

## Influence of the Electron Acceptor Group on the Backbone of *N*-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl)pyrrole-Based Polymer

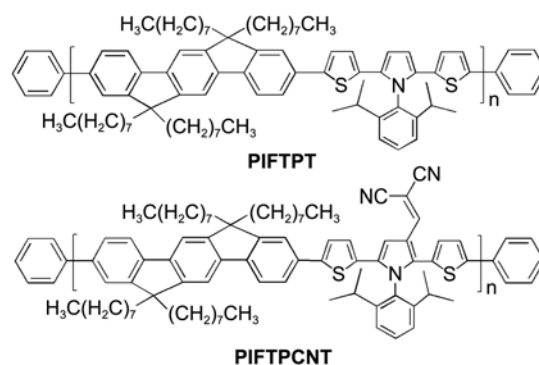
Vellaiappillai Tamilavan, Myungkwan Song,<sup>†</sup> Sung-Ho Jin,<sup>†</sup> and Myung Ho Hyun<sup>\*</sup>

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 690-735, Korea  
<sup>\*</sup>E-mail: mhhyun@pusan.ac.kr

<sup>†</sup>Department of Chemistry Education and Interdisciplinary Program of Advanced Information and Display Materials, Pusan National University, Busan 609-735, Korea  
Received June 21, 2012, Accepted August 6, 2012

**Key Words :** 1-(2,6-Diisopropylphenyl)-2,5-di(2-thienyl)pyrrole, Indenofluorene, Bulk heterojunction solar cell, Conjugated polymer, Copolymerization

Development of structurally new polymers for polymer solar cell (PSC) applications is an attractive research area due to their beneficial properties such as clean energy production, low-cost, light-weight, and roll-to-roll processing on flexible substrates.<sup>1</sup> The power conversion efficiency (PCE) of the PSCs was finally improved to 7.0-8.6% by utilizing suitable polymers as electron donor materials, that have the appropriate energy levels with efficient light harvesting ability, and PC<sub>71</sub>BM as an electron accepting material.<sup>2-8</sup> In our laboratory, we have been interested in preparing *N*-(2,6-diisopropylphenyl)-2,5-di(2-thienyl)pyrrole (*N*-aryl TPT)-based  $\pi$ -conjugated polymers as electron donor materials for PSC applications. Recently, we reported several *N*-aryl TPT-based polymers containing electron rich units such as indenofluorene (**PIFTPT**),<sup>9</sup> 2,5-dioctyloxyphenylene (**PPTPT**),<sup>10</sup> 3-octylthiophene (**PTTPT**),<sup>10</sup> and electron deficient units such as thiophene-benzothiadiazole-thiophene (**PTPTTBT**),<sup>11</sup> benzothiadiazole (**PTPTIFB** and **TPyTBz**),<sup>12,13</sup> and thiadiazoloquinoxaline (**TPyTDzQ**)<sup>14</sup> for PSC applications. The *N*-aryl TPT-based donor (D) polymers showed maximum energy conversion efficiency of 1.35%,<sup>10</sup> whereas the donor-acceptor (D-A) and donor-acceptor-donor (D-A-D) polymers showed maximum PCE of 1.57%.<sup>11</sup> The comparison studies of the *N*-aryl TPT-based polymers indicated that the incorporation of strong electron acceptor unit in polymer main chain significantly broadens the absorption band of the polymers and usually raises the HOMO energy levels of the polymers. Consequently, the PSCs made from the D-A or D-A-D polymers showed improved current density ( $J_{sc}$ ) and decreased open circuit voltage ( $V_{oc}$ ) with similar or slightly higher PCEs compared with *N*-aryl TPT-based donor polymers. In general, the  $V_{oc}$  is defined as the energy difference between the valance and conduction band energy levels of the polymer and PCBM.<sup>15</sup> In this instance, we anticipate that introducing a strong electron acceptor unit on *N*-aryl TPT polymer backbone might offer better photovoltaic results because the incorporation of electron acceptor group on the polymer backbone usually lower its HOMO energy level.<sup>4,5</sup> In this study, we wish to introduce a methylene bridged malononitrile electron acceptor group on the

