

## Electronic Supplementary Information

### **Dialkoxyphenyldithiophene -based small molecules with enhanced absorption for solution processed organic solar cells**

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## 1. Experimental section

### 1.1 Measurements and instruments

**<sup>1</sup>H-NMR, <sup>13</sup>C-NMR and MALDI-TOF-MS spectra:** <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (400 MHz) spectra were carried out in a Bruker DMX-400 NMR Spectrometer using tetramethylsilane (TMS) as internal standard. MS spectra (MALDI-TOF-MS) were determined on Micromass GCT-MS spectrometer. Element analysis were carried out on Thermo Fisher Scientific Flash EA 1112. DSC results were obtained by using a DSC Q100 V9.0 Build 275 analyzer under purified nitrogen gas flow with a 10°C min<sup>-1</sup> heating rate. **Absorption spectra measurement:** UV-Vis spectra were carried out in a JASCO-V570 spectrophotometer in dilute solutions of chloroform and thin films cast from chloroform solution (10 mg/mL). **Electrochemical properties measurement:** The electrochemical cyclic voltammetry was carried out on an electrochemical workstation (VMP3 Biologic, France) with a Pt plate coated with the organic thin film as the working electrode, A Pt plate as the counter electrode, and a Ag<sup>+</sup>/Ag electrode as the reference electrode in a 0.1 mol L<sup>-1</sup> tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>) solution in acetonitrile. **DFT calculation:** The HOMO and LUMO energy levels were calculated by density functional theory (DFT) at the B3LYP/6-31G(d,p) level. The alkyl groups were replaced by methyl or ethyl for convenience. All the calculations were performed in the gas phase with Gaussian 09 program. **Current density-voltage (*J-V*) measurement:** The *J-V* curves were obtained by a Keithley 2420 source-measure unit. Photocurrent was measured under AM 1.5G spectrum at 100 mW/cm<sup>2</sup> using a Newport Thermal Oriel 92250A-1000 solar simulator. Light intensity is calibrated with a Newport Oriel PN 91150V Si-based solar cell. **External Quantum Efficiency (EQE) measurement:** The EQE measurements of the devices were performed in air with an Oriel QE/IPCE measurement kit (Model QE-PV-SI). **Atomic force microscope (AFM)** images were obtained on a Nanoscope Ia AFM (Digital Instruments) in tapping mode. **Transmission electron microscope (TEM)** images were analyzed with a transmission electron microscope (Tecnai G2F20 U-TWIN, FEI Co., USA). **Grazing-incidence wide-angle X-ray scattering (GIWAXS)** were conducted on a Xenoces-SAXS/WAXS system (wavelength of 1.5418 Å, incidence angle of 0.2°). The AFM, TEM and GIWAXS samples were prepared on

PEDOT:PSS coated ITO substrates using the same preparation conditions as for devices. The **thickness** of active layers were obtained by a Kla Tencor D120 profilometer.

## 1.2 Solar cell fabrication and measurement

A layer (~35 nm) of PEDOT:PSS was spin-coated on a cleaned ITO-coated glass, followed by spin coating of active layers using a solution of small molecules/PC<sub>71</sub>BM. The additive (DIO) was added prior to spin-coating process. Ca/Al cathode (20 nm/100 nm) was then deposited on substrates by physical vapor deposition at a pressure of  $2 \times 10^{-6}$  Torr. Active area of a cell is designed as 0.04 cm<sup>2</sup> controlled by a shadow mask.

## 1.3 Hole-only device fabrication and measurement

Hole mobility of blend films were investigated by a hole-only space-charge limited current (SCLC) method with device structures: ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Ag. A layer (~35 nm) of PEDOT:PSS was spin-coated on a cleaned ITO-coated glass, followed by spin coating of active layers using a solution of small molecules/PC<sub>71</sub>BM. The additive (DIO) was added prior to spin-coating process. MoO<sub>3</sub>/Ag cathode (5 nm/160 nm) was then deposited on substrates by physical vapor deposition at a pressure of  $2 \times 10^{-6}$  Torr. Active area of a device is 0.04 cm<sup>2</sup> controlled by a shadow mask. The dark current density– Voltage (*I-V*) curves were by a Keithley 2420 source–measure unit within the range of 0–5 V and the results were fitted to a space charge limited form as below:

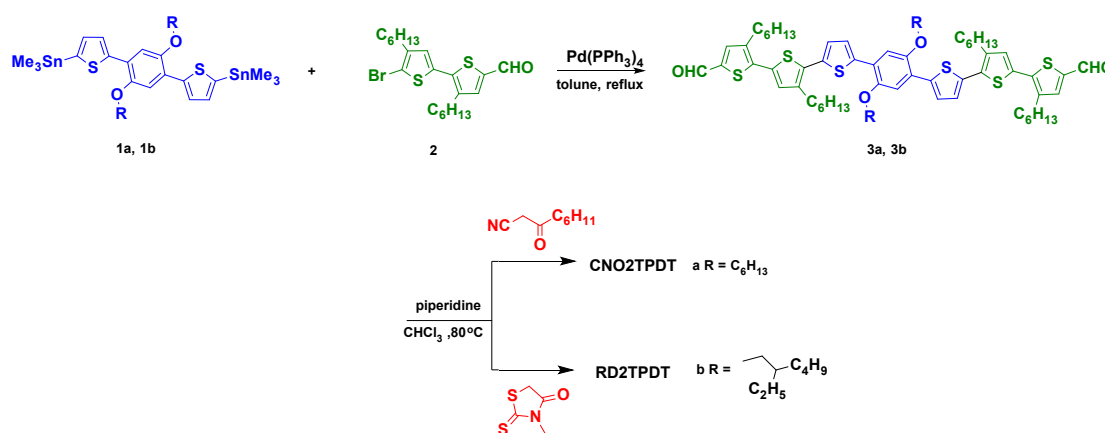
$$I = \frac{9\varepsilon_0\varepsilon_r\mu V^2 A}{8L^3}$$

