

Supporting Information

for

An A-D-A'-D-A Type Small Molecule Acceptor with Broad Absorption Spectrum for Organic Solar Cells

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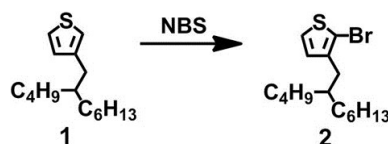
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1. Experimental details

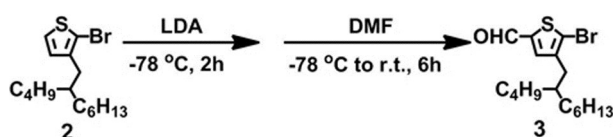
Characterization. ^1H and ^{13}C NMR spectra were measured using Bruker Avance 400 MHz NMR spectrometer. Mass spectra were measured on a Bruker Daltonics Flex matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectroscopy (MS). Elemental analysis was recorded on a VarioEL elemental analyzer. Thermal analyses were performed on a Perkin-Elmer 7 instrument under nitrogen flow at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. UV/Vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer, in spectral grade solvents. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical workstation using Bu_4NClO_4 ($0.1\text{ mol}\cdot\text{L}^{-1}$) in acetonitrile as electrolyte solution and ferrocene as an internal reference at a scan rate of 100 mV s^{-1} . The CV cell consisted of a Pt wire counter electrode, a glassy carbon electrode, and a standard calomel reference electrode. The small molecular was casted on the working electrode for measurements. The ferrocene/ferrocenium (Fc/Fc^+) was used as an internal standard, which was assigned an absolute energy of -4.80 eV . The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the material was estimated by the equations: $E_{\text{HOMO/LUMO}} = -(4.80 + E_{\text{onset}}^{\text{ox}}/E_{\text{onset}}^{\text{red}})\text{ eV}$. Atomic force microscopy (AFM) was performed with a SPA300HV (Seiko Instruments, Inc., Japan) in tapping mode. The thickness of various layers was measured with a Dektak 6M Stylus Profile. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Toluene, THF and CHCl_3 were dried using sodium or calcium hydroxide before use.

General synthesis.



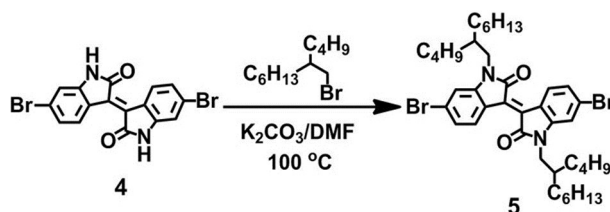
2-bromo-3-(2-butyloctyl)thiophene (2). To the solution of 3-(2-butyloctyl)-thiophene (**1**) (2.50 g, 9.9 mmol) in dichloromethane/chloroform (50 mL/25 mL), *N*-bromosuccinimide (1.76 g, 9.9 mmol) was added at $0\text{ }^\circ\text{C}$ in dark. The mixture was stirred at room temperature for 3 h. Then, the reaction mixture was poured into water

and extracted with dichloromethane. The organic phase was washed with water for three times, dried over anhydrous Na_2SO_4 , filtered and concentrated. The crude product was purified by silica gel chromatography to give **2** (2.67 g, yielded 81%) as a yellowoil. ^1H NMR (400 MHz, CHCl_3) : δ (ppm) 7.18 (d, J = 5.3 Hz, 1H), 6.76 (d, J = 5.5 Hz, 1H), 2.49 (d, J = 7.0 Hz, 2H), 1.64 (m, 1H), 1.41–1.15 (m, 16H), 0.87 (t, J = 5.9 Hz, 6H). ^{13}C NMR (100 MHz, CHCl_3) : δ (ppm) 141.17, 128.80, 124.89, 109.44, 38.56, 34.08, 33.43, 33.12, 31.89, 29.67, 28.81, 26.54, 23.04, 22.68, 14.09.



