Ternalization Approach for Tuning Light Absorption and Crystalline Structure of Diketopyrrolopyrrole-Based Polymer Using Bisthiadiazole Unit

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Diketopyrrolopyrrole (DPP) and bisthiadiazole (BTDz)-based terpolymers were developed to obtain tunable optical properties and crystalline structures. Using dibromo-compounds of DPP and BTDz with distannylated thienylene vinylene (TV) moieties, high molecular weight polymers (44,100-99,200) with varied BTDz compositions (25, 50, or 75 mol%) were obtained. The introduction of BTDz generated a complementary light absorption band in the short-wavelength region (≤550 nm), while the DPP units created an intramolecular charge transfer band at ~730 nm. As a result, terpolymers with a deep highest occupied molecular orbital energy of ~5.50 eV and narrow bandgap of <1.5 eV were obtained. In addition, the crystal orientation of the DPP-based polymer was changed from edge-on to face-on by copolymerizing with only 25 mol% BTDz units.

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Manuscript submitted December 28, 2017; revised manuscript received January 15, 2018. Published February 13, 2018. This paper is part of the JES Focus Issue on Ubiquitous Sensors and Systems for IoT.

The global utilization of photovoltaics (PVs) is growing at an accelerated pace. The total installed capacity, which was only 1.7 GW in 2005, reached 303 GW worldwide in 2016.1 Accordingly, the cost of photovoltaic electricity has decreased dramatically and is now comparable to that of other renewable energy sources. To realize a sustainable social system, the widespread use of PV systems in the building walls, room interiors, and automobile roofs is desirable. Therefore, the demand for organic photovoltaics (OPVs), which is a thin-film, lightweight and highly flexible, is increasing more and more.2–4 OPV is also expected as a potential energy source for a wide variety of sensors in internet of things (IoT) in the near future.

To harvest solar energy efficiently, the light absorption characteristics of the photoelectric conversion material are important factors. Because there is a theoretical limitation on the photoelectric conversion efficiency (PCE) of a single semiconductor, called the Shockley–Queisser limit,5 an approach combining several semiconductors has been widely used for both inorganic and organic PVs.6–8 Particularly in OPVs, a photoelectric conversion layer in which two to three kinds of organic semiconductors are mixed is used to take advantage of their solution processability. Except for examples such as fullerene derivatives9 and ITIC,10 electron or exciton transfer between mixed semiconductors or organic small molecules.

Moreover, the third component gives additional freedom in the polymer backbone can overcome this drawback.11,12 Since different light absorbers are chemically bonded with continual conjugation, a wide wavelength of light can be absorbed by a single polymer film. Moreover, the third component gives additional freedom in the polymer chain packing and solubility. In addition, synergetic effects on the crystalline structure and charge carrier mobility can be achieved by finely tuning the composition. These features represent the unique and advantageous characteristics of polymeric semiconductors, compared with inorganic semiconductors or organic small molecules.

Diketopyrrolopyrrole (DPP)-based polymer is one of the best semiconducting polymers in terms of balanced performance, solubility, and synthetic facility.13 Due to the high electron withdrawing properties of DPP, it has a deep LUMO energy level of (−3.5)−(−4.0) eV with an optical bandgap of 1.5–1.7 eV, which is optimal for harvesting sunlight. In addition, DPP-based polymers with optimized main and side chains show very high charge carrier mobilities, even for solution-processed polycrystalline films.14,15 However, the DPP-based polymer tends to form edge-on oriented crystals suitable for charge transfer in the in-plane direction, which is not preferable for OPVs requiring charge transport in the out-of-plane direction. Therefore, the modification of the side chains and main chain structures has been done to control the crystal orientation.16–18

Based on the previous research, we attempted to expand the absorption spectrum and control the crystalline orientation of DPP-based polymer using a terpolymer approach. We previously developed a short-wavelength absorber using PBTTzDzV, an alternating copolymer composed of a strongly electron-deficient unit, 2,2’-bis(1,3,4-thiadiazole) (BTDz), and a weakly electron-rich unit, thienylene vinylene (TV).19 Due to the strong electron withdrawing properties of BTDz, PBTTzDzV has a deep HOMO energy level of −5.5 eV and a wide bandgap of 1.9 eV. In addition, due to enhanced intermolecular interactions, this material exhibits a highly crystalline nature with face-on orientation. Therefore, the hole mobility in the out-of-plane direction was 6.22 × 10⁻² cm²V⁻¹s⁻¹, which is high among polymer semiconductors. The OPVs using mixed films with PC71BM showed a high PCE exceeding 8%. Thus, in this work, DPP, BTDz, and TV are copolymerized to obtain a terpolymer, BTDz_25DPP_75, where xx and yy are molar ratio (%) of BTDz and DPP respectively, that shows a complementary absorption spectrum and a face-on oriented crystalline structure.

