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PAPER

# New low band gap thieno[3,4-b]thiophene-based polymers with deep HOMO levels for organic solar cells

Salem Wakim,<sup>a</sup> Salima Alem,<sup>a</sup> Zhao Li,<sup>b</sup> Yanguang Zhang,<sup>a</sup> Shing-Chi Tse,<sup>a</sup> Jianping Lu,<sup>\*a</sup> Jianfu Ding<sup>b</sup> and Ye Tao<sup>\*a</sup>

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Two new soluble alternating alkyl-substituted benzo[1,2-*b*:4,5-*b*']dithiophene and ketone-substituted thieno[3,4-*b*]thiophene copolymers were synthesized and characterized. We found that grafting 3-butyloctyl side chains to the benzo[1,2-*b*:4,5-*b*']dithiophene unit at C4 and C8 afforded the resulting polymer (**P1**) a high hole mobility ( $\sim 10^{-2}$  cm<sup>2</sup> Vs<sup>-1</sup>) and a low-lying HOMO energy level (5.22 eV). Preliminary experiments in bulk heterojunction solar cells using **P1** as the electron donor demonstrated a high power conversion efficiency of 4.8% even with PC<sub>61</sub>BM as the electron acceptor. The introduction of an electron-withdrawing fluorine atom into the thieno[3,4-*b*]thiophene unit at the C3 position (**P2**) lowers the HOMO energy level and consequently improves the open circuit voltage from 0.78 to 0.86 V. These values are about 0.1 V higher than those reported for their analogues based on alkoxy-substituted benzo[1,2-*b*:4,5-*b*']dithiophene unit with less electron-donating alkyl chains is able to lower the HOMO energy levels of this class of polymers without increasing their band gap energy.

### Introduction

Organic solar cells based on conjugated polymers and soluble fullerene derivatives have the potential to offer low-cost solar electricity by using spin-coating, ink-jet printing, or roll-to-roll printing techniques to fabricate large-area photovoltaic devices on flexible and light-weight substrates.<sup>1-4</sup> The power conversion efficiencies (PCEs) of solution-processed bulk heterojunction (BHJ) solar cells<sup>5</sup> have recently exceeded 6%, primarily due to the development of low band gap p-type materials<sup>6,7</sup> and better control of the interpenetrating electron donor/acceptor network by using processing additives.8-10 Among these materials, alternating thieno[3,4-b]thiophene and benzo[1,2-b:4,5-b']dithiophene copolymers show the best performance with a PCE up to 7.4% when [6,6]-phenyl  $C_{71}$ -butyric acid methyl ester (P $C_{71}$ BM) was used as an electron acceptor.<sup>11,12</sup> These materials are very interesting not only because of their small band gaps but also due to the possibility of tuning the HOMO and LUMO energy levels simultaneously without affecting the optical properties or the band gap energies of the polymers. Chen et al. showed that substitution of the ester group with a ketone group or/and the introduction of an electron-withdrawing fluorine atom into the

thieno[3,4-b]thiophene unit further lowered both the HOMO and LUMO energy levels of the resulting polymers.<sup>11</sup> This structureproperty relation allows us to increase the open circuit voltage  $(V_{\rm oc})$  but without increasing the band gap and reducing the short circuit current  $(J_{sc})$ . The polymer based on 3-fluorothieno[3,4-b] thiophene with ketone side chain showed the lowest LUMO and HOMO energy levels (3.45 and 5.22 eV respectively) and the best  $V_{\rm oc}$  (0.76 V) recorded for this class of materials.<sup>11</sup> We noticed that a large energy offset ( $\sim 0.9$  eV) exists between the LUMO levels of this series of polymers and the commonly used electron acceptor materials ([6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester  $(PC_{61}BM)$  or  $PC_{71}BM$ ). This energy offset is overly generous for efficient exciton dissociation;<sup>13</sup> a slight reduction in this energy offset should not affect the donor-acceptor charge transfer. This gives us an opportunity to further lower the LUMO and HOMO energy levels of this series of polymers to increase the  $V_{\rm oc}$  without losing the  $J_{sc}$ . One effective method to lower the HOMO energy level is to replace the alkoxy side chains on the benzo[1,2-b:4,5-b']dithiophene unit with less electron-donating alkyl chains.14,15 The combination of such monomer with the ketone-substituted thieno[3,4-b]thiophene monomers will offer new low band gap copolymers with deep HOMO energy levels. In order to keep the copolymers soluble in organic solvents for solution processing, new branched alkyl side chains have to be designed. In this paper, we report the synthesis of new alternating benzo[1,2-b:4,5-b']dithiophene and thieno[3,4-b]thiophene copolymers, P1 and P2, and their photovoltaic performance in BHJ solar cells using  $PC_{61}BM$  as the electron acceptor. P1 and P2 showed  $V_{oc}$  of 0.77 and 0.86 V, respectively, and a PCE up to 4.8%.

