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Synthesis and Photovoltaic Properties of Diketopyrrolopyrrole-Based Donor−Acceptor Copolymers

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Three kinds of diketopyrrolopyrrole-based donor−acceptor (D-A) type copolymers, poly{9,9-di(2-ethylhexyl)fluorene-2,7-diyl-*alt*-3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-5′,5″-diyl} (PF-DTDPP), poly{*N*-(1-decylundecyl)carbazole-2,7-diyl-*alt*-3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-5′,5″-diyl} (PC-DTDPP), and poly{*N*-[1-(2-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-*b*:2′,3′-*d*]pyrrole-3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione-5′,5″-diyl} (PDTP-DTDPP) were synthesized. By changing the donor segments, the absorption ranges of DTDPP-containing copolymers can be tuned. PF-DTDPP and PC-DTDPP showed absorption bands in the range of 500−700 nm, while PDTP-DTDPP showed broad absorption in the range of 500−1000 nm in the solutions. The power conversion efficiencies (PCE) of the polymer solar cells (PSCs) based on these copolymers and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) were 0.88% (PF-DTDPP), 2.26% (PC-DTDPP), and 1.12% (PDTP-DTDPP), respectively, under the illumination of AM 1.5 (100 mW/cm^2). The monochromatic photocurrent responses of the PSCs based on PDTP-DTDPP:PCBM blends extend to the near-infrared region around 1 μm, which makes this material a promising candidate for the application in the multilayer or tandem photovoltaic devices combined with the conventional visible light absorbing materials.

Introduction

After the first synthesis as a byproduct by Farnum et al. in 1974,[1] diketopyrrolopyrrole (DPP) derivatives, with the pyrrolo[3,4-*c*]pyrrole-1,4-dione unit as the underlying chromophore system, have been extensively studied. Some of the derivatives have been commercialized as high performance pigments used in paints, plastics, and inks because of their exceptionally high stability against light, weather, and heat.[2] To use the DPP chromophore in the opto-electrical devices, however, it is necessary to improve the solubility and film forming ability of DPP-containing materials, since 2,5-dihydro-pyrrolo[3,4-*c*]pyrrole-1,4-dione is not soluble in most common organic solvents because of the concurrent $\pi-\pi$ intermolecular interactions and a strong hydrogen-bonding structure in the solid state. After attaching the solubilizing groups at the 2,5-positions of the DPP moiety (N atoms in the lactam), many molecules[3] or polymers[4] containing 3,6-diphenyl-2,5-dialkyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DPDPP) have been synthesized and their interesting opto-electrical characteristics have been reported.

Very recently, significant progress was made for the application of DPP-containing materials in the polymer solar cells (PSCs) and field effect transistor (FET) following the useful synthesis of the 3,6-dithien-2-yl-2,5-dialkyl-pyrrolo[3,4-*c*]pyrrole-1,4-dione (DTDPP) segment. A copolymer containing bithiophene and DTDPP units (BBTDPP1) exhibits excellent ambipolar charge transport properties with high hole (0.1 cm^2/(V s)) and electron mobilities (0.09 cm^2/(V s)).[5] When a similar copolymer (BBTDPP2) was applied to PSCs, a high power conversion efficiency (PCE) of 4% was achieved.[6] Many small molecules were also synthesized and used in the PSCs resulting in the PCEs of 2.3−3%[7] and in the FETs with the charge mobility above 0.02 cm^2/(V s).[8] Besides

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(1) Farnum, D. G.; Mehta, G.; Moore, G. G. I.; Siegel, F. P. *Tetrahedron Lett.* **1974**, *29*, 2549.
(2) (a) Hao, Z. M.; Iqbal, A. *Chem. Soc. Rev.* **1997**, *26*, 203. (b) Wallquist, O.; Lenz, R. *Macromol. Symp.* **2002**, *187*, 617.
(3) (a) Hofkens, J.; Verheijen, W.; Shukla, R.; Dehaen, W.; De Schryver, F. C. *Macromolecules* **1998**, *31*, 4493. (b) Behnke, M.; Tieke, B. *Langmuir* **2002**, *18*, 3815.
(4) (a) Beyerlein, T.; Tieke, B. *Macromol. Rapid Commun.* **2000**, *21*, 182. (b) Cao, D. R.; Liu, Q. L.; Zeng, W. J.; Han, S. H.; Peng, J. B.; Liu, S. P. *J. Polym. Sci., Part A* **2006**, *44*, 2395. (c) Rabindranath, A. R.; Zhu, Y.; Heim, I.; Tieke, B. *Macromolecules* **2006**, *39*, 8250. (d) Zhu, Y.; Rabindranath, A. R.; Beyerlein, T.; Tieke, B. *Macromolecules* **2007**, *40*, 6981. (e) Zhang, K.; Tieke, B. *Macromolecules* **2008**, *41*, 7287.
(5) Bürgi, L.; Trubiez, M.; Pfeiffer, R.; Bienewald, F.; Kirner, H. J.; Winnewisser, C. *Adv. Mater.* **2008**, *20*, 2217.
(6) Wienk, M. M.; Turbiez, M.; Gilot, J.; Janssen, R. A. J. *Adv. Mater.* **2008**, *20*, 2556.
(7) (a) Tamayo, A. B.; Walker, B.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 11545. (b) Tamayo, A. B.; Dang, X.-D.; Walker, B.; Seo, J.; Kent, T.; Nguyen, T.-Q. *Appl. Phys. Lett.* **2009**, *94*, 103301.
(8) Tantiwiwat, M.; Tamayo, A.; Luu, N.; Dang, X.-D.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 17402.

