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Synthesis and Electronic Properties of Oxidized Benzo[1,2-*b*:4,5-*b*′]dithiophenes

Ted M. Pappenfus,*[†] Daniel T. Seidenkranz,[†] Matthew D. Lovander,[†] Travis L. Beck,[†] Brandon J. Karels,[†] Katsu Ogawa,[‡] and Daron E. Janzen[§]

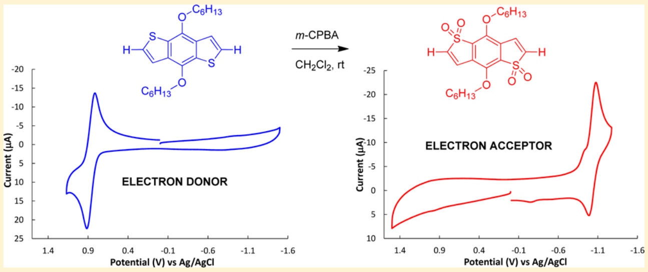
[†]Division of Science and Mathematics, University of Minnesota, Morris, Minnesota 56267, United States

[‡]Department of Chemistry and Biochemistry, California State University Northridge, Northridge, California 91330, United States

[§]Department of Chemistry and Biochemistry, St. Catherine University, St. Paul, Minnesota 55105, United States

Ⓢ *Supporting Information*

ABSTRACT: Benzo[1,2-*b*:4,5-*b*′]dithiophenes were oxidized under mild conditions with *m*-CPBA to yield the corresponding bis-sulfones (or tetraoxides). These sulfones possess red-shifted absorption and emission spectra relative to the parent molecules. Electrochemical analyses reveal that the benzodithiophene molecules are transformed from electron donors to electron acceptors.

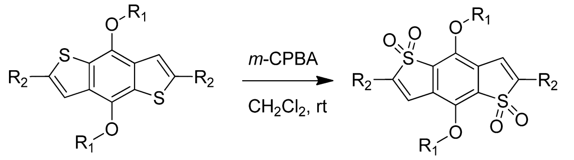


Benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT)-based materials have emerged as leading candidates for a number of organic electronic applications.[1] Initially, these building blocks were used as active materials in organic field effect transistors (OFETs), including devices with small molecules[2] or polymers.[3] In recent years, BDTs have emerged as prominent building blocks in small molecule[4] and polymeric[5] materials for use as donor materials in organic photovoltaic (OPV) devices. Of particular note is the fact that power conversion efficiencies have exceeded 8% when benzodithiophene-based materials have been used in the active layer of bulk heterojunction (BHJ) solar cells for *both* small molecule[4a] and polymeric[5a] donors.

Although benzodithiophenes are viewed as electron donors, with an appropriate chemical modification, it is conceivable one could transform this class of materials into an electron acceptor. The pioneering works of Barbarella,[6] Rozen,[7] and their respective co-workers have achieved this goal in oligothiophene-based materials. Their research has shown that oxidation of sulfur atoms in oligothiophenes to form sulfones (or *S*,*S*-dioxides) provides materials with enhanced electron affinity and reduced HOMO−LUMO gaps. This chemistry has also been applied to fused-ring heterocycles including the oxidation of thienothiophenes,[8] and thienopyrroles.[9] Most recently, during the preparation of our manuscript, Mohanakrishnan and co-workers reported the oxidation of benzodithiophenes with H_2O_2.[10] To further investigate the rich chemistry of benzo[1,2-*b*:4,5-*b*′]dithiophenes, we now report the preparation and physical properties of fully oxidized benzo[1,2-*b*:4,5-*b*′]-dithiophenes.

