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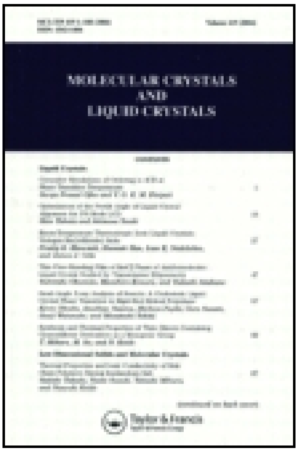

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Synthesis of Copolymer Thieno[3,4-b]Thiophene and Benzodithiophene for Application in Solar Cells

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Synthesis of Copolymer Thieno[3,4-b]Thiophene and Benzodithiophene for Application in Solar Cells

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Synthesis of poly(2-hexylthieno[3,4-b]thiophene-co-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene) (PTB) is presented using a simple and low cost method. Anhydrous DMF and toluene was added into the mixture of 4,6-dibromo-2-hexylthieno[3,4-b]thiophene,2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene and $Pd(PPh_3)_4$*. The polymerization was carried out at 120°C for 12 h. The PTB product was precipitated in methanol and dried in vacuum. The HOMO and LUMO energies of the polymer were calculated using Density Functional Theory (DFT) calculations to be compared with the experimental results.*

Keywords Heterojunction polymer solar cells; HOMO and LUMO levels; PTB/$PC_{61}BM$

Introduction

Our future for energy production on a global scale relies on a technology that is renewable and competitive with fossil fuels. This is due to the increasing need for our society to become independent of foreign oil. Photovoltaic (PV) devices offer us this technology. The first PV cells were developed by Bell Labs in the 1950s. Their silicon–based solar cells were found to have power conversion efficiencies upwards of 6% [1].

The bulk heterojunction solar cells (BHJ) is the self–assembly of nanoscale heterojunctions by spontaneous phase separation of the polymer acts as a donor and the fullerene

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acts as an acceptor. For an efficient transfer of electrons from a donor to an acceptor, charge–separating is formed throughout the bulk of the materials [2–3]. Conjugated polymer based PVs provide lower cost way to convert light to electricity than their inorganic counterparts. The first conjugated polymer–based solar cell incorporating both a donor and an acceptor was developed in 1986 and had an efficiency of 1% [4]. Since then, research has focused on trying to manipulate the device architectures and active layer materials to improve performance. Recently, efficiencies of over 6% have been achieved in polymer solar cells based on alternating thieno[3,4-b]thiophene (TT) and benzodithiophene (BDT) monomers with [6,6]-phenyl–C61–butyric acid methyl ester (PTB/PC$_{61}$BM) from mixed solvents [5]. In this work we sought to find an efficient route to TT monomers. Herein, we discuss our efforts towards preparing TT-based monomers and polymers in an efficient manner. Scheme 1 shows synthesis routes for poly(2-hexylthieno[3,4-b]thiophene-co-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene (PTB).

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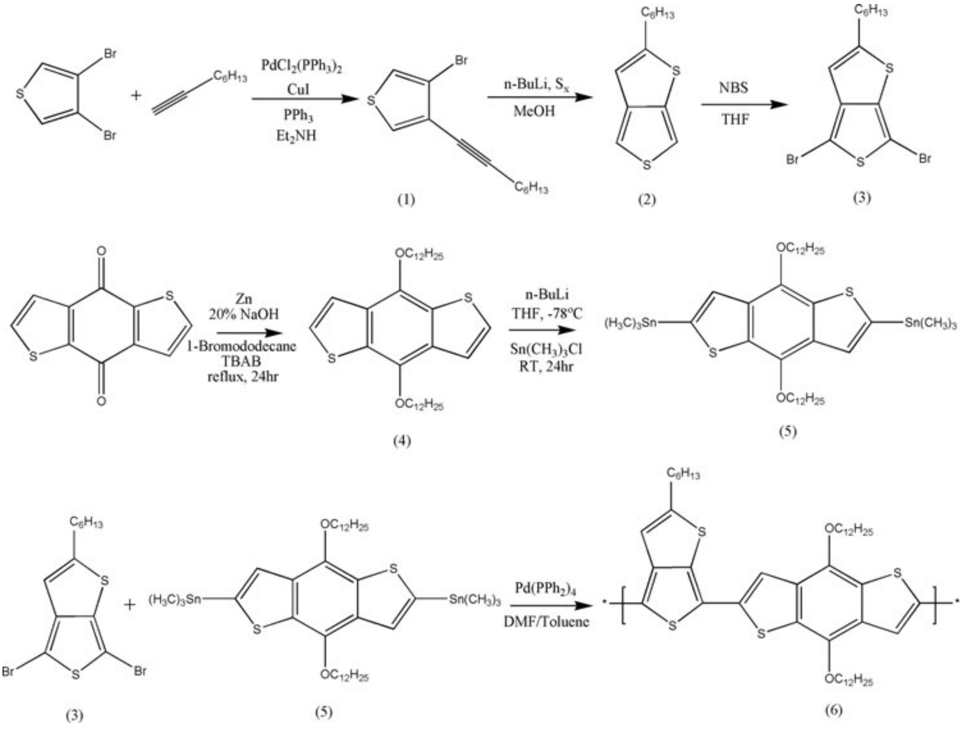

