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Introduction

Solution-processed bulk-heterojunction (BHJ) organic solar cells (OSCs) have been considered a green and effective technology to harvest sun-light and generate electricity because of the potential for low cost manufacturing of large area solar cells through the roll-to-roll coating technique on various substrates.1-6 In the past few years, polymer-based BHJ solar cells have been dominant, and a power conversion efficiency (PCE) of over 9% has been acquired⁷ for single junction devices. Meanwhile, tremendous progress has also been made by designing novel small molecules as the donor in the BHJ architecture, and a PCE over 9%8 was most recently achieved for single junction devices. Compared to the polymer-based OSCs (PSCs), small-molecule-based OSCs (SMSCs) possess numerous advantages, including a relatively simple synthesis and purification process, monodispersity, a well-defined structure, no end-group contaminants, less batch-to-batch variation,^{9,10} a versatile molecular structure, easier band structure control,^{11,12} a high charge carrier mobility, etc. Even so, solution-processed SMSCs have not been investigated as extensively as the PSCs, and their overall efficiencies are still behind those of their polymer counterparts. Currently, many techniques and lessons

Indacenodithiophene core-based small molecules with tunable side chains for solution-processed bulk heterojunction solar cells

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Two indacenodithiophene (IDT) core-based small molecules with different side chains of bulky 4-hexylphenyl and flexible *n*-dodecyl with the same number of carbon atom, namely **SM1** and **SM2**, respectively, were designed and synthesized as the donor materials in organic solar cells (OSCs). The impacts of the different side chains combined with the IDT core on the optical absorption, electrochemical property, hole mobility, film morphology, and solar cell performance were studied thoroughly. The two compounds possess a broad absorption covering the wavelength range of 450–700 nm and relatively low HOMO energy levels of -5.46 and -5.52 eV. The power conversion efficiency (PCE) of the OSCs based on **SM2** as the donor material and PC₆₁BM as the acceptor material (1 : 2, w/w) is 2.33%. In contrast, a PCE of 4.72% was achieved for the device based on **SM1** as the donor and PC₇₁BM as the acceptor (1 : 2, w/w) without any treatment such as thermal annealing or the utilization of a solvent additive.

for the polymer-based BHJ solar cells could be applied for SMSCs.¹³ The active materials, especially the donor materials, are still the most important factor for obtaining high PCEs of SMSCs.13,14 To address this issue, it is believed that several requirements should be considered systematically to design molecular structures for high-performance and solution-processed SMSCs, that is, (1) an excellent film-formation ability, (2) a wide and efficient absorption, (3) matched energy levels with acceptors, (4) a planar structure for high hole mobility, (5) a good solubility and chemical and thermal stability.15 It is notable that the design of small molecules with a good filmformation ability is a prerequisite for high-performance solution-processed BHJ devices, since it has been generally difficult for small molecules to form a comparably good quality film as polymers, especially for those molecules with relatively low molecular weights and rigid planar structures owing to their intrinsic aggregation.16,17

To date, there are three typical types of solution-processed organic molecular photovoltaic donor materials reported in the literatures, that is, (1) triphenylamine (TPA)-based molecules,^{18–25} (2) hyperbranched molecules,^{26–30} and (3) planar and linear structured molecules based on thiophene oligomers^{31–35} or other donor and acceptor units.^{36–41} Although the TPA-based molecules and hyperbranched molecules possess a good solubility, their photovoltaic properties are limited owing to their weak intermolecular interaction when blended with the acceptor like 6,6-phenyl C-butyric acid methyl ester (PC₆₁BM), which results in a lower hole mobility and poorer fill factor (FF) for the BHJ OSCs based on these molecules as the donor. Currently, the maximum PCE of the BHJ OSCs based on these



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types of molecules is only 4.3%.²³ In contrast, the planar and linear molecules embody prospective photovoltaic performances with a PCE surpassing 6%,^{34,38,39,41} which is benefitted from their stronger intermolecular interactions resulting in a higher hole mobility and a higher FF of the BHJ OSCs.

Recently, the indacenodithiophene (IDT) unit has been emerging as an attractive donor building block for the conjugated polymer used in high performance OSCs, because the IDT unit possesses many desirable features for incorporation into semiconducting materials. The three aromatic rings are in conjugation, and a bridging atom fixes coplanarity between the adjacent rings, thus maximizing the π orbital overlap as well as reducing the conformational energetic disorder.42 As a result, the IDT-based polymers generally show a high and stable fieldeffect hole mobility, and a hole mobility as high as $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from an alternating polymer of IDT and benzothiadiazole (BT) units has been reported by Zhang et al.43 The polymers combining IDT as the donor unit and various electron-deficient moieties as the acceptor unit were extensively investigated in the previous article reports. For example, Jen and co-workers44 have reported two donor-acceptor (D-A) copolymers consisting of a 4-hexylphenyl-substituted IDT donor unit and two quinoxaline derivatives as the acceptor unit, and PCEs of 6.24% and 5.69% were achieved for the devices based on PIDT-phanQ/ PC71BM and PIDT-diphQ/PC71BM, respectively. Li and coworkers45 have reported four D-A copolymers consisting of a tetradodecyl-substituted IDT donor unit and different acceptor units, including bis(thiophen-2-yl)-bithiazole, bis(thiophen-2yl)thiazolothiazole, bis(thiophen-2-yl)-tetrazine and bis(thiophen-2-yl)-benzothiadiazole.

