Journal Pre-proof

Structure evolution from D-A-D type small molecule toward D-A-D-A-D type oligomer for high-efficiency photovoltaic donor materials

Hao Xia, Xiaopeng Xu, Jiali Guo, Can Qian, Kai Zhang, Mengbing Zhu, Bin Zhang, Wenhong Peng, Qiang Peng, Weiguo Zhu

PII: S0143-7208(20)31647-8

DOI: https://doi.org/10.1016/j.dyepig.2020.108950

Reference: DYPI 108950

To appear in: Dyes and Pigments

Received Date: 31 July 2020

Revised Date: 19 October 2020

Accepted Date: 19 October 2020

Please cite this article as: Xia H, Xu X, Guo J, Qian C, Zhang K, Zhu M, Zhang B, Peng W, Peng Q, Zhu W, Structure evolution from D-A-D type small molecule toward D-A-D-A-D type oligomer for high-efficiency photovoltaic donor materials, *Dyes and Pigments*, https://doi.org/10.1016/j.dyepig.2020.108950.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier Ltd.



The authors declare no conflict of interest.

building

Graphical Abstract

A D-A-D-A-D type oligomer of 5BDTBDD and its D-A-D type small molecule of 3BDTBDD were primarily designed and synthesized using benzo[1,2-c:4,5-c']dithio-phene-4,8-dione (BDD) as electron-accepting (A) unit. By structure evolution of inserting a repeated D-A unit, the 5BDTBDD shows much improved crystallization, absorption, mobility, morphology and photovoltaic properties than the 3BDTBDD.



Structure evolution from D-A-D type small molecule toward D-A-D-A-D type oligomer for high-efficiency photovoltaic donor materials

Hao Xia,^a Xiaopeng Xu,^b Jiali Guo,^a Can Qian,^a Kai Zhang,^a Mengbing Zhu,^a Bin Zhang,^a Wenhong Peng,^a Qiang Peng,^{*b} Weiguo Zhu^{*a}

^aSchool of Materials Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Key Laboratories of Environment-Friendly Polymers, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China.

^bKey Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, P. R. China

*Corresponding author

E-mail: zhuwg18@126.com E-mail: qiangpengjohnny@yahoo.com

Abstract:

In order to study the influence of structure evolution on properties, a D-A-D-A-D-type oligomer of **5BDTBDD** and its D-A-D type small molecule of **3BDTBDD** were designed and synthesized, which consist of electron-accepting (A) unit of benzo[1,2-c:4,5-c'] dithiophene-4,8-dione (BDD) and electron-donating (D) unit of 4,8-di(6-ethylhexylthiophen-2-yl)benzo [1,2-b:4,5-b']dithiophene (BDT). The effect of structure evolution on crystallinity, absorption, mobility, morphology and photovoltaic properties was primarily investigated. It is found that, by simply inserting a D-A repeat unit, **5BDTBDD** shows more improved crystallization, absorption, mobility and morphology than **3BDTBDD**. As a result, **5BDTBDD** exhibits better photovoltaic properties than **3BDTBDD** in their non-fullerene organic solar cells using 9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-di thieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b'] dithiophene (**ITIC**) as acceptor material. An increasing power conversion efficiency of 7.89% is obtained in the **5BDTBDD**:**ITIC** cells. It indicates that structure evolution from D-A-D type small molecule toward D-A-D-A-D type oligomer is an efficient strategy to achieve high-efficiency donor materials in organic solar cells.

KEYWORDS: Oligomer, Benzodithiophene-4,8-dione, Benzodithiophene, Non-fullerene, Organic solar cells.

1. Introduction

Organic photovoltaics (OPVs) with buck-heterojunction (BHJ) structure as a promising clean energy have attracted great attention due to their low cost, light weight, flexibility, and large-area roll-to-roll fabrication [1-4]. Recently, through development of non-fullerene acceptors and optimization of device structure, polymer-based organic solar cells (P-OSCs) have been made much progress with an encouraging PCE (power conversion efficiency) over 16% in single-junction binary devices fabricated in the laboratory [5-7]. The small molecules based organic solar cells (SM-OSCs) in single-junction binary devices have also received a PCE value over 14% [8,9]. However, higher PCE and device repeatability are still critical issue for the commercialization of organic solar cells.

Conjugated polymers are a type of the important donor materials owing to their excellent film-formation and charge transfer resulting from the extensional conjugated backbone and good electron delocalization. Using polymers as donors, the P-OSCs have showed high PCE, but exist the unexpected batch-to-batch variations [10,11]. In contrast, small molecules, another type of donor materials, have well-defined structure without batch-to-batch variations [12]. But their film-formation and morphology are difficult to be controlled [13]. Thus, a special class of donor materials with multiple electron donating-accepting (D-A) repeat units, that is so-called D-A type oligomers, has been developed in recent years [14-21]. The advanced PCEs about 8.10% ~ 9.25% have been obtained in the oligomer-based organic solar cells (OM-OSCs). The results show these OM-OSCs often take fullerenes (PCBMs) as acceptors. And the D-A structures and attaching terminal groups are crucial factor for oligomers to get advanced photovoltaic properties.

Non-fullerene-based organic solar cells (NF-OSCs) have received rapid progress owing to the adjustable absorption spectra and energy levels of non-fullerene acceptor recently [22-31].

In order to obtain high-performance non-fullerene acceptors (NFAs), some electron-accepting π -fused conjugated units, such as diketopyrrolopyrrole (DPP), perylenediimide (PDI), naphthalene diimide (NDI), anthene diimide (ADI) and indacenothiophene diimide (IDT), have been employed to construct NFAs [32-36]. It is found that the NFAs show more outstanding advantage than fullerene acceptors in enhancing solar absorption and reducing energy loss, which is available to increase short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) for their OSCs [37-39]. High PCE over 12% was recently obtained in NF-OSCs using polymer PBDB-T as donor material [40-42], which indicates that using suitable non-fullerene acceptor is an advisably choice to improve the efficiency of OSCs. However, highperformance NF-OSCs using D-A type oligomers as donor materials were seldom reported.