<sup>&</sup>lt;sup>a</sup>Institute for Microstructural Sciences, National Research Council of Canada, 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada. E-mail: jianping.lu@nrc-cnrc.gc; caye.tao@nrc-cnrc.gc.ca

<sup>&</sup>lt;sup>b</sup>Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada

### **Results and discussion**

### Material synthesis

Scheme 1 shows the synthesis of monomers 3 and 8. First, compound 1 was prepared in three steps according to the procedure reported for its analogue with a branched alkyl chain.<sup>16</sup> Then, compound 1 was converted to the fully aromatic derivative 2 in an 81% yield. The latter was brominated with Nbromosuccinimide to give monomer 3 as a light pink solid in an 83% yield. The monomer 8 was already published in the literature<sup>11</sup> but no information was given about its preparation. Therefore, we have developed independently a synthetic pathway for the preparation of monomer 8 in five steps starting from 1. As shown in Scheme 1, the treatment of 1 with ethylene glycol in refluxing benzene in the presence of a catalytic amount of p-toluenesulfonic acid offered the desired ketal 4 in a 95% yield. Lithiation of 4 with *n*-BuLi in THF and subsequent treatment with N-fluorobenzenesulfonimide furnished the fluorinated compound 5 in a 37% yield. Deprotection of 5 in THF in the presence of 3 N HCl solution provided compound 6 in an 89% yield. Finally, the conversion of 6 to the fully aromatic derivative 7 followed by the bromination of the latter gave the desired monomer 8 as an orange-pink solid in excellent yields.

The new branched alkyl substituted benzo[1,2-*b*:4,5-*b*']dithiophene **12** was prepared in three steps according to the procedure reported by Ong *et al.*<sup>17</sup> using benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione and alkyne as starting materials (Scheme 2). In our case, the 3-butyl-1-octyne **9** was prepared from 1-octyne. The latter was first treated with 2 equiv. of *n*-BuLi in hexane. Then, the regioselective alkylation at C-3 position<sup>18</sup> with bromobutane gave compound **9** in a 36% yield. Compound **9** was treated with isopropylmagnesium chloride to give the corresponding alky-nylmagnesium chloride, which then reacted with benzo[1,2-*b*:4,5-*b*']dithiophene-4,8-dione. After reduction with SnCl<sub>2</sub>, compound **10** was obtained in a 50% yield. Finally, the treatment of **11** with *n*-BuLi in THF, followed by the addition of trimethyltin

chloride, provided compound 12 as white needles in a 70% yield. As described in Scheme 2, P1 and P2 were synthesized by Stille coupling reaction between monomer 12 and the corresponding thieno[3,4-b]thiophene derivative in refluxing toluene/DMF (10/1) using  $Pd(PPh_3)_4$  as the catalyst. P1 and P2 were easily dissolved in chlorinated solvents such as chloroform, chlorobenzene and dichlorobenzene. P1 and P2 have relatively high number-average molecular weights  $(M_n)$  of 27 and 20 kDa and polydispersity indexes (PDI) of 2.0 and 1.75, respectively.<sup>16</sup> We note here that when the two 4-butyloctyl side chains of P2 were replaced by the shorter and more symmetric 3-propylhexyl, the resulting polymer had a lower solubility and precipitated out of the solution during the polymerization. Therefore, the soluble fraction extracted with refluxing chlorobenzene has a lower molecular weight ( $M_{\rm p} = 17$  kDa; PDI = 1.60) than P2 and forms aggregates quickly after cooling to room temperature. Interestingly, using our synthetic approach, the substitution pattern and length of the branched alkyl chain of the benzo[1,2-b:4,5-b']dithiophene unit could be easily tuned to obtain a balance between good solubility and efficient interchain packing of the resulting polymer.19

### Optical and electrochemical properties

The optical properties of **P1** and **P2** thin films were characterized by UV-vis absorption spectroscopy. As shown in Fig. 1, **P1** and **P2** showed absorption maxima at 687 and 676 nm, respectively. These values coincide well with the maximum photon flux region in the solar spectrum ( $\sim$ 700 nm).<sup>2</sup> The optical band gaps of **P1** and **P2** calculated from the onset of the films absorption are 1.63 and 1.65 eV, respectively. These values are consistent with their analogues based on alkoxy-substituted benzo[1,2-*b*:4,5-*b'*] dithiophene,<sup>11</sup> which means the replacement of the alkoxy chains by alkyl chains almost has little influence on the band gaps of **P1** and **P2** were evaluated by cyclic voltammetry (CV) measurement. Both polymers underwent reversible cathodic reduction



Scheme 1 Synthetic route for thieno[3,4-b]thiophene monomers.



Scheme 2 Synthetic route for benzo[1,2-b:4,5-b']dithiophene monomer and corresponding polymers.



Fig. 1 Absorption spectra of P1 and P2 in thin films.

and anodic oxidation (Fig. 2). The onset potentials of the oxidation wave of P1 and P2 appeared at 0.82 and 0.94 V, corresponding to HOMO energy levels of 5.22 and 5.34 eV, respectively. Based on the onset potentials of the first reduction wave, the LUMO energy levels of P1 and P2 were estimated to be at 3.41 and 3.53 eV, respectively. Both HOMO and LUMO energy levels of P1 and P2 are about 0.1 eV lower than the values obtained from their analogues based on alkoxy-substituted benzo[1,2-b:4,5-b']dithiophene,<sup>11</sup> confirming that the replacement of the alkoxy chains on the benzo[1,2-b:4,5-b']dithiophene unit with less electron-donating alkyl chains lowers both the HOMO and LUMO energy levels of this class of polymers and meanwhile keeps their band gap energy almost unchanged. It is worth noting that the electrochemical band gaps of P1 and P2 are higher than the optically measured ones, as already observed by Chen et al. for the similar polymers based on alkoxy-



**Fig. 2** Cyclic voltammograms of **P1** and **P2** films cast on a platinum electrode in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN solution.

substituted benzo[1,2-*b*:4,5-*b'*]dithiophene.<sup>11</sup> This could be related to the interface charge injection barrier due to the presence of insulating side chains between the polymer film and the electrode surface.<sup>20,21</sup>

