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Solution-processable tetrazine and oligothiophene based linear A–D–A small molecules: Synthesis, hierarchical structure and photovoltaic properties

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ABSTRACT

A series of high coplanar alternative linear small molecules with acceptor-donor-acceptor (A-D-A) structure containing electron-accepting tetrazine (Tz) moiety and electron-donating oligothiophenes (OTs) moiety, alkylated thiophene attached to both sides of the Tz moiety were designed and synthesized. The influences of varied oligothiophene length on small molecules' optical and electrochemical properties, crystallization, self assembling morphology in blend film with (6,6)-phenyl- C_{61} -butyric acid methyl ester ($PC_{61}BM$), and photovoltaic properties for the application as donor materials in organic solar cells (OSCs) were studied. The optical and electrochemical properties of small molecules showed that the HOMO and LUMO energy levels were determined by the number of OTs moiety and electron-accepting ability of Tz in the alternative small molecules, respectively. Meanwhile, the varied OT moieties can significantly affect the hierarchical structures when mixed with PC₆₁BM. The molecule with intermediate conjugate moity length showed the highest ordering in its crystalline state, as revealed by differential scanning calorimetry (DSC) and X-ray diffraction experiments, and best photovoltaic properties when blended together with PC₆₁BM or (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) as active layer in photovoltaic devices. The results indicate that hierarchical structures controlled by adjusting the conjugate moity length of small molecules is an effective way to improve the performance of OSCs. The photovoltaic device based on TT(HTTzHT)₂:PC₇₁BM with 1% DIO additives showed the best performance, with a I_{sc} of 7.87 mA/cm² and a PCE of 3.24%. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, small molecules (SMs) for bulk-heterojunction (BHJ) organic solar cells (OSCs) have attracted more and more attention for photovoltaic applications due to their high purity, solution processability, well-defined molecular structures and definite molecular weight [1–4]. They do not suffer from batch-to-batch variations, difficulty of purification, and broad molecular weight distribution problems as their polymer counterparts. Their band structures could be tuned easily with much more choices of chemical modification, and generally have higher charge mobility and open voltages [5–6]. However, even with these advantages, SM-based OSCs have not been investigated intensively due to their generally poor film quality compared with their polymer counterparts when using the simple solution spinning process [7]. Until recently, profound progress has been achieved in the synthesis of new solution processable SMs and the corresponding photovoltaic applications, such as donor–acceptor (D–A) molecules [8–10], oligothiophenes [11–13], star-shaped molecules [3,14], and organic dyes [4]. To date, the highest





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published PCEs for solution-processed SM based BHJ OSCs is more than 7% by carefully molecular designing to control the hierarchical structures like crystallization and nanoscale phase separation morphology [15–17]. It is thus expected that better PCE could be achieved if the intrinsic poor film quality and hierarchical structures in BHJ architecture could be improved. In order to achieve this, careful molecule design has to be carried out to address many factors simultaneously, including the materials solar light absorption associated with its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) positions, crystallization of donor materials and its morphology compatibility with the acceptors, and so on.

Donor-Acceptor (D-A) chromophores involving electron-donating and electron-accepting moieties have been widely investigated for OSCs molecules [18]. Well-chosen donor and acceptor groups are particularly desirable for low band-gap materials due to a significant enhancement of the ICT intensity and conjugated length, which lead to a better extended absorption and higher absorption coefficient [19]. Recently, the acceptor-donor-acceptor (A-D-A) molecules, which is a type of D-A structure molecule, have caused more and more interests due to their outstanding photovoltaic performance [17,20-22]. The A-D-A molecules have demonstrated some advantages. First, they have 6-10 effective conjugated units and two electron-accepting moieties, resulting in high conjugated length and hence similar solar cell absorption to that for the corresponding polymers. Furthermore, the HOMO and LUMO energy levels can also be tuned through designing different central donor moiety and two conjugated electron-accepting moiety on both sides [23]. Third, the central donor moiety based on varied conjugated backbone generally could offer a high mobility, crystallization and improved miscibility between donor and acceptor materials, which can contribute to formation of good film quality with high ordered structure using spin-coating method [24]. It is thus expected that great improvement could be made to the photovoltaic performance for SM with A-D-A structure through delicate chemical structure design and modification.

Oligothiophenes (OTs) have attracted comprehensive interest and been advanced to the most frequently used π -conjugated materials, in particular, as active components in organic optoelectronic devices, such as organic field effect transistors [25,26] and solar cells [2,27]. This is due to their intriguing electronic, optical, and electrochemical properties of OTs and the high coplanarity of thiophene rings lead to a better π - π interaction and excellent charge transport properties, which is one of the most crucial assets for applications in organic electronics. Moreover, the OTs, which are not alkylated, can increase the conjugated length, π - π stacking, and assure the coplanarity of the molecules [28]. In addition, one-dimensional OTs with pull-push structure exhibited promising OSCs performance. For example, OTs with electron-accepting end groups yielded very high PCEs up to 6.1% when blending with PC₆₁BM [17]. Because low dimensional oligomer is molecular and crystal orientation, especially the OTs based materials with high crystallization, which can result in a

ordered structure and continuous carrier transport channel even in composite form. On the other hand, tetrazine (Tz) has a very high electron affinity, and would behave as a strong electron-deficient unit in a conjugated molecule to lower its HOMO level [29]. Tetrazines have a rare and useful physical chemistry characteristic directing several types of applications in various domains. Audebert et al. have reported some donor-acceptor-donor s-tetrazines deriatives possessing excellent fluorescence [30,31].When incorporated into D-A conjugated materials, both HOMO and LUMO levels of Tz based materials are generally lower than other acceptor moiety-based materials, indicating a stronger electron affinity of the Tz moiety. Interestingly, the Tz moiety shows more impact on HOMO levels than on LUMO levels, which is different from most acceptor units [32]. This results in slightly broader band gaps of Tz based materials when compared with other acceptor moiety based materials. Thus, introducing the electron-accepting Tz moiety and low dimensional OTs into A-D-A structure SM may produce surprising and superb results in BHJ OSCs.

