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A bipolar small molecule based on indacenodithiophene and diketopyrrolopyrrole for solution processed organic solar cells[†]

Huitao Bai,^{ab} Pei Cheng,^{ab} Yifan Wang,^{ab} Lanchao Ma,^{ab} Yongfang Li,^a Daoben Zhu^a and Xiaowei Zhan^{*ac}

A new linear A–D–A type low band gap small molecule (IDT-2DPP) based on 4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene (IDT) and 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP) was designed and synthesized by Pd-catalyzed Stille coupling reaction. IDT-2DPP exhibits good solubility and good thermal stability with a decomposition temperature of 395 °C. IDT-2DPP shows strong absorption from 500 to 700 nm with a high molar extinction coefficient of 1.3×10^5 M⁻¹ cm⁻¹ at the absorption peak (640 nm) in chloroform solution. The HOMO and LUMO levels of IDT-2DPP were estimated to be –5.11 and –3.32 eV, respectively. Solution processed bulk-heterojunction solar cells using IDT-2DPP as a donor material blending with PC₇₁BM as an acceptor yielded a power conversion efficiency of 2.82%, and solar cells using IDT-2DPP as an acceptor material blending with P3HT as a donor yielded a power conversion efficiency of 0.83% with a high V_{oc} of 1.17 V.

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1. Introduction

Regarded as promising candidates for renewable energy sources, organic photovoltaic cells (OPV) have attracted considerable interest among scientific community because of their advantages such as solution processability, low-cost, lightweight and large area preparation.¹⁻⁸ Over the last few decades, great effort has been devoted to improving the power conversion efficiency (PCE) of solution processed polymer solar cells (PSCs). By optimizing polymer structure and device architecture, PCEs of over 8% have been achieved based on polymer donors and fullerene acceptors.⁹⁻¹⁵ To date, the highest PCE of PSCs achieved is 10.6%.¹⁶

Small molecules possess some advantages over their polymer counterparts such as well-defined structure, definite molecular weight, simple synthesis, and high purity without batch to batch variations.^{17–20} Recently, a variety of small molecule donor materials containing triphenylamine,^{21–27} diketopyrrolopyrrole,^{28–32} benzo[1,2-*b*:4,5-*b'*]dithiophene,^{32–36} silolo[3,2-*b*:4,5-*b'*]dithiophene^{37–40} and oligothiophenes^{41–44} have been designed and synthesized, and have achieved encouraging PCEs up to over 8%.

In recent years, an indaceno[2,1-b:6,5-b']dithiophene (IDT) unit has been attracting considerable attention due to its excellent performance in constructing conjugated polymers for organic field-effect transistors (OFETs) and PSCs.45-51 Due to the rigid and coplanar structure of the IDT unit, conjugated polymers based on IDT exhibited strong intermolecular π - π interaction, which could enhance the π conjugation degree and lead to high hole mobility.52 When applied in OPVs, IDT based low band gap conjugated polymers exhibited broad absorption and relatively high molar extinction coefficient, which is beneficial to obtaining high short circuit current (J_{sc}) .⁵³ Some IDT based polymers have been synthesized and explored in OPV application.52,54-56 PSCs based on blends of IDT polymer donors and PC71BM acceptor yielded the best PCE of 7.51%.54 PSCs based on blends of IDT polymer acceptors and poly(3-hexylthiophene) (P3HT) donor yielded the best PCE of 1.18%.57 However, to our knowledge, there has been only one report on IDT based small molecules for application in OPVs as an electron donor,⁵⁸ but no report on IDT based small molecule electron acceptors.

