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Perylene Diimide Based Isomeric Conjugated Polymers as Efficient Electron Acceptors for All-polymer Solar Cells

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Electronic Supplementary Information

Abstract We present here a series of perylene diimide (PDI) based isomeric conjugated polymers for the application as efficient electron acceptors in all-polymer solar cells (all-PSCs). By copolymerizing PDI monomers with 1,4-diethynylbenzene (*para*-linkage) and 1,3-diethynylbenzene (*meta*-linkage), isomeric PDI based conjugated polymers with parallel and non-parallel PDI units inside backbones were obtained. It was found that *para*-linked conjugated polymer (PA) showed better solubility, stronger π - π stacking, more favorable blend morphology, and better photovoltaic performance than those of *meta*-linked conjugated polymers (PM) did. Device based on PTB7-Th:PA (PTB7-Th:poly{4,8-bis[5-(2-ethylhexyl)-thiophen-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-*alt*-3-fluoro-2-[(2-ethylhexyl)-carbonyl]thieno[3,4-*b*]thiophene-4,6-diyl}) showed significantly enhanced photovoltaic performance than that of PTB7-Th:MA (3.29% versus 0.92%). Moreover, the photovoltaic performance of these polymeric acceptors could be further improved *via* a terpolymeric strategy. By copolymerizing a small amount of *meta*-linkages into PA, the optimized terpolymeric acceptors enabled to enhance photovoltaic performance with improved the short-circuit current density (J_{sc}) and fill factor (FF), resulting in an improved power conversion efficiency (PCE) of 4.03%.

Keywords Isomeric conjugated polymers; All-polymer solar cells; Electron acceptors; Perylene diimide

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INTRODUCTION

All polymer solar cells (all-PSCs), consisting of both conjugated polymeric donor and acceptor, have received wide attention in the past several years.^[1–13] Compared to PSCs with small molecular acceptors, all-PSCs possess unique advantages, including mechanical strength and good stability, which are especially favorable for the commercial application of polymer solar cells in the future.^[14] Although remarkable progress has been made in the past two years, the device performance of all-PSCs is still inferior to that of PSCs with fullerene and non-fullerene acceptors due to the great challenge in developing high-performance polymeric electron acceptors with high electron transport abilities, optimized molecular packing structure/orientation, as well as blend morphologies with polymeric donors.^[14]

To achieve highly-efficient all-PSCs, it is critical to design high-performance conjugated polymeric donors and acceptors, and enable good morphologies between them.^[15–17] *N*-

type conjugated polymers are studied intensively. Among them, conjugated polymers based on naphthalene diimide (NDI) and perylene diimide (PDI) exhibited the most promising performance.^[18–27] For NDI-based copolymers, N2200 is the most studied electron acceptor and the high-performance all-PSCs based on N2200 have been achieved.^[28] For example, Li *et al.* reported an all-PSC with a PCE over 8%, which utilized a wide band-gap polymer J51 as donor and N2200 as acceptor.^[29] Our group reported an all-PSC with a PCE over 10% by employing a novel wide band-gap polymer, PTzBI-Si, and N2200 as donor and acceptor, respectively.^[30]

Aside from the intensive development on NDI-based polymeric acceptors, PDI-based polymeric acceptors are also widely explored. PDI derivatives share features of high electron affinity and high conductivity, thus making PDI-based copolymers good candidates for the electron acceptor of all-PSCs. For example, Zhan *et al.* firstly reported a PDI-based *n*-type polymeric acceptor, which can enable efficient all-PSC with a PCE over 1%.^[31] Bao *et al.* reported an all-PSC based on P11-2T-PS10:PDI-Th with a PCE of 4.4%.^[32] Hou *et al.* fabricated an all-PSC containing PDI-based acceptor (PPDIOTD) which achieved a high PCE of 6.5%.^[33] Zhao *et al.* reported vinylene-linked PDI-based acceptors (PDI-V

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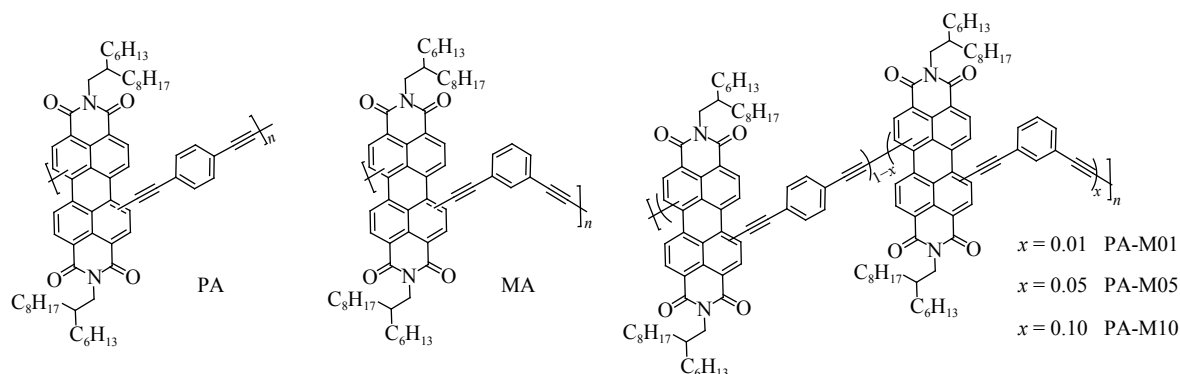
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and NDP-V), which could largely improve the performance of all-PSCs to 7.57% and 8.59%, respectively.^[34,35]

Compared to the boosted performance of polymer:small molecular blend, the inferior performance of all-PSCs requires more efforts to establish the structure-performance relationship. To optimize the photovoltaic performance of *n*-type conjugated polymeric acceptors, it is encouraging to optimize their molecular structures, electron mobilities of conjugated polymers, and blend morphologies with donor polymers.^[36–38] Copolymerizing NDI and PDI monomers with different donor moieties proves an efficient strategy to achieve high-performance *n*-type acceptors.^[39–43] Besides, terpolymeric strategy is also an effective method to improve the performance of polymeric acceptors.^[44–47] Moreover, from the successful cases of small molecular acceptors, it can be learned that the configurations of small molecular acceptors show a great impact on their photovoltaic performance.^[48–53] However, the configurations of *n*-type conjugated polymers as well as their effects on photovoltaic performance have rarely been studied.