where *I* is the dark current,  $\varepsilon_0$  is the vacuum permittivity,  $\varepsilon_r$  is the relative permittivity of the transport medium (assumed to be 3),  $\mu$  is the hole mobility, *V* is the internal voltage in device and defined as  $V = V_{appl} - V_{bi}$  (where  $V_{appl}$  is the applied voltage,  $V_{bi}$  is the built-in voltage due to the relatively different workfunction of the two electrodes), *A* is the area of a single cell (defined as 0.04 cm<sup>2</sup>), *L* is the thickness of active layers.

## 1. 4 Materials

All reagents and chemicals were purchased from Aldrich, Alfa and used as received. Solvents and other common reagents were obtained from the Beijing Chemical Plant. Toluene, chloroform and THF were freshly distilled prior to use. Two important intermediates, ((2,5-dialkoxy-1,4-phenylene)bis(thiophene-5,2-diyl))bis(trimethylstannane) (PDT, **compound 1a and 1b**)<sup>1</sup> and 3,4'-dihexyl-2,2'-bithiophene (Br2TCHO, **compound 2**)<sup>2</sup>, were prepared according to the literature.

Scheme S1. Synthesis routes of CNO2TPDT and R2D2TPDT.



### Compound 3a

Compound 1a (2.00 g, 2.60 mmol) and compound 2 (2.87 g, 6.51 mmol) was dissolved in redistilled toluene (60 ml). Pd(PPh<sub>3</sub>)<sub>4</sub> (150 mg, 5%) catalyst was added and the solution was degassed thrice. After stirring and refluxing overnight, the solvent was evaporated under vacuum and the product purified by column chromatography on silica gel using petroleum ether/chloroform (2:1) as eluent to afford **compound 3a** as a red solid (2.1 g, 1.80 mmol, yield: 69.31%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.83 (s, 2H), 7.59 (s, 2H), 7.53 (d, *J* = 4.0 Hz, 2H), 7.28 (s, 2H), 7.18 (s, 2H), 7.15 (s, 2H), 4.14 (t, *J* = 6.6 Hz, 5H), 2.91 – 2.78 (m, 8H), 2.01 – 1.91 (m, 5H). Elem. Anal. calcd for (C<sub>68</sub>H<sub>90</sub>O<sub>4</sub>S<sub>6</sub>): C 70.18, H 7.79, O 5.50, S 16.53; found: C 70.10, H 7.72, O 5.60, S 16.58.

### Compound 3b

Compound 3b was prepared in a similar way to compound 3a using compound 1b (2.00 g, 2.43 mmol) instead, to give **compound 3b** (1.9 g, 1.56 mmol, yield: 64.20%) as a red solid (1.8 g, 1.48 mmol, yield: 60.82%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.81 (s, 2H), 7.55 (d, *J* = 19.2 Hz,

5H), 7.16 (d,  $J = 10.6$  Hz, 4H), 4.11 (d,  $J = 7.5$  Hz, 4H), 2.84 (q,  $J = 7.9$  Hz, 8H). Elem. Anal. calcd for (C<sub>72</sub>H<sub>98</sub>O<sub>4</sub>S<sub>6</sub>): C 70.89, H 8.10, O 5.25, S 15.77; found: C 70.95, H 8.16, O 5.19, S 15.70.

#### **CNO2TPDT.**

Compound 3a (200 mg, 0.172 mmol) and compound 1 (263 mg, 1.72 mmol) was dissolved in a dry chloroform (50 ml), and then piperidine (three drops) was added to the solution under the argon. After stirring and refluxing for 12 hours, the solvent was evaporated under vacuum. The crude product was purified by silica gel using chloroform and petroleum ether (1:2) as eluent to afford **CNO2TPDT** (110 mg, 0.77 mmol, yield: 44.63%) as a black solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.17 (s, 2H), 7.60 (s, 2H), 7.54 (d,  $J = 4.0$  Hz, 2H), 7.28 (s, 2H), 7.22 (s, 2H), 7.19 (d,  $J = 3.9$  Hz, 2H), 4.15 (t,  $J = 6.5$  Hz, 4H), 2.85 (dq,  $J = 7.8, 5.1, 4.6$  Hz, 13H), 2.01 – 1.91 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  193.70, 149.31, 144.08, 142.59, 141.88, 140.52, 140.18, 139.79, 135.50, 134.26, 133.07, 132.13, 131.00, 126.09, 125.61, 122.76, 118.09, 111.94, 104.10, 76.70, 69.81, 40.63, 31.72, 31.62, 31.57, 30.57, 30.11, 29.51, 29.40, 29.37, 29.34, 29.18, 28.80, 25.97, 24.04, 22.67, 22.66, 22.62, 22.51, 14.11, 14.09, 14.07, 14.04, 1.03. *m/z* (MALDI-TOF) 1433.6 ca. for C<sub>86</sub>H<sub>116</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub> 1434.24. Elem. Anal. calcd for (C<sub>86</sub>H<sub>116</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>): C 72.02, H 8.15, N 1.95, O 4.46, S 13.41; found: C 71.90, H 8.09, N 2.00, O 4.57, S 13.44.

