

## **Electronic Supplementary Information**

### **A Cyclopentadithiophenes-Bridged Small Molecule Acceptor with Near-Infrared Light Absorption for Efficient Organic Solar Cells**

*Yuan-Qiu-Qiang Yi, Huanran Feng, Xin Ke, Jing Yan, Meijia Chang, Xiangjian Wan,  
Chenxi Li and Yongsheng Chen\**

\*E-mail: [yschen99@nankaie.edu.cn](mailto:yschen99@nankaie.edu.cn)

## Measurements and Instruments

The  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were performed on a Bruker Autoflex III instrument. The thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a  $10\text{ }^\circ\text{C min}^{-1}$  heating rate. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputerbased Electrochemical Analyzer in dichloromethane solutions. All CV measurements were carried out at room temperature with a conventional three-electrode configuration 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 argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was  $100\text{ mV s}^{-1}$ . Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G2 F20 at 200 kV. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

The current density-voltage ( $J$ - $V$ ) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. All masked and unmasked tests gave consistent results with relative errors within 5%. The photocurrent was measured under illumination simulated  $100\text{ mW cm}^{-2}$  AM 1.5G irradiation using an Oriel 96000 solar simulator, calibrated with a standard Si solar cell. The average PCE was obtained using 20 devices under the same conditions. External quantum efficiency (EQE) values of the devices were measured using Stanford Research Systems SR810 lock-in amplifier. The

thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer.

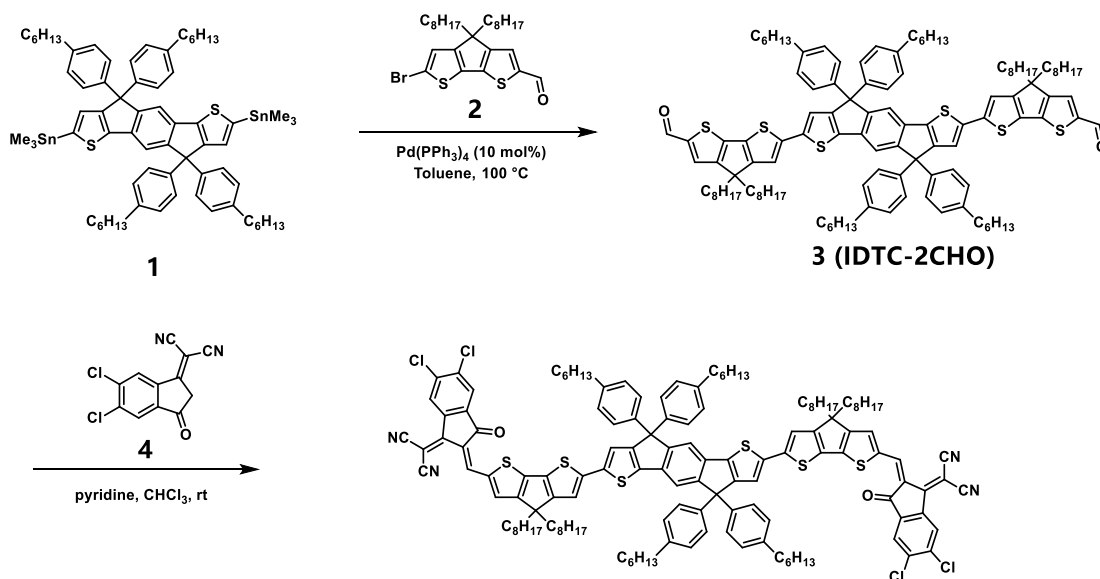
SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/Active layer/Au for hole and Al/Active layer/Al for electron by taking the dark current density in the range of 0-2 V and fitting the results to a space charge limited form, where SCLC is described by:

$$J = \frac{9\epsilon_0\epsilon_r\mu_0V^2}{8L^3} \exp\left(0.89\beta \sqrt{\frac{V}{L}}\right)$$

where  $J$  is the current density,  $L$  is the film thickness of the active layer,  $\mu_0$  is the hole or electron mobility,  $\epsilon_r$  is the relative dielectric constant of the transport medium,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12}$  F m<sup>-1</sup>),  $V$  ( $= V_{\text{appl}} - V_{\text{bi}}$ ) is the internal voltage in the device, where  $V_{\text{appl}}$  is the applied voltage to the device and  $V_{\text{bi}}$  is the built-in voltage due to the relative work function difference of the two electrodes.

