

## Supporting Information

### **Efficient polymer solar cells processed by environmental friendly halogen-free solvents**

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#### **Experimental Part**

##### **1. Materials**

The catalyst precursor Pd(PPh<sub>3</sub>)<sub>4</sub> was prepared according to the literature and stored in a Schlenk tube under nitrogen atmosphere. Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone under nitrogen atmosphere. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh).

##### **2. Material Synthesis and Characterization**

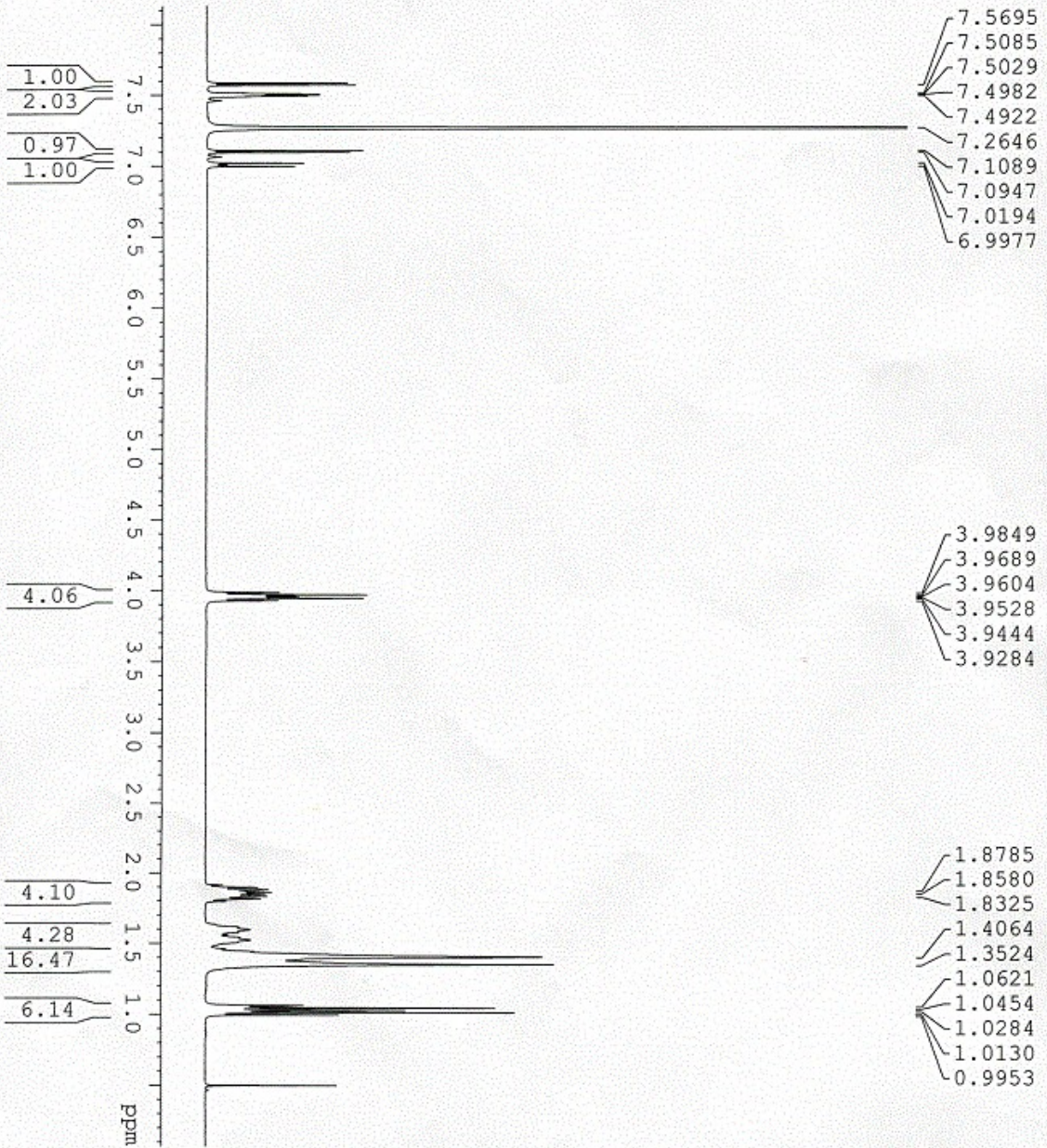
Compound 3 was synthesized in a yield of 85% by the reaction of commercially available diketone and phenyl derivatives 2. The new monomer 4 was easily lithiated by n-BuLi, and then reacted with trimethyltin chloride in 87% yield. The <sup>1</sup>H NMR spectroscopy and <sup>13</sup>C NMR spectroscopy of the compounds 3 and 4 are shown in Fig. S1. 4 was copolymerized with the dibromide derivatives (M1) through Stille coupling reactions to obtain the target polymers P1. The polymers were subjected to Soxhlet extraction with methanol, hexane and DCM. The DCM fraction was concentrated and precipitated into methanol, and extracted by filtration, to yield black-blue solid. The <sup>1</sup>H NMR spectroscopy of polymer is shown in Fig. S2.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 400 spectrometer. Gel permeation chromatography (GPC) measurements were performed at room temperature on a PL-GPC 50 Plus integrated GPC system (Polymer Laboratories, Inc.) with a differential refractive index detector with THF as an eluent. The electrochemical behavior of the compounds was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in acetonitrile at room temperature under an atmosphere of nitrogen with a scanning rate of 30 mV/s. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. UV-visible absorption spectra were obtained on a PerkinElmer UV-vis spectrometer model Lambda 750. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) measurements were performed on a Pyris 1 TGA instrument under a nitrogen atmosphere at a heating rate of 10 °C/min to record the TGA curves. DSC measurements were carried out on a DSC8000 (Perkin Elmer) instrument with indium and zinc employed for the temperature calibration. Samples of ca. 2.0 mg were sealed in aluminum pans, and a nitrogen gas purge with a flux of ca. 20 mL/min was used to prevent oxidative degradation of samples during the temperature scan. The samples were heated at a rate of 20 °C/min. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu KR radiation.

