Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

For

An A–D–A'–D–A Type Small Molecule Acceptor with Wide Absorption Spectrum and Near-Infrared Absorption

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Contents

1. ^{1}H and ^{13}C NMR spectra

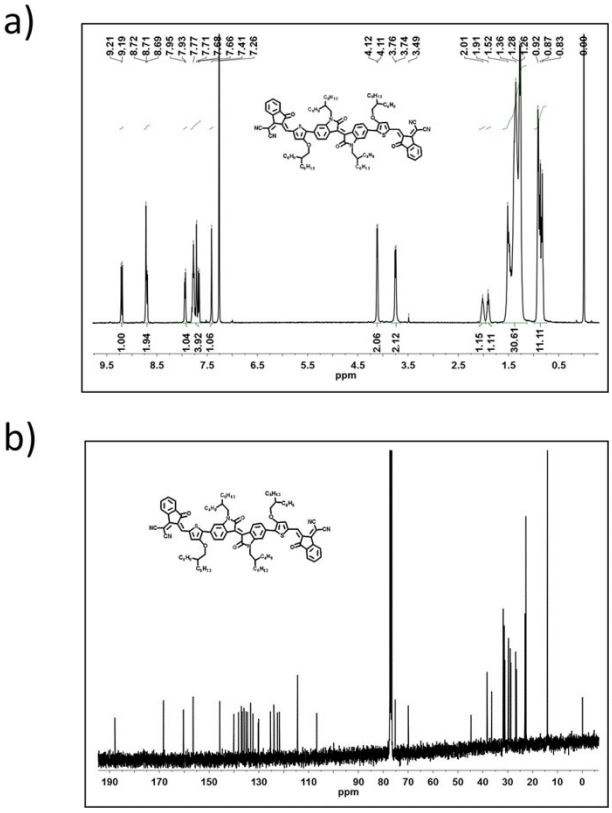


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of IID-IC-O.

2. Thermal properties

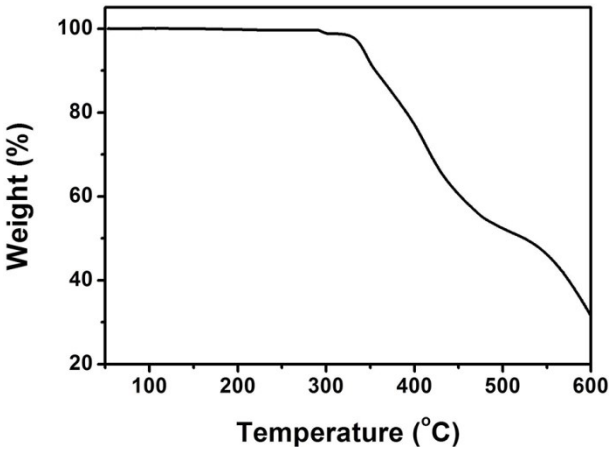


Figure S2. TGA curve of IID-IC-O.

3. Density functional theory calculations

Density functional theory (DFT) calculations were performed using Gaussian 09. The geometry structure of IID-IC-O was optimized by using DFT calculations with the B3LYP/6-31G* basis set. Figure S3 shows the frontier molecular orbitals and

LUMO/HOMO energy levels of IID-IC and IID-IC-O. Time-dependent DFT (TD-DFT) calculations were performed to elucidate the absorption spectrum of IID-IC-O. TD-DFT calculations for the $S_0 \rightarrow S_n$ transitions using the same functional and basis set were performed based on the optimized structure at ground state.

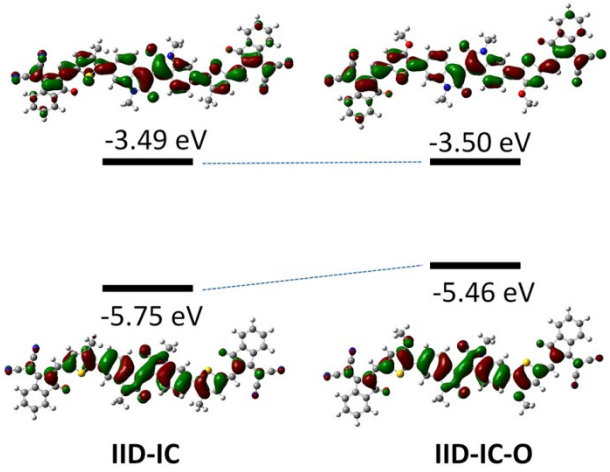


Figure S3. Kohn-sham LUMOs/HOMOs and the LUMO/HOMO energy levels based on DFT calculations at the B31LYP/6-31G* level for the model molecules of IID-IC and IID-IC-O with all the long alkyl chains being replaced by methyl groups for simplification.