the thiophene segment, the DTDPP segment was also copolymerized with carbazole unit. The resulting polymer showed a good hole mobility (0.02 cm^2/(V s)) and a moderate PCE (1.6%).[9]

To design the polymers with a low band gap for the application to the PSCs, the concept of donor−acceptor (D-A) type copolymers is promising because of the vast possibility in the unit combinations. Many D−A type copolymers have been used in PSCs to achieve PCEs above 5% with extensive device engineering efforts.[11] Although DTDPP is a promising building block for the D−A type copolymer, it is still relatively unexplored from the viewpoint of the band gap narrowing. This is in contrast to another donor segment, 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT), which has been studied extensively for the design of the low band gap polymers for the PSC application.[10]

In this paper, we report the synthesis of novel copolymers combining 3,6-di(2-bromothien-5-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione with three kinds of donor segments; fluorene, carbazole, and dithieno-[3,2-b:2′,3′-*d*]pyrrole. These donor segments have similar structures but different electron-donating abilities. The effects of the different donor segments on the absorption spectra, energy levels, and the photovoltaic performances of the resulting DTDPP-containing D−A copolymers are also included.

Results and Discussions

Material Synthesis. To improve the solubility and the film-forming ability of DPP-containing D−A copolymers, two 2-ethylhexyl groups were introduced at the 2,5-positions (N atoms in the lactam ring) of the DPP moiety. 3,6-Dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (monomer **1**) was synthesized according to the procedure in the literature.[12] Dibromination of the monomer **2** in CHCl$_3$ yielded 3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4-dione (monomer **3**). For the donor segments, 9,9-di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester was commercially available. 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(1-decy-

lundecyl)carbazole (monomer **8**) was synthesized with a similar method reported in the literature.[10a] 2,6-Di-(trimethyltin)-*N*-[1-(2′-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2′,3′-d]pyrrole (monomer **9**) has been synthesized as we reported before.[10f]

The alternative copolymers of PF-DTDPP and PC-DTDPP were synthesized by Suzuki coupling reaction, and PDTP-DTDPP was synthesized by Stille coupling reaction (Schemes 1 and 2). All the polymers have good solubility in common organic solvents such as chloroform, toluene, and chlorobenzene. Molecular weights and polydispersity indices (PDIs) of the polymers are determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. PC-DTDPP has a high number-averaged molecular weight (M_n) of 91.3 kg/mol with a PDI of 1.77. The other two polymers have relatively lower M_n of 15.3 kg/mol with a PDI of 1.77 for PF-DTDPP and 8.5 kg/mol with a PDI of 1.70 for PDTP-DTDPP. The difference of the molecular weights may be resulted from the reactivity and steric hindrance of the donor segments.

Optical Properties. The UV−visible absorption spectra of the copolymers in CHCl$_3$ solutions are shown in Figure 1. PF-DTDPP and PC-DTDPP show similar absorption spectra with the absorption maxima at 652 and 658 nm, respectively. In contrast, PDTP-DTDPP shows the absorption band in the significantly longer wavelength compared to the other two copolymers with two absorption peaks at 780 and 847 nm. The absorption coefficients of PF-DTDPP, PC-DTDPP, and PDTP-DTDPP in the CHCl$_3$ solutions are 9.55×10^4, 9.94×10^4, and 6.28×10^4 L mol^{-1} cm^{-1}, respectively, at their absorption maxima. The absorption spectra of the polymer films are shown in Figure 2, and the detailed optical data are summarized in Table 1. The absorption maximum of PC-DTDPP in film shows a red-shift by 18 nm compared with that in solution, indicating there is intermolecular interaction in the solid state. However, there is just 2 nm red-shift for PF-DTDPP from the solutions to the films, likely due to the larger steric hindrance of the two bulky 2-ethylhexyl side chains than that of 1-decylundecyl side chain. These results suggest that by changing the donor segments with different electron-donating ability, the absorption spectra can be tuned, which is very useful for the design of the photovoltaic materials.

Energy Level Measurements Using the Electrochemical Method. Electrochemical cyclic voltammetry (CV) is performed to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated polymers.[13] The CV curves were recorded referenced to an Ag/Ag$^+$ (0.01 M of AgNO$_3$ in acetonitrile) electrode, which was calibrated by a ferrocene−ferrocenium (Fc/Fc$^+$) redox couple (4.8 eV below the vacuum level). As shown in Figure 3, all the copolymers showed a reversible

(9) Zou, Y. P.; Gendron, D.; Badrou-Aïch, R.; Najari, A.; Tao, Y.; Leclerc, M. *Macromolecules* **2009**, *42*, 2891.

(10) (a) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295. (b) Boudreault, P. T.; Michaud, A.; Leclerc, M. *Macromol. Rapid Commun.* **2007**, *28*, 2176. (c) Song, S.; Jin, Y.; Kim, S. H.; Moon, J.; Kim, K.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2008**, *41*, 7296. (d) Moulé, A. J.; Tsami, A.; Bünnagel, T. W.; Forster, M.; Kronenberg, N. M.; Scharber, M.; Koppe, M.; Morana, M.; Brabec, C. J.; Meerholz, K.; Scherf, U. *Chem. Mater.* **2008**, *20*, 4045. (e) Liao, L.; Dai, L. M.; Smith, A.; Durstock, M.; Lu, J. P.; Ding, J. F.; Tao, Y. *Macromolecules* **2007**, *40*, 9406. (f) Zhou, E. J.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q. S.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302.

(11) (a) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497. (b) Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (c) Liang, Y. Y.; Wu, Y.; Feng, D. Q.; Tsai, S. T.; Son, H. J.; Li, G.; Yu, L. P. *J. Am. Chem. Soc.* **2009**, *131*, 56. (d) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Hegger, A. J. *Nat. Photonics* **2009**, *3*, 297.