Based on the above idea, a series of high coplanar linear SMs with A-D-A structure were designed and synthesized consisting of OTs with unalkylated as central donor moiety, Tz moiety as acceptor on both sides and alkylated thiophene as bridge between oligothiophene and Tz moieties. As expected, these linear OTh based SMs with A-D-A structure show relatively low band gap and high efficient sunlight harvesting, owing to their high π conjugated backbone. To understand the relationship between structure and properties, the crystallization, self-assembling morphology and the photovoltaic properties of the SMs with different thiophene unit number as building block of donor part were studied and compared. OSCs were fabricated using these SMs as donor and PC₆₁BM or PC₇₁BM as the acceptor. A PCE of 3.24% was achieved with a V_{oc} of 0.86 V, J_{sc} of 7.87 mA/cm² and a FF of 0.48 for TT(HTTzHT)₂.

2. Experimental section

2.1. Materials and synthesis

2,5-bis(trimethylstannyl)thiophene (**5**), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (**7**) and 5,5"-bis(trimethylstannyl)-2,2':5',2"-terthiophene (**9**) were synthesized according to Li et al. reported [13,28]. All reagents and chemicals were purchased from commercial sources (Aldrich, Across, Fluka) and used without further purification unless stated otherwise. Toluene, tetrahydrofuran (THF), and Et₂O were distilled over Na/benzophenone. N,N-dimethylformamide (DMF) was purified by heating over CaH₂ followed by vacuum distillation.

4-hexylthiophene-2-carbaldehyde (1) 3-hexylthiophene 10 g (59.5 mmol) and 100 mL THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 °C by a liquid nitrogen-acetone bath, and 40.9 mL of *n*-butyllithium (65.4 mmol, 1.6 M in *n*-hexane) was added dropwise. After being stirred at -78 °C for 2 h, a great deal of white solid precipitates appeared in the flask. DMF 5.73 g (78.4 mmol) was added in one portion,

and the reactant turned to clear rapidly. The cooling bath was removed, and the reactant was stirred at ambient temperature for 24 h. Then, it was poured into 200 mL of cool water and extracted by ether three times. The organic layer was washed by water two times and then dried by anhydrous MgSO₄. After removing solvent under vacuum, the residue was purified with column chromatography (EtOAc/petroleum ether = 1/8 v/v) to give yellow liquid 9.68 g (49.3 mmol, yield 83%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.95 (s, 1H), 7.51 (d, 1H, *J* = 1.4 Hz), 7.19 (d, 1H, *J* = 1.4 Hz), 2.66 (t, 2H, *J* = 8.0 Hz), 1.62 (m, 2H), 1.28 (m, 6H), 0.88 (m, 3H).

4-hexylthiophene-2-carbonitrile (2) A mixture solution of 4-hexylthiophene-2-carbaldehyde (5.9 g, 30.0 mmol) and hydroxylamine hydrochloride salt (3.15 g, 45 mmol) in pyridine/ethanol (20 mL, 1/1 v/v) was stirred at 80 °C overnight. Then the solvent was removed using a rotary evaporator. The residue was dissolved in chloroform, and the solution was washed with distilled water and dried over anhydrous MgSO₄. The solvent was removed under vacuum, and the viscous liquid residue was dissolved in acetic anhydride containing potassium acetate (0.1 g) and then refluxed for 3 h. The mixture was poured into distilled water and extracted with hexane. The organic phase was washed with 5% aqueous sodium hydroxide solution and then water, dried over anhydrous MgSO₄ before the solvent was removed by a rotate evaporator. The yellow liquid residue was purified by silica-gel column chromatograph (EtOAc/petroleum ether = 1/10, v/v) to yield a clear light yellow liquid product. (5.1 g, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.41 (d, 1H, I = 1.4 Hz), 7.15 (d, 1H, J = 1.4 Hz), 2.62 (t, 2H, J = 8.0 Hz), 1.60 (m, 2H), 1.28 (m, 6H), 0.88 (m, 3H).

3,6-bis(4-hexyl-2-thienyl)-1,2,4,5-tetrazine (3) To a mixture of compound 2 (5.0 g, 25.9 mmol) and sulfur (0.576 g, 18.2 mmol) in anhydrous ethanol (2 mL) was slowly added fresh hydrazine monohydrate (3.91 g, 77.6 mmol) at room temperature. The solution turned into vellow and large amount of gas evolved. The solution was heated up to reflux for 2 h. Then it was cooled down to room temperature with crystal formed in solution. The crystal was collected by filtration and rinsed with cold ethanol before dried under vacuum. To a chloroform solution of the obtained solid, isoamylnitrite (6.06 g, 51.7 mmol) was added and the solution was stirred at room temperature overnight. The solvent was removed and the resulting red solid was washed with methanol twice before purified by silica-gel column chromatography (CHCl₃/Petroleum ether = 1/2, v/v) to yield red needle-like crystal (0.51 g, yield: 58%). ¹H NMR(400 MHz, CDCl₃): δ (ppm) 8.10 (s, 2H), 7.29 (s, 2H), 2.69 (t, 4H, J = 7.8 Hz), 1.67 (m, 4H), 1.35 (m, 12H), 0.89 (m, 6H).