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

Excited State 1: Energy: 1.7098 eV, Wavelength: 725.14 nm, Oscillator strength: 2.1818, Configulations: HOMO → LUMO (0.70095);

Excited State 5: Energy: 2.3680 eV, Wavelength: 523.57 nm, Oscillator strength: 0.4806, Configulations: HOMO – 2 → LUMO (0.66541), HOMO → LUMO + 2 (0.16487);

Excited State 7: Energy: 2.4567 eV, Wavelength: 504.68 nm, Oscillator strength: 0.2302, Configulations: HOMO – 1 → LUMO + 1 (0.67710), HOMO → LUMO + 4 (–0.12467);

Excited State 9: Energy: 2.6313 eV, Wavelength: 471.18 nm, Oscillator strength: 0.1142, Configulations: HOMO – 4 → LUMO (–0.12580), HOMO – 3 → LUMO + 1 (–0.15366).

The simulated absorption spectrum using the TD-DFT calculations for IID-IC-O

shows two absorption bands with a peak in the long wavelength region and a shoulder peak in the short wavelength region, which agree well with the measured absorption spectrum (Figure S4). The long wavelength peak is attributed to the HOMO→LUMO transition (Excited State 1), which corresponding to the energy of 1.7098 eV (wavelength at 725.14 nm). The shoulder peak in the short wavelength region mainly come from the transitions of HOMO – 2 → LUMO, HOMO → LUMO + 2, HOMO – 1→ LUMO + 1, HOMO → LUMO + 4, HOMO – 4 → LUMO and HOMO – 3 → LUMO + 1 (illustrated by the Excited State 5, 7 and 9).

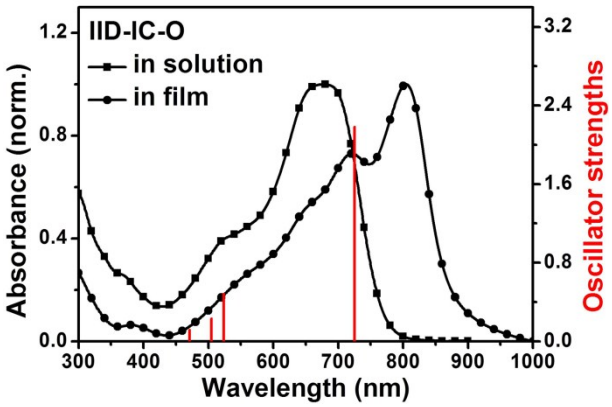


Figure S4. Normalized UV-vis absorption spectra of IID-IC-O in solution and in thin film. The red bars show the transition energies and oscillator strengths simulated by the TD-DFT (B3LYP/6-31G*) calculations.