Herein, we present a series of isomeric PDI-based conjugated polymers (PA and MA, in Scheme 1) as efficient electron acceptors in all-PSCs. By copolymerizing PDI monomers with 1,4-diethynylbenzene (*para*-linkage) and 1,3-diethynylbenzene (*meta*-linkage), isomeric PDI-based conjugated polymers with parallel and non-parallel PDI units inside backbones were obtained. It was found that *para*-linked conjugated polymers (PA) showed better solubility, stronger π - π stacking, more favorable blend morphology, and higher photovoltaic performance. The performance of the device based on PTB7-Th:PA (PTB7-Th:poly{4,8-bis[5-(2-ethylhexyl)-thiophen-2-yl]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl-*alt*-3-fluoro-2-[(2-ethylhexyl)-carbonyl]thieno[3,4-*b*]thiophene-4,6-diyl}) was significantly higher than that of PTB7-Th:MA (3.29% versus 0.92%). Moreover, we found that the photovoltaic performance of these polymeric acceptors can be further improved *via* a terpolymeric strategy. By copolymerizing a small amount (1%) of *meta*-linkages into PA, the optimized terpolymeric acceptors enabled to enhance photovoltaic performance with improvement of J_{sc} and FF, resulting in an improved PCE of 4.03%. The structure-performance relationships from these isomeric polymeric acceptors provide useful information for the designing of high-performance polymeric acceptors.



Scheme 1 Chemical structures of designed conjugated polymers

EXPERIMENTAL

Materials

All reagents and solvents were commercially available and were used as received. Tetrahydrofuran was distilled over sodium before use. Monomers 1,7/1,6-dibromoperylene-3,4:9,10-tetracarboxylic acid dianhydride (1), 1,4-bis((trimethylsilyl)ethynyl)benzene (2), and 1,3-bis((trimethylsilyl)ethynyl)benzene (3) were prepared according to previously reported literatures.^[54,55]

Preparation of Monomers

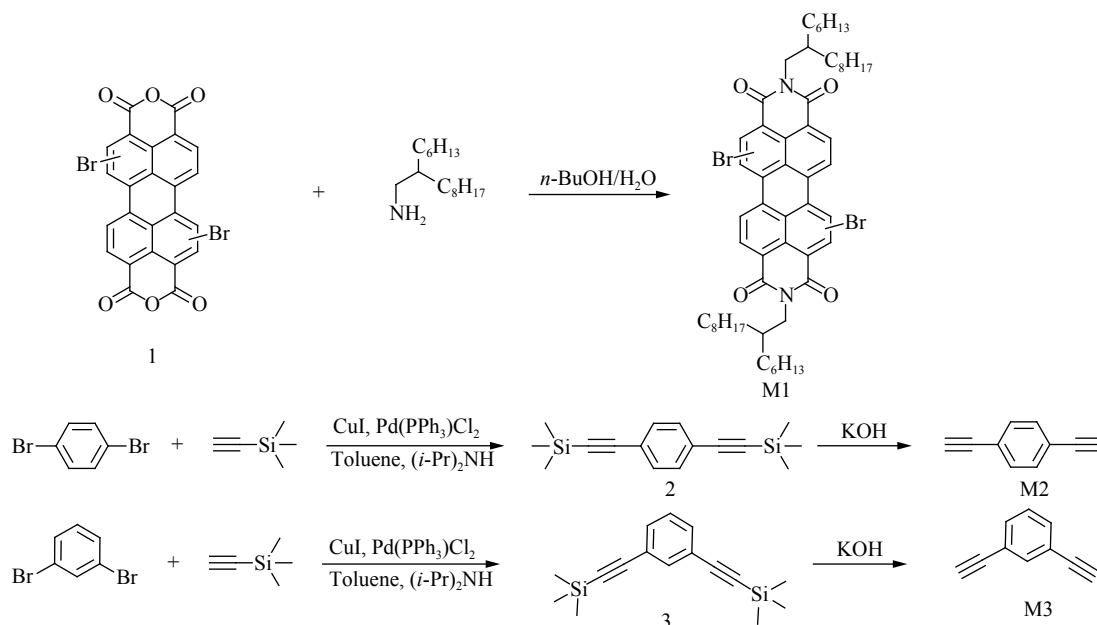
Synthetic routes to the monomers are presented in Scheme 2, while the ¹H-NMR and ¹³C-NMR spectra of monomers are given in Fig. S1 (in electronic supplementary information, ESI).

N,N'-bis(2-hexyldecyl)-1,7/1,6-dibromo-3,4:9,10-perylene diimide (M1)

Monomer 1 (5 mmol, 2.75 g) was firstly dispersed in 120 mL of *n*-BuOH/H₂O (1/1, *V/V*) and sonicated for 10 min. Then 2-hexyldecylamine (20 mmol, 4.83 g) was added. The reaction mixture was stirred at 80 °C for 24 h under nitrogen. The mixture was extracted with dichloromethane (3 × 90 mL) and washed with water (3 × 180 mL). The organic fraction was then dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography eluting with CH₂Cl₂/petroleum ether (1/2, *V/V*) to give a red solid (3.02 g, 61%). ¹H-NMR (500 MHz, CDCl₃, δ , ppm): 9.46 (d, 2H), 8.91 (s, 2H), 8.69 (d, 2H), 4.13 (d, 4H), 1.99 (m, 2H), 1.4–1.1 (m, 48H), 0.83 (m, 12H). ¹³C-NMR (126 MHz, CDCl₃, δ , ppm): 163.13, 162.64, 138.02, 132.71, 129.97, 129.11, 128.38, 126.88, 123.12, 122.68, 120.79, 44.85, 36.65, 31.81, 30.04, 29.66, 29.31, 26.47, 22.67, 14.11. Elemental analysis: Calcd. for [(C₅₆H₇₂Br₂N₂O₄)]_n: C 67.46; H 7.28; O 6.42; N 2.81; Found: C 67.49; H 7.21; O 6.48; N 2.86. LC-MS (APCI) *m/z* for C₅₆H₇₂Br₂N₂O₄ [M⁺]: 996.3; Found: 996.8.

