JOC The Journal of Organic Chemistry

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Synthesis and Characterization of a Series of Annelated Benzotriazole Based Polymers with Variable Bandgap

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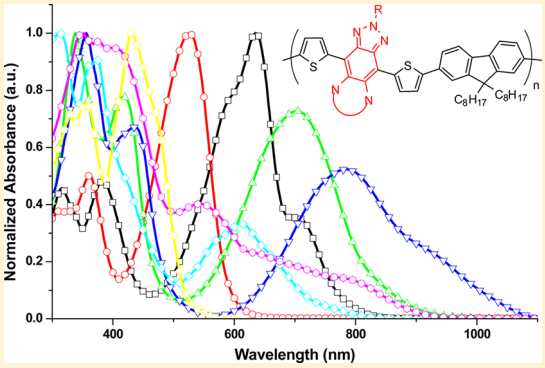
Supporting Information

ABSTRACT: Here we report the synthesis and characterization of a series of annelated benzotriazole based polymers with variable bandgap. Benzobistriazole monomers reported by us previously were desymmetrized using partial reduction ring opening followed by ring closure to produce a wide range of annelated benzotriazole based monomers. These monomers were co-polymerized with a fluorene moiety to give polymers with bandgaps ranging from 1.16 to 2.41 eV.



INTRODUCTION

Benzotriazole based polymers have been recently attracting attention as active materials for use in organic photovoltaics (OPV), organic electrochromics (OEC), and organic light emitting diodes (OLED) due to the easy synthesis and modification of the triazole moiety.[1−12] As our interest is to expand the variety of functional materials available for such application, we have sought to exploit the benzo[1,2-*d*;4,5-*d*′]bistriazole (BBTa) monomer units reported by us previously[13] by co-polymerizing them with a fluorene moiety. The relatively high combined overall yield of the 2,6- and 1,6-dialkylated BBTa monomers also led us to investigate possible desymmetrization by selective reduction of the BBTa core, as we have previously demonstrated in the case of benzo[1,2-*c*;4,5-*c*′]bis[1,2,5]thiadiazole (BBT),[14] so as to test the synthetic versatility of using them as starting materials for other annelated benzotriazole based materials. Such materials, especially donor−acceptor co-polymers containing such units, are of great interest as possible active components in applications such as LEDs[15] or solar cells[16] where the tuning of the optical bandgaps and/or orbital energies is an important aspect in designing materials with optimal device performance.

Reduction of benzotriazole (BTa) has been reported by several groups using different reducing agents such as sodium in liquid ammonia,[17] and N-substituted benzotriazoles can be reduced with sodium in butanol[18] or zinc[19] or polarographically[20] to give N-substituted *o*-phenylenediamines. Reduction of 3,4,5,6-tetrachlorobenzotriazole was also reported by using zinc with hydrochloric acid to give the corresponding diamine.[21] However, reductions of BBTa and its derivatives are to the best of our knowledge unreported to date.

RESULTS AND DISCUSSION

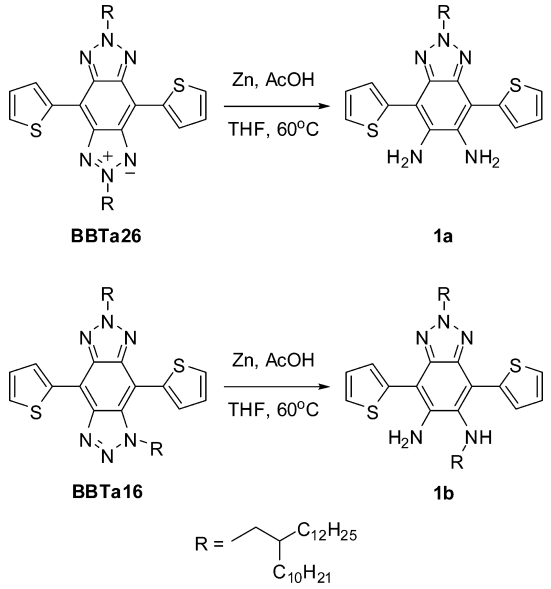
BBTa26 and **BBTa16** were synthesized as previously reported.[13] Treatment of the BBTa derivatives with iron in acetic acid yielded no reaction, unlike BBT, which underwent reduction of one heterocyclic ring under these conditions.[22] Instead, treatment with zinc gave rise to reductive ring opening at one of the triazole rings in the BBTa core. By contrast this reagent reduces both heterocyclic rings in BBT,[22] thus demonstrating the greater resistance of the triazole over the thiadiazole ring toward reduction. Interestingly, reductive ring opening involves the expulsion of a 2-position nitrogen in both **BBTa26** and **BBTa16**, which leads to the diamines **1a** and **1b**, respectively (Scheme 1). Both **1a** and **1b** appear to be unstable as their colors darken rapidly upon standing.[23]

The partial reduction of **BBTa26** provides an alternate route to the synthesis of the diamine **1a**, which we have previously obtained in a five-step synthesis with an overall yield of 7.6% (Scheme 2).[24] This alternate route takes one less step starting from tetraaminobenzene tetrahydrobromide, requires less forceful conditions, and produces potentially higher overall yield (for isolatable shorter alkyl chains).

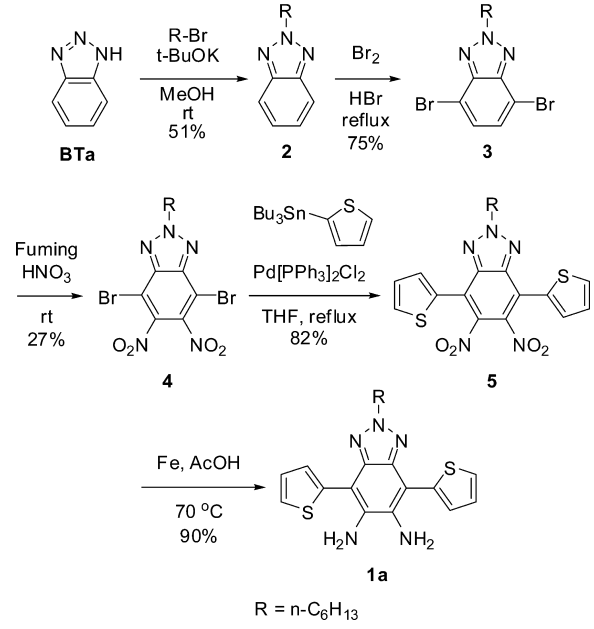
Syntheses of **SBTa**, **SeBTa**, **TaQ1**, and **TaQ2** here were analogous to that reported by us earlier[24] except that the diamine was not purified due to its instability. To synthesize