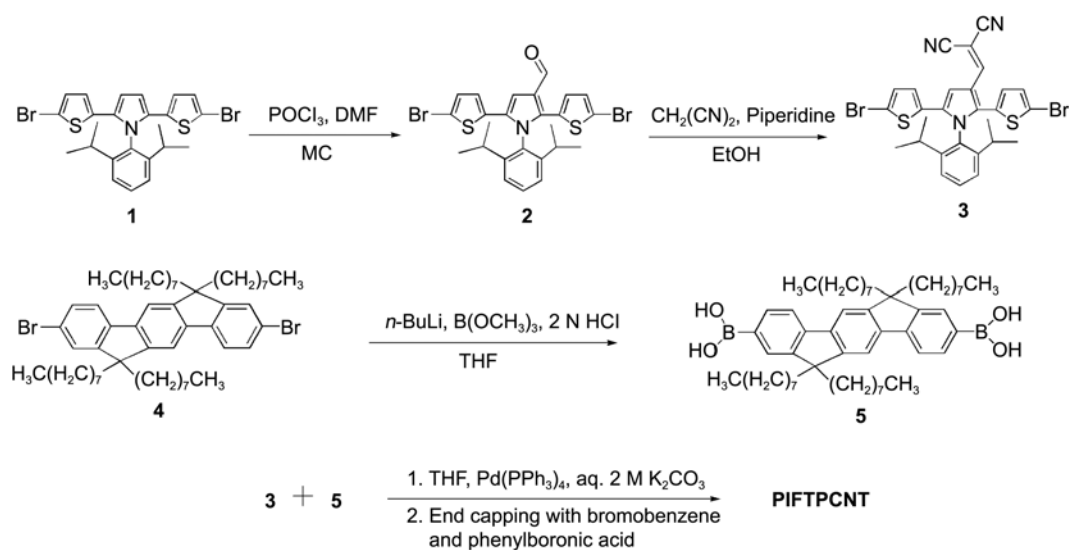


**Figure 1.** Structures of polymers **PIFTPT** and **PIFTPCNT**.

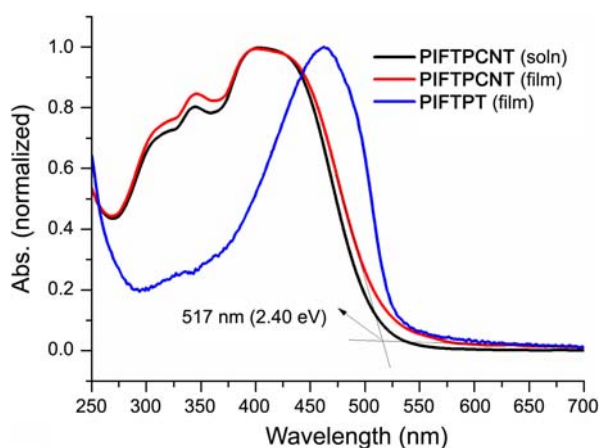
pyrrole ring of the known *N*-aryl TPT-based polymer, **PIFTPT**, to afford new  $\pi$ -conjugated polymer **PIFTPCNT** (Figure 1).

Polymer **PIFTPCNT** was prepared *via* the procedure shown in Scheme 1. Compound **1**, 2,5-bis(5-bromothiophen-2-yl)-1-(2,6-diisopropylphenyl)-1H-pyrrole, was synthesized *via* the known procedure.<sup>9</sup> Compound **1** was subjected to Vilsmeier formylation reaction with DMF and POCl<sub>3</sub> to afford compound **2**. The Knoevenagel condensation reaction of compound **2** with malononitrile in the presence of piperidine yielded monomer **3**. Among the *N*-aryl TPT-based polymers, polymer **PIFTPT** showed higher  $V_{oc}$  and  $FF$  values than other polymers. From these results, we expect that the presence of indenofluorene unit in polymer main chain enhances the carrier mobility and, consequently, improves the  $V_{oc}$  and  $FF$  values. In fact, indenofluorene is known to be a very good candidate for balanced carrier mobility.<sup>16,17</sup> In this instance, indenofluorene comonomer (**5**) prepared from 2,8-dibromo-6,6',12,12'-tetraoctylindeno-fluorene (**4**) *via* the procedure similar to that reported<sup>18</sup> was subjected to the Suzuki polycondensation with monomer **3** and then end capping followed by purification gave pure polymer, **PIFTPCNT**, as a red solid.

