

## Supplementary Information

### **An isoindigo-based low band gap polymer for efficient solar cells with high photo-voltage**

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## Experimental Section

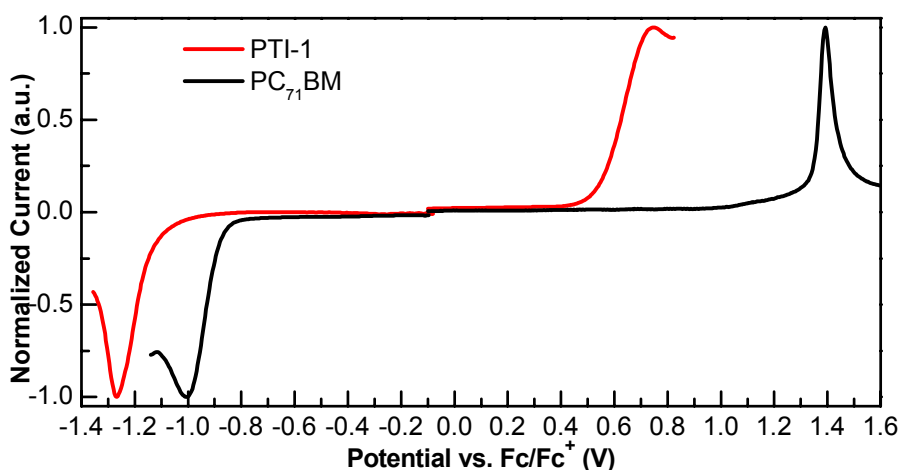
### Characterization:

$^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}$  NMR (125 MHz) spectra were acquired from a Varian Inova 500 MHz NMR spectrometer. Tetramethylsilane was used as an internal reference with deuterated chloroform as solvent. TGA and DSC were performed on Perkin Elmer TGA7 and Perkin Elmer Pyris 1, respectively. Size exclusion chromatography (SEC) was performed on Waters Alliance GPCV2000 with a refractive index detector. Columns: Waters Styvigel HT GE $\times$ 1, Waters Styvigel HMW GE $\times$ 2. The eluent was 1,2,4-trichlorobenzene. The working temperature was 135 °C, and the resolution time was 2 h. The concentration of the samples was 0.5 mg mL $^{-1}$ , which were filtered (filter: 0.45  $\mu\text{m}$ ) prior to the analysis. The molecular weights were calculated according to relative calibration with polystyrene standards. UV-Vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer.

### Electrochemical studies

Square-wave voltammetry (SWV) measurements were carried out on a CH-Instruments 650A Electrochemical Workstation. A three-electrode setup was used with platinum wires both as working electrode and counter electrode, and Ag/Ag $^+$  was used as reference electrode calibrated with ferrocene/ferrocenyl couple (Fc/Fc $^+$ ). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu $_4$ NPF $_6$ ) in anhydrous acetonitrile was used as supporting electrolyte. The polymer was deposited onto the

working electrode from chloroform solution. In order to remove oxygen from the electrolyte, the system was bubbled with nitrogen prior to each experiment. The nitrogen inlet was then moved to above the liquid surface and left there during the scans. HOMO and LUMO levels were estimated from peak potentials of the third scan by setting the oxidative peak potential of Fc/Fc<sup>+</sup> vs. the normal hydrogen electrode (NHE) to 0.63 V,<sup>1</sup> and the NHE vs. the vacuum level to 4.5 V.<sup>2</sup> The HOMO and LUMO levels were calculated according to the formula HOMO =  $-(E^{\text{ox}} + 5.13)$  eV and LUMO =  $-(E^{\text{red}} + 5.13)$  eV, where  $E^{\text{ox}}$  and  $E^{\text{red}}$  were determined from oxidation and reduction peaks respectively.<sup>3</sup>



