Synthesis and Physical Properties of Decylbithiophene End-Capped Oligomers Based on Naphthalene, Anthracene and Benzo[1,2-b:4,5-b']dithiophene

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The new candidates for OTFTs, which were composed of naphthalene, anthracene, benzo[1,2-b:4,5-b']dithiophene and 2-decylbithiophene end-capper were synthesized under Suzuki coupling reaction conditions. All of the oligomers were characterized by FT-IR, mass analysis, UV-vis, PL spectrum, cyclic voltametry (CV), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), ^{1}H-NMR and ^{13}C-NMR. Investigation of physical properties showed that all of the oligomers have higher oxidation potential and good thermal stability. Especially, DBT-DtB-DBT is soluble in common solvents and suitable for low cost processing technologies.

Key Words: Suzuki coupling, Photoluminescence, Cyclic voltametry, Thermal gravimetric analysis, Differential scanning calorimetry

Introduction

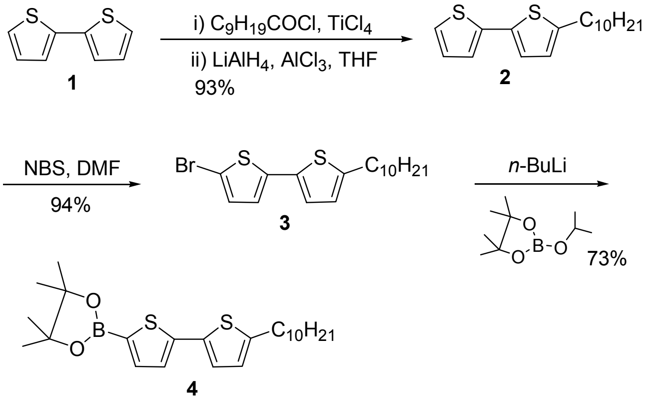
During the past decades, organic semiconducting materials have been interest of electronic industry due to their high potential applications as a low-cost alternative to silicon. A many kinds of conjugated oligomers and polymers were synthesized and investigated for their electrochemical property as new organic semiconductor candidates.[1-5] Among the most potential materials for organic semiconductor, thiophene and anthracene based oligomers have received special attentions due to their good electrochemical properties and thermal properties.[6-9] Recently, hybrid thiophene-phenylene oligomers were reported as good organic materials for OTFTs (organic thin film transistors).[10-12] Ponomarenko and co-worker also reported the synthesis and characterization of the bithiophene-phenylene-bithiophene conjugated cores, which have good oxidation and thermal stability as well as good characterizations for OTFTs.[13,14] As an example, the mobility of 1,4-bis(5-decyl-2,2-bithien-5-yl)benzene (Dec-2T-Ph-2T-Dec) is up to 0.3 cm^2/V.s. This result was explained due to the effect of the long decyl end group, which is leading improved molecular order. More recently, it was also reported that semiconducting materials based on naphthalene and anthracene core units exhibited excellent field effect performances with mobility as high as 0.14 cm^2/V.s and on/off ratio up to 6.3×10^6.[15]

In this paper, we report the synthesis of a new candidates for OTFTs, which were composed of core units such as naphthalene, anthracene and benzo[1,2-b:4,5-b']dithiophene and 2-decylbithiophene as an end-capper. And also we report the electrochemical properties of synthesized molecules.