Scheme 1. Synthesis routes for poly(2-hexylthieno[3,4-b]thiophene-co-4,8-didodecyloxybenzo [1,2-b:4,5-b′]dithiophene (PTB).

Experimental

Materials

Chemicals were purchased from Aldrich and Acros. Benzo[1,2-b:4,5-b′]dithiophene-4,8-dione[6]was synthesized according to the procedures reported in the literature.

3-bromo-4-(oct-1-ynyl)thiophene (1). Compound 1 was synthesized via the Sonogashira cross–coupling reaction [7–8]. The three–necked flask was charged with diethylamine 15 g, 3,4-dibromothiophene (0.1 mmol), 1-Octyne (0.05 mmol), PdCl$_2$(PPh$_3$)$_2$

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125 mg, Ph_3P 50 mg, and copper(I)iodide 40 mg. The mixture was stirred under argon gas at 80°C for 5 h. After cooling to RT, 100 mL of hexane and 50 mL of ice water were added into the mixture. The hexane layer extract was washed with water and dried over $MgSO_4$. The solvent was evaporated. The remaining liquid was purified by distillation to give colorless liquid, yield 57% (17.30 g). ^{1}H NMR ($CDCl_3$), δ (ppm): 7.37 (d, $J = 3.4$ Hz, 2H), 7.24 (d, $J = 3.4$ Hz, 2H), 2.49 (t, 2H), 1.36–1.73 (m, 8H), 0.99 (t, 3H).

2-hexylthieno[3,4-b]thiophene (2). A three–necked flask equipped with a thermometer was charged with 30 mL of dry diethyl ether and 1.00 g (3.67 mmol) of product **1** while under argon. This solution was maintained at a temperature of –78°C and stirred for 30 min, after which 2.375 mL of *n*–BuLi (1.6 M in hexanes, 3.8 mmol) was slowly added. After addition, the solution was stirred for 30 min at –78°C, and then the solution was cooled to –45°C. Sulfur (0.1216 g, 3.8 mmol) was added, and the reaction mixture was allowed to warm to –35°C for fully dissolution of the sulfur. After sulfur addition the reaction mixture had changed to clear yellow solution, was then cooled to –45°C, and stirring was continued for an additional of 30 min. Then the reaction was allowed to warm to ambient temperature and the diethyl ether was removed under reduced pressure. The reaction flask was then charged with a methanol solution of KOH and refluxed for 20 h. Methanol was removed. 50 mL of water was added into the mixture, which was extracted with diethyl ether and dried over $MgSO_4$. The solvent was evaporated and purified by chromatography, yield 78% (0.72 g) as a colorless liquid. ^{1}H NMR (CD_2Cl_2), δ (ppm): 7.21 (s, 2H), 6.69 (s, 1H), 2.83 (t, 2H), 1.34–1.81 (m, 8H), 0.97 (m, 3H).

