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Organic Photovoltaics

High-Molecular-Weight Regular Alternating Diketopyrrolopyrrole-based Terpolymers for Efficient Organic Solar Cells**

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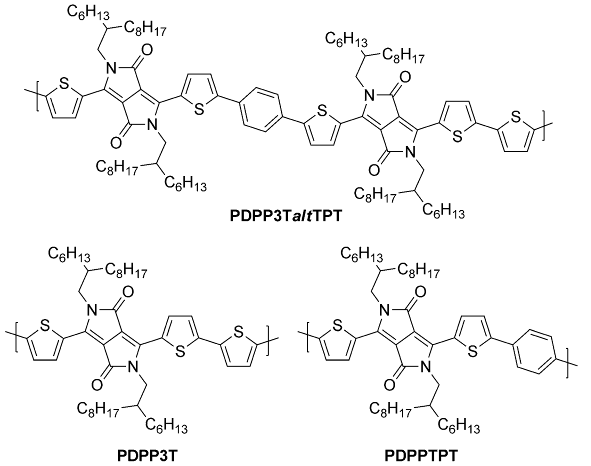
The recent significant increase in power conversion efficiency (PCE) of polymer–fullerene solar cells largely originates from the successful development of new electron donor polymers. The donor–acceptor (D-A) or push-pull design, where electron-rich and electron-deficient units alternate along the copolymer chain- is commonly used to tune the HOMO and LUMO energy levels and the optical band gap of these polymers.[1,2] While structure–property relationships for energy levels are well-established, these are less clear for the actual photovoltaic performance. Creating morphologies in which nanometer-sized, interconnected, semi-crystalline domains of both polymer and fullerene exist seems crucial for high photovoltaic performance.[3,4] These semi-crystalline domains optimize the conjugation along the polymer backbone and allow delocalizing the carrier wave functions to assist efficient charge separation.[5] A high molecular weight and a tendency to crystallize are important in achieving such morphologies.

Herein we present the advantageous effect of high molecular weight and refined energy level control through the synthesis of a regular alternating D_1-A-D_2-A terpolymer and demonstrate its superior performance in polymer–fullerene solar cells compared to the corresponding D_1-A and D_2-A copolymers. The regular alternating D_1-A-D_2-A design motif presents a versatile way to fine-tune energy levels and the optical band gap. Compared to random alternation of D_1 and D_2 with A, the regular D_1-A-D_2-A alternation allows quantifying the exact chemical composition.[6–9] Furthermore, regular alternation of units along the polymer chain reduces local variations in HOMO and LUMO energy levels that broaden the density of states and reduce charge carrier mobility.[10]

The new terpolymer uses diketopyrrolopyrrole (DPP) as the electron-deficient unit (A), alternating with electron-rich terthiophene ($D_1 = 3T$) and thiophene-phenylene-thiophene ($D_2 = TPT$) segments in a regular fashion: PDPP3T*alt*TPT (Scheme 1). The DPP unit has previously been copolymerized with several different electron-rich units, providing polymers with excellent performance in photovoltaic cells and field-effect transistors.[4,11–18] The choice for the 3T and TPT segments is based on our previous work on the individual PDPP3T and PDPPTPT polymers (Scheme 1), for which we obtained favorable PCEs of 4.7% and 5.5%.[11,12] Herein we demonstrate that by improving the polymerization reaction of PDPP3T, PDPPTPT, and of the new PDPP3T*alt*TPT, a dramatic enhancement of the PCEs to 7.1%, 7.4%, and 8.0%, respectively, can be achieved. These PCEs are the highest values reported for DPP-based polymers to date.



Scheme 1. Molecular structures of PDPP3T*alt*TPT, PDPP3T, and PDPPTPT.