#### Thermal properties

Differential scanning calorimetry (DSC) analysis showed that both polymers **P1** and **P2** are crystalline materials with melting points at 203.2 and 208.5 °C, respectively (Fig. 3). However, **P1** has a higher crystallinity and its melting enthalpy reaches 7.14 J  $g^{-1}$ . In contrast, the melting enthalpy of **P2** is only 3.53 J  $g^{-1}$ . In addition, **P1** tends to form crystalline structures when it is cooled from the melted state. Therefore, no obvious glass transition is observed during the second DSC heating scan. **P2** shows a different thermal behavior. Its second DSC scan reveals a glass



Fig. 3 DSC curves of P1 and P2 collected under  $N_2$  at a heating rate of 10 °C min<sup>-1</sup>.

transition at 143.7 °C, and a broad melting process above 185 °C. This means that the substitution of the F atom on the polymer backbone slightly increases the melting point but retards the recrystallization process probably due to the asymmetric molecular structure of the new polymer (**P2**). In fact, it has been shown with some poly(2,7-carbazole) derivatives that symmetric polymers have higher structural organization in the solid state than their corresponding asymmetric polymers.<sup>22</sup>

### Field-effect transistor mobility

The hole mobilities of **P1** and **P2** were measured using an organic field-effect transistor (OFET) technique. Bottom contact OFETs of these two copolymers were fabricated on SiO<sub>2</sub>/Si substrates as described in the Experimental section. **P1** and **P2** were found to exhibit typical p-type organic semiconductor characteristics (Fig. 4) with hole mobilities of  $1 \times 10^{-2}$  and  $4 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. The higher hole mobility of **P1** is probably related to its superior crystallinity, as observed by the DSC analysis. It is well known that crystalline polymers produce organized

structures in the solid state, leading to considerable improvement in their charge transport properties.<sup>23–25</sup>

#### Photovoltaic response

Photovoltaic properties of **P1** and **P2** were investigated in BHJ solar cells, using a device structure of ITO/PEDOT:PSS/polymer:  $PC_{61}BM/LiF/A1$  with a device active area of 1.0 cm<sup>2</sup>. Due to the good solubility of **P1** and **P2** in both chloroform (CF) and 1,2-dichlorobenzene (ODCB) at room temperature, these two solvents were used to prepare the polymer: $PC_{61}BM$  composite films in order to compare their effect on the device performance. The photovoltaic performances of **P1** and **P2** were evaluated using a polymer :  $PC_{61}BM$  weight ratio of 1 : 2 and an active layer thickness of ~100 nm. The devices were tested under AM 1.5G irradiation of 100 mW cm<sup>-2</sup> calibrated with a KG5 filter covered silicon photovoltaic solar cell. The device performance data are summarized in Table 1, where the PCEs were calculated using the  $J_{sc}$  obtained from the integration of the external quantum efficiency and the AM 1.5G solar spectrum.

As we can see in Table 1, using only chloroform as the solvent, **P1** and **P2** exhibited a similar PCE of 2.3% with relatively low  $J_{sc}$ of 6.1 and 5.4 mA cm<sup>-2</sup>, respectively. In both cases, the AFM images of the polymer:PC<sub>61</sub>BM composites show large domains with a diameter of about 150–200 nm (Fig. 5). Such big domain size favors the exciton recombination and consequently reduces the charge separation efficiency.<sup>1,26</sup> As a result, the photocurrent density values are low. We note here that when 1,2-dichlorobenzene is used as the processing solvent for **P1** and **P2**, the PCE values and films morphology (Fig. 5) are very similar to those obtained with the chloroform. According to these results, one can suggest that the observed large domains are not related to the solubility of **P1** and **P2** in chloroform or 1,2-dichlorobenzene but to the low miscibility of these polymers with PC<sub>61</sub>BM.

The use of processing additives, such as 1,8-diiodooctane (DIO), has been proven an effective method to modify and control the nano-scale morphology in polymer solar cells.<sup>8-10</sup> Therefore, new **P1** and **P2** based devices have been prepared using chloroform/DIO (97/3, v/v) mixture as the solvent. The



Fig. 4 Source–drain current ( $I_{DS}$ ) versus source–drain voltage ( $V_{DS}$ ) at different gate voltages ( $V_G$ ) and transfer characteristics in the saturation regime at constant source–drain voltage ( $V_{DS} = -100$  V) for OFET using spin-coated P1 on SiO<sub>2</sub>/Si substrate as the active channel.

Table 1 Performance parameters of polymer solar cells using PC<sub>61</sub>BM as an electron acceptor

Polymer	Solvent	$V_{\rm oc}/{ m V}$	$J_{\rm sc}{}^a/{\rm mA~cm^{-2}}$	FF	PCE <sup><i>a</i></sup> (%)
P1	CHCl <sub>3</sub>	0.82	6.1	0.47	2.3
P1	$CHCl_3 + 3\% DIO$	0.78	9.8	0.63	4.8
P1	ODCB	0.81	5.6	0.49	2.2
P1	ODCB + 3% DIO	0.77	9.5	0.64	4.7
P2	CHCl <sub>3</sub>	0.90	5.4	0.48	2.3
P2	CHCl <sub>3</sub> + 3% DIO	0.86	7.3	0.62	3.9
P2	ODCB	0.89	5.0	0.50	2.2
P2	ODCB + 3% DIO	0.84	6.7	0.54	3.1