Diketopyrrolopyrrole (DPP) based semiconductors have been exploited for OFETs and OPVs because of some advantages such as good photochemical stability, excellent charge carrier motilities and superior optical properties.^{59–61} The planar skeleton of DPP and its ability of readily forming hydrogen bonds facilitate π - π stacking, which is beneficial to obtaining high mobilities.^{62,63} OPVs based on DPP polymers and small molecules have exhibited PCEs as high as 6.5% (ref. 60 and 64) and

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^aBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. *E-mail: xwzhan@iccas.ac.cn*

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

^cDepartment of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China

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5.8%,³² respectively, when blending with fullerene acceptors. As a versatile electron deficient unit, DPP was also applied in constructing small molecule acceptors.^{65,66} In our previous work, a PCE of up to 2.05% was achieved when blending DPP based acceptor DBS-2DPP with P3HT.⁶⁶

In this paper, we designed and synthesized a novel bipolar A–D–A type small molecule (IDT-2DPP, Scheme 1) based on IDT as core and DPP as arms. IDT-2DPP exhibited broad and strong absorption in the visible region. OPV devices based on the IDT-2DPP:PC₇₁BM blend exhibited the highest PCE of 2.82%. OPV devices using IDT-2DPP as an acceptor and P3HT as a donor were also fabricated, and achieved the highest PCE of 0.83%.

2. Experimental section

2.1. Measurements and characterization

The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 400 MHz and 600 MHz spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as an internal standard. Elemental analysis was carried out using a FLASH EA1112 elemental analyzer. The mass spectrum was recorded on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Solution (chloroform) and thinfilm (on quartz substrate) UV-vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. Electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile at a potential scan rate of 100 mV s⁻¹ using a computer-controlled Zahner IM6e electrochemical workstation, a glassy-carbon working electrode coated with IDT-2DPP films, a platinum-wire auxiliary electrode, and an Ag wire anodized with AgCl as a pseudo-reference electrode. Potentials were referenced to the ferrocenium/ferrocene $(FeCp_2^{+/0})$ couple by using ferrocene as an external standard. Thermogravimetric analysis (TGA) measurements were performed on a Shimadzu thermogravimetric analyzer (model DTG-60) under a nitrogen flow at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurements were performed using a METTLER differential scanning calorimeter (DSC822e) under nitrogen at a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) of thin films was performed in the reflection mode at 40 kV and 200 mA with Cu-Ka radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer or PANalytical B.V. Empyrean X-ray diffractometer. The nanoscale morphology of the blend film was observed by using a Veeco Nanoscopy V atomic force microscope (AFM) in tapping mode.

2.2. Fabrication and characterization of photovoltaic cells

Organic solar cells were fabricated with the structure: ITO/ PEDOT:PSS/IDT-2DPP:PC71BM/Ca/Al and ITO/PEDOT:PSS/ P3HT:IDT-2DPP/Ca/Al, respectively. The patterned indium tin oxide (ITO) glass (sheet resistance = $15 \Omega \square^{-1}$) was pre-cleaned in an ultrasonic bath of acetone and isopropanol, and treated in an ultraviolet-ozone chamber (Jelight Company, USA) for min. A thin layer (35 nm) of poly(3,4-ethyl-23 enedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Baytron PVP AI 4083, Germany) was spin-coated onto the ITO glass and baked at 150 °C for 20 min. IDT-2DPP:PC71BM (30 mg mL⁻¹ in total) or IDT-2DPP:P3HT (20 mg mL⁻¹ in total) in o-dichlorobenzene (DCB) solvent was spin-coated on the PEDOT:PSS layer to form a photosensitive layer. Thermal annealing was used after spin-coating the active layer. A calcium (ca. 20 nm) and aluminium layer (ca. 100 nm) was then evaporated onto the surface of the photosensitive layer under vacuum (ca. 10^{-5} Pa) to form the negative electrode. The active area of the device was 4 mm². The *J–V* curve was obtained with a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp coupled to AM 1.5G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm⁻². The incident photon to converted current efficiency (IPCE) spectrum was recorded using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled to a WDG3 monochromator and a 500 W xenon lamp. Hole-only or electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/active layer/ Au for holes and Al/active layer/Al for electrons. Mobilities were extracted by fitting the current density-voltage curves using the Mott–Gurney relationship (space charge limited current).