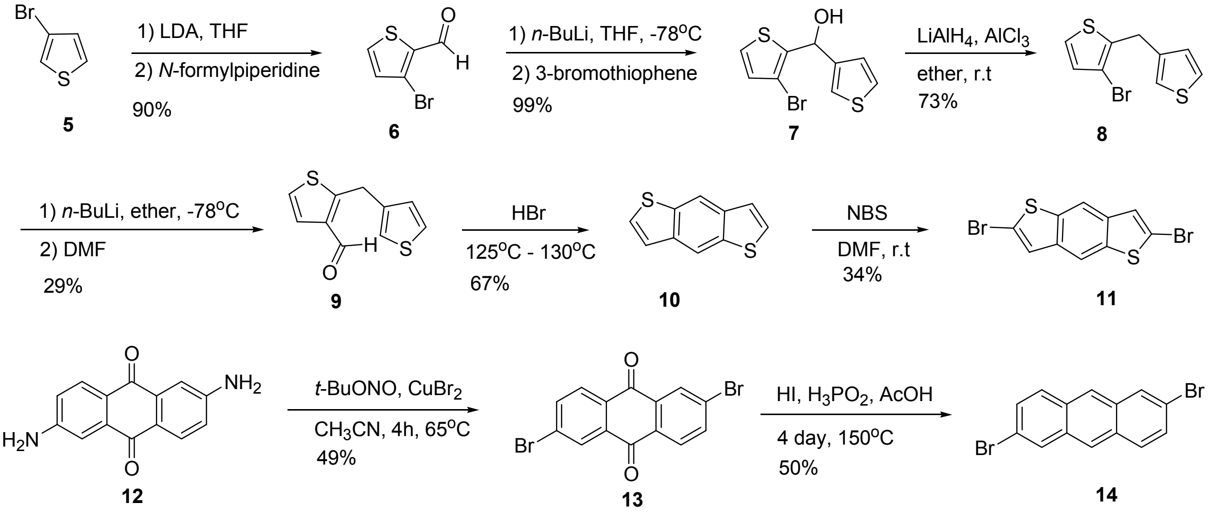
Results and Discussion

Synthesis. The synthetic strategy to the desired molecules is illustrated in Scheme 1, 2 and 3. Compound **4** was prepared from bithiophene **1** as starting material (Scheme 1). A starting material bithiophene **1** was prepared according to literature[16] and easily converted into 2-decylbithiophene **2**, which was brominated with NBS in DMF to give **3** in 94% yield. Compound **3** was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in the presence of n-BuLi to give **4** in 73% yield.

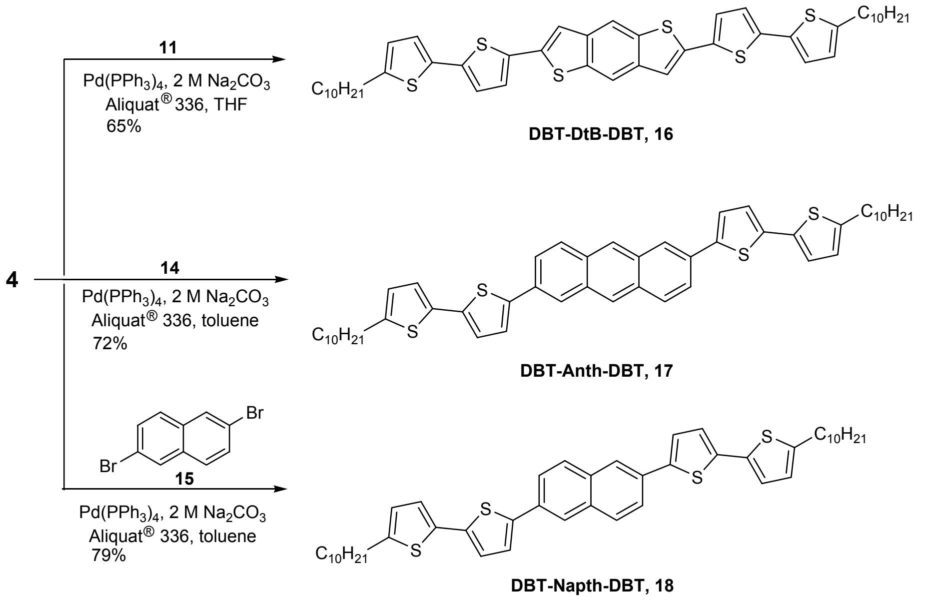
The preparation of 2,6-dibromobenzo[1,2-b:4,5-b']dithiophene **11**[17] and 2,9-dibromoanthracene **14**[18] were synthesized according to literature procedures, respectively (Scheme 2). The 2,6-dibromonaphthalene **15** was purchased from Alfa Aesar Co.