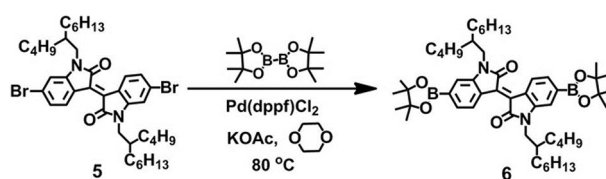
5-bromo-4-(2-butyloctyl)thiophene-2-carbaldehyde (3). Lithium

diisopropylamide (LDA) (2.10 mL, 2.0 mol/L) was added dropwise to the solution of 2-bromo-3-(2-butyloctyl)thiophene (**2**) (1.30 g, 3.9 mmol) in anhydrous THF (15 mL) at $-78\text{ }^\circ\text{C}$ under argon atmosphere. After stirred at $-78\text{ }^\circ\text{C}$ for 2 h, the mixture was added *N,N*-dimethylformamide (DMF) (0.91 mL, 11.8 mmol), followed by stirred at room temperature for 6 h. Then the mixture was quenched by water and extracted by ethyl acetate for three times. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography to give **3** (1.30 g, yielded 92%) as a yellow oil. ^1H NMR (400 MHz, CHCl_3) : δ (ppm) 9.76 (s, 1H), 7.42 (s, 1H), 2.53 (d, J = 7.1 Hz, 2H), 1.66 (m, 1H), 1.41–1.15 (m, 16H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, CHCl_3) : δ (ppm) 181.61, 143.18, 142.82, 137.16, 122.46, 38.47, 34.05, 33.33, 33.02, 31.82, 29.59, 28.74, 26.49, 22.97, 22.63, 14.06, 14.04.

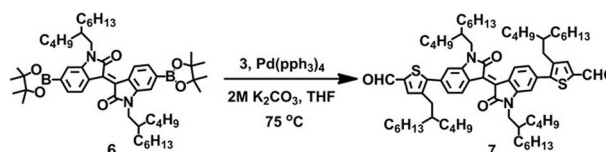


6,6'-dibromo-*N,N'*-(2-butyloctyl)-isoindigo (5). 1-Bromo-2-butyloctane (8.90 g, 35.7 mmol) was added to a suspension of 6,6'-dibromo- isoindigo (**4**)¹ (5.00 g, 11.9 mmol) and potassium carbonate (8.23 g, 59.5 mmol) in DMF (100 mL). The mixture was stirred at $100\text{ }^\circ\text{C}$ for 12 h. After workup, the mixture was poured to water and

extracted with dichloromethane for three times. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography to give **5** (7.00 g, yielded 78%) as a deep-red solid. ^1H NMR (400 MHz, CHCl_3) : δ (ppm) 9.06 (d, J = 8.6 Hz, 2H), 7.16 (dd, J = 8.8 Hz, J = 2.0 Hz, 2H), 6.89 (d, J = 1.8 Hz, 2H), 3.62 (d, J = 7.5 Hz, 4H), 1.88 (m, 2H), 1.40–1.18 (m, 32H), 0.92–0.82 (m, 12H). ^{13}C NMR (100 MHz, CHCl_3) : δ (ppm) 168.08, 146.21, 132.53, 131.03, 126.66, 125.08, 120.39, 111.51, 44.69, 36.12, 31.79, 31.49, 31.23, 29.64, 28.59, 26.33, 23.05, 22.63, 14.06, 14.04. Anal. Calcd. for $\text{C}_{40}\text{H}_{56}\text{Br}_2\text{N}_2\text{O}_2$: C, 63.49; H, 7.46; N, 3.70. Found: C, 63.55; H, 7.40; N, 3.59.

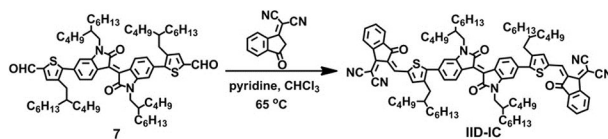


6,6'-(N,N'-2-butyloctyl)-Pinacoldiboronisoindigo (6). A mixture of 6,6'-dibromo-N,N'-(2-butyloctyl)-isoindigo (**5**) (6.41 g, 8.5 mmol), bis(pinacolato)diboron (6.45 g, 25.4 mmol), potassium acetate (4.99 g, 50.8 mmol), Pd(dppf)Cl_2 (372 mg, 0.51 mmol) and anhydrous 1,4-dioxane (100 mL) were stirred at 80 °C for 12 h. After cooled down, the mixture was extracted with dichloromethane and water for three times. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography and recrystallization in acetone/acetonitrile to give **6** (5.37 g, yielded 75%) as a dark red crystal. ^1H NMR (400 MHz, CHCl_3) : δ (ppm) 9.13 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.16 (s, 2H), 3.69 (d, J = 7.2 Hz, 4H), 1.95 (m, 2H), 1.46–1.16 (m, 56H), 0.94–0.79 (m, 12H). ^{13}C NMR (100 MHz, CHCl_3) : δ (ppm) 168.10, 144.48, 134.31, 128.83, 128.70, 124.24, 113.51, 84.04, 44.40, 36.09, 31.81, 31.61, 31.28, 29.63, 28.61, 26.40, 24.87, 23.05, 22.60, 14.10, 14.07. Anal. Calcd. for $\text{C}_{52}\text{H}_{80}\text{B}_2\text{N}_2\text{O}_6$: C, 73.41; H, 9.48; N, 3.29. Found: C, 73.42; H, 9.55; N, 3.25.