While the powerful oxygen-transfer agent $HOF{\cdot}CH_3CN$ has shown exceptional performance in oxidizing oligothiophenes and related heterocycles,[11] in this study, we chose to use *m*-CPBA due to its convenient availability/use and because of our past experience with this reagent in forming thiophene-based sulfones.[12] Scheme 1 outlines the oxidation of alkoxy-substituted BDTs using *m*-CPBA. Whereas the yields for molecules **2** and **2a** are expectedly similar, compound **4** formed in reduced yield. This is most likely due to the presence of bromine atoms in **3** that suppress the reactivity of its sulfur atoms with the electrophilic oxygen of *m*-CPBA. Furthermore, according to our observations, the reduced yield of this reaction is not due to unreacted starting material but rather to the presence of additional products (not isolated), one of which was less polar than **4** and may suggest the presence of a monosulfone. Additional experiments (e.g., changing oxidant stoichiometry and/or reaction temperatures) to improve the conversion of these intermediates or to prepare monosulfones were not performed, however.

Scheme 1. Oxidation of Benzo[1,2-*b*:4,5-*b*′]dithiophenes



1 R_1 = *n*-hexyl; R_2 = H
1a R_1 = 2-ethylhexyl; R_2 = H
3 R_1 = 2-ethylhexyl; R_2 = Br

2 R_1 = *n*-hexyl; R_2 = H (57%)
2a R_1 = 2-ethylhexyl; R_2 = H (60%)
4 R_1 = 2-ethylhexyl; R_2 = Br (35%)

The formation of the bis-sulfones (or tetraoxides) was confirmed with mass spectral data, single-crystal X-ray structures, and combustion analyses. NMR data (^1H and ^{13}C)

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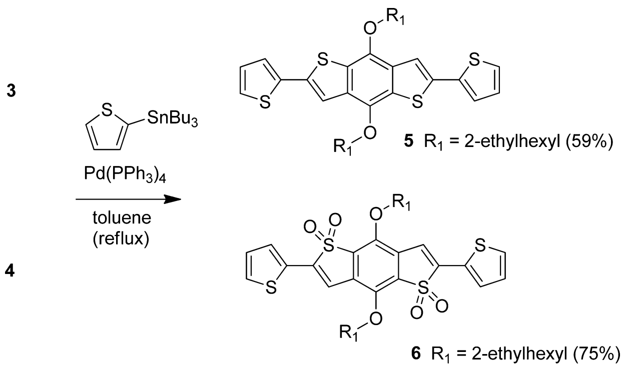
are also consistent with the symmetric structures. Crystallographic analyses of **2** and **2a** reveal layered structures for each with no π-stacking, whereas **4** exhibits a herringbone-type structure with no π-stacking but with a notable $\pi-\pi$ interaction (see the Supporting Information for details).

One approach in the design of conjugated organic materials is to combine the stability of the thiophene ring with the planarity of fused-ring systems, such as dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) and dithieno[3,2-*b*:2′,3′-*d*]pyrrole (DTP),[13] which results in materials with improved carrier mobilities and photophysical properties. Along these lines, we have prepared thiophene-capped conjugated oligomers with and without oxidized BDT cores (Scheme 2). Oligomers **5** and **6** were prepared in good yield using conventional Stille coupling methods and were characterized with NMR (^{1}H and ^{13}C), mass spectroscopy, and combustion analysis.

Scheme 2. Synthesis of Thiophene-Capped Oligomers 5 and 6



UV−vis absorption, emission, and cyclic voltammetry data of the BDT-based molecules are summarized in Table 1. Consistent with previously reported oligothiophene and related sulfones,[6−9,11,12] red shifts in both the absorption and emission bands are observed upon oxidation. Although both the HOMOs and the LUMOs are stabilized upon oxidation of one or more sulfur atoms in these conjugated systems, the extent of stabilization is consistently more (~50%) for the LUMO than the HOMO, which helps account for the red shift.[14,15] Table S1 (Supporting Information) provides energy gap data and redox potentials for all compounds to illustrate this point. The electronic spectra were also recorded in a variety of solvents, and small solvent shifts are observed (average shift of 5 nm for the eight molecules), presumably due to the symmetrical fused structure of the BDT core (complete electronic data and spectra can be found in the Supporting Information). For the BDT molecules **1**−**4**, quantum efficiencies decrease upon oxidation. The opposite is observed, however, for oligomers **5** and **6** where the quantum efficiency is more than 150% higher for **6** than **5**. This feature suggests that oxidized BDTs may be useful building blocks in materials for applications in devices such as organic light-emitting diodes where oxidized oligothiophenes have already shown promising performance.[16]