4. Normalized UV-vis absorption spectra

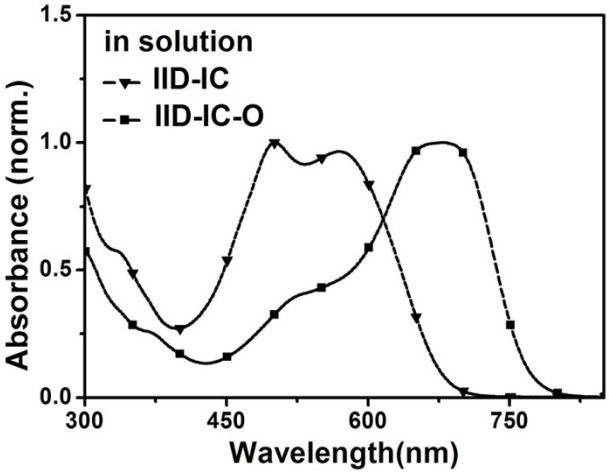


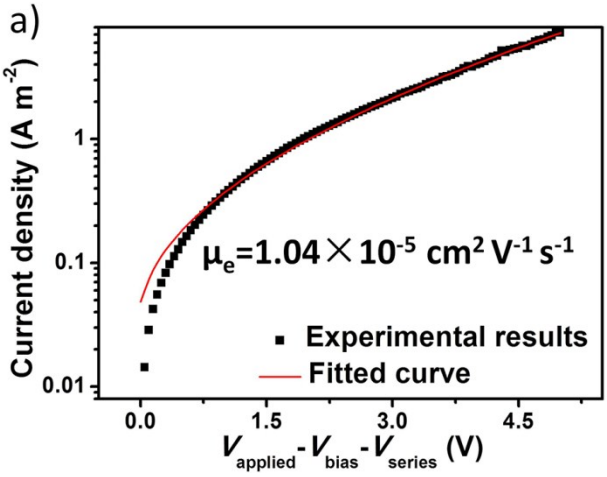
Figure S5. Normalized UV-vis absorption spectra of IID-IC and IID-IC-O in chlorobenzene solution.

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-O film is ITO/PEIE/IID-IC-O/Ca/Al. The electron-only and hole-only device structures for the J61:IID-IC-O blend film are ITO/PEIE/J61:IID-IC-O/Ca/Al and ITO/PEDOT:PSS/J61:IID-IC-O/MoO_3/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:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}\exp\left(0.89\beta\frac{\sqrt{V}}{\sqrt{L}}\right)$$

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 ($V = V_{applied} - V_{bias} - V_{series}$), 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/MoO_3/Al. The range of 0–5 V was used to extract the mobility values.



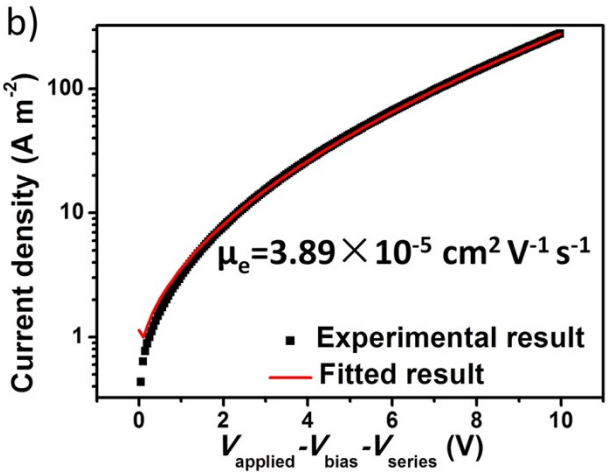


Figure S6. *J–V* curves and SCLC fittings of the electron-only devices of a) IID-IC film and b) IID-IC-O film.

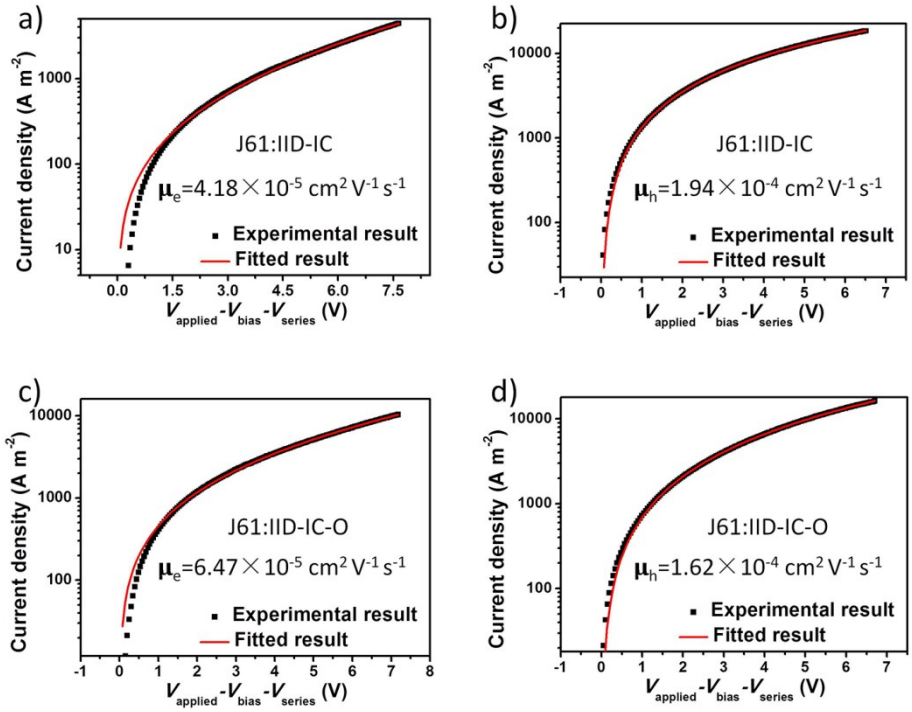


Figure S7. *J–V* curves and SCLC fittings of a, c) the electron-only device and b, d) the hole-only device based on the J61:IID-IC blend and the J61:IID-IC-O blend, respectively.