1,4-Diethynylbenzene (M2)

Monomer 2 (0.271 g, 1 mmol) was dissolved in dichloromethane (10 mL) and methanol (5 mL). NaOH (0.160 g, 4 mmol) was added. The mixture was degassed twice and then stirred at room temperature for 1 h. The obtained product was extracted with dichloromethane (40 mL), washed with water (3 × 40 mL), and dried over anhydrous MgSO₄. The organic phase was collected and solvent was removed to



Scheme 2 Synthesis routes to the monomers

give a crude product, which was purified by chromatography (petroleum ether) to give a colorless solid (0.115 g, 91%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 7.44 (d, 4H), 3.17 (s, 2H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3 , δ , ppm): 132.03, 122.57, 83.04, 79.10. Elemental analysis: Calcd. for $[(\text{C}_{10}\text{H}_6)]_n$: C 95.21; H 4.79. Found: C 95.17; H 4.83. LC-MS (APCI) m/z for C_{10}H_6 $[\text{M}^+]$: 126.1; Found: 126.0.

1,3-Diethynylbenzene (M3)

M3 was synthesized using a similar procedure to that of M2. Yield, 0.110 g (88%). $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 7.62 (t, 1H), 7.47 (d, 2H), 7.28 (t, 1H), 3.09 (s, 2H). $^{13}\text{C-NMR}$ (126 MHz, CDCl_3 , δ , ppm): 135.66, 132.39, 128.45, 122.52, 82.64, 78.05. Elemental analysis: Calcd. for $[(\text{C}_{10}\text{H}_6)]_n$: C 95.21; H 4.79. Found: C 95.28; H 4.72. LC-MS (APCI) m/z for C_{10}H_6 $[\text{M}^+]$: 126.1; Found: 126.1.

Preparation of Polymers

Synthetic routes to the polymers are depicted in Scheme 3.

PA

M1 (219.4 mg, 0.22 mmol), M2 (27.9 mg, 0.22 mmol), dry chlorobenzene (5 mL), and $(i\text{-Pr})_2\text{NH}$ (2 mL) were added into a pressure tube (15 mL). The tube was purged with N_2 for 15 min to remove O_2 . $\text{Pd}(\text{PPh}_3)_4\text{Cl}_2$ (7 mg) and CuI (4 mg) were then added to the stirred solution. The solution was stirred at 60 °C for 30 min. After cooling to room temperature, the resultant dark purple viscous solution was poured into methanol. The polymer precipitate was filtered and dried under vacuum conditions for 12 h. The target polymer was extracted successively with acetone, dichloromethane, and chlorobenzene. The chlorobenzene fraction was concentrated and precipitated from methanol again. Finally, the polymer was dried under vacuum and obtained as a dark purple solid (185 mg, 84%). M_n (GPC, TCB, 150 °C) = 34.0 kDa, $D = 2.53$. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.84–9.41 (2H), 8.92–8.23 (4H), 7.86–7.34 (4H), 4.54–3.89 (4H), 2.51–0.51 (62H).

MA

MA was synthesized using a similar procedure to that of PA. Yield, 153 mg (69%). M_n (GPC, TCB, 150 °C) = 27.0 kDa, $D = 2.58$. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.94–9.40 (2H), 8.92–8.26 (4H), 8.03–7.78 (1H), 7.73–7.34 (3H), 4.47–3.76 (4H), 2.51–0.52 (62H).

