



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

### Novel Thienyl-dibenzothiophene Oligomers End-capped by Hexylphenyl Groups as Potential Organic Semiconductor Materials

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Version of record first published: 17 Sep 2012.

To cite this article: Zongfan Duan, Zhigang Yang, Daiki Hoshino, Toshio Hirao, Mitsumasa Taguchi, Hirokuni Ohuch, Yuichiro Yanagi & Yasushiro Nishioka (2012): Novel Thienyl-dibenzothiophene Oligomers End-capped by Hexylphenyl Groups as Potential Organic Semiconductor Materials, *Molecular Crystals and Liquid Crystals*, 567:1, 28-33

To link to this article: <http://dx.doi.org/10.1080/15421406.2012.702376>

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# Novel Thienyl-dibenzothiophene Oligomers End-capped by Hexylphenyl Groups as Potential Organic Semiconductor Materials

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*Novel thienyl-dibenzothiophene oligomers end-capped by hexylphenyl groups, 2,8-bis[5-(4-n-hexylphenyl)-2-thienyl]dibenzothiophene (28HPTDBT) and 3,7-bis[5-(4-n-hexylphenyl)-2-thienyl]dibenzothiophene (37HPTDBT), have been synthesized using Stille cross-coupling reactions. Newly synthesized oligomers were investigated by Ultraviolet-visible (UV-vis) and photoluminescence (PL) spectroscopy, cyclic voltammogram, and thermal analysis. Strong intermolecular  $\pi$ - $\pi$  interactions, appropriate energy band gaps and low HOMO energy levels imply that the two oligomers are promising candidate materials for durable organic electronic devices.*

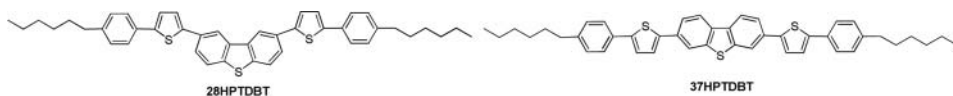
**Keywords** Dibenzothiophene; phenylene-thiophene oligomers; organic semiconductor

## 1. Introduction

There has been growing interest in  $\pi$ -conjugated polymers and oligomers over the last few years because of their unique photo-electronic properties and potential applications in different electronic devices, such as organic light emitting diodes (OLEDs), solar cells and organic field effect transistors (OFETs) [1]. Phenylene (P)-thiophene (T) oligomers with various P:T ratios are a promising class of semiconductor materials, and many of them have been employed in OLEDs [2], solar cells [3], and p-channel OFETs [4,5]. Previous work with OFETs fabricated from phenylene-thiophene oligomers suggests that phenylene substitutes introduced at the 2-position or within the oligothiophene backbone can result in a small lowering of the  $E_{\text{HOMO}}$  level, and provide stability against oxidation and polymerization while minimizing steric interactions [4–6]. Dibenzothiophene unit with coplanar

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**Scheme 1.** Structures of 28HPTDBT and 37HPTDBT

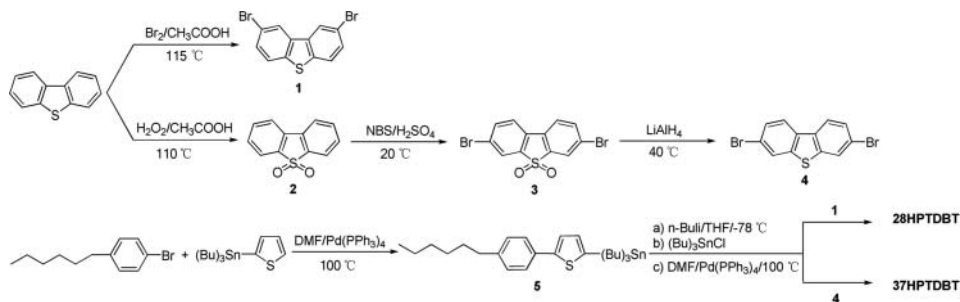
benzene rings has excellent hole-injection/transportation character and dibenzothiophene derivatives are potential high mobility semiconductor materials [7,8].

Bearing in mind the above factors, we have designed, synthesized and characterized two novel thienyl-dibenzothiophene oligomers 28HPTDBT and 37HPTDBT (Scheme 1). Their intrinsic potentials as organic materials for electronics and photonics were also assessed.