#### **RD2TPDT.**

Compound 3b (200 mg, 0.164 mmol) and 3-ethyl-2-thioxothiazolidin-4-one (264 mg, 1.64 mmol) was dissolved in a dry chloroform (50 ml), and then piperidine (1 ml) was added to the solution under the argon. After stirring for 24 hours, the solvent was evaporated under vacuum. The crude product was purified by silica gel using chloroform and petroleum ether (1:1) as eluent to afford **RD2TPDT** (120 mg, 0.80 mmol, yield: 48.59%) as a black solid. <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79 (s, 2H), 7.52 (s, 2H), 7.28 (s, 2H), 7.23 (s, 2H), 7.18 (s, 2H), 7.14 (s, 2H), 4.18 (p,  $J = 9.1, 8.1$  Hz, 8H), 2.84 (s, 8H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  192.28, 167.48, 167.48, 149.45, 141.11, 137.60, 133.36, 130.14, 130.07, 126.05, 125.21, 120.47, 112.14, 112.11, 106.11, 93.52, 69.95, 40.08, 32.00, 31.88, 31.78, 29.59, 29.56, 29.48, 29.45, 29.35, 27.37, 26.45, 25.67, 22.83, 22.77, 14.27, 14.24, 12.45. *m/z* (MALDI-TOF) 1504.3 ca. for C<sub>82</sub>H<sub>108</sub>N<sub>2</sub>O<sub>4</sub>S<sub>10</sub> 1504.55. Elem. Anal. calcd for (C<sub>82</sub>H<sub>108</sub>N<sub>2</sub>O<sub>4</sub>S<sub>10</sub>): C 65.38, H 7.23, N 1.86, O 4.25, S 21.28; found: C 65.52, H 7.12, N 1.97, O 4.23, S 21.16.

## 1.5 Supporting Figures

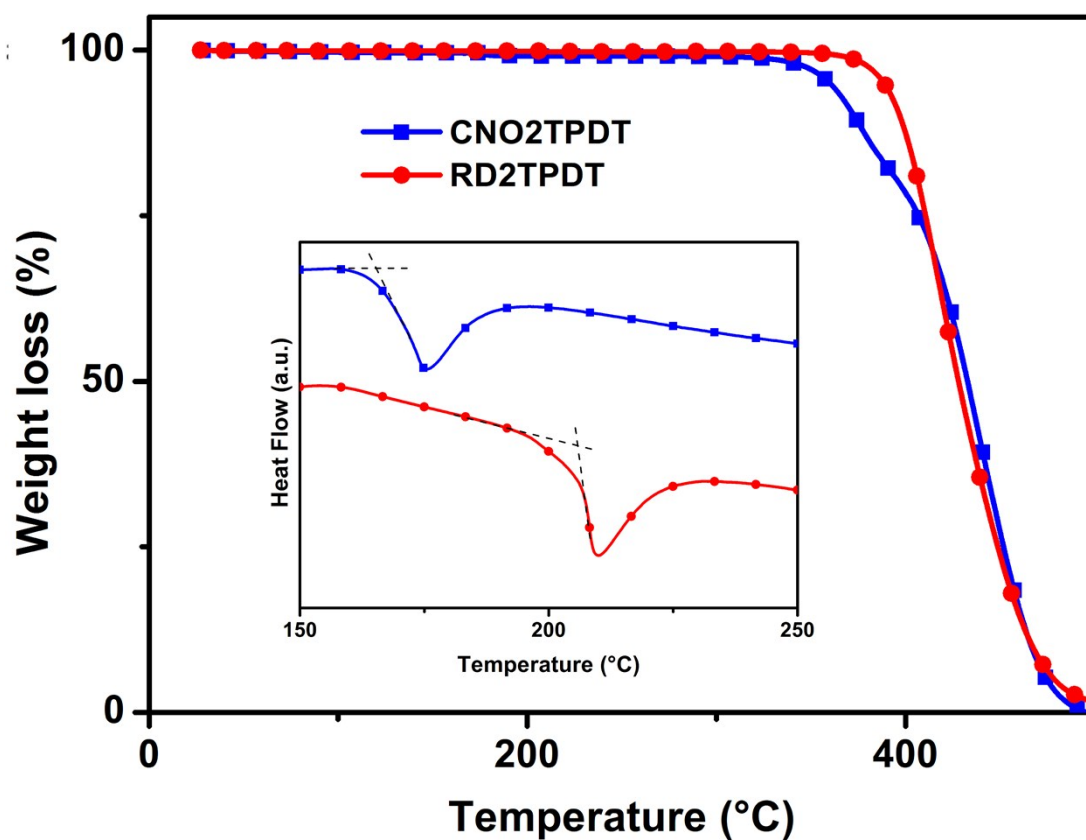


Fig. S1. TGA curve and DSC melting curve (embedded) for small molecules.

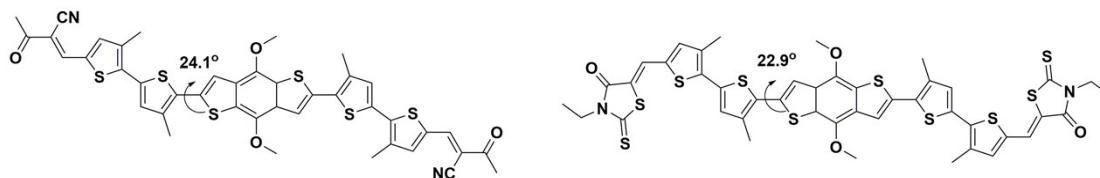


Fig. S2. Chemical structures of BDT analogues.