Compared to previous synthesis,[11,12] the improved cross-coupling polymerization procedure involves a slight decrease in the amount of palladium (4–6 mol% vs. 8-9 mol%) and using a higher triphenylphosphine to palladium ligand ratio (Pd/PPh_3 of 1:2 vs. 1:1.2). The higher ligand ratio serves to prevent decomposition of the palladium catalyst.[19] We find that these conditions improve both Suzuki and Stille polymerizations. Accordingly, PDPPTPT was prepared in a Suzuki reaction, while PDPP3T was obtained from a Stille reaction (Scheme 2). PDPP3T*alt*TPT was synthesized from the extended monomer **4** under the same conditions used for PDPP3T to give PDPP3T*alt*TPT in excellent yield (Scheme 2). The addition of DMF to the Stille polymerizations proved crucial for accelerating the reaction and obtaining high molecular weights.[19] Typically, the polymer-

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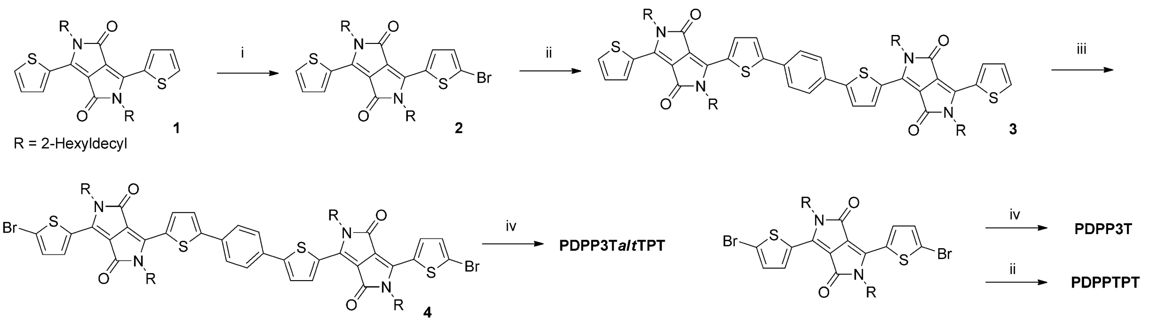

Scheme 2. Synthetic route to PDPP3T*alt*TPT, PDPPTPT, and PDPP3T. Conditions: i) NBS, $CHCl_3$, 0 °C; ii) 1,4-phenylenebis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane), $[Pd_2dba_3]$, PPh_3, K_3PO_4, Aliquat 336, toluene, H_2O, 115 °C; iii) NBS, $CHCl_3$, 0 °C; iv) 2,5-bis(trimethylstannyl)thiophene, $[Pd_2dba_3]$, PPh_3, toluene, DMF, 115 °C.

ization reaction mixtures gelated within 30 min, indicating the high rate of conversion. Because of their low solubility, PDPP3T and PDPP3T*alt*TPT were isolated using hot 1,1,2,2-tetrachloroethane (TCE) after Soxhlet extraction with acetone, hexanes, and chloroform. The high yields (> 90 %) and the lack of recovering oligomers during Soxhlet purification indicate the formation of high-molecular-weight polymers. GPC at 80 °C in *o*-dichlorobenzene (*o*-DCB) confirms that all three polymers have high molecular weights (Figure 1 a, Table 1). For PDPP3T we find $M_n = 147\ \mathrm{kg\,mol^{-1}}$, which is significantly higher than the value obtained previously ($54\ \mathrm{kg\,mol^{-1}}$).[11] PDPP3T*alt*TPT showed a higher peak molecular weight than PDPPTPT but also tailing on the GPC column, giving rise to a high polydispersity index (PDI) and a lower estimated value of $M_n = 42\ \mathrm{kg\,mol^{-1}}$.

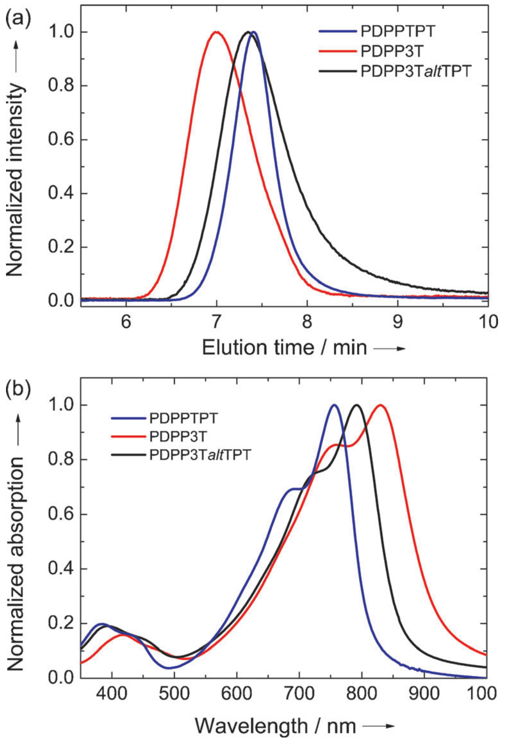

Figure 1. a) GPC traces recorded at 80 °C in *o*-DCB and b) absorption spectra of thin films of PDPPTPT, PDPP3T, and PDPP3T*alt*TPT.