The redox properties of all oligomers were investigated by cyclic voltammetry. Unoxidized BDTs **1**, **1a**, and **3** exhibit a quasi-reversible oxidation, followed by a second irreversible oxidation, whereas oxidized BDTs **2**, **2a**, and **4** exhibit a quasi-reversible reduction, followed by a second irreversible reduction. These features are shown in Figure 1 for compounds **1** and **2**. In short, the BDTs are transformed from electron-rich to electron-deficient materials upon oxidation. Similar results are seen for the extended oligomers where two quasi-reversible oxidations or reductions are observed for **5** and **6**, respectively (Figures S30−S31, Supporting Information). The electrochemical results reported here are consistent with the recent work of Jung et al.[17] that suggests that oxidized BDTs are very good electron acceptors, falling somewhere between the well-studied building blocks benzothiadiazole (BT) and naphthalene/perylene diimides.

In conclusion, benzodithiophenes were reacted under mild conditions to form fully oxidized bis-sulfones (or tetraoxides). Thiophene-capped oligomers have also been prepared, which demonstrates the utility of these molecules in the preparation of both small molecule and polymeric systems. All oxidized BDT molecules exhibit red-shifted electronic spectra and increased electron affinities. These features suggest that oxidized BDTs are promising building blocks for use in organic electronic materials.

■ EXPERIMENTAL SECTION

Materials and Methods. All syntheses were performed under an inert nitrogen atmosphere. 4,8-Bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene **1a**, $Pd(PPh_3)_4$, 2-(tributylstannyl)thiophene, and *m*-CPBA were purchased from chemical suppliers and used as received. Compounds **1**[18] and **3**[19] were prepared as previously reported. NMR spectra were recorded on 300 or 400 MHz instruments. The chemical shifts are reported in parts per million (ppm) and referenced to the residual chloroform peak (7.26 or 77.2 ppm). Mass spectra were obtained on an EI mass spectrometer using a direct insertion probe. X-ray crystallographic data were obtained on a benchtop single-crystal diffractometer using methods described previously.[20]

Table 1. Spectroscopic and Electrochemical Data

molecule	Abs_{Max}, nm^{a,b}	ε, M^{-1} cm^{-1}	Em_{max}, nm^{c}	Φ_{Em}, %	E°_{ox}, V^{d}	E°_{red}, V^{d}
1	351	11 700	385	12	0.86, 1.33^f	^{h}
1a	351	13 300	384	12	0.86, 1.35^f	^{h}
2	388	8300	454	1.5	^{g}	−1.04, −1.47^i
2a	389	7200	451	1.7	^{g}	−1.06, −1.53^i
3	355	15 000	^{e}	^{e}	1.04, 1.43^f	^{h}
4	408	11 200	475	2.4	^{g}	−0.89, −1.39^i
5	413	28 100	467	13	0.85, 1.18	^{h}
6	466	30 200	538	33	1.61^f	−0.95, −1.38

[a] Measured in THF. [b] Lowest energy absorption peak. [c] Measured in THF. [d] Potentials vs Ag/AgCl in 0.1 M $TBAPF_6/CH_2Cl_2$ solution. [e] No observable emission. [f] Irreversible process; E_{pa} value provided. [g] No observable oxidation processes. [h] No observable reduction processes. [i] Irreversible process; E_{pc} value provided.

