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ONE-POT SYNTHESES OF 4,8-DIALKYLBENZO[1,2-*b*:4,5-*b*′]-DITHIOPHENES

Ted M. Pappenfus,[1,*] Daniel T. Seidenkranz,[1] and Eric W. Reinheimer[2]

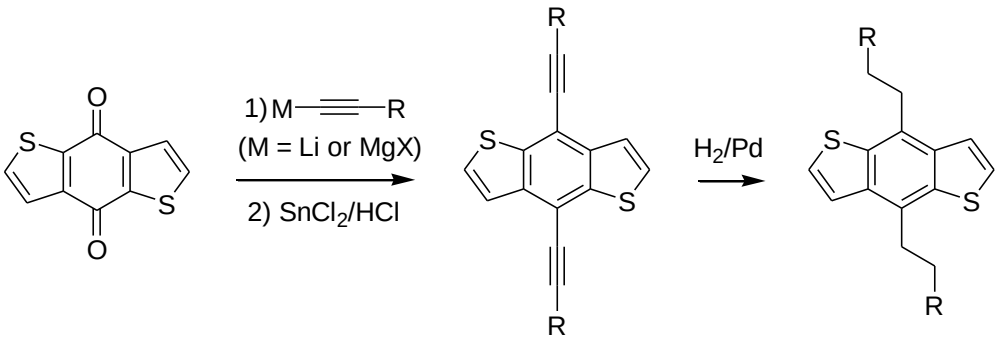
[1]Division of Science and Mathematics, University of Minnesota, Morris, Minnesota 56267, United States. [2]W.M. Keck Foundation Center for Molecular Structure, California State University System, United States. Email: pappe001@morris.umn.edu

Abstract – Two-step, one-pot syntheses are described for the preparation of 4,8-dialkylbenzo[1,2-*b*:4,5-*b*′]dithiophenes (BDTs) from alkyllithium or alkyl Grignard reagents. The yields for various alkyl groups used in this procedure are comparable with or exceed those of previously reported methods. The electronic and redox properties of dialkyl-BDTs are compared with the dialkoxy-BDT, 4,8-bis(hexyloxy)benzo[1,2-b:4,5-b']dithiophene. The stabilized HOMO levels of dialkyl-BDTs suggest they are promising building blocks for use in organic photovoltaics such as bulk heterojunction solar cells.

INTRODUCTION

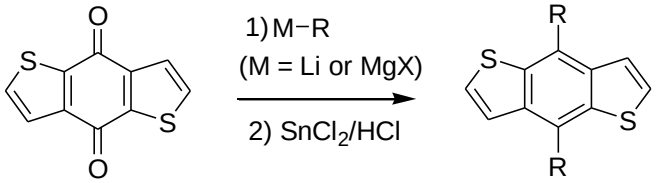
Recently, benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) based materials have emerged as leading candidates for a number of organic electronic applications including thin-film transistors[1] and organic solar cells.[2] The high performance in these devices has been attributed to (a) the planar structure of BDT which may lead to improved intermolecular interactions (i.e., π-π stacking) and (b) reduced steric hindrance between BDT and adjacent rings since substitution on the BDT generally occurs at the 4 and 8 positions.[2g] The replacement of alkoxy with alkyl in these building blocks will reduce the electron donating effect of the solubilizing group and has been shown to lower HOMO energy levels of the resulting polymers.[3] This is attractive for polymers in OPV bulk heterojunction devices as a low-lying HOMO energy level (relative to the acceptor material) can provide a larger open circuit voltage (V_{OC}) which assists in achieving maximum power conversion efficiency.[4] Our present work describes a one-pot synthetic strategy toward 4,8-dialkyl-BDTs from alkyllithium or alkyl Grignard reagents including reagents with branched alkyl chains for the preparation of more soluble building blocks.

Although synthetic strategies towards 4,8-dialkoxy-BDTs have been well established,[5] approaches toward 4,8-dialkyl-BDTs are less efficient. Current literature approaches toward 4,8-dialkyl-BDTs are outlined in Scheme 1.[6] This three step process begins with the addition of an alkynyllithium or alkynylmagnesium reagent to benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione followed by reduction with tin(II) chloride. This alkynyl intermediate is isolated and reduced with hydrogen gas.