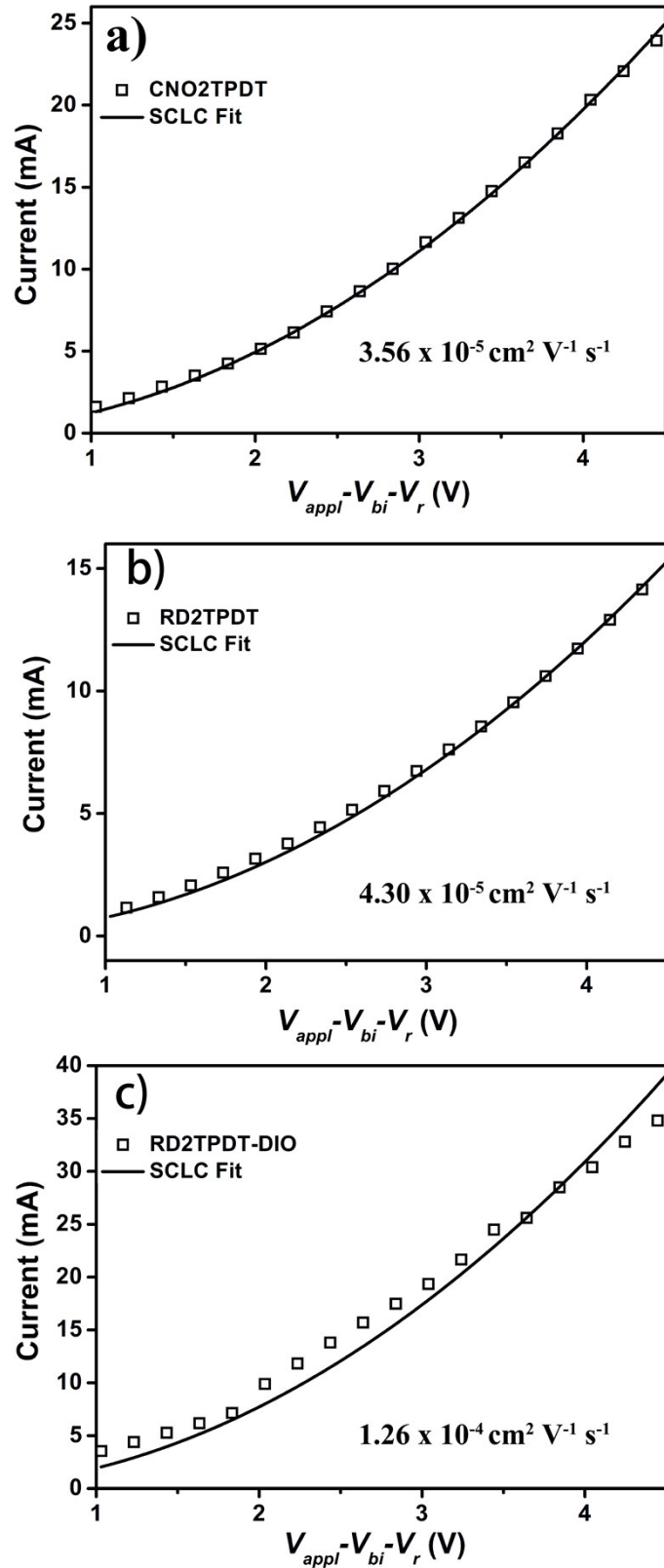


Fig. S3. Typical dark-current-electric field plots for hole only devices: a. CNO2TPDT/PC<sub>71</sub>BM (w/w, 1.5:1); b. RD2TPDT/PC<sub>71</sub>BM (w/w, 1:1); c. RD2TPDT/PC<sub>71</sub>BM (w/w, 1:0.8) with DIO (v/v, 0.8%).

Table S1. Photovoltaic performances of **CNO2TPDT/PC<sub>71</sub>BM** devices under AM 1.5G solar illumination

D:A ratio	Additives	<i>PCE</i> (%)	<i>J<sub>sc</sub></i> (mA cm <sup>-2</sup> )	<i>V<sub>oc</sub></i> (V)	<i>FF</i> (%)
1.5:1	No	4.16	6.74	0.87	67.6
1:1	No	3.27	5.18	0.82	70.6
1:1.5	No	2.63	4.64	0.83	62.6
1.5:1 <sup>a</sup>	No	4.03	6.69	0.84	70.6
1.5:1	0.25% DIO	1.61	4.03	0.75	50.6
1.5:1	0.25% CPE	1.52	3.53	0.72	56.5

<sup>a</sup> Thermal annealing.