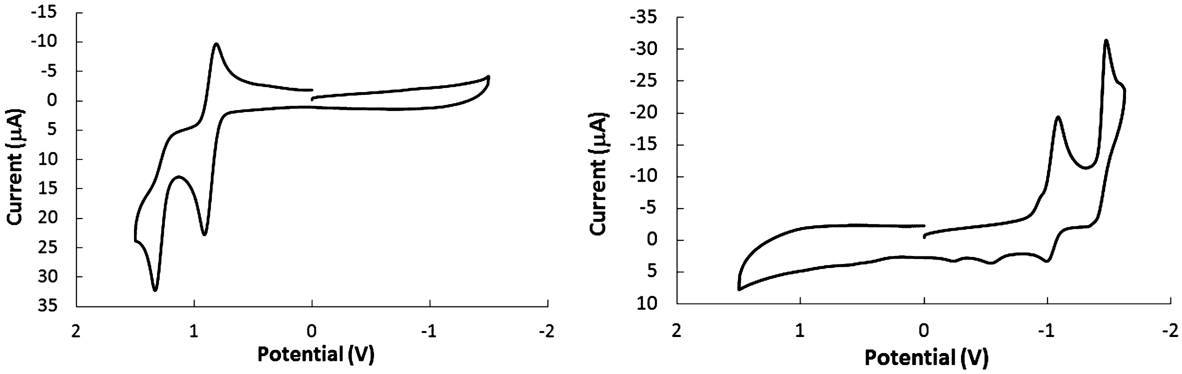


Figure 1. Cyclic voltammograms for **1** (left) and **2** (right) in 0.1 M $TBAPF_6/CH_2Cl_2$ solutions at a carbon electrode; ν = 100 mV/s.

Synthesis of 4,8-Bis(hexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-textraoxide (2). To a 50 mL round-bottom flask equipped with a magnetic stir bar was added **1** (0.437 g, 1.12 mmol) and dichloromethane (15 mL). Three portions of *m*-CPBA (0.500 g, 77% max, 2.23 mmol) were added over a 30 min period in 10 min increments (6.69 mmol total *m*-CPBA added). The reaction vessel was covered in foil to prevent light exposure and stirred for 21 h. The reaction mixture was quenched using 5 mL of $NaHCO_3$ (aq, sat). The organic layer was washed 3× with $NaHCO_3$ (aq, sat) and dried with $MgSO_4$. After filtering, the product was concentrated under vacuum, producing a light yellow oil that solidified upon standing. The crude product was dissolved in acetone, adsorbed onto silica gel, and purified via column chromatography using 75% CH_2Cl_2 in hexanes. The compound was further purified by dissolving in CH_2Cl_2/ethanol and subsequent rotary evaporation until the formation of a suspension. The product was filtered and washed with cold ethanol to provide 0.291 g (57%) of **2** as a light yellow solid. We obtained identical analytical data as given in ref 10. Combustion analysis data are provided here for evidence of purity. Anal. Calcd for $C_{22}H_{30}O_6S_2$: C, 58.12; H, 6.65. Found: C, 57.93; H, 6.56.

Synthesis of 4,8-Bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-tetraoxide (2a). To a 50 mL round-bottom flask equipped with a stir bar was added **1a** (0.500 g, 1.11 mmol) and dichloromethane (15 mL). Three portions of *m*-CPBA (0.506 g, 77% max, 2.26 mmol) were added over a 30 min period in 10 min increments (6.77 mmol total *m*-CPBA added). The reaction vessel was covered in foil and stirred for 21 h. The reaction mixture was quenched with 10 mL of $NaHCO_3$ (aq, sat). The organic layer was washed 2× with $NaHCO_3$ (aq, sat) and dried using $MgSO_4$. After filtering, the product was concentrated under vacuum, producing a yellow solid. The crude product was dissolved in CH_2Cl_2, adsorbed onto silica gel, and purified via column chromatography using 50% CH_2Cl_2 in hexanes and increasing the polarity to 75% CH_2Cl_2 in hexanes after 300 mL was eluted. Further purification was obtained by dissolving the product in CH_2Cl_2/methanol and subjecting the solution to rotary evaporation until a precipitate formed. The suspension was then filtered and washed with cold methanol to yield 0.344 g (60%) of **2a** as a yellow solid (mp = 166–167 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, 2H, J = 6.9 Hz), 6.70 (d, 2H, J = 6.9 Hz), 4.36 (d, 4H, J = 5.4 Hz), 1.79 (m, 2H), 1.61–1.26 (m, 16H), 1.0–0.87 (m, 12H). ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 145.2, 131.3, 130.8, 128.4, 127.3, 79.0, 40.5, 30.4, 29.1, 23.8, 23.2, 14.2, 11.3. EI-MS *m*/*z* (relative intensity) 510.22 (0.4), 301.96 (7.6), 287.97 (16.3), 286.97 (15.6), 285.95 (89.6), 256.96 (17.3), 113.14 (15.4), 112.13 (100.0). Anal. Calcd for $C_{26}H_{38}O_6S_2$: C, 61.15; H, 7.50. Found: C, 60.86; H, 7.48.