2.3. Materials

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Toluene was distilled from sodium-benzophenone under nitrogen prior to use. Compound 1 (ref. 46) and compound 2 (ref. 29) were synthesized according to the literature.

2.4. Synthesis

To a three-necked round bottom flask were added compound **1** (123.3 mg, 0.1 mmol), compound **2** (132.6 mg, 0.22 mmol) and toluene (20 mL). The mixture was degassed with argon for 15 min, and then $Pd(PPh_3)_4$ (30 mg, 0.026 mmol) was added. The



Fig. 1 (a) TGA curve of IDT-2DPP and (b) DSC curve of IDT-2DPP.

mixture was refluxed for 24 h and then cooled to room temperature. 5 mL aqueous KF (0.1 g mL⁻¹) solution was added and stirred at room temperature overnight to remove the tin impurity. 100 mL water was added and the mixture was extracted with CHCl₃ (2 × 100 mL). The organic phase was dried over anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography on silica gel using petroleum ether-CHCl₃ (1 : 2) as eluent yielding a blue black solid (130 mg, 66%). ¹H-NMR (400 MHz, CD₂Cl₂): δ 8.90 (d, *J* = 4 Hz, 2H), 8.83 (s, 2H), 7.60 (s, 2H), 7.48 (s, 2H), 7.32 (d, *J* = 4 Hz, 2H), 7.24 (m, 4H), 7.19 (d, *J* = 8 Hz, 8H), 7.11 (d, *J* = 8 Hz, 8H), 3.98 (m, 8H), 2.57 (t, *J* = 8 Hz, 8H), 1.84 (m, 4H), 1.58



Fig. 2 UV-vis absorption spectra of IDT-2DPP and P3HT in chloroform solution and in thin film. (The line with solid triangles represents the P3HT solution; the line with hollow triangles represents the P3HT film; the line with solid squares represents the IDT-2DPP solution; the line with hollow squares represents the IDT-2DPP film.)

(m, 8H), 1.29 (m, 56H), 0.86 (m, 36H) (see Fig. S1 in the ESI†). ¹³C NMR (150 MHz, CDCl₃): δ 161.93, 161.67, 157.39, 153.94, 143.74, 142.30, 141.95, 141.40, 139.98, 139.78, 138.91, 136.86, 135.35, 135.21, 130.43, 130.09, 128.63, 128.53, 127.99, 127.87, 124.38, 121.15, 117.69, 108.37, 108.24, 63.27, 46.06, 39.33, 39.22, 35.71, 31.84, 31.46, 30.48, 30.36, 29.27, 28.69, 28.50, 23.82, 23.71, 23.20, 23.19, 22.72, 14.21, 14.14, 10.69, 10.64 (see Fig. S2 in the ESI†). MS (MALDI-TOF): *m/z* 1953 (M⁺). Anal. calcd for C₁₂₄H₁₅₀N₄O₄S₆: C, 76.19; H, 7.68; N, 2.86. Found: C, 76.11; H, 7.90; N, 2.58%. $\lambda_{max,s} = 640$ nm (1.3 × 10⁵ M⁻¹ cm⁻¹).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route to IDT-2DPP is outlined in Scheme 1. Stille coupling reaction of compound 1 with compound 2 afforded



Fig. 3 (a) Cyclic voltammogram for IDT-2DPP in CH₃CN-0.1 M Bu₄NPF₆ at 100 mV s⁻¹; (b) the electronic energy level diagram of P3HT, IDT-2DPP and PC₇₁BM.