Scheme 1. Previous approach for the preparation of 4,8-dialkyl-BDTs

We felt a more direct approach toward 4,8-dialkyl-BDTs would be to add the appropriate alkyllithium or alkyl Grignard reagent to the benzoquinone (followed by reduction with tin(II) chloride) in place of the alkynyl reagents to avoid the need for the subsequent hydrogen reduction step. Herein we describe the results of this alternative approach (Scheme 2) using a number of different alkyllithium reagents. Extension of this method to Grignard reagents has also been tested.[7]

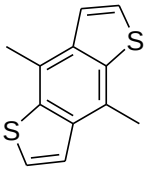
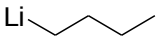
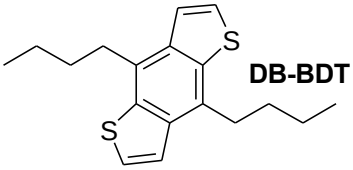
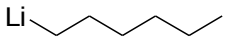
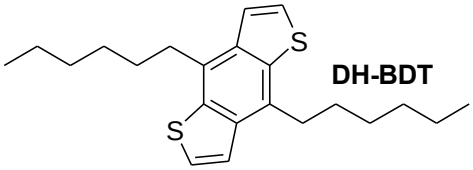
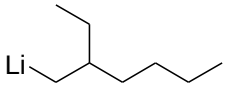
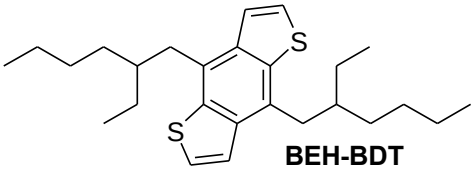
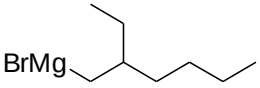
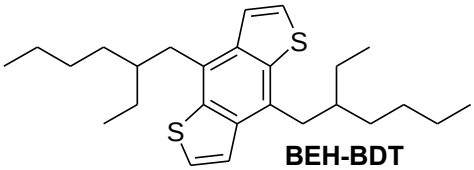
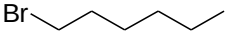
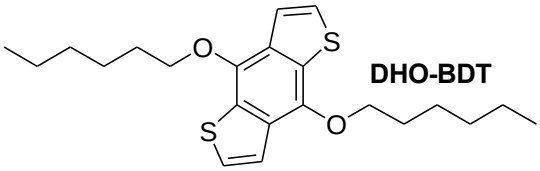


Scheme 2. Preparation of 4,8-dialkyl-BDTs in this investigation (Methods A and B)

RESULTS AND DISCUSSION

The results of our synthetic approach to 4,8-dialkyl-BDTs are summarized in Table 1. Our initial approach (Method A) involved the addition of excess alkyllithium (3.2 equiv) to commercially available benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (1.0 equiv) at room temperature under anhydrous conditions. After an additional hour of stirring at room temperature, the reaction is quenched with water, then tin(II) chloride (4.2 equiv) is added in the presence of aqueous HCl. This mixture is refluxed for three hours and is subjected to a normal workup and purification by silica gel column chromatography. We initially focused on *n*-alkyllithium reagents including methyllithium, *n*-butyllithium, and *n*-hexyllithium which provide 4,8-dialkyl-BDTs in low to modest yields (Table 1, Entries 1-3). As a comparison to our one-pot, two step procedure, the three step process outlined in Scheme 1 has reported overall yields of 40%.[1d]

Table 1. Synthetic outcomes for 4,8-dialkyl- and 4,8-dialkoxybenzo[1,2-*b*:4,5-*b*′]dithiophenes

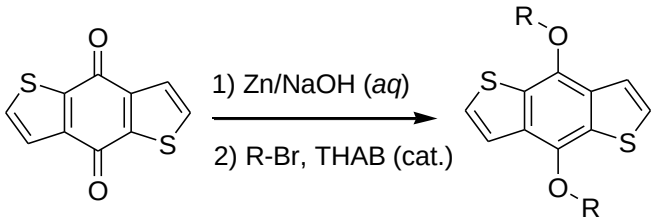
Entry	Alkyl Reagent	Product	Method (**A**, **B** or **C**): Yield (%)
1	Li—Me	 **DM-BDT**	**A**: 30
2		 **DB-BDT**	**A**: 42
3		 **DH-BDT**	**A**: 35 **B**: 45
4		 **BEH-BDT**	**A**: 21
5		 **BEH-BDT**	**A**: 15 **B**: 30
6		 **DHO-BDT**	**C**: 79