Synthesis of 2,6-Dibromo-4,8-bis(2-ethylhexyloxy)benzo-[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-tetraoxide (4). To a 100 mL two-neck round-bottom flask equipped with a stir bar was added **3** (1.005 g, 1.66 mmol) and dichloromethane (30 mL). Three portions of *m*-CPBA (0.746 g, 77% max, 3.33 mmol) were added over a 30 min period in 10 min increments (9.99 mmol total *m*-CPBA added). The reaction vessel was covered in foil and stirred for 23 h. The reaction mixture was quenched with 15 mL of $NaHCO_3$ (aq, sat), and the organic layer was washed 2× with $NaHCO_3$ (aq, sat) and dried with $MgSO_4$. After filtering, the product was concentrated via rotary evaporation to produce an off-orange solid. The crude product was dissolved in CH_2Cl_2, adsorbed onto silica gel, and purified via column chromatography using 35% CH_2Cl_2 in hexanes and increasing the polarity to 50% CH_2Cl_2 in hexanes after 600 mL was eluted. Further purification was obtained by dissolving the material in CH_2Cl_2/ethanol and subsequent rotary evaporation until a precipitate formed. The suspension was then filtered and washed with cold ethanol to provide 0.384 g (35%) of **4** as a bright yellow solid (mp = 106–110 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 2H), 4.35 (d, 4H, J = 5.4 Hz), 1.81 (m,2H), 1.61–1.27 (m, 16H), 1.01–0.89 (m, 12H) ^{13}C NMR (75.6 MHz, $CDCl_3$) δ 144.9, 130.3, 127.6, 125.6, 122.7, 79.2, 40.4, 30.3, 29.1, 23.8, 23.1, 14.2, 11.2. EI-MS *m*/*z* (relative intensity) 668.13 (0.2), 666.08 (0.1), 445.80 (21.6), 443.80 (35.3), 441.81 (19.5), 411.82 (7.8), 365.89 (5.5), 336.89 (5.1), 334.90 (4.8), 112.16 (100.0). Anal. Calcd for $C_{26}H_{36}Br_2O_6S_2$: C, 46.71; H, 5.43; O, 14.36. Found: C, 46.68; H, 5.34; O, 14.27.