current density-voltage characteristics (J-V) of these devices are shown in Fig. 6a and the data are summarized in Table 1. One can see that using DIO as an additive considerably increases the  $J_{\rm sc}$  and fill factor (FF) for both polymers. In the case of **P1**, the device exhibited a  $J_{sc}$  of 9.8 mA cm<sup>-2</sup>, a  $V_{oc}$  of 0.78 V, and a FF of 63% with an overall PCE of 4.8%. As expected, the fluorinated polymer P2 showed a significantly enhanced  $V_{oc}$  of 0.86 V, as compared to that of P1. These  $V_{oc}$  values are about 0.1 V higher than those obtained with their analogues based on alkoxy-substituted benzo[1,2-b:4,5-b']dithiophene<sup>11</sup> indicating, as expected from HOMO energy levels, that replacement of the alkoxy chains by alkyl chains is an effective method to increase the  $V_{\rm oc}$  of the devices based on this class of polymers. The 1,2dichlorobenzene/DIO (97/3, v/v) mixture has also been tested as the processing solvent. As shown in Table 1, adding DIO to the 1,2-dichlorobenzene significantly improves the device performance but without exceeding those obtained with the chloroform/DIO (97/3, v/v) mixture. The significant enhancement in the  $J_{\rm sc}$  and FF, when DIO is used, could be explained by the change

in the morphology of the blend, as we can see from the AFM images (Fig. 5). In the case of **P1**, no large domains are present after adding DIO to the chloroform or 1,2-dichlorobenzene, and the domain structure becomes much smaller, indicating a better nano-scale phase separation between the polymers and PC<sub>61</sub>BM. We believe there is still more room for further optimizations to realize optimum morphology of the active layer, particularly for **P2**. It is worth noting that there was a slight drop in the  $V_{oc}$  when DIO was used as the processing additive. This phenomenon was typically observed in the literature.<sup>9</sup> The mechanism is not very clear at this moment. We think it may be related to the formation of a very thin PC<sub>61</sub>BM-enriched layer on PEDOT-PSS as DIO selectively dissolves PC<sub>61</sub>BM and has a high density (1.84 g mL<sup>-1</sup>).

The EQE spectra (Fig. 6b) show that **P1** and **P2** based solar cells harvest light very efficiently between 600 and 700 nm, as expected from the UV-vis spectra of **P1** and **P2** (Fig. 1). However, their absorption below 550 nm is weak, resulting in low EQE values in this spectral region. The use of  $PC_{71}BM$  as an



**Fig. 5** AFM phase images (surface scan area:  $1 \times 1 \ \mu\text{m}^2$ ) of the **P1**:PC<sub>61</sub>BM [(a), (b), (e) and (f)] and **P2**:PC<sub>61</sub>BM [(c), (d), (g) and (h)] composite films prepared using the chloroform [(a) and (c)], the 1,2-dichlorobenzene [(b) and (d)], chloroform/DIO (97/3, v/v) mixture [(e) and (g)] and 1,2-dichlorobenzene/DIO (97/3, v/v) mixture [(f) and (h)].



Fig. 6 Current density–voltage curves measured under AM 1.5G irradiation of 100 mW cm<sup>-2</sup> (a) and EQE spectra (b) of polymer:PC<sub>61</sub>BM BHJ solar cells prepared from mixed solvents chloroform/DIO (97/3, v/v).

electron acceptor could potentially overcome this problem since  $PC_{71}BM$  has stronger absorption between 400 and 600 nm. This work is presently in progress. In addition, the molecular weight of  $P2 (M_n = 20 \text{ kDa})$  may be not high enough. We are optimizing our synthetic procedure to further increase its molecular weight.

### Conclusions

In conclusion, we report the synthesis of new alternating alkyl-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene and ketone-substituted thieno[3,4-*b*]thiophene copolymers. When branched 3-butyloctyl side chains were introduced to the benzo[1,2-*b*:4,5-*b'*]dithiophene unit at C4 and C8 positions, the resulting polymer **P1** showed excellent solubility, high hole mobility ( $\sim 10^{-2}$  cm<sup>2</sup> Vs<sup>-1</sup>) and low-lying HOMO energy level (5.22 eV). **P1** blended with PC<sub>61</sub>BM, demonstrated a  $V_{oc}$  of 0.78 V and a high PCE of 4.8%. **P2** with fluorinated thieno[3,4-*b*]thiophene exhibited a significantly improved  $V_{oc}$  of 0.86 V, as compared to that of **P1**. To the best of our knowledge, these are the highest  $V_{oc}$  values

reported for this class of materials. The results presented here show that the replacement of the alkoxy chains on the benzo[1,2b:4,5-b']dithiophene unit with less electron-donating alkyl chains allows us to increase the  $V_{\rm oc}$  of these polymers by 0.1 V but without increasing their band gap energy which remains around 1.64 eV. Further improvement in device performance is expected after the device optimization, such as replacing PC<sub>61</sub>BM with PC<sub>71</sub>BM and optimization of the active layer morphology by using new fabrication processes.

### **Experimental section**

### Materials

All starting materials, unless otherwise specified, were purchased from Aldrich Co. and used without further purification. The THF used in the reactions was freshly distilled over sodium under argon. Column chromatography was carried out on silica gel (size  $40-63 \mu m$ , pore size 60 Å, Silicycle). 1-(4,6-Dihydrothieno[3,4-*b*]thiophen-2-yl)octane-1-one (1) was synthesized according to the literature methods.<sup>16</sup> All other compounds were synthesized following the procedures described below.