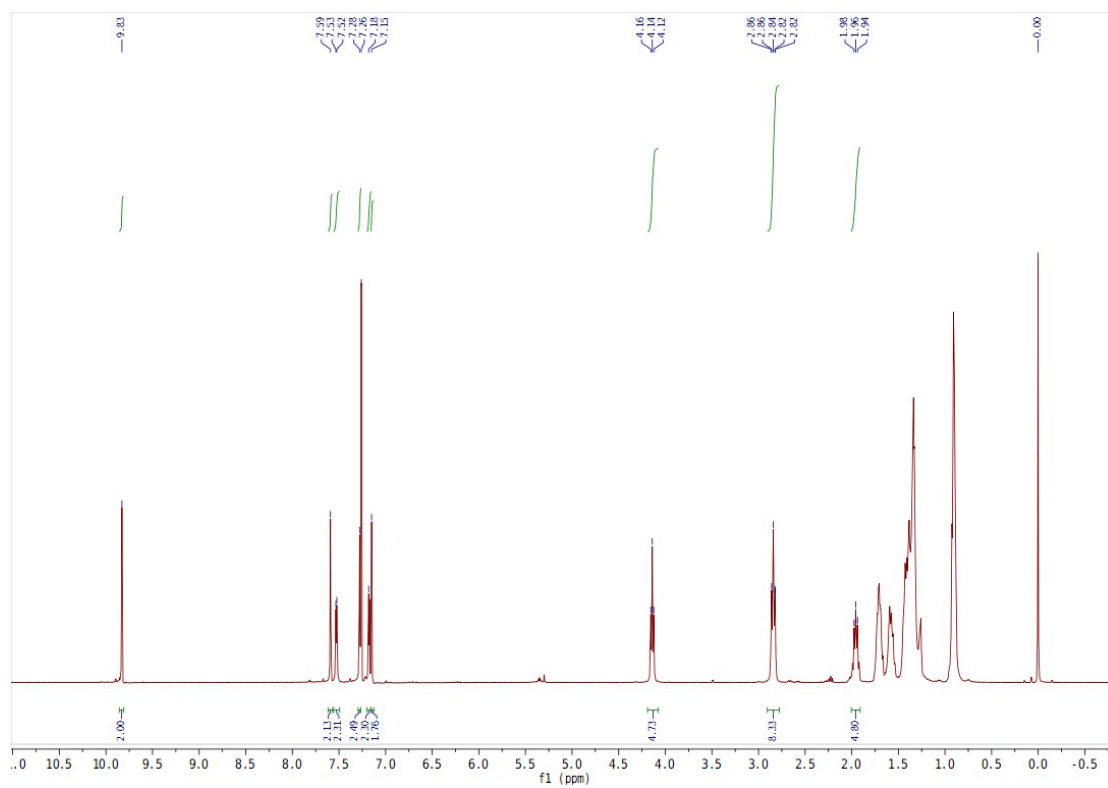
Table S2. Photovoltaic performances of **RD2TPDT/PC<sub>71</sub>BM** devices under AM 1.5G solar illumination

D:A ratio	DIO	<i>PCE</i> (%)	<i>J<sub>sc</sub></i> (mA cm <sup>-2</sup> )	<i>V<sub>oc</sub></i> (V)	<i>FF</i> (%)
1.5:1	0	2.09	7.86	0.79	45.8
1:1	0	3.01	8.85	0.84	39.4
1:1.5	0	4.50	9.77	0.89	50.6
1:1.2	0.8%	6.42	11.96	0.77	68.2
1:1	0.8%	6.54	12.33	0.76	68.5
1:0.8	0.8%	6.64	12.61	0.77	66.8
1:0.8	1.0%	6.60	12.84	0.76	66.1
1:0.8	1.2%	6.40	12.30	0.78	65.4