(12) Tamayo, A. B.; Tantiwiwat, M.; Walker, B.; Nguyen, T.-Q. *J. Phys. Chem. C* **2008**, *112*, 15543.

(13) (a) Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth. Met.* **1999**, *99*, 243. (b) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.

Scheme 1. Synthetic Routes for the Monomers
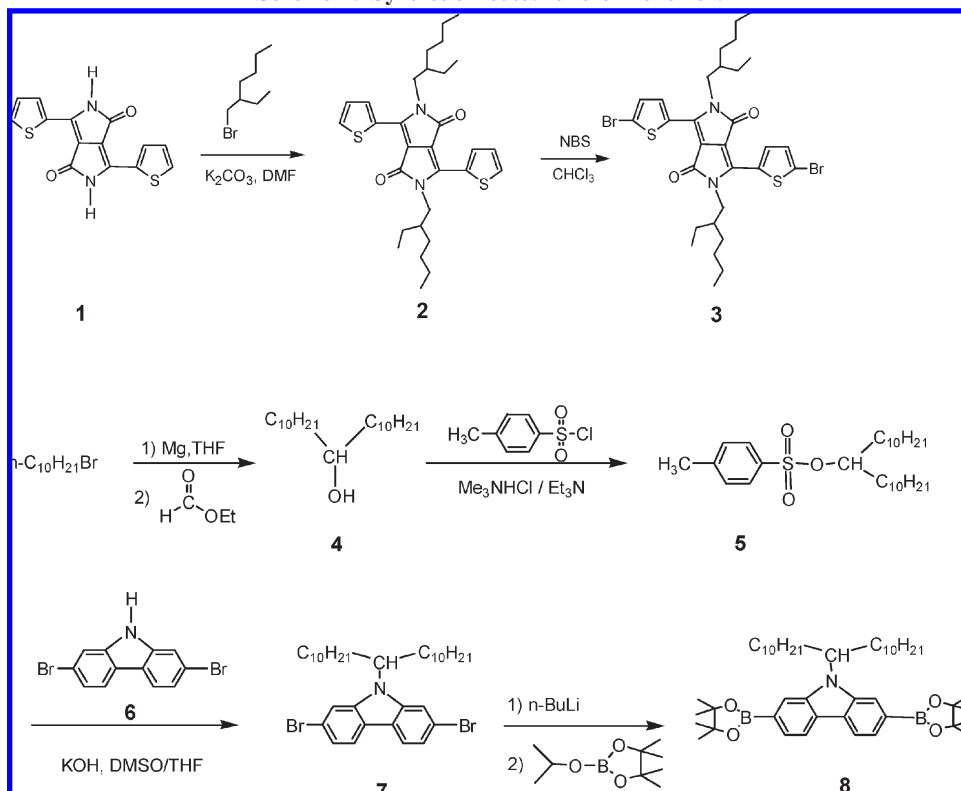
Scheme 2. Synthetic Route for the Three Diketopyrrolopyrrole-Based Donor−Acceptor Type Copolymers
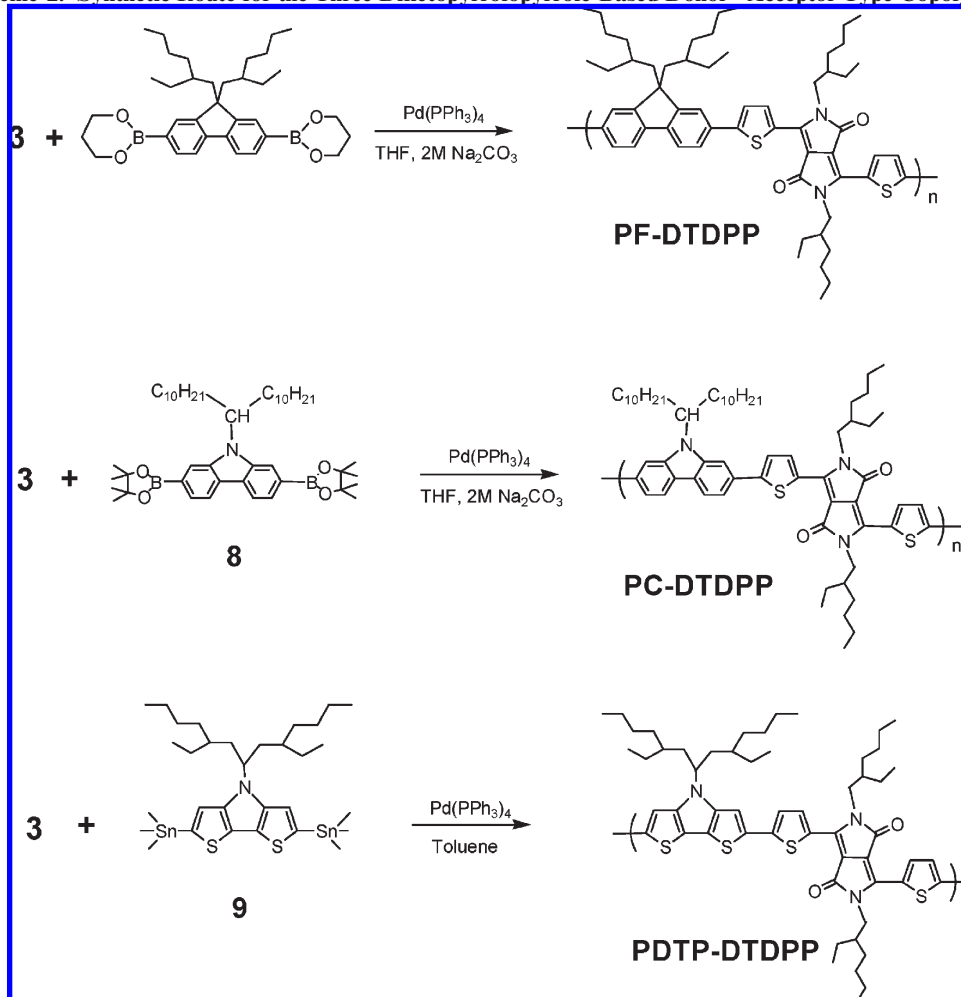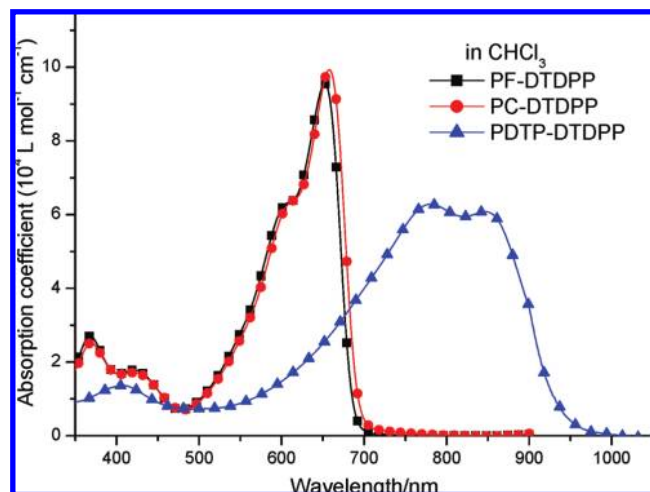
Figure 1. UV−vis absorption spectra of the copolymers in CHCl₃ solution.
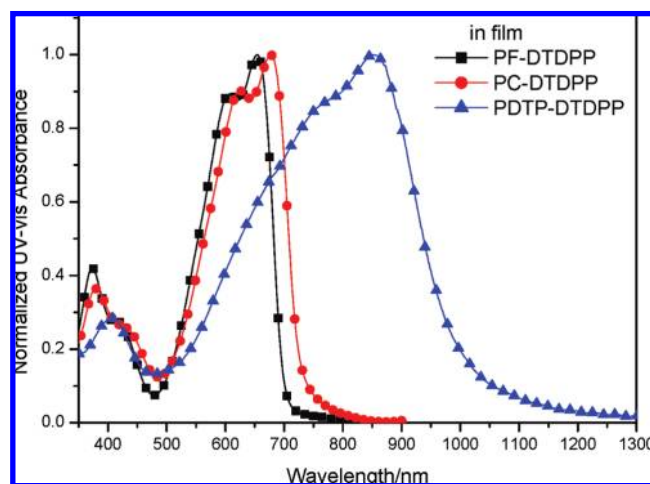