## **Material Synthesis and Characterization**

All starting materials were purchased from commercial suppliers and used without further purification unless otherwise indicated.



### Synthesis of Compound 3 (IDTC-2CHO)

A solution of compounds **1** (1.00 g, 0.81 mmol) and **2** (1.03 g, 2.30 mmol) in toluene (80 mL) was degassed with argon for three time. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (1.16 g, 1.00 mmol) was added and the mixture was stirred at 100 °C for 24 h under argon, after which the mixture was added with saturated KF aqueous solution (100 mL), and extracted with EA (50 mL × 2). The organic layer was washed with water and brine, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by a rotating evaporator and the residue was purified by silica gel chromatography to obtain compound **2** (3.84 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.81 (s, 2H), 7.53 (s, 2H), 7.41 (s, 2H), 7.19 (d, *J* = 8.3 Hz, 8H), 7.13 (s, 2H), 7.09 (d, *J* = 8.1 Hz, 9H), 7.01 (s, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 8H), 1.84 (tq, *J* = 13.5, 6.7, 6.2 Hz, 8H), 1.65 – 1.52 (m, 8H), 1.38 – 1.07 (m, 60H), 0.96 (dd, *J* = 10.7, 5.0 Hz, 8H), 0.85 (dt, *J* = 14.0, 6.8 Hz, 24H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 182.41, 171.17, 163.26, 157.78, 156.94, 153.60, 147.62, 143.31, 143.09, 141.80, 141.61, 140.76, 140.17, 135.22, 134.09, 129.90, 128.54, 127.97, 119.72, 117.50, 117.37, 63.17, 60.47, 54.21, 37.78, 35.69, 31.89, 31.83, 31.47, 30.06, 29.42, 29.36, 29.26, 24.68, 22.71, 21.13, 14.31, 14.20.

MS (MALDI-TOF): calcd for C<sub>116</sub>H<sub>146</sub>O<sub>2</sub>S<sub>6</sub> [M<sup>+</sup>], 1764.802; found: 1764.196.

## Synthesis of IDTC-4Cl

Under the protection of argon, compound **3** (0.20 g, 0.11 mmol) and IC-2Cl (0.21 g, 0.88 mmol) was dissolved in a dry CHCl<sub>3</sub> (40 mL) solution, and then pyridine (0.5 mL) was added to the mixture. After stirring at room temperature for 12 h, the mixture was poured into water and then extracted with CHCl<sub>3</sub> (30 ml x 2), the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> for 0.5 h. After removal of solvent, the crude product was purified by silica gel and recrystallized from CHCl<sub>3</sub> and hexane to give IDTC-4Cl as a dark green solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (s, 2H), 8.71 (s, 2H), 7.86 (s, 2H), 7.57 (s, 2H), 7.43 (s, 2H), 7.25 (s, 2H), 7.20 (d, *J* = 8.1 Hz, 8H), 7.12 (d, *J* = 8.1 Hz, 8H), 7.07 (s, 2H), 2.59 (t, *J* = 7.8 Hz, 8H), 2.00 – 1.81 (m, 8H), 1.60 (dd, *J* = 14.2, 6.5 Hz, 8H), 1.43 – 1.08 (m, 72H), 0.98 – 0.86 (m, 12H), 0.82 (t, *J* = 6.9 Hz, 12H).

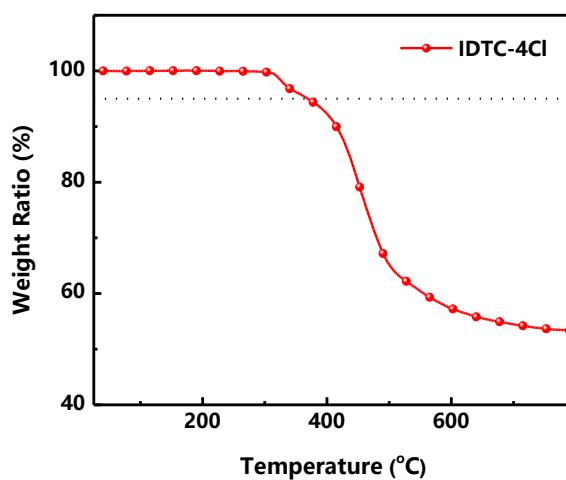
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 186.19, 167.71, 158.40, 157.52, 153.96, 148.21, 142.44, 141.95, 141.16, 139.83, 139.49, 138.92, 138.68, 138.64, 138.29, 135.97, 135.31, 134.87, 128.53, 127.84, 126.66, 124.67, 120.95, 118.46, 117.58, 117.49, 115.10, 114.91, 66.89, 63.12, 54.15, 37.91, 35.59, 31.76, 31.72, 31.37, 29.87, 29.28, 29.23, 29.16, 24.63, 22.60, 14.10, 14.07.