In addition, the bridging position of IDT offers the opportunity to attach substituents, typically aliphatic hydrocarbon chains, which can aid solubility and impact the intermolecular interactions. Aside from the various acceptor units, the role of the side chains on a conjugated polymer is also of importance because it can be used to tune its crystallinity in the solid state as well as its miscibility with other materials in thin blend films. For example, McCulloch and co-workers have reported a PCE of 6.5% from an alternating polymer consisting of 2-ethylhexylsubstituted IDT as the donor unit and BT as the acceptor unit.46 In comparison, a polymer incorporating 4-hexylphenylsubstituted IDT as the donor unit, thiophene as the bridge, and BT as the acceptor unit gives a PCE of 4.4% and a hole mobility of 3.4×10^{-3} cm² V⁻¹ s⁻¹.⁴⁷ A PCE of 6.17% and a hole mobility of 2.24×10^{-3} cm² V⁻¹ s⁻¹ were achieved for the PSCs based on an alternating polymer consisting of tetradodecyl-substituted IDT as the donor unit and bis(thiophen-2-yl)-benzothiadiazole as the acceptor unit.45 It is well known that polymer materials generally suffer from batch-to-batch variations, broad molecular weight distributions, end-group contamination, or difficult purification methods, which may be significant problems for understanding their molecular structure-property relationships. Moreover, although the acceptor units for these polymers are different which may result in the difference in device performance, the effect of the different side chains should not be omitted. Accordingly, it is more meaningful to study the relationships between the side chain structure and the properties in a small molecular platform because of the welldefined molecular structure. However, there are few publications that report on the effects of the side chain variation on the SMSCs.

In this article, two small molecules with the same conjugated backbone in an acceptor- π -donor- π -acceptor (A- π -D- π -A) framework comprised of an IDT core as the donor, two BT units as the acceptor, and thiophene π bridges were designed and synthesized as the platform for investigating the effect of the different side chains. 4-Hexylphenyls and n-dodecyls are attached on the IDT core to give 7,7'-(5,5'-(4,4,9,9-tetrakis(4hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2, 7-diyl)bis(thiophene-5,2-diyl))bis(4-(5'-dodecyl-[2,2'-bithiophen]-5-yl)benzo[c]^{1,2,5} thiadiazole) (SM1) and 7,7'-(5,5'-(4,4,9,9-tetradodecyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7diyl)bis(thiophene-5,2-diyl))bis(4-(5'-dodecyl-[2,2'-bithiophen]-5-yl)benzo $[c]^{1,2,5}$ thiadiazole) (SM2), respectively (Scheme 1). n-Dodecyl-substituted thiophene terminals are incorporated to extend the π -conjugated structure and to improve the solubility and film-formation property. As one of the most extensively exploited acceptor units in linear donor-acceptor type molecules, two BT acceptor units are linked with the IDT core through thiophene π bridges, leading to intramolecular charge transfer and thus broad optical absorption. Rigid and bulky aromatic 4-hexylphenyls and flexible aliphatic n-dodecyls with the same number of carbon atoms are attached onto the IDT unit on both sides, which can facilitate solubility and regulate intermolecular interactions between the molecular chains for tuning their solution processability and film morphology. The planarity of the small molecule is desirable to promote intramolecular π -delocalization and intermolecular π - π stacking, both are beneficial for a high charge carrier mobility.48 Both materials show a good solubility in common organic solvents, such as chloroform, dichloromethane, tetrahydrofuran (THF) and toluene, and can be readily solution-processed to form smooth and pinhole-free films upon spin-coating. Small molecular BHJ devices were fabricated using these materials as the donor and PC₆₁BM or PC₇₁BM as the acceptor. A PCE of 4.72% was achieved with an open circuit voltage (V_{oc}) of 0.87 V, a short circuit current density (J_{sc}) of 9.85 mA cm⁻² and a FF of



Scheme 1 The molecular structures of SM1 and SM2.

0.55 for the device based on **SM1** and $PC_{71}BM$. In contrast, the device based on **SM2** and $PC_{71}BM$ displays a much lower PCE of 1.52%, and it is even lower than that of the device with $PC_{61}BM$ as the acceptor (2.33%).

Experimental

Measurement and characterization

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV-300 spectrometer operating at 300 and 75 MHz, respectively, in a deuterated chloroform solution at room temperature. Differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 209 under an N2 flow at a heating and cooling rate of 10 °C min⁻¹. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under an N_2 flow at a heating rate of 10 °C min⁻¹. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a platinum working electrode and a Pt wire counter electrode at a scanning rate of 100 mV s^{-1} against a Ag/Ag⁺ (0.1 M of AgNO₃ in acetonitrile) reference electrode with a nitrogen-saturated anhydrous acetonitrile solution of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate. The thin solid films used for the absorption spectral measurement were prepared by spincoating their chloroform solutions on quartz substrates. Atom force microscopy (AFM) measurements were carried out by using a Digita Instrumental DI Multimode Nanoscope IIIa in the tapping mode. The processing conditions to make the blend films for the morphology study were the same as those for the fabrication of the solar cell devices.