Figure 2. Normalized UV−vis absorption spectra of the copolymer films on quartz plates.

oxidation/reduction process. However, the reduction/reoxidation process was irreversible, which was different from the behaviors of the polythiophene derivatives.[14] From the value of onset oxidation potential (E_{on}^{ox}) and onset reduction potential (E_{on}^{red}) of the polymers, the HOMO and the LUMO as well as the bandgaps (E_g^{EC}) were calculated and are listed in Table 1. The data show that the different donor segments have almost no effect on the LUMO energy level but affect the HOMO energy level largely. For PDTP-DTDPP, the HOMO energy level shift upward by 0.3 eV compared with those of the other two polymers, which results in the decrease of the band gap. The electrochemical band gaps of PF-DTDPP and PC-DTDPP are similar with the optical band gaps

estimated from the UV−vis absorption onset. For PDTP-DTDPP, the electrochemical band gap is 1.38 eV, which is slightly higher than the optical band gap.

Photovoltaic Properties. The bulk heterojunction PSCs were fabricated with the device structure of ITO/PEDOT: PSS/polymer:[6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM)/Al. To accurately evaluate the PCEs of the photovoltaic devices, it is essential to determine the device area correctly.[15] Here, the effective areas of the PSCs are defined using a metal photo mask during the irradiation of the simulated solar light (Scheme 3).

Figure 4 shows the $I-V$ curves of the devices with best photovoltaic performance under the illumination of AM 1.5 (100 mW/cm²). The corresponding open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor (FF), and PCE of the devices are summarized in Table 2. The V_{OC} of photovoltaic devices based on PF-DTDPP and PC-DTDPP showed similar values above 0.7 V, while the photovoltaic devices based on PDTP-DTDPP showed a lower V_{OC} of 0.44 V. This difference of V_{OC} could result from the upward shift of the HOMO energy levels of PDTP-DTDPP because the V_{OC} is related to the energy difference between the LUMO of the acceptor (PCBM) and the HOMO of the donor (the conjugated polymer).[16]

The photovoltaic device based on PC-DTDPP:PCBM gave a PCE of 2.26%, which has above 40% improvement compared with the PCE (1.6%) of similar polymer with different side chain.[9] This result might be attributed to the higher molecular weight of PC-DTDPP in this study.

The mixing morphology of the polymer and PCBM composite film has proven to be extremely important in determining the photovoltaic properties of PSCs, which mainly affects the interpenetrated network of the donor and the acceptor.[17] The morphology of the blend films with polymer and PCBM was observed by atomic force microscopy (AFM) as shown in Figure 5. PF-DTDPP: PCBM blend film showed a rough surface and coarse phase separation (Figure 5A); however, a rather smooth surface and more intimate mixing for PC-DTDPP: PCBM (Figure 5B) and PDTP-DTDPP:PCBM were observed (Figure 5C). The improved miscibility of PC-DTDPP:PCBM and PDTP-DTDPP:PCBM compared to PF-DTDPP:PCBM explained, at least in part, the increased photocurrent because of the short exciton diffusion lengths generally reported in the conjugated polymers.