Received: July 17, 2012
Published: October 23, 2012

Scheme 1. Reduction of BBTa26 and BBTa16 Using Zinc and Acetic Acid



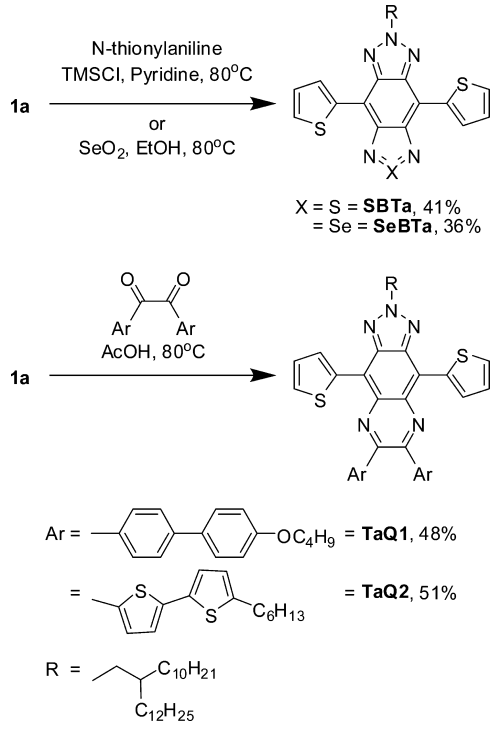
Scheme 2. Synthesis of the C6 Analogue of 1a According to the Literature; Overall Yield = 7.6%



SBTa and **SeBTa**, **BBTa26** was reduced, and the reaction mixture was extracted. The crude **1a** was then treated with *N*-thionylaniline and TMSCl in pyridine or SeO_2 in ethanol to give **SBTa** and **SeBTa** ,respectively (Scheme 3). For **TaQ1** and **TaQ2**, after reduction of **BBTa26**, the reaction mixture was filtered, and 1,2-diketone **2** or **3** was reacted with the filtrate to give **TaQ1** and **TaQ2**, respectively (Scheme 3). The yields obtained via reduction of **BBTa26** were all higher than by our previous synthesis despite the instability of **1a** (**SBTa**, 12.3% vs lit. 6.4%; **SeBTa**, 10.8% vs lit. 6.6%; **TaQ1**, 14.4% vs lit. 6.2%; **TaQ2**, 15.3% vs lit. 5.8%), suggesting this is a viable alternative synthesis.

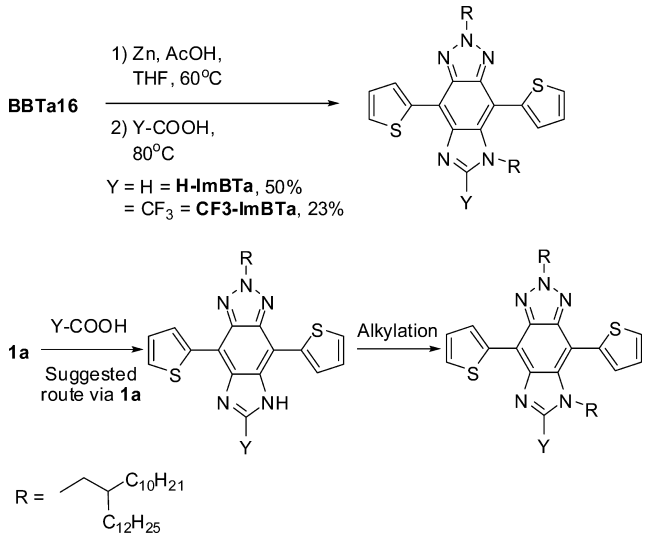
Though the alkyl amine on **1b** does not allow aromatic cyclization to form a six-membered ring using 1,2-diketones or

Scheme 3. Ring Closure of 1a



a five-membered ring by incorporating sulfur/selenium, it is possible to form an aromatic five-member imidazole ring by adding a carbon atom. Thus **H-ImBTa** and **CF3-ImBTa** were synthesized via an one-pot reductive ring opening of **BBTa16** using the procedure above followed by ring closure using formic acid or trifluoroacetic acid, respectively (Scheme 4). Ring closure with benzoic acid did not yield the corresponding ImBTa but gave a complex mixture of unidentified products. A conventional route via benzotriazole would suggest the diamine **1a** as the likely intermediate, followed by ring closure using the appropriate acids and then alkylation. This would take a total of

Scheme 4. Synthesis of H-ImBTa and CF3-ImBTa via BBTa16 (Five Steps in Total Starting from Tetraaminobenzene Tetrahydrobromide) versus via Benzotriazole (7 Steps in Total)



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Scheme 5. Synthesis of the Annelated Benzotriazole Based Polymers

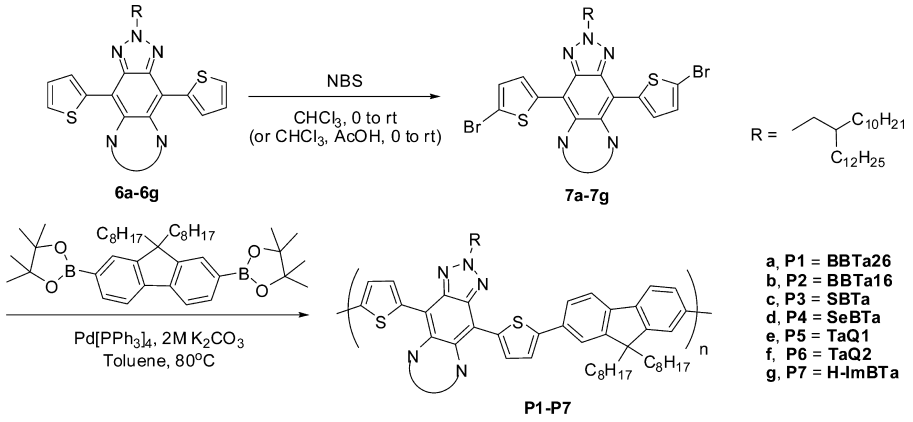

Table 1. Characterization of P1−P7[a]

	HOMO (eV)	LUMO (eV)	CV E_g (eV)	solution opt E_g (eV)	thin film opt E_g (eV)	$M_w \times 10^{-4}$	PDI
P1	−5.04	−3.45[b]		1.59	1.51	2.53	2.93
P2	−5.38	−3.27[b]		2.11	2.04	2.15	2.87
P3	−5.09	−3.64 (−3.73)[b]	1.45	1.36	1.22	0.88	1.87
P4	−5.02	−3.74 (−3.86)[b]	1.28	1.16	1.10	0.83	1.95
P5	−5.22	−3.71 (−3.71)[b]	1.51	1.52	1.36	0.77	1.79
P6	−5.18	−3.82 (−3.81)[b]	1.36	1.37	1.23	0.84	1.52
P7	−5.35	−2.94[b]		2.41	2.32	0.91	1.66

[a]Electrochemical and photophysical properties were measured in chloroform. [b]Determined from HOMO and optical bandgap.

