Synthesis, Characterization, and Solar Cell and Transistor Applications of Phenanthro[1,2-*b*:8,7-*b*']dithiophene–Diketopyrrolopyrrole Semiconducting Polymers

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ABSTRACT: Synthesis, characterization, and polymer solar cell and transistor application of a series of phenanthro[1,2-*b*:8,7*b'*]dithiophene-based donor-acceptor (D-A)-type semiconducting polymers combined with a diketopyrrolopyrrole unit are reported. The present polymers showed some unique features such as strong aggregation behavior, high thermal stability, and short π - π stacking distance (3.5–3.6 Å), which are suitable for high performance organic materials. In addition, they have a significantly extended absorption up to 1000 nm with a band gap of ca. 1.2 eV. However, such strong intermolecular interaction reduced their solubility and molecular weights, which

INTRODUCTION Donor-acceptor (D–A)-type semiconducting polymers have been widely used high-performance semiconductors in organic electronics.^{1–11} Recent developments in this field have made a remarkable progress. Indeed, power conversion efficiencies (PCEs) and field-effect mobilities ($\mu_{\rm FET}$ s) have reached over 10% for the polymer solar cells (PSCs),^{12,13} and >10 cm² V⁻¹s⁻¹ for organic field-effect transistors (OFETs),^{14–17} respectively. However, further improvements of the device performance are required to achieve the high-performance electronics in practical applications.

In order to maximize the device performance, it is essential to facilitate the dense π - π stacking structure with the high long-range orders, which enables efficient carrier transport through π - π orbitals between polymer backbones.^{6-8,18} An incorporation of the highly fused π -electron system into a polymer backbone is the most effective strategy to enhance an intermolecular interaction, which is highly desirable for high-performance D-A polymers. Such strong intermolecular interaction may lead to high self-assembling nature, which can lead to the low conformational disorders^{19,20} and form

resulted in low crystalline nature and moderate field-effect mobility of 0.01 cm² V⁻¹ s⁻¹. Furthermore, such strong aggregation behavior led to the large-scale phase separation in the blend films, which may prevent the effective photocurrent generation, limiting J_{sc} and power conversion efficiency of 2.0%. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

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the suitable phase separation structure without any additives or conducting a post-annealing process in PSCs.²¹⁻²⁴ In addition, a rigid and planar structure provides a high thermal stability.²⁰⁻²⁴ Among a large number of the developed high performance D-A polymers,^{12-17,19,21-29} the polymers with such highly extended π -electron system still limited. Thus, the development of such new building unit is highly desirable for high-performance electronics.

Linear π -extension typically elevates the HOMO energy levels, which significantly reduces $V_{\rm oc}$ and the chemical stability. From this viewpoint, phenacene-type molecules, such as picene ([5]phenacene]^{30,31} and fulminene ([6]phenacene),³² are one of the promising candidate for organic electronics. Although such molecules have highly extended π -electron system, they have deep HOMO energy levels and high air stability. Such rigid and extended π -electron core leads to high crystal-linity and strong intermolecular interaction, resulting in superior hole mobility over 1 cm² V⁻¹ s⁻¹.^{33,34} From these features, phenacene-type molecules are also potent building units for high performance semiconducting polymers. Actually,

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naphtho[1,2-b:5,6-b']dithiophene ([4]phenacene type molecule)-based semiconducting polymers showed excellent hole mobility of 0.77 cm² V⁻¹ s⁻¹ (Ref. 35) and PCE of over 8%.²² However, in spite of promising features, only few example of phenacene-based polymers has been reported due to a synthetic difficulty. Very recently, we have developed the efficient synthetic route of phenanthro[1,2-*b*:8,7-*b*']dithiophene (PDT), which is analogue of picene, a representative highperformance semiconductor.^{36,37} Such new phenacene-type molecule was found to have a deep HOMO energy level (-5.7)eV) and the high air and chemical stability. Indeed, PDT is an air-stable compound and its HOMO orbital highly delocalized over an entire molecule, leading to high crystalline nature and high hole mobility as high as $0.11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1.36}$ An excellent rigidity and a high planarity of PDT as additional features may lead to the effective π - π overlaps of the polymer main chain, which can allow the efficient carrier transport.

Herein, we report the synthesis and characterization of novel PDT-based semiconducting polymers (**P-PDT-DPP-R; R** denotes branched alkyl chains) in conjunction with diketopyrrolopyrrole (DPP) known as a representative acceptor unit. Furthermore, we evaluated properties of PDT as the new building block of the high-performance D-A polymers in solar cell and transistor fabrications.