 Table 1
 Photovoltaic parameters of solar cells using IDT-2DPP as donor and acceptor

| Blend | Ratio (wt%) | $V_{\rm oc}$ (V) | $J_{\rm sc}$ (mA cm ⁻²) | FF (%) | PCE (%) |
|----------------------------|----------------|------------------|-------------------------------------|-----------|------------|
| | () | 00() | , | () | () |
| IDT-2DPP:PC71BM | 1:1 | 0.87 | 5.26 | 34.8 | 1.59 |
| IDT-2DPP:PC71BM | 1:1.5 | 0.88 | 6.71 | 35.1 | 2.07 |
| IDT-2DPP:PC71BM | 1:2 | 0.86 | 4.87 | 35.3 | 1.49 |
| IDT- | 1:1.5 | 0.88 | 8.53 | 37.6 | 2.82 |
| 2DPP:PC71BMa | | | | | |
| IDT-2DPP:P3HT | 1:0.8 | 1.13 | 0.78 | 36.5 | 0.32 |
| IDT-2DPP:P3HT | 1:1.2 | 1.13 | 1.05 | 38.2 | 0.45 |
| IDT-2DPP:P3HT | 1:1.8 | 1.15 | 0.66 | 36.8 | 0.28 |
| IDT-2DPP:P3HT ^a | 1:1.2 | 1.17 | 1.43 | 49.5 | 0.83 |
| | | | | | |

^a Annealing at 130 °C for 15 min.



Fig. 4 (a) J-V characteristics of the solar cells based on IDT-2DPP/ PC₇₁BM (1 : 1.5, w/w) and P3HT/IDT-2DPP (1.2 : 1, w/w) under the illumination of AM 1.5G, 100 mW cm⁻²; (b) the IPCE spectra. (The line with solid squares represents the as-cast IDT-2DPP/PC₇₁BM blend; the line with hollow squares represents the annealed IDT-2DPP/PC₇₁BM blend; the line with solid triangles represents the as-cast P3HT/IDT-2DPP (1.2 : 1, w/w) blend; the line with hollow triangles represents the annealed P3HT/IDT-2DPP (1.2 : 1, w/w) blend.)

IDT-2DPP in 66% yield. IDT-2DPP is soluble in common organic solvents such as dichloromethane, dichlorobenzene and chloroform at room temperature. The thermal properties of IDT-2DPP were investigated by TGA and DSC methods. The material exhibits excellent thermal stability with a decomposition temperature (T_d , 5% weight loss) of 395 °C in a nitrogen atmosphere (Fig. 1a). According to the DSC traces in Fig. 1b, IDT-2DPP shows glass transition at *ca.* 100 °C, and no melting peak from room temperature to 250 °C, indicating that it is amorphous. This result is also supported by the melting point measurement and X-ray diffraction (XRD) pattern of IDT-2DPP (see Fig. S3 in the ESI†). The phenyl alkyl substituents on the IDT seem to hinder any proper alignment of this molecule, making the films amorphous.

3.2. Optical properties

The UV-vis absorption spectra of IDT-2DPP and P3HT were recorded in chloroform solution (10^{-6} M) and in thin solid film and are shown in Fig. 2. IDT-2DPP exhibits strong absorption in solution with a maximum molar extinction coefficient of 1.3×10^5 M⁻¹ cm⁻¹ at 640 nm. IDT-2DPP shows a broader absorption band in film relative to that in solution. The optical band gap estimated from the absorption edge (712 nm) of the thin film is 1.74 eV. The absorption peak of IDT-2DPP in thin solid film is located at 620 nm, while the absorption peak of P3HT in thin solid film is located at 520 nm. The complementary absorption of IDT-2DPP and P3HT is beneficial to harvesting light in the visible region when using IDT-2DPP as an acceptor to blend with P3HT.

3.3. Electrochemical properties

The electrochemical properties of IDT-2DPP were studied by the cyclic voltammetry (CV) method with IDT-2DPP films on glassy carbon as working electrodes in acetonitrile solution containing 0.1 mol L⁻¹ Bu₄NPF₆. IDT-2DPP exhibits irreversible oxidation and quasi-reversible reduction waves (Fig. 3a). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of IDT-2DPP are estimated to be -5.11 and -3.32 eV from the onset oxidation and reduction potentials, assuming the absolute energy level of FeCp₂^{+/0} to be 4.8 eV below vacuum. The electrochemical band gap (LUMO-HOMO) estimated by CV is 1.79 eV, which is close to the optical band gap (1.74 eV).