**HR-FTMS**: calcd for C<sub>140</sub>H<sub>150</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>2</sub>S<sub>6</sub> [M<sup>+</sup>], 2254.9260; found: 2254.8935.

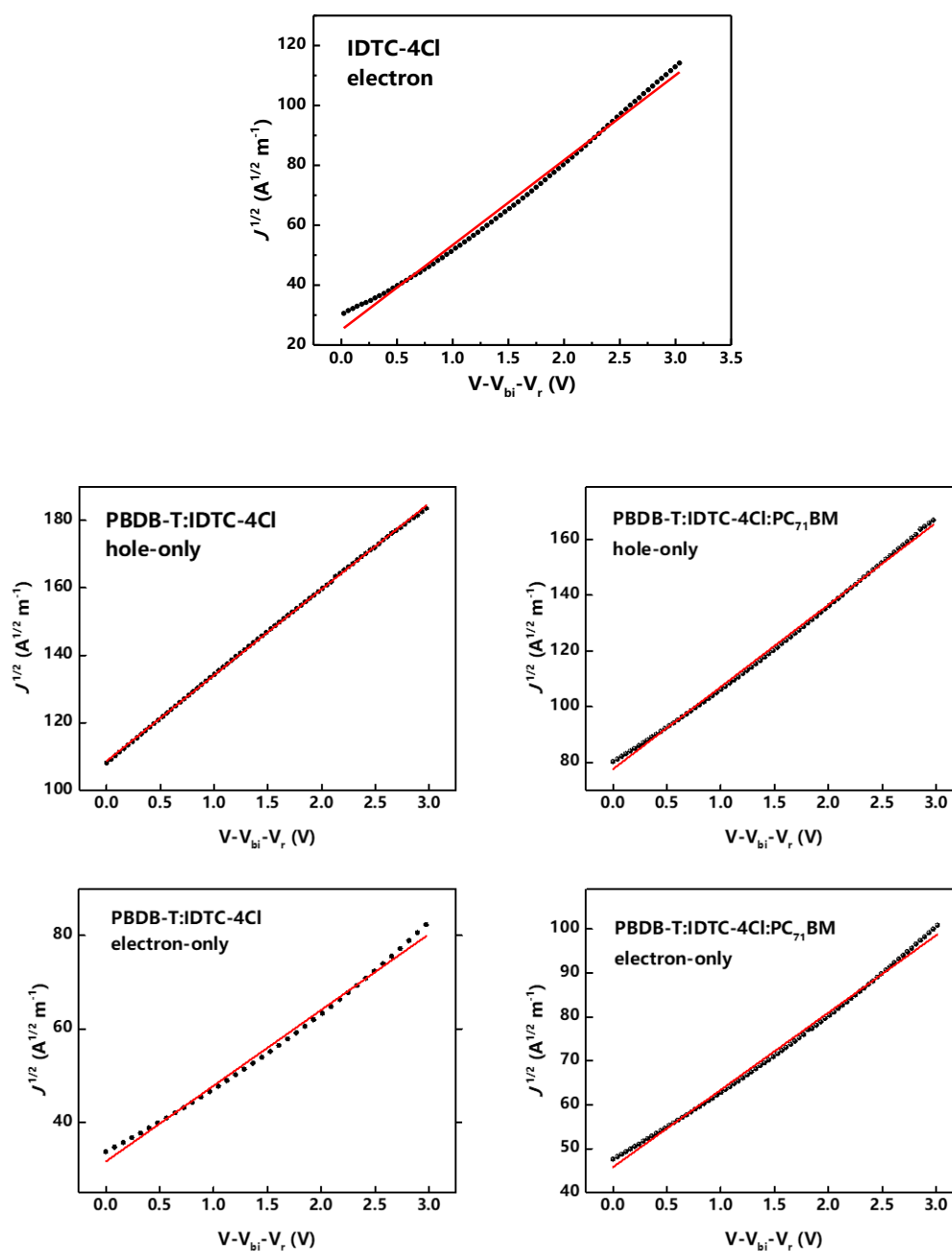
## Fabrication of OPV Devices

The photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/Donor:Acceptor/PDINO/Al. The ITO coated glass substrates were cleaned by indetergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and dried by a nitrogen blow. PEDOT:PSS layer was spin-coated (ca. 30 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.