Polymer **PIFTPCNT** exhibited good solubility in chloroform, tetrahydrofuran, chlorobenzene and dichlorobenzene. The weight average molecular weight ( $M_w$ ) and polydispersity (PDI) of **PIFTPCNT** determined from the GPC analysis



**Scheme 1.** Scheme for the synthesis of polymer **PIFTPCNT**.

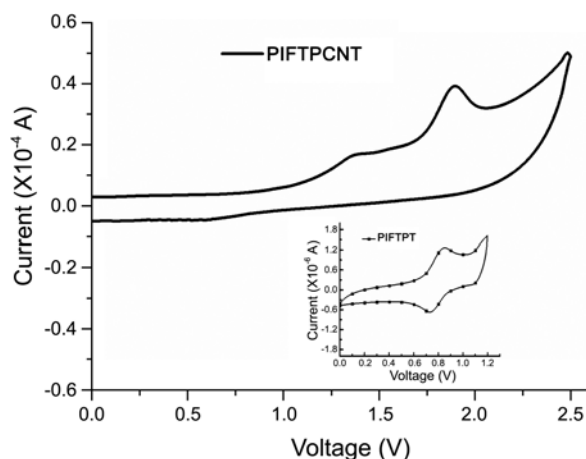


**Figure 2.** UV-Visible absorption spectra of polymers **PIFTPCNT** and **PIFTPT**. The spectrum of **PIFTPT** was quoted from reference 9.

were  $1.54 \times 10^4$  and 1.73, respectively. Polymer **PIFTPCNT** was estimated to have high thermal stability from the thermogravimetric analysis (TGA), and the 5% weight loss temperature was 354 °C.

The absorption spectra of **PIFTPCNT** in chloroform solution and as thin film on quartz are shown in Figure 2. The absorption bands of **PIFTPCNT** in solution and as film were found to be almost identical, and the absorption band width was quite broad from 270 nm to 530 nm with maximum absorption peak at around 400 nm. The optical band gap of polymer **PIFTPCNT** was calculated from the onset wavelength of the optical absorption as thin film to be 2.40 eV, which is slightly higher than that of the reported polymer **PIFTPT** band gap.<sup>9</sup> The strong electron acceptor group on the polymer backbone of **PIFTPCNT** was found to induce the blue shift in the absorption maximum and broaden the absorption band quite significantly compared to the absorption of **PIFTPT** as shown in Figure 2.

The HOMO energy level of the polymer was determined from cyclic voltammetry analysis, and the CV spectrum of



**Figure 3.** Cyclic voltammogram of polymer **PIFTPCNT** as film (Inset: CV spectrum of polymer **PIFTPT** quoted from reference 9).

the polymer is represented in Figure 3. The HOMO energy level of the polymer **PIFTPCNT** was estimated to be  $-5.24$  eV and the LUMO energy level of the polymer **PIFTPCNT** was calculated to be  $-2.84$  eV by using the known equations.<sup>9</sup>

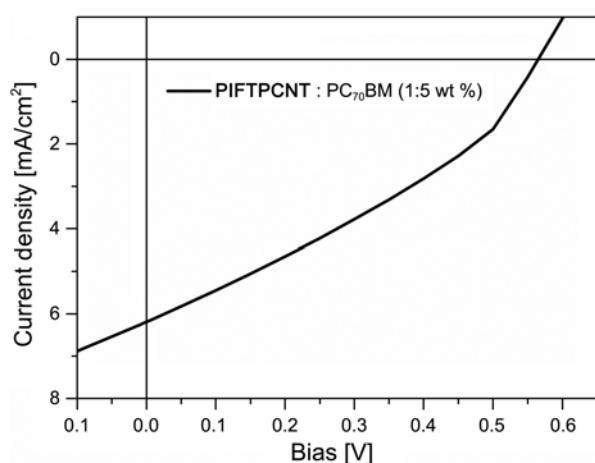
The optical and electrochemical properties of **PIFTPCNT** were summarized and compared with those of **PIFTPT** in Table 1.

The polymer solar cell (PSC) was fabricated with the device structure of ITO/PEDOT:PSS/**PIFTPCNT**:PC<sub>71</sub>BM (1:5 wt %)/TiO<sub>2</sub>/Al. In our previous studies, high PCEs were observed when the ratio of polymer:PC<sub>71</sub>BM was 1:5 wt % in the active layer.<sup>9-14</sup> Consequently, in this study, the ratio of donor:acceptor was also set at 1:5 wt %. The current density-voltage ( $J$ - $V$ ) characteristic curve of the PSC device measured under the AM 1.5 G irradiation ( $100 \text{ mWcm}^{-2}$ ) from a solar simulator is shown in Figure 4. The PSC device made from **PIFTPCNT** showed maximum PCE of 1.16% with a  $V_{oc}$  of 0.56 V, a  $J_{sc}$  of  $6.19 \text{ mAcm}^{-2}$ , and a FF of 32%. The photovoltaic properties of the PSC made from **PIFTPCNT** are included in Table 1 and compared with

**Table 1.** Summary of the optical and electrochemical properties of **PIFTPCNT** and **PIFTPT** and the photovoltaic properties of **PIFTPCNT** and **PIFTPT** as an electron donor with PC<sub>71</sub>BM as an electron acceptor in ITO/PEDOT:PSS/**PIFTPCNT** or **PIFTPT**:PC<sub>71</sub>BM/TiO<sub>2</sub>/Al device<sup>a</sup>