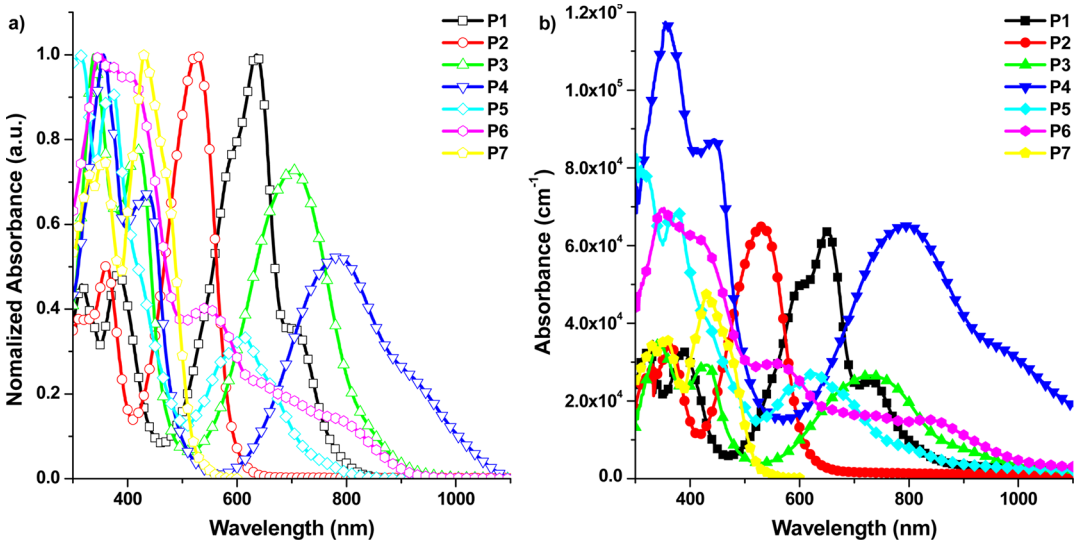

Figure 1. (a) Solution (chloroform) and (b) thin film UV−vis−NIR absorption of **P1**−**P7**.

seven steps, versus five steps via tetraaminobenzene tetrahydrobromide with **BBTa16** as intermediate.

The annelated benzotriazole based monomers, with the exception of **CF3-ImBTa** because of its low yield, were brominated using NBS, and the resultant dibromo derivatives were Suzuki co-polymerized with fluorene diboronic acid pinacol ester to yield the polymers **P1**−**P7** (Scheme 5). These polymers were characterized using UV−vis−NIR absorption spectroscopy and cyclic voltammetry, the results of which are shown in Table 1 and Figure 1. The reduction onsets for polymers **P1**, **P2**, and **P7** could not be detected, while those for **P3**−**P6** could not be determined unambiguously. We therefore estimated the LUMO values for these polymers using the HOMO values from the oxidation onsets and the optical bandgap. For polymers **P3**−**P6** these values match closely those we obtained from our best estimate of the reduction onsets. Polymer **P3** with a different alkyl chain has recently been reported by another group, with properties almost identical to those reported here by us.[25] This polymer has been used as an electron donor in a BHJ solar cell with a promising efficiency of 2.56%.

Table 1 shows the series of annelated benzotriazole based polymers with optical bandgap ranging from 1.16 to 2.41 eV that can be achieved by simply changing the annelated ring in the benzotriazole core. The increase in the bandgaps is in accordance with the decreasing electron-accepting ability of the

dx.doi.org/10.1021/jo301281d | J. Org. Chem. 2012, 77, 10035−10041

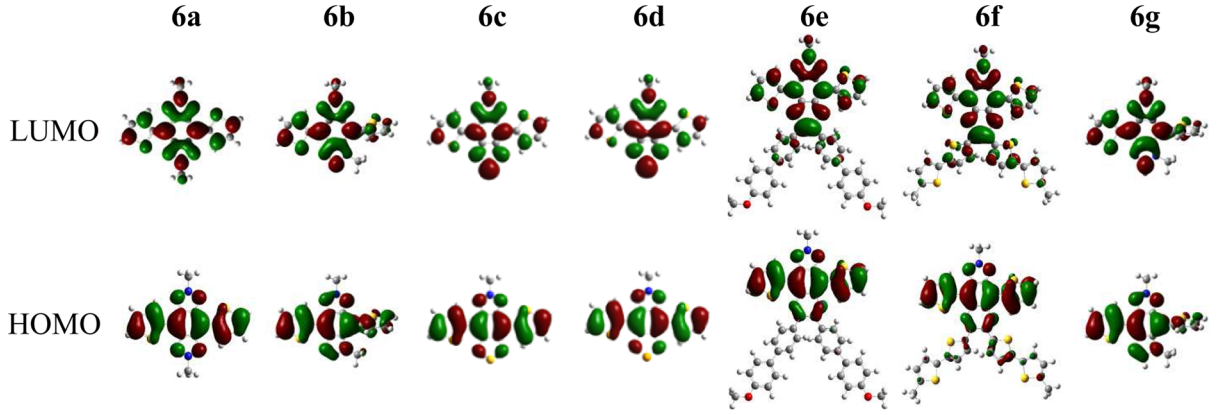

Figure 2. DFT calculation of **6a−g** via geometry optimization using B3LYP 6-31G^{+2}(d,p) for **6a,b**[13] and **6e−g**, 6-31G^{+2}(3d,3p) for **6c**,[13] and 6-31++(3df,3pd) for **6d**. The large alkyl groups were reduced to methyl groups for simplicity.