PA-M01

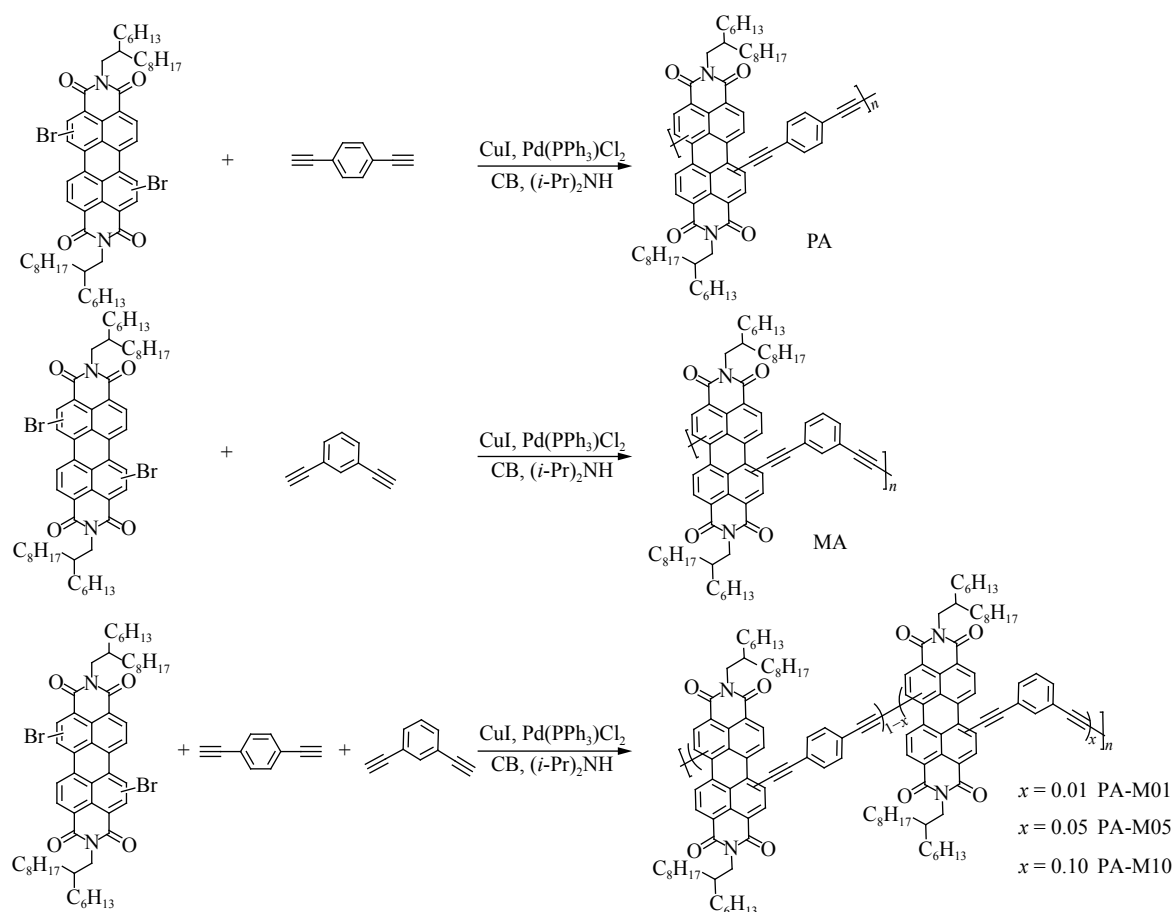
M1 (219.4 mg, 0.22 mmol), M2 (27.6 mg, 0.22 mmol), M3 (0.3 mg, 0.002 mmol), $\text{Pd}(\text{PPh}_3)_4\text{Cl}_2$ (7 mg), and CuI (4 mg) were dissolved in anhydrous chlorobenzene (5 mL) and $(i\text{-Pr})_2\text{NH}$ (2 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 30 min. After cooling to room temperature, the resultant dark purple viscous solution was poured into methanol. The polymer precipitate was filtered and dried under vacuum conditions for 12 h. The following procedure was similar to that used for the acquisition of PA. Yield: 160 mg (73%). M_n (GPC, TCB, 150 °C) = 37.6 kDa, $D = 1.96$. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.88–9.40 (2H), 8.92–8.23 (4H), 7.83–7.37 (4H), 4.55–3.82 (4H), 2.52–0.50 (62H).

PA-M05

PA-M05 was synthesized using a similar procedure to that of PA-M01 starting with M1 (219.4 mg, 0.22 mmol), M2 (26.2 mg, 0.21 mmol), and M3 (1.4 mg, 0.01 mmol). Yield, 165 mg (75%). M_n (GPC, TCB, 150 °C) = 38.3 kDa, $D = 2.20$. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.85–9.41 (2H), 8.94–8.25 (4H), 7.93–7.5 (4H), 4.56–3.85 (4H), 2.55–0.45 (62H).

PA-M10

PA-M10 was synthesized using a similar procedure to that of PA-M01, starting with M1 (219.4 mg, 0.22 mmol), M2 (24.8 mg, 0.19 mmol), and M3 (2.8 mg, 0.02 mmol). Yield, 167 mg (76%). M_n (GPC, TCB, 150 °C) = 31.4 kDa, $D = 2.51$. $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 9.97–9.40 (2H), 9.01–8.28 (4H), 7.86–7.45 (4H), 4.51–3.85 (4H), 2.51–0.55 (62H).



Scheme 3 Synthetic routes to the polymers

Characterization

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on a Bruker AV500 spectrometer in deuterated chloroform solution using tetramethyl silane as the reference. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda-9 spectrophotometer in chlorobenzene solution and as thin films, which were spin-coated with $10 \text{ mg}\cdot\text{mL}^{-1}$ chlorobenzene solution. Cyclic voltammetry (CV) measurements were carried out using a platinum-carbon working electrode, a Pt wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode, in a $0.1 \text{ mol}\cdot\text{L}^{-1}$ tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile electrolyte solution. Thermogravimetric analysis (TG) was performed on a Netzsch TG 209 instrument at heating rate of $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under nitrogen. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 instrument under nitrogen and the heating/cooling rate was $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The transmission electron microscopy (TEM) images of the polymers were taken by JEM-100CXII on the copper grid. High temperature gel permeation chromatography (HTGPC) was measured by Agilent Technologies PL-GPC 220 high temperature chromatography at $150 \text{ }^\circ\text{C}$ using 1,2,4-trichlorobenzene as the solvent. The atomic force microscopy (AFM) measurements of the surface morphologies of blend films were carried out with a Digital Instrumental DI Multimode Nanoscope IIIa in tapping mode microscopy with $5 \text{ }\mu\text{m}$ scanners.

All-PSCs were fabricated using the conventional device structures of ITO/PEDOT:PSS/PTB7-Th:acceptor/PFN/Ag. Firstly, PEDOT:PSS solution was spin-coated onto cleaned indium tin oxide (ITO) substrates, followed by the deposition of active layer *via* spin-coating. All the blend films were spin-coated from chlorobenzene (CB) solutions. The donor and acceptor polymers were dissolved and fabricated at a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$. Poly[(9,9-bis(3'-((*N,N'*-dimethyl)-*N*-ethylammonium)-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) with a thickness of 5 nm was spin-coated on the active layer as electron transporting layer. Finally, Ag electrode was thermally deposited in vacuo with a base pressure of $2.0 \times 10^{-4} \text{ Pa}$ through a shadow mask on the top of the active layer. The J - V curves were measured on a computer-controlled Keithley 2400 sourcemeter under 1 sun , AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), the light intensity was $100 \text{ mW}\cdot\text{cm}^{-2}$ as calibrated by a China general certification center (CGC) certified reference monocrystal silicon cell (Enlitech). Before the J - V test, a physical mask of an aperture with precise area of 4 mm^2 was used to define the device area. The external quantum efficiency (EQE) spectra were recorded on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011).