IID-Th-CHO (7). A mixture of 6,6'-(N,N'-2-butyloctyl)-Pinacoldiboronisoindigo (**6**)

(0.50 g, 0.6 mmol), 5-bromo-4-(2-butyloctyl)thiophene-2-carbaldehyde (**3**) (0.53 g, 1.5 mmol), Pd(PPh₃)₄ (17 mg, 0.015 mmol), potassium carbonate (2.20 mL, 2.0 mol/L in H₂O) and THF (10 mL) were stirred at 75 °C for 12 h. Then the mixture was poured into water, the organic phase was extracted by dichloromethane for three times. The organic phase was dried over anhydrous Na₂SO₄ and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography to give **7** (0.31 g, yielded 46%) as a brown black solid. ¹H NMR (400 MHz, CHCl₃) : δ (ppm) 9.90 (s, 2H), 9.27 (d, J = 8.2 Hz, 2H), 7.64 (s, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.86 (s, 2H), 3.71 (d, J = 7.2 Hz, 4H), 2.70 (d, J = 7.0 Hz, 4H), 1.93 (m, 2H), 1.66 (m, 2H), 1.48–1.07 (m, 64H), 0.94–0.75 (m, 24H). ¹³C NMR (100 MHz, CHCl₃) : δ (ppm) 182.74, 168.32, 148.33, 145.61, 141.68, 140.36, 138.72, 137.68, 133.00, 130.15, 123.15, 121.91, 108.75, 44.79, 39.16, 36.35, 33.46, 33.14, 31.83, 31.79, 31.70, 31.42, 29.67, 29.61, 28.76, 28.73, 26.50, 23.05, 22.96, 22.62, 22.59, 14.04, 14.01. MS (MALDI): m/z 1154.8 (M⁺). Anal. Calcd. for C₇₄H₁₁₀N₂O₄S₂: C, 76.90; H, 9.59; N, 2.42. Found: C, 76.81; H, 9.94; N, 2.37.



IID-IC. IID-Th-CHO (**7**) (0.29 g, 0.3 mmol) and 1,1-dicyanomethylene-3-indanone (0.24 g, 1.2 mmol) were dissolved in anhydrous CHCl₃ (50 mL), and then 1.1 mL pyridine was added to the mixture. After refluxed for 10 h, the reaction mixture was extracted by water and CHCl₃ for three times. The organic phase was dried over anhydrous Na₂SO₄ and the solvent was then removed by rotary evaporation. The crude product was purified by silica gel chromatography and recrystallization in n-hexane/dichloromethane to give **IID-IC** (0.30 g, yielded 80%) as a black solid. ¹H NMR (400 MHz, CHCl₃) : δ (ppm) 9.30 (d, J = 8.3 Hz, 2H), 8.86 (s, 2H), 8.73 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 7.0 Hz, 2H), 7.84 – 7.72 (m, 6H), 7.24 (s, 2H), 6.95 (s, 2H), 3.75 (d, J = 7.2 Hz, 4H), 2.74 (d, J = 7.1 Hz, 4H), 1.97 (m, 2H), 1.68 (m, 2H), 1.48–1.04 (m, 64H), 0.94–0.73 (m, 24H). ¹³C NMR (100 MHz, CHCl₃) : δ (ppm) 188.05, 168.31, 160.54, 155.29, 147.33, 145.62, 141.17, 140.01, 137.88, 137.54, 137.03, 135.72, 135.27, 134.66, 133.10,

130.18, 125.42, 123.94, 123.52, 123.30, 122.30, 114.40, 114.32, 108.59, 70.32, 44.79, 39.17, 36.43, 33.48, 33.20, 33.14, 31.84, 31.80, 31.75, 31.45, 29.70, 29.65, 28.80, 28.69, 26.56, 26.48, 23.07, 22.99, 22.62, 22.60, 14.05, 14.02. MS (MALDI): m/z 1506.9 (M^+). Anal. Calcd. for $C_{98}H_{118}N_6O_4S_2$: C, 78.05; H, 7.89; N, 5.57. Found: C, 77.92; H, 7.83; N, 5.72.