Table 1: Molecular weight, optical absorption, and redox potentials.

	PDPP3T*alt*TPT	PDPPTPT	PDPP3T
M_p [kg mol^{-1}]	141	122	369
M_n [kg mol^{-1}]	42	72	147
M_w [kg mol^{-1}]	154	143	400
PDI	3.68	1.98	2.72
λ_{max} [nm]	792	756	830
E_g^{sol} [eV]	1.47	1.57	1.37
E_g [eV]	1.43	1.53	1.33
E_{ox} [V][a]	n.a.	0.25[b]	0.07[b]
E_{red} [V][a]	−1.50	−1.57[b]	−1.49[b]
E_g^{CV} [eV]	n.a.	1.82	1.56
E(HOMO) [eV][c]	n.a.	−5.48	−5.30
E(LUMO) [eV][c]	−3.73	−3.66	−3.74

[a] Versus Fc/Fc^+. [b] Values from reference [11] and [12]. [c] Determined using a work-function value of −5.23 eV for Fc/Fc^+.

The absorption spectra of solid-state films (Figure 1 b) reveal that the optical absorption band of PDPP3T*alt*TPT is positioned in between those of PDPPTPT and PDPP3T. Hence, the electronic structure of the terpolymer is better described by the average of the two parent copolymers than by the sum. In the latter case, the density of states and the absorption spectrum would broaden. The optical band gap of 1.43 eV (Table 1) is nearly ideal for maximum efficiency in a single-junction organic solar cell.[20] The HOMO and LUMO energy levels estimated by cyclic voltammetry place the LUMO energy level in between those of PDPPTPT and PDPP3T. Unfortunately, an oxidation potential could not be determined for PDPP3T*alt*TPT.

Bulk heterojunction solar cells were fabricated from photoactive layers comprising PDPP3T*alt*TPT, PDPPTPT, or PDPP3T as electron donor with [70]PCBM as electron acceptor. The solar-cell performance was carefully optimized for each polymer by varying the layer thickness, the polymer:[70]PCBM weight ratio, the solute concentration and the composition of the spin coating solvent. The similar chemical structure of the three polymers resulted in nearly identical optimized conditions. The optimal polymer:[70]PCBM weight ratio was 1:2 in each case. The best solvent combination was chloroform with *o*-DCB as co-solvent at 6, 7.5, and 10 vol % for PDPPTPT, PDPP3T, and PDPP3T*alt*TPT, respectively. It is notable that PDPP3T and PDPP3T*alt*TPT had to

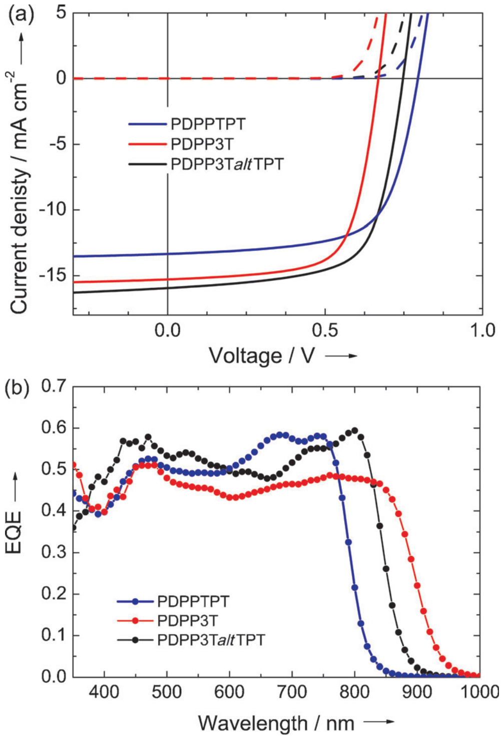

Figure 2. a) *J*–*V* characteristics and b) spectrally resolved external quantum efficiencies of PDPPTPT:[70]PCBM, PDPP3T:[70]PCBM, and PDPP3T*alt*TPT:[70]PCBM solar cells.

be processed from a solution containing only 3 $\mathrm{mg\,mL^{-1}}$ polymer owing to gelation at higher concentrations.