Synthesis of 2,6-Di-2-thienyl-4,8-bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b*′]dithiophene (5). To a 100 mL two-neck round-bottom flask equipped with a condenser was added **3** (0.497g, 0.822 mmol) and 2-(tributylstannyl)thiophene (0.921 g, 2.47 mmol). The apparatus was purged with N_2 for 10 min, followed by the addition of $Pd(PPh_3)_4$ (47 mg, 0.041 mmol) and toluene (15 mL). The resulting suspension was bubbled directly with N_2 via a Teflon needle for 15 min and then refluxed for 24 h. Once cool, the mixture was filtered over Celite to remove insoluble impurities. The filtrates were concentrated, and the resulting mixture was suspended and washed with ethanol (30 mL total). The resulting solid was purified via silica gel column chromatography using 100% CH_2Cl_2. Further purification was obtained by dissolving the material in CH_2Cl_2/ethanol and subsequent rotary evaporation until a precipitate was formed. The suspension was then filtered and washed with cold ethanol to provide 0.296 g (59%) of **5** as a yellow-orange solid (mp = 110–112 °C). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 2H), 7.33 (m, 4H), 7.08 (dd, 2H, J = 5.2, 3.6 Hz), 4.19 (d, 4H, J = 5.6 Hz), 1.84 (m, 2H), 1.78–1.37 (m, 16 H), 1.06 (t, 6H), 0.98 (t, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 144.3, 137.6, 136.7, 132.5, 129.4, 128.2, 125.8, 125.4, 116.2, 76.2, 40.8, 30.6, 29.40, 24.0, 23.4, 14.4, 11.5. EI-MS *m*/*z* (relative intensity) 610.27 (14.5), 498.11 (10.9), 387.96 (21.6), 386.99 (33.5), 385.98 (100.0), 384.96 (70.8), 383.96 (13.4), 192.97 (26.9), 126.99 (11.0). Anal. Calcd for $C_{34}H_{42}O_2S_4$: C, 66.84; H, 6.93. Found: C, 66.81; H, 6.88.

Synthesis of 2,6-Di-2-thienyl-4,8-bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-tetraoxide (6). To a 50 mL two-neck round-bottom flask equipped with a condenser was added **4** (0.130 g, 0.194 mmol) and 2-(tributylstannyl)thiophene (0.217 g, 0.581 mmol). The apparatus was purged with N_2 for 10 min, followed by the addition of $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol) and toluene (7.5 mL). The resulting suspension was bubbled directly with N_2 via a Teflon needle for 15 min and then refluxed for 24 h. Once cool, the mixture was concentrated via rotary evaporation. The resulting solid was purified via silica gel column chromatography using 100% CH_2Cl_2. Further purification was obtained by dissolving the material in CH_2Cl_2/ethanol and subsequent rotary evaporation until a precipitate formed. The suspension was then filtered and washed with cold ethanol to provide 0.099 g (75%) of **6** as a bright fluorescent orange solid (mp = 227−230 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, 2H, J = 3.8, 1.0 Hz), 7.52 (dd, 2H, J = 5.3, 1.0 Hz), 7.19 (s, 2H), 7.18 (dd, 2H, J = 5.3, 3.9 Hz), 4.40 (d, 4H, J = 5.4 Hz), 1.87 (m, 2H), 1.68−1.33 (m, 16 H), 1.02 (t, 6H), 0.94 (t, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 145.4, 137.9, 131.2, 129.2, 129.2, 129.0, 128.9, 127.7, 115.8, 79.2, 40.5, 30.4, 29.2, 23.8, 23.2, 14.3, 11.4. EI-MS m/z (relative intensity) 674.24 (2.6), 562.10 (3.4), 451.95 (12.4), 450.97 (14.6), 449.95 (62.6), 338.96 (9.4), 290.99 (6.6), 112.09 (11.4), 111.01 (100.0). Anal. Calcd for $C_{34}H_{42}O_6S_4$: C, 60.50; H, 6.27. Found: C, 60.71; H, 6.49.

Electrochemical Measurements. Room-temperature electrochemical measurements were performed with a potentiostat and cell stand in a three-electrode configuration with a glassy carbon working electrode (A = 0.07 cm^2), a platinum counter electrode, and a standard Ag|AgCl|KCl (1.0 M) reference electrode. A single compartment, low volume cell was used for all measurements. Tetrabutylammonium hexafluorophosphate electrolyte solution was added to the cell (5 mL, 0.1 M/CH_2Cl_2), and background cyclic voltammograms of the electrolyte solution were recorded prior to the addition of the sample. Suitable amounts of sample were added to create 0.5−1.0 mM solutions. The $E^{0\prime}$ values for the ferrocenium/ferrocene couple for concentrations similar to those used in this study were 0.43 V for dichloromethane solutions at a glassy carbon electrode. Anodic−cathodic peak separations were typically 80−90 mV for this redox couple.