RESULTS AND DISCUSSION

Synthesis and Characterization

Copolymers PA and MA were synthesized *via* Sonogashira

polymerization^[56] from monomer *N,N'*-bis(2-hexyldecyl)-1,7-dibromo-3,4,9,10-perylene diimide (M1) with 1,4-diethynylbenzene (M2) and 1,3-diethynylbenzene (M3), respectively. The three random terpolymers (PA-M01, PA-M05, and PA-M10) were synthesized by varying the molar ratio of M2 and M3. All the polymers are soluble in common organic solvents (such as chloroform, CB, and *o*-dichlorobenzene). However, MA showed apparent lower solubility than that of PA, and copolymers showed gradually reduced solubility with increasing *meta*-linkage ratios, indicating that the *meta*-linkage can induce more aggregation of copolymers, result-

ing in lower solubility.^[57] The molecular weights of the polymers were measured *via* gel permeation chromatography in 1,2,4-trichlorobenzene at 150 °C. As summarized in Table 1, the number-average molecular weights (M_n) of PA and terpolymers were ranging from 30 kDa to 38 kDa, while MA had the lowest M_n of 27.0 kDa, which can be ascribed to the low solubility of MA that decreases the chain propagation during polymerization. The thermal stabilities of these copolymer acceptors were investigated using thermogravimetric analysis, as shown in Fig. S2 (in ESI). It can be observed that these polymers can be stable up to 400 °C.

Table 1 Summary of M_n , D , optical band gap, oxidation/reduction potentials of copolymer acceptors

Polymer	M_n (kDa)	D	E_{ox} (eV)	E_{red} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
PA	34.0	2.53	1.41	−0.95	−6.21	−3.85	2.36
MA	27.0	2.58	1.28	−1.03	−6.08	−3.77	2.31
PA-M01	37.6	1.96	1.40	−0.98	−6.20	−3.82	2.38
PA-M05	38.3	2.20	1.41	−0.99	−6.21	−3.81	2.40
PA-M10	31.4	2.51	1.38	−1.02	−6.18	−3.78	2.40

Density Functional Theory Calculations

Triple bonds, well-known linkages with high rigidity, can eliminate the twisting between donor and acceptor moieties inside polymer backbones.^[58] Herein, two dimers of PA and MA were subjected to density functional theory (DFT) modelling with ignorance of the side chains, based on the Gaussian 09 with B3LYP/6-31G (d, p) basis set.^[59] As shown in Fig. 1, the PDI units in the dimer of PA are parallel with each other, while those in the dimer of MA are not due to an angle of 120 °C between two triple bonds in 1,3-diethynylbenzene. Moreover, it can be observed that small dihedral angles about 15° appear between benzene and PDI chromophore in the two dimers due to the distortion of PDI chromophore. These results indicate that the distortion degrees of PDI units in the two polymers are similar, while the configurations between PDI units inside the polymers are different. The different configurations of PA and MA can result in different properties (such as solubility, as discussed above) and might affect their performance in photovoltaic cells by manipulating their crystallinity, blend morphologies with donor polymers, *etc.*

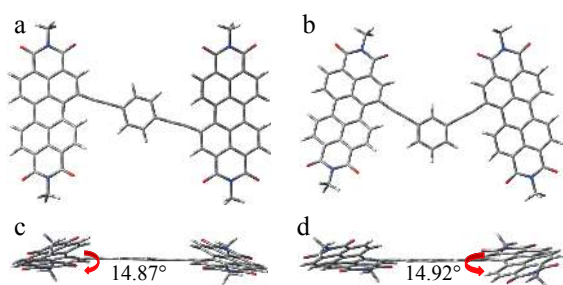


Fig. 1 Density functional theory (DFT) modelling of the *para*-linked and *meta*-linked PDI dimers: (a) top view of PA, (b) top view of MA, (c) side view of PA, and (d) side view of MA

Optical Properties

The optical absorption of these copolymers was investigated in chlorobenzene and as thin films *via* UV-Vis absorption

spectroscopy. As shown in Fig. 2, it can be observed that both the absorption spectra of PA and MA covered the absorption range from 300 nm to 650 nm. However, the absorption peaks in the short wavelengths of PA were red-shifted than that of MA. Moreover, PA showed apparent shoulder peaks around 610 nm, which can be attributed to the π - π stacking between the backbones of PA. Interestingly, it can be observed that with the increase of *meta*-linkage, the absorption spectra of PA-M05 and PA-M10 in the range from 450 nm to 650 nm showed slight enhancement in comparison with those of both PA and MA. In the thin-film state, all the copolymers showed limited difference from those in CB, indicating that these polymers were pre-aggregated in solution.^[60] Similarly, the trend in the absorption spectra of these polymers in CB was also maintained in their thin-film state. The absorption of PTB7-Th in thin film was also recorded. All the copolymers exhibited complementary absorption with that of PTB7-Th, indicating potential good utilization of sunlight and higher performance in all-PSCs.