4,6-dibromo-2-hexylthieno[3,4-b]thiophene(3). NBS (0.810 g 4.56 mmol) in 15 mL of THF was added into the solution of **2** (0.51 g, 2.28 mmol) under argon protection in the dark. The reaction was stirred at RT for 24 h. 50 mL of water was added into the mixture which was extracted with dichloromethane and dried with $MgSO_4$. After the removal of the solvent, the residue was purified by column chromatography on silica gel with hexane, yield 76% (0.66 g) as a colorless liquid. ^{1}H NMR (CD_2Cl_2), δ (ppm): 6.53 (s, 1H), 2.78 (m, 2H), 1.39–1.74 (m, 8H), 0.96 (t, 3H).

4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene(4). [9]. Benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (1.5973 g, 7.25 mmol) was added to a flask containing Zn dust (1.0744 g, 16.43 mmol) and NaOH (25 mL, 25%) solution. The red mixture was allowed to reflux for 1 h. The color changed to orange and 1-bromododecane (5.5 mL, 22.9 mmol) and TBAB (20.0 mg) were added and the mixture was refluxed overnight. After cooling, the mixture was quenched with H_2O and separated with ether. The organic phase was dried over $MgSO_4$, yield as an orange solid. ^{1}H–NMR ($CDCl_3$), δ (ppm): 7.48 (d, 2H); 7.36 (d, 2H); 4.28 (t, 4H); 1.87 (q, 4H); 1.55 (m, 4H); 1.40–1.20 (br, 32H) 0.88 (t, 6H).

2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene(5). 4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene (4.49 g, mmol) in dry THF (150 mL) was cooled to –78°C in an acetone/dry ice bath. N–butyllithium (11.0 mL, 1.6 M) in hexane was added drop–wise. The solution was stirred at –78°C for 30 min and at RT for 30 min. The solution was then cooled to –78°C and trimethyltin chloride (8.5 mL, 1 M in hexanes) was added drop–wise and the solution was allowed to stir at RT overnight. The solution was quenched in 50 mL of cold water and extracted with ether. The solution was washed with water and the organic phase was dried over $MgSO_4$ and evacuated to give an orange oil. ^{1}H–NMR ($CDCl_3$), δ (ppm): 7.53 (s, 2H); 4.31 (d, 4H); 1.89 (q, 4H); 1.58 (m, 4H); 1.35–1.25 (m, 32H); 0.89 (t, 6H).

Poly(2-hexylthieno[3,4-b]thiophene-co-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene(6). Anhydrous DMF and toluene was added into the mixture of compound **3**, compound **5** and $Pd(PPh_3)_4$. The polymerization was carried out at 120°C for 12 h. The product was precipitated in methanol and dried in vacuum.

Table 1. HOMO–LUMO energy levels by DFT calculation

PTB	HOMO (eV)	LUMO (eV)	$\Delta_{H\text{–}L}$ (eV)
$n = 1$	–5.03	–1.73	3.30
$n = 2$	–4.75	–2.19	2.57
$n = 3$	–4.67	–2.31	2.34
$n = 4$	–4.62	–2.39	2.24
$n = \infty$	–4.49	–2.60	1.89

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Characterization

1H–NMR spectra were recorded using a Bruker 300 UltraShield (300 MHz), which the chemical shifts were recorded in δ (ppm). The UV–vis spectrum was recorded on a Varian Cary 50 Scan UV–visible spectrophotometer with baseline corrections and normalizations performed using Cary Scan software. Cyclic voltammetry (CV) was used to assess the electrochemical behavior of the polymer. The measurement was performed in a solution of n–Bu_4NPF_6 (0.1 M) and polymer **6** (10 mg) in dried CH_2Cl_2 at scan rate of 50 mV/s at room temperature. A glassy carbon electrode, a platinum electrode and a Ag/Ag^+ electrode were used as the working electrode, the counter electrode and a guasi–reference electrode respectively.