In order to study the influence of structure evolution on photovoltaic properties and get highperformance photovoltaic donor materials used in NF-OSCs, a D-A-D-A-D type oligomer of **5BDTBDD** and a D-A-D type small molecule (SM) of **3BDTBDD** were primarily designed and synthesized, in which a weak electron-accepting (A) unit of benzo[1,2-c:4,5-c']dithio phene-4,8-dione (BDD) and an electron-donating (D) unit of 4,8-di(6-ethylhexylthiophen-2yl)benzo[1,2-b:4,5-b']dithiophene (BDT) are employed. Their molecular structures are showed in Figure 1. And their crystallinity, absorption, mobility, morphology and photovoltaic properties were systematically studied. Our results demonstrate that, **5BDTBDD** oligomer, by simply embedding a D-A skeleton into D-A-D type SM, exhibited stronger π - π stacking and intermolecular dipolar interaction, as well as better crystallinity and morphology than **3BDTBDD** small molecule. As a result, **5BDTBDD** oligomer exhibits more intense redshifted absorption, higher carrier mobility, and more ordered molecular packing than **3BDTBDD** small molecule. Benefited from these qualities, **5BDTBDD** exhibit significantly improved photovoltaic properties with a higher PCE of 7.89% than **3BDTBDD** in the NF-OSCs using **ITIC** as NFA. This is first example using a weak electron-accepting BDD unit to construct high-performance oligomer. This work provides an effective strategy to improve photovoltaic properties of photovoltaic donor materials by structure evolution from D-A-D-type SM toward D-A-D-A-D type oligomer in the NF-OSCs.



Figure 1. Molecular structures of 5BDTBDD oligomer and 3BDTBDD small molecule.2. Experimental section

2.1 Materials and Synthesis

The synthetic route of **3BDTBDD** and **5BDTBDD** is depicted in Scheme 1. Compounds 1 and **4** were purchased from Chemical Corporation [43,44]. The synthetic details of compounds **2**, **3**, **5**, **6** and **7** are depicted in Electronic Supporting Information (ESI) [43,44]. **3BDTBDD** and **5BDTBDD** were respectively prepared by Stille coupling reaction as follows. Both molecules were characterized by ¹H, ¹³C NMR, and HRMS. They show good solubility in common solvents, such as dichloromethane, chloroform and chlorobenzene.



Scheme 1. Synthetic routes of **5BDTBDD** and **3BDTBDD**.

Synthesis of compound 3BDTBDD

In a 50 mL two-neck round-bottom flask, a mixture of compound **3** (0.167 g, 0.22 mmol), compound **5** (0.358 g, 0.48 mmol), and Pd₂(dba)₃ (10 mg, 0.011 mmol), tri(o-tolyl)phosphine (13.4 mg, 0.044 mmol) in toluene was degassed under the N₂ atmosphere and stirred at refluxing temperature for 12 h. After cooled to room temperature, the mixture was poured into water (150 mL) and extracted with CH₂Cl₂(30 mL×3). The organic phases were combined and dried over anhydrous MgSO₄. The solvents were removed off under reduced pressure and the red residue was purified by silica gel chromatography, eluting with PE-CH₂Cl₂ (4:1) to give purplish red solid (225 mg, 62%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.79 (s, 2H), 7.72 (d, *J* = 4.0 Hz, 2H), 7.62 (d, *J* = 5.7 Hz, 2H), 7.45 (d, *J* = 5.7 Hz, 2H), 7.32 (dd, *J* = 3.4, 2.5 Hz, 4H), 7.28 (d, *J* = 4.0 Hz, 2H), 6.92 (t, *J* = 3.8 Hz, 4H), 3.41 – 3.23 (m, 4H), 2.88 (dd,

J = 6.7, 2.7 Hz, 8H), 1.77 - 1.69 (m, 6H), 1.47 - 1.25 (m, 48H), 0.99 - 0.86 (m, 36H). ¹³C NMR (75 MHz, CDCl₃) δ 177.6, 153.6, 145.9, 141.9, 141.2, 139.5, 138.5, 137.3, 137.1, 137.0, 136.9, 133.5, 132.9, 132.6, 131.6, 128.0, 127.8, 125.5, 125.5, 124.1, 123.7, 123.6, 120.0, 41.5, 41.3, 34.3, 33.7, 32.8, 32.6, 32.5, 29.0, 28.8, 26.2, 25.8, 23.1, 23.0, 14.2, 14.2, 11.0. HRMS (m/z) of C₁₀₂H₁₂₀O₂S₁₂ for [M+H]⁺: calcd. 1761.6010; found, 1761.6055.