### **3. Polymer Solar Cell Fabrication and Characterization**

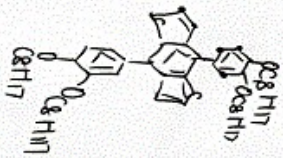
PSCs were fabricated with the device configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/LiF/Al. The conductivity of ITO was 20 Ω/□. PEDOT:PSS is Baytron A1 4083 from

H.C. Starck and was filtered with a 0.45 mm polyvinylidene difluoride (PVDF) film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at a speed of 3500 rpm for 50 s and dried subsequently at 130 °C for 20 min on a hotplate before being transferred into a glove box. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC<sub>71</sub>BM was dissolved in DCB and green solvents, and heated at 70 °C overnight to ensure a sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The additive was added to the blend solutions before spin coating. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, then followed by 100 nm of aluminum at a pressure of 10<sup>-4</sup> Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm<sup>2</sup>. The measurement of devices was conducted in air without encapsulation. Current-voltage characteristics were recorded using an Agilent B2902A Source Meter under an AM 1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mWcm<sup>-2</sup> as the white light source and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the *J-V* curves was approximately 25 °C. The EQE measurements of PSCs were performed by Stanford Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500Wxenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths.

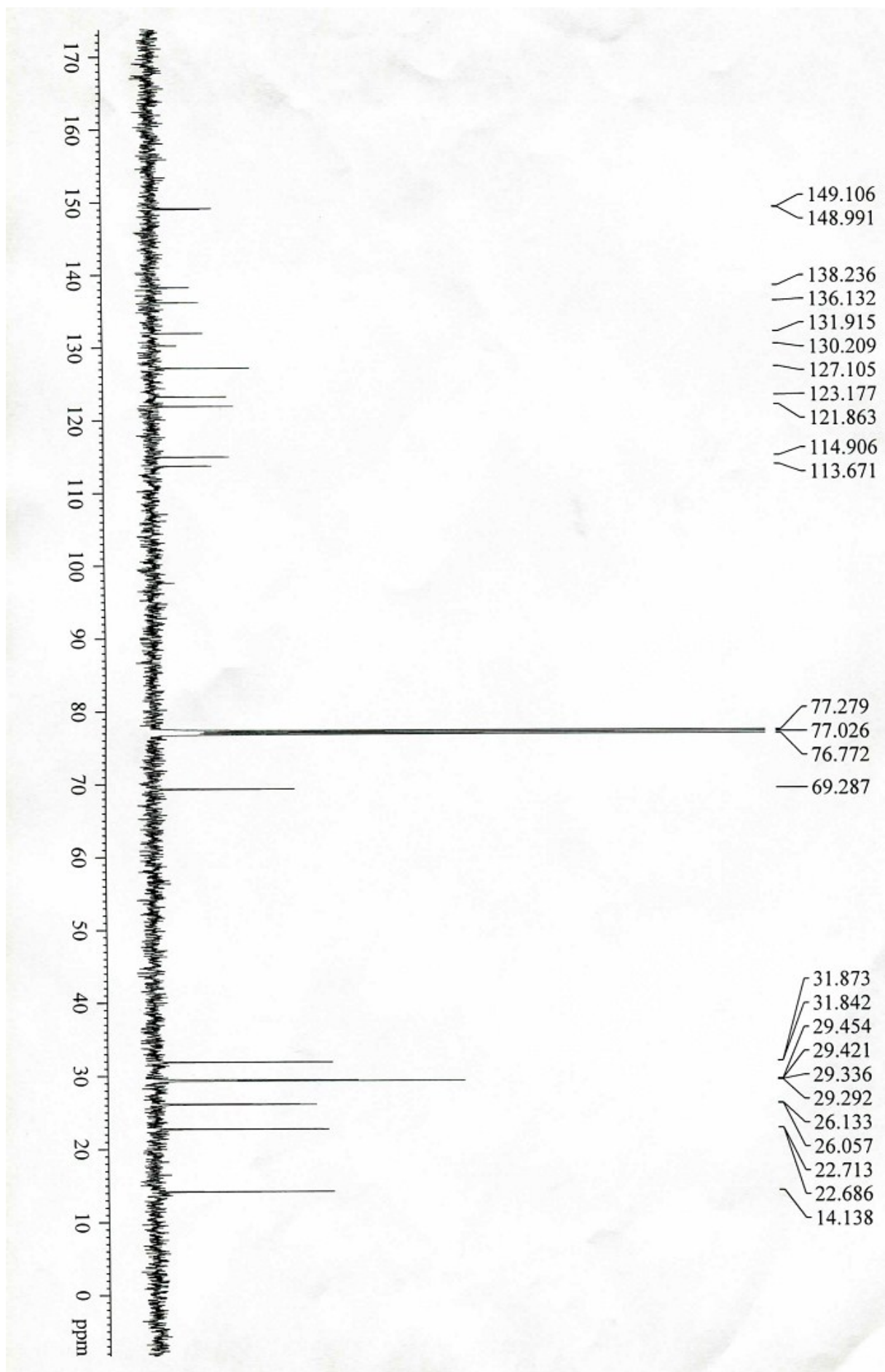


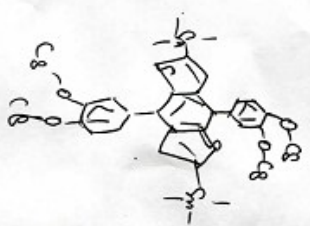
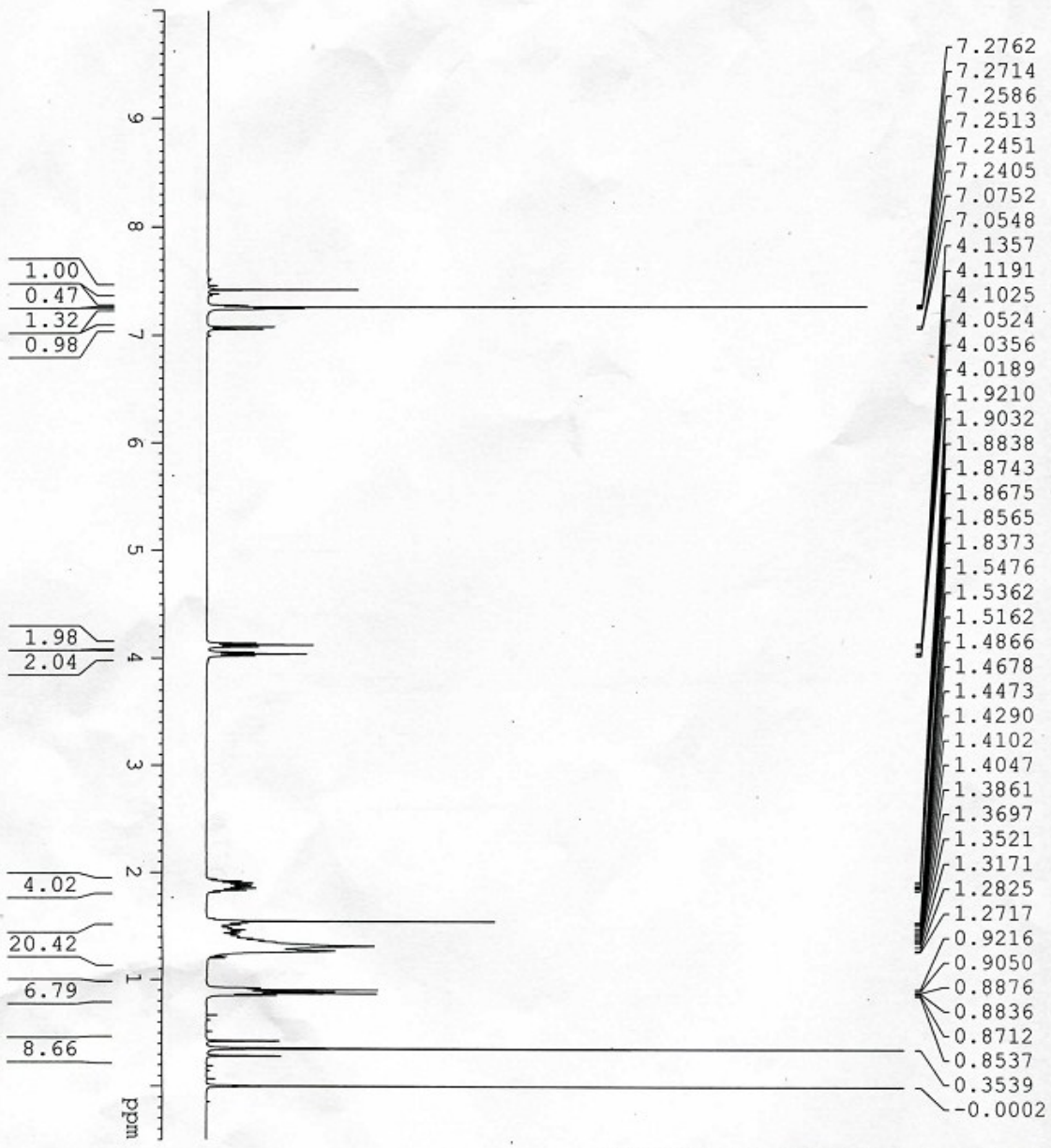
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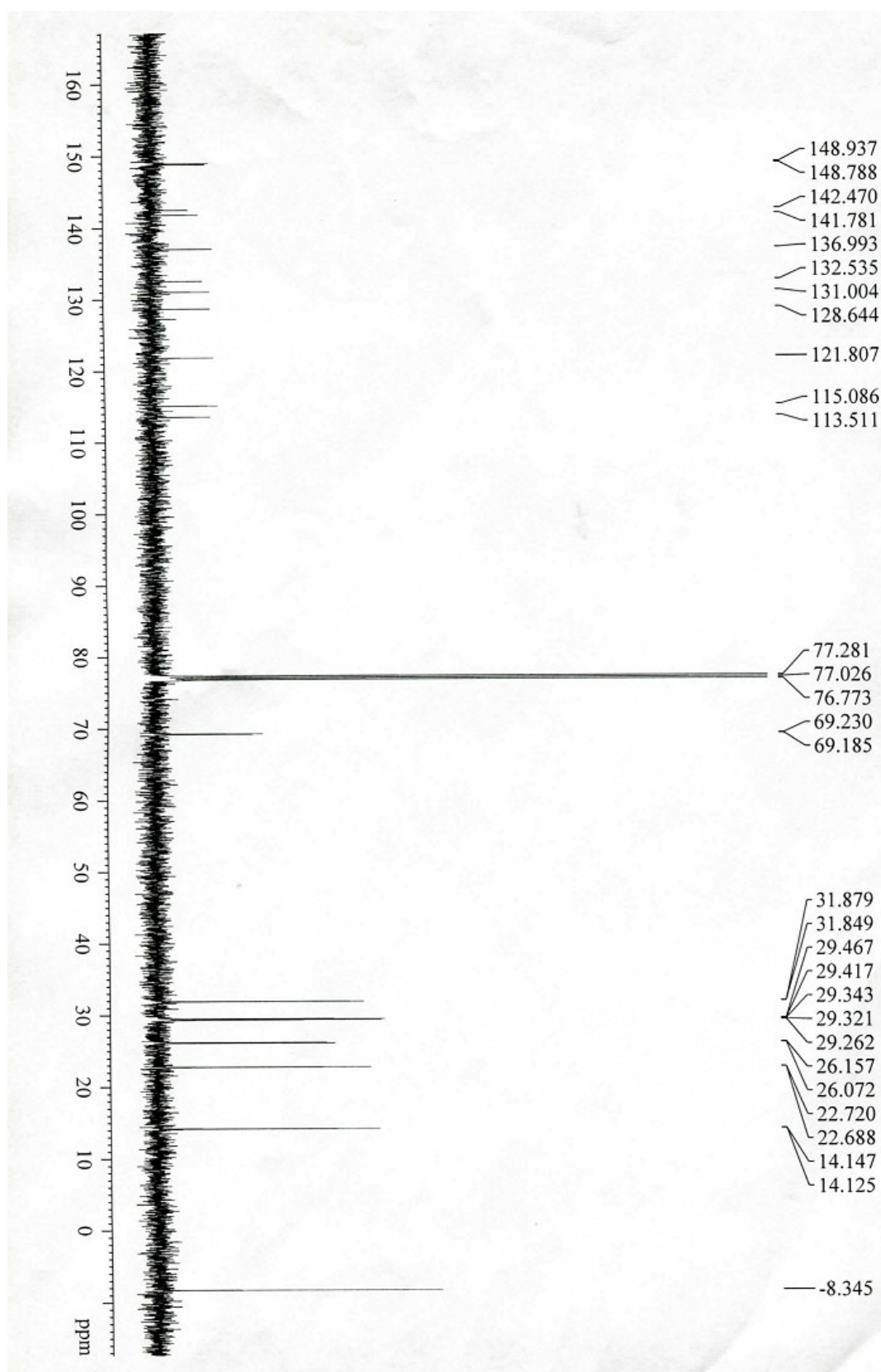