EXPERIMENTAL

General

All the reactions were carried out under an Ar atmosphere using standard Schlenk techniques. Glassware was dried in an oven (130 °C) and heated under reduced pressure prior to use. Solvents employed as eluents and for all other routine operations, as well as the anhydrous solvents and all reagents used, were purchased from commercial suppliers and employed without any further purification. For TLC analyses throughout this work, Merck (Darmstadt, Germany) precoated TLC plates (silica gel 60 GF254, 0.25 mm) were used. Silica gel column chromatography was carried out using silica gel 60 N (spherical, neutral, 40–100 μ m) from Kanto Chemical Co., Ltd. (Tokyo, Japan). The ¹H and ¹³C{¹H} NMR spectra were recorded on Varian Mercury-300 (300 MHz), Varian 400-MR (400 MHz), and Varian INOVA-600 (600 MHz) spectrometers. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer (Shimadzu Co. (Kyoto, Japan)). Elemental analyses were carried out with a PerkinElmer 2400 CHN elemental analyzer (PerkinElmer, Waltham, MA) at Okayama University. Polymerization was performed with a Biotage initiator microwave reactor (Biotage, Uppsala, Sweden). Molecular weights of polymers were determined by GPC with a Polymer Laboratories PL-GPC210 using polystyrene standards and odichlorobenzene (o-DCB) as the eluent at 140 °C.

3,6-Bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**3**),³⁸ 2,5-bis(2-decyltetradecyl)-3,6-bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4a**),³⁹ 3,6-bis(5-bromothioph-ene-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**5a**),³⁹ and phenanthro[1,2-*b*:8,7-*b*']dithio-

phene (PDT, $\mathbf{1}$)³⁷ were prepared in accordance with the corresponding references.

3-Decyl-1-Pentadecyl Bromide

To a mixture of magnesium (1.28 g, 52.8 mmol) in dry THF (200 ml) was added a flake of I_2 as an initiator under an argon atmosphere.⁴⁰ 2-Decyl-1-tetradecyl bromide (20 g, 48 mmol) was added dropwise to a stirring mixture and refluxed for 3 h. To the resultant Grignard reagent solution was added dropwise the solution of paraformaldehyde (1.58 g, 62.4 mmol) in dry THF (50 ml) over 10 min at room temperature. After being stirred for 4 h, the reaction mixture was quenched with 1 M HCl (20 ml) and extracted with hexane (50 ml \times 3). The combined organic layers were washed with brine and dried over MgSO₄. After the removal of the solvent under reduced pressure, the crude product was used for a next step without further purification.

A solution of triphenylphosphine (10.3 g, 40.0 mmol) in CH_2Cl_2 (100 ml) was cooled to 0 °C and bromine (2.0 ml, 40.0 mol) was added slowly under an argon atmosphere. 3-Decyl-1-pentadecanol was added dropwise to the mixture at 0 °C and stirred at room temperature for 12 h. After evaporation, triphenylphosphine oxide precipitated was removed by filtration to afford the mixture, which was purified by column chromatography on silica-gel eluted with hexane ($R_f = 0.85$) to give the title compound as a colorless oil (2-step yield: 70%).

FT-IR (KBr, cm⁻¹): v = 2924 (s), 2853 (s), 1458 (s), 1253 (s), 721 (s), 650 (s), 422 (br). ¹H NMR (600 MHz, CDCl₃, rt, δ): 3.41 (t, J = 7.2 Hz, 2H), 1.81 (q, J = 6.6 Hz, 2H), 1.47 (m, 1H), 1.25–1.35 (m, 40H), 0.87–0.90 (m, 6H); ¹³C{¹H} NMR (150 MHz, CDCl₃, rt, δ): 37.3, 36.5, 33.1, 32.3, 31.9, 29.7, 29.6, 29.4, 26.4, 22.7, 14.1. Anal. Calcd for C₂₅H₅₁Br: C 69.57, H 11.91%; Found: C 69.70, H 11.80%.

Synthesis of 2,5-Bis(3-decylpentadecyl)-3,6-bis(thiophen-2yl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (4b)

A solution of 3-decylpentadecylbromide (5.0 g, 12.0 mmol) in anhydrous DMF (20 ml) was added dropwise to a mixture of 3,6-bis(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)dione (**3**) (1.5 g, 5.0 mmol), K₂CO₃ (1.6 g, 12.0 mmol), 18crown-6 (10 mg, 0.04 mmol) in anhydrous DMF (80 ml). The mixture was maintained at 120 °C overnight. The reaction mixture was cooled to room temperature and poured into water (100 ml). The compound was extracted with CHCl₃ and hexane, washed with brine, dried over MgSO₄. The solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica with 0–50% dichloromethane in hexane as the eluent to give **4b** ($R_f = 0.20$) as dark purple solid (0.96 g, 19%).

