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## ***Electronic Supplementary Information***

### **Akylidenefluorene-Isoindigo Copolymers with an Optimized Molecular Conformation for Spacer Manipulation, $\pi$ - $\pi$ Stacking and Its Application in Efficient Photovoltaic Devices**

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## 1. Synthetic Procedures

### 1.1 N, N'-(2-octyldodecyl)-6, 6'-dithiophen-2-yl-isoindigo (1Tindigo)

To the solution of 0Tindigo-Br (5.5224 g, 5.634 mmol) and 2-(tributylstannyl)thiophene (4.836 g, 13.22 mmol) in toluene (47 mL), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.26 g) were added in one portion. The mixture was stirred under reflux 96 h. Then the mixture was cooled to room temperature and poured into water. The organic phase was extracted by diethyl ether, and then washed with water, dried over MgSO<sub>4</sub>. After the removal of the solvent under reduced pressure, the solids were purified by silica chromatography with dichloromethane: hexane = 2:3. Yield (3.4 g, 61 %) d<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 9.19 (d, 2H), 7.43 (d, 2H), 7.37 (d, 2H), 7.32 (d, 2H), 7.16-7.11 (m, 2H), 7.00 (s, 2H), 3.72 (d, 4H), 1.95 (m, 2H), 1.46-1.19 (br, 48H), 0.89-0.83 (br, 12H)

### 1.2 N, N'-(2-octyldodecyl)-6, 6'-di-2,2'-bithiophen-5-yl-isoindigo (2Tindigo)

2Tindigo was synthesized with the same procedure of 1Tindigo. To the solution of 0Tindigo-Br (1.8 g, 1.83 mmol) and 5-(tributylstannyl)-2,2'-bithiophene (1.483 g, 4.507 mmol) in toluene (15 mL), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) (0.086 g) were added in one portion. The mixture was stirred under reflux 96 h. Then the mixture was cooled to room temperature and poured into water. The organic phase was extracted by diethyl ether, and then washed with water, dried over MgSO<sub>4</sub>. After the removal of the solvent under reduced pressure, the solids were purified by silica chromatography with dichloromethane: hexane = 2:3. Yield (1.681 g, 78.2 %) d<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 9.19 (d, 2H), 7.32-7.17 (m, 10H), 7.07-7.03 (m, 2H), 6.92 (s, 2H), 3.78 (d, 4H), 1.90 (m, 2H), 1.36-1.22 (br, 48H), 0.85-0.83 (br, 12H)

### 1.3 N, N'-(2-octyldodecyl)-6, 6'-di(5-bromothiophen-2-yl)-isoindigo (A1)

To a solution of 1Tindigo (1.92 g, 1.94 mmol) in 58 mL THF, NBS (0.725 g, 4.07 mmol) was added portionwise in 2 h in the dark. The reaction mixture was stirred at room temperature for 12 h. Then it was poured into water and extracted with diethyl ether. Removal of the solvent and column purification on silica gel using dichloromethane:hexane = 1:2. Yield (1.78 g, 80 %) d<sub>H</sub> (400 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 9.19 (d, 2H), 7.20-7.15 (m, 4H), 7.07 (d, 2H), 6.87 (s, 2H), 3.70 (d, 4H), 1.90 (m, 2H), 1.42-1.19 (br, 48H), 0.86-0.83 (br, 12H)

### 1.4 N, N'-(2-octyldodecyl)-6, 6'-di(5-bromo-2,2'-bithiophen-2-yl)-isoindigo (A2)

2Tindigo-Br was synthesized with the same procedure of 1Tindigo-Br. To a solution of 2Tindigo (1.68 g, 1.46 mmol) in 44 mL THF, NBS (0.52 g, 2.92 mmol) was added portionwise in 1 h in the dark. The reaction mixture was stirred at room temperature for 12 h. Then it was poured into water and extracted with diethyl ether. Removal of the solvent and column purification on silica gel using

dichloromethane:hexane = 1:2. Yield (1.88 g, 98.3 %)  $d_H$  (400 MHz;  $CDCl_3$ ;  $Me_4Si$ ): 9.15 (d, 2H), 7.29-7.25 (d, 4H), 7.10-7.09 (d, 2H), 6.99-6.95 (m, 4H), 6.89 (s, 2H), 3.68 (d, 4H), 1.90 (m, 2H), 1.41-1.22 (br, 48H), 0.87-0.83 (br, 12H)