Electrochemical Properties

The electron affinities of polymeric acceptors are correlated with the open-circuit voltage of all-PSCs. Here, the electron affinities of these copolymer acceptors were investigated using cyclic voltammetry (CV) analysis. Ferrocene/ferrocenium (Fc/Fc^+) was used for calibration. The highest occupied molecular orbital (HOMO) energy level (E_{HOMO}) and the lowest unoccupied molecular orbital (LUMO) energy level (E_{LUMO}) were calculated according to the following equations: $E_{HOMO} = E_{ref} - E_{ox}$ (eV) and $E_{LUMO} = E_{ref} - E_{red}$ (eV). E_{ox} and E_{red} of copolymers were estimated from their CV curves, shown in Fig. 2. The E_{HOMO} and E_{LUMO} values are summarized in Table 1. It can be seen that MA possessed both higher E_{HOMO} and E_{LUMO} values (−6.08 and −3.77 eV) than those of PA (−6.21 and −3.85 eV). Moreover, with the increase of *meta*-linkages, the E_{LUMO} values of PA-M01, PA-M05 and PA-M10 were gradually raised from −3.82 eV to −3.77 eV, implying potential higher open-circuit voltage

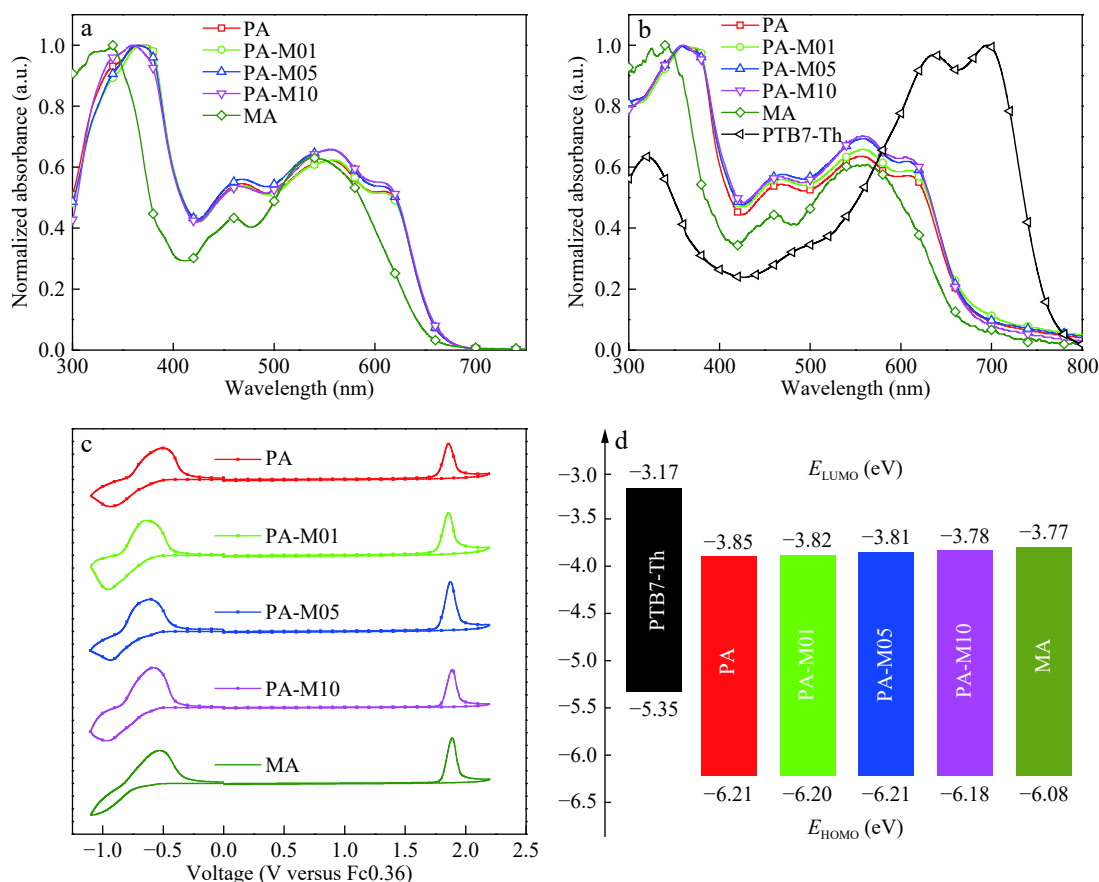


Fig. 2 The UV-Vis-NIR absorption spectra of PDI copolymers (a) in CB and (b) as thin films; (c) CV curves and (d) energy level alignment diagram of PDI copolymers

(V_{oc}) in all-PSCs. The E_{HOMO} and E_{LUMO} of PTB7-Th were estimated to be -5.35 and -3.17 eV, respectively. The differences in both LUMO offset (over 0.6 eV) and HOMO offset (over 0.7 eV) between PTBT-Th and acceptors indicate that sufficient energy offsets for efficient exciton dissociation in PTB7-Th and these copolymer acceptors were obtained.

Photoluminescence (PL)

The PL spectra of the PTB7-Th film and the PTB7-Th:acceptor blend films are depicted in Fig. 3. The PL quenching efficiency, which reflects the efficiency of exciton diffusion and dissociation at the D/A interface, was calculated according to the equation: $\Delta PL = 1 - PL_{blend}/PL_{PTB7-Th}$, where PL_{blend} and $PL_{PTB7-Th}$ were PL intensity of the blend and neat PTB7-Th films, respectively. The PL emission peak of the neat PTB7-Th film is around 760 nm. ΔPL s in the PTB7-Th:acceptor (1:1, $W:W$) blend films were above 95%, suggesting that the exciton generated in the donor PTB7-Th can efficiently dissociate at the D/A interface.^[44]

Photovoltaic Performance

To investigate the photovoltaic performance of the all-PSCs, conventional device structure, ITO/PEDOT:PSS/PTB7-Th:Acceptor/PFN/Ag were fabricated. PFN was used as the interfacial layer. The active layer was spin-coated from CB with a donor/acceptor weight ratio of 1:1. The device characteristics were determined under an illumination of AM

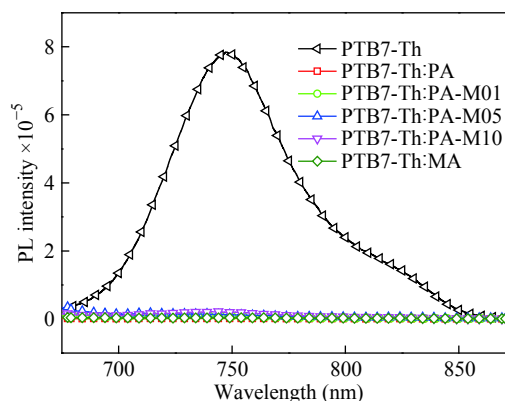


Fig. 3 Photoluminescence spectra of PDI copolymers based active layers and neat PTB7-Th