Synthesis

4,4,9,9-Tetrakis(4-hexylphenyl)-4,9-dihydro-*s*-indaceno[1,2-*b*:5, 6-*b*']dithiophene (1),⁴⁹ 4,4,9,9-tetradodecyl-4,9-dihydro-*s*-indaceno-[1,2-*b*:5,6-*b*']dithiophene (3),⁴³ 4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)benzo[c]^{1,2,5} thiadiazole (5)⁵⁰ and tributyl(5-dodecylthiophen-2-yl)stannane (6)⁵¹ were prepared according to the reported methods. The IDT-based small molecules, **SM1** and **SM2**, were synthesized by a Stille cross-coupling reaction (Scheme 2). All reactions and manipulations were carried out in an inert atmosphere with the use of standard Schlenk techniques. THF was distilled from sodium before use. The other reagents and solvents, unless otherwise specified, were purchased from commercial suppliers and used without further purification.

Compound 2 (ref. 49) 907 mg (1 mmol) of compound 1 and 392 mg (2.2 mmol) of *N*-bromosuccinimide (NBS) were placed in a 100 ml two-necked bottle. 30 ml of chloroform was added to the bottle. Then, the whole bottle was wrapped in Al foil and immersed into an ice bath. The mixed solution was stirred in an N_2 atmosphere overnight. The organic phase was extracted by chloroform and washed with saturated sodium chloride solution and then dried over anhydrous MgSO₄ and filtered. The filtrate was concentrated on a rotary evaporator to give a pale yellow solid 2 (852 mg, 80%). ¹H NMR (CDCl₃, 300 MHz): δ



Scheme 2 The synthetic routes of SM1 and SM2. Reagents and conditions: (i) NBS, CHCl₃, N₂, room temperature, overnight; (ii) NBS, THF/DMF, N₂, room temperature, 3 h; (iii) Pd(PPh₃)₄, toluene, N₂, reflux at 110 °C, two days; (iv) LDA, THF, N₂, -20 °C for 15 min; (CH₃)₃SnCl, -20 °C then room temperature for 2 h.

(ppm) 0.87 (t, J = 6.6 Hz, 12H), 1.29 (m, 24H), 1.57 (m, 8H), 2.56 (t, J = 8.0 Hz, 8H), 6.99 (s, 2H), 7.07–7.09 (m, 16H), 7.32 (s, 2H). ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 157.0, 154.6, 143.2, 142.5, 141.4, 136.3, 129.4, 129.1, 128.5, 124.3, 118.7, 62.8, 35.7, 31.9, 31.5, 29.3, 22.8, 15.4. MS (MALDI-TOF) m/z: calculated for C₆₄H₇₂Br₂S₂, 1065.19; found, 1064.32.

Compound 4 (ref. 43) To a solution of compound 3 (4.0 g, 4.25 mmol) in THF/*N*,*N*-dimethylformamide (DMF) (2 : 1, v/v, 100 ml) NBS (1.66 g, 9.35 mmol) was added. This mixture was stirred for 3 h in the absence of light at room temperature and then poured into water. The precipitate was collected and washed with water and then recrystallized from acetone to give a pale yellow solid (3.96 g, 85%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.17 (s, 2H), 6.96 (s, 2H), 1.89–1.95 (m, 4H), 1.78–1.88 (m, 4H), 1.00–1.53 (m, 68H), 0.74–0.88 (m, 24H); ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 154.2, 152.2, 141.9, 135.6, 124.9, 113.1, 112.5, 55.0, 39.1, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 24.2, 22.8, 14.3.

Compound 7. 6.46 g (17.0 mmol) of 5 and 104 mg (0.09 mmol) tetrakis(triphenylphosphine)palladium(0) $(Pd(PPh_3)_4)$ were placed in a dried round bottom flask under protective gas. 50 ml of dry toluene was added, and the solution was then heated to 110 °C. 9.76 g (18.0 mmol) of **6** was then added to the reaction mixture and the solution was stirred for two days at 110 °C. The crude product was obtained by extraction with chloroform, and the organic phase was subsequently washed with a diluted hydrochloric acid, water and sodium carbonate solution. The organic phase was dried over magnesium sulphate and evaporated, and the residue was recrystallized from ethanol. Further purification was performed by column chromatography on silica with an eluent of hexane-dichloromethane (1 : 1, v/v) to give the product as a red solid (6.1 g,

