2, 29.1, 29.0, 28.2, 27.7, 27.5, 27.2, 13.8, 11.6, 11.5, 9.9, 8.3, 8.2. HRMS calcd for $C_{34}H_{46}BrO_8N_4S_2Sn$ (M-butyl): 897.0958. Found: 897.0975. Anal. calcd for $C_{38}H_{55}BrO_8N_4S_2Sn$: C, 47.61; H, 5.78; N, 5.84. Found: C, 47.82; H, 5.84; N, 5.81.

Polymer 14. To a solution of **2** (0.90 g, 0.94 mmol) in THF (6 mL) in a screw cap tube was added $(Ph_3P)_2PdCl_2$ (0.026 g, 0.04 mmol) under N_2, and the pressure tube was capped and heated to 80 °C for 4 days. The resulting mixture was cooled, concentrated, dissolved in acetone (10 mL), and poured into hexane (500 mL). The precipitate was filtered and dried to give **14** (0.49 g, 83%) as yellow plates. IR (KBr): 2976 (m), 1711 (vs), 1542 (s), 1365 (s), 1150 (vs) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.25−7.68 (m, 4 H), 3.15−3.0 (m, 6 H), 1.58−1.15 (m, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 154.1, 153.6, 153.3, 153.1, 140.4, 139.7, 137.4, 136.5, 135.3, 134.9, 131.0, 129.7, 128.4, 127.9, 120.5, 82.1, 81.9, 81.6, 81.2, 36.8, 36.3, 36.0, 35.7, 35.5, 28.3, 28.2, 27.9. Anal. calcd for $(C_{26}H_{30}O_8N_4S_2)_n$: C, 52.87; H, 5.12; N, 9.49. Found: C, 52.22; H, 4.87; N, 8.59. SEC (THF, PS): $M_n = 14\,500$, $M_w = 24\,700$. Optical spectra (THF): λ_{abs} 341, 500 (edge) nm; λ_{emis} 554 nm.

Polymer 1. To a solution of **14** (0.075 g, 0.127 mmol) in THF (25 mL) was added $ZnCl_2$ (7 mg, 0.05 mmol), and the solution was capped in a screw cap tube and heated at 140−145 °C for 2 days. The reaction mixture was cooled, and the deprotected polymer was filtered, washed with ether (2 × 30 mL), and dried to give **1** (0.045 g, 91%). IR (KBr): 3361 (m), 2950 (m), 1671 (m), 1518 (vs), 1326 (s) cm^{-1}. No Boc signal (1710 cm^{-1}) was detected. Optical spectrum (solid): λ_{abs} 453 (max), 500 (br), 900 (edge) nm. Since **1** was insoluble in every solvent tested, further data was not obtained.

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Supporting Information Available: Spectra data for the monomer **2** and polymers **1** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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