cores, and this can be taken with referral to previously studied benzazoles and quinoxaline systems (ring 2 and 3).[11,26] The lowest bandgap was observed for **P3** and **P4**, which seems to be due to the hypervalent sulfur and selenium in the diazole ring.[27−29] A thorough study by Schanze et al. has shown that these systems are better described by a three-center-four-electron bond in which the central sulfur/selenium atom is expected to have a +1 charge.[30] This condition produces an electron deficiency in these systems, which reduces the energy of the LUMO. The selenium analogue **P4** has lower bandgap than the sulfur analogue **P3** due to larger polarizability (as shown by a larger contribution to the LUMO of **6d** in Figure 2) and electrochemical amphotericity of selenium.[11] This is followed by **P5** and **P6**, which have the electron-accepting pyrazine ring. **P5** shows higher bandgap than **P6** because the biphenyls on the triazoloquinoxaline are less conjugated than the bithienyls, leading to lower/less LUMO contribution/stabilization. These trends are similar to those observed for thiadiazoloquinoxalines reported by us previously.[31,32] Replacement of sulfur/selenium in **P3**/**P4** with nitrogen resulted in a higher bandgap **P1** due to the significantly smaller contribution from the nitrogen to the LUMO. According to the theoretical calculations reported by us previously, changing the position of the alkyl chain from the 2- to the 1-position from **BBTa26** to **BBTa16** results to a large dihedral angle between the core and thiophene on one side of the latter.[13] This reduced conjugation in **BBTa16** is expected to repeat in the polymer backbone, and thus **P2** has a higher bandgap than **P1**. Replacement of the 2-azo-nitrogen in the annelated triazole ring of **P2** with carbon in **P7** results in a weaker electron-accepting imidazole ring. Thus bandgap of **P7** is expected to be higher than that of **P2**.

The optical bandgaps show that the electron-accepting strength of the core can be assigned as **SeBTa** > **SBTa** > **TaQ** > **BBTa26** > **BBTa16** > **H-ImBTa**. The results can also be translated as 1,2,5-selenadiazole >1,2,5-thiadiazole > pyrazine >2-triazole >1-triazole > imidazole. Instructively, the trend of the optical bandgaps of these polymers follows the trend of the theoretical bandgaps of the acceptor unit due to the common fluorene donor unit.

UV−vis−NIR spectra in Figure 1 show a slight bathochromic shift of the band edge from solution to thin film for **P2** and **P7**, while larger shifts were observed for **P1**, **P3**, **P4**, **P5**, and **P6**. The amount of bathochromic shift can be viewed as the amount of aggregation existing in the solid state. **P2** and **P7** are the only polymers with highly twisted backbones and are also non-regioregular. Such small shifts would be expected of **P2** and **P7** since packing of their polymer chains would be inefficient. On the other hand, **P1** is a planar and regioregular polymer, and thus packing should be efficient, The same goes for **P5** and **P6** since their aromatic substituents would provide stronger $\pi-\pi$ interactions. The heavy sulfur and selenium atom in **P3** and **P4**, respectively, result in stronger aggregation since there are presence of strong electrostatic effect[33] and secondary bonding interaction.[34]

■ CONCLUSION

In conclusion, we have demonstrated the reductive ring opening of **BBTa26** and **BBTa16** using zinc and acetic acid. The diamine obtained from the reduction of the former can be ring closed with the appropriate reagents to yield **SBTa**, **SeBTa**, **TaQ1**, and **TaQ2**, by a more convenient and efficient route than previously reported. The diamine obtained from the reduction of the latter on the other hand can be ring closed with formic acid or trifluoroacetic acid to yield **H-ImBTa** or **CF3-ImBTa**, respectively. The annelated benzotriazole based monomers were co-polymerized with a fluorene moiety, and the resulting polymers showed bandgaps as low as 1.16 eV to as high as 2.41 eV. Using this strategy of varying the annelated ring, a wide variety of benzotriazole based derivatives with different energy levels and bandgaps can be obtained. These derivatives may find application in the field of organic photovoltaics, organic field effect transistors, organic light emitting diodes, and electrochromic displays where such electronic properties are important.

■ EXPERIMENTAL SECTION

All reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Column chromatography was carried out with silica gel (230−400 mesh), and thin layer chromatography (TLC) were performed on silica gel 60 Al-backed plates (20 cm × 20 cm). ^{1}H NMR data were obtained on a 400 MHz spectrometer with chemical shifts referenced to $CDCl_3$. Thin film UV−vis−NIR samples were prepared by spincoating 10 mg/mL of polymer in chloroform. Cyclic voltammetry measurements were recorded in ACS grade $CHCl_3$ with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV s^{-1}). The electrolyte was bubbled with nitrogen gas for 5 min prior to measurement. The experiments were performed at room temperature with a conventional three electrodes configuration consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3 M KCl reference electrode. The measured potentials were

dx.doi.org/10.1021/jo301281d | J. Org. Chem. 2012, 77, 10035−10041

converted to SCE (saturated calomel electrode with reduction potential of −4.4 eV relative to vacuum).

Atomistic simulation, using density function theory (DFT) at B3LYP[35,36] (which includes the gradient corrected exchange and correlation functionals along with the exact exchange) method with double-ζ quality basis functions 6-31G* (augmented with polarized function for all non-hydrogen atoms) was used to optimize the geometry of **6d−g** molecules. Geometry was fully relaxed, and no symmetry constraints were imposed during optimization using Gaussian 09 code[3] with a convergence criterion of 10^{-3} au on the gradient and displacement and 10^{-6} auon energy and electron density. Harmonic vibrational analyses showed no imaginary frequency, indicating these structures are a local minimum. The obtained HOMOs and LUMOs were visualized using GaussView 5.0.

During reduction of **1a**, the reaction mixture changes from red (PL orange) to yellow (PL blue) upon completion. For **1b**, reaction mixture changes from PL green to PL blue. All reductions were monitored using thin layered chromatography.