### 1.5 General polymerizations

To a mixture of tetrakis(triphenyl-phosphine)  $Pd(PPh_3)_4(0)$  (12mg, 0.010mmol, 5 mol%), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(1-decylundecylidene)fluorene (AF) (0.213 g, 0.3 mmol), and equivalent of halogen compound, e.g. A0, A1 and A2, was added a degassed mixture of toluene: DMF = 1:1 and 2 M  $K_2CO_3$  aqueous solution (3:2 in volume). The mixture was vigorously stirred at 90 °C for 48 h under the nitrogen. After the mixture was cooled to room temperature, poured into water. The organic mixture was separated and washed with aqueous HCl, ammonium solution and deionized water, respectively. Then, remove the solvent under the reduced pressure. The organic fraction was precipitated in methanol. The polymer was further purified by washing methanol and acetone, respectively, in a Soxhlet apparatus for 24 h. The chloroform part was reprecipitated with methanol and filtrated then, dried under reduced pressure at 50 °C.

## 2. $^1\text{H-NMR}$ Spectrum of polymers

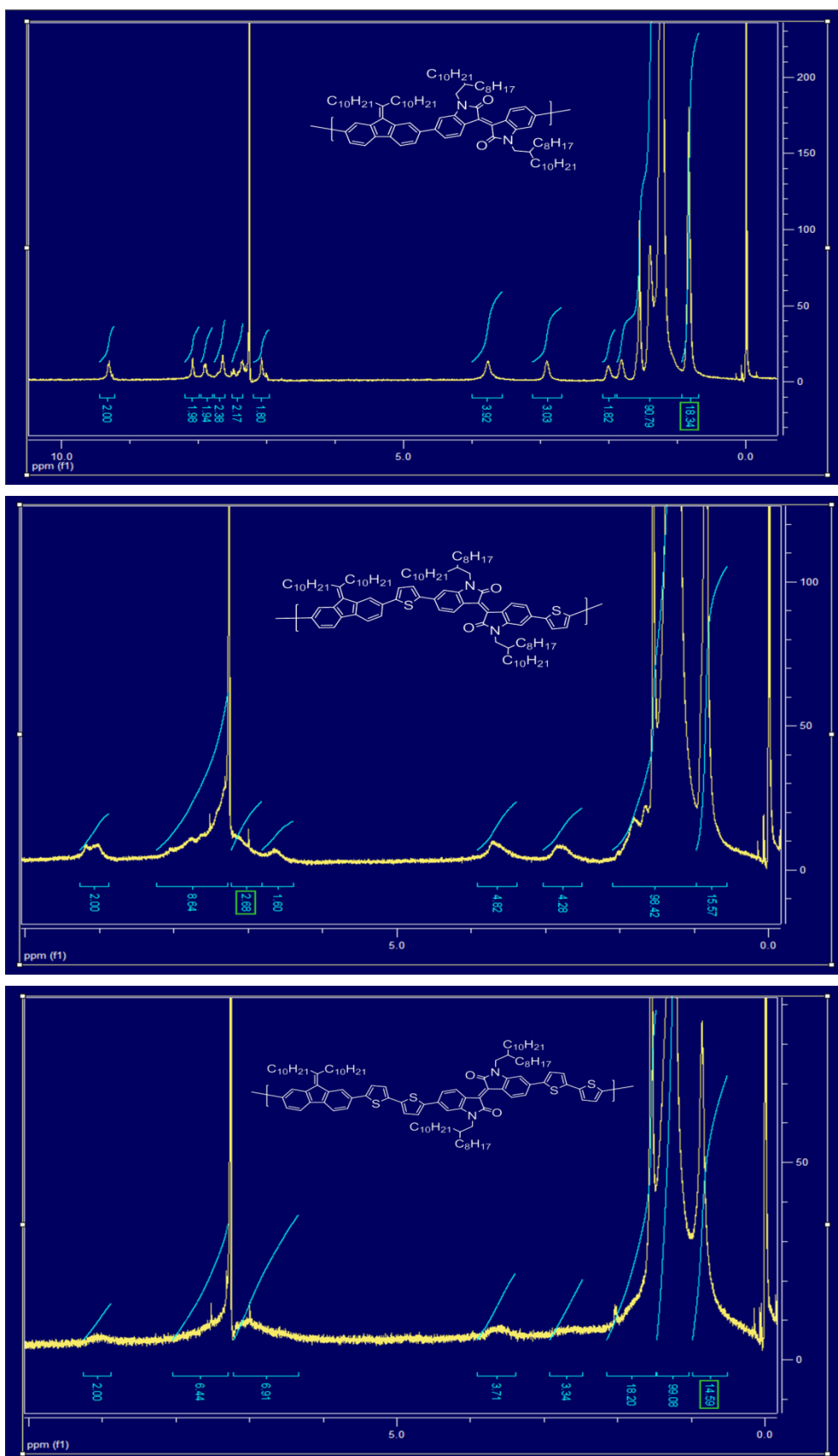
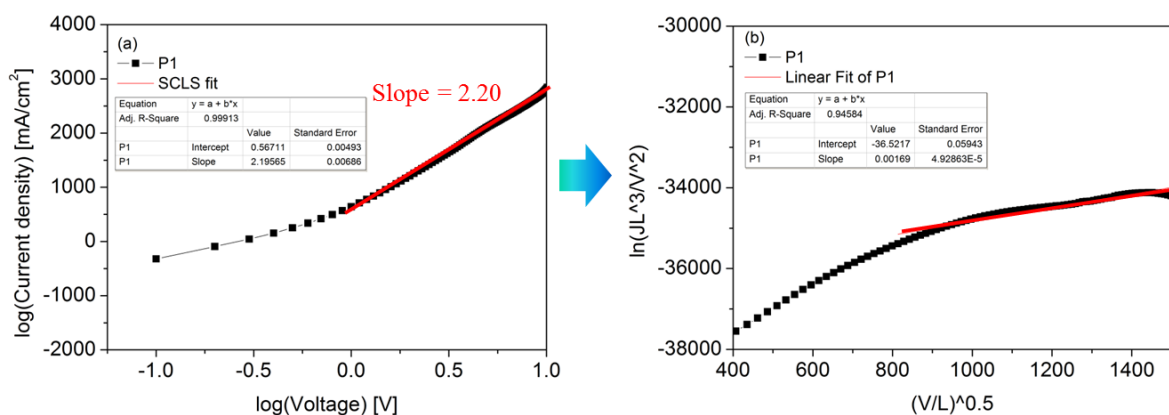
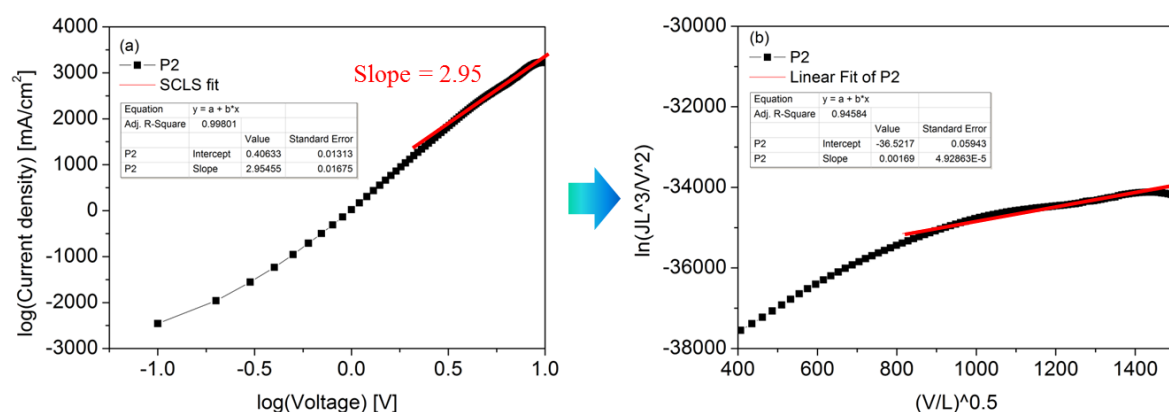