3-(5-bromo-4-hexyl-2-thienyl)-1,2,4,5-tetrazine **(4).** To a suspension solution of compound **3** (0.75 g, 1.8 mmol) in chloroform (20 mL) and acetic acid (20 mL) was added N-Bromosuccinimide (NBS, 0.32 g, 1.8 mmol) at room temperature. The mixture was stirred at room temperature under dark for 1 h before heated at 80 °C for 5 h. Then the solution was poured into distilled water and extracted with chloroform. The organic phase was washed with water, dried over anhydrous MgSO₄. The solvent was re-

moved by a rotate evaporator and the residue was purified by silica-gel chromatography (CHCl₃/Petroleum ether = 1/5, v/v) to yield red needle-like crystal (3.11, yield: 58%).¹H NMR(400 MHz, CDCl₃): δ (ppm) 8.08 (s, 1H), 7.94 (s, 1H), 7.28 (s, 1H), 2.67 (t, 4H, *J* = 7.8 Hz), 1.65 (m, 4H), 1.35 (m, 12H), 0.89 (m, 6H).

2,5-bis{5-(6-(4-hexylthiophen-2-yl)-1,2,4,5-tetrazine-3-yl)-(3-hexylthiophene-2-yl)}thiophene (T(HTTzHT)₂). 2.2 mmol compound 4, 1.0 mmol of 2,5-bis(trimethylstannyl)thiophene 5, and 40 mL of toluene were put into a flask with oil bath. The solution was flushed with argon for 10 min, and then 25 mg of $Pd(PPh_3)_4$ was added into the flask. The solution was flushed again for 20 min. The oil bath was heated to 110 °C carefully, and the reactant was stirred for 48 h at this temperature under an argon atmosphere. Then, the reactant was cooled to room temperature. The solution was poured into distilled water and extracted with chloroform. The organic phase was washed with water, dried over anhydrous MgSO4. The solvent was removed by a rotate evaporator and the residue was purified by silica-gel chromatography, the obtained material was further purified by redissolving in chloroform and deposited in 100 mL of methanol. The solid was dried under vacuum for 1 day to get the final product. The yield of the coupling reaction was 72%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.06 (s, 4H), 7.27 (d, 2H), 7.23 (s, 2H), 2.87 (t, 4H, *I* = 1.9 Hz), 2.68 (t, 4H, *I* = 1.9 Hz), 1.76 (m, 4H), 1.68 (m, 4H), 1.37 (m, 24H), 0.89 (m, 12H). MALDI-TOF MS: Calcd for C₄₈H₆₀N₈S₅: 908.35; Found: 908.48.

5,5'-*bis*{5-(6-(4-*hexylthiophen*-2-*yl*)-1,2,4,5-*tetrazine*-3-*yl*)-(3-*hexylthiophene*-2-*yl*)}-2,2'-*bithiophene* (**TT(HTT2HT)**₂). This compound was prepared with the same procedure as T(HTT2HT)₂. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.08 (s, 4H), 7.27 (d, 2H), 7.23 (s, 4H), 2.88 (t, 4H, *J* = 1.9 Hz), 2.69 (t, 4H, *J* = 1.9 Hz), 1.74 (m, 4H), 1.68 (m, 4H), 1.38 (m, 24H), 0.89(m, 12H). MALDI-TOF MS: Calcd for C₅₂H₆₂N₈S₆, 990.34; Found 990.89.

5,5"-bis{5-(6-(4-hexylthiophen-2-yl)-1,2,4,5-tetrazine-3-yl)-(3-hexylthiophene-2-yl)}-2,2':5',2"-terthiophene (**TTT(HTTzHT)**₂). This compound was prepared with the same procedure as T(HTTzHT)₂. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.08 (s, 4H), 7.27 (d, 2H), 7.21 (s, 2H),7.15 (s, 4H), 2.87 (t, 4H, *J* = 1.9 Hz), 2.68 (t, 4H, *J* = 1.9 Hz), 1.76 (m, 4H), 1.68 (m, 4H), 1.36 (m, 24H), 0.90 (m, 12H). MALDI-TOF MS: Calcd for C₅₆H₆₄N₈S₇, 1072.33; Found 1072.87.

2.2. Measurements and characterization

Differential scanning calorimetry (DSC) was performed under nitrogen flushing at a heating rate of 10 °C/min with a NETZSCH (DSC-204) instrument. Thermal gravimetric analysis (TGA) was carried out on a Perkin–Elmer Pyris 6, with a heating rate of 10 °C/min under nitrogen flow. Electrochemical measurements of these derivatives were performed with a Bioanalytical Systems BAS100 B/W electrochemical workstation. The cyclic voltammetry (CV) diagrams of the SMs were obtained by using n-Bu₄NPF₆ as supporting electrolyte in acetonitrile solution with a glass carbon working electrode, a platinum wire counter electrode and a Ag/AgNO₃ reference electrode under N₂ atmosphere. Ferrocene was used as the internal standard. The redox potential of Fc/Fc⁺ which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration is located at 0.17 V in 0.1 M n-Bu₄NPF₆/acetonitrile solution [33]. ¹H NMR spectra were measured using a Varian Mercury-400 NMR. Time-of-flight mass spectra were recorded with a Kratos MALDI-TOF mass system. UV-visible absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. Atomic force Microscopy (AFM) images were recorded under ambient conditions, using a Vecco Digital Instrument Multimode Nanoscopellla operating in the tapping mode regime. The samples were prepared by spin-coating onto silica at 800 rpm from sample solutions in chloroform. X-ray diffraction (XRD) analysis was performed on an X'Pert-Pro MPD diffractometer with a Cu K radiation source at room temperature. The transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-Twin transmission electron microscope operated at 200 kV.