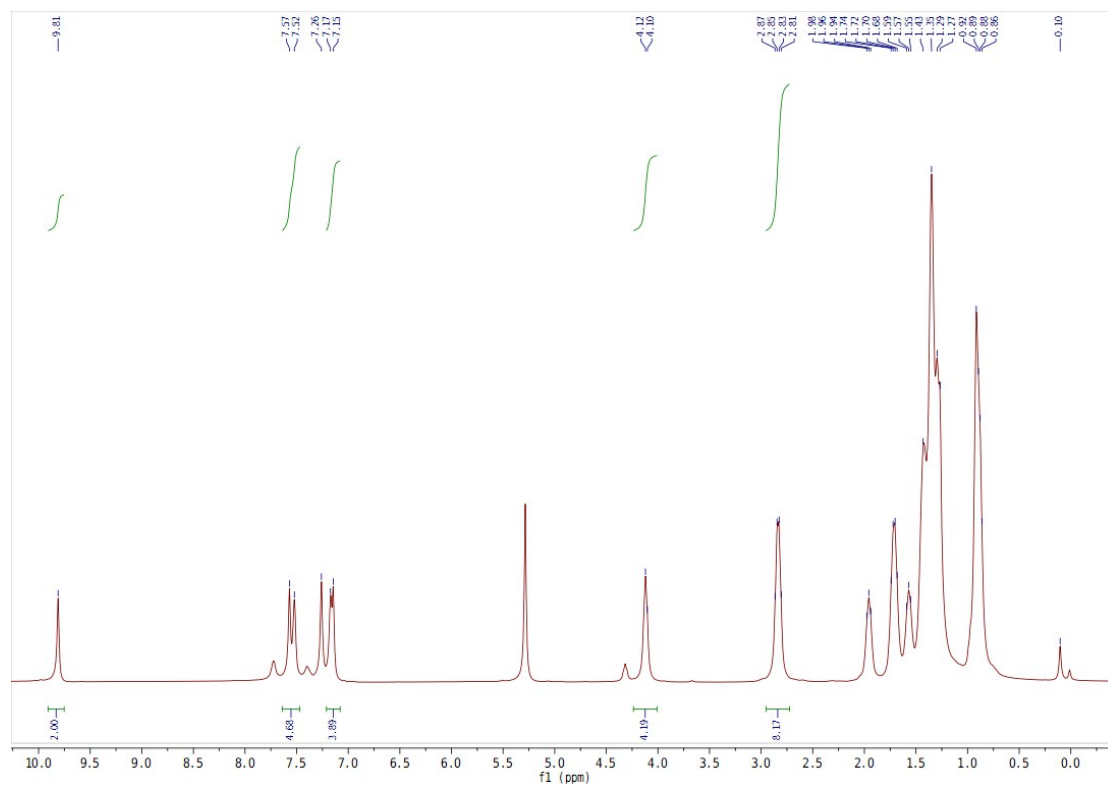


## NMR and MS spectra

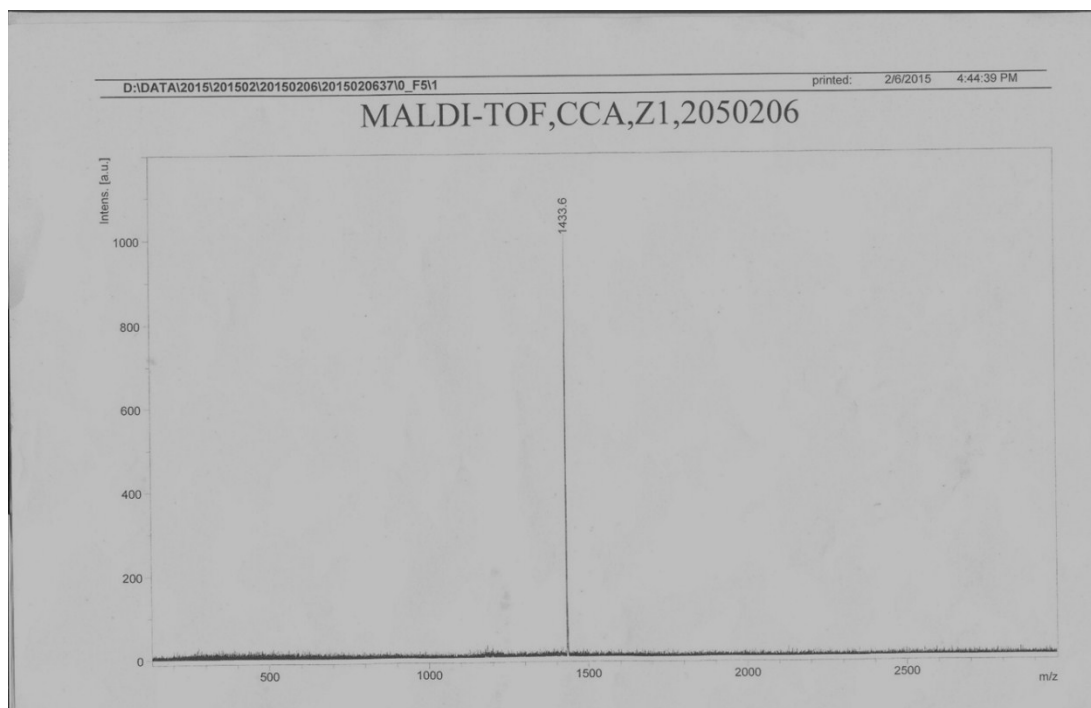
### <sup>1</sup>H-NMR spectra of Compound 3a



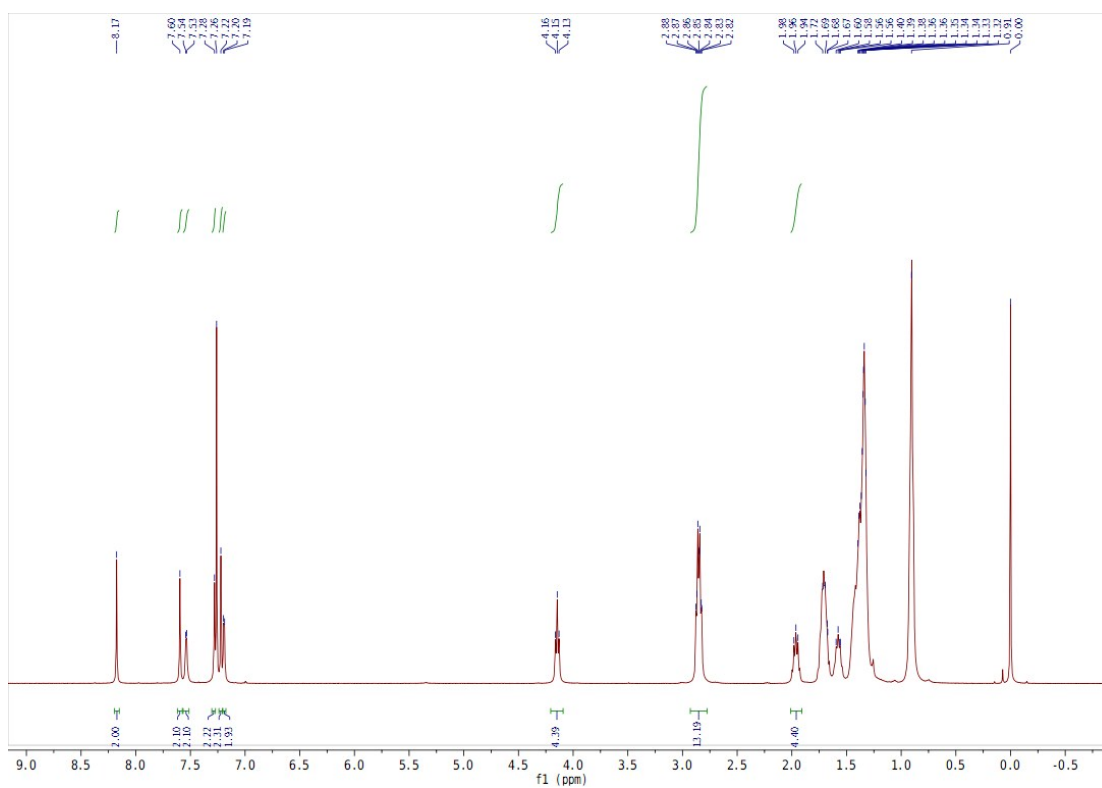
### <sup>1</sup>H-NMR spectra of Compound 3b