Scheme 1



Scheme 2



Scheme 3

The obtained **4** was used for coupling reaction with **11**, **14** and **15** in next step. The target material DBT-DtB-DBT (**16**), DBT-Anth-DBT (**17**) and DBT-Napth-DBT (**18**) were synthesized under the conditions of Suzuki coupling reaction in the presence of Aliquat®336 as a phase transfer catalyst in toluene to give 65%, 72% and 79% yield, respectively. The coupling reaction between **4** and **14** or **15** were carried out in toluene as an usual solvent of Suzuki reaction conditions to give **17** and **18** easily. However, the coupling reaction between **4** and **11** were carried out in THF instead of toluene (Scheme 3).

Compound **16** was soluble in common solvents and the structure was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR and mass analysis. However, compound **17** and **18** were soluble in hot toluene, chlorobenzene and dichlorobenzene only. Therefore, their structures were confirmed by mass and IR spectroscopy because of their poor solubility.

Optical and electrochemical properties. The optical properties of synthesized oligomers were investigated using UV-vis absorption and photoluminescence (PL) in dilute $CHCl_3$ solution and on thin film. The results are shown in Figure 1 and 2 and summarized in Table 1. UV absorption maxima in dilute $CHCl_3$ solution were exhibited at 346 nm for **16**, at 310 and 404 nm for **18** and at 361, 430, 452 nm for **17**, respectively. The experimental results of UV absorption of **16**, **17** and **18** were almost coincident with the increasing of conjugation length in their structures. In PL spectra, all of the oligomers exhibited blue fluorescence in solution. The emission spectra of oligomers in solid state displayed a large red shift about 60-80 nm. These results can be originated from the formation of aggregation or excimer in thin film due to π-π* stacking or intermolecular interaction caused by their planar structures. The electrochemical behaviors of oligomers were investigated by cyclic voltametry (CV). The cyclic voltammograms (CVs) of oligomers were recorded in a 1.0×10^{-3} M $CHCl_3$ solution containing 0.1 M Bu_4NClO_4. The oxidation peak potentials of oligomers were summarized in Table 1. In

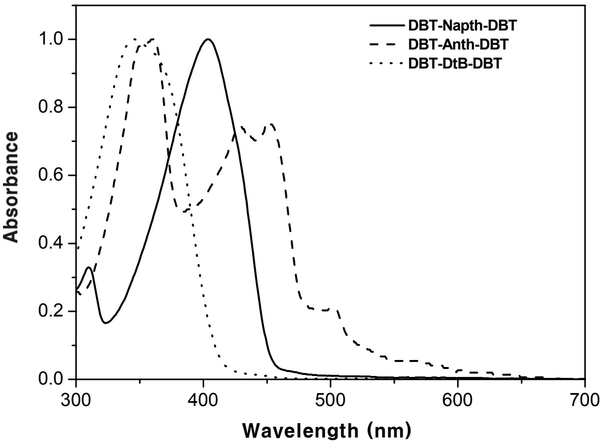


Figure 1. UV-vis spectra of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT in dilute $CHCl_3$ solution.

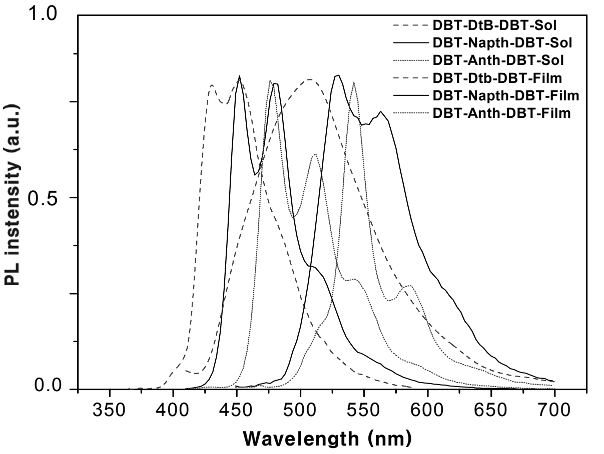


Figure 2. PL spectra of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT in dilute $CHCl_3$ solution and solid state.