**Fig. S1** SWV of the thin films of **PTI-1** and PC<sub>71</sub>BM.

#### **Device fabrication and characterization:**

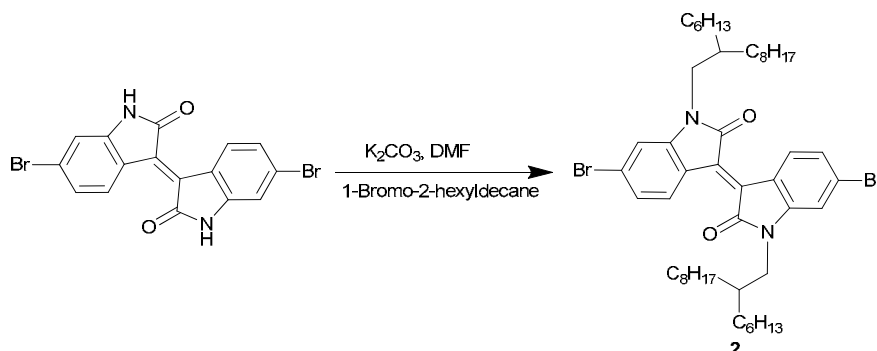
The structure of the solar cells was Glass/ITO/PEDOT:PSS/Active Layer/LiF/Al. As a buffer layer, the conductive polymer, PEDOT:PSS (Baytron P VP Al 4083), was spin-coated onto ITO-coated glass substrates, followed by annealing at 120 °C for 10 minutes to remove water. The thickness of the PEDOT:PSS layer was about 45 nm, as determined by a Dektak 6M surface profilometer. The active layer consisting of

polymer and PC<sub>71</sub>BM was spin-coated from ODCB solution (or with DIO additive) onto the PEDOT:PSS layer. The spin-coating was done in a glove box and the material was directly transferred to a vapor deposition system mounted inside of the glove box. LiF (0.6 nm) and Al (80 nm) were used as top electrodes and were deposited via a mask in vacuum onto the active layer. The accurate area of every device (4-6 mm<sup>2</sup>), defined by the overlap of the ITO and metal electrode, was measured carefully by microscope image. EQEs were calculated from the photocurrents at short-circuit conditions. The currents were recorded by a Keithley 485 picoammeter under illumination of monochromatic light (MS257) through the ITO side of the devices. PCE was calculated from *J-V* characteristics recorded by a Keithley 2400 source meter under illumination of an AM1.5G solar simulator with an intensity of 100 mW cm<sup>-2</sup> (Model SS-50A, Photo Emission Tech., Inc.). The light intensity was determined by a standard silicon photodiode. Device characterization was conducted in ambient environment.

### **Synthetic Procedures**

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. 6-Bromoisatin and 6-bromooxindole were obtained from Puyang Huicheng Chemical Co. Ltd.. 6,6'-Dibromoisindigo and 1-bromo-2-hexyldecane were prepared according to the literature methods.<sup>1-3</sup>