The external quantum efficiency (EQE) of the devices under the illumination of monochromatic light is shown in Figure 6. The shape of the EQE curves of the devices is very similar to the absorption spectra, indicating that all the absorption of the polymers contributed to the photovoltaic conversion. The photocurrent response wavelengths of the

(14) (a) Zhou, E. J.; Hou, J. H.; Yang, C. H.; Li, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2206. (b) Zhou, E. J.; He, C.; Tan, Z. A.; Yang, C. H.; Li, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4916. (c) Zhou, E. J.; Tan, Z. A.; Yang, C. H.; Li, Y. F. *Macromol. Rapid Commun.* **2006**, *27*, 793. (d) Zhou, E. J.; Tan, Z. A.; Huo, L. J.; He, Y. J.; Yang, C. H.; Li, Y. F. *J. Phys. Chem. B* **2006**, *110*, 26062. (e) Zhou, E. J.; Tan, Z. A.; He, Y. J.; Yang, C. H.; Li, Y. F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 629. (f) Zhou, E. J.; Tan, Z. A.; Yang, Y.; Huo, L. J.; Zou, Y. P.; Yang, C. H.; Li, Y. F. *Macromolecules* **2007**, *40*, 1831.

(15) Sol. Energy Mater. Sol. Cells **2008**, *92*, 371.
(16) (a) Mihailetchi, V. D.; M.; Blorn, P. W.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849. (b) Dyakonov, V. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 21.
(17) Chen, L.-M.; Hong, Z. R.; Li, G.; Yang, Y. *Adv. Mater.* **2009**, *21*, 1434.

Table 1. Optical and Electrochemical Properties of the Polymers

| | UV–vis absorption spectra | | | | cyclic voltammetry | | |
| | solution | film | | | *p*-doping | *n*-doping | |
polymer	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{opt} (eV)	E_{on}^{ox}/HOMO (V)/(eV)	E_{on}^{red}/LUMO (V)/(eV)	E_g^{EC} (eV)
PF-DTDPP	652	654	710	1.75	0.62/−5.42	−1.16/−3.64	1.78
PC-DTDPP	658	676	760	1.63	0.55/−5.35	−1.14/−3.66	1.69
PDTP-DTDPP	780	852	1100	1.13	0.22/−5.02	−1.16/−3.64	1.38

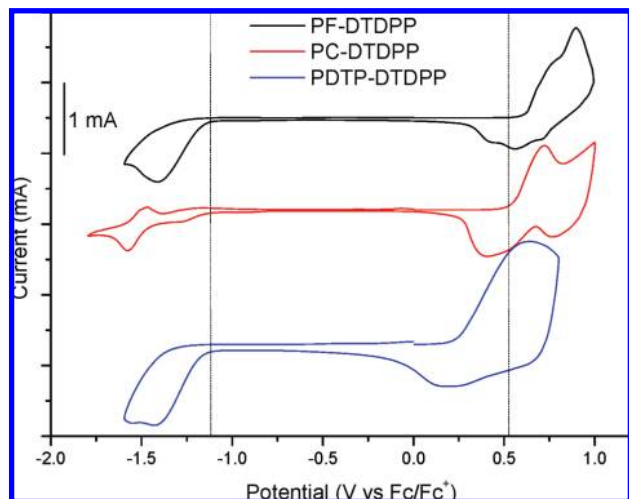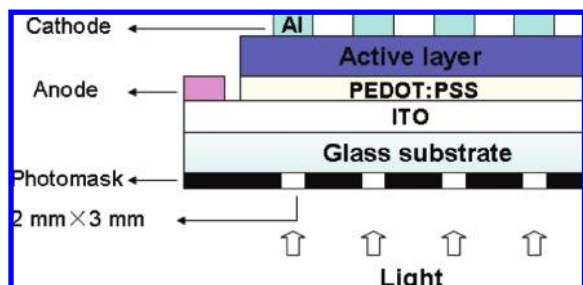**Figure 3.** Cyclic voltammogram of three polymers films on a platinum plate in an acetonitrile solution of 0.1 mol/L [Bu$_4$N]PF$_6$ (Bu = butyl) at a scan rate of 50 mV/s.

Scheme 3. Schematic Representation of the Polymer/Fullerene Bulk-Heterojunction PSCs

PSCs based on PDTP-DTDPP:PCBM blends extend to above 1 μm. To our knowledge, PDTP-DTDPP has the highest PCEs (1.12%) in all the low band gap photovoltaic polymers with the photocurrent response wavelengths above 1 μm.[18] In addition, since this response is complementary with the semiconducting polymers such as P3HT that is commonly used for high performance PSCs, the use of PDTP-DTDPP in the multilayer or tandem devices[19]