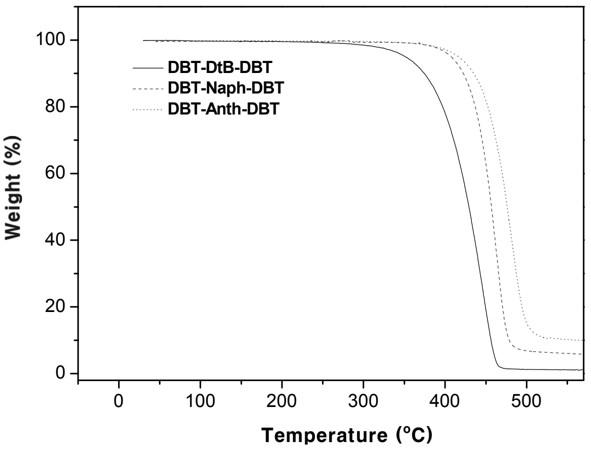


Figure 3. TGA curves of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT.

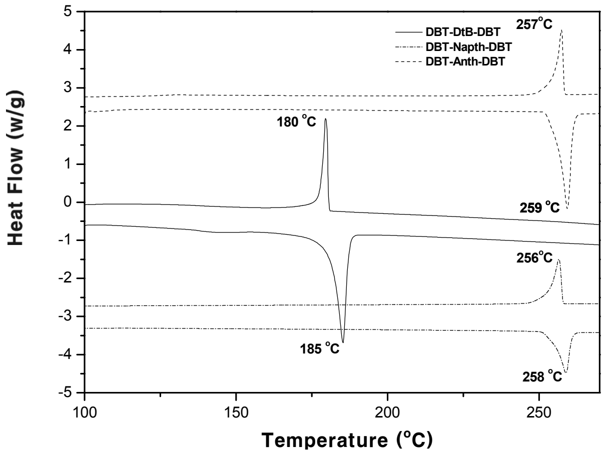


Figure 4. DSC thermograms of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT.

Table 1. Summary of the physical data of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT.

Compound	$\lambda_{abs/nm}$[a]	$\lambda_{em/nm}$[b]		E_{ox}/eV	T_{5d}/℃[c]	E_g/eV	HOMO/eV[d]	LUMO/eV[e]
		Solution	Film					
DBT-DtB-DBT	346	431, 452	509	1.0	351	3.00	-5.4	-2.40
DBT-Anth-DBT	361, 430, 452	476, 512	542, 587	0.89	412	2.55	-5.3	-2.75
DBT-Napth-DBT	310, 404	479, 452	530, 563	1.1	406	2.74	-5.4	-2.66

[a]Measured in dilute $CHCl_3$ solution [b]Excited at the absorption maxima [c]Obtained from DSC and TGA measurements under N_2 at a heating rate of 10 °C/min [d]Calculated using the empirical equation: HOMO = −(4.44 + E_{onset}) [e]Calculated from LUMO = HOMO + E_g

addition, the optical band gaps (E_g) of oligomers were determined from the absorption onset. The optical band gaps of **16**, **17** and **18** were found to be 3.00, 2.55 and 2.74, respectively. Table 1 summarizes the HOMO/LUMO energies of DBT-DtB-DBT, DBT-Anth-DBT and DBT-Napth-DBT estimated from the relation $E_{(LUMO)} = E_{(HOMO)} + E_{gap}$, where $E_{(HOMO)}$ is classically estimated from E_{onset} [x].[19] HOMO energy level of the oligomers were shown in the range of -5.3 eV to -5.4 eV, which are lower than that of α-sexithiophene (**α 6T**, HOMO level of -5.0 eV).[20] These results indicated that the synthesized oligomers have low band gap. For p-type semiconductors, the majority carriers are holes. For this reason, it is important to reduce the energy barrier between gold electrode and organic semiconductor so that the HOMO levels of p-type semiconductors should be closed to the work function of gold electrode (-5.4 eV).[21] Therefore, it can be assumed that the injection of charge carriers may be hindered. In addition, the determined HOMO levels of p-type semiconductors match well to the work function of gold metal used in OTFTs, which leads increasing of efficiency of the injection and transport of holes.