SBTa. **BBTa26** (1.36 g, 1.36 mmol) and zinc powder (3.57 g, 54.53 mmol) in 130 mL of acetic acid and 65 mL of THF were heated at 60 °C for 1 day. Dichloromethane and water were added, and the organic layer was washed thoroughly with water. The organic layer was dried over anhydrous magnesium sulfate, and all volatiles were removed to yield crude **1a**. *N*-Thionylaniline (0.31 mL, 2.76 mmol) followed by trimethylsilyl chloride (1.73 mL, 13.63 mmol) were added to the crude **1a** dissolved in dry pyridine (15 mL) in a round-bottom flask purged with nitrogen. The mixture was heated at 80 °C for 1 day and cooled to room temperature. The mixture was poured into dichloromethane and washed repeatedly with dilute hydrochloric acid. The organic layer was collected, dried over anhydrous $MgSO_4$, and filtered, and solvent was removed. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (4:1) to yield pure **SBTa** as a purple amorphous solid (379 mg, 41% overall). ^{1}H NMR ($CDCl_3$): δ [ppm] 0.89 (t, 3 H, J = 7.2 Hz), 0.90 (t, 3 H, J = 7.2 Hz), 1.34 (m, 40 H), 2.34 (m, 1 H), 4.75 (d, 2 H, J = 6.4), 7.26 (dd, 2 H, J = 3.6, 4.8), 7.58 (dd, 2 H, J = 0.8, 4.8), 8.73 (dd, 2 H, J = 0.8, 3.6). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.82, 22.83, 26.4, 29.5, 29.78, 29.80, 30.0, 31.7, 32.0, 39.3, 61.2, 111.8, 127.6, 129.3, 131.0, 137.3, 142.5, 149.7. Anal. Calcd for $C_{38}H_{55}N_5S_3$: C, 67.31; H, 8.18; N, 10.33; S, 14.19. Found: C, 67.46; H, 8.46; N, 10.10; S, 13.98. MALDI-TOF-MS m/z: 676.51; calcd for $C_{38}H_{55}N_5S_3$ = 678.07.

SeBTa. **BBTa26** (0.97 g, 0.972 mmol) was reduced in the similar manner as above. SeO_2 (129 mg, 1.17 mmol) was added to the crude **1a** in ethanol (40 mL) in a round-bottom flask purged with nitrogen. The mixture was refluxed for 1 day and cooled to room temperature. The ethanol solvent was removed using rotary evaporator, and the residue was dissolved in dichloromethane and washed repeatedly with water. The organic layer was collected, dried over anhydrous $MgSO_4$, and filtered, and solvent was removed. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (7:3) to yield pure **SeBTa** as (253 mg, 36% overall).^{1}H NMR ($CDCl_3$): δ [ppm] 0.89 (t, 3 H, J = 7.2 Hz), 0.90 (t, 3 H, J = 7.2 Hz), 1.32 (m, 40 H), 2.34 (m, 1 H), 4.70 (d, 2 H, J = 6.8), 7.25 (dd, 2 H, J = 3.6, 1.2), 7.59 (dd, 2 H, J = 0.8, 5.2), 8.75 (dd, 2 H, J = 0.8, 2.8). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.81, 22.82, 26.4, 29.47, 29.48, 29.76, 29.79, 30.0, 31.7, 32.0, 32.1, 39.3, 61.3, 112.1, 127.5, 129.8, 131.2, 138.0, 143.3, 156.0. Anal. Calcd for $C_{38}H_{55}N_5S_2Se$: C, 62.96; H, 7.65; N, 9.66; S, 8.85; Se, 10.89. Found: C, 63.16; H, 7.71; N, 9.69; S, 8.87. MALDI-TOF-MS m/z: 724.40; calcd for $C_{38}H_{55}N_5S_2Se$ = 724.97.

TaQ1. **BBTa26** (0.48 g, 0.48 mmol) was reduced in the similar manner as above. The reaction mixture was filtered, and 1,2-bis(4′-butoxybiphenyl-4-yl)ethane-1,2-dione (293 mg, 0.58 mmol) was added. The reaction flask was purged with nitrogen and heated at 80 °C for 1 day. The reaction mixture was cooled to room temperature and dichloromethane was added. The organic layer was washed thoroughly with water, collected, and dried over anhydrous $MgSO_4$, and solvent was removed. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (3:1) to yield pure **TaQ1** as a brown amorphous solid (260 mg, 48% overall). ^{1}H NMR ($CDCl_3$): δ [ppm] 0.92 (t, 3 H, J = 6.8 Hz), 0.93 (t, 3 H, J = 6.8 Hz), 1.04 (t, 6 H, J = 7.6 Hz), 1.36 (m, 44 H), 1.83 (quintet, 4 H, J = 7.6 Hz), 2.38 (m, 1 H), 4.03 (t, 4 H, J = 6.4 Hz), 4.79 (d, 2 H, J = 6.4), 6.99 (d, 4 H, J = 8.8 Hz), 7.28 (dd, 2 H, J = 4.0, 0.8), 7.63 (m, 10 H), 7.89 (d, 4 H, J = 8.4), 8.96 (dd, 2 H, J = 0.8, 3.6). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.0, 14.3, 19.4, 22.8, 26.4, 27.1, 29.5, 29.78, 29.82, 30.1, 31.5, 31.7, 32.1, 39.3 57.9, 60.8, 67.9 114.9, 119.3, 126.2, 126.6, 128.2, 130.7, 131.4, 131.8, 132.7, 133.3, 136.0, 136.9, 141.3, 142.1, 151.3, 159.2. Anal. Calcd for $C_{72}H_{89}N_5O_2S_2$: C, 77.17; H, 8.00; N, 6.25; O, 2.86; S, 5.72. Found: C, 77.38; H, 8.14; N, 6.13; S, 5.54. MALDI-TOF-MS m/z: 1117.27; calcd for $C_{72}H_{89}N_5O_2S_2$ = 1120.64.

TaQ2. The synthetic procedures were exactly the same as **TaQ1**. **BBTa26** (480 mg, 0.48 mmol) and 1,2-bis(5′-hexyl-2,2′-bithiophen-5-yl)ethane-1,2-dione (320 mg, 0.58 mmol) were used. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (4:1) to yield pure **TaQ2** as a black amorphous solid (287 mg, 51% overall). ^{1}H NMR ($CDCl_3$): δ [ppm] 0.92 (m, 12 H), 1.35 (m, 52 H), 1.73 (quintet, 4 H, J = 7.6 Hz), 2.36 (m, 1 H), 2.84 (t, 4 H, J = 7.6 Hz), 4.78 (d, 2 H, J = 6.4 Hz), 6.74 (d, 2 H, J = 3.6 Hz), 7.04 (d, 2 H, J = 4.0 Hz), 7.18 (d, 2 H, J = 3.2 Hz), 7.27 (dd, 2 H, J = 1.2, 4.0), 7.50 (d, 2 H, J = 4.0 Hz), 7.66 (dd, 2 H, J = 0.8, 4.4), 8.87 (dd, 2 H, J = 1.2, 4.0). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.2, 14.3, 22.7, 22.8, 26.4, 28.9, 29.5, 29.79, 29.83, 30.1, 30.4, 31.70, 31.72, 32.1, 39.2, 60.7, 118.8, 123.2, 124.6, 125.1, 126.6, 130.6, 131.8, 131.9, 132.7, 134.6, 135.8, 139.9, 142.3, 142.6, 144.1, 146.6. Anal. Calcd for $C_{68}H_{89}N_5S_6$: C, 69.87; H, 7.67; N, 5.99; S, 16.46. Found: C, 69.98; H, 7.90; N, 5.67; S, 16.45. MALDI-TOF-MS m/z: 1165.13; calcd for $C_{68}H_{89}N_5S_6$ = 1168.86.