Synthesis of compound 5BDTBDD

In a 50 mL two-neck round-bottom flask, a mixture of compound 6 (0.041 g, 0.045 mmol), compound 7 (0.12 g, 0.095 mmol) and Pd₂(dba)₃ (2.1 mg, 0.0023 mmol), tri(otolyl)phosphine (2.7 mg, 0.009 mmol) in toluene was degassed toluene and stirred at refluxing temperature for 12 h under the N₂ atmosphere. After cooled to room temperature, the mixture was poured into water (150 mL), and extracted with CH₂Cl₂ (30 mL×3). The organic phases were combined, and then dried over with anhydrous MgSO₄. The solvents were removed off under reduced pressure. The red residue was purified by silica gel chromatography eluting with PE-CH₂Cl₂ (3:1) to give purple black solid (80 mg, 60 %).¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.80 (s, 2H), 7.76 (s, 2H), 7.72 (d, J = 4.0 Hz, 4H), 7.63 (d, J = 5.7 Hz, 2H), 7.46 (d, J = 5.7 Hz, 2H), 7.37 (d, J = 3.5 Hz, 2H), 7.34 (dd, J = 3.4, 2.1)Hz, 4H), 7.29 (d, J = 1.4 Hz, 4H), 6.97 (d, J = 3.5 Hz, 2H), 6.95 – 6.91 (m, 4H), 3.41 - 3.27(m, 8H), 2.95 - 2.87 (m, 12H), 1.80 - 1.70 (m, 5H), 1.49 - 1.36 (m, 40H), 1.00 - 0.93 (m, 30H). ¹³C NMR (75 MHz, CDCl₃) δ 177.4, 153.2, 145.8, 142.0, 141.6, 141.1, 139.3, 138.8, 138.4, 137.3, 137.1, 136.9, 133.5, 132.9, 132.2, 131.9, 128.5, 128.0, 127.8, 127.6, 125.5, 125.4, 125.1, 124.0, 123.6, 119.8, 118.3, 41.4, 41.2, 34.4, 34.3, 33.6, 32.8, 32.6, 32.5, 29.8, 29.0, 28.8, 26.2, 25.7, 23.2, 23.1, 23.1, 14.3, 14.2, 14.2, 11.1, 11.0. HRMS (m/z) of $C_{170}H_{198}O_4S_{20}$ for [M]⁺: calcd. 2942.9704; found, 2942.9731.

7

3. Results and discussion

3.1. Thermal Property and Crystallinity

Figure S1 shows the thermogravimetry (TG) curves of **3BDTBDD** and **5BDTBDD**. Under a nitrogen atmosphere, high decomposition temperature of 380 °C at 5% weight loss is observed for both molecules. It indicates that D-A-D-A-D type oligomer and its D-A-D type SM have good thermal stability. Figure S2 depicts the differential scanning calorimetry (DSC) curves of two molecules. It is found that there aren't obvious melting temperature (T_m) upon heating process and crystallization temperatures (T_c) upon cooling process for **3BDTBDD** small molecule. However, **5BDTBDD** oligomer displays obvious melting and crystalling peaks. It indicates that **5BDTBDD** oligomer has stronger intermolecular forces and crystallinity than **3BDTBDD** small molecule. Inserting D-A repeat unit into a D-A-D type small molecule can efficiently tune molecular crystallinity.

3.2. Absorptive and Electrochemical Properties

The UV-vis absorption spectra of **5BDTBDD** and **3BDTBDD** are depicted in Figure 2. Their absorptive data are summarized in Table 1. Two typical absorption bands are observed for both molecules, which contain a high-lying band at $300 \sim 400$ nm and a low-lying band at $400 \sim 600$ nm in diluted chloroform solution. Therein, **5BDTBDD** oligomer shows a remarkably red-shifted absorption spectrum peaked at 512 nm with an increasing molar extinction coefficient of 1.32×10^5 M⁻¹ cm⁻¹ in comparison with **3BDTBDD** small molecule. It indicates that the embedding D-A repeat unit is available to increase conjugation degree and intramolecular charge transfer (ICT) effect for this **5BDTBDD** oligomer. The observed maximum absorption peak at 562 nm for the **5BDTBDD** film and 516 nm for the **3BDTBDD** film further support this speculation. As a result of calculation, the optical band gaps are 1.87 eV

for **5BDTBDD** and 2.03 eV for **3BDTBDD** from their absorption band edges (E_g^{opt}) in the thin films. It is noted that the **5BDTBDD** film rather than the **3BDTBDD** film displays another pronounced shoulder peak at 606 nm. It implies that **5BDTBDD** oligomer has better crystallinity and stronger π - π stacking effect than **3BDTBDD** small molecule [45]. This phenomenon is consistent with the DSC testing results.



Figure 2. UV-vis absorption spectra of **5BDTBDD** and **3BDTBDD** in chloroform solution (a) and in their neat films (b).

Table 1. Absorptive and	electrochemical p	properties of	5BDTBDD	and 3BDTBDD
--------------------------------	-------------------	---------------	---------	--------------------

Donor -	λ_{max} (nm)		$\lambda_{onset.film}$	$E_{\rm g}^{\rm opt}$	$E_{\rm HOMO}$	E_{LUMO}
	Solution	Film	(nm)	(eV) ^a	$(eV)^{b}$	$(eV)^{b}$
3BDTBDD	484	516	610	2.03	-5.50	-3.38
5BDTBDD	512	562, 606	663	1.87	-5.46	-3.51

^a Calculated from the absorption band edge of the films, $E_{\rm g}^{\rm opt}$ =1240/ $\lambda_{\rm onset}$

^b Calculated from empirical equation: $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ eV, $E_{\text{LUMO}} = (E_{\text{red}} + 4.8)$ eV (The formal potential of Fc/Fc⁺ was 0.48V vs. Ag/AgCl measured in this work)

Figure S3 shows cyclicvoltammetry curves of **5BDTBDD** and **3BDTBDD** in chloroform solution. Similar reversible redox processes are presented for both molecules. The calculated electrochemical data are listed in Table 1. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels (E_{HOMO} / E_{LUMO}) are calculated to be -5.46 eV /-3.51 eV for **5BDTBDD** and -5.50 eV/ -3.38 eV for **3BDTBDD** by empirical

equation [46]. It is found that the inserting D-A repeat unit plays an important role in decreasing the E_{LUMO} value. In comparison with the energy levels of photovoltaic materials used in photoactive layer depicted in Figure 3(a), this decreasing E_{LUMO} value for **5BDTBDD** oligomer can diminish the LUMO energy level difference between **5BDTBDD** donor and **ITIC** acceptor and further promote excition separation in photoactive layer. Therefore, **5BDTBDD** oligomer should exhibit better photovoltaic properties than **3BDTBDD** in the ITIC-based OSCs [47].