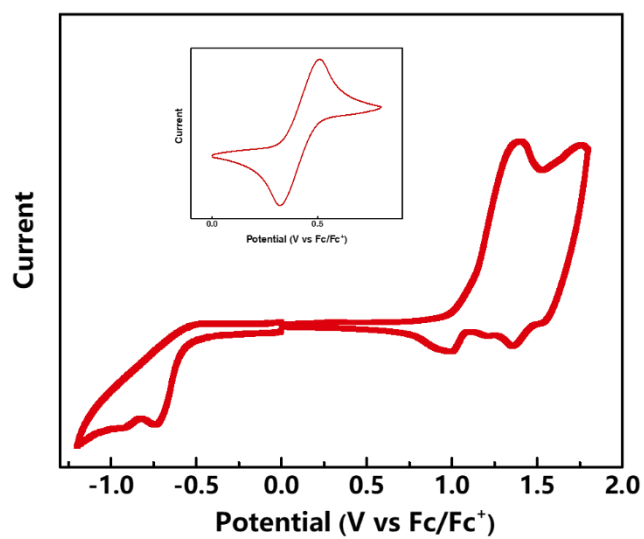
Subsequently, the active layer was spin-coated from donor (5 mg/mL) and acceptor (4 mg/mL) in chloroform solution at 1500 rpm for 20 s on the ITO/PEDOT:PSS substrate. The active layer thickness was measured using a Dektak150 profilometer. And then, PDIN, with the concentration of 1.5 mg/ml using CH<sub>3</sub>OH/AcOH (v:v = 100:0.2%) as mixed solvent, was spin-coated at 3000 rpm for 40 s on the active layer. Finally, a 60 nm Al layer were deposited on the PDINO layer under high vacuum ( $< 1.5 \times 10^{-4}$  Pa). The effective area of each cell was 4 mm<sup>2</sup>, defined by masks for the solar cell devices.



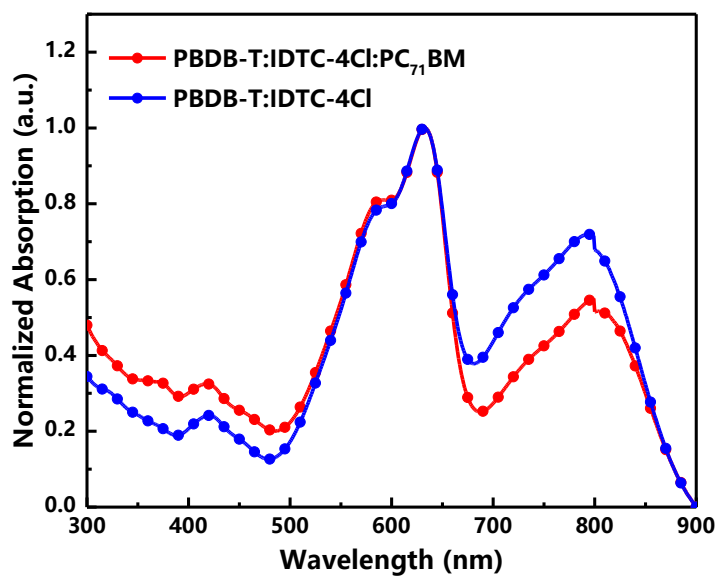
**Figure. S1** TGA curve with a heating rate of 10 °C/min under N<sub>2</sub> atmosphere.



**Figure. S2** Electron-only device based on pure IDTC-4Cl, electron-only and hole-only devices based on PBDB-T:IDTC-4Cl and PBDB-T:BDTC-4Cl:PC<sub>71</sub>BM, respectively. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility. The  $J_D$ - $V$  characteristics are corrected for the built-in voltage  $V_{bi}$  that arises from the work function difference between the contacts.