65%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.10–8.12 (dd, J = 3.9 Hz, 1H, Ar-H), 8.01–8.03 (d, J = 3.9 Hz, 1H, Ar-H), 7.84–7.87 (d, J = 7.5 Hz, 1H, Ar-H), 7.80–7.83 (d, J = 7.5 Hz, 1H, Ar-H), 7.44–7.46 (dd, J = 5.1, 0.9 Hz, 1H, Ar-H), 7.19–7.22 (dd, J = 5.1, 3.9 Hz, 1H, Ar-H), 7.10–7.11 (d, J = 3.9 Hz, 1H, Ar-H), 7.10–7.11 (d, J = 3.9 Hz, 1H, Ar-H), 6.71–6.73 (d, J = 3.9 Hz, 1H, Ar-H), 2.79–2.84 (t, J = 7.5 Hz, 2H, CH₂), 1.65–1.75 (m, 2H, CH₂), 1.25–1.42 (m, 18H, CH₂), 0.88–0.96 (m, 3H, CH₃). ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 152.7, 152.6, 146.2, 139.60, 139.55, 137.5, 134.8, 128.5, 128.2, 127.6, 126.9, 125.91, 125.85, 125.76, 125.1, 123.9, 31.78, 31.76, 30.4, 29.0, 22.8, 14.3. MS (MALDI-TOF) m/z: calculated for C₃₀H₃₄N₂S₄, 550.86; found, 550.15.

Compound 8. To a solution of compound 7 (551 mg, 1 mmol) in dry THF (50 ml) in an N_2 atmosphere at -20 °C a lithiumdiisopropylamide (LDA) solution (1 M in THF/hexane, 1.1 ml) was added dropwise. The mixture was then stirred at -20 °C for 15 min. Trimethyltin chloride (1.2 ml, 1.2 mmol) was dissolved in THF and added in small portions. The reaction was stirred at -20 °C for 10 min before being warmed to room temperature and then stirred for 2 h. The resulting mixture was poured into water and extracted with ether. The organic phase was then washed with brine (60 ml \times 3) and water (60 ml \times 3). Further purification was performed by recrystallization from ethanol to give the product as a red solid. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.21-8.18 (d, 1H), 8.05-8.02 (d, 1H), 7.89-7.82 (dd, 2H), 7.31-7.28 (d, 1H), 7.21-7.18 (d, 1H), 7.12-7.08 (d, 1H), 6.72-6.70 (d, 1H), 2.85-2.78 (t, 2H), 1.73-1.69 (m, 2H), 1.35-1.21 (m, 18H), 0.90-0.82 (t, 3H), 0.45-0.32 (t, 9H). MS (MALDI-TOF) *m/z*: calculated for C₃₃H₄₂N₂S₄Sn, 713.67; found, 712.13.

Compound SM1. Compound 2 (213 mg, 0.2 mmol) and compound 8 (357 mg, 0.5 mmol) were placed in a dried round bottom flask under protective gas. 10 ml of dry toluene was added to the flask which then was sealed and degassed with argon for 15 min. Then Pd(PPh₃)₄ (10 mg) was added and the solution was heated to 110 °C. The reaction mixture was stirred for two days at 110 °C. The crude product was obtained by extraction with chloroform, and the organic phase was subsequently washed with a diluted hydrochloric acid, water and sodium carbonate solution. The organic phase was dried over magnesium sulfate and filtered. The filtrate was concentrated on a rotary evaporator. After the removal of solvent, the crude product was purified by silica gel using a mixture solvent of hexane-dichloromethane (2:1, v/v) as an eluent. The crude solid was recrystallized from CH2Cl2 several times to afford SM1 as a black solid (150 mg, 37%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.05-8.03 (d, 2H), 8.01-7.98 (d, 2H), 7.84-7.82 (m, 4H), 7.43-7.41 (m, 2H), 7.25-7.18 (m, 16H), 7.12-7.08 (m, 6H), 7.00-6.98 (m, 2H), 6.73-6.71 (d, 2H), 2.85-2.80 (t, 4H), 2.61-2.53 (t, 8H), 1.78-1.73 (m, 4H), 1.59-1.52 (m, 8H), 1.40-1.20 (m, 60H), 0.91-0.82 (m, 18H). ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 154.2, 152.7, 152.6, 152.2, 146.2, 141.9, 139.60, 139.55, 137.5, 135.6, 134.8, 128.5, 128.2, 127.6, 126.9, 125.91, 125.85, 125.76, 125.1, 124.9, 123.9, 113.1, 112.5, 55.0, 39.1, 32.1, 31.78, 31.76, 30.4, 29.9, 29.8, 29.7, 29.5, 29.4, 29.0, 24.2, 22.8, 14.3. MS (MALDI-TOF) *m/z*: calculated for C₁₂₄H₁₃₈N₄S₁₀, 2003.82; found, 2003.52.

Compound SM2. SM2 was synthesized and purified in a similar manner to that of **SM1** and was obtained as a dark solid

(182 mg, 45%). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.05–8.03 (d, 4H), 7.90–7.82 (m, 3H), 7.18–7.12 (m, 8H), 7.15–7.08 (m, 2H), 7.00–6.94 (s, 1H), 6.74–6.72 (m, 2H), 2.85–2.80 (t, 4H), 2.61–2.53 (t, 8H), 1.78–1.73 (m, 4H), 1.40–1.10 (m, 108H), 0.91–0.82 (m, 26H). ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 154.2, 152.7, 152.6, 152.2, 146.2, 141.9, 139.60, 139.55, 137.5, 135.6, 134.8, 128.5, 128.2, 127.6, 126.9, 125.91, 125.85, 125.76, 125.1, 124.9, 123.9, 113.1, 112.5, 55.0, 39.1, 32.1, 31.78, 31.76, 30.4, 29.9, 29.8, 29.7, 29.5, 29.4, 28.0, 23.2, 22.6, 13.3. MS (MALDI-TOF) *m/z*: calculated for C₁₂₄H₁₇₀N₄S₁₀, 2036.07; found, 2035.76.