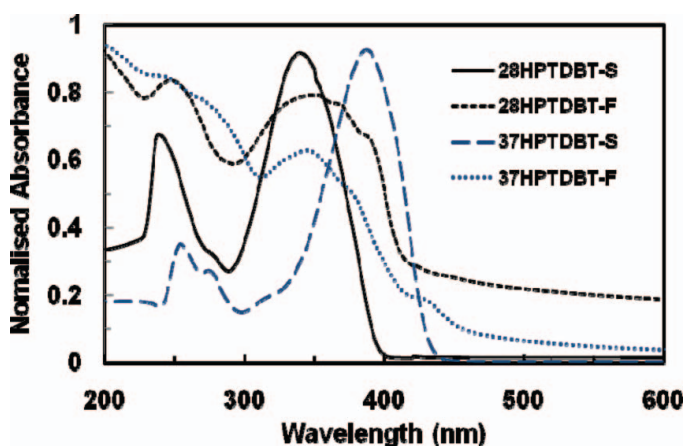
## 2. Experimental

The synthetic pathways to 28HPTDBT and 37HPTDBT are outlined in Scheme 2. Starting from the commercially available dibenzothiophene, 2,8-dibromodibenzothiophene was obtained by bromination [9], 3,7-dibromodibenzothiophene can be attained by three steps [10]. The key precursor 2-(tri-*n*-butylstannyl)-5-(4-*n*-hexylphenyl)thiophene was synthesized according to the literature [4]. The desired oligomers 28HPTDBT and 37HPTDBT were prepared by Stille cross-coupling reactions. All compounds were fully characterized with  $^1\text{H}$  NMR, MS (EI-HR) and elemental analysis and found to be in good agreement with their structures.

**Synthesis of 2,8-bis[5-(4-*n*-hexylphenyl)-2-thienyl]dibenzothiophene (28HPT-DBT).** To a 100 ml three-neck round-bottomed flask were added 2,8-dibromodibenzothiophene (0.342g, 1 mmol), 2-(tri-*n*-butylstannyl)-5-(4-*n*-hexylphenyl)thiophene (1.60g, 3 mmol), and dry DMF (30 ml). The mixture was deoxygenated with nitrogen for 30 min. After tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{PPh}_3)_4$ ) (46 mg, 0.04 mmol) was added, the mixture was stirred at  $110^\circ\text{C}$  for 48 hours under nitrogen. The resulting large amount of yellow solid was collected by filtration and washed with aqueous 8% aqueous KF (100 ml), 5% aqueous HCl (100 ml), 10% aqueous  $\text{Na}_2\text{CO}_3$  (100 ml), water (200 ml) and methanol (100 ml) successively. The residue was purified by column chromatography using hexane/dichloromethane (10:1) as eluent. After recrystallization from ethyl acetate, pale yellow solid was obtained (0.434 g, 65%). mp  $175\text{--}177^\circ\text{C}$ .  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.38 (d, 2H,  $J = 1.4$  Hz), 7.82 (d, 2H,  $J = 8.2$  Hz), 7.73 (dd, 2H,  $J = 8.2$  Hz, 1.7 Hz), 7.59 (d, 4H,  $J = 8.3$  Hz), 7.41 (d, 2H,  $J = 3.8$  Hz), 7.30 (d, 2H,  $J = 3.8$  Hz), 7.22 (d, 4H,  $J = 8.3$  Hz), 2.64 (t, 4H,  $J = 7.7$  Hz), 1.66-1.63 (m, 4H), 1.37-1.32 (m, 12H), 0.90 (t,



**Scheme 2.** Synthetic pathways to oligomers 28HPTDBT and 37HPTDBT



**Figure 1.** Normalized UV-Vis absorption spectra: 28HPTDBT in chloroform (28HPTDBT-S) and in thin film (28HPTDBT-F); 37HPTDBT in tetrachloroethane (37HPTDBT-S) and in thin film (37HPTDBT-F).