Figure 3. (a) Energy levels of 5BDTBDD, 3BDTBDD and ITIC and (b) the device structure.

3.3. Theoretical Calculations

The molecular geometries and frontier orbitals of **5BDTBDD** and **3BDTBDD** were theoretically simulated with the hybrid density functional theory (DFT) at the B3LYP/6-31G* level using Gaussian 09W program. In order to simplify calculation, long alkyl chains were replaced by methyl. Figure 4 shows the simulated electrostatic potential distribution of the electron-donating (D) unit of BDT and the electron-accepting (A) unit of BDD, as well as their **5BDTBDD** oligomer and **3BDTBDD** small molecule. It is observed that the dipole moment of BDT is 0.0002 D, which is significantly smaller than that of BDD (1.1341 D). Therefore, while inserting D-A repeat unit on **3BDTBDD**, the resulting **5BDTBDD** oligomer

should have an increasing proportion of A unit and molecular dipole moment. It implies that **5BDTBDD** oligomer has stronger intermolecular effect than **3BDTBDD** small molecule. Here, lower electrostatic potential observed for **5BDTBDD** oligomer than **3BDTBDD** small molecule is consistent with the intermolecular effect.



Figure 4. Electrostatic potentials of BDT, BDD, 5BDTBDD and 3BDTBDD.

The optimal geometries (front and side view) and wave functions (HOMO and LUMO) of **5BDTBDD** and **3BDTBDD** are shown in Figure 5. It is found that the electron densities of LUMO are most localized on the central electron-deficient BDD unit for **3BDTBDD**, but on the central backbone of two BDD and one BDT units for the **5BDTBDD**. It implies that the **5BDTBDD** oligomer is in favor of intramolecular charge transfer. However, the electron densities of HOMO are distributed across the molecular backbone for **5BDTBDD** and **3BDTBDD**. Based on the dihedral angles of the optimal geometries of **5BDTBDD** and **3BDTBDD** in Figure 5(a), it is further found that both molecular backbones of **5BDTBDD** and **3BDTBDD** have good planarity, which is favorable for their π - π stacking. And the backbone planarization of **5BDTBDD** is more available for the HOMO-LUMO wave



function overlap to yield a higher extinction coefficient [13]. As a result, **5BDTBDD** exhibits more intense absorption than **3BDTBDD**.

Figure 5. Optimized geometries of the (a) front and (b) side views. Electron densities of (c) LUMO and (d) HOMO for **3BDTBDD** and **5BDTBDD** calculated by Gaussian at the B3LYP/6-31G* level.

3.4. Photovoltaic Properties

The organic solar cells were fabricated using **ITIC** as acceptor and **5BDTBDD** or **3BDTBDD** as donor in active layer. The device structure is Glass/ITO/ZnO/active layer /MoO₃/Ag, as shown in Figure 3(b). In these cells, 1,8-diiodoctane (DIO) was used as an additive at various concentrations from 0.1 wt% to 0.3 wt%. The measured photovoltaic

parameters are summarized in Table S1 and S2 under an illumination of AM 1.5G simulated solar light at 100 mW/cm². It is found that the optimal donor/acceptor weight ratio and DIO concentration are respectively 1:0.8 and 0.2 wt%. Figure 6(a) depicts the current density-voltage (J–V) curves of the cells at the optimal processing conditions and Table 2 summarizes the corresponding photovoltaic parameters. The maximum PCE value of 7.89% with a short-circuit current density (J_{sc}) of 13.23 mAcm² is observed in the **5BDTBDD:ITIC** cells. Here, the PCE and J_{sc} are 1.8 and 1.4 times higher than those corresponding values in the **3BDTBDD:ITIC** cells, respectively. Higher J_s value for the **5BDTBDD:ITIC** cells is consistent with the wider UV-Vis absorption spectrum for the **5BDTBDD** oligomer. It is noted that the **PBDB-T:ITIC**-based devices exhibit a decreasing PCE of 7.14% under the same processing conditions. It indicates that oligomers have great potential as photovoltaic materials.

The *EQE* spectra of the optimal cells are depicted in Figure 6(b). The maximum *EQE* values of 65% and 47% are observed for the **5BDTBDD**:**ITIC** and **3BDTBDD**:**ITIC** blend films, respectively. The broader photo-response region from 350 nm to 750 nm and higher *EQE* value indicate that **5BDTBDD** oligomer has more efficient photo-response than **3BDTBDD** small molecule in their **ITIC** blend films. As a result, it can further facilitate **5BDTBDD** exhibit higher J_{sc} values in their cells.



Figure 6. (a) J - V curves of the **5BDTBDD:ITIC**, **3BDTBDD:ITIC** and **PBDB-T:ITIC** cells under a simulated AM 1.5 G irradiation (100 mW cm⁻²) and (b) *EQE* curves of **5BDTBDD:ITIC**, **3BDTBDD:ITIC** and **PBDB-T:ITIC** cells.

Table 2. Photovoltaic parameters of the 5BDTBDD:ITIC, 3BDTBDD:ITIC and PBDB-
T:ITIC cells.

Donor	V _{oc} (V)	$\frac{J_{\rm sc}^{a}}{(\rm mA~cm^{-2})}$	$J_{\rm sc}^{\rm b}$ (mA cm ⁻²)	FF (%)	PCE _{max} ^c (%)	$PCE_{(ave)}^{c}$ (%)
3BDTBDD	0.90	9.51	9.38	50.6	4.33	4.02
5BDTBDD	0.91	13.23	13.15	65.6	7.89	7.66
PBDB-T	0.91	14.66	13.96	53.5	7.14	7.00

^a J_{sc} measured from solar cells. ^b J_{sc} estimated from *EQE* spectra. ^c PCE obtained from 20 cells, at 0.2% DIO additive.