### 1-(Thieno[3,4-b]thiophen-2-yl)octan-1-one (2)

In a 100 mL flask, 1.66 g (6.19 mmol) of 1 was dissolved in 21 mL of chloroform and cooled down to -40 °C. Then, 1.52 g (6.19 mmol) of 3-chloroperoxybenzoic acid (77%) dissolved in 10 mL of chloroform was added dropwisely and the resulting mixture was stirred for 30 min at -40 °C. The mixture was warmed up to room temperature and stirred for 30 min. The chloroform was removed under reduced pressure, and 6.2 mL of acetic acid anhydride was added and the mixture was refluxed for 20 min. The volatile substance was removed under reduced pressure and the oily crude material residue was purified by column chromatography (silica gel, 5% ethyl acetate in hexanes as eluent) to provide 1.33 g of the title product as a white solid (81% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.63 (d, 1H, J = 2.8 Hz), 7.59 (s, 1H), 7.27 (d, 1H, J = 2.8 Hz), 2.90 (t, 2H, J = 7.4 Hz), 1.74 (m, 2H), 1.32 (m, 8H), 0.88 (t, 3H, J = 6.8 Hz). HRMS (EI) calculated for C<sub>14</sub>H<sub>18</sub>OS<sub>2</sub> 266.0799, found 266.0803.

### 1-(4,6-Dibromothieno[3,4-b]thiophen-2-yl)octan-1-one (3)

In a 25 mL flask, 319 mg (1.2 mmol) of **2** was dissolved in 3 mL of DMF under argon. Then, 534 mg (3 mmol) of *N*-bromosuccinimide dissolved in 3 mL of DMF was added, and the mixture was stirred for 25 min at room temperature in the absence of light. The mixture was quenched with 20 mL of 5% sodium thiosulfate solution in an ice bath and extracted three times with diethyl ether. The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (silica gel, 4% ethyl acetate in hexanes as eluent) to provide 420 mg of the title product as a light pink-orange solid (83% yield). <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>, ppm)  $\delta$  6.86 (s, 1H), 2.27 (t, 2H, J = 7.2 Hz), 1.57 (m, 2H), 1.26 (m, 2H), 1.18 (m, 6H), 0.90 (t, 3H, J = 7.0 Hz). HRMS (EI) calculated for C<sub>14</sub>H<sub>16</sub>Br<sub>2</sub>OS<sub>2</sub> 421.9409, found 421.9016.

### 2-(4,6-Dihydrothieno[3,4-*b*]thiophen-2-yl)-2-heptyl-1,3dioxolane (4)

A mixture of 2.0 g (7.5 mmol) of compound 3, 4.65 g (75 mmol) of ethylene glycol, 52 mL of benzene and 0.14 g (0.75 mmol) of p-toluenesulfonic acid monohydrate was heated at reflux under argon in a 100 mL flask equipped with a Dean-Stark apparatus. After 72 h, the reaction mixture was cooled to room temperature and 125 mL of ethyl acetate and 48 mL of water were added. The mixture was extracted three times with ethyl acetate. The combined organic fractions were washed with 80 mL of 5% NaHCO<sub>3</sub> solution, dried over magnesium sulfate and the solvents were removed under reduced pressure. The oily crude material was purified by column chromatography (silica gel, 50%) dichloromethane in hexanes as eluent) to provide 2.2 g of the title product as a pale yellow oil (95% yield): <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ , ppm)  $\delta$  6.74 (s, 1H), 4.12 (m, 2H), 3.99 (m, 4H), 3.91 (m, 2H), 1.91 (m, 2H), 1.38 (m, 2H), 1.27 (m, 8H), 0.87 (t, 3H, J = 7.2 Hz).

### 2-(3-Fluoro-4,6-dihydrothieno[3,4-*b*]thiophen-2-yl)-2-heptyl-1,3-dioxolane (5)

In a 100 mL flame-dried flask, 1.51 g (4.85 mmol) of 4 was dissolved in 42 mL of dry THF. The solution was cooled at -78 °C and 2.50 mL of *n*-BuLi solution (2.5 M in hexanes, 6.31 mmol) was added dropwise under argon. After addition, the mixture was stirred at -78 °C for 2 h. A solution of 1.99 g (6.31 mmol) N-fluorobenzenesulfonimide in 12 mL of THF was added dropwise at -78 °C. After 1.5 h, the cold bath was removed and the mixture was stirred at room temperature for 2.5 h. The reaction was quenched with cold NH<sub>4</sub>Cl solution and extracted three times with ethyl acetate. The combined organic fractions were washed with H<sub>2</sub>O, dried over magnesium sulfate and the solvents were removed under reduced pressure. The oily crude material was purified by column chromatography (silica gel, 50% dichloromethane in hexanes as eluent) to provide 0.64 g of the title product as a pale yellow oil (37% yield, purity by <sup>1</sup>H NMR 92%). Compound 5 was not stable and was used immediately. <sup>1</sup>H NMR of compound 5 (400 MHz, acetone-d<sub>6</sub>, ppm)  $\delta$  4.13 (m, 2H), 4.00 (m, 2H), 3.96 (m, 4H), 1.98 (m, 2H), 1.40 (m, 2H), 1.27 (m, 8H), 0.87 (t, 3H, J = 6.8 Hz).

