

## Effect of substituted side chain on donor-acceptor conjugated copolymers

Shinuk Cho,<sup>1,a)</sup> Jung Hwa Seo,<sup>1</sup> Sun Hee Kim,<sup>2</sup> Suhee Song,<sup>3</sup> Youngeup Jin,<sup>3</sup>  
Kwanghee Lee,<sup>2,a)</sup> Hongsuk Suh,<sup>3,a)</sup> and Alan J. Heeger<sup>1</sup>

<sup>1</sup>Center for Polymers and Organic Solids, University of California at Santa Barbara,  
Santa Barbara, California 93106-5090, USA

<sup>2</sup>Department of Materials Science and Engineering, Gwangju Institute of Science and Technology,  
Gwangju 500-712, Republic of Korea

<sup>3</sup>Department of Chemistry, Pusan National University, Busan 609-735, Republic of Korea

(Received 15 September 2008; accepted 9 December 2008; published online 29 December 2008)

The effects of substitute side chain (alkyl or alkoxy) on optical and electrical properties of low-band-gap conjugated copolymers were investigated using poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-di-2-thienyl-2,1,3-benzothiadiazole), poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-bis(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole) (PININE-DHTBT), and poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-bis[3-(hexyloxy)-2-thienyl]-2,1,3-benzothiadiazole) (PININE-DHOTBT). Alkyl introduced PININE-DHTBT exhibits blueshifted absorption spectrum, while alkoxy introduced PININE-DHOTBT exhibits redshifted absorption spectrum. Because of steric hindrance of alkyl or alkoxy side chain, highest occupied molecular orbitals of PININE-DHTBT and PININE-DHOTBT highly localized on donor segments, thereby decreasing hole mobilities of PININE-DHTBT and PININE-DHOTBT. Consequently, despite the spectral advantage of PININE-DHOTBT for photovoltaic cells, the actual solar cell property of PININE-DHOTBT was not enhanced. © 2008 American Institute of Physics. [DOI: 10.1063/1.3059554]

Conjugated copolymers with electron donor-acceptor (D-A) units in the repeat unit have drawn considerable attention for bulk heterojunction photovoltaic (PV) cells because their intramolecular delocalization over the electron-donating and electron-accepting segments can lead to low-band-gap conjugated polymers that enable efficient harvesting of the solar spectrum.<sup>1-10</sup> By using donor units with highest occupied molecular orbital (HOMO) corresponding to high ionization potential, one can also expect large open circuit voltages in bulk heterojunction (BHJ) PV cells.<sup>6</sup> Because they exhibit relatively high hole mobilities, such D-A conjugated copolymers are also of interest as the active materials in polymer field-effect transistors (PFETs).<sup>8-11</sup>

A number of D-A copolymers have been generated and subsequently characterized, including 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DTBT) combined with conventional conjugated donor units, such as fluorene,<sup>1,3,11</sup> 2,7-carbazole,<sup>8,9</sup> and 4,4-dialkyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl.<sup>2</sup> Although conjugated core unit possesses solubilizing power, D-A copolymers have relatively low solubility if it has high molecular weight (Mw) fraction. Achieving high Mw with good solubility is one of the important factors for polymer electronic devices; generally, the highest performance was obtained from highest Mw material.<sup>12,13</sup>

The general approach to improve the solubility in D-A copolymers is the introduction of either alkyl or alkoxy side chains at the thiophene unit.<sup>3,14-17</sup> Substituted side chains, however, often significantly alter the conjugated chain configuration and thereby affect their electronic properties. Thus, resultant polymers have somewhat different properties compared to the original analogs.<sup>7,18</sup> Although the effects of side chain substitution in conventional conjugated polymers are

well known, the effect of side chain in D-A alternating copolymers has not yet been fully explored.

We have investigated the effect of substituted side chain (alkyl or alkoxy) on the optical and electrical properties of D-A conjugated copolymers, poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-di-2-thienyl-2,1,3-benzothiadiazole) (PININE-DTBT), poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-bis(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole) (PININE-DHTBT), and poly(2,7-dihydroindeno[2,1-a]indene-co-4,7-bis[3-(hexyloxy)-2-thienyl]-2,1,3-benzothiadiazole) (PININE-DHOTBT).