2.3. Device fabrication and characterization

The active layer contained a blend of SM as electron donor and PC₆₁BM or PC₇₁BM as electron acceptor, which was prepared from varied weight ratios by solution (6 mg/mL of SMs) in chloroform. After spin coating the blend from solution at 800-1400 rpm, the devices were completed by evaporating a 0.8 nm LiF layer protected by 100 nm of Al at a base pressure of 4×10^{-4} Pa. The effective photovoltaic area defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 12 mm². Current-voltage characteristics of the solar cells in the dark and under illumination of 100 mW/cm² white light from a Hg-Xe lamp filtered by a Newport 81094 Air Mass Filter, using a GWinstek SFG-1023 source meter. Monochromatic light from a Hg-Xe lamp (Newport 67005) in combination with monochromator (Oriel, Cornerstone 260) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Newport 70104 Merlin). A calibrated Si cell was used as reference. All the measurements were performed under ambient atmosphere at room temperature.

3. Results and discussion

3.1. Synthesis and structural characterization

Scheme 1 outlines the synthetic approach and depicts the structures of the final products of T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂. Compound **3** was obtained through a known procedure²⁷ and then reacted with NBS in CHCl₃/AcOH to provide compound **4** in 58% yield. The bis(trimethylstannyl)thiophene derivatives **5**, **7** and **9** were synthesized from the corresponding oligothiophene or their bromides after successive treatments with n-BuLi and trimethyltin chloride. The final products T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂ were produced through Pd(0)-catalyzed Stille crosscoupling reaction of compound **4** with **5**, **7** and **9**, respectively. T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂ were soluble in common organic solvents, including CH_2Cl_2 , $CHCl_3$, THF, chlorobenzene (CB) and dichlorobenzene (DCB).

3.2. Thermal properties

The thermal stability of all the compounds was investigated by TGA at a heating rate of 10 °C/min under N₂. The 5% weight loss temperatures (T_d) of these SMs were determined from TGA curves (Fig. S1, Supporting Information). Each SM exhibits high thermal stability with a T_d greater than 257 °C. DSC experiments were performed to investigate the thermal properties of T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂. Fig. 1 shows the DSC curves of these molecules after they are purified through recrystallization, and it clearly reveals these SMs are in the crystalline state at room temperature. The effect of number of thiophene repeating units in oligothiophene as building block of donor part in these SMs on crystalline properties is studied. With the repeating number of central thiophene increases from T(HTTzHT)₂ to TT(HTTzHT)₂ and TTT(HTTzHT)₂, the melting temperature (T_m) varied from 177 to 205 and 174 °C, concomitantly with a strong tendency to crystallize during the heating scan with the crystallization enthalpy of 45.4 kJ/mol, 55.4 kJ/mol and 37.6 kJ/mol, respectively. The largest crystallization enthalpy of TT(HTTzHT)₂ indicates that it has the highest tendency to crystallize by its enhanced interchain interaction. It should also be noted that the corresponding entropy at crystal melting changed from 102 J/mol K for T(HTTzHT)₂ to 116 J/mol K for TT(HTTzHT)₂ and 83.5 J/mol K for TTT(HTTzHT)₂. Generally, the entropy should increase with increasing thiophene repeating units due to the similar molecules structure. The largest change of entropy for TT(HTTzHT)₂ indicates that molecules are packed more regularly in crystalline state than the others. This would be beneficial for applications in organic solar cells since a highly ordered heterojunction nanostructure enhanced by the crystallization of the SM in the active layer is desirable for charge separation and transport [34].

3.3. Optical properties

Among three SMs, there is a symmetrical A-D-A structure, where D represents the electron-donating OTs moiety (1T, 2T, 3T) in center, while A represents the electronaccepting Tz moieties (bisthiophene-tetrazine) at both sides. The normalized UV-vis absorption spectra of these SMs in dilute chloroform solution (10^{-5} M) are shown in Fig. 2a, and the main optical properties are listed in Table 1. One absorption peak is apparent in the range of 300-400 nm for the π - π ^{*} transition between OT and TTTz moieties in the backbone, and the other absorption maximum in the 450–500 nm range is for the intramolecular charge transfer (ICT) transition [4]. As the incorporated the number of OT units increase from T(HTTzHT)₂ to TT(HTTzHT)₂ and TTT(HTTzHT)₂, the ICT transition red-shifted from 447 to 463 and 473 nm, respectively. This phenomenon is because that the increasing OT units enhance the conjugated backbone [28]. Moreover, the relatively high absorption coefficients (ε_{max}) could be calculated from the Beer's law equation with the same dilute concentration of the SMs in chloroform, which are listed in Table 1.



Scheme 1. Molecular structures and synthesis of T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂.



Fig. 1. DSC traces of T(HTTzHT)_2, TT(HTTzHT)_2 and TTT(HTTzHT)_2 measured under N_2 flow at a heating rate of 10 $^\circ C/min.$

Fig. 2b shows the optical absorption spectra of thin films of the SMs, and the optical properties are summarized in Table 1. The thin film absorption spectra are generally similar in shapes to those in dilute solution. The maximum absorption peaks and absorption edges (λ_{edge}) in film were red shifted significantly compared with those in solution, suggesting that intermolecular interactions existed in the solid state. Compared to T(HTTzHT)₂, compounds TT(HTTzHT)₂ and TTT(HTTzHT)₂ showed stronger absorption intensity due to strong intermolecular interactions and the high crystallization in the solid state, which results in a longer effective conjugation length than in the solution state (Fig. S2, Supporting Information). The optical band gaps $(E_{g,opt})$ of the compounds $TT(HTTzHT)_2$ and TTT(HTTzHT)₂ derived from the absorption edge of the thin film spectra are around 1.85 eV (Table 1). These



Fig. 2. Normalized UV–Vis absorption spectra of the SMs. (a) In chloroform solutions with the concentration of 10^{-5} mol/L and (b) films spincoating from a 10 mg/mL chloroform solution.

low band gaps can improve light harvesting and enhance the photocurrent of the OSCs since they are very close to the photon flux maximum of the solar spectrum (1.77 eV).