Results

Density Functional Theory (DFT) Calculations

To get insight into the molecular structure and electronic distribution, the geometries of oligomers ($n = 1$–4) were fully optimized using density functional theory (DFT) on Beck′s three–parameter hybrid exchange functional and Lee–Yang–Parr correlation functional (B3LYP) [10–11] with 6–31G(d,p) basis set, as implemented in Gaussian 03 program package [12]. There is no any symmetric constraint on optimization calculation and long alkyl groups were replaced with methyl group to reduce calculation time [13]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) distributions ($n = 4$) are plotted in Figure 1 and the calculated HOMO and LUMO energies are collected in Table 1. As shown, both the HOMO and LUMO shape spread over the whole π–conjugated backbone indicating that the transition character of studied molecules is π–π^* transition. The HOMO and LUMO energy levels of ground–state optimized geometry are calculated to be –4.49 eV and –2.60 eV, respectively. The theoretical energy gap was estimated from the difference energy between HOMO and LUMO energies, which is 1.89 eV. In addition, although there are some discrepancies between the calculated HOMO

Table 2. The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} of polymer

Polymer	E_{onset} (V)	E_{HOMO} (eV)	E_{gap} (eV)	E_{LUMO} (eV)
PTB	1.38	–5.82	1.82	–4.00

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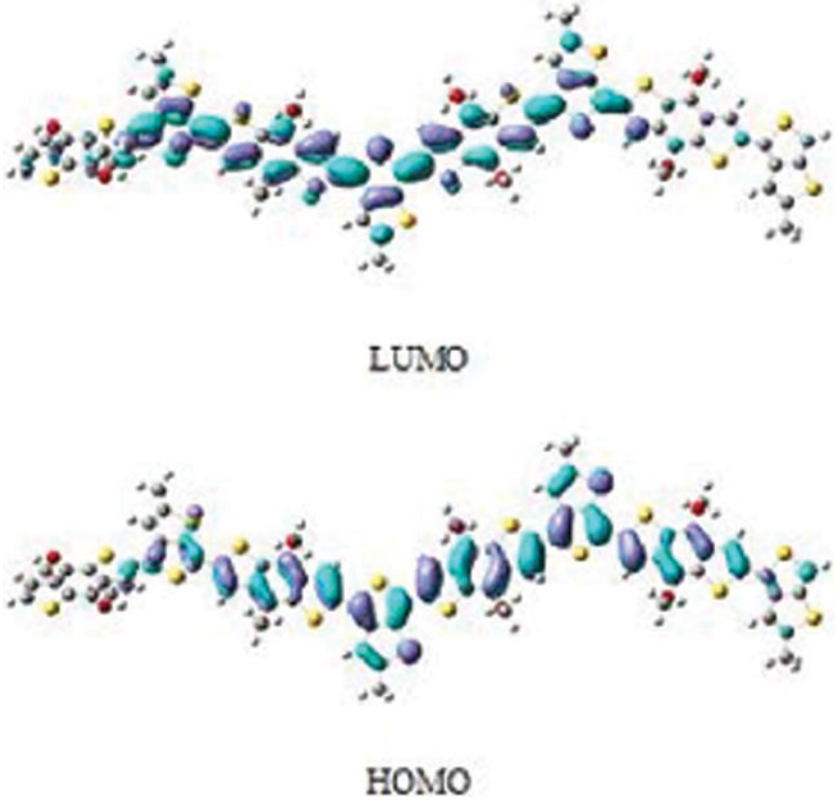

Figure 1. HOMO and LUMO surface plots for alkyl-substituted analogues of polymer.

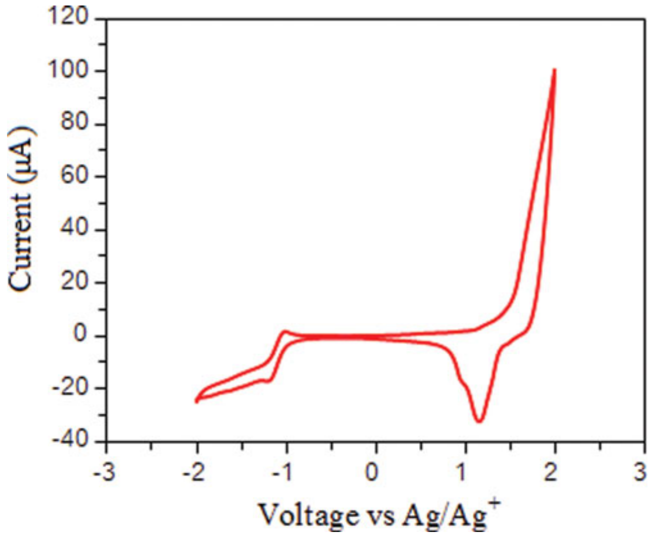

Figure 2. Cyclic voltammogram of polymer in CH_2Cl_2 with 0.1 M of n-Bu_4NPF_6 at a scan rate of 50 mV/s.