Mp. 44–46 °C. FT-IR (neat, cm⁻¹): v = 2918 (s), 2891 (s), 2851 (s), 2808 (w), 1732 (m), 1665 (s), 1558 (m), 1466 (w), 1404 (m). ¹H NMR (300 MHz, CDCl₃, rt, δ): 8.90 (dd, J = 3.9 and 1.2 Hz, 2H), 7.60 (dd, J = 5.1 and 1.2 Hz, 2H), 7.25 (dd, J = 5.0 and 3.9 Hz, 2H), 4.06 (t, J = 8.1 Hz, 4H), 1.68–1.65 (m, 4H), 1.30–1.25 (m, 80H), 0.88 (t, J = 6.9 Hz,

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12H). ${}^{13}C{}^{1}H$ NMR (75 MHz, CDCl₃, rt, δ): 161.1, 139.8, 135.1, 130.3, 129.6, 128.5, 107.7, 40.8, 35.9, 33.8, 33.4, 31.9, 30.0, 29.7, 29.6, 29.3, 26.5, 22.6, 14.1; Anal. Calcd for $C_{64}H_{108}N_2O_2S_2$: C 76.74, H 10.87, N 2.80%; Found: C 76.31, H 11.00, N 2.77%.

Synthesis of 3,6-Bis(5-bromothiophene-2-yl)-2,5-bis(2-

decyltetradecyl)pyrrolo[3,4-*c*]*pyrrole*-1,4(2H,5H)-*dione* (5b) *N*-Bromosuccinimide (NBS, 0.36 g, 2.0 mmol) was added slowly to a solution of **4b** (0.96 g, 0.95 mmol) in CHCl₃ (30 ml). The solution was protected from light and stirred at room temperature for 5 h. The reaction mixture was poured into MeOH (100 ml) and filtrated. After being dried under vacuum, the crude product was purified by twice recrystallization from ethyl acetate to give **5b** as purple solid (0.75 g, 68%).

Mp 78–80 °C. FT-IR (neat, cm⁻¹): v = 2920 (s), 2893 (m), 2851 (s), 2808 (w), 1867 (w), 1668 (s), 1558 (m), 1467 (w), 1406 (w). ¹H NMR (400 MHz, CDCl₃, rt, δ): 8.64 (d, J = 4.0Hz, 2H), 7.19 (d, J = 4.0 Hz, 2H), 3.95 (d, J = 8.0 Hz, 4H), 1.64–1.59 (m, 4H), 1.44–1.43 (m, 2H), 1.30–1.25 (m, 80H), 0.88 (t, J = 7.2 Hz, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃, rt, δ): 160.8, 138.8, 135.3, 131.5, 131.0, 118.9, 107.8, 40.9, 35.9, 33.7, 33.4, 31.9, 30.0, 29.7, 14.1. Anal. Calcd for C₆₄H₁₀₆N₂O₂S₂Br₂: C 66.30, H 9.21, N 2.42%; Found: C 66.27, H 8.91, N 2.34%.

Synthesis of 2,9-Bis(trimethylstannyl)-phenanthro [1,2-b:8,7-b']dithiophene (2)

To a solution of phenanthro[1,2-*b*:8,7-*b*']dithiophene (1) (1.0 g, 3.43 mmol) in anhydrous THF (100 ml) was added *n*-BuLi (1.6 M hexane solution, 6.45 ml, 10.3 mmol) at -78 °C, and the mixture was stirred at room temperature for 1 h. After the mixture was cooled to -78 °C, trimethyltin chloride (2.75 g, 13.7 mmol) was slowly added and the mixture was stirred at room temperature for 3 h. Then the mixture was treated with water (100 ml) and extracted with dichloromethane (50 ml \times 3). The combined organic layers were washed with brine and dried over MgSO₄. After a removal of the solvent under reduced pressure, the precipitate was collected by filtration and washed with hexane to give **2** as white solid (2.07 g, 98%).

Mp 277–279 °C. FT-IR (KBr, cm⁻¹): v = 3433 (br), 2946 (m), 1282 (s), 910 (s), 843 (s), 773 (m), 727 (s), 534 (s). ¹H NMR (600 MHz, CDCl₃, rt, δ): 8.65 (d, J = 9.0 Hz, 2H), 8.25 (s, 2H), 8.03 (d, J = 9.0 Hz, 2H), 7.61 (s, 2H), 0.49 (s, $J_{\text{Sn-H}}$ satellite = 28 Hz, 18H). ¹³C{¹H} NMR (150 MHz, CDCl₃, rt, δ): 143.8, 139.6, 139.2, 133.1, 127.3, 126.9, 124.0, 122.0, 120.3, -8.1 ($J_{\text{C-Sn satellite}} = 186$ Hz). Anal. Calcd for C₂₄H₂₆S₂Sn₂: C 46.79, H 4.25%; Found: C 46.88, H 4.11%.