Device fabrication and characterization

The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/donor:acceptor/PFN/Al. Indium tin oxide (ITO)-coated glass substrates were cleaned by sonication in detergent, deionized water, acetone and isopropyl alcohol, and dried in a nitrogen stream, followed by an oxygen plasma treatment. A 40 nm-thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at 0.45 µm) was spin-coated (3000 rpm) onto the ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into a nitrogen-filled glove box. Subsequently, a 90-100 nm-thin active layer was spin-casted from different blend ratios (w/w) of donor (SM1 or SM2) and acceptor (PC71BM or PC61BM) in a chloroform solution (10 mg ml⁻¹) at 1500 rpm for 20 s on the ITO/PEDOT:PSS substrate without further special treatment. The active layer thickness was measured using a Dektak 150 profilometer. A 5 nm-thin PFN layer was spin-coated from its solution in methanol. Finally, a 90 nm-thin Al layer was deposited on top of the PFN layer under a high vacuum (3 \times 10⁻⁶ torr). The effective device area was patterned to be 0.15 cm² by using a shadow mask. The PCEs were measured in an AM 1.5G solar simulator (Oriel model 91192) under ambient conditions. The power of the sun simulator was calibrated before the testing using a standard silicon solar cell, giving a value of 100 mW cm^{-1} in the test. The current density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter. The spectral response was measured with a commercial photomodulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity. The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight System (Bunkoh-Keiki SM-250).

The hole mobilities were measured with the hole-only devices by using the space charge limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/**SM1** or **SM2** (90 nm)/MoO₃ (10 nm)/Al. The device fabrication and mobility measurements were conducted in a nitrogen-filled glove box. The mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the Mott–Gurney law, which is described as

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{L^3} \tag{1}$$

where *J* is the current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ_h is the hole mobility, *L* is the film thickness of the active layer, and *V*, the

internal voltage, is defined as $V = V_{\rm appl} - V_{\rm r} - V_{\rm bi}$, where $V_{\rm appl}$ is the applied voltage to the device, $V_{\rm r}$ is the voltage drop due to contact resistance and series resistance across the electrodes, and $V_{\rm bi}$ is the built-in voltage due to the relative work-function difference of the two electrodes.

Results and discussion

Thermal stability and optical absorption

The thermal property of the developed materials was investigated by TGA and DSC. TGA suggests that **SM1** and **SM2** show a good thermal stability with a decomposition temperature (T_d) greater than 350 and 321 °C, respectively, in an N₂ atmosphere, indicating that they can effectively resist the thermal degradation at the operating temperatures in the resultant solar cells. **SM1** has a higher decomposition temperature due to its bulky and rigid 4-hexylphenyl side chains, while **SM2** contains flexible aliphatic *n*-dodecyl side chains. The DSC traces for these two materials do not show any peaks from room temperature to 250 °C, indicating that no phase transition was found in this temperature range.

To study the relationships between the chemical structure and the photophysical property, the UV-vis absorption spectra of **SM1** and **SM2** in diluted chloroform solutions (10^{-5} M) and in thin solid films (90 nm) prepared by spin-coating were recorded as shown in Fig. 1. Benefited from their D–A molecular structures with thiophene π -bridges, the absorption spectra of the compounds in diluted chloroform solutions exhibit strong



Fig. 1 The UV-vis absorption spectra of SM1 (solid lines) and SM2 (dashed lines) (a) in chloroform solutions and (b) in thin solid films.

and broad absorption bands in the wavelength range from 300 to 700 nm with clear vibronic peaks at 360, 440 and 570 nm. The absorption bands at 360 and 440 nm should be commonly ascribed to the π - π * transition of the conjugated backbone, and the absorption band at the longer wavelength region could be attributed to the intramolecular charge transfer (ICT) interaction between their donor moieties and acceptor groups.⁵²