(18) (a) Wang, X. J.; Perzon, E.; Delgado, J. L.; de la Cruz, P.; Zhang, F. L.; Langa, F.; Andersson, M.; Inganäs, O. *Appl. Phys. Lett*. **2004**, *85*, 5081. (b) Xia, Y. L.; Wang, L.; Deng, X. Y.; Li, D. Y.; Zhu, X. H.; Cao, Y. *Appl. Phys. Lett*. **2006**, *89*, 81106. (c) Wienk, M. M.; Turbiez, M. G. R.; Struijk, M. P.; Fonrodona, M.; Janssen, R. A. J. *Appl. Phys. Lett*. **2006**, *88*, 153511. (d) Perzon, E.; Zhang, F. L.; Andersson, M.; Mammo, W.; Inganäs, O.; Andersson, M. R. *Adv. Mater*. **2007**, *19*, 3308. (e) Yi, H. N.; Johnson, R. G.; Iraqi, A.; Mohamad, D.; Royce, R.; Lidzey, D. G. *Macromol. Rapid Commun*. **2008**, *29*, 1804. (f) Zoombelt, A. P.; Fonrodona, M.; Wienk, M. M.; Sieval, A. B.; Hummelen, J. C.; Janssen, R. A. J. *Org. Lett*. **2009**, *11*, 903.
(19) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T.-Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222.
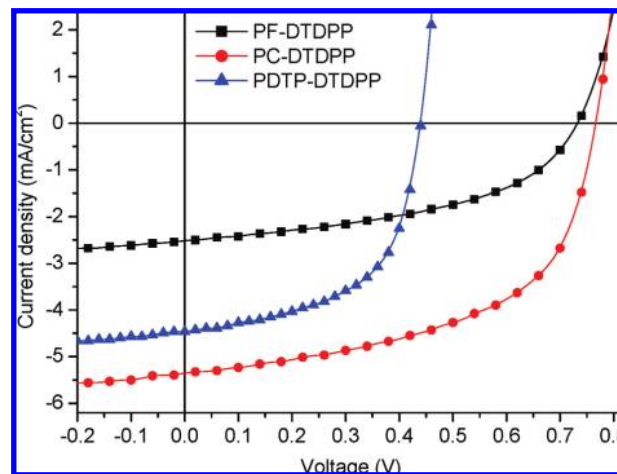
Figure 4. *I*–*V* curves of the polymer solar cells based on three polymers under the illumination of AM 1.5, 100 mW/cm^2.

Table 2. Device Characteristics of PSCs Based on DPP-Containing Polymers with PCBM

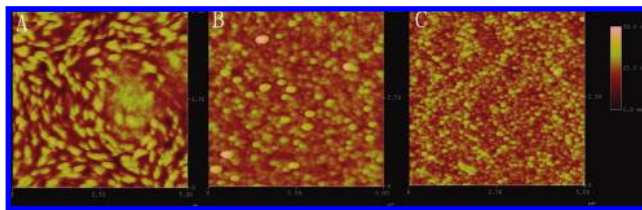| active layer (w/w)	V_{OC} (V)	I_{SC} (mA/cm^2)	FF	PCE (%)
PF-DTDPP:PCBM (1:2)	0.74	2.51	0.47	0.88
PC-DTDPP:PCBM (1:2)	0.76	5.35	0.56	2.26
PDTP-DTDPP:PCBM (1:3)	0.44	4.47	0.57	1.12

Figure 5. AFM height images of PF-DTDPP:PCBM (A), PC-DTDPP:PCBM (B), and PDTP-DTDPP:PCBM (C) composite films, spin-coated from dichlorobenzene solution.
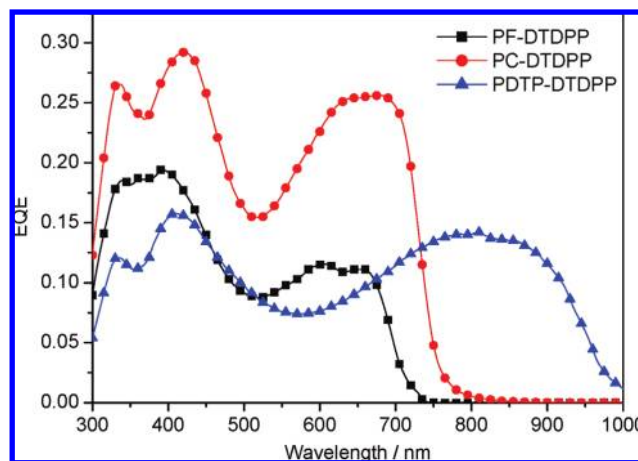

Figure 6. EQE of PSCs based on DPP-containing polymers with PCBM.

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with those materials could further improve the efficiency of the solar light collection.

Conclusion

Three diketopyrrolopyrrole-based donor−acceptor (D-A) type copolymers, PF-DTDPP, PC-DTDPP, and PDTP-DTDPP were successfully synthesized. The absorption spectra and energy level of resulting copolymers can be tuned easily by changing the donor segments. The photovoltaic device based on a PC-DTDPP:PCBM bulk heterojunction gives a higher PCE of 2.26%. The photocurrent response wavelengths of the PSCs based on PDTP-DTDPP:PCBM blends extend to above 1 μm with a moderate PCE of 1.12%. These results indicate DTDPP is a kind of effective acceptor segment for the design of D−A type photovoltaic polymers. Further investigations on these DTDPP-based copolymers, such as charge transport properties both in the pristine polymer films and in the blend films with PCBM, are in progress.

Experimental Section

Synthesis. 9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester solution (monomer **5**, 0.5 mol/L in toluene, Aldrich) and other chemicals were purchased from Alfa, Aldrich, or Wako and used without further purification. The following compounds were synthesized according to the procedure in the literature:, 3,6-dithien-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (**1**),[20] 3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (**2**),[12] 2,7-dibromo-9-*H*-carbazole (**6**),[21] 2,6-di(trimethyltin)-*N*-[1-(2′-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2′,3′-d]pyrrole (**10**).[10f]

Synthesis of 3,6-Di(2-bromothien-5-yl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (3). In a 500 mL double-neck round-bottom flask, compound **2** (6.3 g, 12 mmol) was dissolved in 350 mL of CHCl₃, covered with aluminum foil. *N*-bromo-succinimide (4.7 g, 26.4 mmol) was added portionwise, and the reaction mixture was stirred for 48 h at room temperature. The reaction mixture was poured into water, and the organic phase was separated and washed by water. The organic layers were dried over MgSO₄ and concentrated by rotary evaporation. The crude compound was purified by column chromatography (silica gel; eluent: chloroform/hexane 1/1 (v/v)), and the title compound was isolated as dark-purple solid. Yield: 6.1 g (74%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.65 (d, 2H), 7.22 (d, 2H), 3.93 (m, 4H), 1.84 (m, 2H), 1.4−1.2 (br, 16H), 0.85 (m, 12H).