3.4. Electrochemical properties

Fig. 3 shows the cyclic voltammetry curves of $T(HTTzHT)_2$, $TT(HTTzHT)_2$ and $TTT(HTTzHT)_2$. The results of the electrochemical measurement and calculated energy levels of the SMs are listed in Table 1. The estimated LUMO energy levels of $T(HTTzHT)_2$, $TT(HTTzHT)_2$ and $TTT(HTTzHT)_2$ are -3.54 eV, -3.55 eV and -3.41 eV,

Table 1	
Optical and electrochemical data of the small molecules.	

respectively, which are very similar. It indicates that alternating electron-donating OTs with different number of thiophene units have slight effect on the reduction potential of the SMs with A–D–A structure, as the LUMO energy level is mainly determined by the Tz based acceptor unit. On the other hand, the HOMO energy levels of the three SMs behave quite differently. The HOMO energy levels of the T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂ are -5.5 eV, -5.18 eV, and -5.02 eV, respectively. The improved HOMO energy levels of the three SMs are caused by the enhanced conjugated length, which indicates that the OT with increasing number of thiophene possessed higher electron-donating ability can increase the conjugated length of the molecules and result in a higher HOMO energy level [28].

The electrochemical band gaps ($E_{g,ec}$) of the three SMs, calculated from the difference between HOMO and LUMO values, are well consistent with the $E_{g,opt}$ in trend. The varied HOMO energy level and relative stable LUMO energy level result in the reduced band gaps of the SMs, demonstrated the significance of the intramolecular charge transfer through the A–D–A structures inside the SMs. It clearly indicates the HOMO energy level and band gap of the SM can be controlled strictly by introducing oligothiophene with different number of thiophene.

3.5. Photovoltaic performance

In order to investigate the photovoltaic properties of the SMs, the BHJ photovoltaic cells, with a structure of ITO/ PEDOT:PSS/SM:PCBM/LiF/Al, were fabricated, where the SMs were used as donors and PC₆₁BM or PC₇₁BM as acceptor. The active layers of the photovoltaic cells were fabricated from CHCl₃ solutions of SM and PC₆₁BM or PC₇₁BM by spin-coating. Different conditions including the weight ratio between donor and acceptor and the thickness of the active layer were optimized. The performances were achieved with the varied weight ratios of SM:PC₆₁BM from 1:1 to 1:4 (w/w). The thickness of the active layer is 60-90 nm, which could be controlled by changing both the spin-coating rate and the concentration of the solution. Due to the high performance of TT(HTTzHT)₂, we also fabricated the photovoltaic cell with the active layer (around 100 nm) prepared by spin-coating CHCl₃ solutions consisting of TT(HTTzHT)₂ and PC₇₁BM with the weight ratio at 1:1 (w/w), and 1,8-diiodooctane (DIO, 1% by volume) was added as a processing additive. All devices were characterized in the dark and under AM 1.5 (100 mW/cm²) white

SM	In solution ^a		In film ^b						
	λ_{\max}^{abs} (nm) (ε_{\max}) (M ⁻¹ cm ⁻¹))	$\lambda_{edge} (nm_) \qquad \lambda_{max}^{abs}$		$\lambda_{edge} = E_{ox}^{onset}$ (V)/ HOMO (eV)		E ^{onset} (V)/LUMO (eV)	Electrochem.Optical ^c $E_{g,ec}$ (eV) $E_{g,opt}$ (eV) ^c		
T(HTTzHT) ₂ TT(HTTzHT) ₂ TTT(HTTzHT) ₂	447 (84,500) 463 (96,300) 473 (82,600)	544 559 569	467 498 507	605 664 669	0.87/-5.50 0.55/-5.18 0.39/-5.02	-1.09/-3.54 -1.08/-3.55 -1.22/-3.41	1.96 1.63 1.61	2.05 1.87 1.85	

 $^a~1\times 10^{-5}\,M$ in anhydrous chloroform.

^b Spin-coating from a 10 mg/mL chloroform solution.

^c The optical band gap ($E_{g,opt}$) was obtained from absorption edge.



Fig. 3. Cyclic voltammetry curves of $T(HTT_2HT)_2$, $TT(HTT_2HT)_2$ and $TTT(HTT_2HT)_2$ films on platinum electrode in 0.1 mol/L n-Bu₄NPF₆ in CH₃CN solution, at a scan rate of 100 mV/s.

light with simultaneous recording of their current–voltage characteristics. The photovoltaic performance characteristics of each OSCs are given in Table 2.