As shown in Fig. 3b, the LUMO gap (0.58 eV) and HOMO gap (0.35 eV) between P3HT and IDT-2DPP and the LUMO gap (0.68 eV) and HOMO gap (0.69 eV) between IDT-2DPP and PC₇₁BM are large enough to guarantee efficient exciton dissociation. The difference between the HOMO of P3HT and the LUMO of IDT-2DPP is as large as 1.44 eV, while the difference between the HOMO of PC₇₁BM is 1.11 eV, which is beneficial to obtaining a high open-circuit voltage.

3.4. Photovoltaic properties

Bulk heterojunction (BHJ) solar cells were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/active layer/Ca/Al by using IDT-2DPP as a donor or acceptor material to blend with the PC₇₁BM acceptor or P3HT donor, respectively. Table 1 summarizes the detailed device characteristics at different donor/acceptor ratios with or without thermal annealing. Fig. 4 shows the *J*–*V* curves (a) and IPCE characteristics (b) of four as-cast and annealed champion devices based on IDT-2DPP/PC₇₁BM (1 : 1.5, w/w) and P3HT/IDT-2DPP (1.2 : 1, w/w) under AM 1.5G illumination at an intensity of 100 mW cm⁻².

The ratio of donor to acceptor slightly affects V_{oc} and fill factor (FF) but strongly affects the short circuit current density (J_{sc}). Before thermal annealing, the best PCE of 2.07% was obtained at a ratio of 1 : 1.5 for the IDT-2DPP/PC₇₁BM blend and 0.45% at a ratio of 1.2 : 1 for the P3HT/IDT-2DPP blend. The PCEs for the IDT-2DPP/PC₇₁BM (1 : 1.5, w/w) blend and for the

P3HT/IDT-2DPP (1.2 : 1, w/w) blend were enhanced to 2.82% and 0.83%, respectively, after thermal annealing at 130 $^{\circ}$ C for 15 min.

Atomic force microscope (AFM) tapping-mode images of IDT-2DPP/PC_{71}BM (1:1.5, w/w) and P3HT/IDT-2DPP (1.2:1,



Fig. 5 AFM height images (3 μ m \times 3 μ m) of (a) as-cast IDT-2DPP/PC₇₁BM (1:1.5, w/w) blend films; (c) annealed IDT-2DPP/PC₇₁BM (1:1.5, w/w) blend films; (e) as-cast IDT-2DPP/P3HT (1:1.2, w/w) blend films; (g) annealed P3HT/IDT-2DPP (1.2:1, w/w) blend films. AFM phase images (3 μ m \times 3 μ m) of (b) as-cast IDT-2DPP/PC₇₁BM (1:1.5, w/w) blend films; (d) annealed IDT-2DPP/PC₇₁BM (1:1.5, w/w) blend films; (f) as-cast P3HT/IDT-2DPP (1.2:1, w/w) blend films; (h) annealed P3HT/IDT-2DPP (1.2:1, w/w) blend films;

w/w) blend films before and after annealing are shown in Fig. 5. The IDT-2DPP/PC₇₁BM blend film exhibits a smooth and uniform surface before (Fig. 5a and b) and after (Fig. 5c and d) thermal annealing in the height images.

The P3HT/IDT-2DPP as-cast film (Fig. 5e) exhibits a typical cluster structure with many aggregated domains in the height image, which decrease after thermal annealing (Fig. 5g). In the phase images, the as-cast blend film exhibits a rough surface (Fig. 5f), which becomes more smooth after thermal annealing (Fig. 5h); the RMS roughness decreases from 2.20 to 1.84 nm.