Experimental

Reagents.—Tris(dibenzylideneacetonato)dipalladium(0) (Pd₂dba₃) and tri(o-toly)phosphine (P(o-tol))₁₀, sodium dimethyldithiocarbonate dihydrate were purchased from Tokyo Chemical Industry Co., Ltd. 3,6-Bis(5-bromo-2-thienyl)-2,5-bis(2-hexyldecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP monomer) was purchased from Sigma-Aldrich Co. LLC. Dehydrated toluene was purchased from Kanto Chemical Co., Inc. 5,5’-Bis(5-bromo-3,4-didecyl-2-thienyl)-2,2’-bi-1,3,4-thiadiazole (BTDz monomer), and (E)-1,2-di-(3-(2-ethylhexyl))-5-trimethylammoniumphosphinevinylene (TV monomer) were synthesized according to the literatures.19

Synthesis.—BTDz_25DPP_75.—In a 20 mL of two-neck flask, BTDz monomer (0.75 eq. 0.15 mmol, 174.8 mg), DPP monomer (0.25 eq., 0.05 mmol, 45.4 mg), TV monomer (1.0 eq., 0.20 mmol, 148.5 mg), Pd₂dba₃ (0.060 eq. 0.012 mmol 11.0 mg) and P(o-tol) (0.30 eq.,...
0.060 mmol, 18.3 mg) were dissolved in dehydrated toluene (2 mL). The solution was refluxed for 3 h to afford a viscous solution. The solution was diluted with chloroform and washed with sodium dimethyldithiocarbamate aq., and then, brine. The organic layer was further dried over magnesium sulfate. After filtration to remove the magnesium salt, the filtrate was concentrated and precipitated into methanol. The precipitate was collected by vacuum filtration to afford the crude product. It was then washed by Soxhlet extraction using acetone, hexane, and extracted using chloroform. After evaporating the solvent, the polymer was freeze-dried to afford BTDz50-DPP50.

Yield = 205 mg (76%). SEC (THF, 40 °C): $M_n = 44,100$, $M_w = 81,000$, $D = 1.84$. $^1$H NMR (400 MHz, chloroform-$d$, ppm, 25 °C, Figure S3): 8.91 (br, 0.5H), 6.99–6.67 (br, 4.5H), 4.04 (br, 1H), 2.91 (br, 3H), 2.78 (br, 3H), 2.61 (br, 4.5H), 1.98–0.89 (br, 114H). Anal. Calcd. for $C_{52}H_{123}N_2O_5S_5$ (%): C, 73.15, H, 9.69, N, 3.56. Found (%): C, 73.00, H, 10.06, N, 3.51.

Other syntheses were recorded on JEOL JNM-ECX400 in chloroform-$d$, ppm, 25 °C.

Solar cell characterization.—The solution for active layer was prepared by dissolving 4 mg of polymer and 6 mg of PC$_71$BM in 0.4 mL of the mixed solvent (chloroform/n-dichlorobenzene/1-chloronaphthalene = 3:1:0.12, by vol). The mixture was stirred for 12 h before use. The glass—indium tin oxide (ITO) substrates (obtained from Lumtect, Ltd. (7 Ω/sq)) were first patterned by lithography, then cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, subsequently dried on a hot plate at 120 °C for 5 min, and finally treated with oxygen plasma for 15 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AH4083) was passed through a 0.45 μm filter before being deposited on ITO spin-coating at 5000 rpm for 60 s in the air, and dried at 140 °C for 20 min inside a glove box. The blended film of the polymer/PC$_71$BM (1:1.5, by wt) was prepared by spin-coating the active layer solution on the top of the PEDOT:PSS layer at 600 rpm for 60 s. After drying for 1 h, the devices were completed by thermal evaporation of Ca (30 nm) and Al (100 nm) under high-vacuum condition (<10$^{-6}$ Torr). The active area of the device is 4 mm$^2$. The current density—voltage ($J$–$V$) measurement was conducted by a computer-controlled Keithley 2400 source measurement unit (SMU) with a Peccell solar simulator under the illumination of AM 1.5G, 100 mW/cm$^2$. The illumination intensity was calibrated by a standard Si photodiode detector with KG-5 filter and no additional mask was used under the illumination.