Photophysical Measurements. All solvents used for photophysical measurements were spectroscopy grade and purchased from Fisher Scientific unless otherwise noted. Rhodamine B and 9,10-diphenylanthracene were purchased from Acros Organics. Compounds were dissolved in THF, and concentrations were adjusted by serial dilutions. Steady-state UV−visible absorption spectra were obtained on a dual beam absorption spectrometer using 1 cm quartz cells. Extinction coefficients were calculated using the least-square method based on five data points in the optical density range of 0.1−1.0. Steady-state emission spectra were recorded on a fluorescence spectrometer. Prior to the measurements, THF solutions of the compounds were purged with nitrogen gas for 30 min. Excitation wavelengths for the emission experiments were as follows: **1** and **1a** (330 nm); **2**−**5** (370 nm); and **6** (460 nm). Fluorescence quantum yields of compounds **1**−**5** were determined by the relative actinometry method using 9,10-diphenylanthracene in hexane (Φ_f = 0.90)[21] as the standard, and that of compound **6** was determined using fluorescein in 0.1 N NaOH (aq) (Φ_f = 0.94)[22] as the standard.

X-ray Crystallographic Data for 4,8-Bis(hexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-textraoxide (2). $C_{22}H_{30}O_6S_2$, F.W. = 454.60, triclinic, space group $P\bar{1}$, a = 5.7152(9) Å, b = 10.217(2) Å, c = 11.026(2) Å; α = 63.897(5)°, β = 84.349(6)°, γ = 77.260(5)°; V = 563.9(2) Å^3, Z = 1, D = 1.338 g/cm^3, T = 223 K, 5726 reflections collected and 2586 unique (R_{int} = 0.0264), $F(000)$ = 242.00, μ(MoKα) = 2.712 cm^{-1}, 2θ_{max} = 55.0°, R1 (I > 2.00σ(I)) 0.0362, wR2 (all reflections) = 0.0990.

X-ray Crystallographic Data for 4,8-Bis(2-ethylhexyloxy)-benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-tetraoxide (2a). $C_{26}H_{38}O_6S_2$, F.W. = 510.70, triclinic, space group $P\bar{1}$, a = 5.6618(9) Å, b = 9.055(2) Å, c = 13.657(2) Å; α = 102.316(7)°, β = 90.782(6)°, γ = 96.640(7)°; V = 678.9(2) Å^3, Z = 1, D = 1.249 g/cm^3, T = 223 K, 6942 reflections collected and 3102 unique (R_{int} = 0.0323), $F(000)$ = 274.00, μ(MoKα) = 2.328 cm^{-1}, 2θ_{max} = 55.0°, R1 (I > 2.00σ(I)) = 0.0673, wR2 (all reflections) = 0.1936.

X-ray Crystallographic Data for 2,6-Dibromo-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene-1,1,5,5-tetraoxide (4). $C_{26}H_{36}Br_2O_6S_2$, F.W. = 668.49, monoclinic, space group $P2_1/c$, a = 8.014(2) Å, b = 25.471(5) Å, c = 7.401(2) Å; β = 99.659(7)°; V = 1489.4(5) Å^3, Z = 2, D = 1.491 g/cm^3, T = 223 K, 14 078 reflections collected and 3412 unique (R_{int} = 0.0599), $F(000)$ = 684.00, μ(MoKα) = 29.058 cm^{-1}, 2θ_{max} = 55.0°, R1 (I > 2.00σ(I)) = 0.0673, wR2 (all reflections) = 0.1428.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic files (CIF) for molecules **2**, **2a**, and **4** and crystallographic images; ^{1}H and ^{13}C NMR spectra of all new compounds; UV−vis absorption and emission spectra/data; and cyclic voltammograms of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pappe001@morris.umn.edu. Fax: 320-589-6371. Phone: 320-589-6340 (T.M.P.).

Notes

The authors declare no competing financial interest.

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