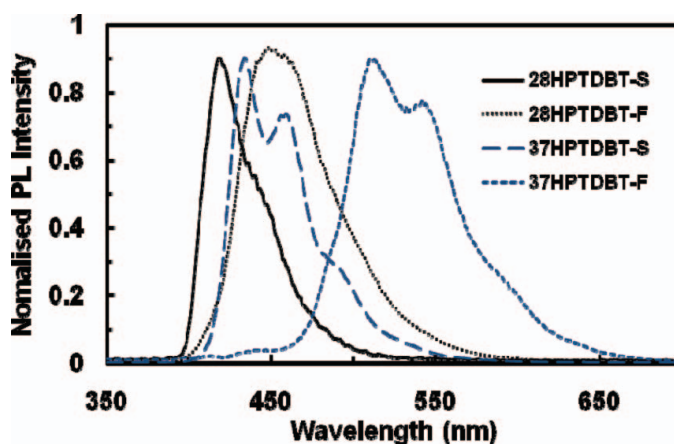
6H,  $J = 6.9$  Hz).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150MHz, ppm): 143.9, 142.9, 142.6, 138.9, 135.9, 131.7, 131.2, 129.0, 125.6, 124.9, 124.2, 123.6, 123.2, 118.4, 35.7, 31.7, 31.4, 29.0, 22.6, 14.1. MS (EI-HR),  $m/z$ :  $[\text{M}]^+$  calcd. for  $\text{C}_{44}\text{H}_{44}\text{S}_3$ , 668.2605; found, 668.2610. Elemental Analysis calcd. for  $\text{C}_{44}\text{H}_{44}\text{S}_3$ : C, 78.99; H, 6.63. Found: C, 79.25; H, 6.34.

**Synthesis of 3,7-bis[5-(4-*n*-hexylphenyl)-2-thienyl]dibenzothiophene (37HPT-DBT).** Applying the same procedure as described for 28HPTDBT, green-yellow solid was obtained with a yield of 66%. mp > 300°C.  $^1\text{H}$  NMR (600 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ , 100°C):  $\delta$  8.14 (d, 2H,  $J = 7.9$  Hz), 8.11 (d, 2H,  $J = 1.7$  Hz), 7.76 (dd, 2H,  $J = 8.3$  Hz, 1.7 Hz), 7.59 (d, 4H,  $J = 7.9$  Hz), 7.40 (d, 2H,  $J = 3.8$  Hz), 7.31 (d, 2H,  $J = 3.4$  Hz), 7.24 (d, 4H,  $J = 7.9$  Hz), 2.68 (t, 4H,  $J = 7.9$  Hz), 1.71–1.69 (m, 4H), 1.44–1.38 (m, 12H), 0.95 (t, 6H,  $J = 7.2$  Hz). MS (EI-HR),  $m/z$ :  $[\text{M}]^+$  calcd. for  $\text{C}_{44}\text{H}_{44}\text{S}_3$ , 668.2605; found, 668.2606. Elemental Analysis calcd. for  $\text{C}_{44}\text{H}_{44}\text{S}_3$ : C, 78.99; H, 6.63. Found: C, 78.75; H, 6.44.

### 3. Results and Discussion

#### 3.1. Photo-physical Properties

The UV-vis absorption and PL spectra of two oligomers in solutions and in thin films prepared by drop-casting of tetrachloroethane solutions on quartz glasses are shown in Figure 1 and 2, respectively, and the photo-physical data are summarized in Table 1. The absorption maxima of 28HPTDBT and 37HPTDBT in solutions peak at 340 and 387 nm, respectively, and there is a substantial red shift ( $\Delta\lambda = 47$  nm) of the absorption maxima upon variation of substituted situations of 4-*n*-hexylphenyl-2-thienyl group at the aryl ring of dibenzothiophene, which is attributed to the asymmetric destabilization of the HOMO and the LUMO energy levels leading to a decrease in the energy gap [11]. In thin films, the absorption bands of two oligomers become relatively broader and less structured. The maximum absorption of 28HPTDBT is red-shifted about 12 nm, while the UV-vis spectra of 37HPTDBT display a large blue-shift more than 30 nm relative to those of their corresponding solutions. The energy band gaps of 28HPTDBT and 37HPTDBT were determined from the absorption onset and were found to be 2.95 and 2.72 eV, respectively



**Figure 2.** Normalized photoluminescence (PL) spectra: 28HPTDBT in chloroform (28HPTDBT-S) and in thin film (28HPTDBT-F); 37HPTDBT in tetrachloroethane (37HPTDBT-S) and in thin film (37HPTDBT-F).