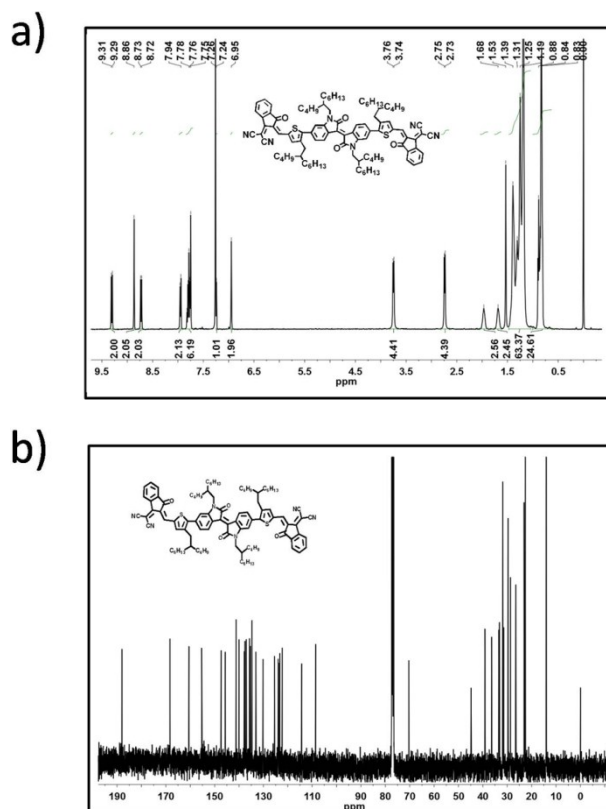


Figure S1. 1H NMR (a) and ^{13}C NMR (b) of IID-IC.

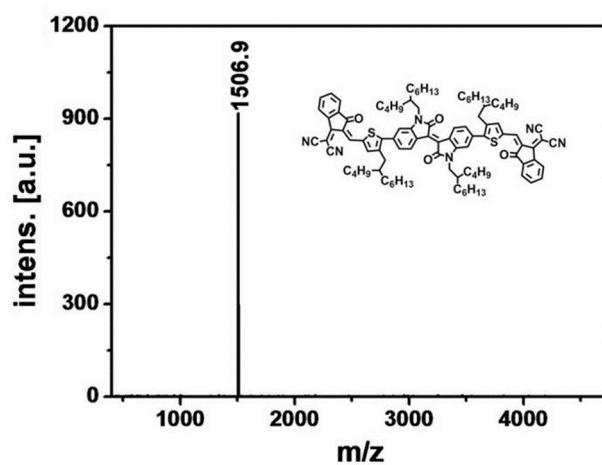


Figure S2. MALDI-TOF MS results of IID-IC.

2. Thermal properties

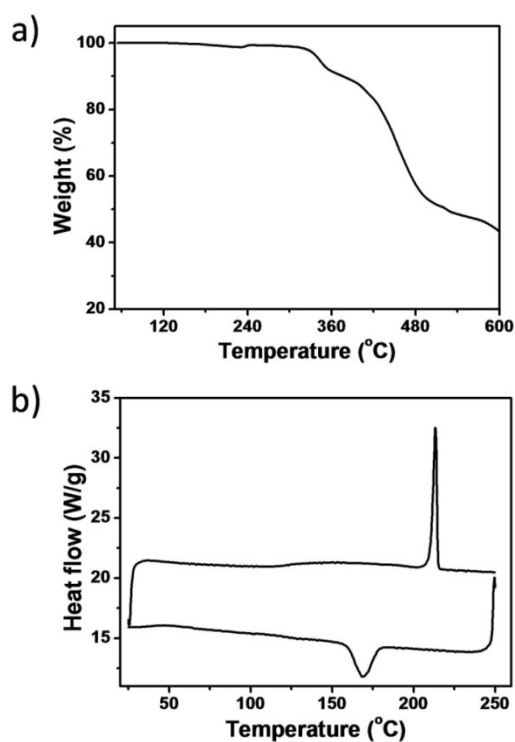


Figure S3. TGA (a) and DSC (b) curves of IID-IC.

3. DFT calculation results

All calculations were performed with the Gaussian 09 program. The geometry structure of IID-IC was optimized by using DFT calculations (B3LYP/6-31G*). Time-dependent DFT (TD-DFT) calculations at the B3LYP/6-31G* level of theory were performed to elucidate the absorption spectrum of IID-IC. TD-DFT calculations for the $S_0 \rightarrow S_n$ transitions using the same functional and basis set were then performed based on the optimized structure at ground state.