Synthesis of Poly[2,9-bisthiophen-2-yl-phenanthro[1,2b:8,7-b']dithiophene-5,5'-diyl-alt-2,5-bis(2-decyltetradecyl-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl) (P-PDT-DPP-DT)

Monomers **2** (28.9 mg, 0.047 mmol) and **5a** (53.0 mg, 0.047 mmol), PdCl₂(PPh₃)₂ (0.66 mg, 0.94 μ mol), and toluene

(2.5 ml) were added to a 5-ml reaction vial. The vial was sealed and heated in a microwave reactor at 110°C for 30 min. After being cooled to room temperature, the reaction mixture was poured into methanol (100 ml) and concentrated hydrochloric acid (2 ml), and vigorously stirred for 1 h at room temperature. The precipitate was filtered and subjected to Soxhlet extraction with methanol, hexane, chloroform, and finally chlorobenzene. The chloroform fraction was concentrated and poured into methanol. The precipitate was isolated by filtration and dried in vacuo to afford the polymer sample (42 mg, 71%) as a metallic purple solid. GPC (o-DCB, 140°C): Almost proceeded the detection limit of typical polystyrene standards due to the strong aggregation tendency, resulting in overestimation of its molecular weight $(M_{\rm n} = 341 \text{ kDa}, \text{PDI} = \sim 250)$. Anal. Calcd for $C_{80}H_{116}N_2O_2S_4$: C 75.89, H 9.24, N 2.21%; Found: C 75.19, H 8.44, N 2.19%.

Synthesis of Poly[2,9-bisthiophen-2-yl-phenanthro[1,2b:8,7-b']dithiophene-5,5'-diyl-alt-2,5-bis(3-decylpentadecyl-2,3,5,6-tetrahyd-ro-3,6-dioxopyrrolo[3,4-c]pyrrole-1,4-diyl) (P-PDT-DPP-DP)

Monomers 2 (30.8 mg, 0.05 mmol) and 5b (58.0 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (0.7 mg, 1.0 μ mol), and toluene (2.5 ml) were added to a 5-ml reaction vial. The vial was sealed and heated in a microwave reactor at 110°C for 25 min. After being cooled to room temperature, the reaction mixture was poured into methanol (100 ml) and concentrated hydrochloric acid (2 ml), and vigorously stirred for 1 h at room temperature. The precipitate was filtered and subjected to Soxhlet extraction with methanol, hexane, chloroform, and finally chlorobenzene. The chloroform fraction was concentrated and poured into methanol. The precipitate was isolated by filtration and dried in vacuo to afford the polymer sample (43.2 mg, 67%) as a metallic purple solid. GPC (o-DCB, 140°C): Almost proceeded the detection limit of typical polystyrene standards due to the strong aggregation tendency, resulting in overestimation of its $M_{\rm w}$ ($M_{\rm n} = 175$ kDa, PDI = \sim 500). Anal. Calcd for C₈₂H₁₂₀N₂O₂S₄: C 76.11, H 9.35, N 2.16%; Found: C 74.73, H 8.76, N 2.17%.

Instrumentations

TGA were carried out using a TG/DTA 6300 (Hitachi High-Tech Science Corporation, Tokyo, Japan) at 10 °C/min under N₂ atmosphere. DSC was performed on a Mettler Toledos DSC-1 at 10 °C/min for both heating and cooling steps. UVvis absorption spectra were measured using a JASCO V670 UV-vis spectrometer (JASCO, Tokyo, Japan). CVs were recorded on CHI 600B Electrochemical Analyzer (CH Instruments, Austin, TX) in acetonitrile containing tetrabutylammonium hexafluorophosphate (TBAP, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. A Pt electrode (surface area: A = 0.071 cm², Bioanalytic Systems, Inc., West Lafayette, IN), an Ag/Ag⁺ (Ag wire in 0.01 M AgNO₃/0.1 M TBAP/CH₃CN), and Pt wire electrodes were used as working, reference, and counter electrode, respectively. Samples of polymer film were prepared by drop-casting on a working electrode from its chloroform solution. All the potentials were calibrated with the standard ferrocene/ferrocenium





SCHEME 1 Synthetic route to phenanthro[1,2-b:8,7-b']dithiophene-based semiconducting polymers.

redox couple (Fc/Fc⁺: $E^{1/2} = +0.08$ V measured under identical conditions). Dynamic force-mode atomic force microscopy was carried out using an SPA 400-DFM (SII Nano Technologies). Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) analyses were measure at the SPring-8 on beamline BL46XU. The sample was irradiated at a fixed angle on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.39 keV ($\lambda = 1$ Å), and the GIXD patterns were recorded with a 2D image detector (Pilatus 300K, Dectris Ltd. Baden, Switzerland). Samples of polymers and polymer/PC₆₁BM blended films were fabricated by spincoating on the (PEDOT:PSS) treated ITO substrate.