Synthesis of 1-Decyl-1-undecanol (4). In a three-neck flame-dried 1 L round-bottom flask, ethyl formate (20.1 mL, 250 mmol) was dissolved in 300 mL of THF and cooled to −78 °C under N₂ atmosphere. A freshly prepared solution of decylmagnesium bromide [obtained by adding a solution of 1-bromodecane (133 g, 600 mmol) in dry THF (200 mL) to a suspension of Mg (15.8 g, 660 mmol) in dry THF (300 mL)] was then added dropwise, and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by the addition of MeOH and then saturated aqueous NH₄Cl. The crude compound was extracted three times with diethyl ether. The combined organic layers were washed with a saturated

NaHCO₃ solution and brine, dried over MgSO₄, and concentrated by rotary evaporation. After vacuum distillation, the title compound was isolated as a white solid. Yield: 72.5 g (93%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 3.59 (s, 1H), 1.5−1.0 (m, 37H), 0.88 (t, 6H).

Synthesis of Toluene-4-sulfonic acid 1-Decylundecyl Ester (5). *p*-Toluenesulfonyl chloride (22.88 g, 120 mmol) in CH₂Cl₂ (80 mL) was added to a stirred solution of 1-decylundecanol (25 g, 80 mmol), Et₃N (27.9 mL, 200 mmol), and Me₃N·HCl (7.65 g, 80 mmol) in CH₂Cl₂ (100 mL) at 0 °C. After stirring for 2 h at room temperature, water was added and the mixture was extracted three times with CH₂Cl₂. The combined organic layers were washed with brine and then dried over MgSO₄. The solvents were removed by rotary evaporation. The crude compound was purified by column chromatography (silica gel; eluent: chloroform/hexane 1/5 (v/v)), and the title compound was isolated as viscous, colorless liquid. Yield: 32.0 g (86%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.79 (d, 2H), 7.32 (d, 2H), 4.54 (m, 1H), 2.40 (s, 3H), 1.57 (m, 4H), 1.3−1.0 (br, 32H), 0.87 (t, 6H).

Synthesis of 2,7-Dibromo-*N*-(1-decylundecyl)carbazole (7). In a double-neck flame-dried 100 mL round-bottom flask, 2,7-dibromo-9-*H*-carbazole (1.625 g, 5.0 mmol) and 1.4 g (25.0 mmol) of freshly powdered potassium hydroxide were dissolved in anhydrous dimethyl sulfoxide (DMSO, 20 mL), and then a solution of 3.50 g (30.00 mmol) of **5** in DMSO (10 mL) and THF (10 mL) was added dropwise through the addition funnel over 2 h at room temperature. After stirring at room temperature overnight, the reaction mixture was poured into water and the aqueous layer was extracted three times with hexane. The combined organic layers were dried over MgSO₄, and the solvents were removed by rotary evaporation. The crude compound was purified by column chromatography (silica gel; eluent:, hexane), and the title compound was isolated as a white solid. Yield: 1.90 g (62%).

¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.90 (m, 2H), 7.69 (s, 1H), 7.53 (s, 1H), 7.33 (m, 2H), 4.41 (m, 1H), 2.18 (m, 2H), 1.90 (m, 2H), 1.3−0.9 (br, 32H), 0.86 (t, 6H).

Synthesis of 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(1-decylundecyl)carbazole (8). *n*-BuLi (1.92 mL, 3.07 mmol, 1.6 M in hexane) was added via a syringe to a solution of 2,7-dibromo-*N*-(1-decylundecyl)carbazole (**7**) (0.929 g, 1.5 mmol) in anhydrous THF (20 mL) at −78 °C under N₂ atmosphere. After the reaction was stirred for 1 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.68 mL, 3.30 mmol) was added rapidly via a syringe. After one additional hour at −78 °C, the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water, and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were dried over MgSO₄, and the solvents were removed by rotary evaporation. Finally, the crude compound was purified by column chromatography (silica gel; eluent: chloroform/hexane 1/10 (v/v)) and isolated as a viscous, colorless solid. Yield: 0.77 g (72%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.12 (m, 2H), 8.02 (s, 1H), 7.88 (s, 1H), 7.66 (m, 2H), 4.69 (m, 1H), 2.32 (m, 2H), 1.94 (m, 2H), 1.3−1.0 (br, 32H), 0.85 (t, 6H).

Synthesis of DTDPP-Containing D-A Copolymers. *Poly-{9,9-di(2-ethylhexyl)fluorene-2,7-diyl-alt-3,6-dithien-2-yl-2,5-di-(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl}* (*PF-DTDPP*). 9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis-(1,3-propanediol) ester (0.4 mL, 0.2 mmol) and monomer **6** (136.5 mg, 0.2 mmol) were dissolved in a mixture of THF (15 mL) and 2 mol/L aqueous solution of Na₂CO₃ (8 mL).

(20) (a) Iqbal, A.; Jost, M.; Kirchmayr, R.; Pfenninger, J. A.; Rochat, A.; Wallquist, O. *Bull. Soc. Chim. Belg* **1988**, *97*, 615. (b) Yamamoto, H. International Patent WO2004/090046, **2004**.
(21) Sonntag, M.; Strohriegl, P. *Chem. Mater.* **2004**, *16*, 4736.