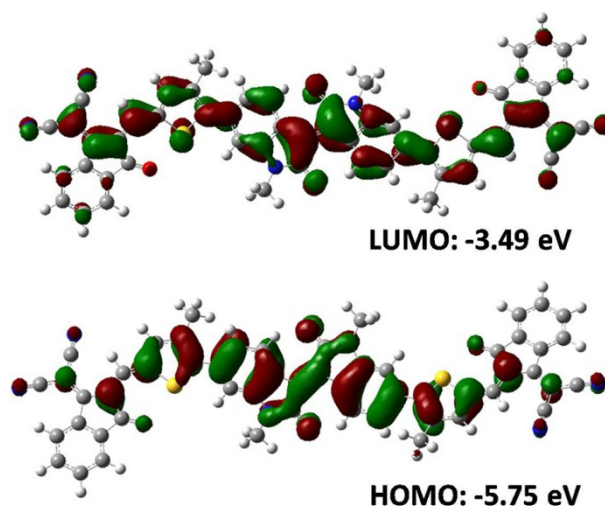


Figure S4. Kohn–Sham LUMO and HOMO of IID-IC based on calculations at the B3LYP/6-31G* level. The LUMO and HOMO energy levels are also shown.

Excitation energies and oscillator strengths (Oscillator strength exceeding 0.1):

Excited State 1: Energy: 1.9486 eV, Wavelength: 636.27 nm, Oscillator strength: 1.8096, Configurations: HOMO $\rightarrow$ LUMO (0.69498);

Excited State 4: Energy: 2.4950 eV, Wavelength: 496.93 nm, Oscillator strength: 0.3894, Configurations: HOMO-4 $\rightarrow$ LUMO (0.15595), HOMO-2 $\rightarrow$ LUMO (0.45893), HOMO-2 $\rightarrow$ LUMO+2 (-0.13145), HOMO $\rightarrow$ LUMO+2 (0.46717);

Excited State 5: Energy: 2.5265 eV, Wavelength: 490.74 nm, Oscillator strength: 0.2517, Configurations: HOMO-2 $\rightarrow$ LUMO (-0.48254), HOMO $\rightarrow$ LUMO+2 (0.49619);

Excited State 7: Energy: 2.7143 eV, Wavelength: 456.79 nm, Oscillator strength: 0.2775, Configurations: HOMO-3 $\rightarrow$ LUMO+1 (0.11641), HOMO-1 $\rightarrow$ LUMO+1 (0.67336);

Excited State 11: Energy: 2.9491 eV, Wavelength: 420.42 nm, Oscillator strength: 0.1567, Configurations: HOMO-4 $\rightarrow$ LUMO (-0.27177), HOMO-3 $\rightarrow$ LUMO+1 (0.53932), HOMO-2 $\rightarrow$ LUMO+1 (-0.20322), HOMO-2 $\rightarrow$ LUMO+2 (-0.14791), HOMO $\rightarrow$ LUMO+4 (-0.17536);

Excited State 30: Energy: 3.5457 eV, Wavelength: 349.67 nm, Oscillator strength: 0.1357, Configurations: HOMO-11 $\rightarrow$ LUMO (0.17821), HOMO-10 $\rightarrow$ LUMO (0.41656), HOMO-6 $\rightarrow$ LUMO (-0.25715), HOMO-5 $\rightarrow$ LUMO+1 (-0.14328), HOMO-4 $\rightarrow$ LUMO+2

(-0.17692), HOMO-3 $\rightarrow$ LUMO+3 (0.27862), HOMO-2 $\rightarrow$ LUMO+4 (0.18403).

The transition energies and oscillator strengths simulated by the TD-DFT (B3LYP/6-31G*) calculations resulted in two absorption bands for IID-IC. The calculation results agree well with the experiment result of absorption spectra (Figure 2a). The low-energy absorption band around 610 nm is attributed to the HOMO $\rightarrow$ LUMO transition (Excited State 1). The high-energy absorption band around 500 nm mainly come from the transitions of HOMO-4 $\rightarrow$ LUMO, HOMO-2 $\rightarrow$ LUMO, HOMO-2 $\rightarrow$ LUMO+2, HOMO $\rightarrow$ LUMO+2, HOMO-3 $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO+1 (illustrated by the Excited State 4, 5 and 7).