Fabrication and Characterization of Bulk-Heterojunction Solar Cells

Conventional bulk-heterojunction solar cell devices were fabricated as follows. The ITO substrates (ITO, Geomatec Co., Ltd., Yokohama, Japan, thickness = 150 nm, sheet resistance <12 Ω sq⁻¹, transmittance ($\lambda = 550$ nm) $\geq 85\%$) were successively washed using ultrasonication in a neutral detergent, deionized water, acetone, and isopropanol for 10 min, respectively. Then ITO substrate was treated with UVozone for 20 min. The substrate was spin-coated with poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios[™] P VP AI 4083, Heraeus, Hanau, Germany) through the 0.45 μ m PVDF syringe filter at 5000 rpm for 30 sec, and dried at 120°C for 10 min. After being dried, the substrate was immediately loaded into a glove box. The thin films of an active layer were deposited by spin-coating from an anhydrous chloroform (CF) and o-dichlorobenzene (DCB) blended solution (v/v, 2:1 for **P-PDT-DPP-DT**, and 9:1 for **P-PDT-DPP-DP**) containing 10 mg/ml polymer samples with respective amount of PC₆₁BM under inert conditions at 600 rpm for 60 sec. After the thin films were dried, a Ca (10 nm)/Al (80 nm) cathode layer with an active cathode area with 0.16 cm^2 was then deposited through a shadow mask.

The characteristics of the solar cell devices were measured through a 4 \times 4 mm photo-mask with a Keithley 2401 source-measure unit using a halogen lamp (BunkoKeiki Co., Tokyo, Japan, OTENTO-SAN III type G2) as the light source under AM 1.5 G simulated solar irradiation at 100 mW cm⁻² at room temperature under an inert atmosphere. The light intensity was determined by a calibrated standard silicon solar cell (Bunkokeiki, BS-520BK). External quantum efficiencies (EQE) were measured on a Bunkokeiki SM-250 hyper monolight system.

Fabrication and Characterization of Organic Field-Effect Transistors

Typical bottom-gate top-contact OFET devices were fabricated as follows. All the processes, except for a substrate cleaning, were performed under an inert atmosphere. A heavily doped n-Si wafer with 200-nm-thick thermally grown SiO₂ ($C_i = 17.3 \text{ nF cm}^{-2}$) as the dielectric layer was used as the substrate. The Si/SiO₂ substrates were washed by immersion in a piranha solution (mixture of H₂SO₄ and H_2O_2 , 4:1 v/v) at 50 °C for 10 min. Then, substrates were carefully cleaned using ultrasonication with deionized water, acetone, and isopropanol, respectively. After being dried, the substrates were irradiated by UV-03 for 20 min, and then treated with octyltriethoxysilane (OTS) to form a self-assembled monolayer. The active layers were deposited on the treated substrate by spin-coating from o-DCB solution (3 g L^{-1}) at 3000 rpm for 30 sec. After its drying or annealing at 200 °C for 30 min, gold electrode (80 nm thick) was deposited through a shadow mask on the top of the active layer under reduced pressure (5 \times 10⁻⁵ Pa).



FIGURE 1 (a) TGA curves and (b) DSC thermograms of P-PDT-DPP-R.

For a typical device, the source-drain channel length (*L*) and width (*W*) are 100 μ m and ca. 2 mm, respectively.

The current-voltage characteristics of the OFET devices were measured at room temperature in air on an Agilent B1500A semiconducting parameter analyzer. Field-effect mobilities in saturation regime were calculated by following equation,

$$I_{\rm D} = (WC_{\rm i}/2L)\mu(V_{\rm G}-V_{\rm th})^2,$$
 (1)

where C_i is the capacitance of the SiO₂ insulator, and V_{gr} V_{thv} and I_D are the gate and threshold voltages, and source-drain current, respectively. Current on/off ratio ($I_{on/off}$) was determined from a minimum I_D at around $V_g = 0-10$ V and maximum I_D at $V_g = -60$ V. All device parameters were collected from more than five different devices.