Figure 7(a) shows the photoluminescence (PL) spectra of the **ITIC** neat film and blend films with **5BDTBDD** or **3BDTBDD**. An intense emission peaked at 680 nm is observed in the **ITIC** neat film. However, its emission is quickly quenched by adding **5BDTBDD** and **3BDTBDD** with a quenching efficiency of 95.0% and 66.5%, respectively. It indicates that the exciton is transferred and separated more efficiently from the **ITIC** to the **5BDTBDD** donor. This can make the **5BDTBDD**:**ITIC** cells have an increasing J_{sc} .

The characteristics of exciton dissociation, charge collection, and charge recombination also support the result of higher *FF* and J_{sc} values for the **5BDTBDD:ITIC** cells, which are

measured by the characteristics of photocurrent density (J_{ph}) versus effective voltage (V_{eff}) and the dependence of J_{sc} on light intensity (P_{light}) [48]. Figure 7(b) shows the curves of J_{ph} versus V_{eff} for the optimized **5BDTBDD:ITIC** and **3BDTBDD:ITIC** cells. It is found that both devices exhibit a saturated photocurrent density (J_{sat}) at ~2 V, suggesting that charge recombination in both cells is minimized at higher voltage due to the high internal electric field. The $J_{ph'}/J_{sat}$ ratio is up to 0.93 for the **5BDTBDD:ITIC** cells under short-circuit conditions, which is higher than that value of 0.85 for the **3BDTBDD:ITIC** cells. Therefore, the **5BDTBDD:ITIC** cells should possess more efficient exciton dissociation and charge collection than the **3BDTBDD:ITIC** cells.



Figure 7. (a) Photoluminescent spectra of the neat and blend films excited at 680 nm, (b)The curves of $J_{\rm ph}$ versus $V_{\rm eff}$ in the optimized **5BDTBDD:ITIC** and **3BDTBDD:ITIC** cells, (c)

The dependence of P_{light} on V_{oc} of the **5BDTBDD**:**ITIC** and **3BDTBDD**:**ITIC** cells, (d) The dependence of P_{light} on J_{sc} of the **5BDTBDD**:**ITIC** and **3BDTBDD**: **ITIC** cells .

Figure 7(c) shows the characteristics of V_{oc} versus P_{light} of the optimized cells. For trapassisted recombination system, it is suggested that the slope of V_{oc} versus $log(P_{light})$ is close to 2kBT/q, here, kB is Boltzmann's constant, T is temperature and q is the elementary charge [49]. It is found that the optimal **5BDTBDD:ITIC** cell shows a lower slope of 1.31 than the **3BDTBDD:ITIC** cell (*kBT/q* = 1.651). Hence, there is a weaker trap-assisted recombination in the **5BDTBDD:ITIC** cells. In general, more compact π - π stacking could reduce the intermolecular interfacial trap densities in the active layer and thus suppressed trap-assisted recombination [50]. Therefore, **5BDTBDD** oligomer with an enhanced π - π stacking exhibits a weaker trap-assisted recombination than **3BDTBDD** small molecule, which is also one of key factors for the **5BDTBDD:ITIC** cells to obtain higher J_{sc} value.

To better probe the charge recombination behavior in the devices, the light-intensity (P_{light}) dependence of J_{sc} was also measured. Figure 7(d) shows the curves of P_{light} versus J_{sc} of the optimal **5BDTBDD:ITIC** and **3BDTBDD:ITIC** cells. It is suggested that the relationship of J_{sc} and P_{light} is usually represented by the power-law equation of $J_{sc} \propto P_{\text{light}}^{\alpha}$, in which the power-law exponent α refers to the extent of bimolecular recombination [51]. In comparison with α values of 0.94 for the optimal **5BDTBDD:ITIC** cell and 0.85 for the optimal **3BDTBDD:ITIC** cell, less bimolecular recombination should occur in the optimal **5BDTBDD:ITIC** cell, which is available to result in high J_{sc} and FF values for this solar cell [48].

3.5. Morphology and Charge Transport

Journal Pre-proof

Figure 8 shows the morphology of the active layers measured by atomic force microscopy (AFM) using the trapping mode. A better-distributed nano-fibrillar interpenetrating network is observed for the **5BDTBDD:ITIC** blend film. The measured root-mean-square (RMS) roughness is 0.87 nm for the **3BDTBDD:ITIC** blend film and 1.23 nm for the **5BDTBDD**: **ITIC** blend film. Here, the enhenced packing and aggregation properties of **5BDTBDD** are responsible for the slightly increasing RMS roughness of the **5BDTBDD:ITIC** blend film. In general, well-distributed interpenetrating network with appropriate domain size is very crucial for exciton separation and transportion [24]. Under this morphology, the **5BDTBDD:ITIC** cells exhibit some increase of J_{sc} and FF values.



Figure 8. AFM height images and tapping phases for the **3BDTBDD:ITIC** blend film (a, c) and for the **5BDTBDD:ITIC** blend film (c, d).