Results and Discussion

According to Scheme 1, the Stille-coupling copolymerization of BTDz, DPP and TV was conducted. The feed ratio of TV/BTDz/DPP was varied from 1.00/0.75/0.25, 1.00/0.50/0.50, 1.00/0.25/0.75, and 1.00/1.0. After the removal of impurities and the low molecular weight fraction by Soxhlet extraction, the target polymers were obtained with number-averaged molecular weights ($M_n$) of 44,000–99,000 and dispersities ($D_n$) of 1.84–5.85, which was summarized in Table I. The structure was confirmed by $^1$H NMR spectroscopy and elemental analysis. All the polymers showed sufficient solubility in chlorinated solvents, and polymers with high DPP content partially dissolved even in hexane.

The thermal properties, listed in Table II and Figure 1, were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All the samples have similar 5 wt% weight loss temperatures ($T_{5\%}$) of ~400°C, which indicates sufficient thermal stability.
Table I. Results of polymerization.

| Polymer         | BTDz (eq.) | DPP (eq.) | TV (eq.) | M<sub>n</sub> \((\times 10^3)\) | M<sub>w</sub> \((\times 10^3)\) | D<sup>c</sup> |
|-----------------|------------|-----------|----------|-------------------------------|-----------------------------|-----------|
| PDPPTV          | 0          | 1.0       | 1.0      | 72.0                          | 421.1                       | 5.85      |
| BTDz<sub>25</sub>DPP<sub>75</sub> | 0.25       | 0.75      | 1.0      | 99.2                          | 254.3                       | 2.57      |
| BTDz<sub>50</sub>DPP<sub>50</sub> | 0.50       | 0.50      | 1.0      | 56.8                          | 126.9                       | 2.23      |
| BTDz<sub>75</sub>DPP<sub>25</sub> | 0.75       | 0.25      | 1.0      | 44.1                          | 81.0                        | 1.84      |

<sup>a</sup>number-averaged molecular weight  
<sup>b</sup>weight-averaged molecular weight  
<sup>c</sup>dispersity  
These parameters were measured by SEC using tetrahydrofuran at 40°C as an eluent, where polystyrene standards were used to obtain a calibration curve.

Table II. Thermal and optical properties of PDPPTV and terpolymers.

| Polymer         | T<sub>d5%</sub> \((°C)\)<sup>a</sup> | T<sub>c</sub> \((°C)\)<sup>b</sup> | T<sub>m</sub> \((°C)\)<sup>c</sup> | λ<sub>max</sub> \((nm)\)<sup>e</sup> | λ<sub>onset</sub> \((nm)\)<sup>f</sup> | E<sub>g</sub><sup>opt</sup> \((eV)\)<sup>g</sup> |
|-----------------|----------------------------------|----------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------|
| PDPPTV          | 397.2                            | -                                | -                               | 794                             | 922                             | 1.34                 |
| BTDz<sub>25</sub>DPP<sub>75</sub> | 397.2                            | 203.9                            | 217.3                           | 737                             | 905                             | 1.37                 |
| BTDz<sub>50</sub>DPP<sub>50</sub> | 397.4                            | 178.3                            | 196.7                           | 551, 735                        | 860                             | 1.44                 |
| BTDz<sub>75</sub>DPP<sub>25</sub> | 397.4                            | - \((239.1)\)<sup>d</sup>       | 551, 732                        | 818                             | 1.52                             |

<sup>a</sup>5 wt% of weight-loss temperature measured at 20°C/min in N<sub>2</sub>  
<sup>b</sup>crystallizing temperature measured at 10°C/min in N<sub>2</sub>  
<sup>c</sup>melting temperatures measured at 10°C/min in N<sub>2</sub>,  
<sup>d</sup>melting temperatures observed in the first heating process at 10°C/min  
<sup>e</sup>absorption maxima  
<sup>f</sup>absorption onsets  
<sup>g</sup>optical bandgaps calculated from the eq.; \(E_{g}^{opt} = \frac{1240}{\lambda_{onset}}\) (eV).

stability to withstand the metal deposition conditions during device fabrication. PDPPTV showed no transition peaks from 50 to 250°C, implying its amorphous nature, which is supported by the grazing incidence wide-angle X-ray scattering (GIWAXS) measurement described below. On the other hand, BTDz<sub>50</sub>DPP<sub>50</sub> and BTDz<sub>25</sub>DPP<sub>75</sub> showed broad but clear melting/crystallizing peaks at 178/197°C and 204/217°C, respectively. The difference between PDPPTV and the terpolymers indicates that the crystallinity is enhanced by the BTDz units. BTDz<sub>75</sub>DPP<sub>25</sub> does not exhibit a phase transition from 25 to 280°C, but an exothermic peak was observed at ∼240°C in the first heating process. Thus, BTDz<sub>75</sub>DPP<sub>25</sub> also has a crystalline nature, though its crystallization rate seems to be slow compared to the time scale of the DSC measurement.