As shown in Fig. 1b, the absorption spectra of the thin solid films display fewer vibronic peaks in comparison with the corresponding solutions, and the absorption band at a longer wavelength is red-shifted and broadened with a slight shoulder at \sim 620 nm. It seems that the relative intensity of the shoulder of the absorption spectrum for SM2 is stronger than that for SM1, giving a further red-shifted and broader absorption band, and it might be attributed to the presence of stronger intermolecular interactions in the solid state. Compared to the absorption peak at 565 nm for the SM1 solution, the SM2 solution has a \sim 9 nm red-shifted band at 574 nm. Similarly, a red-shifted absorption maximum was also observed at 587 nm for the SM2 film, compared with the 576 nm for the SM1 film. Such a difference of these two molecules in the optical absorption should be attributed to the different side chains. The rigid and bulky 4-hexylphenyl substituents seem to offer SM1 a low tendency of self-aggregation compared with the flexible *n*-dodecyl side chains due to the steric hindrance of the side phenyls. The optical band gaps (E_g^{opt}) of **SM1** and **SM2** were estimated to be 1.66 and 1.65 eV, respectively, from the onset of the film absorption spectra (Table 1). In addition, SM1 exhibits higher absorption coefficients of $6.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (565 nm) and 5.0 \times 10⁴ cm⁻¹ (576 nm) in chloroform solutions and in thin solid films, respectively, compared with SM2 (3.0×10^4) M^{-1} cm⁻¹ (574 nm) and 3.2×10^4 cm⁻¹ (587 nm)) (Table 1), indicating a stronger solar light absorption ability which is preferable to light-harvesting.

Electrochemical properties and energy levels

In order to insightfully understand the relationships between the chemical structure and the electronic structure of the resulting materials and consequently provide key parameters for the design of small-molecule-based BHJ solar cells, CV experiments were conducted to measure the HOMO and LUMO energy levels of SM1 and SM2. The potentials were calibrated with the redox couple of ferrocene/ferrocenium (Fc/ Fc⁺) under the same experimental conditions. In the oxidation curves shown in Fig. 2, both the CV curves of SM1 and SM2 in acetonitrile solution show one irreversible p-doping process. The onset oxidation potentials (E_{ox}) versus Ag/AgNO₃ are 0.98 and 0.92 V for SM1 and SM2, respectively. As summarized in Table 1, the HOMO energy levels of SM1 and SM2 are estimated to be -5.52 and -5.46 eV, respectively, according to an equation of $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.54)$ (eV).⁵³ Because the reliable onset reduction potentials of these materials are hardly gained, their LUMO energy levels are thus estimated from the HOMO energy levels and the E_{g}^{opt} based on the relation of $E_{LUMO} = E_{HOMO} + E_{g}^{opt}$. The LUMO energy levels are calculated to be -3.86 and -3.81 eV

Table 1 The optical and electrochemical properties of SM1 and SM2

Compounds	Solution		Film				
	λ_{\max} (nm)	${\epsilon \choose M^{-1} cm^{-1}}$	λ_{\max} (nm)	$\stackrel{arepsilon}{(\mathrm{cm}^{-1})}$	$E_{ m g}^{ m opt}$	НОМО	LUMO
SM1 SM2	565 574	$6.0 imes10^4\ 3.0 imes10^4$	576 587	$5.0 imes10^4\ 3.2 imes10^4$	1.66 1.65	$-5.52 \\ -5.46$	$-3.86 \\ -3.81$



Fig. 2 Cyclic voltammograms of the SM1 (solid line) and SM2 (dashed line) films on the Pd/C electrode in an anhydrous acetonitrile solution of 0.1 mol L^{-1} Bu₄NPF₆ with a scan rate of 100 mV s⁻¹. The arrows indicate the onset oxidation potentials (E_{ox}).

for **SM1** and **SM2**, respectively, as listed in Table 1. Because the V_{oc} is proportional to the energy difference between the HOMO energy level of the electron donor and the LUMO energy level of the electron acceptor in the active layer of the BHJ solar cells,⁵⁴ such low-lying HOMO energy levels are expected to increase the open circuit voltages in the solar cell devices. It has generally been accepted that the HOMO and LUMO energy levels of the D–A type conjugated molecules are mainly governed by those of the D and A units, respectively. Considering the same conjugated main chain structure, their frontier energy levels are almost the same or change little when different side chain groups are introduced.

Hole mobility

It is generally accepted that the charge carrier transporting abilities of the donor materials can tremendously influence the $J_{\rm sc}$ and FF of the resulting BHJ solar cells and consequently the overall device performance.⁵⁵ The hole mobility of the pristine **SM1** and **SM2** films was measured by the SCLC method with a device configuration of ITO/PEDOT:PSS/**SM1** or **SM2** (90 nm)/MoO₃/Al. As plotted in Fig. 3, the $J_{1/2}$ -V plots of the devices are consistent with the corresponding single charge SCLC fitting curves. The **SM1** and **SM2** films show hole mobilities of 2.05 × 10⁻⁴ and 5.49 × 10⁻⁵ cm² V⁻¹ s⁻¹, respectively. The relatively greater hole mobility of **SM1** with 4-hexylphenyl side chains may be attributed to the fact that the aromatic phenyl side groups

possess delocalized π conjugation, which may be advantageous to the charge transport.

Photovoltaic performance

To evaluate the photovoltaic properties of SM1 and SM2, BHJ solar cells using the small molecules as the donor material were fabricated with the conventional solution spin-coating process. The device structure is ITO/PEDOT:PSS/photoactive layer (90-100 nm)/PFN/Al. The device optimizations were conducted by varying the acceptor and the weight ratios of the donor and the acceptor. Aside from PC₆₁BM, PC₇₁BM was also selected to be as an electron acceptor material due to its stronger lightharvesting ability in the visible region from 440 to 530 nm which can complement the absorption valley of the small molecules.56 In addition, a slightly lower (about 0.1 eV) LUMO energy level of PC71BM offers a larger driving force for charge transfer in the resulting SMSCs.57 Typical current densityvoltage (J-V) characterizations of the fabricated devices under 1 sun illumination (AM 1.5, 100 mW cm^{-2}) are displayed in Fig. 4, and the device performances are summarized in Table 2.