Method A conditions: (i) THF, R-Li or RMgX (3.2 equiv), rt, 1 h (ii) $SnCl_2$ (aq) (4.2 equiv), reflux, 3 h.
Method B conditions: (i) THF, R-Li or RMgX (3.2 equiv), reflux, 1 h (ii) $SnCl_2$ (aq) (4.2 equiv), reflux, 3 h.
Method C conditions: (i) H_2O, Zn (3 equiv), NaOH (1.9 equiv), reflux, 2 h. (ii) R-Br (3.0 equiv), tetrahexylammonium bromide (3%), reflux, 16 h.

Given the widespread use of branched alkyl groups to generate more soluble polymers,[2] we next investigated the use of 2-(ethylhexyl)lithium in our reaction procedure. The desired 4,8-dialkyl-BDT, **BEH-BDT**, was generated in even lower yield than the linear alkyllithium reagents (Table 1, Entry 4).

We then investigated extending our initial method to Grignard reagents – specifically using (2-ethylhexyl)magnesium bromide (Table 1, Entry 5). Unfortunately, even lower yields resulted using this particular organometallic reagent.

In an attempt to increase our reaction yields, we modified our initial procedure (Method A) by refluxing the reaction mixture in the 1 hour period after addition of the organometallic reagent (referred to as Method B). In the case of (2-ethylhexyl)magnesium bromide, reaction yields doubled as a result of this simple modification. Application of this method to alkyllithium reagents was tested with n-hexyllithium, which also resulted in an improved reaction yield (Table 1, Entry 3). The remaining alkyllitihium reagents were not subjected to Method B, but similar results are anticipated. We did, however, investigate the preparation of the 4,8-dialkoxy-BDT, **DHO-BDT**, using a slightly modified procedure from the literature (Scheme 3 and Table 1, Entry 6, Method C).[5a] This molecule also serves as a comparison for electronic and redox properties of this series of materials (vide infra).



Scheme 3. Preparation of 4,8-dihexyloxy-BDT in this investigation (Method C)

The structure and purity of the materials were confirmed with NMR, mass spectrometry, and/or combustion analysis. Although we have been unsuccessful in obtaining suitable crystals for many of these materials for single crystal X-ray analysis, we have been able to determine the X-ray structure of **DM-BDT**. The ORTEP plot of **DM-BDT** is shown in Figure 1. A crystallographic inversion center exists within the molecule. A search of the Cambridge Structural Database (CSD) found two structures with

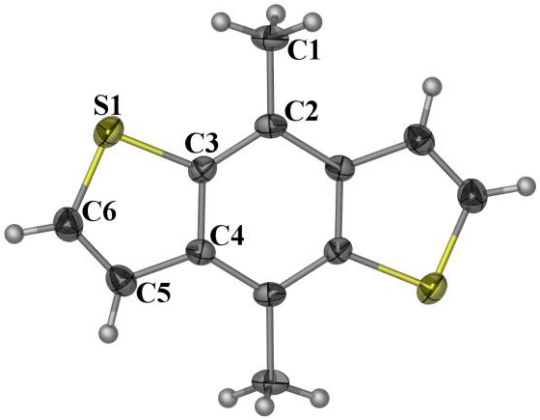


Figure 1. ORTEP diagram for **DM-BDT** (with arbitrary numbering)

substituents in the 4 and 8 positions of the benzodithiophene core,[1c,1d] including 4,8-didodecylbenzo[1,2-*b*:4,5-*b*′]dithiophene.[1d] Whereas the didodecyl-BDT molecule shows close face-to-face π-π stacking, **DM-BDT** does not (packing views of the molecule are found in the Supplementary Data). This demonstrates that the nature of the alkyl group clearly influences the crystal morphology in these materials.