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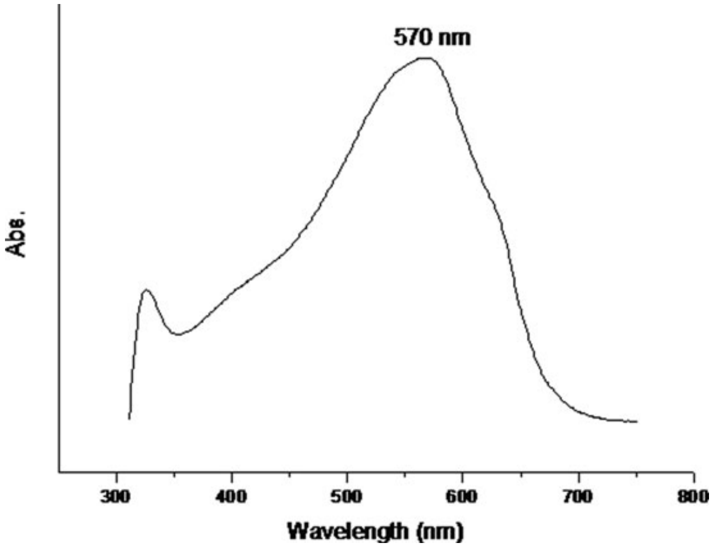

Figure 3. UV–vis absorption spectrum of polymer in chlorobenzene.

and LUMO energies and experimental observation, the trend of estimated energy gap is similar.

Electrochemical and Optical Properties

Cyclic voltammetry (CV) was used to determine the HOMO and LUMO energy levels of the polymer. The results are summarized in Table 2. The UV-vis spectrum was shown in the Fig. 3, with $\lambda_{onset} = 680$ nm. The lower band gap was determined by Planck′s equation that shown alternating TT and BDT monomers can be suitable to use for photovoltaic cells application.

As shown in Figure 2 polymer exhibits quasi–irreversible oxidation processes. The onset oxidation potential (E_{onset}), E_{HOMO}, band gap energy (E_{gap}), and E_{LUMO} were summarized in Table 2.

The E_{HOMO} was calculated according to an empirical equation [14–15] as follows:

$$E_{HOMO} = -(E_{onset} + 4.44)\,(eV)$$

and the E_{gap} was estimated from absorption onset of the polymer, thus, E_{LUMO} was calculated using the equation:

$$E_{LUMO} = E_{HOMO} + E_{gap}$$

Conclusions

Our method for accessing TT monomers started from readily available 3,4-dibromo thiophene. A palladium–catalyzed Sonogashira reaction was allowed to a variety of 3-bromo-4-alkynylthiophenes that can be ring closure in one step to obtain the desired alkyl substituted TT in lesser steps than other TT syntheses reported earlier. Bromination of the TT unit followed by Stille coupling copolymerization with 2,6-Bis(trime thyltin)-4,8-didodecyloxybenzo[1,2-b:4,5-b′]dithiophene and standard work-up yields Poly(2-hexylthieno[3,4-b]thiophene-co-4,8-didodecyloxybenzo[1,2-b:4,5-b′] dithiophene. Solution UV-vis in chlorobenzene revealed that the polymer **6** has $\lambda_{max} = 570$ nm, with an onset of 680 nm. The HOMO and LUMO energy levels of the polymer were calculated from onset energy of UV-vis spectrum and cyclic voltammogram. The E_{gap} estimated from absorption onset of the polymer was 1.82 eV. The theoretical energy gap was estimated from the difference energy between HOMO and LUMO energies, which is 1.89 eV. In our future work we will alter our synthetic methodology to include electron-withdrawing groups at the 2-position in an effort to optimize the HOMO levels of our polymers. Our end goal is to incorporate these materials into fiber-based OPV architectures.

Acknowledgments

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