4. OSC device fabrication and measurement

The device architecture was ITO/PEDOT:PSS/J61:acceptors/Ca/Al. IID-IC and PC₇₁BM were used as electron acceptors, respectively. J61 was purchased from Solarmer materials, Inc. PC₇₁BM was purchased from American Dye Source, Inc. Indium tin oxide (ITO) glass substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol, followed by dried at 120 °C for 30 min and treated with UV-ozone for 30 min. Then PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO glass substrates at 5000 r/min for 40 s to give a thickness of 40 nm, followed by baking at 120 °C for 30 min. The substrates were transferred to a nitrogen-filled glove box. The blend was spin-coated onto the PEDOT:PSS layer to produce the active layer. The blend ratio is 1:1.3 (w:w) for J61:IID-IC in *o*-DCB solution. The active layer of J61:IID-IC blend was annealed at 160 °C for 10 min. The blend ratio is 1:2 (w:w) for J61:PC₇₁BM in chlorobenzene solution with 5 vol% 1,8-diiodooctane, and the active layer of J61:PC₇₁BM was annealed at 120 °C for 10 min. Finally, the active layer was transferred to a vacuum chamber, and Ca (20 nm) and Al (100 nm) were deposited by thermal evaporation at the pressure of about 2×10^{-4} Pa. The active area of each device was 8 mm². The current density (*J*-*V*) curves of the OSC devices were measured using a computer-controlled Keithley 2400 source meter under 100 mW cm⁻² AM 1.5G simulated solar light illumination provided by a XES-40S2-CE Class Solar Simulator (Japan, SAN-EI Electric Co., Ltd.). The EQE spectrum

was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a calibrated monosilicon diode.

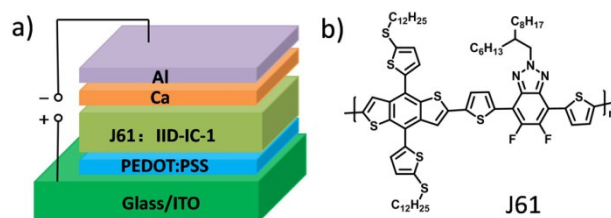


Figure S5. a) OSC device structure; b) chemical structure of J61.

5. Hole/electron-only devices fabrication and hole/electron mobility measurement

The electron/hole mobilities were measured using space charge limited current (SCLC) method. The electron-only device structure for the IID-IC film is ITO/PEIE/IID-IC/Ca/Al. The electron-only and hole-only device structures for the J61:IID-IC blend film are ITO/PEIE/J61:IID-IC/Ca/Al and ITO/PEDOT:PSS/J61:IID-IC/MoO₃/Al, respectively. The current-voltage curves in the range of 0–10 V were recorded using a computer-controlled Keithley 2400 source meter, and the results were fitted to a space-charge limited function:

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

where J is the current density, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of 3 for molecules, μ is the zero-field mobility, V is the potential across the device ($V = V_{\text{applied}} - V_{\text{bias}} - V_{\text{series}}$), L is the thickness of active layer, and β is the field-activation factor. The series and contact resistance (V_{series}) of the device (10–15 Ω) were measured using blank device of ITO/PEIE/Ca/Al or ITO/PEDOT:PSS/MoO₃/Al. The range of 0–5 V was used to extract the mobility values.

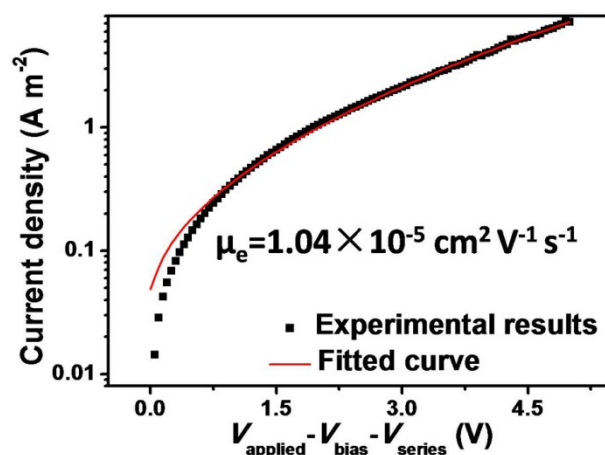


Figure S6. J-V curve and SCLC fitting of the electron-only device of IID-IC film.