Table 2. Spectroscopic and electrochemical data

molecule	λ_{abs} (nm)[a]	E^{o}_{ox}, V[b]
DM-BDT	346	1.21
DB-BDT	347	1.19
DH-BDT	347	1.18
BEH-BDT	348	1.17
DHO-BDT	352	0.86

[a]Lowest energy absorption maxima measured in CH_2Cl_2. [b]Potentials vs Ag/AgCl in 0.1 M $TBAPF_6/CH_2Cl_2$ solution determined from square-wave voltammograms similar to reference 8.

Solution absorption and electrochemical data of the molecules in this investigation are summarized in Table 2. The UV-Vis absorption spectra are rather complex and possess significant fine structure likely due to the planar structure of the molecules (spectra are provided in the Supplementary data). The lowest energy absorption maxima for the dialkyl-BDTs, as expected, are very similar and are all within 2 nm of each other. Upon alkoxy substitution (as with **DHO-BDT**) a slight redshift is observed as anticipated for the more electron-donating group (Figure 2).

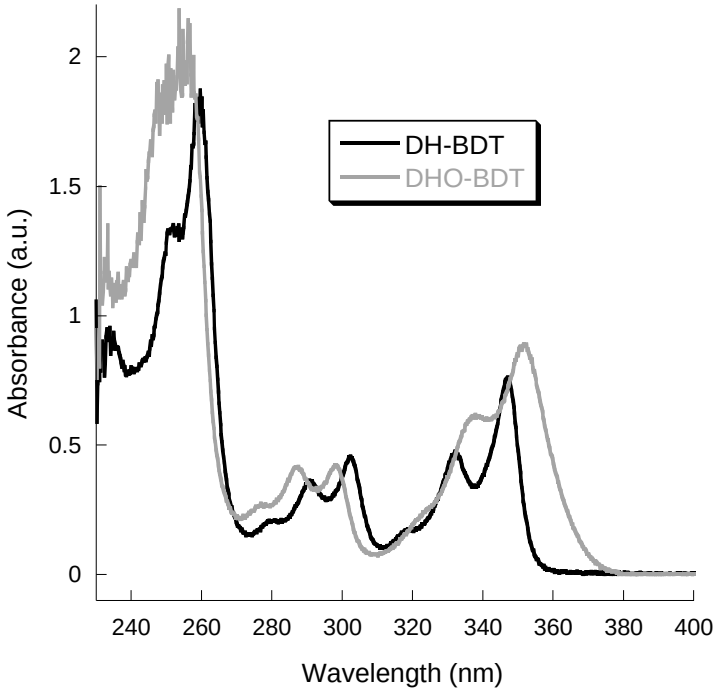


Figure 2. Solution absorption spectra for **DH-BDT** and **DHO-BDT** in dichloromethane

Similar trends are observed in the electrochemical data as the oxidation potentials of the dialkyl oligomers are within 0.04 V of each other. A representative cyclic voltammogram (CV) is presented in the Supplementary data and illustrates quasi-reversibility on the CV timescale. Noteworthy is the significant decrease in oxidation potential upon alkoxy substitution. Figure 3 includes square wave voltammograms of **DH-BDT** and **DHO-BDT** which have oxidation potentials of 1.18 and 0.86 V respectively. This increase in oxidation potential upon alkyl substitution is directly related to the stabilization of the HOMO level of **DH-BDT** relative to **DHO-BDT** and has important implications for utilizing these monomers in materials for OPV applications (vide supra).