H-ImBTa. **BBTa16** (0.82 g, 0.82 mmol) and zinc powder (2.15 g, 32.88 mmol) in 40 mL of acetic acid and 20 mL of THF were heated at 60 °C for 1 day. Ten milliliters of formic acid was added on the second day, and the reaction was heated to 80 °C for another 1 day. Water and dichloromethane was added to the reaction mixture, and the organic layer was washed thoroughly with water. The organic layer was dried over anhydrous magnesium sulfate, and solvent was removed. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (1:1) to yield pure **H-ImBTa** as a yellow amorphous solid (50% yield).^{1}H NMR ($CDCl_3$): δ [ppm] 0.90 (m, 12 H), 1.27 (m, 80 H), 1.63 (m, 1 H), 2.32 (m, 1 H), 3.93 (d, 2 H, J = 7.6 Hz), 4.72 (d, 2 H, J = 6.8), 7.20 (m, 2H), 7.28 (dd, 1 H, J = 1.2 Hz, 4.0 Hz), 7.53 (m, 2 H), 8.00 (s, 1 H), 8.85 (d, 1 H, J = 2.8 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.2, 22.7, 22,8, 25.3, 25.7, 26.3, 29.4, 29.5, 29.6, 29.66, 29.69, 29.71, 29.74, 29.76, 29.95, 30.02, 30.5, 31.5, 31.7, 32.00, 32.03, 34.7, 38.0, 39.2, 51.5, 60.3, 103.0, 113.8, 126.8, 127.0, 127.2, 127.7, 129.7, 130.1, 133.3, 134.7, 136.7, 138.7, 141.6, 143.6, 149.2. Anal. Calcd for $C_{63}H_{105}N_5S_2$: C, 75.92; H, 10.62; N, 7.03; S, 6.43. Found: C, 76.05; H, 10.67; N, 7.11; S, 6.17. MALDI-TOF-MS m/z: 996.20; calcd for $C_{63}H_{105}N_5S_2$ = 996.67.

CF3-ImBTa. The synthetic procedures were exactly the same as **H-ImBTa**. **BBTa16** (0.62 g, 0.62 mmol) and trifluoroacetic acid (7.5 mL) were used. Column chromatography was carried out on silica using hexane to hexane/dichloromethane (3:2) to yield pure **CF3-ImBTa** as a yellow liquid (23% yield). ^{1}H NMR ($CDCl_3$): δ [ppm] 0.89 (m, 12 H), 1.26 (m, 80 H), 1.57 (m, 1 H), 2.32 (m, 1 H), 4.19 (d, 2 H, J = 7.2 Hz), 4.75 (d, 2 H, J = 6.8), 7.25 (m, 2H), 7.29 (dd, 1 H, J = 1.2 Hz, 4.0 Hz), 7.58 (m, 2 H), 8.88 (dd, 1 H, J = 1.2, 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.8, 26,0, 26.4, 29.45, 29.50, 29.64, 29.70, 29.76, 29.79, 29.81, 29.83, 29.84, 30.5, 31.6, 32.04, 32.07, 37.8, 39.2, 51.1, 60.6, 104.5, 115.9, 119.0 (quartet, CF_3, J = 272.3 Hz), 126.9, 127.3, 127.7, 129.0, 130.2, 131.1, 134.3, 134.4, 136.1, 138.5, 139.0, 144.4, 146.04 (quartet, C-2, J = 37.6 Hz). Anal. Calcd for $C_{64}H_{104}F_3N_5S_2$: C, 72.20; H, 9.85; F, 5.35; N, 6.58; S, 6.02. Found: C, 72.13; H, 9.99; N, 6.21; S, 6.17. MALDI-TOF-MS m/z: 1063.33; calcd for $C_{64}H_{104}F_3N_5S$ = 1064.67.

General Procedures for NBS Bromination. A 0.5 g portion of the annelated benzotriazole monomer was dissolved in 40 mL of chloroform (20 mL chloroform + 20 mL acetic acid for **6b** and **6g**), and the reaction setup was filled with N_2 and cooled in an ice bath. Two equivalents of NBS was dissolved in 100 mL of chloroform and was added dropwise. After the addition of NBS, the reaction mixture was allowed to warm to room temperature and stirred overnight.

dx.doi.org/10.1021/jo301281d | J. Org. Chem. 2012, 77, 10035−10041

Dilute aqueous sodium thiosulphate solution was added and stirred well. The organic layer was collected, washed with deionized water, and dried over anhydrous magnesium sulfate. Solvent was removed from the filtrate, and column chromatography was performed using gradient elution from pure hexane to hexane/DCM mixture (15% DCM for **7a**, **7c** and **7d**, 20% DCM for **7b**, **7e** and **7f**, and 30% DCM for **7g**).

7a: 85% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.89 (m, 12 H), 1.25−1.44 (m, 80 H), 2.31 (m, 2 H), 4.75 (d, 4 H, J = 6.0), 7.19 (d, 2H, J = 4.0 Hz), 8.35 (br, 2 H). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.9, 26.5, 29.5, 29.8, 29.9, 30.1, 31.7, 32.1, 39.4, 60.7, 108.9, 116.2, 129.8, 130.5, 139.0, 140.6. Anal. Calcd for $C_{62}H_{102}Br_2N_6S_2$: C, 64.45; H, 8.90; Br, 13.83; N, 7.27; S, 5.55. Found: C, 64.37; H, 8.99; N, 7.36; S, 5.42. MALDI-TOF-MS m/z: 1152.24 (M^+); calcd for $C_{62}H_{102}Br_2N_6S_2$ = 1155.45.