The light absorption properties were evaluated by UV-Vis-Near infrared (NIR) absorption spectroscopy. Figure 2 displays the UV-Vis-NIR spectra of sample films on glass substrates. The sample films were prepared by spin-coating at 400 rpm for 60 s from 25 mg/mL solutions in chlorobenzene (CB), followed by drying at room temperature (15°C) for 1 h. All the terpolymers showed an absorption peak or shoulder at ∼730 nm, corresponding to intramolecular charge transfer (ICT) between DPP and TV. In addition to these peaks, complementary absorption bands were observed at ∼550 nm. Because these peaks are similar to those observed in the PBTDz<sub>TV</sub> absorption spectrum, they are attributed to \(\pi-\pi^*\) transitions resulting from the BTDz-TV structure. The \(\pi-\pi^*\) transition peaks of BTDz<sub>25</sub>DPP<sub>25</sub>

Figure 1. DSC curves of PDPPTV and terpolymers at 10°C/min in N<sub>2</sub>.

Figure 2. UV-Vis-NIR absorption spectra for PDPPTV and terpolymers at thin film states.

Figure 3. a) Oxidative cyclic voltammogram and b) energy diagram for PDPPTV and terpolymers films, where the following eq. were used; HOMO = -(E<sub>onset</sub> + 4.8) (eV), and LUMO = HOMO + E<sub>g</sub><sup>opt</sup> (eV).
Figure 4. Two-dimensional GIWAXS patterns of PDPPTV and terpolymer thin films.

BTDz50TV50 have a shoulder in the long-wavelength region (∼600 nm), indicating aggregated states. The optical bandgaps calculated from the absorption onsets range from 1.34 to 1.52 eV and decrease according to the DPP content. Thus, the ternaryization of the polymer with BTDz successfully expanded the absorption band, tuning the optical bandgap of PDPPTV.

The electrochemical properties of the sample films were obtained from cyclic voltammetry. The oxidation peaks in the positive scans are depicted in Figure 3a. The HOMO energy levels evaluated from the oxidation peak edges and LUMO energy levels, calculated from the HOMO levels and optical bandgaps, are shown in Figure 3b. The sample with a higher BTDz content shows a deeper HOMO energy level (∼-5.5 eV) and a deep LUMO energy level (∼-4.0 eV) due to DPP. Thus, the obtained energy levels in BTDz75DPP25 and BTDz50DPP50 are ideal for OPV applications.

Grazing incident wide-angle X-ray scattering (GIWAXS) was performed on the thin films to analyze the crystal structures. Figure 4 displays the two-dimensional GIWAXS images, the one-dimensional profiles corresponding to the in-plane and out-of-plane directions and the azimuth profile of (100) scattering. The PDPPTV thin film has an amorphous-like nature with a (100) scattering spot at \( q_z = 3.36 \text{ nm}^{-1} \) (1.87 nm). The azimuth profile clearly suggests that the (100) scattering is observed in the out-of-plane direction, indicating the edge-on orientation of the crystallites, as (100) is attributed to their lamellar spacing. When the BTDz unit is incorporated into PDPPTV, the crystalline structure is dramatically changed. All the terpolymers show a semi-crystalline nature with (100) spots in the in-plane direction and (010) spots in the out-of-plane direction, indicating face-on orientation. The volume fractions of the face-on oriented area in the crystalline region were quantified by the integral ratio between the peaks at 0–60 deg and 60–90 deg in the azimuth profiles (Figure 5a, Table III). Overall, 83–93 vol% of the crystals show face-on orientation, which is preferable for charge carrier transport in the out-of-plane direction and thus OPV performance. BTDz75DPP25 and BTDz50DPP50 have similar lamellar spacings (2.37 nm and 2.36 nm, respectively), which are close to that of the PBTDzTV homopolymer (Figures 5b, Table III). Interestingly, the lamellar spacing of BTDz25DPP75, 2.00 nm, is between those of PDPPTV and the other terpolymer. This result indicates that the crystalline region includes not only BTDz but also DPP units. Therefore, it can be concluded that only 25 mol% BTDz can promote enhanced crystallization and drastic orientation change.