The charge transport properties of both active layers were measured by the space-charge limited current (SCLC) method. The hole-only device with a structure of Glass/ITO/ PEDOT: PSS/active layer/ MoO₃ /Au and the electron-only device with a structure of Glass/Al/active layer/Al were made for this purpose. Figure 9 shows the $J^{1/2}$ -V characteristics of these hole-only and electron-only cells. The detail results are summarized in Table 3. A hole mobility (μ_h) of 1.12×10^{-4} cm⁻² V⁻¹ s⁻¹ and an electron mobility (μ_e) of 8.93×10^{-5} cm⁻² V⁻¹ s⁻¹ are obtained with a μ_h/μ_e ratio of 1.25 for the **5BDTBDD:ITIC** cells. The μ_h and μ_e values are 6.5 and 2.3 times higher than the corresponding values for the **3BDTBDD:ITIC** cells with a μ_h/μ_e ratio of 0.45. It indicates that simply embedding a D-A repeat unit into the D-A-D type SM is available for the resulting oligomer to obtain better charge transport properties. The increasing μ_h and μ_e values, as well as the matched μ_h/μ_e ratio are in favour of the **5BDTBDD:ITIC** cells to improve *FF* and PCE values [28].



Figure 9. (a) $J^{1/2}$ -V characteristics of the hole-only devices (a) and the electron-only devices (b) based on **5BDTBDD**:**ITIC** and **3BDTBDD**:**ITIC**.

Active layer	$(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$(\text{cm}^2 \text{V}^{-1} \text{s}^{-1})$	$\mu_{ m h}/\mu_{ m e}$
3BDTBDD:ITIC	1.73×10 ⁻⁵	3.84×10 ⁻⁵	0.45
5BDTBDD:ITIC	1.12×10^{-4}	8.93×10 ⁻⁵	1.25

Table 3. Hole and electron mobilities of the cells based on **5BDTBDD:ITIC** and**3BDTBDD: ITIC** blend films under optimal conditions

4. Conclusion

A D-A-D-A-D type oligomer of **5BDTBDD** and a D-A-D type SM of **3BDTBDD** were primarily obtained using BDD as electron-accepting (A) unit. It is found that the structure evolution from D-A-D type SM toward D-A-D-A-D type oligomer plays an important effect on crystallinity, absorption, mobility, morphology and photovoltaic properties of photovoltaic donor materials. By inserted the D-A repeat unit into **3BDTBDD** small molecule, **5BDTBDD** oligomer exhibits more intense absorption with a red-shifted absorption spectrum, higher carrier mobility, stronger crystallization, and more ordered molecular packing than **3BDTBDD** small molecule. As a result, the **5BDTBDD**:**ITIC** cells present a significantly increasing PCE of 7.89 %, which is 1.8 times higher than that of the **3BDTBDD**:**ITIC** cells. Our work provides an effective strategy to improve photovoltaic properties of donor materials by simply inserting a D-A repeat unit in D-A-D type SM to get D-A-D-A-D type oligomers.

Conflict of Interest

The authors declare no competing financial interest.

Supporting Information.

The characterization and measurement, ¹H, ¹³C NMR spectra and time-of-flight (MALDI-TOF) analyzer data, TGA, DSC and CV measurement, fabrication and characterization of the solar cells and the detail *J-V* curves of the solar cells at different processing conditions.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (51673031, 51573154, 51573107, 91633301 and 21432005), the Major Program of the Natural Science Research of Jiangsu Higher Education Institutions (18KJA480001), the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Jiangsu Provincial Talents Project of High-Level Innovation and Entrepreneurship, the Research Innovation Program for Postgraduate of Jiangsu Province (KYCX19_1751).

Journal Press

References

- [1] Li Y, Acc. Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption. Chem Res 2012;45:723–733.
- [2] Lin Y, Li Y, Zhan X. Small molecule semiconductors for high-efficiency organic photovoltaics. Chem Soc Rev 2012;41:4245-72.
- [3] Yao H, Ye L, Zhang H, Li S, Zhang S, Hou J. Molecular design of benzodithiophenebased organic photovoltaic materials. Chem Rev 2016;116:7397-457.
- [4] Cheng P, Li G, Zhan X, Yang Y. Next-generation organic photovoltaics based on nonfullerene acceptors. Nat Photon 2018;12:131-142.
- [5] Xu X, Feng K, Bi Z, Ma W, Zhang G, Peng Q. Single-junction polymer solar cells with 16.35% efficiency enabled by a platinum(ii) complexation strategy. Adv Mater 2019;31:1901872.
- [6] Cui Y, Yao H, Zhang J, Zhang T, Wang Y, Hong L, Xian K, Xu B, Zhang S, Peng J, Wei Z, Gao F, Hou J. Over 16% efficiency organic photovoltaic cells enabled by a chlorinated acceptor with increased open-circuit voltages. Nat Commun 2019;10:2515.
- [7] Liu Q, Jiang Y, Jin K, Qin J, Xu J, Li W, Xiong J, Liu J, Xiao Z, Sun K, Yang S, Zhang X, Ding L. 18% Efficiency organic solar cells. Science Bulletin 2020;65:272-275.
- [8] Zhou R, Jiang Z, Yang C, Yu J, Feng J, Adil M A, Deng D, Zou W, Zhang J, Lu K, Ma W, Gao F, Wei Z. All-small-molecule organic solar cells with over 14% efficiency by optimizing hierarchical morphologies. Nat Commun 2019;10:5393.
- [9] Gao J, Ge J, Peng R, Liu C, Cao L, Zhang D, Fanady B, Hong L, Zhou E, Ge Z. Over 14% efficiency nonfullerene all-small-molecule organic solar cells enabled by improving the ordering of molecular donors via side-chain engineering. J Mater Chem A

2020;8:7405-7411.