[3]. These energy band gaps are significantly higher than that of pentacene, implying the greater stabilities of 28HPTDBT and 37HPTDBT against photo-degradation [12]. The pronounced changes in the absorption spectra are a result of the delocalization of the exciton within co-facial stacks induced by the  $\pi$ - $\pi$  interactions, which is also evidenced by a related red-shift of the PL spectra. 28HPTDBT and 37HPTDBT show strong blue fluorescence in solutions, while emission color of 37HPTDBT in the solid state is observed in the green region. The remarkable shifts of UV-vis and PL spectra in thin films relative to the solutions correspond to the extremely high intermolecular  $\pi$ - $\pi$  interactions in the film state.

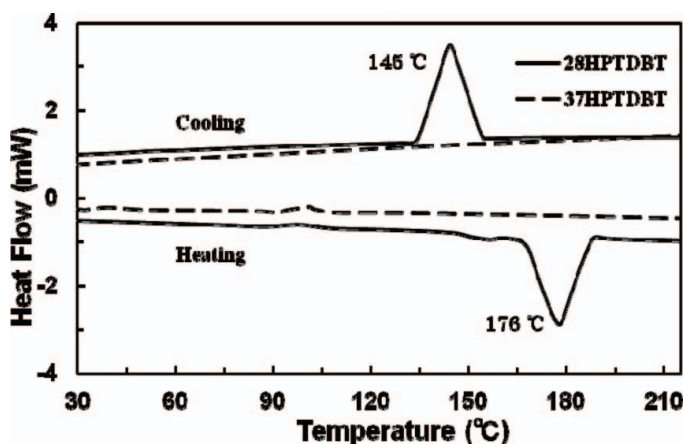
### 3.2. Electrochemical Properties

The cyclic voltammograms of 28HPTDBT and 37HPTDBT, performed by using a three-electrode system, show quasi-reversible and irreversible oxidation waves, respectively. The onset oxidation potentials of 28HPTDBT and 37HPTDBT are 0.96 and 0.77 eV, respectively. Considering the onset oxidation potential of ferrocene/ferrocenium was 0.26V with respect to Ag/AgCl reference electrode and assuming that the energy level of the

**Table 1.** Optical and electrochemical data for 28HPTDBT and 37HPTDBT.

Oligomers	$\lambda_{\max}^{abs}$ (nm)		$E_g^{opt}$ (eV)	$\lambda_{\max}^{pl}$ (nm)		Electrochemical data	
	Solution	Film		Solution	Film	$E_{HOMO}$ (eV)	$^*E_{LUMO}$ (eV)
28HPTDBT	340	352	2.95	418	448	−5.50	−2.55
37HPTDBT	387	356	2.72	434	511	−5.31	−2.59

\*LUMO levels were determined by adding  $E_g^{opt}$  and HOMO energy levels.



**Figure 3.** Differential scanning calorimetry (DSC) trace for 28HPTDBT and 37HPTDBT.

ferrocene/ferrocenium reference is 4.8 eV below vacuum. The HOMO energy levels of 28HPTDBT and 37HPTDBT were calculated to be  $-5.50$  and  $-5.31$  eV, respectively (Table 1). Compared to that of sixthiophene ( $-4.99$  eV) [12], the lower HOMO energy levels of 28HPTDBT and 37HPTDBT suggest that the introduction of the phenylene ring into oligothiophene conjugated chain can really decrease the HOMO energy levels, and therefore increase the oxidative stabilities of the corresponding oligomers. The calculated LUMO energy levels of 28HPTDBT and 37HPTDBT are  $-2.55$  eV and  $-2.59$  eV, respectively. Such energy levels may provide a closer match to the work function of Ca ( $-2.76$  eV) when they are used as electron-transporting materials in the OLEDs.

### 3.3. Thermal analysis

Two oligomers were found to exhibit good thermal stabilities, losing less than 5% of weight upon heating up to  $400^{\circ}\text{C}$  in nitrogen as determined by thermal gravimetric analysis (TGA). 28HPTDBT shows only one endothermal peak at  $176^{\circ}\text{C}$  and exothermal peak at  $145^{\circ}\text{C}$  on the differential scanning calorimeter (DSC) curve (Figure 3). Interestingly, for oligomer 37HPTDBT with a high phase transition temperature, sublimation is complete at the temperature much lower than its melting point.

## 4. Conclusions

In a word, straightforward syntheses, unique photo-electronic properties and durability make oligomers 28HPTDBT and 37HPTDBT very attractive for low-cost organic electronics applications.

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