Fig. S1.  $^1\text{H}$  NMR spectroscopy and  $^{13}\text{C}$  NMR spectroscopy of the compounds 3 and 4.

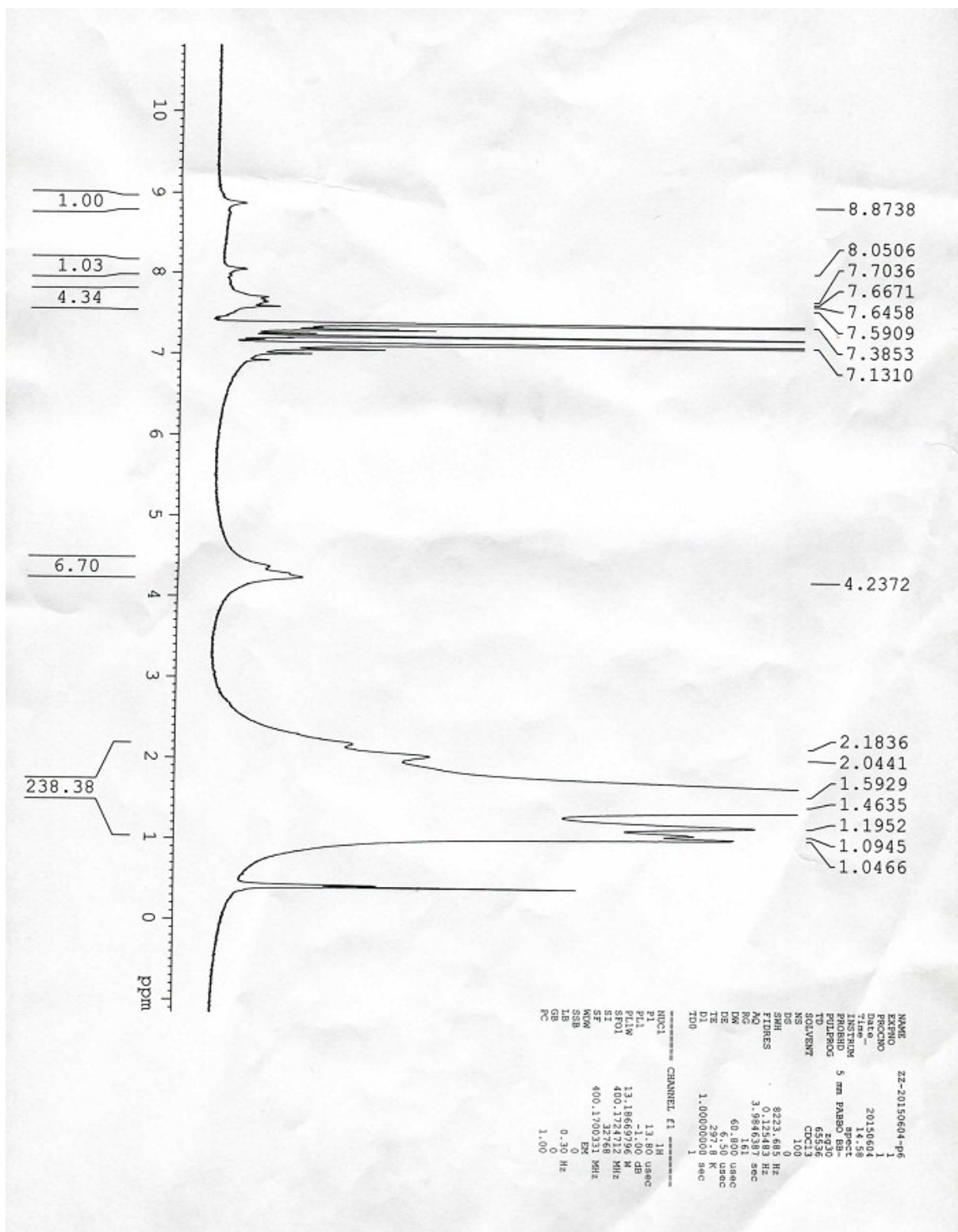


Fig. S2. <sup>1</sup>H NMR spectroscopy of polymer.