RESULTS AND DISCUSSION

Synthesis and GPC Analysis

Scheme 1 shows the synthetic route to the present polymers. PDT (1) was synthesized according to our improved method.³⁷ Stannylation of 1 with a slightly excess of *n*-butyl-lithium followed by addition of trimethyltin chloride afforded distannylated PDT 2 in 98% yield.⁴¹ Alkylation of 3 and a sequential bromination of the formed 4 gave two types of DPP monomers 5a and 5b in moderate yields.³⁹ First, the target polymer P-PDT-DPP-DT was synthesized by Migita-Kosugi-Stille coupling from the prepared monomers 2 and 5a.⁴² Polymerization at 180 °C afforded the poorly soluble polymers of P-PDT-DPP-DT due to the over-polymerization. Finally, we could obtain the soluble polymers by optimizing the polymerization temperature at 110 °C to avoid the over-

polymerization. With this result in hand, **P-PDT-DPP-DP** bearing slightly longer alkyl chains was synthesized from monomers **2** and **5b** to improve the solubility. However, the same tendency was observed at high polymerization temperature. These results indicate that an incorporation of PDT core into polymers significantly reduces the solubility owing to its rigid and large π -electron system even with bulkier alkyl chains. After a removal of low molecular-weight fractions by Soxhlet extraction with methanol and hexane, the two polymers were obtained as soluble products in hot chloroform under the optimized polymerization conditions.

Molecular weights of the two polymers were determined by high-temperature GPC using polystyrene standards (Fig. S1, Supporting Information). The number-average molecular weights (M_n) of the two polymers were ca. 341 kDa for **-DT** and 175 kDa for **-DP**, respectively. From their GPC profiles, both polymers showed intense peaks at shorter retention time regions, which are almost in the range of the detection limit of typical polystyrene standards. This result suggests that the two polymers obtained mainly form the large aggregate even in a hot *o*-DCB at 140 °C.⁴³⁻⁴⁶ Therefore, actual molecular weights could not be determined by GPC due to their strong aggregation behavior. However, broad peaks longer retention time regions were also observed. From these results, we assumed that molecular weights of two polymers may be relatively low, being as an oligomer.

Thermal Properties of the Polymers

We next evaluated their thermal stability using TGA and DSC (Fig. 1). The 5% weight loss temperatures (T_d^5) of the



FIGURE 2 UV-vis absorption spectra of **P-PDT-DPP-R** in chlorobenzene solution at room temperature, in the heated solution around 80 °C, and in thin film; (a) R = DT and (b) R = DP.



Polymer	λ_{max}/nm (solution) ^a		$\lambda_{max}/nm (film)^{b}$	E_{g}^{opt} / eV ^c	E _{HOMO} / eV ^d	E _{LUMO} / eV ^e	E_{g}^{CV}/eV^{f}
P-PDT-DPP-DT	Room temp. 655, 715, 811 (sh)	Heated 654, 712, 795 (sh)	654, 719, 816 (sh)	1.24	-5.24	-3.73	1.41
P-PDT-DPP-DP	658, 720, 800 (sh)	655, 716	663, 723, 811 (sh)	1.23	-5.19	-3.79	1.40

TABLE 1 Physicochemical Properties of P-PDT-DPP-R

^a Absorption maxima in chlorobenzene solution at rt and at ca. 80°C.

^b Absorption maxima in thin film.

^c Optical energy gap estimated from absorption edge (λ_{edge}).

^d Estimated with the oxidation onset versus Fc/Fc⁺; $E_{HOMO} = -4.73$ -

Eonset.

 e Estimated with the reduction onset versus Fc/Fc^+; $\textit{E}_{LUMO} = -4.73 - \textit{E}_{onset}^{red}$

^f Electrochemical gaps.

polymers are over 371 °C for –**DT** and 375 °C for –**DP**, respectively. Furthermore, no transition temperatures were observed in their DSC thermograms. These results indicate that the PDT-based polymers **P-PDT-DPP-DT** and -**DP** have a high thermal stability, owing to their rigid backbone originating from a large π -electron system of PDT.

Physicochemical Properties

Figure 2 shows UV-vis absorption spectra of the polymers in chlorobenzene solution and in thin films. Both polymers in solution showed broad absorption in the visible region and well-defined two absorption peaks and one shoulder with $\lambda_{\rm max}$ of around 660, 720, and 800 nm corresponding to their vibronic structures. When the solution was heated to ca. 80 °C, **P-PDT-DPP-DT** showed the almost identical spectra, while the absorption spectra of **P-PDT-DPP-DP** exhibited slightly blue-shifted and decreased its intensity, which may reflect the partial disaggregation upon heating. This result

suggests that P-PDT-DPP-DT has the stronger aggregation ability than that of P-PDT-DPP-DP. On the basis of the branching point, P-PDT-DPP-DP should have stronger aggregation ability than that of P-PDT-DPP-DT.40 From GPC chromatograms, one possible reason is lower molecular weight of P-PDT-DPP-DP. In fact, the response of P-PDT-DPP-DP in a longer retention time region was higher than that of P-PDT-DPP-DT. In its thin film, P-PDT-DPP-DT showed an identical absorption spectrum to that in solution, indicating that **P-PDT-DPP-DT** has the strong aggregation behavior even in the dilute solution upon heating. Both polymers have very narrow energy gap (E_{g}^{opt}) of 1.24 eV for **-DT** and 1.23 eV for -DP, respectively, which are significantly small values among the reported DPP-based polymers.40,44,46-50 This reason is attributed to their tailing absorption band with the defined shoulder around 800 nm. Although there is no clear explanation of these phenomena, the origin of this absorption band may be originated from their strong aggregation



FIGURE 3 Transfer (a,b) and output (c,d) characteristics of P-PDT-DPP-R-based organic field-effect transistor devices; (a,c) P-PDT-DPP-DT and (b,d) P-PDT-DPP-DP.

