Importance of varying electron-accepting moieties in regular conjugated terpolymers for use in polymer solar cells

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A B S T R A C T

Three A_1-D-A_2-D regular conjugated terpolymers containing diketopyrrolopyrrole, isoindigo, or thienoisoindigo moieties were synthesized. Each terpolymer with the combination of two different acceptors and thiophene as common donor displayed strong absorption from 500 nm to the near-IR region as well as different molecular energy levels. Among three terpolymers, bulk heterojunction polymer solar cell made of the terpolymer containing diketopyrrolopyrrole, isoindigo, and thiophene moieties and phenyl-C71-butyric acid methyl ester showed the highest power conversion efficiency of 6.95% due to its appropriate internal morphology and the high open circuit voltage conferred by the relatively low-lying highest occupied molecular orbital level of the polymer.

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1. Introduction

There has been a large amount of research into the use of donor-acceptor (D-A) conjugated polymers [1–3] for high-performance bulk heterojunction (BHJ) polymer solar cells (PSCs) [4], with their power conversion efficiencies (PCEs) recently reaching close to 11% [5,6]. However, a limited number of backbone structures is available for constituting the structures of D-A conjugated copolymers due to the difficulty of synthesizing novel donor and acceptor monomers. Accordingly, it leads to restriction of optimizing the molecular energy levels of the D-A copolymers [7–10]. For this reason, terpolymers composed of three different monomeric units in a single repeating group have recently begun to be used as a promising way to overcome the critical points associated with binary D-A-based conjugated copolymers.

By introducing a third monomer to a binary D-A system (i.e., A_1-D-A_2-D or A-D_1-A-D_2), various properties such as absorption range, thermal behavior, molecular energy level, charge carrier mobility, and solubility can be fine-tuned, leading to improvements in PCE *via* synergy between the three monomers. There have already been several reports on terpolymers [11], with some demonstrating PCEs exceeding 8% [12,13]. Many studies have looked at the impact of incorporating two different donor monomers, including our previous works [14–18], but there has been relatively little research into the manipulation of the acceptor unit. Unlike random terpolymers [19], terpolymers with regular structures have a unique advantage in that their chemical compositions can be well characterized; however, these polymers have received little attention because of the difficulty of the synthesis of the desired monomers [20–22].

There are a variety of electron acceptors that can be used in polymer-based semiconductors, including diketopyrrolopyrrole (DPP) [23–27], isoindigo (IID) [28,29], benzotriazole (TAZ) [30,31], benzothiadiazole (BTD) [32,33], thienoisoindigo (TID) [34–36], and thienopyrroledione (TPD) [37]. Of the many reported acceptors, DPP, IID, and TID were selected for use in terpolymers in this work to allow comparative analysis of properties and device performances in accordance with changing the acceptor unit on terpolymer. The use of DPP and IID in polymeric semiconductors has been intensely studied due to their abilities to induce high carrier mobilities through their strong intermolecular interactions. Additionally, TID units, which bear a thiophene ring instead of a phenyl ring as seen in IID, is well known because of its unique electron accepting strength [38]. It was expected that when polymerized with a thiophene (T) donor unit, TID, DPP, and IID would result in small, medium, and large polymer bandgaps, respectively.

Furthermore, the three acceptor-containing polymers should absorb in different wavelength regions, making them suitable for studying the physical properties and device performances of ter-polymers combining two different acceptor units.

In this work, we used DPP, IID, and TID to synthesize three regular A$_1$-D-A$_2$-D terpolymers, PDPP-T-IID, PDPP-T-TID, and PIID-T-TID, with the acceptor being tethered by thiophenes to give alternating copolymers. Each terpolymer was a combination of two different acceptors and a single donor, with the polymers absorbing different wavelengths ranging from 500 nm to the near-infrared (near-IR) and displayed different molecular energy levels, including for the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs).

While the PDPP-T-TID and PIID-T-TID terpolymers displayed absorptions in the near-IR region due to the low-bandgap TID unit, their BHJ PSCs showed poor PCEs due to relatively low short-circuit current density (J_{SC}) through the worse internal morphology and low open circuit voltages (V_{OC}). On the other hand, PDPP-T-IID exhibited a PCE of 6.95% due to its high J_{SC} through the fine internal morphology and relatively high V_{OC}, which was conferred by its relatively deep HOMO level compared to those of the other terpolymers.