6. Charge recombination behavior

The monomolecular recombination of IID-IC-O-based device was studied by measuring the light density (*P*) dependence of V_{OC} with the linear law: $V_{OC} \propto \ln P$. The slope for IID-IC-O-based device is 1.33 kT/q, which shown in Figure S8. The big

slope for IID-IC-O-based cell indicates serious trap-assisted recombination occurred in the device. The serious trap-assisted recombination for IID-IC-O-based device may be the main reason of the low fill factor (FF) of 0.51.

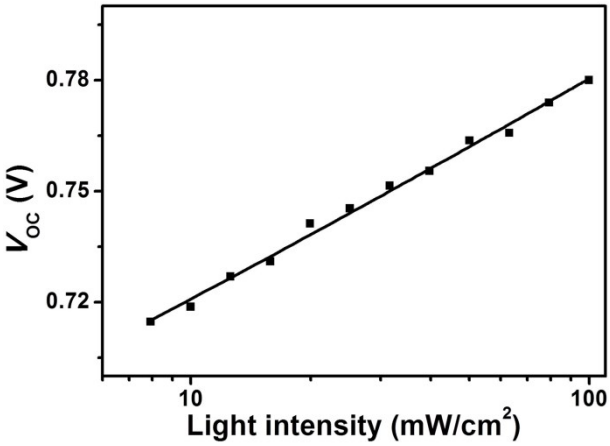


Figure S8. The line fitted to the light-intensity dependence of the V_{oc} values for the IID-IC-O-based OSC device.

7. Stacking in solid state

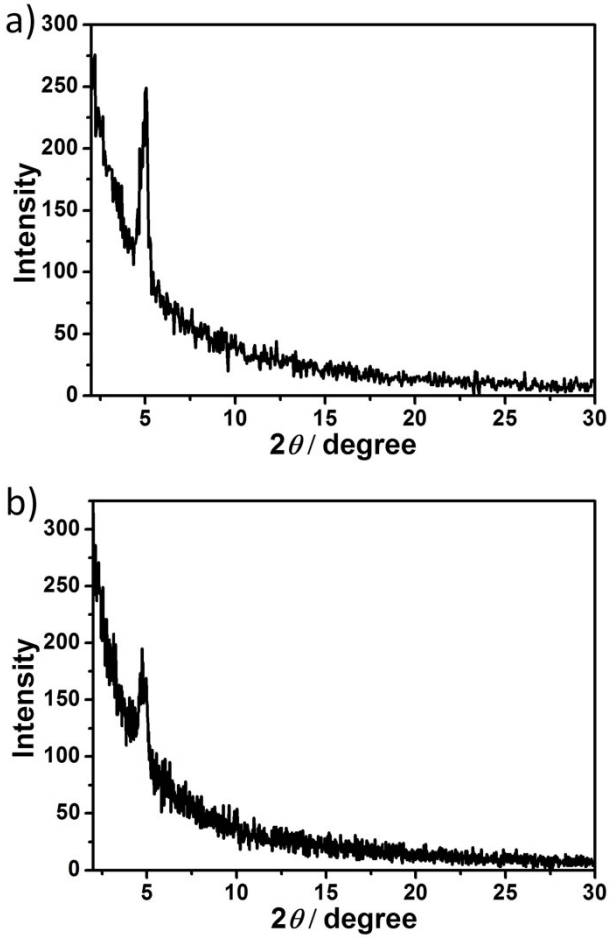


Figure S9. GI-XRD patterns of a) IID-IC-O film and b) J61:IID-IC-O blend film.