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TABLE 2 OFET and Solar Cell Performances of P-PDT-DPP-R ^a	
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Polymer	$\mu_{\rm FET}/{\rm cm}^2 \ {\rm V}^{-1} \ {\rm s}^{-1} \ {\rm b}$	V _{th} /V	I _{on/off}	$J_{\rm sc}/{ m mA~cm^{-2~c}}$	$V_{\rm oc}/V^{\rm c}$	FF ^c	PCE/% ^c
P-PDT-DPP-DT	0.010 (8.7×10 ⁻³)	-15 (-16)	$10^3 - 10^5$	5.06 (4.94)	0.64 (0.63)	0.63 (0.62)	2.03 (1.94)
P-PDT-DPP-DP	9.2×10 ⁻³ (7.8×10 ⁻³)	-7 (-7)	$10^4 - 10^5$	2.82 (2.71)	0.65 (0.65)	0.45 (0.44)	0.83 (0.78)

^a Average values are shown in parentheses.

^b Extracted from transfer curves in saturation regime.

behavior.⁵¹ Energy levels of **P-PDT-DPP-DT** and **-DP** estimated with the oxidation and reduction onsets of their thin films in cyclic voltammograms (Table 1, Fig. S2, Supporting Information). The clear oxidation and reduction waves were observed in both polymers. HOMO and LUMO energy levels can be estimated to be -5.24 and -3.73 eV for **-DT**, and -5.19 and -3.79 eV for **-DP**, respectively. It is found that the difference of alkyl branching point almost did not affect their frontier energy levels.

OFET Characteristics

To investigate their semiconductor character, we fabricated and characterized typical top-contact, bottom-gate OFET devices. The polymer active layers were fabricated by spincoating from DCB solution of polymers onto OTS-modified n^+ -Si/SiO₂ substrate, followed by a thermally annealing at 200 °C for 30 min. Typical transfer and output characteristics are shown in Figure 3 and extracted parameters are summarized in Table 2. Both polymer-based devices showed a typical p-channel FET behavior and no n-channel character.



FIGURE 4 (a) *J-V* characteristics and (b) EQE spectra of **P-PDT-DPP-R**:PC₆₁BM-based solar cells.

 $^\circ$ Extracted from J-V characteristics under 1 sun condition using fabricated conventional bulk-heterojunction polymer solar cells.

In contrast to our expectation, mobilities of both polymers were $1.0 \times 10^{-2} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}$ for **-DT** and $9.2 \times 10^{-3} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}$ for **-DP**, respectively, which are relatively low values in the D-A polymer system. Furthermore, the difference of alkyl branching point significantly affected OFET performances because of structural changes in the solid state, 40,52 but almost no alkyl chain dependency was observed in this system.

Photovoltaic Properties

Conventional bulk-heterojunction solar cells with the device configuration of ITO/(PEDOT:PSS)/(P-PDT-DPP-R:PC₆₁BM)/ Ca (10 nm)/Al (80 nm) were fabricated. Figure 4(a) depicts typical current density-voltage (*J-V*) curves under AM 1.5 G simulated solar irradiation at 1 sun (100 mW cm⁻²) of the fabricated solar cells. As summarized in Table 2, the optimized P-PDT-DPP-DT-based cell exhibited PCE of 2.03% with short-circuit current density (I_{sc}) of 5.06 mA cm⁻², open-circuit voltage (Voc) of 0.64 V, and fill factor (FF) of 0.63, respectively. On the other hand, P- PDT-DPP-DP device showed significantly lower performance than that of the -DT cell. Although the -**DP** device showed almost same V_{oc} (0.65) V) as expected from the same HOMO energy level, J_{sc} and FFwere decreased to 2.82 mA cm^{-2} and 0.45, respectively, resulting in a lower PCE of 0.83%. From the EQE spectra [Fig. 4(b)], P-PDT-DPP-DP showed lower photoresponse throughout the UV-vis and NIR region than that of P-PDT-**DPP-DT**. Moreover, J_{sc} values of two polymers were still low in spite of broad and intense absorption. Thus, some problems such as molecular order, morphology, and energy level offset may suppress the efficient photo-conversion.