1.5 simulated solar light at $100 \text{ mW} \cdot \text{cm}^{-2}$. The $J-V$ curves of PTB7-Th:acceptor solar cells are shown in Fig. 4, with detailed photovoltaic parameters summarized in Table 2. Compared to device based on PTB7-Th:MA with a low PCE of 0.92%, device with PTB7-Th:PA exhibited the significantly enhanced PCE of 3.29%. The V_{oc} s in devices of PTB7-Th:PA and PTB7-Th:MA were 0.639 and 0.658 V, respectively. However, much enhanced J_{sc} ($10.75 \text{ mA} \cdot \text{cm}^{-2}$ versus $3.50 \text{ mA} \cdot \text{cm}^{-2}$) and moderately improved FF (0.47 versus 0.39) were obtained in devices with PTB7-Th:PA. The increased J_{sc} in PTB7-Th:PA based device can be

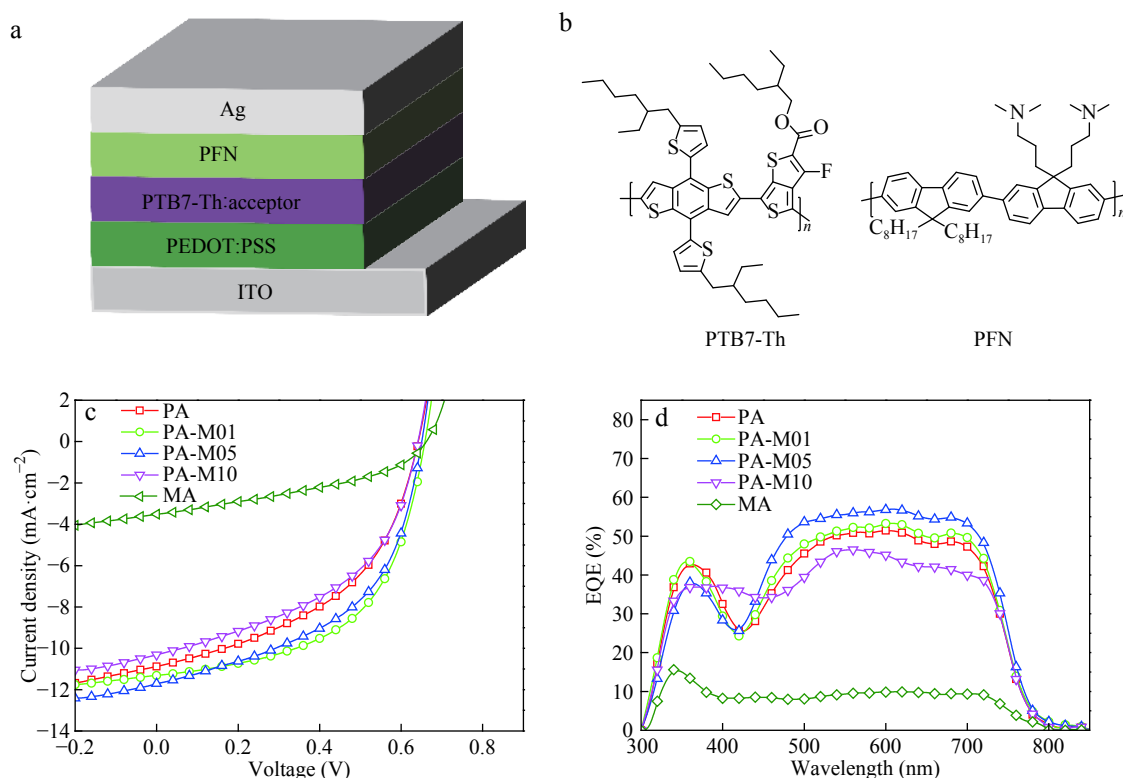


Fig. 4 (a) Device structure of all-PSC, (b) molecular structures of donor and interfacial material, and (c) J - V curves and (d) EQE curves of all-PSCs based on PDI copolymers

Table 2 Photovoltaic data of PSCs with donor:acceptor ($W:W = 1:1$) under the illumination of AM 1.5G at 100 mW·cm⁻²

Donor:Acceptor	V_{oc} (V)	J_{sc} (mA·cm ⁻²)	FF (%)	PCE (%)	Best PCE (%)	$\mu_h \times 10^4$ (cm ² ·V ⁻¹ ·s ⁻¹)	$\mu_e \times 10^4$ (cm ² ·V ⁻¹ ·s ⁻¹)
PTB7-Th:PA	0.639 ± 0.005	10.75 ± 0.18	46.76 ± 0.55	3.21 ± 0.12	3.29	9.76	1.07
PTB7-Th:MA	0.658 ± 0.004	3.50 ± 0.04	39.20 ± 0.16	0.90 ± 0.01	0.92	4.19	0.19
PTB7-Th:PA-M01	0.658 ± 0.002	11.31 ± 0.02	54.16 ± 1.47	4.03 ± 0.12	4.11	10.23	1.13
PTB7-Th:PA-M05	0.649 ± 0.002	11.44 ± 0.25	50.38 ± 0.43	3.74 ± 0.09	3.84	21.10	1.10
PTB7-Th:PA-M10	0.644 ± 0.002	10.18 ± 0.16	46.71 ± 0.67	3.06 ± 0.06	3.13	4.38	0.89

attributed to more regular π - π stacking of PA.^[61] Devices with terpolymeric acceptors PA-M01, PA-M05, and PA-M10 were also fabricated. It can be observed that devices with PTB7-Th:PA-M01 and PTB7-Th:PA-M05 exhibited higher PCE than device with PA as acceptor did. The V_{oc} and J_{sc} in PTB7-Th:PA-M01 and PTB7-Th:PA-M05 based devices were both slightly enhanced in comparison with those in PTB7-Th:PA based devices, which can be attributed to the higher E_{LUMO} values of PA-M01 and PA-M05, and enhanced absorption. Surprisingly, we found that the FF in device with PTB7-Th:PA-M01 was much higher than those of other devices, which might be originated from the optimized BHJ morphology in PTB7-Th:PA-M01 blend.