From Fig. 4 and Table 2, one can see the characteristically high $V_{\rm oc}$ of the devices based on **SM1** and **SM2** (>0.8 V) because of their relatively lower-lying HOMO energy levels, which is predominantly determined by the backbone donor moiety. In addition, the $V_{\rm oc}$ of the devices based on **SM1** is 0.03–0.05 V higher than that of the devices based on **SM2** with the same



Fig. 3 The $J_{1/2}-V$ plots of the devices with a configuration of ITO/ PEDOT:PSS (40 nm)/SM1 or SM2 (90 nm)/MoO₃ (10 nm)/Al. The solid lines are the fitting curves according to the single charge SCLC method.



Fig. 4 Current density–voltage characteristics of the OSC devices in a structure of ITO/PEDOT:PSS (40 nm)/photoactive layer (90–100 nm)/ PFN (5 nm)/Al based on an active layer of SM1 or SM2/PC₆₁BM or PC₇₁BM (1 : 2, w/w) under the illumination of AM 1.5G, 100 mW cm⁻².

acceptor material and their weight ratios due to its further lower-lying HOMO energy level. For the conventional devices with PC61BM as the acceptor material, the active layer of **SM1**:PC₆₁BM with a weight ratio of 1:2 exhibited a high V_{oc} of 0.90 V, a $J_{\rm sc}$ of 4.95 mA cm $^{-2}$, a FF of 0.36, and a PCE of 1.59%. In contrast, the active layer based on SM2:PC₆₁BM with the same weight ratio gave a $V_{\rm oc}$ of 0.87 V, a $J_{\rm sc}$ of 5.00 mA cm⁻², a FF of 0.54, and a PCE of 2.33%. By using PC71BM instead of PC61BM as the acceptor material, the photovoltaic devices based on SM1:PC₇₁BM (1:2, w/w) with a thickness of 100 nm showed a PCE value up to 4.72% with a $V_{\rm oc}$ of 0.87 V, a significantly improved $J_{\rm sc}$ of 9.85 mA cm⁻², and an FF of 0.55. In comparison, the devices based on SM2:PC₇₁BM (1:2, w/w) exhibited a slightly lower $V_{\rm oc}$ of 0.82 V, a very low $J_{\rm sc}$ of 4.27 mA cm⁻², an FF of 0.43, and a PCE of only 1.52%, which is even lower than the devices with PC61BM as the acceptor. Obviously, compared with the SM1/PC₆₁BM devices, the SM1/PC₇₁BM devices showed a 2 times higher J_{sc} and an enhanced FF, which may be attributed to the stronger light absorption from PC71BM and a suitable morphology. Nevertheless, for the SM2 blended with PC71BM, the device performance was lower than that blended with PC₆₁BM. It could be largely attributed to the lower FF which may be due to an undesirable morphology. A further increase of the $PC_{71}BM$ concentration (D : A = 1 : 3, w/w) induced a lower PCE for both **SM1** and **SM2**, possibly due to a reduction in the total light absorption at the same film thickness and undesirable phase segregation, which is critical to the electron-hole charge balance. It is necessary to note that no additive or thermal annealing was utilized for the current device fabrication, and this is an advantage for simplifying the device fabrication and improving the repeatability of the device performance.

To further understand the device performance, the EQE spectra of the fabricated devices were measured as shown in Fig. 5. From the curves, it is observed that all the EQE spectra cover a broad wavelength range from 400 to 700 nm and show a maximum EQE value of 57% at 560 nm, 35% at 470 nm, 31% at 435 nm, and 29% at 467 nm for the SMSCs based on **SM1**:PC₇₁BM (1 : 2, w/w), **SM2**:PC₆₁BM (1 : 2, w/w), **SM1**:PC₆₁BM (1 : 2, w/w), and **SM2**:PC₇₁BM (1 : 2, w/w), respectively. It can be clearly seen that the performance of the above devices is well consistent with the results of the EQE measurements. In addition, the calculated J_{sc} values obtained by the integration of the EQE data for the **SM1** and **SM2**-based devices showed a 3–6% mismatch compared with the J_{sc} values obtained from the J-V measurements. Obviously, the EQE of the devices based on **SM1**:PC₇₁BM is about 2 times higher than that of the devices based on the blend with PC₆₁BM,



Fig. 5 The EQE spectra of the OSC devices in a structure of ITO/ PEDOT:PSS (40 nm)/photoactive layer (90–100 nm)/PFN (5 nm)/Al based on an active layer of SM1 or SM2/PC₆₁BM or PC₇₁BM (1 : 2, w/w).