The optimized current-voltage curves of the three SMs are presented in Fig. 4. The cells based on T(HTTzHT)₂:PC₆₁₋ BM (1:1 w/w in CHCl₃ solution) showed an open circuit voltage (V_{oc}) of 0.73 V, a short circuit current density (I_{sc}) of 1.77 mA/cm^2 , a fill factor (FF) of 0.38, giving a PCE of 0.49%. Interestingly, with the increasing number of thiophene unit in the SM backbone, the photovoltaic cell based on TT(HTTzHT)₂:PC₆₁BM (1:1 w/w in CHCl₃ solution) showed V_{oc} of 0.74 V, J_{sc} of 5.77 mA/cm², FF of 0.52, and significantly increased PCE to 2.22%, which is more than three times higher than that of T(HTTzHT)₂. However, the photovoltaic performances of TTT(HTTzHT)₂ with increasing thiophene number in backbone decreased greatly. Considering the promising photovoltaic properties of TT(HTTzHT)₂ among the three SMs, we performed the optimization on the OSCs based on TT(HTTzHT)₂ by using PC₇₁BM as acceptor instead of PC₆₁BM and adding varied volume ratios DIO as a processing additive. Fig. 5 shows the current-voltage characteristics of the OSCs devices at different mixed solvents device fabrication conditions. We found that the device performance can be further improved by using PC71BM as acceptor instead of PC61BM and adding varied DIO:CHCl₃ volume ratio. The best device,



Fig. 4. Current–voltage characteristics of optimized photovoltaic cells based on $T(HTTzHT)_2:PC_{61}BM$, $TT(HTTzHT)_2:PC_{61}BM$ and $TTT(HTTzHT)_2:PC_{61}BM$ under illumination of AM 1.5, 100 mW/cm² white light.

prepared using CHCl₃ with 1% DIO, reaches a V_{oc} = 0.86 V, J_{sc} = 7.87 mA/cm², *FF* = 0.48 and PCE = 3.24%. All the parameters of optimized photovoltaic devices are list in Table 2. Since the serials of OTs based A–D–A SMs exhibit the similar chemical structure, the greatly increased PCEs of TT(HTTzHT)₂ based photovoltaic device can be attributed to the enhanced interchain interactions, as discussed in the thermal properties part, plus the energy level, crystallization, absorption properties, the hierarchical structures of the SM:PCBM blend films as discussed below.

It is generally considered that the V_{oc} is mainly determined by the difference between the HOMO energy level of the donor (SM) and LUMO energy level of the acceptor (PCBM). However, several other parameters should also be taken into account such as carrier recombination, resistance related to thickness of the active layer, and degree of phase separation between the components in the blend, which can modify the energetically expected V_{oc} value. Although T(HTTzHT)₂ showed lowest HOMO energy levels (around -5.50 eV) and similar LUMO energy level compared with the other two SMs TT(HTTzHT)₂ and TTT(HTTzHT)₂, the TT(HTTzHT)₂ based devices exhibits the highest V_{oc} . Moreover, the V_{oc} of the devices based on TT(HTTzHT)₂ can be further improved by replacing PC₆₁BM with PC71BM as acceptor and adding processing additive. The relatively high V_{oc} of TT(HTTzHT)₂ based device could

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haracteristic Current–voltage Parameters from Device Testing at AM 1.5G White Light Conditio	ons.

	SM/PCBM (w/w ratio)	$V_{oc}\left(V\right)$	J_{sc} (mA/cm ²)	FF	PCE (%)	DIO ^c (volume %)	$R_{sh} \left(\Omega \mathrm{cm}^2 \right)$	$R_s (\Omega \text{ cm}^2)$	RMS ^d (nm)
T(HTTzHT)2 ^a	1:1	0.73	1.77	0.38	0.49	-	857	29.39	2.11
TT(HTTzHT)2 ^a	1:1	0.74	5.77	0.52	2.22	-	1510	5.26	5.18
TTT(HTTzHT)2 ^a	1:1	0.66	1.57	0.41	0.42	-	1394	40.73	3.93
TT(HTTzHT)2 ^b	1:1	0.81	5.59	0.54	2.45	-	1312	8.31	-
TT(HTTzHT)2 ^b	1:1	0.86	7.87	0.48	3.24	1%	632	10.08	-
TT(HTTzHT)2 ^b	1:1	0.84	7.85	0.47	3.08	3%	781	8.00	-
TT(HTTzHT)2 ^b	1:1	0.84	5.96	0.47	2.37	5%	879	11.81	-

 $^{\rm a}$ The active layer based on the blend film of SM and ${\rm PC}_{\rm 61}{\rm BM}.$

^b The active layer based on the blend film of SM and PC₇₁BM.

^c The varied volume mixed ratio between DIO and CHCl₃.

^d Root mean-square (RMS) roughness from AFM measurement.



Fig. 5. Current-voltage characteristics of $TT(HTTzHT)_2:PC_{71}BM$ photovoltaic cell prepared from varied volume mixed solvents CHCl₃:DIO under illumination of AM 1.5, 100 mW/cm² white light.

be explained by using the following theoretical equation [35]:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{sc}}{J_{so}}\right) + \frac{\Delta E_{DA}}{2q}$$

where *q* is the fundamental charge, n is the diode ideality factor, J_{so} is a pre-exponential factor that depends on the molecules and ΔE_{DA} is the energy difference between the LUMO level of the acceptor material and the HOMO level of the donor material. Considering the Materials properties affected the magnitude of J_{so} including the reorganization energy for D–A electron transfer, the intermolecular overlap at the D/A interface, the layer electrical conductivities, the area of the D/A interface. A more ordered TT(HTTzHT)₂ crystalline structure in active layer, and ideal phase separation between donor and acceptor materials can give a lower J_{so} for the optimized TT(HTTzHT)₂ based device [36]. By combining high J_{sc} and low J_{so} , the high V_{oc} of TT(HTTzHT)₂ based devices can be explained according to the above equation.