Polymer	$\lambda_{\max}$ in solution (nm) <sup>b</sup>	$\lambda_{\max}$ as film (nm) <sup>c</sup>	$E_g$ (eV) <sup>d</sup>	HOMO (eV) <sup>e</sup>	LUMO (eV) <sup>f</sup>	$V_{oc}$ (V) <sup>g</sup>	$J_{sc}$ (mA/cm <sup>2</sup> ) <sup>h</sup>	$FF$ (%) <sup>i</sup>	$PCE$ (%) <sup>j</sup>
<b>PIFTPCNT</b>	400	400	2.40	-5.24	-2.84	0.56	6.19	32	1.16
<b>PIFTPT</b>	465	465	2.36	-5.19	-2.83	0.67	3.39	49	1.12

<sup>a</sup>Data for **PIFTPT** are quoted from reference 9. <sup>b</sup>Absorption maximum of the polymers in chloroform solution. <sup>c</sup>Absorption maximum of the polymers as thin film onto the quartz substrate. <sup>d</sup>The optical band gap estimated from the onset wavelength of the optical absorption in thin film. <sup>e</sup>The HOMO level of the polymers estimated from cyclic voltammetry analysis. <sup>f</sup>The LUMO level of the polymers calculated by using the equation of LUMO = HOMO -  $E_g$ . <sup>g</sup>Open-circuit voltage. <sup>h</sup>Short-circuit current density. <sup>i</sup>Fill factor. <sup>j</sup>Power conversion efficiency.



**Figure 4.**  $J$ - $V$  characteristics of the PSC made from polymer **PIFTPCNT**.

those of the PSC made from **PIFTPT**. The  $J_{sc}$  value for **PIFTPCNT** was higher than that for **PIFTPT**, but the  $V_{oc}$  and  $FF$  values for **PIFTPCNT** were lower than those for **PIFTPT**. The broader absorption ability of **PIFTPCNT** compared with that of **PIFTPT** might be one of the reasons for the higher  $J_{sc}$  value of the PSC device made from **PIFTPCNT**. However, the acceptor group on the polymer backbone of **PIFTPCNT** might reduce the carrier mobility and, consequently, lower the  $FF$  and  $V_{oc}$  values. In addition, relatively low molecular weight of **PIFTPCNT** might also be a reason for the decreased  $V_{oc}$  and  $FF$  values.<sup>19,20</sup>

The surface morphology of the **PIFTPCNT**:PC<sub>71</sub>BM (1:5 wt %) blend coated on the glass/ITO/PEDOT:PSS substrate was studied using atomic force microscope (AFM) analysis. The root-mean-square (rms) roughness of the active layer was estimated to be 1.754, which indicates the surface is quite smooth. The main morphological feature of the composite film shows a homogeneous distribution of the two components within the nanoscale.

In summary, we designed and prepared a new *N*-aryl TPT-based polymer (**PIFTPCNT**) containing methylene bridged malononitrile acceptor group on the backbone. The optical, electrical and photovoltaic properties of **PIFTPCNT** were studied and briefly compared with those of **PIFTPT**, which does not contain acceptor group on the backbone. The optical band gaps of the polymers **PIFTPCNT** and **PIFTPT** were quite close, but the absorption band of **PIFTPCNT**

was significantly broader than that of **PIFTPT**. The HOMO energy level of the **PIFTPCNT** was slightly deeper than that of **PIFTPT**. The overall photovoltaic performances ( $PCE = \sim 1.16\%$ ) of the PSCs made from polymers **PIFTPCNT** and **PIFTPT** also found to be similar, but the PSC made from **PIFTPCNT** showed higher  $J_{sc}$  value with decreased  $V_{oc}$  and  $FF$  values compared with those of the PSC made from **PIFTPT**. This study clearly demonstrates that the incorporation of methylene bridged malononitrile acceptor group on *N*-aryl TPT-based polymer backbone alone is not always satisfactory in tuning the photovoltaic properties of polymers.