### 1-(3-Fluoro-4,6-dihydrothieno[3,4-b]thiophen-2-yl)octane-1-one (6)

In a 25 mL flask, 0.62 g (1.88 mmol) of **5** was dissolved in 7 mL of THF. The solution was cooled at 0 °C, and 2.4 mL of 3 N HCl solution was added dropwise. After addition, the mixture was stirred at room temperature for 4 h. 20 mL of ethyl acetate and 100 mL of water were added. The organic layer was separated, and the aqueous layer was extracted three times with ethyl acetate. The combined organic fractions were washed with H<sub>2</sub>O, 5% NaHCO<sub>3</sub> solution, dried over magnesium sulfate and the solvents were removed under reduced pressure. The crude solid material was purified by column chromatography (silica gel, 50% dichloromethane in hexanes as eluent) to provide 0.48 g of the title product as a white solid (89% yield). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>, ppm)  $\delta$  4.24 (t, 2H, J = 3.0 Hz), 4.04 (t, 2H, J = 3.2 Hz), 2.85 (td, 2H,  $J_{(H-H)}$  = 7.2 Hz and  $J_{(H-F)}$  = 2.0 Hz), 1.67

(m, 2H), 1.32 (m, 8H), 0.88 (t, 3H, J = 7.0 Hz). HRMS (EI) calculated for C<sub>14</sub>H<sub>19</sub>FOS<sub>2</sub> 286.0861, found 286.0854.

### 1-(3-Fluorothieno[3,4-b]thiophen-2-yl)octane-1-one (7)

In a 25 mL flask, 0.48 g (1.67 mmol) of 6 was dissolved in 7 mL of chloroform and cooled down to -40 °C. Then, 0.38 g (1.67 mmol) of 3-chloroperoxybenzoic acid (77%) dissolved in 3 mL of chloroform was added dropwise and the mixture was stirred for 30 min at -40 °C. The mixture was warmed up to room temperature and stirred for 75 min. The chloroform was removed under reduced pressure, and 2 mL of acetic acid anhydride was added and the mixture was refluxed for 20 min. The volatile substance was removed under reduced pressure and the crude material was purified by column chromatography (silica gel, 4% ethyl acetate in hexanes as eluent) to provide 0.41 g of the title product as a white solid (86% yield). <sup>1</sup>H NMR (400 MHz, acetone-d<sub>6</sub>, ppm)  $\delta$  8.08 (d, 1H, J = 2.8 Hz), 7.70 (t, 1H, J<sub>(H-H)</sub> = 2.6 Hz and  $J_{(H-F)} = 2.6$  Hz), 2.99 (td, 2H,  $J_{(H-H)} = 7.2$  Hz and  $J_{(H-F)} = 2.4$  Hz), 1.71 (m, 2H), 1.30–140 (m, 8H), 0.89 (t, 3H, J =7.0 Hz). HRMS (EI) calculated for C14H17FOS2 284.0705, found 284.0698.

### 1-(3-Fluoro-4,6-dibromothieno[3,4-b]thiophen-2-yl)octan-1-one (8)

In a 25 mL flask, 200 mg (0.70 mmol) of 7 was dissolved under argon in 2 mL of DMF. Then, 313 mg (1.76 mmol) of *N*-bromosuccinimide dissolved in 2 mL of DMF was added, and the mixture was stirred for 75 min at room temperature in the absence of light. The mixture was quenched with 10 mL of 5% sodium thiosulfate solution cooled with ice bath and extracted three times with diethyl ether. The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (silica gel, 3% ethyl acetate in hexanes as eluent) to provide 250 mg of the title product as a light pinkorange solid (81% yield). <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>, ppm)  $\delta$  2.56 (td, 2H,  $J_{(H-H)} = 7.2$  Hz and  $J_{(H-F)} = 2.4$  Hz), 1.62 (m, 2H), 1.18–1.30 (m, 8H), 0.89 (t, 3H, J = 7.2 Hz). HRMS (EI) calculated for C<sub>14</sub>H<sub>15</sub>Br<sub>2</sub>FOS<sub>2</sub> 439.9315, found 439.8898.

### 3-Butyl-1-octyne (9)

In a 500 mL oven-dried flask, 10.0 g of 1-octyne (90.7 mmol) and 80 mL of anhydrous hexanes were added under argon. After the solution was cooled to -78 °C in a dry ice/acetone bath, 79 mL of *n*-butyl lithium (2.5 M in hexanes) was added *via* a syringe with vigorous stirring. A lot of white solids precipitated out of the solution in the beginning. With more *n*-butyl lithium added, the white solids dissolved to form a clear but very viscous yellow solution. The resulting solution was further stirred at -42 °C in a dry ice/acetonitrile bath for another 1 h. Then, 12.3 g of freshly distilled 1-bromobutane (90 mmol) was added. The solution was allowed to warm to room temperature overnight. 40 mL of 6 M HCl aqueous solution was dropwise added at 0 °C. The organic layer was separated and washed with water. After removal of organic solvents on a rotary evaporator, the target product was separated from byproducts by fractional distillation under vacuum (65-75 °C/0.2 mm Hg). Totally, 5.40 g of clear colorless oil was obtained in 36% yield. <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>,

ppm)  $\delta$  2.23 (m, 1H), 1.89 (d, 1H, J = 2.4 Hz), 1.60–1.15 (m, 14H), 0.92–0.85 (m, 6H). MS (ESI) m/z 204.92 [(M + K)<sup>+</sup> calculated for C<sub>12</sub>H<sub>22</sub> 205.26].