## Synthesis of (E)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (2)

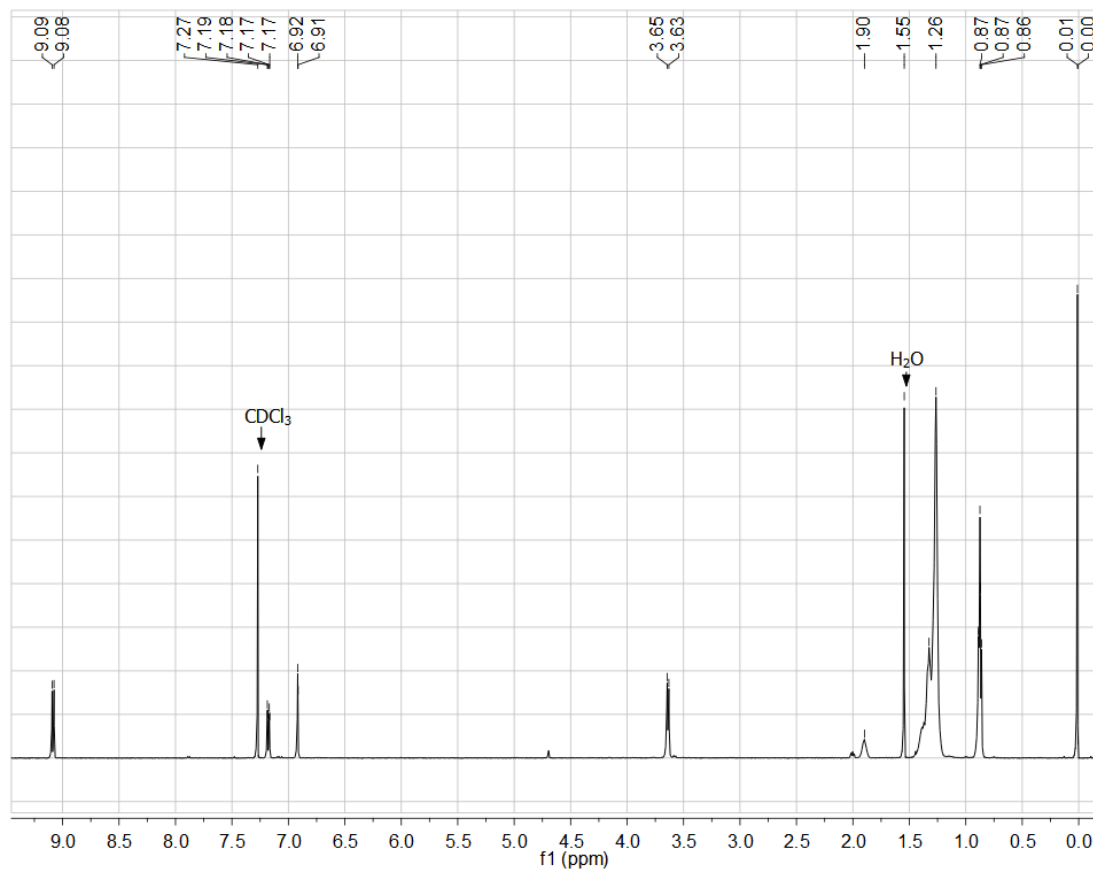


1-Bromo-2-hexyldecane (3.36 g, 11 mmol) was added to a suspension of 6,6'-dibromoisoindigo (2.10 g, 5 mmol) and potassium carbonate (6.90 g, 50 mmol) in dimethylformamide (100 mL). The mixture was heated to 100 °C for 24 h. After cooling to room temperature, the mixture was transferred to a separatory funnel, extracted with diethyl ether and then washed with water. The ether phase was dried over  $MgSO_4$ . Removal of the solvent gave a crude product, which was purified by silica-gel column chromatography using a mixture of hexane:dichloromethane (1:1) as eluent to obtain **2** (3.51 g, 80.8%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ,  $\delta$ ): 9.09 (d,  $J = 8.6$  Hz, 2H), 7.16 (dd,  $J = 8.6$  Hz,  $J = 1.9$  Hz, 2H), 6.91 (d,  $J = 1.8$  Hz, 2H), 3.64 (d,  $J = 7.5$  Hz, 4H), 1.93-1.85 (m, 2H), 1.43-1.20 (m, 48 H), 0.92-0.84 (m, 12H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ,  $\delta$ ): 168.12, 146.20, 132.60, 131.00, 126.66, 125.10, 120.38, 111.56, 44.69, 36.08, 31.86, 31.80, 31.48, 29.98, 29.65, 29.54, 29.29, 26.35, 26.32, 22.67, 22.64, 14.12, 14.09.