The photovoltaic performance was evaluated using the conventional device architecture, ITO/PEDOT:PSS/active layer/Ca/Al, where the composition of the active layer was 1:1.5 (wt/wt) for polymer:[6,6]-phenyl C71 butyric acid methyl ester (PC71BM). The solvent for the active layer was a mixture of chloroform, o-dichlorobenzene and 1-chloronaphthalene (3:1:0.12, vol/vol), where chloroform and 1-chloronaphthalene were used to suppress PC71BM aggregation in the DPP-containing polymers. Figure 6 and Table IV show the J-V curves and characteristic OPV parameters. The PDPPTV-based device showed an open-circuit voltage (VOC) of 0.62 V, which was improved to 0.74 V by increasing the BTDz content. This trend follows that of the HOMO energy levels of the polymers. The short-circuit current density (JSC = 5.65 mA/cm²) and fill factor (FF = 0.645) were determined in the PDPPTV-based device and found to decrease in the BTDz75DPP25 and BTDz50DPP50-based devices. The limited photocurrent can be explained by the energy level and

| Table III. Structural parameters evaluated by GIWAXS measurement. |
|---------------------------------------------------------------|
| Polymer  | Face-on (%) | lamella (nm) | π-π (nm) |
|----------|-------------|--------------|----------|
| PDPPTV   | 0 (edge-on) | 1.87         | 0.38     |
| BTDz25DPP75 | 93         | 2.00         | 0.39     |
| BTDz50DPP50 | 91         | 2.36         | 0.39     |
| BTDz75DPP25 | 83         | 2.37         | 0.39     |

Figure 5. a) In-plane and b) out-of-plane one-dimensional profiles, and c) azimuth profile of (100) scattering.
miscibility. Considering the energy levels in the terpolymers, the local HOMO and LUMO energy levels of BTDz are deep and shallow, respectively, compared with those of DPP. Thus, both holes and electrons prefer to be located at the DPP unit, rather than BTDz. Therefore, BTDz is not a trapping site for charge carriers. Indeed, the terpolymer with the highest BTDz content, BTDz75:DPP25, showed a relatively high $J_{SC}$ of 5.36 mA/cm$^2$. Atomic force microscopy (AFM) was performed to evaluate the miscibility between the terpolymer and PC$_7$BM (Figure 7). The topography image of the BTDz75:DPP25:PC$_7$BM film exhibited a well-mixed structure; on the other hand, strong segregation of PC$_7$BM was observed in BTDz50:DPP50 with a domain size of 200–500 nm. Their root-mean-square roughness were 2.15 and 2.89 nm, respectively, which were also much larger than that of the BTDz75DPP25:PC$_7$BM film, 1.46 nm. The segregation reduces the p/n interfacial area, affording a limited $J_{SC}$ and FF. Further optimization of the solvent composition and additives may suppress aggregation to enhance photocurrent generation.

**Conclusions**

Based on a ternarization strategy, we copolymerized BTDz, DPP and TV to realize an expanded absorption spectrum and desired crystalline orientation. The obtained terpolymers showed two absorption peaks, attributed to BTDz and DPP units, resulting in an expanded absorption band as intended. The HOMO/LUMO energy levels were also tuned to be $-5.5/-4.0$ eV, respectively, which reflected the characteristics of both the BTDz and DPP units. In addition, the introduction of BTDz enhanced the crystalline nature of the polymer thin films and changed the crystalline orientation from edge-on to face-on. Therefore, the absorption spectrum, energy levels and crystalline structure were successfully tuned for OPV applications. Unfortunately, the photocurrent is limited by the aggregation of PC$_7$BM. Further optimization of the fabrication process is ongoing.

**Acknowledgments**

This study was supported by the Japan Society for the Promotion of Science (JSPS) (KAKENHI Grant Number, 16H06049). We thank Dr. Tomoyuki Koyanazawa (the Japan Synchrotron Radiation Research Institute, JASRI) for performing GIWAXS experiments at BL46XU of SPring-8 (Proposal 2017A1767). S. Fukuta appreciates the support by a Grant-in-Aid from JSPS, Research Fellowship for Young Scientists (Proposal No. 17J02989) and Innovative Flex Course for Frontier Organic Material Systems (iFront) at Yamagata University.

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