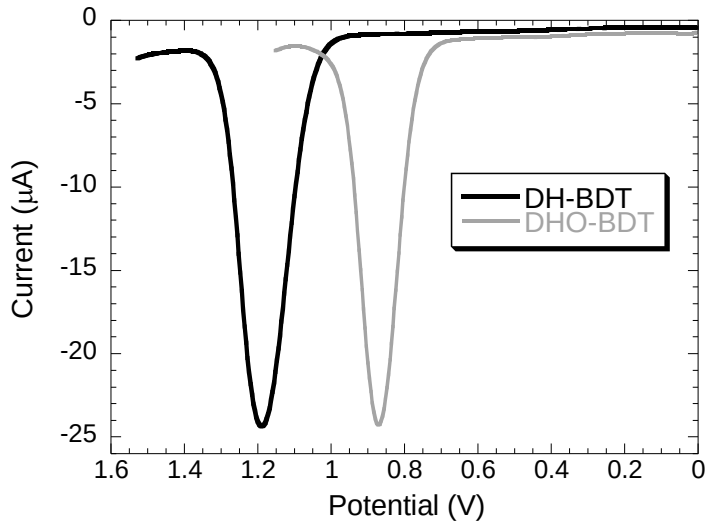


Figure 3. Osteryoung square wave voltammograms for **DH-BDT** and **DHO-BDT**

In summary, we have explored a more direct route for the preparation of 4,8-dialkyl-BDTs using a two step, one-pot procedure. The yields for various alkyl groups used in this procedure are comparable with or exceed the yields of previously reported methods. We have also prepared the 4,8-dialkoxy-BDT molecule, **DHO-BDT**, which is compared to the 4,8-dialkyl-BDTs using spectroscopic and electrochemical methods. The physical data suggests dialkyl substitution may have advantages over dialkoxy substitution for use of these molecules in materials applications such as organic photovoltaics.

EXPERIMENTAL

General Methods. Synthetic procedures were carried out under an inert atmosphere of nitrogen. Tetrahydrofuran was distilled from Na/benzophenone. Grignard and alkyllithium reagents were purchased from Aldrich and titrated prior to use in the reactions using a previously reported procedure.[9] Benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione was purchased from SunaTech Inc. and used as received. NMR spectra were recorded on a JEOL Eclipse 300 MHz instrument. The chemical shifts are reported in

ppm and referenced to the residual chloroform peak (7.26 or 77.1 ppm). Mass spectra were obtained on an Agilent 5973 MSD mass spectrometer and elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. UV-Vis absorption measurements were recorded on an Ocean Optics USB4000 fiber optic spectrometer and room temperature electrochemical measurements were performed with a BAS 100B electrochemical analyzer using methods previously described.[10] Details for the X-ray data collection of **DM-BDT** are found in the Supplementary data.

Typical procedure for the preparation of 4,8-dialkyl-BDTs (Method A). To a 250 mL two-neck flask with large stir bar was added benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (1.00 g, 4.54 mmol) and freshly distilled THF (30 mL). To this stirred suspension, a solution of the appropriate Grignard or alkyllithium reagent (14.5 mmol) was added dropwise over 10 min at room temperature. The mixture was stirred for an additional hour at room temperature and was then quenched with 1 mL water. $SnCl_2$ (4.30 g, 19.1 mmol) in 10 mL of 3M HCl was then added with stirring. The mixture was refluxed for 3 h, then cooled and 15 mL of brine followed by 45 mL of hexanes were added. The organic phase was separated and the aqueous phase was extracted once with hexanes. The organic phases were combined, dried with $MgSO_4$ and concentrated using rotary evaporation. Purification was performed by dissolving the crude material in acetone and adsorbing on silica gel. Column chromatography was performed with 100% hexanes followed by 5% EtOAc in hexanes.

Typical procedure for the preparation of 4,8-dialkyl-BDTs (Method B). To a 250 mL two-neck flask with large stir bar was added benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione (1.00 g, 4.54 mmol) and freshly distilled THF (30 mL). To this stirred suspension, a solution of the appropriate Grignard or alkyllithium reagent (14.5 mmol) was added dropwise over 10 min at room temperature. The mixture was stirred for an additional hour under reflux conditions, cooled down, and then quenched with 1 mL water. $SnCl_2$ (4.30 g, 19.1 mmol) in 10 mL of 3M HCl was then added with stirring. The mixture was refluxed for 3 h, then was cooled and 15 mL of brine followed by 45 mL of hexanes were added. The organic phase was separated and the aqueous phase was extracted once with hexanes. The organic phases were combined, dried with $MgSO_4$ and concentrated using rotary evaporation. Purification was performed by dissolving the crude material in acetone and adsorbing on silica gel. Column chromatography was performed with 100% hexanes followed by 5% EtOAc in hexanes.