Figure S1.  $^1\text{H-NMR}$  Spectrum of polymers

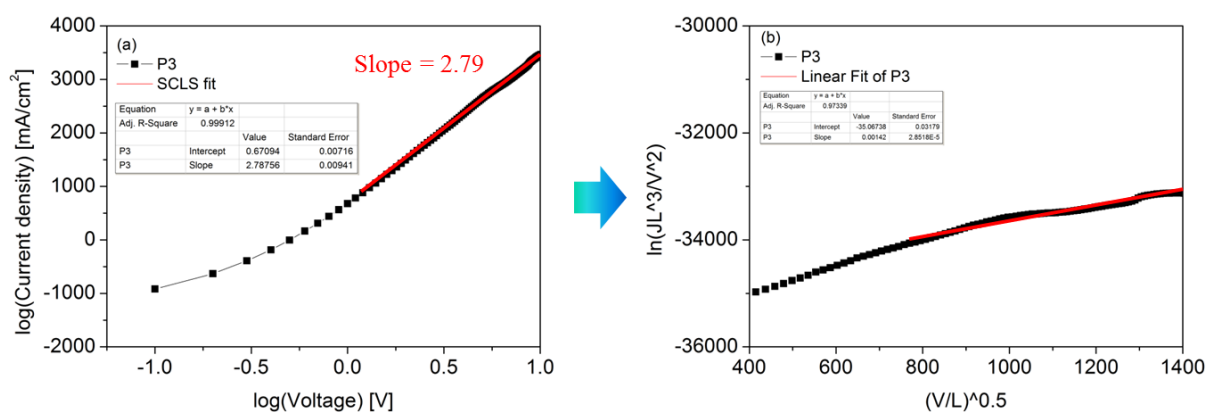
### 3. J-V characteristics of the hole-only devices based on Polymer:PC<sub>70</sub>BM blend



**Figure S2.** (a) log J vs. log V plot and (b)  $\ln(JL^3/V^2)$  vs  $(V/L)^{1/2}$  plot of the hole-only devices (ITO(170nm)/PEDOT:PSS(40 nm)/P1:PC<sub>70</sub>BM (42.3nm)/MoO<sub>3</sub> (30 nm)/Al(100nm)).