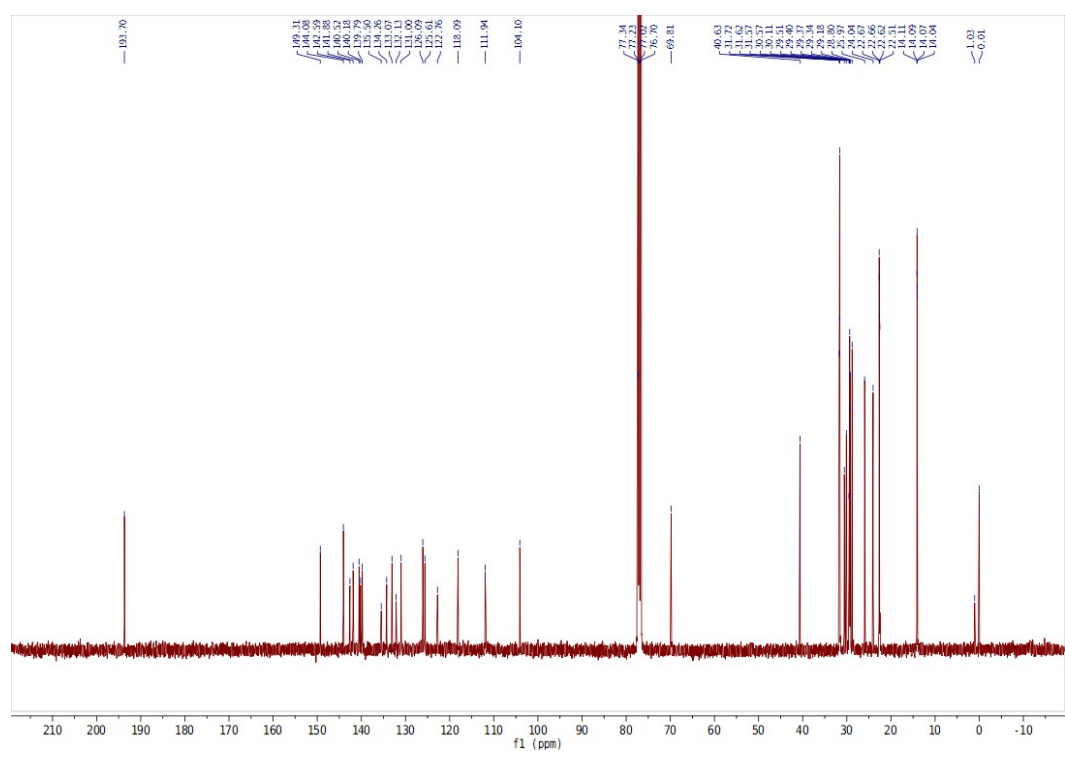
## MS spectra of CNO2TPDT



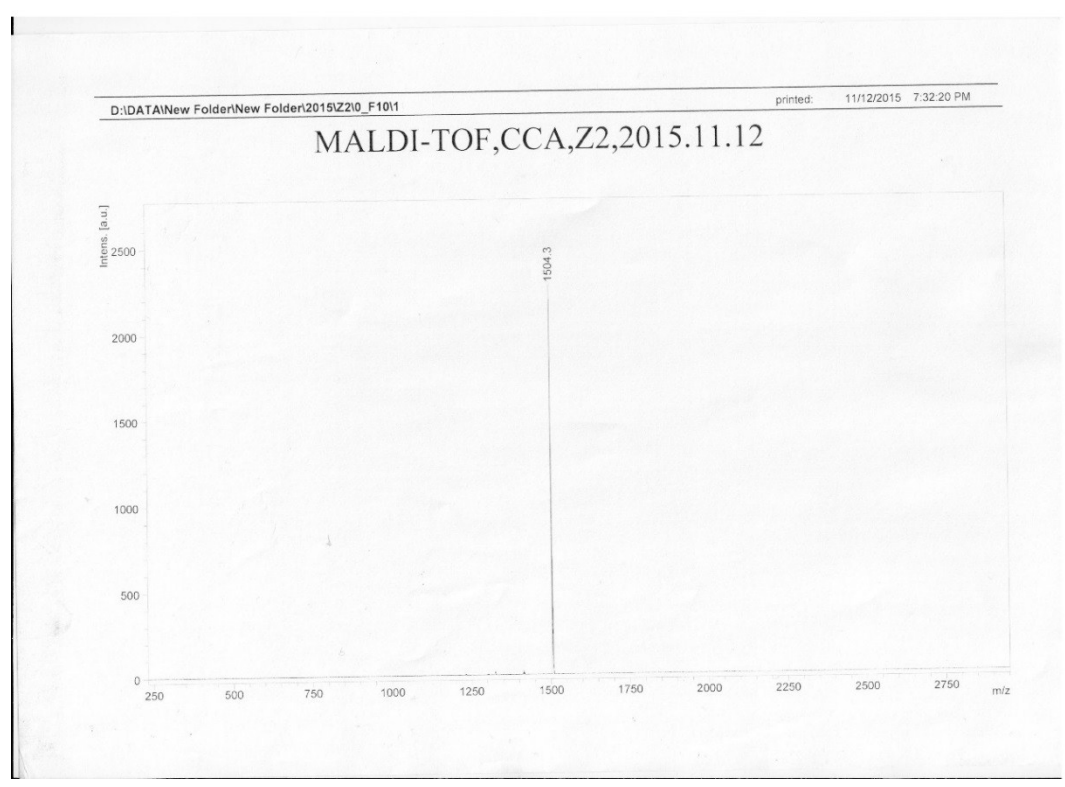
## <sup>1</sup>H-NMR spectra of CNO2TPDT