The current-density–voltage (*J*–*V*) characteristics and spectrally resolved external quantum efficiencies (EQEs) of the optimized cells are collected in Figure 2 and Table 2. Mixed with [70]PCBM, all three polymers provide very good performance with PCEs between 7.1 % and 8.0 % for the best cells and 6.9 % to 7.8 % for the average performance. Compared to the previous reports on solar cells of PDPP3T and PDPPTPT,[11,12] the solar cell parameters are virtually identical, except for a significant, more than 30 % increase in the short-circuit current density (J_{sc}). We note that upon testing the original batches of PDPP3T and PDPPTPT again, their performance was entirely consistent with the previously reported data.[11,12] To test reproducibility of the new synthetic procedure, three additional batches of PDPPTPT were synthesized that all showed the favorable increase in J_{sc} (PCE > 7 %). The increase in PCE for the new polymer batches arises from their higher molecular weight. The positive effect of molecular weight on the PCE has previously been discussed,[11,21,22] but we find it remarkable that the effect continues to be so strong even above the $M_n = 54\ \mathrm{kg\,mol^{-1}}$ value of the PDPP3T previously reported.[11] We note that for the new batch of PDPP3T we could not reproduce the beneficial effect of using a ternary solvent mixture ($CHCl_3$, *o*-DCB, 1,8-diiodooctane) as reported recently by Ye et al. for the same polymer.[18]

Of course it would be very interesting to investigate whether further enhancing the molecular weight or reducing the polydispersity can increase the performance. However, both changes will further reduce the already limited solubility, making processing of the polymers into thin films more challenging.

The V_{oc} of the PDPP3T*alt*TPT:[70]PCBM cells at 0.75 V is between the values of 0.67 and 0.80 V of the parent copolymers. This reveals that the HOMO level of PDPP3T*alt*TPT lies in between those of PDPP3T and PDPPTPT, analogous to the electrochemically determined LUMO levels and the optical band gaps (Table 1).[2]

With a PCE of up to 8 %, the new PDPP3T*alt*TPT terpolymer outperforms the two parent copolymers in solar cells with [70]PCBM. To rationalize the origin of the improvement, it is useful to compare the maximum EQE in the region of the main polymer absorption ($\mathrm{EQE_{max}}$) to the photon energy loss, defined as $E_g - eV_{oc}$, where e is the elementary charge and V_{oc} the open-circuit voltage. $E_g - eV_{oc} \approx 0.6$ eV serves as a lower threshold for efficient charge generation.[23] Table 2 shows that for PDPP3T, the photon energy loss is only 0.66 eV, but it is slightly larger for PDPP3T*alt*TPT and PDPPTPT (0.69–0.73 eV). The higher photon energy loss scales with $\mathrm{EQE_{max}}$, which increases from 0.49 for PDPP3T to 0.58 and 0.59 for PDPPTPT and PDPP3T*alt*TPT, respectively.

The advantageous effect of the high molecular weight on the PCE is most likely also related to the morphology of the bulk heterojunction blends that are obtained during layer deposition. TEM of the photoactive layers reveals clear fibrillar structures arising from aggregated polymer chains (Figure 3). Comparing the morphologies of films from the old and new batches of PDPPTPT with [70]PCBM by TEM (see the Supporting Information) reveals that finer dispersed fibrils are achieved from the polymer synthesized by the new method, which is beneficial for charge generation. Furthermore, compared to PDPP3T, the fibrils of PDPPTPT and PDPP3T*alt*TPT that give higher EQEs seem somewhat more finely dispersed with [70]PCBM and more narrow (Figure 3 a–c). At higher magnification, clear lattice fringes can be observed in the TEM images of PDPPTPT and PDPP3T with average *d*-spacings of 18.5 Å and 18.7 Å, respectively, determined by detailed analysis of multiple images. For PDPP3T*alt*TPT, only some fringes ($d \approx 20$ Å) could be observed owing to the sensitivity of the layer to the electron beam. These distances correspond to the lamellar stacking distance of this class of polymers.[18,24] It indicates that the fibrils are composed of pure polymeric material and PCBM can be intermixed between these domains.