Thermal properties. The thermal properties of obtained oligomers were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. TGA curve reveals that the oligomers have high thermal stability. Five percent weight loss (T_{5d}) was observed at 351 °C, 412 °C and 406 °C for **16**, **17** and **18**, respectively. The results are shown in Figure 3 and summarized in Table 1.

These decomposition temperatures are higher than that of **α 6T** (T_{5d} = 322 °C) under similar conditions.[11] The decomposition of **16** is lower than those of **17** and **18,** this result can be explained due to less thermal stability of benzo[1,2-b:4,5-b']-dithiophene. The thermal characterization of **16**, **17** and **18** were investigated by DSC thermogram. Compound **16** exhibits an endothermic peak at 185 °C and an exothermic transition at 180 °C. The results are summarized in Table 1. DSC thermogram of **17** reveals an endothermic peak at 259 °C and an exothermic peak at 257 °C. Compound **17** also displayed good thermal feature under heating and cooling cycle. DSC thermogram of **18** reveals an endothermic peak at 316 °C and an exothermic peak was observed at 309 °C. All revealed thermal features of **16, 17** and **18** showed that all of the three oligomers are crystalline and it is expected that their thin films are well ordered under heat treatment.

Conclusions

We reported the synthesis of new 2-decylbithiophene end-capped oligomers, which were synthesized from Suzuki coupling reaction of naphthalene, anthracene and benzo[1,2-b:4,5-b']-dithiophene with compound **4** and their properties were investigated. Investigation of thermal properties revealed that all of the oligomers have good thermal stability from 350 °C to 410 °C as compared to **α6T** (T_{5d} = 322 °C). The optical and electrochemical properties showed that the synthesized oligomers have higher oxidation potential due to their high HOMO energy levels (-5.4 eV for **16**, -5.4 eV for **18** and -5.3 eV for **17**). In particularly, compound **16** exhibited good solubility in common solvents and can be used in low cost fabrication technologies. The fabrication of OTFTs using performance will be reported in the future.

Experimental

Materials. 2-Bromothiophene, 3-bromothiophene, 2,6-diaminoanthraquinone, decanoyl chloride, *N*-bromosuccinimide (NBS), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, *N*-formylpiperidine, *N,N*-dimethylformamide (DMF), copper (II) bromide, tetrakis(triphenylphosphine)palladium, Aliquat® 336 were purchased from Aldrich Chemical Co. The 2,6-dibromonaphthalene (**15**) was purchased from Alfa Aesar Co. All reagents purchased commercially were used without further purification except for diethylether, tetrahydrofuran (THF) dried with sodium/benzophenone.

Synthesis of 2,2'-bithiophene (1),[16] **2,6-dibromobenzo[1,2-b:4,5-b']dithiophene (11)**[17] **and 2,9-dibromoanthracene (14)**[18] were carried out according to literature procedures.

2-Decyl-5-(thiophen-2-yl)thiophene (2). To a solution of 2,2'-bithiophene **1** (3.17 g, 19.1 mmol) in anhydrous benzene (20 mL) was added decanoyl chloride (4.07 mL, 20.0 mmol) at r.t. $TiCl_4$ (2.25 mL, 20.5 mmol) was added to the reaction mixture at 0 °C and stirred for 15 min at 0 °C. Ice water was added to the reaction mixture and the resulting mixture was diluted with CH_2Cl_2 (50 mL), washed successively with water (200 mL) and saturated aqueous solution of $NaHCO_3$ (100 mL), dried over $MgSO_4$ and evaporated under reduced pressure to afford 5.00 g (85%) of yellow solid expected as the desired ketone intermediate. The intermediate was used for next step without purification.