The EQE spectra of these devices were collected to examine the spectral responses of the all-PSCs. As depicted in Fig. 4, compared to device of PTB7-Th:MA, PTB7-Th:PA based device showed apparently enhanced EQE in a broad range of 300–800 nm, corresponding well with the higher J_{sc} in PTB7-Th:PA based device. Similarly, devices with terpolymeric acceptors PA-M01 and PA-M05s exhibited

higher EQE responses than that in the PTB7-Th:PA based device. These observations suggested that PA contributed to the higher PCE by providing a more regular molecular stacking, while the terpolymers PA-M01 and PA-M05 could improve the BHJ morphologies.

Carrier Mobility

We also probed carrier mobilities of these blend films to obtain a deep understanding of differences in device performance. Hole-only and electron-only devices were fabricated with ITO/PEDOT:PSS/PTB7-Th:acceptor/MoO₃/Ag and ITO/ZnO/PTB7-Th:acceptor/Ag, respectively. The hole mobility (μ_h) and electron mobility (μ_e) were calculated based on the space charge limited current (SCLC) model using the following equation: $J = 9/8\epsilon_0\epsilon_r\mu V^2/d^3$, where J is the current, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, μ is the zero-field mobility, d is the thickness of the active layer, and V is the effective voltage. The SCLC curves of all-polymer blends are given in Fig. S3 (in ESI). The mobility μ was calculated from the slope of the $J^{1/2}$ - V curve. The electron and hole

mobility of PTB7-Th:PA blend film were 1.07×10^{-4} and $9.76 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, respectively, which are higher than those of 0.19×10 and $4.19 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the blend film based on MA. The higher electron mobility in PA may be originated from its more ordered backbone, which is favorable for charge transporting. Moreover, the PTB7-Th:PA blend film possessed a more balanced $\mu_{\text{h}}/\mu_{\text{e}}$ ratio of 9 compared to that of 22 for the PTB7-Th:MA blend film. The more balanced hole and electron mobility can reduce bimolecular recombination in the blend film and thus maximize the photocurrent,^[62] which is consistent with the higher J_{sc} of PA based device. The higher carrier mobility and more balanced $\mu_{\text{h}}/\mu_{\text{e}}$ ratio of the PTB7-Th:PA blend film than those of the PTB7-Th:MA blend film coincide well with the enhanced J_{sc} and FF in PTB7-Th:PA based devices. Surprisingly, we found that the incorporation of *meta*-linkages into PA can further improve both electron and hole mobilities of blend films. PTB7-Th:PA-M01 and PTB7-Th:PA-M05 blends showed slightly enhanced μ_{h} and μ_{e} in

comparison with those in PTB7-Th:PA blend, resulting in enhanced J_{sc} s and FFs in PTB7-Th:PA-M01 and PTB7-Th:PA-M05 based devices.

Film Morphology

We probed the surface morphologies of active layers using atomic force microscopy (AFM). As shown in Fig. S4 (in ESI), all the blend films showed similar root-mean-square (RMS) roughness around 1.4–1.5 nm. To give a deeper understanding of the different photovoltaic performance, we also probed the blend morphologies of active layers using transmission electron microscopy (TEM). As shown in Fig. 5, both PTB7-Th:PA and PTB7-Th:MA showed homogenous blend morphologies. However, the blend film of PTB7-Th:PA-M01 showed apparent phase separation, which can efficiently facilitate charge transportation and dissociation, indicating that the PA-M01 can be used as effective electron acceptors in all-PSCs. These results also strongly prove that terpolymeric strategy is an efficient tool to tune the blend morphologies of all-PSCs.

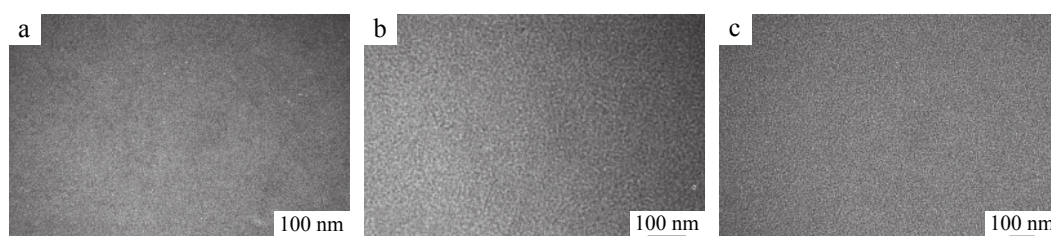


Fig. 5 TEM images of (a) PA, (b) PA-M01, and (c) MA

CONCLUSIONS

In conclusion, we have presented a series of isomeric conjugated polymers as electron acceptors of all-PSCs. By altering the linkage types between PDI units in the backbones, the properties and photovoltaic performance of these polymers can be well-regulated. The *para*-linked conjugated polymers showed better solubility, stronger π - π stacking, more favorable morphology, and higher photovoltaic performance. It was also found that the photovoltaic performance of these polymers can be further improved *via* a terpolymeric strategy with improvement in morphologies and electron/hole mobilities of blend active layer. As a result, a PCE of 4.11% was obtained in devices with the optimized isomeric polymer as acceptors. These results give a clear relationship between polymer configuration and device performance and will provide useful information in the design of polymeric acceptors for high-performance all-PSCs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2188-1>.

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