- [10]Collins S D, Ran N A, Heiber M C, Nguyen T-Q. Small is powerful: recent progress in solution-processed small molecule solar cells. Adv Energy Mater 2017;7:1602242.
- [11]Roncali J, Leriche P, Blanchard P. Molecular materials for organic photovoltaics: small is beautiful. Adv Mater 2014;26:3821-38.
- [12]Li M, Qiu Z, Zhang G, Liu Y, Xiong L, Bai D, Zhu M, Peng Q, Zhu W. Efficient chemical structure and device engineering for achieving difluorinated 2,2'-bithiophenebased small molecular organic solar cells with 9.0% efficiency. J Mater Chem A 2018;6:12493-12505.
- [13]Gu Z, Guo J, Hao R, Lin Z, Qian Y, Ma C, Fan Y, Deng X, Zhang G, Peng W, Xia H, Peng Q, Zhu W. An efficient strategy to supervise absorption, mobility, morphology of photovoltaic molecule by inserting a D-A unit. Dyes and Pigments 2019;166:515-522.
- [14] Yuan L, Zhao Y, Zhang J, Zhang Y, Zhu L, Lu K, Yan W, Wei Z. Oligomeric donor material for high-efficiency organic solar cells: breaking down a polymer. Adv Mater 2015;27:4229-33.
- [15]Li W, Wang D, Wang S, Ma W, Hedstrom S, James D I, Xu X, Persson P, Fabiano S, Berggren M, Inganas O, Huang F, Wang E. One-step synthesis of precursor oligomers for organic photovoltaics: a comparative study between polymers and small molecules. ACS Appl Mater Interfaces 2015;7:27106-14.
- [16] Wang J L, Liu K K, Yan J, Wu Z, Liu F, Xiao F, Chang Z F, Wu H B, Cao Y, Russell T P. Series of Multifluorine substituted oligomers for organic solar cells with efficiency over 9% and fill factor of 0.77 by combination thermal and solvent vapor annealing. J Am Chem Soc 2016;138:7687-97.

- [17] Yuan L, Lu K, Xia B, Zhang J, Wang Z, Wang Z, Deng D, Fang J, Zhu L, Wei Z. Acceptor end-capped oligomeric conjugated molecules with broadened absorption and enhanced extinction coefficients for high-efficiency organic solar cells. Adv Mater 2016;28:5980-5.
- [18]Nitti A, Signorile M, Boiocchi M, Bianchi G, Po R, Pasini D. Conjugated thiophenefused isatin dyes through intramolecular direct arylation. J Org Chem 2016;81:11035-11042.
- [19]Nitti A, Bianchi G, Po R, Swager T M, Pasini D. Domino direct arylation and cross-aldol for rapid construction of extended polycyclic π -scaffolds. J Am Chem Soc 2017;139: 8788-8791.
- [20]Nitti A, Osw P, Calcagno G, Botta C, Etkind S I, Bianchi G, Po R, Swager T M, Pasini D. One-pot regiodirected annulations for the rapid synthesis of π -extended oligomers. Org Lett 2020;22:3263-3267.
- [21]Osw P, Nitti A, Abdullah M N, Etkind S I, Mwaura J, Galbiati A, Pasini D. Synthesis and evaluation of scalable D-A-D π -extended oligomers as p-type organic materials for bulkheterojunction solar cells. Polymers 2020;12:720.
- [22]Zhao W, Qian D, Zhang S, Li S, Inganas O, Gao F, Hou J. Fullerene-free polymer solar cells with over 11% efficiency and excellent thermal stability. Adv Mater 2016;28:4734-9.
- [23]Zhang S, Qin Y, Zhu J, Hou J. Over 14% efficiency in polymer solar cells enabled by a chlorinated polymer donor. Adv Mater 2018;30:1800868.
- [24]Zhou Z, Xu S, Song J, Jin Y, Yue Q, Qian Y, Liu F, Zhang F, Zhu X. High-efficiency small-molecule ternary solar cells with a hierarchical morphology enabled by synergizing

fullerene and non-fullerene acceptors. Nat Energy 2018;3:952-959.

- [25]Peng W, Zhang G, Zhu M, Xia H, Zhang Y, Tan H, Liu Y, Chi W, Peng Q, Zhu W. Simple-structured NIR-Absorbing small-molecule acceptors with a Thiazolothiazole core: multiple noncovalent conformational locks and D-A effect for efficient OSCs. ACS Appl Mater Interfaces 2019;11:48128-48133.
- [26] Yuan J, Zhang Y, Zhou L, Zhang G, Yip H-L, Lau T-K, Lu X, Zhu C, Peng H, Johnson P A, Leclerc M, Cao Y, Ulanski J, Li Y, Zou Y. Single-junction organic solar cell with over 15% efficiency using fused-ring acceptor with electron-deficient core. Joule 2019;3:1140-1151.
- [27] Yan T, Song W, Huang J, Peng R, Huang L, Ge Z. 16.67% rigid and 14.06% flexible organic solar cells enabled by ternary heterojunction strategy. Adv Mater 2019;31:1902210.
- [28] Wu Y, Zheng Y, Yang H, Sun C, Dong Y, Cui C, Yan H, Li Y. Rationally pairing photoactive materials for high-performance polymer solar cells with efficiency of 16.53%. Sci China Chem 2019.
- [29]Peng W, Zhang G, Shao L, Ma C, Zhang B, Chi W, Peng Q, Zhu W. Simple-structured small molecule acceptors constructed by a weakly electron-deficient thiazolothiazole core for high-efficiency non-fullerene organic solar cells. J Mater Chem A 2018;6:24267-24276.
- [30] Tan H, Zheng X, Zhu J, Yu J, Zhu W. An A–D–D–A-type non-fullerene small-molecule acceptor with strong near-infrared absorption for high performance polymer solar cells. J Mater Chem C 2019;7:13301-13306.
- [31] Yue Q, Liu W, Zhu X. n-type molecular photovoltaic materials: design strategies and

device applications. J Am Chem Soc 2020.