The absorption spectrum, and the morphology formed by the blends of the SM and fullerene are generally considered as the main factors that influence the J_{sc} of SM/fullerene BHJ solar cells. For all the optimized photovoltaic devices, a higher J_{sc} based on TT(HTTzHT)₂:PC₆₁BM (5.77 mA/cm²) was obtained than that of the device based on T(HTTzHT)₂:PC₆₁BM (1.77 mA/cm²) and TTT(HTTzHT)₂: PC₆₁BM (1.41 mA/cm²). This could be explained by the relative higher absorption coefficients of TT(HTTzHT)₂ as indicated in Table 1, and the different hierarchical structures in blend film as discussed in the following part.

The structural ordering of pristine T(HTTzHT)₂, TT(HTTzHT)₂ and TTT(HTTzHT)₂ in spin-coating films from CHCl₃ solutions onto glass substrates with same condition was investigated by X-ray diffraction (XRD) (Fig. S3, Supporting Information). The strong diffraction peaks of T(HTTzHT)₂, TT(HTTzHT)₂, and TTT(HTTzHT)₂ at *q* values of 0.328 Å⁻¹, 0.272 Å⁻¹, and 0.331 Å⁻¹ suggest that they are in the crystalline state in the film, with corresponding *d* spacing (d_{100}) of 19.2 Å, 23.1 Å and 19.0 Å, respectively. These results indicate these small molecules are easy to



Fig. 6. XRD patterns of SM:PCBM blend films spin-coating onto glass substrate: (a) chloroform solution of SM:PC₆₁BM; (b) chloroform solution of SM:PC₇₁BM; (c) DIO:chloroform (1%) mixed solution of SM:PC₇₁BM.

crystallize and form a well ordered packing structure during the spin-coating process. This is further supported by the XRD of the blend films of small molecules with $PC_{61}BM$, as indicated in Fig. 6, showing the corresponding similar diffraction peaks. It should also be noted that the full width at half maxim intensity (FWHM) of XRD peaks for SMs increased in the blend film, indicates that crystalline domain size decreased when blended with $PC_{61}BM$, according to Debye–Scherrer's equation [37,38].

Combining the length of SMs in the range of 28–36 Å obtained from the B3LYP functional and employing the 6-31G* basis set method (see Fig. S4, Supporting Information), the much smaller *d* spacing calculated from XRD of blend films indicates that the diffraction peaks should come from the lamella packing of SMs in the crystalline structure [39,40]. It is very interesting to find that the lamella packing distances (d_{100}) in blend films of TT(HTTzHT)₂:PC₆₁BM is higher than that of T(HTTzHT)₂:-PC₆₁BM and TTT(HTTzHT)₂:PC₆₁BM blend films, although it possesses intermediate side alkyl chain density per conjugated moiety. Since this molecule shows the best photovoltaic properties among the three studied SMs with similar chemical structure, the different molecular packing in the crystalline structure may play the main role. Attempts to grow single crystals of the above molecules to reveal the molecular packing in the crystal are under current investigation.

It is noted that the lamella distance of $TT(HTTzHT)_2$ molecules in crystalline part reduced from 23.1 Å to 21.4 Å (see in Fig. 6), when PC₇₁BM was used as acceptor to replace PC₆₁BM. This means that the donor molecules are packing more closely, and more efficient BHJ hole transporting domains formed. As a result, the photovoltaic performances are improved, with the PCE increased from 2.22% to 2.45%. Note in the optimized photovoltaic cell that replacing PC₆₁BM with PC₇₁BM as acceptor and adding DIO (Fig. 6 TT(HTTzHT)^c₂), can not only reduce the stacking distance (20.9 Å) but also increase the crystallization of the blend film, which could form more closed stacking crystalline state and improved photovoltaic performance (J_{sc} = 7.87 mA/cm², PCE = 3.24%). Therefore, we can



Fig. 7. Topography images obtained by tapping mode AFM showing the morphology of the blend films spin-coating from chloroform for: (a) $T(HTTzHT)_2:PC_{61}BM$ (w/w, 1:1); (b) $TT(HTTzHT)_2:PC_{61}BM$ (w/w, 1:1); (c) $TTT(HTTzHT)_2:PC_{61}BM$ (w/w, 1:1) with (size: $5 \ \mu m \times 5 \ \mu m$).



Fig. 8. TEM images obtained by the blend films spin-coating from chloroform for: (a) $T(HTTzHT)_2:PC_{61}BM (w/w, 1:1);$ (b) $TT(HTTzHT)_2:PC_{61}BM (w/w, 1:1);$ (c) $TTT(HTTzHT)_2:PC_{61}BM (w/w, 1:1)$. The insets are the corresponding electron diffraction (SAED) patterns.

conclude that a more closed lamella stacking and high crystallization of donor molecules in blend film will lead to better photovoltaic properties by adding DIO or replacing PC₆₁BM with PC₇₁BM. The reason is that excitons and charges are hopping easier in ordered structure and continuous transport channel, leading to significantly increased J_{sc} [41].

As OSCs properties are linked not only to molecular stacking and crystallization, but also to the morphology and relative miscibility of the components, we employed AFM and TEM to assess the correlation between spatial dimensions of phase-separated domains and OSCs properties. Fig. 7 shows the AFM height images of T(HTTzHT)₂:-PC₆₁BM, TT(HTTzHT)₂:PC₆₁BM and TTT(HTTzHT)₂:PC₆₁BM blend films with the same weight ratio (1:1 w/w) spin-coating from chloroform solutions. As clearly evidenced by AFM, the as-cast blend films of T(HTTzHT)2:PC61BM and TTT(HTTzHT)₂:PC₆₁BM show relatively low surface roughness of 2.11 and 3.93 nm (Fig. 7a and c and Table 2), respectively. As for the TT(HTTzHT)₂:PC₆₁BM blend film, it shows a relatively higher coarse surface with the root mean square (RMS) of 5.18 nm (Fig. 7b and Table 2), which may come from the high crystallization tendency of molecule, as revealed by DSC. This will result in an ordered structure, continuous carrier transport channel, and hence increase the distance of carrier transport and decrease recombination, leading to the greatly improved short circuit current densities from 1.57 mA/cm² for TTT(HTTzHT)₂:PC₆₁BM to 5.77 mA/cm² for TT(HTTzHT)₂:PC₆₁BM.