2. Experimental section

2.1. Materials

All reagents and solvents used for synthesizing the polymers were purchased from Tokyo Chemical Industry (TCI), Alfa Aesar, Sigma-Aldrich, and Acros Organics.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**1**) [39], (E)-2,2′-dibromo-4,4′-bis(2-hexyldecyl)-[6,6′-bithieno[3,2-b]pyrrolylidene]-5,5′(4H,4′H)-dione (**3**) [34], (E)-1,1′-bis(2-hexyldecyl)-6,6′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3′-biindolinylidene]-2,2′-dione (**M$_3$**) [40], and 2,5-bis(2-hexyldecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4 (2H,5H)-dione (**M$_4$**) [41] were synthesized according to synthetic procedures found in the literature.

2.2. Synthesis

Synthetic procedures for 3,6-di([2,2′-bithiophen]-5-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**2**), 3,6-bis(5′-bromo-[2,2′-bithiophen]-5-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c] pyrrole-1,4(2H,5H)-dione (**M$_1$**), (E)-4,4′-bis(2-hexyldecyl)-2,2′-di(thiophen-2-yl)-[6,6′-bithieno [3,2-b]pyrrolylidene]-5,5′(4H,4′H)-dione (**4**), and (E)-2,2′-bis(5-bromothiophen-2-yl)-4,4′-bis(2-hexyldecyl)-[6,6′-bithieno [3,2-b]pyrrolylidene]-5,5′(4H,4′H)-dione (**M$_2$**) are shown in Scheme S1.

2.2.1. Synthesis of 3,6-di([2,2′-bithiophen]-5-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (2)

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**1**) (1.0 g, 1.1 mmol) and tributyl(thiophen-2-yl)stannane (1.0 g, 2.7 mmol) were added to 60 mL of anhydrous toluene in a 250 mL three-neck round bottom flask, then degassed with nitrogen. Subsequently, tris(dibenzylideneacetone)dipalladium(0) (0.02 g, 0.022 mmol) and tri-o-tolylphosphine (0.026 g, 0.088 mmol) were added. The reaction was heated to 90 °C for 24 h then cooled to room temperature. The reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over sodium sulfate and purified by silica-gel column chromatography (dichloromethane: hexane = 1:2 v/v). The product was obtained as a dark-purple powder in a 72% yield

(0.72 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.94 (d, J = 4.1 Hz, 2H), 7.31–7.35 (m, 6H), 7.06 (d, J = 4.0 Hz, 2H), 4.02 (d, 4H), 1.94 (m, 2H), 1.15–1.4 (m, 48H), 0.8–0.9 (m, 12H). Anal. Calcd for C$_{54}$H$_{76}$N$_2$O$_2$S$_4$: C, 71.00; H, 8.39; N, 3.07; O, 3.50; S, 14.04. Found: C, 71.50; H, 8.62; N, 2.98; O, 3.34; S, 13.56.

2.2.2. Synthesis of 3,6-bis(5′-bromo-[2,2′-bithiophen]-5-yl)-2,5-bis(2-hexyldecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (M$_1$)

3,6-Di([2,2′-bithiophen]-5-yl)-2,5-bis(2-hexyldecyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) (0.5 g, 0.547 mmol) was added to 40 mL of chloroform in a 100 mL two-neck round bottom flask and degassed with the nitrogen. N-bromosuccinimide (NBS) (0.2 g, 1.15 mmol) was added, and then the solution was stirred at room temperature for 6 h in the dark. The reaction was extracted with chloroform and the organic phase was dried over sodium sulfate. The compound was purified by silica-gel column chromatography (dichloromethane: hexane = 1:1 v/v). The product was obtained as a dark-purple powder in a 56% yield (0.33 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.89 (d, J = 5.0 Hz, 2H), 7.23 (d, J = 5.0 Hz, 2H), 7.06 (d, J = 5.0 Hz, 2H), 7.02 (d, J = 5.0 Hz, 2H), 4.02 (d, 4H), 1.94 (m, 2H), 1.20–1.35 (m, 48H), 0.8–0.9 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ(ppm) 161.60; 141.40; 139.43; 137.65; 136.48; 131.08; 128.47; 125.14; 124.89; 113.17; 108.58; 46.31; 37.94; 31.90; 31.82; 31.31; 30.05; 29.71; 29.31; 26.34; 26.31; 22.68; 22.63; 14.13; 14.10. Anal. Calcd for C$_{54}$H$_{74}$Br$_2$N$_2$O$_2$S$_4$: C, 60.54; H, 6.96; N, 2.62; O, 2.99; S, 11.97. Found: C, 59.54; H, 7.02; N, 2.58; O, 3.04; S, 12.81.