- [32] Wu Q, Zhao D, Schneider A M, Chen W, Yu L. Covalently bound clusters of alphasubstituted pdi-rival electron acceptors to fullerene for organic solar cells. J Am Chem Soc 2016;138:7248-51.
- [33]Gao K, Li L, Lai T, Xiao L, Huang Y, Huang F, Peng J, Cao Y, Liu F, Russell T P, Janssen R A, Peng X. Deep absorbing porphyrin small molecule for high-performance organic solar cells with very low energy losses. J Am Chem Soc 2015;137:7282-5.
- [34] Tang A, Zhan C, Yao J, Zhou E. Design of diketopyrrolopyrrole (DPP)-based small molecules for organic-solar-cell applications. Adv Mater 2017;29.
- [35]Hwang Y J, Earmme T, Courtright B A, Eberle F N, Jenekhe S A. n-Type semiconducting naphthalene diimide-perylene diimide copolymers: controlling crystallinity, blend morphology, and compatibility toward high-performance all-polymer solar cells. J Am Chem Soc 2015;137:4424-34.
- [36] Tan H, Long Y, Zhang J, Zhu J, Yang J, Yu J, Zhu W. Spirobifluorene-cored wide bandgap non-fullerene small molecular acceptor with 3D structure for organic solar cells. Dyes and Pigments 2019;162:797-801.
- [37] Yao H, Cui Y, Yu R, Gao B, Zhang H, Hou J. Design, synthesis, and photovoltaic characterization of a small molecular acceptor with an ultra-narrow band gap. Angew Chem Int Ed 2017;56:3045-3049.
- [38]Zhang H, Li S, Xu B, Yao H, Yang B, Hou J. Fullerene-free polymer solar cell based on a polythiophene derivative with an unprecedented energy loss of less than 0.5 eV. J Mater Chem A 2016;4:18043-18049.
- [39] Baran D, Kirchartz T, Wheeler S, Dimitrov S, Abdelsamie M, Gorman J, Ashraf R S,

Holliday S, Wadsworth A, Gasparini N, Kaienburg P, Yan H, Amassian A, Brabec C J, Durrant J R, McCulloch I. Reduced voltage losses yield 10% efficient fullerene free organic solar cells with >1 V open circuit voltages. Energy Environ Sci 2016;9:3783-3793.

- [40]Li S, Ye L, Zhao W, Zhang S, Mukherjee S, Ade H, Hou J. Energy-level modulation of small-molecule electron acceptors to achieve over 12% efficiency in polymer solar cells. Adv Mater 2016;28:9423-9429.
- [41]Cui Y, Yao H, Gao B, Qin Y, Zhang S, Yang B, He C, Xu B, Hou J. Fine-tuned photoactive and interconnection layers for achieving over 13% efficiency in a fullerenefree tandem organic solar cell. J Am Chem Soc 2017;139:7302-7309.
- [42]Zhao W, Li S, Zhang S, Liu X, Hou J. Ternary polymer solar cells based on two acceptors and one donor for achieving 12.2% efficiency. Adv Mater 2017;29.
- [43]Qian D, Ye L, Zhang M, Liang Y, Li L, Huang Y, Guo X, Zhang S, Tan Z a, Hou J. Design, application, and morphology study of a new photovoltaic polymer with strong aggregation in solution state. Macromolecules 2012;45:9611-9617.
- [44] Warnan J, El Labban A, Cabanetos C, Hoke E T, Shukla P K, Risko C, Brédas J-L, McGehee M D, Beaujuge P M. Ring substituents mediate the morphology of PBDTTPD-PCBM bulk-heterojunction solar cells. Chem. Mater. 2014;26:2299-2306.
- [45] Anthony J. Functionalized acenes and heteroacenes for organic electronics. Chem Rev 2006;106:5028-5048.
- [46] Wang R, Yuan J, Wang R, Han G, Huang T, Huang W, Xue J, Wang H C, Zhang C, Zhu C, Cheng P, Meng D, Yi Y, Wei K H, Zou Y, Yang Y. Rational tuning of molecular interaction and energy level alignment enables high-performance organic photovoltaics.

Adv Mater 2019;31:1904215.

- [47]Scharber M C, Mühlbacher D, Koppe M, Denk P, Waldauf C, Heeger A J, Brabec C J. Design rules for donors in bulk-heterojunction solar cells-towards 10% energyconversion efficiency. Advanced Materials 2006;18:789-794.
- [48]Blom P W M, Mihailetchi V D, Koster L J A, Markov D E. Device physics of polymer:fullerene bulk heterojunction solar cells. Adv Mater 2007;19:1551-1566.
- [49]Koster L J A, Mihailetchi V D, Ramaker R, Blom P W M. Light intensity dependence of open-circuit voltage of polymer:fullerene solar cells. Appl Phys Lett 2005;86:123509.
- [50]Nian L, Gao K, Jiang Y, Rong Q, Hu X, Yuan D, Liu F, Peng X, Russell T P, Zhou G. Small-molecule solar cells with simultaneously enhanced short-circuit current and fill factor to achieve 11% efficiency. Adv Mater 2017;29.
- [51]Riedel I, Parisi J, Dyakonov V, Lutsen L, Vanderzande D, Hummelen J C. Effect of temperature and illumination on the electrical characteristics of polymer–fullerene bulkheterojunction solar cells. Advanced Functional Materials 2004;14:38-44.

Research Highlights

- A D-A-D-A-D type oligomer of 5BDTBDD and its D-A-D type small molecule \triangleright of 3BDTBDD were synthesized.
- \triangleright The crystalline, absorption, mobility and photovoltaic properties were primarily investigated.
- \triangleright 5BDTBDD shows better photovoltaic properties than 3BDTBDD in the ITIC based organic solar cells.
- The PCE in the 5BDTBDD-based cell is 1.8 times higher than that in the \triangleright 3BDTBDD-based cell.

times h

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.