7b: 91% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.88 (m, 12 H), 1.08−1.38 (m, 80 H), 1.57 (m, 1 H), 2.31 (m, 1 H), 4.53 (d, 2 H, J = 7.6 Hz), 4.75 (d, 2 H, J = 6.4), 7.01 (d, 1 H, J = 3.6 Hz), 7.20−7.23 (m, 2 H), 8.69 (d, 1 H, J = 4.4 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.79, 22.84, 26.0, 26.3, 29.48, 29.51, 29.6, 29.75, 29.76, 29.79, 29.81, 30.0, 30.1, 30.9, 31.6, 32.1, 38.5, 39.3, 54.4, 61.0, 100.5, 114.2, 114.7, 118.2, 130.0, 130.3, 130.7, 131.2, 132.3, 135.4, 137.3, 138.6, 142.5, 145.3. Anal. Calcd for $C_{62}H_{102}Br_2N_6S_2$: C, 64.45; H, 8.90; Br, 13.83; N, 7.27; S, 5.55. Found: C, 64.33; H, 9.01; N, 7.33; S, 5.43. MALDI-TOF-MS m/z: 1154.03 (M^+); calcd for $C_{62}H_{102}Br_2N_6S_2$ = 1155.45.

7c: 82% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.88 (m, 6 H), 1.23−1.40 (m, 40 H), 2.27 (m, 1 H), 4.66 (d, 2 H, J = 6.4), 7.10 (d, 2H, J = 4.0 Hz), 8.26 (d, 2 H, J = 3.2 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.9, 26.4, 29.5, 29.8, 29.9, 30.1, 31.7, 32.1, 39.4, 61.2, 110.8, 117.8, 130.5, 131.1, 138.7, 141.8, 149.0. Anal. Calcd for $C_{38}H_{53}Br_2N_5S_3$: C, 54.60; H, 6.39; Br, 19.12; N, 8.38; S, 11.51. Found: C, 54.49; H, 6.45; N, 8.43; S, 11.53. MALDI-TOF-MS m/z: 836.83 (M^+); calcd for $C_{38}H_{53}Br_2N_5S_3$ = 835.86.

7d: 88% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.88 (m, 6 H), 1.23−1.38 (m, 40 H), 2.24 (m, 1 H), 4.58 (d, 2 H, J = 6.4), 7.09 (d, 2H, J = 4.0 Hz), 8.23 (d, 2 H, J = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.3, 22.8, 26.4, 29.5, 29.8, 29.9, 30.1, 31.6, 32.1, 39.3, 61.3, 110.9, 118.5, 130.3, 131.2, 139.3, 142.4, 154.9. Anal. Calcd for $C_{38}H_{53}Br_2N_5S_2Se$: C, 51.70; H, 6.05; Br, 18.10; N, 7.93; S, 7.26; Se, 8.94. Found: C, 51.55; H, 6.16; N, 8.03; S, 7.33. MALDI-TOF-MS m/z: 884.77 (M^+); calcd for $C_{38}H_{53}Br_2N_5S_2Se$ = 882.76.

7e: 95% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.90 (m, 6 H), 1.04 (t, 6 H, 7.2 Hz), 1.23−1.30 (m, 40 H), 1.56 (sextet, 4 H, J = 7.2 Hz), 1.84 (quintet, 4 H, J = 6.8 Hz), 2.19 (m, 1 H), 4.04 (t, 4 H, J = 6.4 Hz), 4.54 (d, 2 H, J = 7.0), 7.01 (d, 4 H, J = 8.4 Hz), 7.13 (d, 2H, J = 4.0 Hz), 7.64 (m, 8 H), 7.76, (d, 4 H, J = 8.0 Hz), 8.51 (d, 2 H, J = 4.4 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.1, 14.3, 19.4, 22.9, 26.3, 29.5, 29.77, 29.81, 29.83, 29.86, 30.1, 31.5, 31.6, 32.1, 39.2, 60.6, 67.9, 115.0, 118.3, 119.5, 126.2, 128.3, 129.4, 131.6, 131.8, 132.5, 132.6, 136.3, 137.3, 141.2, 141.5, 151.6, 159.2. Anal. Calcd for $C_{72}H_{87}Br_2N_5O_2S_2$: C, 67.64; H, 6.86; Br, 12.50; N, 5.48; O, 2.50; S, 5.02. Found: C, 67.53; H, 6.91; N, 5.50; S, 5.20. MALDI-TOF-MS m/z: 1279.70 (M^+); calcd for $C_{72}H_{87}Br_2N_5O_2S_2$ = 1278.43.

7f: 93% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.90 (t, 6 H, J = 6.8 Hz), 0.95 (t, 6 H, 6.4 Hz), 1.22−1.45 (m, 52 H), 1.75 (quintet, 4 H, J = 7.6 Hz), 2.17 (m, 1 H), 2.86 (t, 4 H, J = 7.6 Hz), 4.57 (d, 2 H, J = 6.4 Hz), 6.76 (d, 2 H, J = 3.2 Hz), 7.01 (d, 2 H, J = 4.0 Hz), 7.04 (d, 2 H, J = 4.4 Hz), 7.19 (d, 2H, J = 3.6 Hz), 7.41 (d, 2 H, J = 4.0 Hz), 8.38 (d, 2 H, J = 3.6 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.28, 14.30, 22.8, 22.9, 26.3, 29.0, 29.6, 29.82, 29.85, 29.89, 30.1, 30.4, 31.6, 31.7, 31.8, 32.1, 39.2, 60.5, 117.7, 119.2, 123.0, 124.7, 125.3, 129.2, 131.7, 131.9, 132.1, 134.7, 137.1, 139.4, 141.3, 142.8, 144.1, 146.7. Anal. Calcd for $C_{68}H_{87}Br_2N_5S_6$: C, 61.56; H, 6.61; Br, 12.05; N, 5.28; S, 14.50. Found: C, 61.44; H, 6.73; N, 5.64; S, 14.55. MALDI-TOF-MS m/z: 1327.58 (M^+); calcd for $C_{68}H_{87}Br_2N_5S_6$ = 1326.65.