2.2.3. Synthesis of (E)-4,4′-bis(2-hexyldecyl)-2,2′-di(thiophen-2-yl)-[6,6′-bithieno[3,2-b]pyrrolylidene]-5,5′(4H,4′H)-dione (4)

The synthetic procedure was similar to that of **2**, with (E)-2,2′-dibromo-4,4′-bis(2-hexyldecyl)-[6,6′-bithieno[3,2-b]pyrrolyli-dene]-5,5′(4H,4′H)-dione (**3**) being used under the same conditions. The product was obtained as a bluish-purple powder in a 70% yield (0.62 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.40 (d, J = 3.52 Hz, 2H), 7.30 (d, J = 5.08 Hz, 2H), 7.08 (m, 2H), 6.85 (s, 2H), 3.70 (d, 4H), 1.85 (m, 2H), 1.37–1.19 (m, 48H), 0.8–0.9 (m, 12H). Anal. Calcd for C$_{52}$H$_{74}$N$_2$O$_2$S$_4$: C, 70.38; H, 8.41; N, 3.16; O, 3.16; S, 14.45. Found: C, 69.89; H, 8.62; N, 3.28; O, 3.04; S, 14.73.

2.2.4. Synthesis of (E)-2,2′-bis(5-bromothiophen-2-yl)-4,4′-bis(2-hexyldecyl)-[6,6′-bithieno[3,2-b]pyrrolylidene]-5,5′(4H,4′H)-dione (M$_2$)

The synthesis was similar to that of **M$_1$**. (E)-4,4′-bis(2-hexyldecyl)-2,2′-di(thiophen-2-yl)-[6,6′-bithieno[3,2-b]pyrrolyli-dene]-5,5′(4H,4′H)-dione (**4**) (0.5 g, 0.56 mmol) was used for this reaction under the same conditions. The product was obtained as a bluish-purple powder in an 80% yield (0.47 g). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.12–7.14 (d, J = 3.92 Hz, 2H), 7.02–7.05 (d, J = 3.92 Hz, 2H), 6.78 (s, 2H), 3.70 (d, 4H), 1.90 (m, 2H), 1.15–1.4 (m, 48H), 0.8–0.9 (m, 12H). Anal. Calcd for C$_{52}$H$_{72}$Br$_2$N$_2$O$_2$S$_4$: C, 59.75; H, 6.94; N, 2.68; O, 3.06; S, 12.27. Found: C, 60.09; H, 7.02; N, 2.38; O, 3.04; S, 12.42.

2.2.5. Synthesis of poly((E)-6-(5′-(2,5-bis(2-hexyldecyl)-3,6-dioxo-(thiophen-2-yl)-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)-[2,2′-bithiophen]-5-yl)-1,1′-bis(2-hexyldecyl)-6′-(thiophen-2-yl)-[3,3′-biindolinylidene]-2,2′-dione) (PDPP-T-IID)

M$_1$ (110 mg, 0.10 mmol) and (E)-1,1′-bis(2-hexyldecyl)-6,6′-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3′-biindolinyli-dene]-2,2′-dione (**M$_3$**) (99 mg, 0.10 mmol) were added to 10 mL of anhydrous toluene in a 100 mL two-neck round bottom flask and degassed with nitrogen. A potassium carbonate solution (2 M, 2 mL) and a few drops of Aliquat 336, which acted as a phase-transfer catalyst, were added to the solution. Subsequently, tris(-dibenzylideneacetone)dipalladium(0) (2.0 mg, 2.06 μmol) and tri(o-tolyl)phosphine (2.5 mg, 8.24 μmol) were added, and the