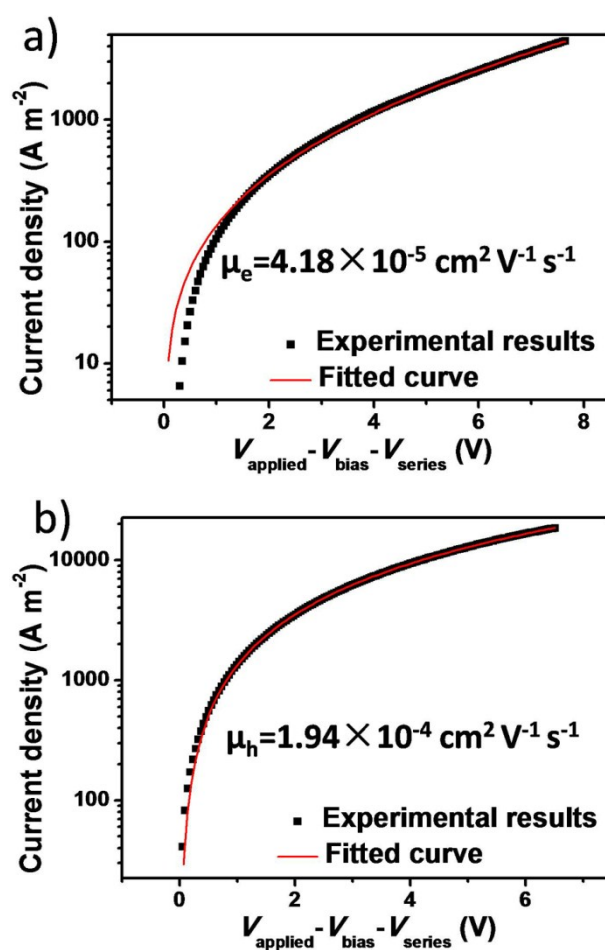


Figure S7. J-V curves and SCLC fittings of (a) the electron-only device and (b) the hole-only device based on the J61:IID-IC blend film.

6. Charge recombination behavior and charge dissociation process

The charge recombination behavior is estimated by measuring the dependence of J_{SC} on light density (P). The relationship between J_{SC} and P can be described as $J_{SC} \propto$

P^α . If all the charges are swept out and collected by the electrode before recombination, α should be equal to 1, while $\alpha < 1$ means the existence of charge recombination. The α value of IID-IC based OSCs is 0.94, suggesting negligible bimolecular charge recombination at the short circuit condition.

The exciton dissociation probability of the OSC device are estimated by measuring the photocurrent density (J_{ph}) versus the effective voltage (V_{eff}) curve. J_{ph} is defined as $J_L - J_D$, where J_L and J_D are the photocurrent densities under illumination and in dark, respectively. V_{eff} is defined as $V_0 - V_{bias}$, where V_0 is the voltage at which photocurrent is zero and V_{bias} is the applied voltage bias. The charge dissociation probability ($P(E, T)$) can be calculated from J_{ph}/J_{sat} . Under short-circuit condition, the $P(E, T)$ of IID-IC based OSCs is 60.6%, which indicates ineffective exciton dissociation.

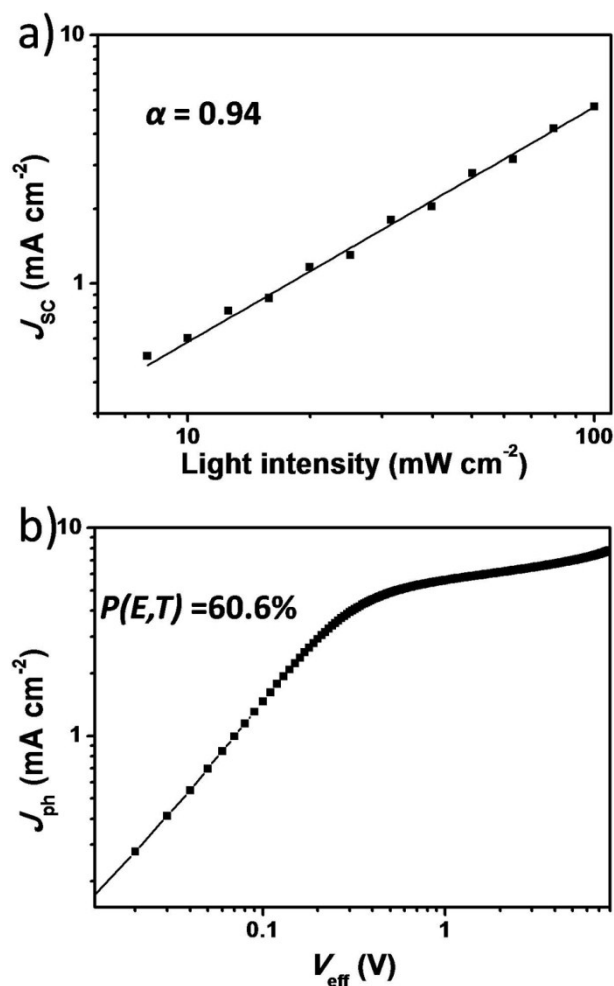


Figure S8. a) Dependence of J_{sc} on light density and b) photocurrent versus effective voltage curve of the IID-IC-based OSC device.