Polymer solar cells were prepared according to the following procedure. Conducting poly(3,4-ethylenedioxyethiophene)-polystyrene sulfonic acid (PEDOT:PSS, Baytron P) was spin cast (5000 rpm) with thickness of ~40 nm from aqueous solution on the pre-cleaned indium tin oxide glass. The dichlorobenzene solution comprised of PININE-DTBT (1 wt %): [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) (3.5 wt %), PININE-DHTBT (1 wt %): PCBM (4 wt %), and PININE-DHOTBT (1 wt %): PCBM (4 wt %) was then spin cast at 3000 rpm with thickness ~80 nm on top of the PEDOT layer. Finally, a ~120 nm Al electrode was deposited on top. Measurements were done with the solar cells inside the glove box filled with N<sub>2</sub> gas using a high quality optical fiber to guide the light from a solar simulator (AM1.5G) outside the glovebox. Current density-voltage curves were measured with a Keithley 236 source measurement unit.

PFETs (with the top contact geometry) were fabricated on heavily doped *n*-type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO<sub>2</sub>) layer with thickness of 200 nm. The active layer was deposited by spin coating at 2500 rpm. Prior to active layer deposition, SiO<sub>2</sub> surfaces were treated with octyltrichlorosilane to make surface hydrophobic. All solutions were prepared at 0.5 wt %

<sup>a)</sup>Authors to whom correspondence should be addressed. Electronic addresses: sucho@physics.ucsb.edu, klee@gist.ac.kr and hssuh@pusan.ac.kr.

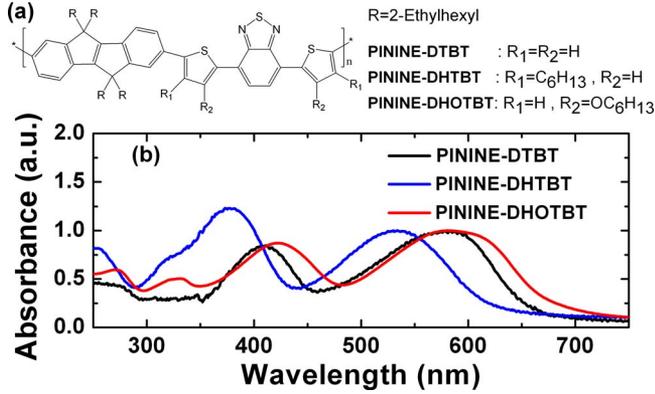


FIG. 1. (Color online) (a) Chemical structure of PININE derivatives and (b) UV-visible absorption spectra of thin films.

concentration in chlorobenzene. The thickness of the deposited films was about 60 nm. Prior to deposition of source-drain electrodes, the films were dried on hot plate stabilized at 80 °C for 30 min. All fabrication processes were carried out in the glovebox filled with  $N_2$ . Source and drain electrodes using Au were deposited by thermal evaporation using shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length ( $L$ ) and channel width ( $W$ ) were 50  $\mu\text{m}$  and 1.5 mm, respectively. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200) under  $N_2$  atmosphere.

All thin film samples for UV-visible absorption were prepared by spin coating (3000 rpm, 60 s) on quartz substrates using 1 wt % solution. UV-visible absorption spectra were taken using a Varian 5E UV/visible/near infrared spectrometer.

Figure 1 shows UV-visible absorption spectra of the PININE-DTBT, PININE-DHTBT, and PININE-DHOTBT thin films along with their molecular structures. The details of synthesis and the chemical properties of these copolymers are described elsewhere.<sup>19</sup> All absorption spectra are typical of D-A conjugated copolymers films that show two distinct broad absorption peaks. Although the precise origin of the two absorption peaks is not known, the short-wavelength absorption peaks have been attributed to a delocalized  $\pi$ - $\pi^*$  transition in the polymer chains and long-wavelength absorption peaks attributed to a localized transition between the D-A-D charge transfer states in DTBT segment.<sup>5,20,21</sup> Although all the absorption spectra in Fig. 1 are similar in shape, substituted side chains on the thiophene moiety induce dramatic shifts in the absorption spectrum. For the PININE-DHTBT, the onset of absorption is blueshifted by 50 nm compared to the PININE-DTBT. In case of PININE-DHOTBT, however, the onset of absorption is redshifted by 20 nm compared to the PININE-DTBT. The redshift of the absorption spectrum of PININE-DHOTBT might originate from stronger ICT due to the oxygen in the alkoxy chain (the oxygen in alkoxy chain tends to make the thiophene unit more electron rich).

