



## Diketopyrrolopyrrole based small molecules with near infrared absorption for solution processed organic solar cells



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### ABSTRACT

Two small molecules DOR2TDPP and DCAO2TDPP with a diketopyrrolopyrrole (DPP) unit as the central building block have been designed and synthesized for solution-processed bulk-heterojunction (BHJ) solar cells. The two molecules in films exhibited broad absorption ranging from 300 to 900 nm with optical bandgaps of around 1.40 eV. The BHJ solar cell devices based on the DOR2TDPP and DCAO2TDPP as donors and PC<sub>71</sub>BM as acceptors gave a PCE of 2.05% and 1.09%, respectively, under the illumination of AM.1.5G, 100 mW cm<sup>-2</sup>. The influence of blend ratio of donor/acceptor and amount of additive on the performance of the solar cell were studied systematically.

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### 1. Introduction

Organic solar cells (OSCs) have attracted great attentions due to the potential advantages such as low cost, flexibility and etc. In contrast to the widely studied polymer based OSCs, small molecular organic solar cells (SM-OSCs) demonstrated many outstanding advantages, such as well-defined structure and definite molecular weight, easiness to purification, and thus little batch-to-batch variation. Recently, the power conversion efficiency (PCE) of ~10% [1–3] has been achieved for SM-OSCs, indicating that the PCE of SM-OSCs could be indeed comparable with that of polymer solar cells [4–11] and even higher PCEs could be expected for SM-OSCs through combination of delicate molecule design and device

optimization. The PCE of OSC are determined by three parameters, open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ) and fill factor (FF). Generally, SM-OSCs have a high  $V_{oc}$  and FF over 70% have also been achieved for many SM-OSCs. So, to improve the  $J_{sc}$  without sacrificing the  $V_{oc}$  and FF is one of the effective strategies to get high PCE for OSCs. There are many methods to improve the  $J_{sc}$ , such as active layer morphology controlling by adding additives [12–14], thermal annealing [15], solvent vapor annealing [16,17], modification of buffer layer [18], applying anti-reflection coating [19,20], and so on. In fact, the direct and fundamental strategy to improve the  $J_{sc}$  is to design new donor molecules with broad light absorption range and high harvest efficiency.

The diketopyrrolopyrrole (DPP) unit, as a well known dye unit with many excellent properties such as strong light absorption, photochemical stability, good charge carrier mobility and etc., have been widely used not only in polymers based OSCs but also in SM-OPVs. In 2009, a DPP unit based molecule was reported with a PCE of 4.4%, which was the highest PCE in the field of solution processed SM-OSCs at that time [21]. Nowadays, various DPP based small molecules have been designed [22]. All of them have symmetric molecule structures, in which the DPP unit serves as the central core or end unit. Recently, our group have reported series of donor molecules with an acceptor-donor-acceptor (A-D-A) structure and

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PCEs around 10% have been achieved [1–3,23–25]. In order to extend the light absorption range, herein, we introduce the DPP unit as the central core, two electron withdrawing groups (octyl cyanoacetate and 3-octyl rhodanine) as end groups and design two small molecules DOR2TDPP and DCAO2TDPP. As expected, the two molecules exhibit broad and red shift solar absorption in contrast to our reported molecules. Initial PCEs of 2.07% and 1.10% were achieved for the molecules DOR2TDPP and DCAO2TDPP based devices with PC<sub>71</sub>BM as acceptors, respectively.

## 2. Materials and methods

### 2.1. Materials

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. Unless otherwise specified, all the starting materials were purchased from commercial suppliers which were used without any purification. The intermediate M2 was synthesized according to the method we have reported [26].

### 2.2. Instruments and measurements

Nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>13</sup>C NMR) spectra were taken on a Bruker AV400 Spectrometer. MALDI-TOF spectra were performed on a Bruker Autoflex III instrument. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA409PC instrument under nitrogen gas flow with a 10 °C min<sup>-1</sup> heating rate. UV–Vis spectra were obtained with a JASCO V-570 spectrophotometer. The organic molecule films on quartz used for absorption spectral measurement were prepared by spin-coating their chloroform solutions. X-Ray diffraction (XRD) experiments were performed on a Rigaku D/max-2500 X-ray diffractometer with Cu-K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ) at a generator voltage of 40 kV and a current of 100 mA. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based electrochemical analyzer in CH<sub>2</sub>Cl<sub>2</sub> solutions which were carried out at room temperature employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scanning rate was 100 mV s<sup>-1</sup>.