The reaction container was purged with N_2 for 30 min to remove O_2. Pd(PPh$_3$)$_4$ (3%, 7 mg) was added, and the mixture was heated under reflux for 48 h. Phenylboric acid (100 mg in 1 mL THF) was added, and after 2 h, bromobenzene (1 mL) was introduced. The mixture was allowed to reflux for 2 h and cooled to room temperature, and the polymer was precipitated by slowly adding the mixture into CH$_3$OH. The precipitates were collected by filtration and then washed with MeOH and hexane. The solid was dissolved in CHCl$_3$ (150 mL) and passed through a column packed with alumina, Celite, and silica gel. The column was eluted with CHCl$_3$. The combined polymer solution was concentrated and was poured into MeOH. After this, the precipitates were collected and dried under vacuum overnight. Yield: 120 mg (66%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 9.06 (br, 2H), 7.78–7.40 (m, 8H), 4.14 (br, 4H), 2.10–2.01 (m, 6H), 1.5–0.6 (m, 58H). Anal. Calcd for C$_{59}$H$_{78}$N$_2$O$_2$S$_2$: C, 77.75; H, 8.63; N, 3.07. Found: C, 77.78; H, 8.77; N, 2.93. M_n = 15.3 kg/mol; polydispersity = 1.94.

Poly{N-(1-decylundecyl)carbazole-2,7-diyl-alt-3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl} (*PC-DTDPP*). A procedure was followed that was similar to the synthesis of PF-DTDPP starting with monomer **8** (0.26 mmol, 186 mg) and monomer **3** (0.26 mmol, 177 mg). Yield: 190 mg (75%).

^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 9.06 (br, 2H), 8.14–7.40 (m, 8H), 4.65 (br, 1H), 4.17 (br, 4H), 2.35 (br, 2H), 2.03 (br, 4H), 1.5–0.8 (m, 66H). Anal. Calcd for C$_{63}$H$_{87}$N$_3$O$_2$S$_2$: C, 77.01; H, 8.93; N, 4.28. Found: C, 76.59; H, 9.09; N, 4.20. M_n = 91.3 kg/mol; polydispersity = 1.77.

Poly{N-[1-(2-ethylhexyl)-3-ethylheptanyl]-dithieno[3,2-b:2′,3′-d]-pyrrole-3,6-dithien-2-yl-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-5′,5″-diyl} (*PDTP-DTDPP*). Monomer **9** (349 mg, 0.47 mmol), monomer **3** (321 mg, 0.47 mmol), and dry toluene (20 mL) were added to a 50 mL double-neck round-bottom flask. The reaction container was purged with N_2 for 30 min to remove O_2. Pd(PPh$_3$)$_4$ (5%, 27 mg) was added and heated up to 110 °C. The solution was stirred at 110 °C for 48 h. The dark blue sticky solution was cooled down to room temperature and poured into MeOH (200 mL), and the precipitates were collected by filtration and then washed with MeOH. The solid was dissolved in CHCl$_3$ (150 mL) and passed through a column packed with alumina, Celite, and silica gel.

The column was eluted with CHCl$_3$. The combined polymer solution was concentrated and poured into MeOH. After which, the precipitates were collected and dried. Yield: 310 mg (70%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.96 (br, 2H), 7.5–6.8 (m, 4H), 4.50 (br, 1H), 4.09 (br, 4H), 2.0–0.5 (m, 60H). Anal. Calcd for C$_{55}$H$_{75}$N$_3$O$_2$S$_4$: C, 70.39; H, 8.06; N, 4.48. Found: C, 69.59; H, 8.04; N, 4.22. M_n = 8.5 kg/mol; polydispersity = 1.70.

Characterization. ^{1}H NMR (400 MHz) spectra were measured using a JEOL Alpha FT-NMR spectrometer equipped with an Oxford superconducting magnet system. Absorption spectra were measured using a SHIMADZU spectrophotometer MPC-3100. Cyclic voltammograms (CVs) were recorded on an HSV-100 (Hokuto Denkou) potentiostat. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag$^+$ (0.01 M of AgNO$_3$ in acetonitrile) electrode were used as the counter and the reference electrodes (calibrated vs Fc/Fc$^+$), respectively. AFM measurement was carried out using a Digital Instrumental Nanoscope 31 operated in the tapping mode.

Fabrication and Characterization of Polymer Solar Cells. PSCs were constructed in the traditional sandwich structure through several steps. ITO-coated glass substrates were cleaned by ultrasonication sequentially in detergent, water, acetone, and 2-propanol. After drying the substrate, PEDOT:PSS (Baytron P) was spin-coated (4000 rpm for 30 s) on ITO. The film was dried at 150 °C under N_2 atmosphere for 5 min. After cooling the substrate, a dichlorobenzene solution of the polymer and PCBM mixture was spin-coated. After drying the dichlorobenzene, the substrate was transferred into an evaporation chamber (ALS technology H-2807 vacuum evaporation system with E-100 load lock). An Al electrode (~60 nm) was evaporated onto the substrate under high vacuum (10^{-4}–10^{-5} Pa). Postdevice annealing was carried out at 110 °C for 5 min inside a nitrogen-filled glovebox. The current–voltage characteristics of the photovoltaic cells were measured using the Keithley 2400 I–V measurement system. The measurements were conducted under the irradiation of AM 1.5 simulated solar light (100 mW cm^{-2}, Peccell Technologies PCE-L11). Light intensity was adjusted by a standard silicon solar cell with an optical filter (Bunkou Keiki BS520). The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight System (Bunkoh-Keiki SM-250F).