We have fabricated BHJ PV cells using the copolymer as donor with PCBM as the acceptor. The initial PV cell results are promising, as summarized in Table I. The PV cell fabricated using the BHJ mixture of PININE-DTBT and PCBM yields maximum power conversion efficiency (PCE) of 2%. With PININE-DHTBT and PCBM, because of the blueshifted absorption spectrum, the maximum PCE is 1.1%.

TABLE I. Photovoltaic properties and FET mobilities of PININE derivatives.

|   | PININE-DTBT          | PININE-DHTBT         | PININE-DHOTBT        |
|---|----------------------|----------------------|----------------------|
| $V_{oc}$  | $0.71 \pm 0.03$      | $0.76 \pm 0.02$      | $0.64 \pm 0.01$      |
| $J_{sc}$ (mA/cm <sup>2</sup> )                              | $5.85 \pm 0.13$      | $3.50 \pm 0.45$      | $4.35 \pm 0.29$      |
| FF  | $0.40 \pm 0.02$      | $0.32 \pm 0.02$      | $0.41 \pm 0.02$      |
| PCE (%)   | $1.67 \pm 0.32$      | $0.87 \pm 0.23$      | $1.15 \pm 0.15$      |
| Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ) | $9.1 \times 10^{-3}$ | $3.1 \times 10^{-4}$ | $3.9 \times 10^{-3}$ |

With PININE-DHOTBT and PCBM, the maximum PCE is 1.3%. Differences in the BHJ morphology presumably play a role since the PININE-DHOTBT has the longest wavelength absorption cutoff.

Because good charge transport mobility is also an important factor for high PCE, we examined the field-effect mobilities of the three copolymers. Figure 2 shows the transfer characteristics,  $I_{ds}$  versus  $V_{gs}$  and  $I_{ds}^{1/2}$  versus  $V_{gs}$  of the polymer FETs fabricated with PININE-DTBT, PININE-DHTBT, and PININE-DHOTBT. The polymer FET properties were significantly influenced by the side chain substitutions. Linear plots of  $I_{ds}^{1/2}$  versus  $V_{gs}$  deduced from the  $I_{ds}$  versus  $V_{gs}$  measurements yield hole mobilities of  $\mu_1 = 9.1 \times 10^{-3}$  cm<sup>2</sup>/V s,  $\mu_2 = 3.1 \times 10^{-4}$  cm<sup>2</sup>/V s,  $\mu_3 = 3.9 \times 10^{-3}$  cm<sup>2</sup>/V s for PININE-DTBT ( $\mu_1$ ), PININE-DHTBT ( $\mu_2$ ), and PININE-DHOTBT ( $\mu_3$ ). The mobility of the PININE-DTBT is significantly higher than that of PININE-DHTBT and PININE-DHOTBT. In addition, these measured mobilities show strong correlation with PV cell performance. The highest mobility PININE-DTBT shows better PCE value, while relatively lower mobility PININE-DHOTBT shows lower PCE value (see Table I).

Steric hindrance is the most serious effect of side chain functionalization because it affects the coplanarity of the conjugated backbone. In order to investigate how much the side chain disturbs the chain conformation, we carried out semiempirical quantum chemical simulations using the parametrized model 3.<sup>22</sup> Since the alkyl side chains in PININE moiety do not contribute significantly to the variation in chain conformation and charge-density isosurface, they were excluded from our calculation. Figure 3 shows the charge-density isosurfaces for the HOMO and lowest unoccupied molecular orbital (LUMO) levels of PININE-DTBT, PININE-DHTBT, and PININE-DHOTBT with the most en-