Preparation of 4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*']dithiophene, DHO-BDT (Method C). To a 250 mL three-neck flask with large stir bar was added in the following order: benzo[1,2-*b*:4,5-*b*']-dithiophene-4,8-dione (1.00 g, 4.54 mmol), Zn dust (0.890 g, 13.6 mmol), 100 mL water, and NaOH (4 x 0.880 g, 8.80 mmol). After stirring the mixture for 2 h under reflux, 1-bromohexane (2.24 g, 13.6 mmol) and tetrahexylammonium bromide (0.059 g, 0.136 mmol) was added. After an additional 16 h reflux, the mixture was cooled and extracted with CH_2Cl_2 (3 x 30 mL). The organic layers were combined, dried

with $MgSO_4$ and concentrated via rotary evaporation. The compound was purified by dissolving in 10 mL CH_2Cl_2 and 10 mL EtOHl. This solution was subjected to rotary evaporation until the formation of a suspension. The product was filtered and washed with cold EtOH to provide 1.41 g (79%) of **DHO-BDT** as an off-white solid.

Analytical data for BDT molecules

4,8-dimethylbenzo[1,2-*b*:4,5-*b*′]dithiophene (DM-BDT).[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, 2H, *J* = 5.5 Hz), 7.47 (d, 2H, *J* = 5.5 Hz), 2.82 (s, 6H). ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 137.66, 136.15, 126.12, 123.60, 122.10, 18.15. EI-MS *m/z* (relative intensity) 218 (100), 203 (33), 184 (13), 171 (12). Anal. Calcd for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62. Found: C, 66.05; H, 4.65.

4,8-dibutylbenzo[1,2-*b*:4,5-*b*′]dithiophene (DB-BDT). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, 2H, *J* = 5.5 Hz), 7.45 (d, 2H, *J* = 5.8 Hz), 3.21 (t, 4H), 1.81 (m, 4H), 1.49 (m, 4H), 0.99 (t, 6H). ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 137.48, 135.99, 129.06, 125.94, 121.99, 33.34, 31.96, 23.19, 14.14. EI-MS *m/z* (relative intensity) 302 (60), 259 (100), 217 (14), 203 (16), 184 (11), 171 (8). Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33. Found: C, 71.60; H, 7.40.

4,8-dihexylbenzo[1,2-*b*:4,5-*b*′]dithiophene (DH-BDT).[1b] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 2H, *J* = 5.8 Hz), 7.45 (d, 2H, *J* = 5.5 Hz), 3.19 (t, 4H), 1.82 (m, 4H), 1.48 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H). ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 137.45, 135.97, 129.10, 125.95, 121.96, 33.63, 31.82, 29.78, 29.75, 22.74, 14.23. EI-MS *m/z* (relative intensity) 358 (98), 287 (100), 217 (18), 203 (16), 184 (9), 171 (6). Anal. Calcd for $C_{22}H_{30}S_2$: C, 73.68; H, 8.43. Found: C, 73.79; H, 8.61.

4,8-bis(2-ethylhexyl)benzo[1,2-*b*:4,5-*b*']dithiophene (BEH-BDT).[7b,7c] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47 (d, 2H, *J* = 5.8 Hz), 7.43 (d, 2H, *J* = 5.5 Hz), 3.13 (m, 4H), 1.98 (m, 2H), 1.45-1.19 (m, 16H), 0.96-0.82 (m, 12H). ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 138.19, 136.61, 128.50, 125.83, 122.31, 40.14, 38.28, 33.20, 29.03, 26.41, 23.21, 14.24, 11.21. EI-MS *m/z* (relative intensity) 414 (100), 315 (92), 217 (70), 203 (5), 184 (8), 171 (5). Anal. Calcd for $C_{26}H_{38}S_2$: C, 75.30; H, 9.24. Found: C, 75.58; H, 9.42.

4,8-bis(hexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene (DHO-BDT).[5a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, 2H, *J* = 5.5 Hz), 7.37 (d, 2H, *J* = 5.5 Hz), 4.28 (t, 4H), 1.87 (m, 4H), 1.58 (m, 4H), 1.37 (m, 8H), 0.93 (t, 6H). ^{13}C NMR (75.6 MHz, $CDCl_3$): δ 144.63, 131.72, 130.28, 126.10, 120.42, 74.08, 31.77, 30.61, 25.86, 22.77, 14.20. EI-MS *m/z* (relative intensity) 390 (43), 306 (8), 221 (100). Anal. Calcd for $C_{22}H_{30}O_2S_2$: C, 67.65; H, 7.74. Found: C, 67.81; H, 7.74.

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SUPPLEMENTARY DATA

Supplementary data associated with this article, including crystallographic data for **DM-BDT**,[12] can be found in the online version.

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12. CCDC file 832357 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.