2D-GIXD Measurement of Thin Films

To investigate the molecular orientation of two polymers, 2D grazing incidence X-ray diffraction (2D-GIXD) analyses were performed (Fig. 5). In P-PDT-DPP-DT, two orders diffraction corresponding to lamellar structure of the polymer along with the q_z axis at q = 0.31 Å⁻¹ and diffraction of the π - π stacking along with the q_{xy} axis at q = 1.74 Å⁻¹ were observed. This indicates that P-PDT-DPP-DT preferentially forms the edge-on orientation in its thin film. After blended with PC₆₁BM, both diffractions provided the ring, indicating that P-PDT-DPP-DT has no preferred crystallographic orientation in the blend film. Polymer P-PDT-DPP-DP also showed similar orientation ($q_z = 0.29$ and $q_{xy} = 1.79$ Å⁻¹, respectively) with a slightly higher crystalline nature than that of P- PDT-DPP-DT in the polymer-only film. In addition, **P-PDT-DPP-DP** has shorter $\pi - \pi$ stacking distance of $d_{\pi} = 3.5$ Å than that of **P-PDT-DPP-DT** ($d_{\pi} = 3.6$ Å). In contrast,



FIGURE 5 2D-GIXD images of (a,c) polymer-only films and (b,d) (polymer:PC₆₁BM) blend films on (PEDOT:PSS) treated with ITO substrate; (a,b) P-PDT-DPP-DT and (c,d) P-PDT-DPP-DP.

although diffraction shapes of two polymers became slightly arc in their blend films, **P-PDT-DPP-DP** still maintain the edge-on orientation with a slightly disordered structure. This unfavorable orientation for an efficient carrier transport in PSC limited *FF* of the **P-PDT-DPP-DP**-based device.^{22,53} From this result, we conclude that increasing the number of a

methylene chain may lead to more dense packing structure and enhance the edge-on orientation.^{40,52} However, their OFET devices showed almost same mobilities. One possible reason is their relatively low crystallinity in thin film state, and hence the molecular order did not significantly affect their OFET performances.



FIGURE 6 AFM images (2 \times 2 μ m) of **P-PDT-DPP-R** on Si/SiO₂ (a,b) and of their blended films with PC₆₁BM on ITO/(PEDOT:PSS) (c,d). (a,c) P-PDT-DPP-DT and (b,d) P-PDT-DPP-DP.

Surface Morphologies

We further investigated the surface morphology of P-PDT-DPP-**R** using AFM. Their thin films on n^+ -Si/SiO₂ substrate exhibited no defined crystalline grains and very smooth surface with root mean square (RMS) of 0.25 (-DT) and 0.62 (-DP) nm, respectively. Such low crystalline nature may limit their carrier transporting ability, resulting in a moderate field-effect mobility. The reason of this low crystalline nature may be attributed to their oligomeric feature, because it is known that high molecularweight polymers typically show high crystalline and the better connected crystalline domain, which lead to high charge carrier mobility.^{54,55} Furthermore, another possible reason of this low crystalline nature may be its low symmetry of the polymer backbone. The backbone structure of P-PDT-DPP-R with an axisymmetric structure change the direction of alkyl side chains. This difference of the direction may limit the effective π - π overlaps, and thus **P-PDT-DPP-R** showed low crystalline nature. On the other hand, the films of P-PDT-DPP-R blended with PC₆₁BM showed a relatively rough surface with RMS of 2.45 and 5.71 nm, respectively (Fig. 6). Typically, large-scale phase separation with discontinuous domain is not favorable for efficient exciton dissociation and charge transport, resulting in the limited J_{sc} .^{56,57} Thus, the present **P-PDT-DPP-R**-based cell showed the low J_{sc} .

CONCLUSIONS

In summary, we have successfully synthesized a series of new PDT-based D-A-type semiconducting polymers. The superior features of the present polymers are strong aggregation behavior, high thermal stability, and short π - π stacking distance (3.5–3.6 Å), which indicates that an incorporation of the rigid and large π -electron system into the polymer backbone leads to strong intermolecular interactions. In addition, the present polymers have a significantly extended absorption up to 1000 nm with a small band gap of 1.2 eV. However, such strong intermolecular interaction significantly decreased their solubility, thus giving rise to their low molecular weights. In spite of such strong aggregation behavior, their thin films showed low crystalline nature owing to their oligomeric features, which resulted in a moderate field-effect mobility up to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In contrast, large-scale phase separation was observed in the blend film with PC₆₁BM, which may prevent an effective photocurrent generation, resulting in the limited J_{sc} and at most PCE of 2.0%. However, since an installation of other alkyl groups can improve solubility and molecular weights of the polymers, one can expect that further modified PDT-based polymers show the better performance owing to their superior features. Thus, the development of new PDT-containing polymers is currently underway.

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