7g: 95% yield. ^{1}H NMR ($CDCl_3$): δ [ppm] 0.90 (m, 12 H), 1.09−1.36 (m, 81 H), 2.28 (m, 1 H), 3.93 (d, 2 H, J = 7.2 Hz), 4.69 (d, 2 H, J = 6.4), 6.95 (d, 1 H, J = 3.6 Hz), 7.15 (d, 1 H, J = 3.6 Hz), 7.19 (d, 1 H, J = 4.0 Hz), 7.92 (s, 1 H), 8.56 (d, 1 H, J = 4.0 Hz). ^{13}C NMR ($CDCl_3$): δ [ppm] 14.2, 22.8, 25.8, 26.3, 29.4, 29.5, 29.6, 29.7, 29.75, 29.77, 29.98, 30.04, 30.7, 31.5, 32.0, 38.1, 39.2, 51.6, 61.2, 102.3, 113.2, 114.0, 116.0, 129.7, 129.9, 130.0, 130.4, 133.1, 136.2, 138.2, 138.3, 141.5, 143.3, 149.3. Anal. Calcd for $C_{63}H_{102}Br_2N_5S_2$: C, 65.54; H, 8.99; Br, 13.84; N, 6.07; S, 5.55. Found: C, 65.47; H, 9.01; N, 6.16; S, 5.49. MALDI-TOF-MS m/z: 1153.49 (M^+); calcd for $C_{63}H_{102}Br_2N_5S_2$ = 1154.46.

General Procedures for Suzuki Polymerization. A 0.4 g portion of the dibromo annelated benzotriazole monomer, 1 equiv of fluorene diboronic acid pinacol ester, and 8 mol % $Pd[PPh_3]_4$ in 20 mL of toluene and 20 mL of 2 M K_2CO_3 was added into a round-bottom flask purged with N_2. The reaction was allowed to stirred at 80 °C for 2 days. The reaction mixture was extracted using dichloromethane and deionized water, and the organic layer was collected and dried over anhydrous magnesium sulfate. The collected filtrate was concentrated and precipitated in methanol twice.

P1: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.80−0.86 (br, -CH_3), 1.13−1.63 (br, -CH_2), 2.11 (br, fluorene-CH_2), 2.48 (br, -CH), 4.96 (br, N-CH_2), 7.47−7.80 (br, Ar-H), 8.77 (br, Th-H). Anal. Calcd for $(C_{91}H_{144}N_6S_2)_n$: C, 78.84; H, 10.47; N, 6.06; S, 4.63. Found: C, 78.47; H, 10.40; N, 6.16; S, 4.62.

P2: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.80−0.87 (br, -CH_3), 1.07−1.39 (br, -CH_2), 1.73 (br, -CH), 2.09 (fluorene-CH_2), 2.42 (br, -CH), 4.70 (br, N-CH_2), 4.84 (br, N-CH_2), 7.51−7.85 (br, Ar-H), 9.00 (br, Th-H). Anal. Calcd for $(C_{91}H_{144}N_6S_2)_n$: C, 78.84; H, 10.47; N, 6.06; S, 4.63. Found: C, 78.45; H, 10.41; N, 6.20; S, 4.66.

P3: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.79 (br, -CH_3), 0.87 (br, -CH_3), 1.10−1.46 (br, -CH_2), 2.09 (br, fluorene-CH_2), 2.43 (br, -CH), 4.89 (br, N-CH_2), 7.12−7.77 (br, Ar-H), 8.58 (br, Ar-H), 8.88 (br, Th-H). Anal. Calcd for $(C_{67}H_{95}N_5S_3)_n$: C, 75.44; H, 8.98; N, 6.57; S, 9.02. Found: C, 75.27; H, 8.99; N, 6.61; S, 8.81.

P4: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.79 (br, -CH_3), 0.87(br, -CH_3), 1.09−1.39 (br, -CH_2), 2.07 (br, fluorene-CH_2), 2.42 (br, -CH), 4.84 (br, N-CH_2), 7.12−7.74 (br, Ar-H), 8.58 (br, Ar-H), 8.88 (br, Th-H). Anal. Calcd for $(C_{67}H_{95}N_5S_2Se)_n$: C, 72.26; H, 8.60; N, 6.29; S, 5.76; Se, 7.09. Found: C, 72.02; H, 8.52; N, 6.38; S, 5.55.

P5: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.74 (br, -CH_3), 0.86 (br, -CH_3), 1.00−1.42 (br, -CH_2), 1.81 (br, OCH_2-CH_2), 2.03(br, fluorene-CH_2), 2.37 (br, -CH), 4.02 (br, O-CH_2), 4.83 (br, N-CH_2), 7.00−8.00 (br, Ar-H), 8.74 (br, Ar-H), 9.00 (br, Th-H). Anal. Calcd for $(C_{101}H_{129}N_5O_2S_2)_n$: C, 80.38; H, 8.62; N, 4.64; O, 2.12; S, 4.25. Found: C, 80.09; H, 8.51; N, 4.74; S, 4.18.

P6: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.79−0.92 (br, -CH_3), 1.09−1.34 (br, -CH_2), 1.72 (br, $ArCH_2$-CH_2), 2.02 (br, fluorene-CH_2), 2.29 (br, -CH), 2.83 (Th-CH_2), 4.75 (br, N-CH_2), 6.75−7.94 (br, Ar-H), 8.58 (br, Ar-H), 8.90 (br, Th-H). Anal. Calcd for $(C_{97}H_{129}N_5S_6)_n$: C, 74.80; H, 8.35; N, 4.50; S, 12.35. Found: C, 74.67; H, 8.30; N, 4.61; S, 12.18.

P7: ^{1}H NMR ($CDCl_3$): δ [ppm] 0.79−0.88 (br, -CH_3), 1.09−1.24 (br, -CH_2), 1.63 (br, -CH), 2.04 (fluorene-CH_2), 2.31 (br, -CH), 4.00 (br, N-CH_2), 4.72 (br, N-CH_2), 6.97−8.08 (br, Ar-H), 8.56 (br, Ar-H), 8.84 (br, Th-H). Anal. Calcd for $(C_{92}H_{145}N_5S_2)_n$: C, 79.77; H, 10.55; N, 5.06; S, 4.63. Found: C, 79.67; H, 10.49; N, 5.19; S, 4.47.

■ ASSOCIATED CONTENT

Supporting Information

NMR and MALDI-TOF spectra of **6c−6g**, **CF3-ImBTa**, **7a−7g**, and **P1−P7**; CV plots for **P1−P7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Robert Bosch (SEA) Pte. Ltd.

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