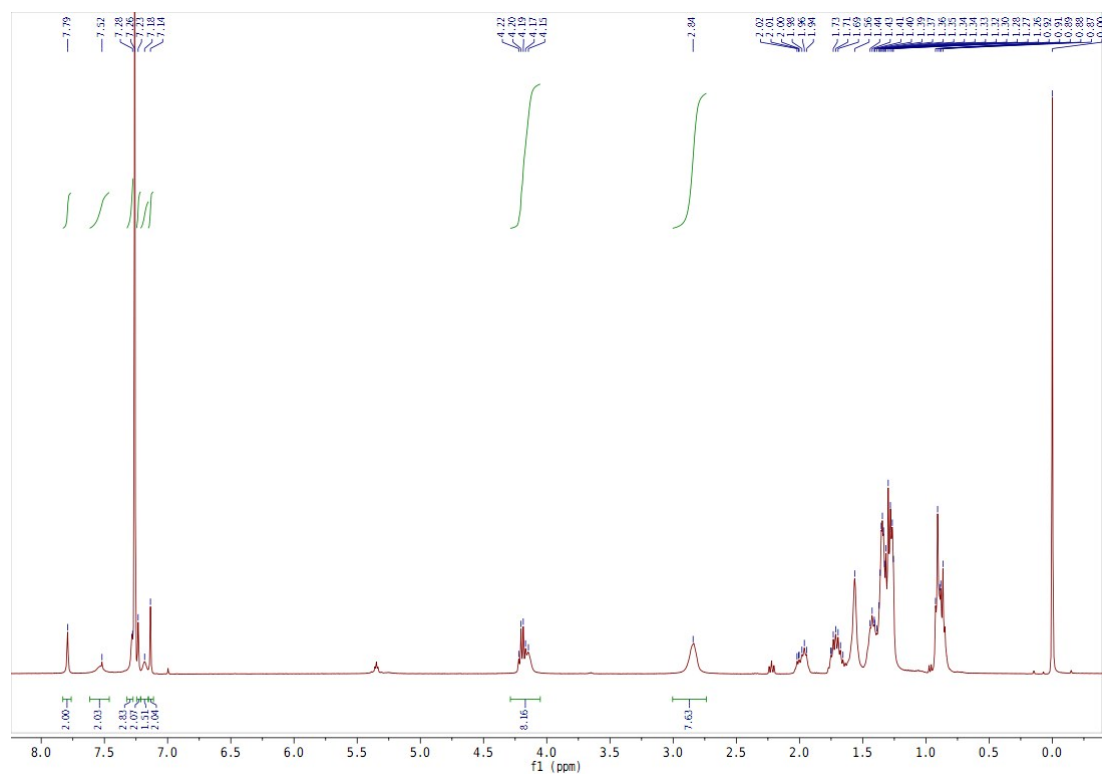
### <sup>13</sup>C-NMR spectra of CNO2TPDT



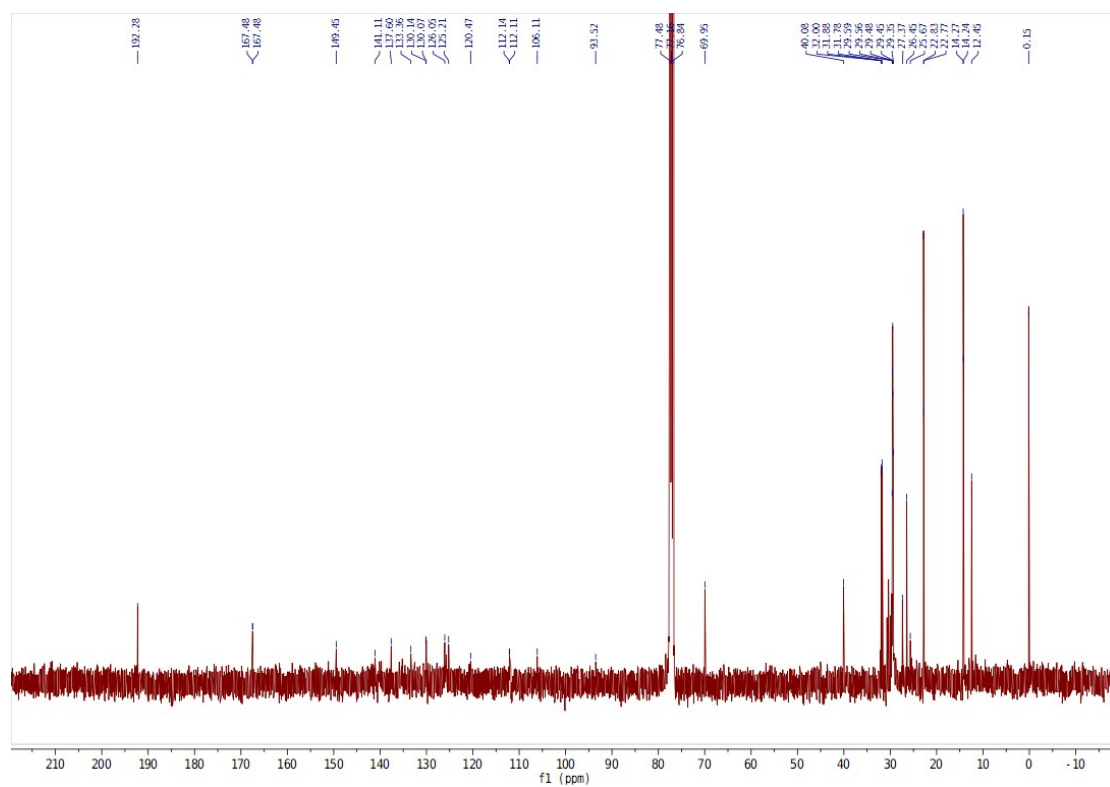
### MS spectra of RD2TPDT



### <sup>1</sup>H-NMR spectra of RD2TPDT



### <sup>13</sup>C-NMR spectra of RD2TPDT



## Reference

1. Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian and Y. Chen, *Adv. Mater.*, 2011, **23**, 5387-5391.
2. J. E. Carlé, J. W. Andreasen, M. Jørgensen and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2010, **94**, 774-780.