### 4,8-Bis(3-butyloct-1-ynyl)benzo[1,2-b:4,5-b']dithiophene (10)

This compound was synthesized following a literature procedure<sup>17</sup> except that 1-dodecyne was replaced with 3-butyl-1-octyne. Briefly, 4.53 g (27.3 mmol) of 3-butyl-1-octyne in 7 mL of dry THF was first treated with 13 mL of isopropylmagnesium chloride (2 M in THF, 26 mmol). The resulting 3-butyloct-1-ynylmagnesium chloride directly reacted with 1.00 g of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (4.54 mmol) in anhydrous THF, and the intermediate product was reduced with SnCl<sub>2</sub>/HCl solution (7 g in 18 mL 10% HCl) to give crude 4,8-bis(3-butyloct-1-ynyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**10**), which was purified by column chromatography (silica gel, 10% dichloromethane in hexanes as eluent) to give 1.20 g of bright yellow solids (50% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.55 (d, 2H, *J* = 5.6 Hz), 7.49 (d, 2H, *J* = 5.6 Hz), 2.74 (m, 2H), 1.75–1.32 (m, 28H), 1.00–0.85 (m, 12H).

### 4,8-Bis(3-butyloctyl)benzo[1,2-b:4,5-b']dithiophene (11)

This compound was synthesized following a literature procedure.<sup>17</sup> Briefly, 1.15 g of compound **10** (2.22 mmol) was reduced by hydrogen reduction using 10% Pd/C (0.24 g) as the catalyst in 40 mL of anhydrous THF overnight. After purification by column chromatography using hexanes as an eluent, the target product was obtained in 70% yield as a white solid (0.82 g). <sup>1</sup>H NMR (400 MHz, benzene-d<sub>6</sub>, ppm)  $\delta$  7.37 (d, 2H, J = 5.6 Hz), 7.35 (d, 2H, J = 5.6 Hz), 3.22–3.15 (m, 4H), 1.85–1.78 (m, 4H), 1.52–1.22 (m, 30H), 0.98–0.85 (m, 12H).

### 2,6-Bis(trimethyltin)-4,8-bis(3-butyloctyl)benzo[1,2-*b*:4,5-*b'*] dithiophene (12)

0.81 g of compound 11 (1.53 mmol) was dissolved in 20 mL of anhydrous THF, and cooled to -78 °C in a dry ice/acetone bath. 1.5 mL of n-butyl lithium (2.5 M in hexanes) was added via a syringe with stirring. After stirring at -78 °C for 0.5 h, the cold bath was removed, and the reaction mixture was further stirred at room temperature for 2 h. A lot of white solids formed. The mixture was cooled down to -78 °C again, and 4.4 mL of trimethyltin chloride (1 M) was added in one potion. After stirring at -78 °C for 0.5 h, the cold bath was removed, and the clear reaction solution was stirred at room temperature for another 2 h. 50 mL of water was added, and the mixture was extracted with hexanes. The organic layer was separated, dried over MgSO<sub>4</sub>, and concentrated under reduced pressure. Recrystallization of the residue from isopropanol two times yielded the product as white needles (0.92 g, 70% yield). <sup>1</sup>H NMR (400 MHz, acetoned<sub>6</sub>, ppm) δ 7.65 (s, 2H), 3.25–3.18 (m, 4H), 1.80–1.65 (m, 4H), 1.55-1.25 (m, 30H), 0.98-0.85 (m, 12H), 0.46 (m, 18H). MS (ESI) m/z 889.62 [(M + K)<sup>+</sup> calculated for C<sub>40</sub>H<sub>70</sub>S<sub>2</sub>Sn<sub>2</sub> 889.39].

### Polymer P1

In a 50 mL oven-dried one-necked flask, 151 mg (0.356 mmol) of monomer **3** and 303.5 mg (0.356 mmol) of monomer **12** were added. The flask was purged 3 times with argon, then 25 mg (0.02

mmol) of Pd(PPh<sub>3</sub>)<sub>4</sub> and a condenser were added under argon atmosphere. 7 mL of degassed toluene/DMF (10:1, v/v) was added and the reaction mixture was stirred at 110 °C under argon atmosphere. After 41 h of reaction time, 110 mg of bromobenzene (0.7 mmol) in 1 mL of degassed toluene/DMF (10:1, v/v) was added to the reaction and the reaction was kept at 110 °C for an additional 5 hours. The polymerization solution was cooled to room temperature and precipitated into methanol. The resultant polymer was collected by filtration, dried, and extracted with hexanes and dichloromethane using a Soxhlet extraction apparatus. The remaining solid was extracted with 250 mL of toluene. After evaporation of the toluene under reduced pressure, methanol was added and 240 mg of the polymer was collected by filtration (85% yield). Molecular weight (by GPC using chlorobenzene as eluent and monodispersed polystyrene as standard):  $M_n = 27$  kDa and PDI = 2.0. <sup>1</sup>H NMR (400 MHz, 1,2-dichlorobenzene-d<sub>4</sub>, 140 °C, ppm) δ 7.87 (br, 1H), 7.60–7.40 (br, 2H), 3.15 (br, 6H), 2.00–1.35 (m, 44H), 0.95–1.25 (m, 15H).