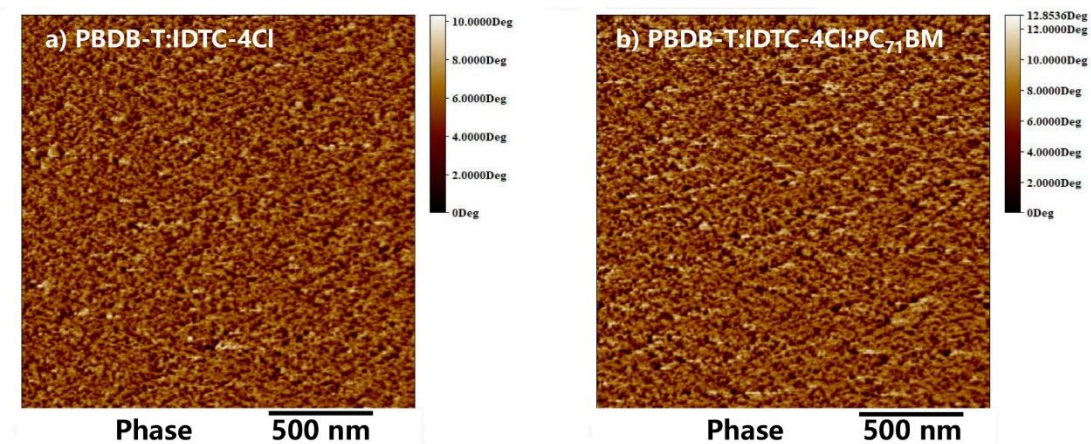


**Figure. S3** Electrochemical properties of IDTC-4Cl.



**Figure. S4** UV-vis-NIR absorptions of IDTC-4Cl based binary and ternary blend films.



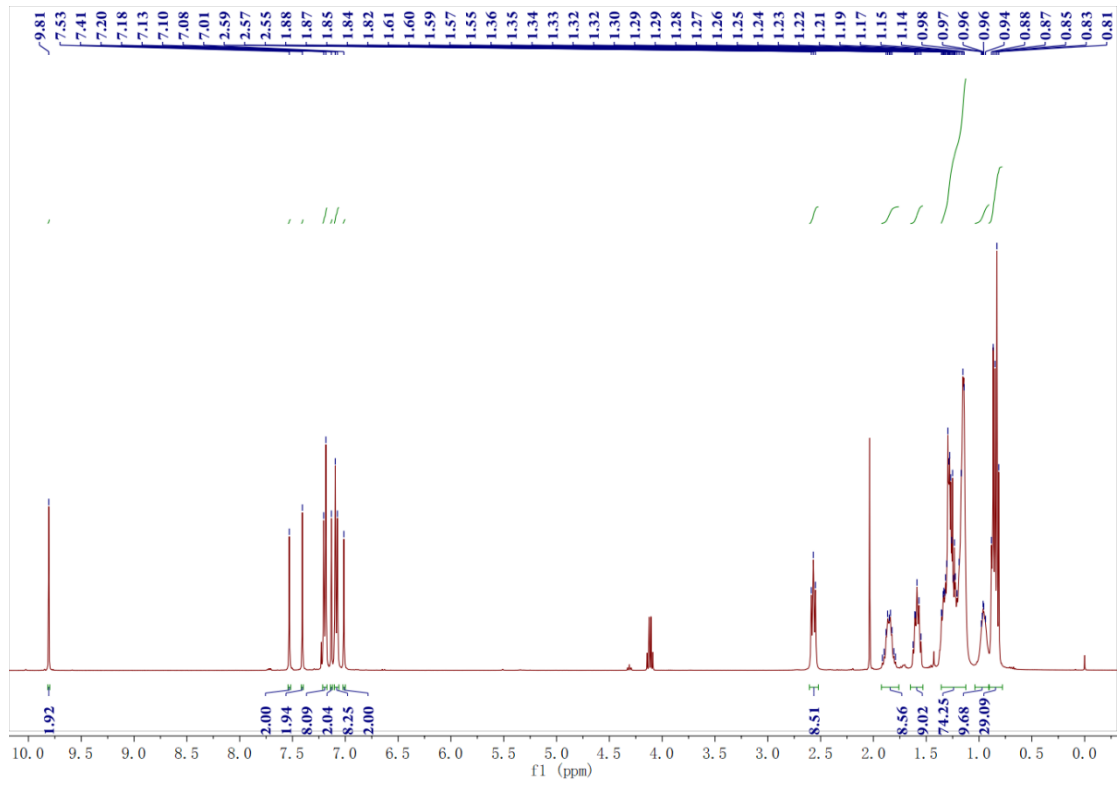


**Figure. S5** AFM phase images of IDTC-4Cl based binary and ternary blend films.

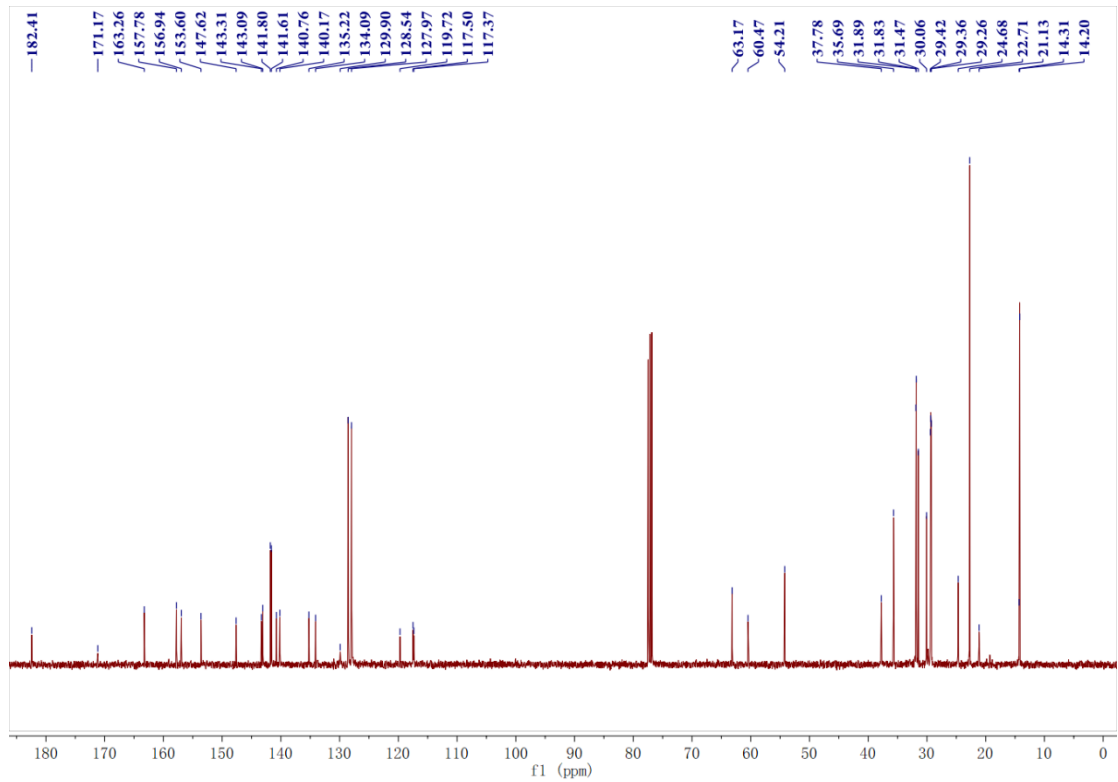
**Table S1.** Photovoltaic performance of the solar cells based on **PBDB-T:IDTC-4Cl:PC<sub>71</sub>BM** blend films with different ratios under illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>. Chlorobenzene as solvent.

<b>PBDB-T: IDTC- 2Cl:PC<sub>71</sub>BM</b>	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
<b>1:1:0</b>	0.820	18.95	61.2	9.50
<b>1:0.8:0.2</b>	0.829	19.14	65.6	<b>10.41</b>
<b>1:0.6:0.4</b>	0.837	18.23	65.8	10.04
<b>1:0.4:0.6</b>	0.843	18.11	66.1	10.09
<b>1:0.8:0.2</b>	0.854	15.86	66.2	8.97
<b>1:0:1</b>	0.857	12.87	69.2	7.63