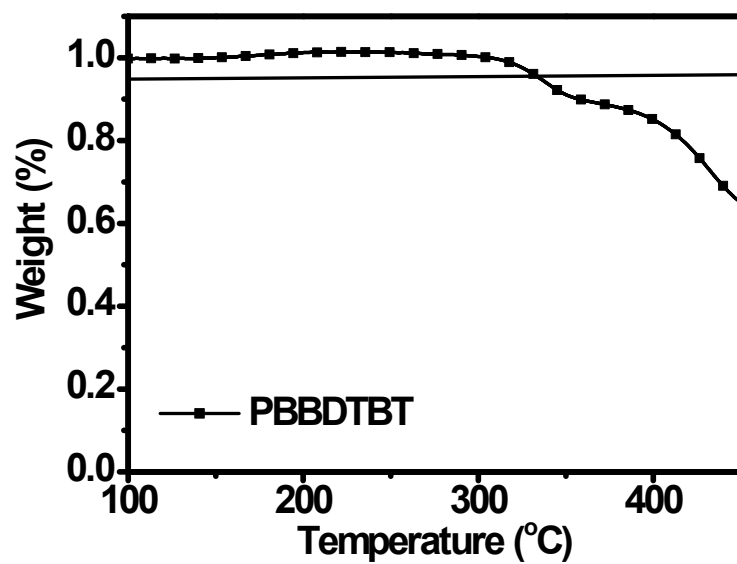


Fig. S3. TG curves of PBBDTBT powdery samples.

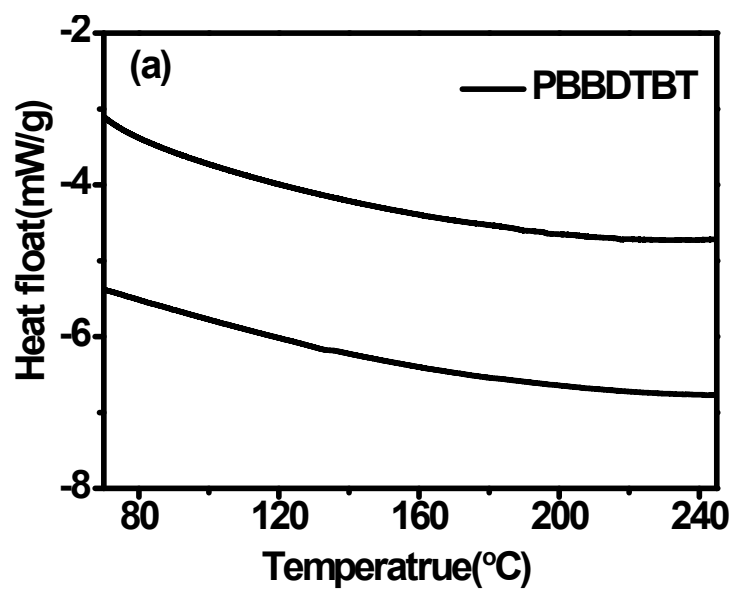


Fig. S4. DSC curves of PBBDTBT powdery samples.

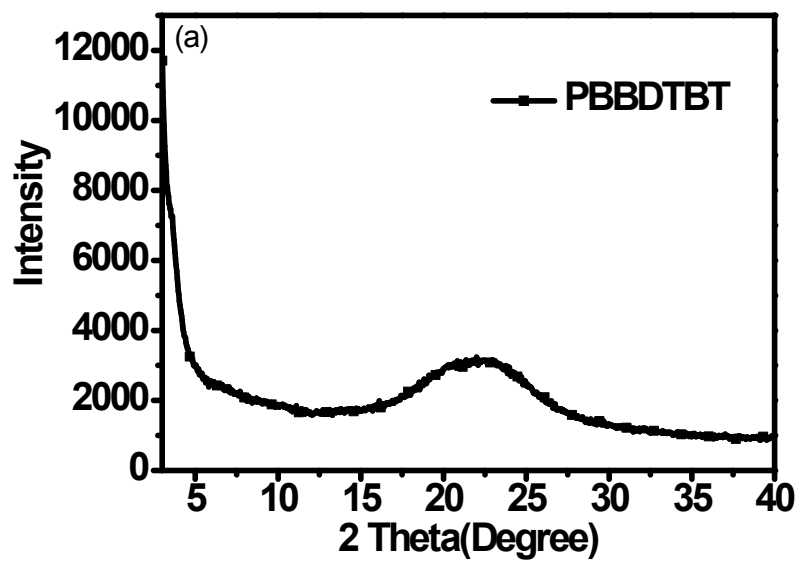


Fig. S5. XRD curves of **PBBDTBT** powdery samples.