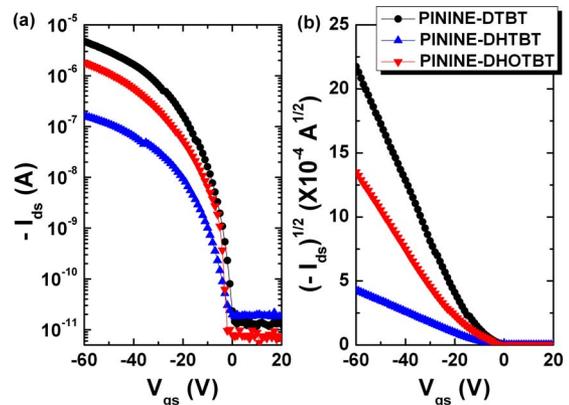


FIG. 2. (Color online) Transfer characteristics (a)  $I_{ds}$  vs  $V_{gs}$  and (b)  $I_{ds}^{1/2}$  vs  $V_{gs}$  of PFET devices measured in saturation regime ( $V_{ds} = -60$  V).

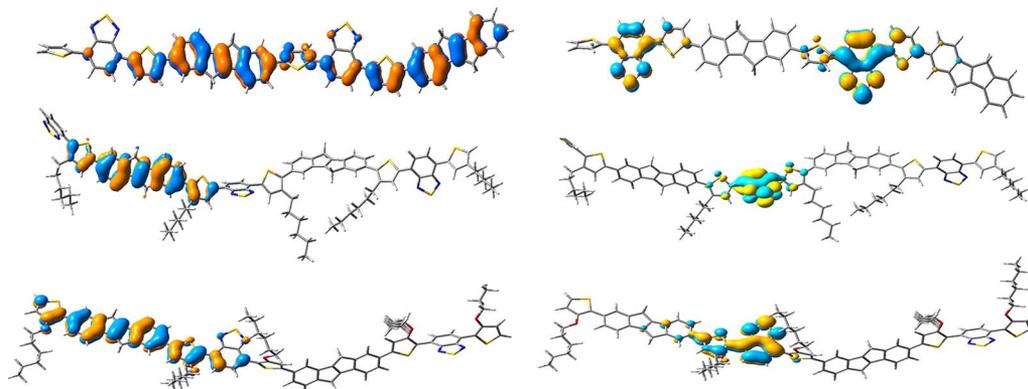


FIG. 3. (Color online) Charge-density isosurface for the HOMO (left) and LUMO (right) levels of PININE-DTBT (top), PININE-DHTBT (middle), and PININE-DHOTBT (bottom).

ergetically favorable geometry. For the PININE-DTBT, the HOMO isosurface shows delocalization on both donor and acceptor sites. In addition, the conjugated backbone is relatively flat. The LUMO isosurface of PININE-DTBT, however, tends to be localized on the benzothiadiazole (BT). This localization might be one of the reasons of the absence of *n*-channel behavior in the FETs. For the PININE-DHTBT, because of steric hindrance by alkyl side chain, the structure of the conjugated backbone is seriously twisted. Moreover, both the LUMO orbital and the HOMO orbital are localized, consistent with the lower values obtained for the hole mobilities. For the PININE-DHOTBT, although the isosurfaces of HOMO and LUMO orbitals are similar to those of PININE-DHTBT, the backbone is more nearly planar than that of PININE-DHTBT; only the BT moiety tilted from the backbone plane. Thus, we attribute the somewhat higher mobility of PININE-DHOTBT to better planarity of conjugated backbone.

In conclusion, alkyl or alkoxy side chains were introduced onto the D-A conjugated copolymer, PININE-DTBT, to obtain better solubility. The alkyl or alkoxy side chains alter the optical and electrical properties. Because of steric hindrance, the HOMOs of PININE-DHTBT and PININE-DHOTBT are localized on the donor segments, thereby decreasing the hole mobilities. Thus, in spite of the spectral advantage of PININE-DHOTBT for PV cells, the power conversion efficiency of PININE-DHOTBT was less than that obtained from the PININE-DTBT:PCBM cells.

This work was supported by the Heeger Center for Advanced Materials at the Gwangju Institute of Science and Technology and by the GRL Program of the Korean Government (Grant No. M60605000005-06A0500-00510).