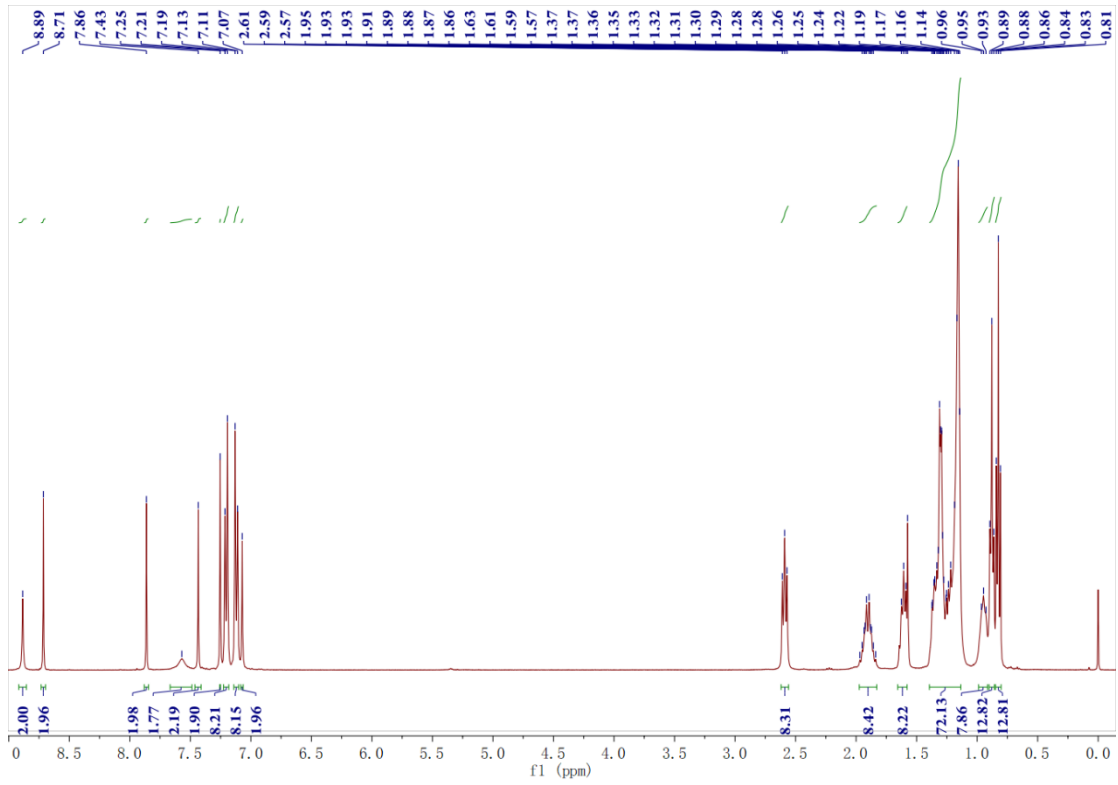
### <sup>1</sup>H NMR of IDTC-2CHO



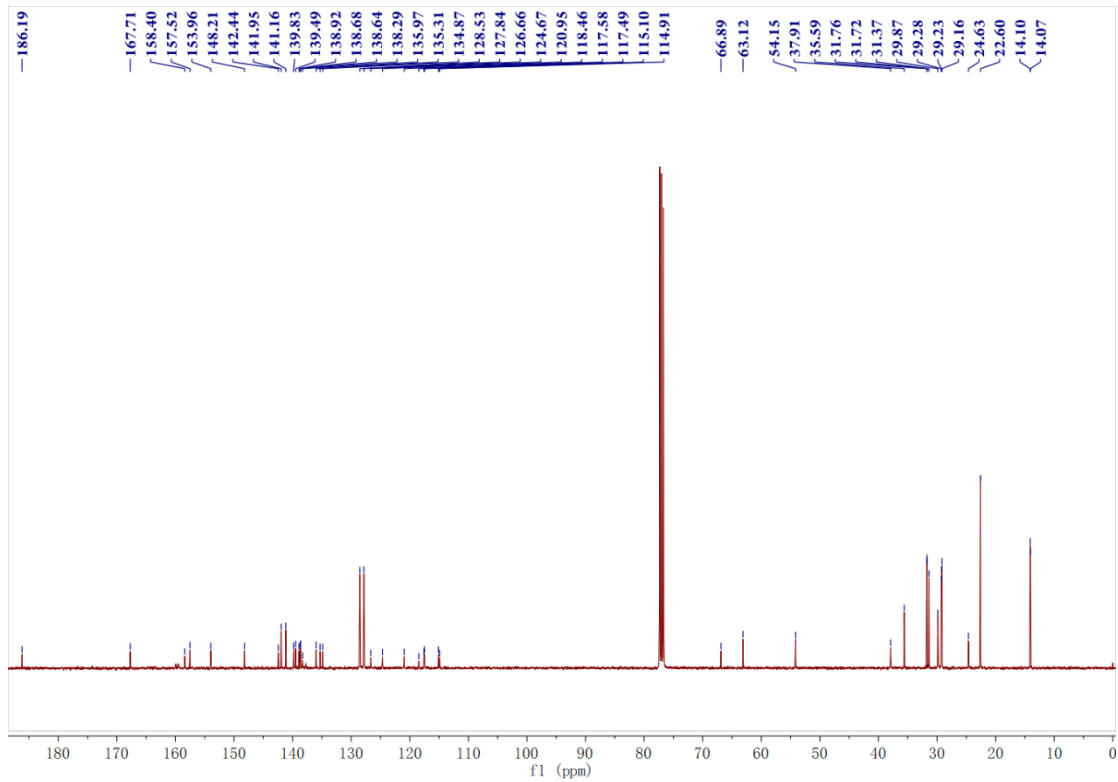
### <sup>13</sup>C NMR of IDTC-2CHO



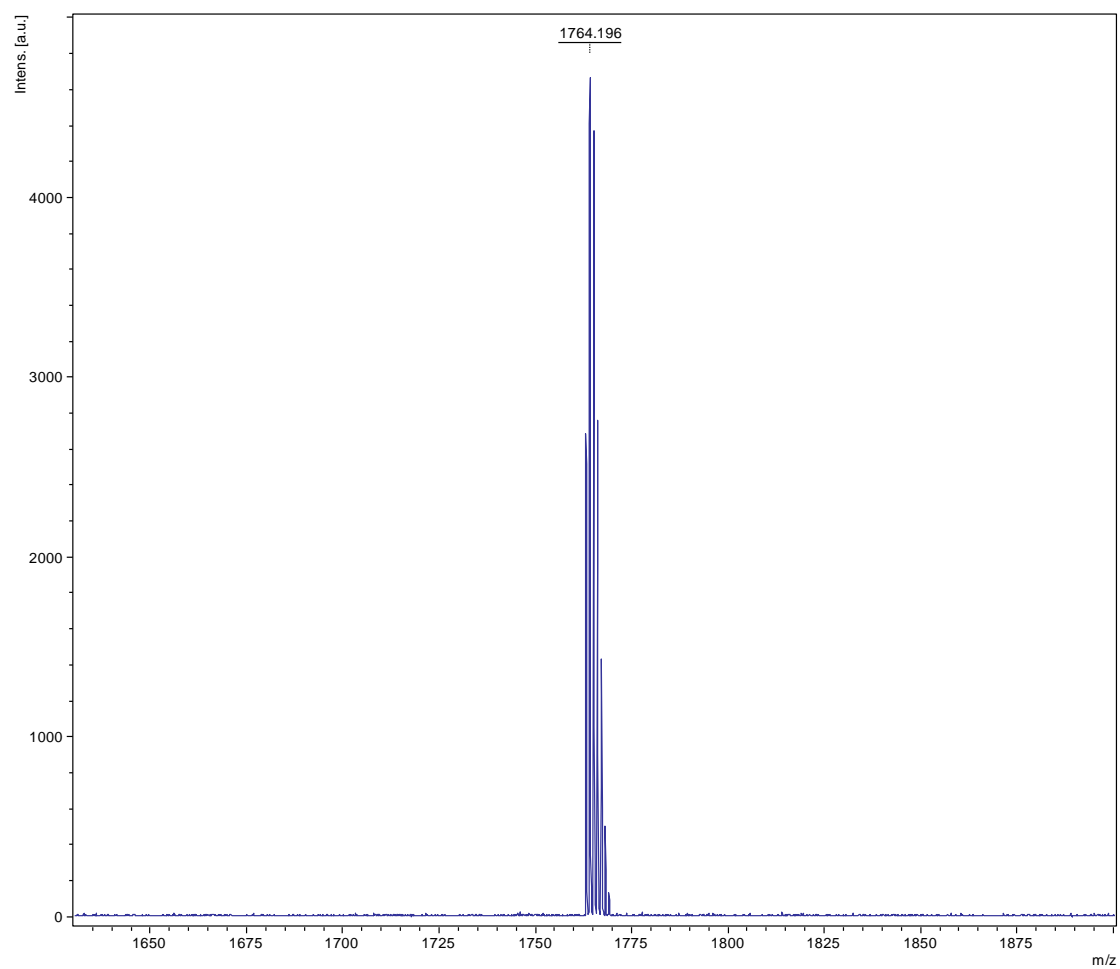
### <sup>1</sup>H NMR of IDTC-4Cl



### <sup>13</sup>C NMR of IDTC-4Cl



# MULTI-TOF MS of IDTC-2CHO



# HR-FTMS of IDTC-4Cl

Varian ProMALDI  
File: I\_MALDI.trans

Mode: Positive  
Scans: 1

Date: 08-JUN-2018  
Time: 08:32:27  
Scale: 45.1701