To the solution of intermediate in toluene (40 mL) was added a suspension of $LiAlH_4$ (4.6 g, 121 mmol) and $AlCl_3$ (4.03 g, 30.3 mmol) in anhydrous Et_2O (100 mL) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred for 1h at r.t. The reaction mixture was cooled to 0 °C, EtOAc (20 mL) and 6M HCl (50 mL) were added. The resulting mixture was extracted with Et_2O (2 × 300 mL), washed with water (100 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether) to give compound **2** (6.00 g, 93%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (dd, J = 5.4Hz, 1.3Hz, 1H), 7.09 (dd, J = 3.5Hz, 1.3Hz, 1H), 6.99 (dd, J = 5.4Hz, 3.5Hz, 1H), 6.98 (d, J = 3.5Hz, 1H), 6.67 (d, J = 3.5Hz, 1H), 2.78 (t, J = 7.6Hz, 7.5Hz, 2H), 1.67 (m, 2H), 1.34 (m, 14H), 0.90 (t, J = 7.0Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 138.0, 134.8, 127.7, 124.7, 123.7, 123.4, 123.0, 32.0, 31.7, 30.2, 29.7, 29.6, 29.5, 29.4, 29.2, 22.8, 14.2; MS m/z 306 (M^+).

5-Bromo-5'-decyl-2,2'-bithiophene (3). In the absence of light, NBS (1.22 g, 6.86 mmol) was added in one portion to a solution of compound **2** (2.00 g, 6.53 mmol) in DMF (30 mL) and the reaction mixture was stirred for 0.5 h. After diluting with petroleum ether (50 mL), the reaction mixture was washed with saturated aqueous solution of NH_4Cl (100 mL), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether) to give compound **3** (2.36 g, 94%) as a white solid. mp 35-38 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 6.93 (d, J = 3.5Hz, 1H), 6.91 (d, J = 3.5Hz, 1H), 6.82 (d, J = 3.7Hz, 1H), 6.66 (d, J = 3.7Hz, 1H), 2.78 (t, J = 7.6Hz, 2H), 1.67 (m, 2H), 1.34 (m, 14H), 0.90 (t, J = 6.9Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.8, 139.7, 133.9, 130.5, 124.8, 123.7, 123.0, 110.2, 32.2, 31.8, 30.3, 29.9, 29.9, 29.6, 29.5, 29.4, 22.9, 14.4; MS m/z 384 (M^+).

2-{5-(5-Decylthiophen-2-yl)thiophen-2-yl}-4,4,5,5-tetra methyl-1,3,2-dioxaborolane (4). To a solution of **3** (1 g, 2.64 mmol) in THF (30 mL) was added *n*-BuLi (1.6 M, 3.17 mmol) at -78 °C under nitrogen condition. The reaction mixture was warmed slowly to -50 °C during 20 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.58 mL, 5.27 mmol) was added at -50 °C and the temperature was increased slowly to r.t. The reaction mixture was stirred for 3 h at r.t and 2N HCl (20 mL) was added. The resulting mixture was extracted with ether (2 × 30 mL), washed with water (100 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The obtained residue was recrystallized from hexane (10 mL) to give compound **4** (0.85 g, 93.6%) as a white solid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 3.6Hz, 1H), 7.19 (d, J = 3.6Hz, 1H), 7.07 (d, *J* = 3.5Hz, 1H), 6.71 (d, *J* = 3.5Hz, 1H), 2.81 (t, *J* = 7.6Hz, 2H), 1.70 (m, 2H), 1.37 (m, 14H), 0.91 (t, *J* = 6.6Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.1, 144.8, 137.9, 134.7, 124.9, 124.2, 124.1, 84.1, 31.9, 31.6, 30.2, 29.6, 29.5, 29.4, 29.3, 29.1, 24.8, 22.7, 14.2; MS m/z 432 (M^+).