8. The morphology of active layer

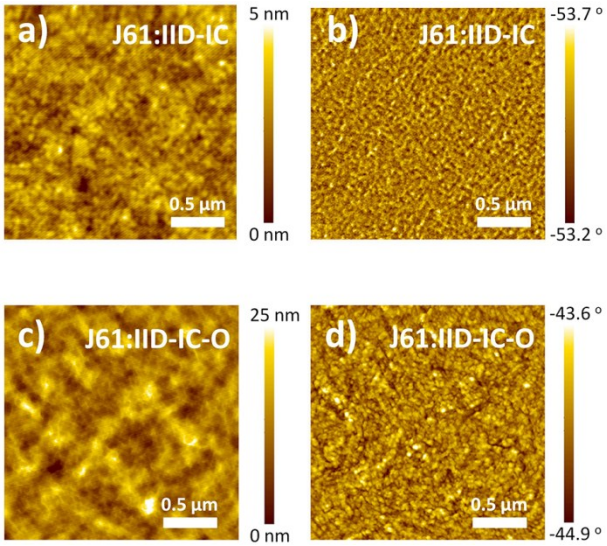


Figure S10. AFM height a) and AFM phase b) of the J61:IID-IC blend film. AFM height c) and AFM phase d) of the J61:IID-IC-O blend film.

9. The photoluminescence (PL) measurements

Photoluminescence (PL) spectroscopy was employed to study the exciton dissociation and charge transfer behavior in the blends. The excitation wavelengths of 550 nm for J61 and 600 nm for IID-IC or IID-IC-O were selected according to their maximum absorptions. Figure S11 shows the PL spectra of the blend films in comparison with those of pristine polymer donor J61 or small molecular acceptor IID-IC/IID-IC-O films. The pristine J61 shows PL with emission peak at 661 nm. For the J61:IID-IC and J61:IID-IC-O blend films, their emissions are effectively quenched (by 91% for IID-IC and 92% for IID-IC-O), suggesting effective electron transfer from J61 to IID-IC or IID-IC-O for the excitons present in the donor phase. The pristine IID-IC and IID-IC-O show PL with emission peak at 798 nm and 830 nm, respectively. For the blend films, the PL quenching efficiency of J61:IID-IC is 90% while the PL quenching efficiency of J61:IID-IC-O is 84% when using the photo excitation at 600 nm.

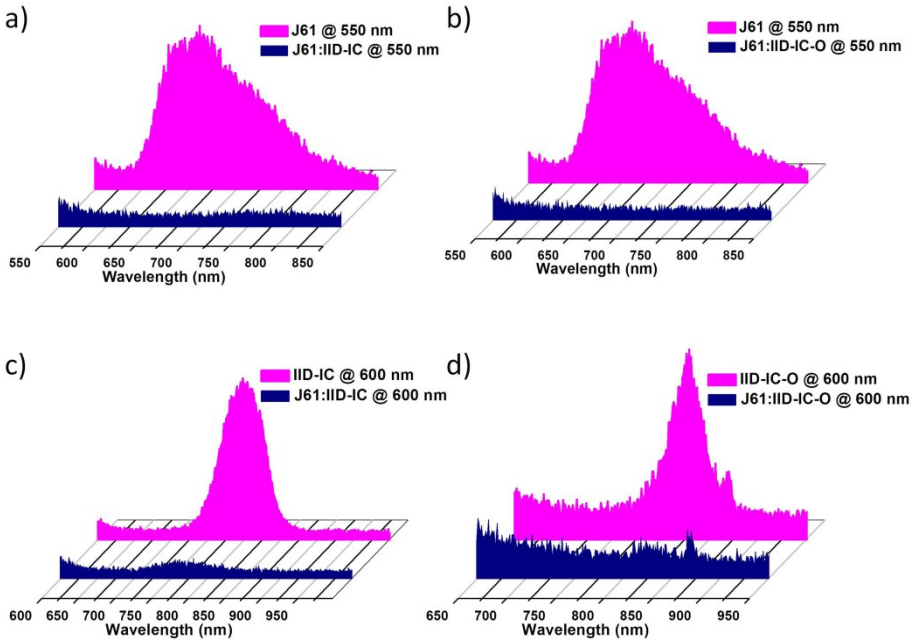


Figure S11. Photoluminescence spectra of pure J61 (excited at 550 nm) and IID-IC or IID-IC-O (excited at 600 nm) as well as the blend films of J61/IID-IC, and J61/IID-IC-O (excited at 550 and 600 nm).