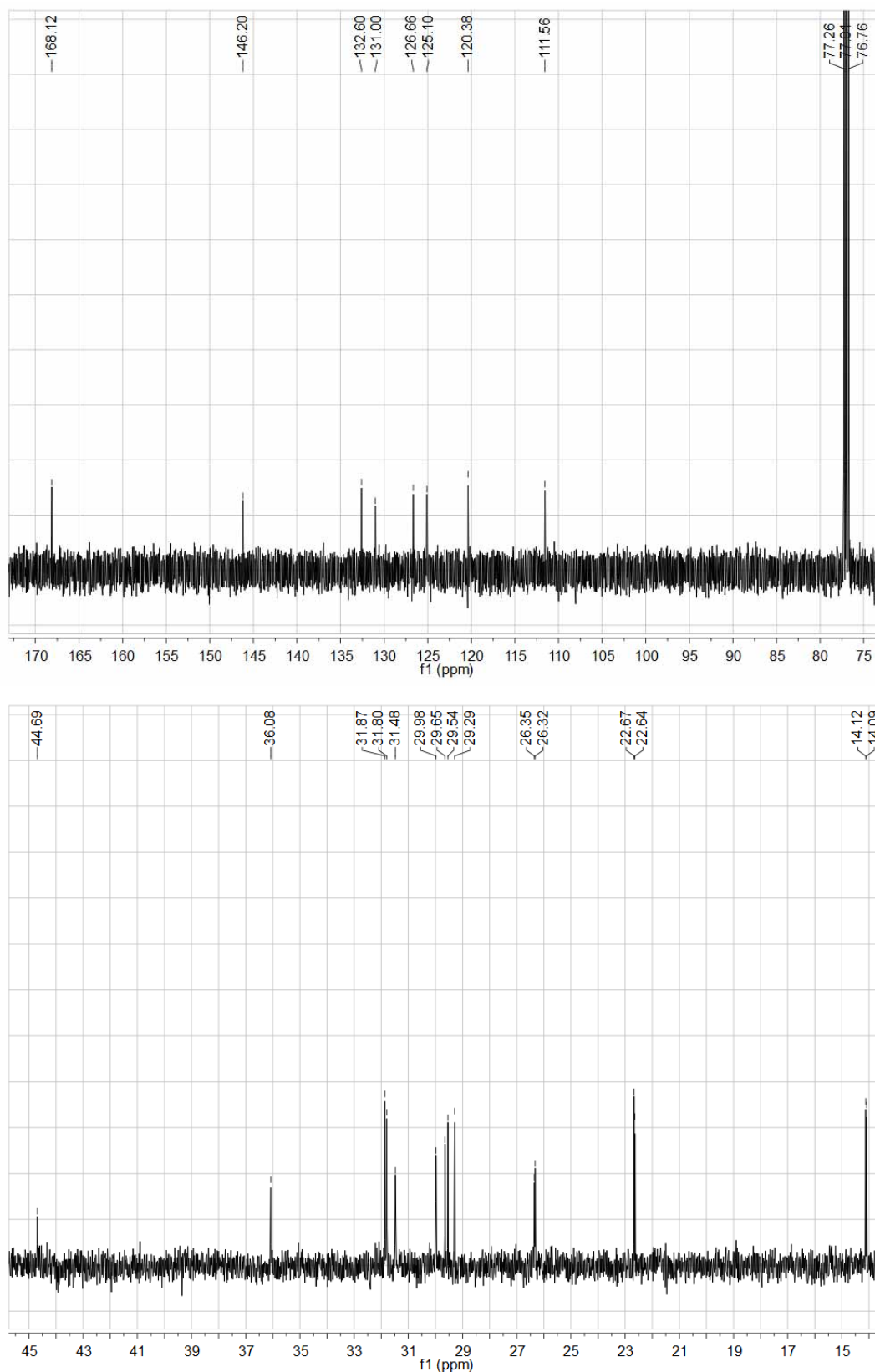
## Synthesis of PTI-1

In a 25 mL dry flask, 2,5-bis(trimethylstannyl)thiophene (**1**) (86 mg, 0.21 mmol), **2** (182 mg, 0.21 mmol), tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ ) (6 mg) and tri(*o*-tolyl)phosphine ( $\text{P}(\text{o-Tol})_3$ ) (10 mg) were dissolved in degassed toluene (5 mL). The mixture was vigorously stirred at 100 °C for 24 h under nitrogen, cooled to r. t., and the solution was poured into acetone. The polymer was collected by filtration through 0.45  $\mu\text{m}$  Teflon filter. And then the polymer was washed in a Soxhlet extractor with acetone and diethyl ether for 24 h each. After that, the polymer was Soxhlet-extracted with chloroform. The chloroform fraction was purified by passing it through a short silica gel column and then precipitated from acetone. Finally, the polymer was collected by filtration through 0.45  $\mu\text{m}$  Teflon filter and dried under vacuum at 40 °C overnight (155 mg, 93%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 9.3-8.6 (br, 2H), 7.5-6.2 (br, 6H), 4.2-3.5 (br, 4H), 1.5-1.1 (br, 48H), 1.0-0.7 (br, 12H).

1. J. Mei, K. R. Graham, R. Stalder and J. R. Reynolds, *Org. Lett.*, 2010, **12**, 660-663.
2. L. Burgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H. J. Kirner and C. Winnewisser, *Adv. Mater.*, 2008, **20**, 2217-2224.
3. N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295-2300.



**Figure S2.** <sup>1</sup>H NMR spectrum of **(E)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (2)**



**Figure S3.**  $^{13}\text{C}$  NMR spectrum of **(E)-6,6'-dibromo-1,1'-bis(2-hexyldecyl)-[3,3'-biindolinylidene]-2,2'-dione (2)**. (To see it clearly, it was divided into two parts.)