To probe further the morphology throughout the entire film, TEM experiments were carried to obtain a real-space image of the phase separated morphology of the SM:PCBM blend film structure, where the domains can be distinguished from their different electron densities [42]. Fig. 8a shows the TEM image of T(HTTzHT)₂:PC₆₁BM (w/ w, 1:1) blend film. PCBM grain-aggregation with the size around 60 nm is almost homogeneously dispersed in the T(HTTzHT)₂ matrix. The large aggregation may result in a decreased diffusional escape probability for mobile charge carriers, and hence increased recombination. The diffused ring from its corresponding electron diffraction pattern (inset of Fig. 8a) shows the low crystallization of T(HTTzHT)₂ and PCBM. As for the TTT(HTTzHT)₂, the TEM image of blend film (Fig. 8c) shows weak bean-like aggregation and lamella phase separation with domain size about 15 nm. Meanwhile, the weak inner and outer reflection rings of corresponding SAED pattern is from the TTT(HTTzHT)₂ crystals. Although the crystallization has been increased, the deteriorated morphology owning to the relatively poor solubility gives a more important influence on the recombination of charge carrier, thus the low FF [43]. All above are fully consistent with the relative low short circuit current densities and high series resistance (R_s) obtained for the T(HTTzHT)₂:PC₆₁BM (J_{sc} =1.77 mA/cm², $R_s = 29.39 \Omega \text{ cm}^2$) and TTT(HTTzHT)₂:PC₆₁BM $(J_{sc} = 1.57 \text{ mA/cm}^2, R_s = 40.73 \Omega \text{ cm}^2)$ photovoltaic cells. The relative low shunt resistances (R_{sh}) of T(HTTzHT)₂:- $PC_{61}BM$ and $TTT(HTTzHT)_2:PC_{61}BM$ based OSCs ($R_{sh} = 857$



Fig. 9. The IPCE spectra of devices based on $TT(HTTzHT)_2:PC_{71}BM$ with 1% DIO additive.

and 1394 Ω cm²) are also observed from the *I*–*V* curve, and the V_{oc} (0.73 and 0.66 V) and *FF* (0.38 and 0.41) deteriorated significantly. For blend films of TT(HTTzHT)₂:PC₆₁-BM, elongated fibrillar structure was observed (Fig. 8b), which can greatly increase the interface area and construct the continuous transport channel. It is notable that the SAED pattern of TT(HTTzHT)₂:PC₆₁BM blend film shows stronger intensity than the others, indicating a more ordered structure formed. This leads to the lower R_s (5.26 Ω cm²) and higher R_{sh} (1510 Ω cm²) of the photovoltaic cell, and hence greatly improved J_{sc} to 5.77 mA/cm² and *FF* to 0.52.

The incident photon-to-current conversion efficiency (IPCE) curve of the optimized OSCs based on $TT(HTT_2HT)_2$:PC₇₁BM (w:w, 1:1) with 1% DIO additive under monochromatic light is shown in Fig. 9. The IPCE curve exhibits monochromatic IPCE maximum of 60% at 430 nm and a broad response covering 300–700 nm, consistent with the optical absorption spectrum (Fig. 2b). This IPCE value indicates that the photoresponse is very efficient for this SM based OSCs device. The J_{sc} calculated from the integral of IPCE curve based on TT(HTT2HT)₂ with an AM1.5G reference spectrum were 7.87 mA cm⁻², consistent with the J_{sc} value obtained from the I-V measurement.

4. Conclusions

We have designed and synthesized a series of high coplanar A–D–A SMs with varied electron donor or acceptor moieties containing Tz moiety and electron-donating OTs moiety, alkylated thiophene attached to both sides of the Tz moiety for the application as donor materials in OSCs. We observed that band gaps of these three SMs are gradually lowered due to the A–D–A structure and varied OTs, indicating that the band gaps and energy levels of these SMs can be tuned through changing the number of OT based on the A–D–A structure, and also the A–D–A structure SMs can lead to high absorption coefficients. Moreover, the OT moiety of the Tz based A–D–A SMs plays a great role in crystallization. The photovoltaic performances of these SMs are varied significantly, and the per-

formance of OSCs by using SM:PC₆₁BM as the active layer was obtained in the order of TT(HTTzHT)₂ > T(HTTzHT)₂ > -TTT(HTTzHT)₂. XRD experiments of the SM:PC₆₁BM blend films showed well ordered packing structure in the crystalline state, and the more closed lamella stacking of donor material in blend film lead to better photovoltaic properties. AFM and TEM experiments also revealed morphology control by adjusting the crystallization of SM and PCBM is an effective way to improve the performance of OSCs. OSCs with the highest power conversion efficiency of 3.24% was also observed when the TT(HTTzHT)₂ was blended with PC71BM and 1% DIO as additives. Our results indicated that careful molecular design can improve the photovoltaic properties of A-D-A based small molecules by incorporation oligothiophene moiety with proper conjugated length and two sets of Tz moieties. This would be very useful in designing photovoltaic cell materials with high efficiency.

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Appendix A. Supplementary material

TGA, umnormalized UV–Vis absorption spectra of small molecule film, XRD spectra of small molecules, calculated optimized molecule structures of small molecules and molecule dimension. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2013.02.038.

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