DBT-DtB-DBT (16). To a solution of 2,6-dibromobenzo[1,2-b:4,5-b']dithiophene **11** (0.52 g, 1.49 mmol) and **4** (1.41 g, 3.27 mmol) in anhydrous THF (20 mL) under nitrogen atmosphere were added $Pd(PPh_3)_4$ (0.069 g, 0.059 mmol), Aliquat®366 (0.34 mL, 0.745 mmol) and Na_2CO_3 (2 N, 0.80 g, 7.45 mmol) at r.t. The reaction mixture was degassed and stirred at reflux during overnight and then poured into the mixed solution [toluene (200 mL) + water (100 mL) + 1N HCl (20 mL)]. The light orange precipitate was filtered off, washed with water (100 mL), 2N HCl (100 mL), methanol (100 mL) and then with acetone (100 mL) to remove starting material as well as the mono-substituted by-product. The resulting precipitate was purified by Soxhlet to give compound **16** (0.77 g, 65%) as a yellow solid. mp 185 °C; ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 2H), 7.60 (s, 2H), 7.32 (d, *J* = 3.6Hz, 2H), 7.20 (d, *J* = 3.7Hz, 2H), 7.09 (d, *J* = 3.5Hz, 2H), 6.75 (d, *J* = 3.4Hz, 2H), 2.84 (t, *J* = 7.5Hz, 4H), 1.73 (m, 4H), 1.38 (m, 28H), 0.91 (t, *J* = 6.4Hz, 6H); MS m/z 798 (M^+), HRMS(ESI) Calcd for: $C_{46}H_{54}S_6$ (M^+): 798.2550. Found: 798.2546.

DBT-Anth-DBT (17). To a solution of 2,6-dibromoanthacene **14** (0.50 g, 1.49 mmol) and **4** (1.41 g, 3.27 mmol) in anhydrous toluene (20 mL) under nitrogen atmosphere were added $Pd(PPh_3)_4$ (0.069 g, 0.059 mmol), Aliquat®366 (0.34 mL, 0.745 mmol) and Na_2CO_3 (2N, 0.80 g, 7.45 mmol) at r.t. The reaction mixture was degassed and stirred at reflux during overnight and then poured into the mixed solution [toluene (200 mL) + water (100 mL) + 1N HCl (20 mL)]. The light orange precipitate was filtered off, washed with water (100 mL), 2N HCl (100 mL), methanol (100 mL) and then with acetone (100 mL) to remove starting material as well as the mono-substituted by-product. The resulting precipitate was purified by Soxhlet to give compound **17** (0.84 g, 72%) as a yellow solid. mp 347 °C; MS m/z 786 (M^+), HRMS(ESI) Calcd for: $C_{50}H_{58}S_4$ (M^+): 786.3421. Found: 786.3414.

DBT-Napth-DBT (18). To a solution of 2,6-dibromonapthalene, **15** (0.43 g, 1.49 mmol) and **4** (1.41 g, 3.27 mmol) in anhydrous toluene (20 mL) under nitrogen atmosphere were added $Pd(PPh_3)_4$ (0.069 g, 0.059 mmol), Aliquat®366 (0.34 mL, 0.745 mmol) and Na_2CO_3 (2N, 0.80 g, 7.45 mmol) at r.t. The reaction mixture was degassed and stirred at reflux for 12 h and then poured into the mixed solution [toluene (200 mL) + water (100 mL) + 1N HCl (20 mL)]. The yellow precipitate was filtered off, washed with water (100 mL), 2N HCl (100 mL), methanol (100 mL) and then with acetone (100 mL) to remove starting material as well as the mono-substituted by-product. The resulting precipitate was purified by Soxhlet to give compound **18** (0.87 g, 79%) as a yellow solid. mp: 302 °C; MS m/z 736 (M^+), HRMS(ESI) Calcd for: $C_{46}H_{56}S_4$ (M^+): 736.3265. Found: 736.3260.

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