Table 2A summary of the device performances under the illumination of AM 1.5, 100 mW cm $^{-2}$ for the devices in a structure of ITO/PEDOT:PSS(40 nm)/photoactive layer (90–100 nm)/PFN (5 nm)/Al. At least 10 solar cell devices were fabricated for each composition

Active layer	Ratio (w/w)	$V_{\rm oc}$ (V)	$J_{\rm sc}~({ m mA~cm^{-2}})$	FF (%)	PCE _{max} (PCE _{ave}) (%)
SM1/PC ₆₁ BM	1:2	0.90	4.95	35.7	1.59(1.36)
SM2/PC ₆₁ BM	1:2	0.87	5.00	53.6	2.33(2.09)
SM1/PC ₇₁ BM	1:2	0.87	9.85	55.1	4.72(4.50)
SM2/PC ₇₁ BM	1:2	0.82	4.27	43.4	1.52(1.34)
SM1/PC ₇₁ BM	1:3	0.86	10.16	51.0	4.46(4.20)
SM2/PC ₇₁ BM	1:3	0.83	3.04	42.5	1.07(0.95)

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and it can be attributed to the stronger light absorption of $PC_{71}BM$ and the appropriate film morphology as proven by the following AFM images. For the devices based on **SM2**, the EQE of the devices based on the blend with $PC_{61}BM$ is higher than that of the devices based on the blend with $PC_{71}BM$ due to the unfavourable film morphology. Such a difference in the EQE spectra agrees well with the observed different J_{sc} of the solar cell devices. At the same time, the relatively higher hole mobility of **SM1** may also contribute to the higher EQE of the corresponding SMSCs.

Film morphology

In order to deeply understand the photovoltaic properties of the resulting small molecular materials, the active layer morphology was studied by AFM in the tapping-mode. Similar to the OSC devices, the films for the AFM measurements were also prepared by spin-coating their chloroform solutions on top of the PEDOT:PSS layer, which was spin-coated on the ITO glass substrates. As shown by the topography images presented in Fig. 6, it can be obviously seen that the different side chains of these two small molecules result in substantial morphology variation in the condensed state. The root-mean-square (rms) roughness of the pure SM1, pure SM2, SM1/PC₆₁BM (1 : 2, w/w), SM2/PC61BM (1:2, w/w), SM1/PC71BM (1:2, w/w), and SM2/ PC₇₁BM (1:2, w/w) films are 0.418, 3.753, 0.455, 3.149, 0.439, and 5.715 nm, respectively. The surfaces of the SM1-based films are quite smooth and uniform. The smaller rms roughness of the SM1-based blend films with PC61BM or PC71BM indicates that SM1 has a good miscibility with both PC₆₁BM and PC₇₁BM to give a favourable donor-acceptor interpenetrating network (IPN). The well-defined IPN structure ensures large D-A interfaces and



Fig. 6 Tapping mode AFM topography images (5 \times 5 μ m²) of (a) pure SM1, (b) pure SM2, (c) SM1:PC₆₁BM (1 : 2, w/w), (d) SM2:PC₆₁BM (1 : 2, w/w), (e) SM1:PC₇₁BM (1 : 2, w/w), and (f) SM2:PC₇₁BM (1 : 2, w/w).

efficient percolation channels for charge transport, thus improving the exciton separation and carrier collection efficiency and leading to a high Jsc and FF. In comparison, the films blended with SM2 exhibit a larger roughness, which indicates an unfavourable film morphology that is a major disadvantage for charge separation from the donor to the acceptor, thus leading to lower $J_{\rm sc}$ and FF. From a structural point of view, the intermolecular interactions among the SM2 molecules with flexible aliphatic side chains should be stronger than the SM1 molecules with aromatic 4-hexylphenyl side chains for their stronger self-aggregation tendency, which may greatly increase the phase separation in the blended thin films with the acceptors, as can be observed in the corresponding AFM images. In contrast, there might be π - π intermolecular interactions between the phenyl side groups of the SM1 molecules and PC₆₁BM or PC₇₁BM that may improve their miscibility with each other, leading to a desirable film morphology for exciton separation and charge transport.

Conclusions

Two IDT-core-containing molecules were successfully synthesized and characterized for use in solution-processed small molecular BHJ solar cells. These two molecules employ the same conjugated backbone but different side chains of rigid and bulky aromatic 4-hexylphenyls and flexible aliphatic ndodecyls with the same number of carbon atoms. Such a structural difference in the side chains combined with the central IDT moiety leads to different intermolecular interactions, self-aggregation tendency, film morphology, charge transport ability, and thus device performance, as evidenced by the results from thermogravimetric analysis, optical absorption, cyclic voltammetry, the single carrier space charge limited current, and AFM topography images. Compared with the ndodecyl side chains, the introduction of 4-hexylphenyl side chains onto the IDT unit significantly improves the solar light absorption and gives a favourable blend film morphology for exciton separation and charge transport, leading to a high PCE of 4.72% under the illumination of AM. 1.5, 100 mW cm $^{-2}$. The current results indicate the potential impact of the aromatic or aliphatic side chains of the donor molecules with the same backbone on the performance of the SMSCs to guide the next molecular design for highly efficient OSCs.

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