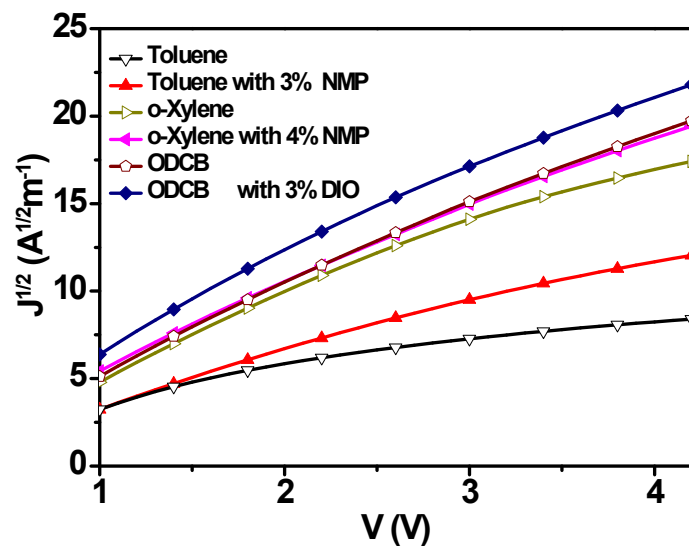


Fig. S6.  $\ln(J^{1/2}/A^{1/2})$  vs  $(V)$  plot of the blends for the hole mobility by SCLC method.



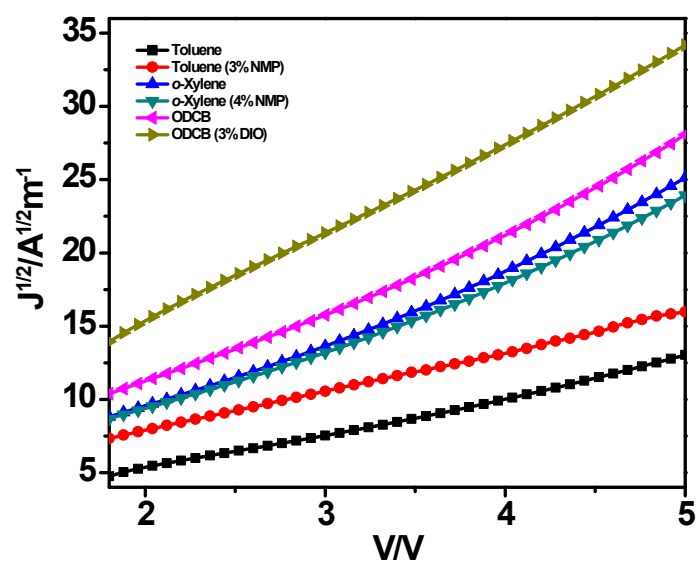


Fig. S7.  $\ln(J^{1/2}/A^{1/2})$  vs  $(V)$  plot of the blends for the electron mobility.

**Table S1** Photovoltaic Properties of the Solar Cells with varied D/A ratios in DCB/DIO (3%)

D/A ratios	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF	PCE (%) best/ave <sup>a</sup>
1:0.5	0.72	7.07	0.33	1.68/1.63
1:1	0.70	8.47	0.62	3.68/3.61
1:1.5	0.71	8.97	0.68	<b>4.33/4.25</b>
1:2	0.71	8.16	0.67	3.88/3.81
1:2.5	0.70	7.10	0.65	3.23/3.19
1:3	0.71	7.28	0.58	3.00/2.94

<sup>a</sup> The average PCEs were based on ten devices.

**Table S2.** Hole and electron mobility of the Photovoltaic Properties of the Solar Cells.

Solvent	Solvent additive	Hole Mobility ( $\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$ )	Electron Mobility ( $\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$ )
Toluene	no	$4.15 \times 10^{-6}$	$1.59 \times 10^{-5}$
	3% NMP	$1.05 \times 10^{-5}$	$1.83 \times 10^{-5}$
<i>o</i> -Xylene	no	$8.73 \times 10^{-6}$	$1.79 \times 10^{-5}$
	4% NMP	$1.48 \times 10^{-5}$	$2.41 \times 10^{-5}$
DCB	no	$1.18 \times 10^{-5}$	$2.07 \times 10^{-5}$
	3% DIO	$1.52 \times 10^{-5}$	$2.66 \times 10^{-5}$