## Experimental

**Synthesis of Polymer PIFTPCNT.** The stirred solution of monomer **3** (0.32 g, 0.5 mmol) and **5** (0.40 g, 0.5 mmol) in THF (60 mL) was purged well with nitrogen for 45 min. Subsequently, Pd(PPh<sub>3</sub>)<sub>4</sub> (0.04 g, 8 mol %) and aqueous 2 M K<sub>2</sub>CO<sub>3</sub> (7 mL) were added and the mixture was refluxed with vigorous stirring for 72 h under nitrogen atmosphere. After that, to this refluxing solution was added 50 mg of phenylboronic acid. The whole mixture was refluxed for 6 h and then 0.1 mL of bromobenzene was added and refluxed again for 6 h. The reaction mixture was cooled and then poured into the mixed solvent of methanol and water (200 mL:100 mL) with vigorous stirring. The precipitate was recovered by filtration, washed well with 2 N HCl solution, and then extracted with methanol for 24 h and hexane for 24 h in a Soxhlet apparatus. After drying, polymer **PIFTPCNT** was obtained as a red solid. Yield 0.32 g (48%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (s, 1 H), 7.26-7.80 (m, 10 H), 6.70-6.88 (m, 3 H), 6.40 (s, 1 H), 6.18 (s, 1 H), 2.34-2.56 (m, 2 H), 1.88-2.14 (m, 8 H), 0.82-1.30 (m, 52 H), 0.77 (s, 12 H), 0.58-0.64 (m, 8 H).

**Acknowledgments.** This research was supported by the New & Renewable Energy program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20103020010050) funded by the Ministry of Knowledge Economy, Republic of Korea.

**Supporting Information.** The detailed synthetic procedures for the monomers and PSC device preparation were presented in supplementary.

## References

1. Zhou, H.; Yang, L.; You, W. *Macromolecules* **2012**, *45*, 607.
  2. Liang, Y.; Xu, Z.; Xia, J.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. *Adv. Mater.* **2010**, *22*, E135.
  3. Chu, T.-A.; Lu, J.; Beaupre, S.; Zhang, Y.; Pouliot, J. R.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250.
  4. Price, S. C.; Stuart, A. C.; Yang, L.; Zhou, H.; You, W. *J. Am. Chem. Soc.* **2011**, *133*, 4625.
  5. Son, H. J.; Wang, W.; Xu, T.; Liang, Y.; Wu, Y.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1885.
  6. Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 10062.
  7. Small, C. E.; Chen, S.; Subbiah, J.; Amb, C. M.; Tsang, S.-W.; Lai, T.-H.; Reynolds, J. R.; So, F. *Nat. Photonics* **2012**, *6*, 115.
  8. Dou, L.; You, J.; Yang, J.; Chen, C.-C.; He, Y.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. *Nat. Photonics* **2012**, *6*, 180.
  9. Tamilavan, V.; Sakthivel, P.; Li, Y.; Song, M.; Kim, C.-H.; Jin, S.-H.; Hyun, M. H. *J. Polym. Sci. Part. A: Polym. Chem.* **2010**, *48*, 3169.
  10. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *J. Polym. Sci. Part. A: Polym. Chem.* **2010**, *48*, 5514.
  11. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *Polymer* **2011**, *52*, 2384.
  12. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *Curr. Appl. Phys.* **2012**, doi:10.1016/j.cap.2012.02.034.
  13. Tamilavan, V.; Song, M.; Ban, T.-W.; Jin, S.-H.; Hyun, M. H. *Polym. Bull.* **2012**, doi 10.1007/s00289-012-0740-z.
  14. Tamilavan, V.; Song, M.; Jin, S.-H.; Hyun, M. H. *Synthetic Met.* **2011**, *161*, 1199.
  15. Dennler, G.; Scharber, M. C.; Brabec, C. *J. Adv. Mater.* **2009**, *21*, 1323.
  16. Kim, H.; Schulte, N.; Zhou, G.; Mullen, K.; Laquai, F. *Adv. Mater.* **2011**, *23*, 894.
  17. Kim, J.; Kim, S. H.; Jung, I. H.; Jeong, E.; Xia, Y.; Cho, S.; Hwang, I.-W.; Lee, K.; Suh, H.; Shim, H.-K.; Woo, H. Y. *J. Mater. Chem.* **2010**, *20*, 1577.
  18. Yen, W.-C.; Pal, B.; Yang, J.-S.; Hung, Y.-C.; Lin, S.-T.; Chao, C.-Y.; Su, W.-F. *J. Polym. Sci. Part. A: Polym. Chem.* **2009**, *47*, 5044.
  19. Moet, D. J. D.; Lenes, M.; Kotlarskia, J. D.; Veenstra, S. C.; Sweelssen, J.; Koetse, M. M.; de Boer, B.; Blom, P. W. M. *Org. Electron.* **2009**, *10*, 1275.
  20. Muller, C.; Wang, E.; Andersson, L. M.; Tvingstedt, K.; Zhou, Y.; Andersson, M. R.; Inganas, O. *Adv. Funct. Mater.* **2010**, *20*, 2124.
-