7. The morphology of active layer of J61:IID-IC

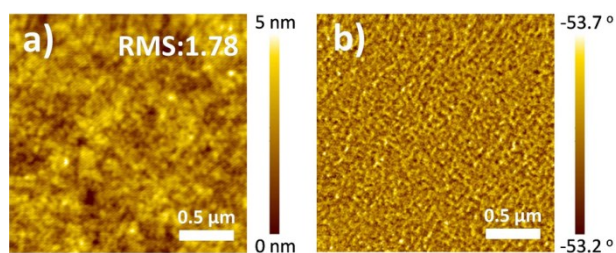


Figure S9. AFM height (a), phase (b) images of the J61:IID-IC active layer.

8. Photovoltaic properties of OSC devices based on IID-IC blending with various polymer electron donors (P3HT, PBDB-T, PTB7-Th and PffBT4T-2OD)

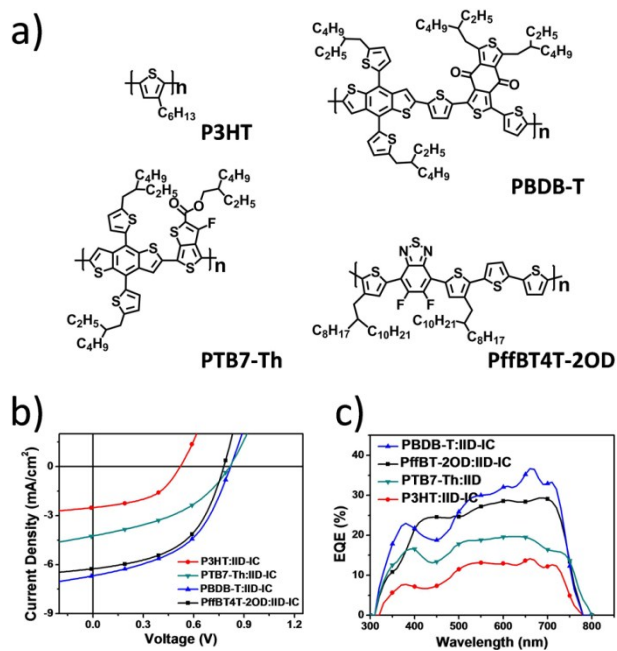


Figure S10. a) Chemical structures of P3HT, PBDB-T, PTB7-Th and PffBT4T-2OD; b) *J*-*V* curves and c) EQE curves of OSC devices based on donor:IID-IC.

Table S1. Photovoltaic performance of OSC devices based on donor:IID-IC.

Donor	$V_{oc}(V)$	$J_{sc}(mA\ cm^{-2})$	FF(%)	PCE(%)
P3HT	0.52	2.51	0.49	0.64
PTB7-Th	0.82	4.25	0.42	1.46

PBDB-T	0.82	6.68	0.48	2.63
PffBT4T-2OD	0.78	6.25	0.51	2.50

The preliminary PCE of IID-IC is not very high, and the main limit is its poor morphology, which may be ascribed to its sub-optimal blend morphology. Further optimization of the J61:IID-IC blend morphology and fine-tuning the chemical structure of IID-IC are in progress in our lab and is expected to give OSC device performance enhancement.

9. Photovoltaic properties of OSC device based on J61:PC₇₁BM

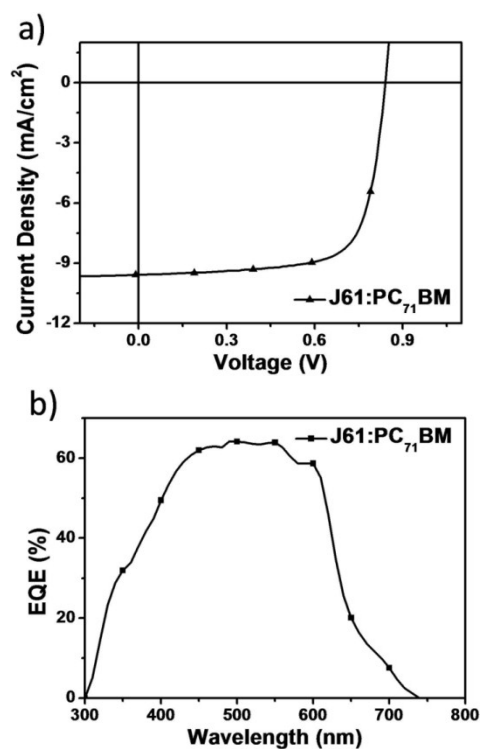


Figure S11. a) *J*-*V* curve and b) EQE curve of the OSC device using J61:PC₇₁BM as the active layer.

10. References

- 1 J. Mei, K. R. Graham, R. Stalder and J. R. Reynolds, *Org. Lett.*, 2010, **12**, 660.