### Polymer P2

Polymer P2 was synthesized according to the procedure for the synthesis of polymer P1. Equimolar monomer 8 (153 mg, 0.346 mmol) and monomer 12 (295 mg, 0.346 mmol) were used. After 62 h of reaction time, 12 mg of trimethylphenyltin (0.05 mmol) in 0.5 mL of degassed toluene/DMF (10: 1, v/v) was added, and the reaction was kept at 110 °C for an additional 5 hours. 50 mg of bromobenzene (0.32 mmol) in 1 mL of degassed toluene/DMF (10:1, v/v) was then added, and the reaction was kept at 110 °C for an additional 6 hours to complete the end-capping reaction. The polymerization solution was cooled to room temperature and precipitated into methanol. The resultant polymer was collected by filtration, dried, and extracted with hexanes and dichloromethane using a Soxhlet extraction apparatus. The remaining solid was extracted with 250 mL of toluene. After evaporation of the toluene under reduced pressure, methanol was added and 202 mg of the polymer was collected by filtration (70%) yield). Molecular weight (by GPC using chlorobenzene as eluent and monodispersed polystyrene as standard):  $M_{\rm n} = 20$  kDa and PDI = 1.75. <sup>1</sup>H NMR (400 MHz, 1,2-dichlorobenzene-d<sub>4</sub>, 140 °C, ppm) & 7.82 (br, 1H), 7.46 (br, 1H), 3.22 (br, 6H), 2.00–1.35 (m, 44H), 0.95–1.25 (m, 15H).

### Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrometer. Chemical shifts were reported as  $\delta$  values (ppm) relative to internal tetramethylsilane. The number-average ( $M_n$ ) molecular weight and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography (GPC) using a Waters Breeze HPLC system with a 1525 binary HPLC pump and a 2414 differential refractometer. Chlorobenzene was used as eluent and commercial polystyrenes were used as standards. UV-visible absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer. The differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC 2920. DSC traces were measured at a scanning rate of 10 °C min<sup>-1</sup>, under a nitrogen flow (50 mL min<sup>-1</sup>). Cyclic voltammetry (CV) Downloaded by University of Virginia on 01 July 2012 Published on 17 June 2011 on http://pubs.rsc.org | doi:10.1039/C1JM11229E measurements were carried out under argon in a three-electrode cell using 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in anhydrous CH<sub>3</sub>CN as the supporting electrolyte. The polymers were coated on a platinumworking electrode. The CV curves were recorded referenced to an Ag quasi-reference electrode, which was calibrated using a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (4.8 eV below the vacuum level) as an external standard. The  $E_{1/2}$  of the Fc/Fc<sup>+</sup> redox couple was found to be 0.40 V versus the Ag quasi-reference electrode. Therefore, the HOMO and LUMO energy levels of the polymers can be estimated using the empirical  $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.40)$  eV and  $E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} + 4.40)$  eV, respectively, where  $E_{\text{ox}}^{\text{onset}}$  and  $E_{\text{red}}^{\text{onset}}$  are the onset potentials for oxidation and reduction relative to the Ag quasi-reference electrode, respectively.

### Device fabrication and characterization

The hole mobilities of P1 and P2 were measured using organic field-effect transistor (OFET) measurements. A heavily doped n-Si wafer with an overlayer of SiO<sub>2</sub> (230 nm,  $C_i = 15 \text{ nF cm}^{-2}$ ) was used as the substrate. With bottom contact configuration, sputtered gold source and drain electrodes were used to contact the polymer film. An interdigitated layout was used for the OFET where the channel length and width are 20 µm and 1 mm, respectively. A chloroform or 1,2-dichlorobenzene solution of the desired polymer was spin cast to cover the source and drain electrodes. The OFETs were characterized inside a dark box at room temperature under nitrogen protection with a semiconductor parameter analyser (HP4145A). The hole mobilities were calculated in the saturation regime at  $V_{\text{DS}} = -100 \text{ V}$  using the following equation  $I_{\rm DS} = (W/2L)\mu C_{\rm i}(V_{\rm G} - V_{\rm T})^2$ , where  $V_{\rm DS}$ is the source-drain voltage, IDS is the source-drain current, W and L are, respectively, the channel width and length,  $\mu$  is the field-effect mobility,  $C_i$  is the capacitance per unit area of the  $SiO_2$  layer, and  $V_G$  and  $V_T$  are, respectively, the gate voltage and threshold voltage.27,28

The BHJ solar cells were prepared on commercial glass slides coated with patterned ITO. The thickness and sheet resistance of the ITO are 150 nm and 12  $\Omega$  per square, respectively. The active area of each solar cell device is 1.0 cm<sup>2</sup> with a length : width ratio of 4 : 1. The substrates were cleaned by sonicating sequentially in detergent, DI water, acetone, and isopropanol. Immediately prior to device fabrication, the substrates were treated in a UV-ozone oven for 15 min. First, a poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS) thin film (30 nm) was spin-coated and then baked at 140 °C for 15 min. Secondly, an active layer was spin-coated on top of the PEDOT-PSS from a chloroform or 1,2-dichlorobenzene solution of polymer:  $PC_{61}BM$  with a weight ratio of 1 : 2. In the case of the devices using an additive, 1,8-diiodooctane with a 3% volume ratio was added to the solutions before use. Finally, 2 nm of LiF and 120 nm of Al were deposited on the top of the active layer in a vacuum of  $5 \times 10^{-7}$  Torr to form the top electrode. The solar cells (with no protective encapsulation) were then tested in air under AM 1.5G irradiation of 100 mW cm<sup>-2</sup> (ScienceTech Inc., SS 500W solar simulator) calibrated with a KG5 filter covered silicon photovoltaic solar cell traced to the National Renewable Energy Laboratory (NREL). Current-voltage (I-V) characteristics were recorded using a computer-controlled

Keithley 2400 source meter. The external quantum efficiency (EQE) was performed using a Jobin-Yvon Triax spectrometer, a Jobin-Yvon xenon light source, a Merlin lock-in amplifier, a calibrated Si UV detector, and an SR570 low noise current amplifier.

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