<sup>1</sup>M. Svensson, F. Zhang, S. C. Veenstra, W. J. H. Verhees, J. C. Hummelen, J. M. Kroon, O. Inganäs, and M. R. Andersson, *Adv. Mater. (Weinheim, Ger.)* **15**, 988 (2003).

<sup>2</sup>A. J. Moulé, A. Tsami, T. W. Bünnagel, M. Forster, N. M. Kronenberg, M. Scharber, M. Koppe, M. Morana, C. J. Brabec, K. Meerholz, and U. Scherf, *Chem. Mater.* **20**, 4045 (2008).

<sup>3</sup>Y. Zhu, R. D. Champion, and S. A. Jenekhe, *Macromolecules* **39**, 8712 (2006).

<sup>4</sup>P. T. Boudreault, A. Michaud, and M. Leclerc, *Macromol. Rapid Commun.* **28**, 2176 (2007).

<sup>5</sup>A. Gadisa, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson, and O. Inganäs, *Adv. Funct. Mater.* **17**, 3836 (2007).

<sup>6</sup>M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec, *Adv. Mater. (Weinheim, Ger.)* **18**, 789 (2006).

<sup>7</sup>J. Roncali, *Macromol. Rapid Commun.* **28**, 1761 (2007).

<sup>8</sup>N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, and M. Leclerc, *J. Am. Chem. Soc.* **130**, 732 (2008).

<sup>9</sup>N. Blouin, A. Michaud, and M. Leclerc, *Adv. Mater. (Weinheim, Ger.)* **19**, 2295 (2007).

<sup>10</sup>E. Wang, L. Wang, L. Lan, C. Luo, W. Zhuang, J. Peng, and Y. Cao, *Appl. Phys. Lett.* **92**, 033307 (2008).

<sup>11</sup>M. Chen, X. Crispin, E. Perzon, M. R. Andersson, T. Pullerits, M. Andersson, O. Inganäs, and M. Berggren, *Appl. Phys. Lett.* **87**, 252105 (2005).

<sup>12</sup>R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, and J. M. J. Fréchet, *Adv. Mater. (Weinheim, Ger.)* **15**, 1519 (2003).

<sup>13</sup>A. Zen, J. Pfluam, S. Hirschmann, W. Zhuang, F. Jaiser, U. Asawapirom, J. P. Rabe, U. Schref, and D. Neher, *Adv. Funct. Mater.* **14**, 757 (2004).

<sup>14</sup>C. Edder, P. B. Armstrong, K. B. Pradob, and J. M. J. Fréchet, *Chem. Commun. (Cambridge)* **2006**, 1965.

<sup>15</sup>C. Shi, Y. Yao, Y. Yang, and Q. Pei, *J. Am. Chem. Soc.* **128**, 8980 (2006).

<sup>16</sup>C. R. McNeill, A. Abruci, J. Zaumseil, R. Wilson, M. J. McKiernan, J. H. Burroughes, J. J. M. Halls, N. C. Greenham, and R. H. Friend, *Appl. Phys. Lett.* **90**, 193506 (2007).

<sup>17</sup>E. Wang, C. Li, W. Zhuang, J. Peng, and Y. Cao, *J. Mater. Chem.* **18**, 797 (2008).

<sup>18</sup>M. Jayakannan, P. A. Van Hal, and R. A. J. Janssen, *J. Polym. Sci., Part A: Polym. Chem.* **40**, 251 (2002).

<sup>19</sup>S. Song, Y. Jin, S. H. Kim, J. Moon, K. Kim, J. Y. Kim, S. H. Park, K. Lee, and H. Suh, *Macromolecules* **41**, 7296 (2008).

<sup>20</sup>K. G. Jespersen, W. J. D. Beenken, Y. Zaushitsyn, A. Yartsev, M. Andersson, T. Pullerits, and V. Sundström, *J. Chem. Phys.* **121**, 12613 (2004).

<sup>21</sup>E. Perzon, X. Wang, S. Admassie, O. Inganäs, and M. R. Andersson, *Polymer* **47**, 4261 (2006).

<sup>22</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN03 package, Gaussian, Inc., Pittsburgh, Pennsylvania, 2003.