The space-charge limited current (SCLC) method was used to measure hole and electron mobilities of the blends. Hole-only and electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/IDT-2DPP:PC₇₁BM (1 : 1.5, w/w) or P3HT:IDT-2DPP (1.2 : 1, w/w)/Au for holes and Al/IDT-2DPP:PC₇₁BM (1 : 1.5, w/w) or P3HT:IDT-2DPP (1.2 : 1, w/w)/Al for electrons. Fig. 6 shows the *J*–*V* curves for hole-only (a) and electron-only (b) devices as-cast and annealed at 130 °C for 15 min, and the detailed hole and electron mobility data are summarized in Table 2.

After thermal annealing, the hole mobility of the IDT-2DPP/ $PC_{71}BM$ (1 : 1.5, w/w) blend film slightly increases from 9.88 \times 10⁻⁴ to 1.27 \times 10⁻³ cm² V⁻¹ s⁻¹, while the electron mobility slightly decreases from 2.94 \times 10⁻⁴ to 1.82 \times 10⁻⁴ cm² V⁻¹ s⁻¹.



Fig. 6 J-V curves for (a) hole-only and (b) electron-only devices based on IDT-2DPP/PC₇₁BM (1 : 1.5, w/w) and P3HT/IDT-2DPP (1.2 : 1, w/w) blend films as-cast and annealed at 130 °C for 15 min. (The line with solid squares represents the as-cast IDT-2DPP/PC₇₁BM blend; the line with hollow squares represents the annealed IDT-2DPP/PC₇₁BM blend; the line with solid triangles represents the as-cast P3HT/IDT-2DPP blend; the line with hollow triangles represents the annealed P3HT/IDT-2DPP blend.)

| Blend | Ratio (wt%) | Annealing (°C)/time (min) | $\mu_{\rm h}~({ m cm}^2~{ m V}^{-1}~{ m s}^{-1})$ | $\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})$ |
|-----------------|-------------|---------------------------|---|---|
| IDT-2DPP:PC71BM | 1:1.5 | As cast | 9.88×10^{-4} | $2.94	imes 10^{-4}$ |
| IDT-2DPP:PC71BM | 1:1.5 | 130/15 | 1.27×10^{-3} | 1.82×10^{-4} |
| IDT-2DPP:P3HT | 1:1.2 | As cast | 6.76×10^{-4} | $1.11	imes 10^{-5}$ |
| IDT-2DPP:P3HT | 1:1.2 | 130/15 | 1.58×10^{-3} | 8.16×10^{-5} |

For the P3HT/IDT-2DPP (1.2 : 1, w/w) blend film, the hole mobility increases from 6.76×10^{-4} to 1.58×10^{-3} cm² V⁻¹ s⁻¹, and the electron mobility also increases from 1.11×10^{-5} to 8.16×10^{-5} cm² V⁻¹ s⁻¹. The more smooth surface and more balanced charge transport are beneficial to FF and PCE enhancement after thermal annealing.

4. Conclusions

A new bipolar small molecule IDT-2DPP based on IDT and DPP is designed and synthesized. IDT-2DPP exhibits good solubility and good thermal stability with a decomposition temperature of 395 °C. IDT-2DPP shows strong absorption from 500 to 700 nm with a high molar extinction coefficient of $1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ in chloroform solution, which is complementary to that of P3HT. The HOMO (-5.11 eV) and LUMO (-3.32 eV) levels of IDT-2DPP are also appropriate as a donor blending with PCBM as an acceptor and an acceptor blending with P3HT as a donor. Solution processed bulk-heterojunction solar cells based on IDT-2DPP/PC₇₁BM (1 : 1.5, w/w) yield the best PCE of 2.82% after thermal annealing, and solar cells based on P3HT/IDT-2DPP (1.2 : 1, w/w) yield the best PCE of 0.83% with a high $V_{\rm oc}$ of 1.17 V after thermal annealing.

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