Table 2: Solar-cell characteristics.

Photoactive layer	d [nm]	V_{oc} [V]	J_{sc} [$\mathrm{mA\,cm^{-2}}$][a]	FF[b]	PCE [%][c]	$\mathrm{EQE_{max}}$	$E_g - eV_{oc}$ [eV]
PDPP3T*alt*TPT:[70]PCBM	110	0.75	15.9	0.67	8.0 (7.8)	0.59	0.69
PDPPTPT:[70]PCBM	115	0.80	14.0	0.67	7.4 (7.3)	0.58	0.73
PDPP3T:[70]PCBM	134	0.67	15.4	0.69	7.1 (6.9)	0.49	0.66

[a] Determined by integrating the EQE spectrum with AM 1.5 G spectrum. [b] Fill factor. [c] Value in brackets is the average over six nominally identical devices.

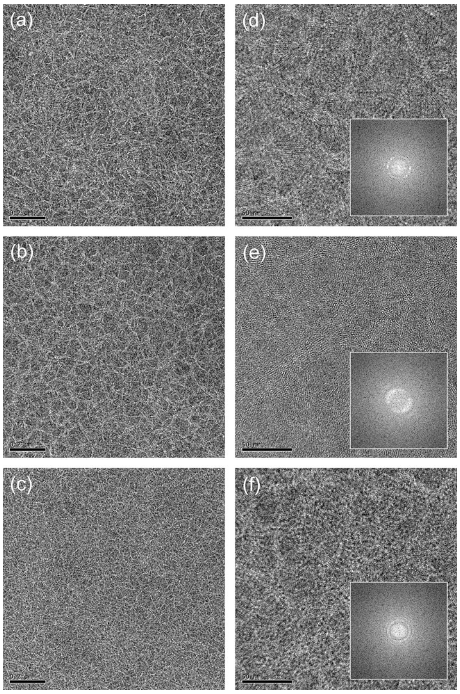

Figure 3. TEM images of the photoactive layers: a),d) PDPPTPT:[70]PCBM, b),e) PDPP3T:[70]PCBM, and c),f) PDPP3T*alt*TPT:[70]PCBM with lower ((a–c); scale bar 200 nm) and higher magnification ((d–f); scale bar 50 nm). Inserts: Fourier transform of part of the images to determine *d*-spacings.

In conclusion, the modified synthetic procedure resulted in a significant improvement of the photovoltaic performance of the PDPPTPT and PDPP3T donor–acceptor copolymers in combination with [70]PCBM as a result of high molecular weights. Combining the two 3T and TPT donor segments with DPP in a new regular alternating PDPP3T*alt*TPT terpolymer provides a material with optimized energy levels and optical band gap positioned in between those of the parent copolymers, providing PCEs up to 8.0% in combination with [70]PCBM. These results show the feasibility of combining multiple D-A copolymer systems into new, superior, terpolymer materials with tailored energy levels.

Experimental Section

Details of solar-cell fabrication and the synthesis of compounds **2**, **3**, **4**, and the polymers are described in the Supporting Information. Molecular-weight distributions of the polymers were estimated by GPC at 80°C on a PL-GPC 120 system using a PL-GEL 10 μm MIXED-B column with *o*-DCB as the eluent and using polystyrene internal standards. UV/Vis/NIR spectroscopy was conducted on a PerkinElmer Lambda 900 spectrophotometer. *J–V* characteristics were measured with a Keithley 2400 source meter under ca. 100 mW cm^{-2} white-light illumination from a tungsten–halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. Short-circuit currents under AM 1.5 G conditions were estimated by convoluting the spectral response with the solar spectrum (see the Supporting Information for details). The thickness of the active layers was determined on a Veeco Dektak150 profilometer. TEM was performed on a Tecnai G^2 Sphera TEM (FEI) operated at 200 kV. Digital micrograph software was used to determine *d*-spacing from bright-field TEM images using line integration and Fourier transforms.

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