### 2.3. Fabrication and characterization of SM-OSCs

The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/Donor:Acceptor/LiF/Al. The ITO coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and dried by a nitrogen blow. PEDOT:PSS layer was spin-coated (3000 rpm, ca. ~40 nm thick) onto the cleaned ITO surface. The substrates were then placed into an argon-filled glove box after being baked at 150 °C for 20 min. Subsequently, the active layer was spin-coated from different blend ratios (weight-to-weight) of donor (8 mg mL<sup>-1</sup>) and PC<sub>71</sub>BM in chloroform solution at 1700 rpm for 20 s on the ITO/PEDOT:PSS substrate. The active layer thickness was measured using a Dektak150 profilometer. Finally, a ~1 nm LiF layer and a ~80 nm Al layer were deposited on the active layer under high vacuum (<1.5 × 10<sup>-4</sup> Pa) respectively. The effective area of each cell was 4 mm<sup>2</sup>, defined by masks for all the solar cell devices discussed in this work. The current density–voltage (J–V) curves of the photovoltaic devices

were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under simulated illumination at 100 mW cm<sup>-2</sup> AM 1.5G irradiation using a xenon-lamp-based solar simulator (Oriel 96000) in an argon filled glove box. The simulator irradiance was calibrated using a certified silicon diode.

### 2.4. Synthesis

The synthesis routes of DOR2TDPP and DCAO2TDPP are shown in Scheme 1.

#### 2.4.1. Synthesis of compound M1

LDA (2.0 M in hexane, 2.4 ml, 4.8 mmol) was added dropwise to a solution of DPP (1.0 g, 1.9 mmol) in anhydrous tetrahydrofuran (60 ml) at –78 °C under an argon atmosphere, the mixture was stirred for 2 h, then the mixture was stirred at room temperature for 12 h. Afterwards, tri-n-butyltin chloride (1.0 M in THF, 4.8 ml, 4.8 mmol) was added to the mixture at –78 °C and the reaction mixture was stirred for 2 h, then stirred at room temperature for 24 h. The solution was poured into water and the organic phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> for three times, and the merged solution was dried with anhydrous sodium sulfate for over 5 h. Solvent was removed by evaporation under vacuum, the product was obtained as dark pink liquid and used in the next step without further purification.

#### 2.4.2. Synthesis of compound M3

A solution of M2 (2 g, 4.0 mmol) and M1 synthesized above in dry toluene (100 ml) was degassed twice with argon followed by the addition of Pd(PPh<sub>3</sub>)<sub>4</sub> (80 mg, 0.06 mmol). After being stirred at 120 °C for 24 h under argon, the reaction mixture was poured into water (100 ml) and extracted with CHCl<sub>3</sub>. The organic layer was washed with water for three times, and then dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (1:3) to afford compound M3 (1.40 g, 56%) as a blue-black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.868 (s, 2H), 9.028 (d, 2H), 7.629 (s, 2H), 7.367 (d, 2H), 7.189 (s, 2H), 4.112 (m, 4H), 2.893 (m, 8H), 1.739 (m, 10H), 1.329 (m, 67H), 0.905 (m, 24H). MS (MALDI-TOF): calculated for C<sub>80</sub>H<sub>112</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub> [M]<sup>+</sup>, 1358.14; found, 1359.03.

#### 2.4.3. Synthesis of compound DOR2TDPP

A solution of M3 (500 mg, 0.37 mmol) and 3-octyl rhodanine (900 mg, 3.7 mmol) in dry chloroform was degassed twice with argon followed by the addition of three drops of piperidine. After refluxing for 12 h under argon, the reaction mixture was poured into water (300 ml) and extracted with CHCl<sub>3</sub>. The organic layer was washed with water for three times, and then dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and petroleum ether (2:1) to afford compound DOR2TDPP (420 mg, 63%) as a black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ 9.09 (s, 2H), 7.78 (s, 2H), 7.34 (s, 2H), 7.25 (d, 2H), 7.16 (d, 2H), 4.12 (d, 8H), 2.85 (t, 8H), 1.98 (m, 2H), 1.75 (m, 14H), 1.44 (m, 98H), 0.95 (m, 30H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 201.180, 192.168, 167.504, 141.831, 141.497, 141.057, 139.422, 138.967, 137.301, 136.606, 135.525, 134.630, 134.324, 132.311, 131.547, 130.102, 129.316, 126.824, 124.692, 120.887, 108.459, 44.891, 39.369, 31.880, 31.784, 30.399, 30.218, 29.749, 29.536, 29.431, 29.370, 29.341, 29.284, 29.145, 28.434, 26.997, 26.805, 23.607, 23.174, 22.688, 22.641. MS (MALDI-TOF): calculated for C<sub>102</sub>H<sub>146</sub>N<sub>4</sub>O<sub>4</sub>S<sub>10</sub> [M]<sup>+</sup>, 1811.86; found, 1812.83.

#### 2.4.4. Synthesis of compound DCAO2TDPP

A solution of M3 (500 mg, 0.37 mmol) and doctylcyanoacetate (0.78 ml, 3.7 mmol) in dry chloroform was degassed twice with

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