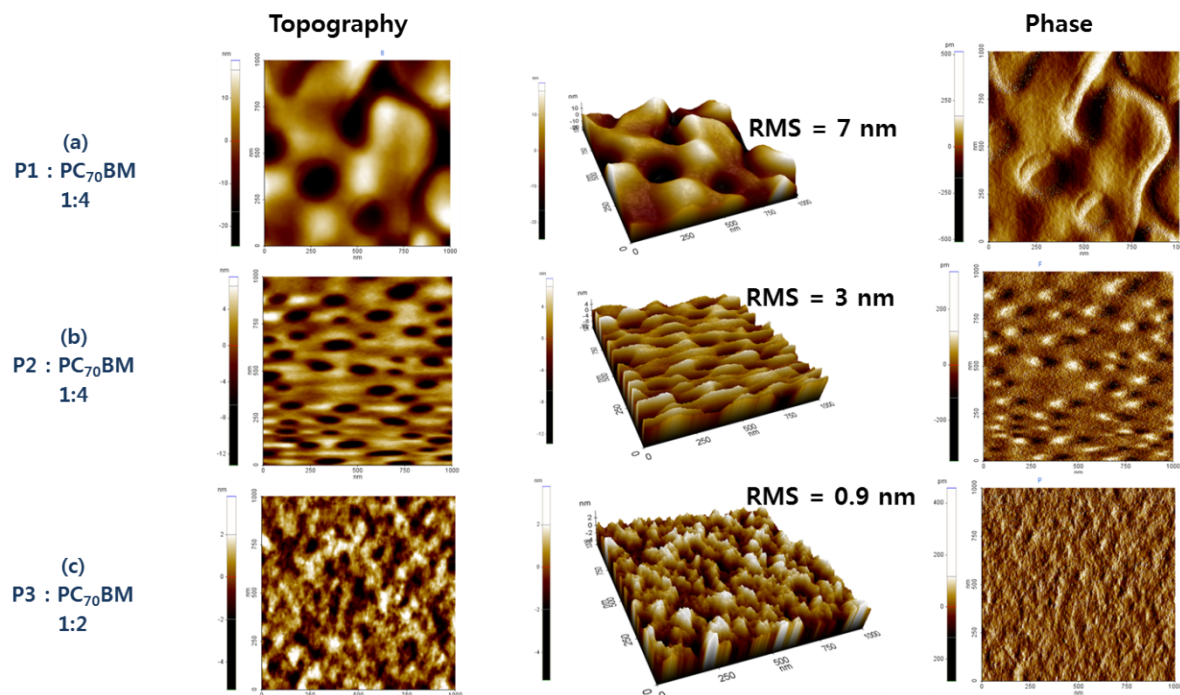


**Figure S3.** (a) log J vs. log V plot and (b)  $\ln(JL^3/V^2)$  vs  $(V/L)^{1/2}$  plot of the hole-only devices (ITO(170nm)/PEDOT:PSS(40 nm)/ P2:PC<sub>70</sub>BM (52.3nm)/MoO<sub>3</sub> (30 nm)/Al(100nm)).



**Figure S4.** (a) log J vs. log V plot and (b)  $\ln(JL^3/V^2)$  vs  $(V/L)^{1/2}$  plot of the hole-only devices (ITO(170nm)/PEDOT:PSS(40 nm)/ P3:PC<sub>71</sub>BM (17.7nm)/MoO<sub>3</sub> (30 nm)/Al(100nm)).

#### 4. Morphologies of the Polymer:PCBM blend films



**Figure S5.** Topographic AFM images of Polymer:PC<sub>70</sub>BM

(a) P1: PC<sub>70</sub>BM 1:4w/w ( $1 \times 1 \mu\text{m}^2$ ), (b) P2: PC<sub>70</sub>BM 1:4w/w ( $1 \times 1 \mu\text{m}^2$ ),

and (c) P3: PC<sub>70</sub>BM 1:2w/w ( $1 \times 1 \mu\text{m}^2$ ).

**Table S1. Hole mobility of polymers blended with PC<sub>71</sub>BM**

Polymer	PC <sub>71</sub> BM ratios (w:w)	Film thickness [nm]	Hole mobility [cm <sup>2</sup> (V <sup>-1</sup> s <sup>-1</sup> )]
P1	1:4	42.3	5.76 X 10 <sup>-5</sup>
P2	1:4	52.3	4.61 X 10 <sup>-4</sup>
P3	1:2	17.7	1.97 X 10 <sup>-3</sup>

**Table S2. Photovoltaic properties of polymers with different PC<sub>70</sub>BM ratio**

polymer	PC <sub>70</sub> BM ratios	Voc[V]	Jsc[mA/cm <sup>2</sup> ]	FF[%]	PCE[%]
P1	1:2	1.0	0.07±0.003	43.5±0.3	0.03±0.005
	1:4	1.0	0.07±0.003	49.1±1.4	0.04±0.006
P2	1:2	0.858±0.04	1.2±0.1	53.1±3.0	0.55±0.03
	1:4	0.858±0.02	1.4±0.2	54.2±1.4	0.66±0.04
P3	1:1	0.798	6.8	46.2±1.5	2.50±0.1
	1:2	0.798±0.02	7.3±0.3	51.6±0.9	3.00±0.1
	1:3	0.798±0.02	6.2±0.3	51.0±1.0	2.50±0.1
	1:4	0.778±0.02	6.4±0.4	50.3±3.0	2.50±0.1