

Supporting Information

All-Small-Molecule Efficient Ternary Organic Solar Cells Employing a Coumarin Donor and Two Fullerene-Free Acceptors

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Device fabrication and characterization:

Indium tin oxide (ITO) coated glass substrates with a sheet resistance of 10-12 Ω cm⁻² were thoroughly cleaned prior to device fabrication by soaking in detergent solution followed by ultrasonication in deionized water, acetone and isopropyl alcohol sequentially for 15 min. The substrates were dried in vacuum overnight and a 40 nm thick poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 2500 rpm for 30 s. The substrates were dried at 110 °C for 10 min in under air conditions. The active layers were spun from solutions of C1-CN and F13 or IDT-IC at different weight ratios of 1:0.4, 1:0.8, 1:1.2 and 1:1.4 with an overall concentration of 14 mg/mL from chloroform. In order to prepare the ternary bulk heterojunction active layer, the weight ratio between two acceptors is varied and kept C1-CN

concentration constant. Solvent vapor annealing (SVA) of active layers spin coated from solution in a binary blend of CF with weight ratio of 1:2 and ternary C1-CN:IDT-IC:F13 (1:0.3:0.9) was carried out by placing the substrate in a glass petri dish containing 0.3 mL THF for 40 s. On top of the active layer, a thin PFN layer was spin coated at a concentration of 1.5 mg/mL on at 3000 rpm for 30 s. Finally, the aluminum (Al) top electrode was thermally deposited on the top in a vacuum of 10^{-5} Torr through a shadow mask area of 20 mm². All devices were fabricated and tested in an ambient atmosphere without encapsulation. The hole-only devices and electron only devices with architectures of ITO/PEDOT:PSS/active layer/Au and ITO/Al/active layer/Al, respectively were also fabricated in a similar way in order to measure the hole and electron mobility. The current-voltage (J - V) characteristics of the BHJ organic solar cells were measured using a computer-controlled Keithley 2400 source meter in the dark and under simulated AM1.5G illumination of 100 mW/cm². A xenon light source coupled with an optical filter was used to provide stimulated irradiance at the surface of the devices. The incident photon-to-current efficiency (IPCE) of the devices was measured by Bentham IPCE system.

The exciton generation rate (G_{\max}), exciton dissociation probability (P_{diss}) and charge collection probability (P_{coll}) were determined by the examination of the variation of photocurrent density (J_{ph}) with effective voltage (V_{eff}). The $J_{\text{ph}}=J_{\text{L}}-J_{\text{D}}$, where J_{L} and J_{D} are the current densities under illumination and in dark, respectively. $V_{\text{eff}} = V_{\text{o}}-V_{\text{a}}$, where V_{o} is the voltage when $J_{\text{ph}}=0$ and V_{a} is the applied voltage.

The transmission electron microscope (TEM) images were taken on the Tecnai 20 (FEI) S-Twin system, and the thin film of the samples were deposited on Cu-grid. The XRD patterns of the thin films were recorded using X-ray diffractometer (Panalytical X-Pert Pro).

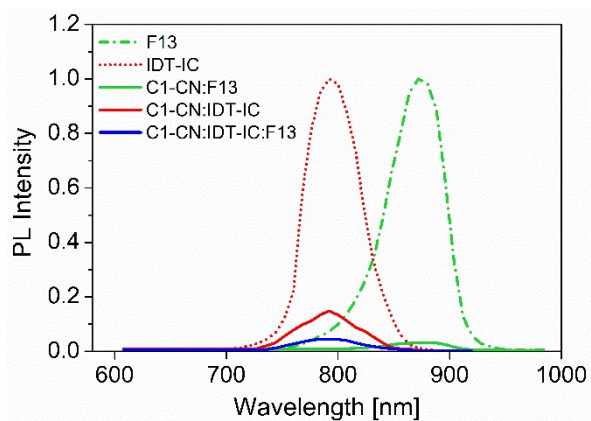


Figure S1. Thin film PL spectra of neat IDT-IC, F13, their binary blends with C1-CN and ternary blend.

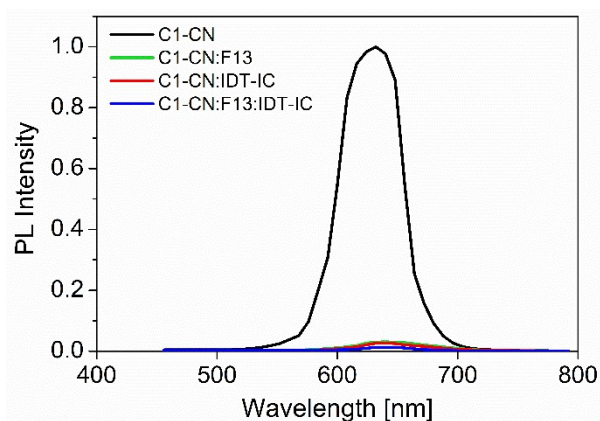


Figure S2. Thin film PL spectra of pristine C1-CN, C1-CN:F13, C1-CN:IDT-IC and C1-CN:IDT-IC:F13, when excited at wavelength corresponds to the absorption maxima of C1-CN

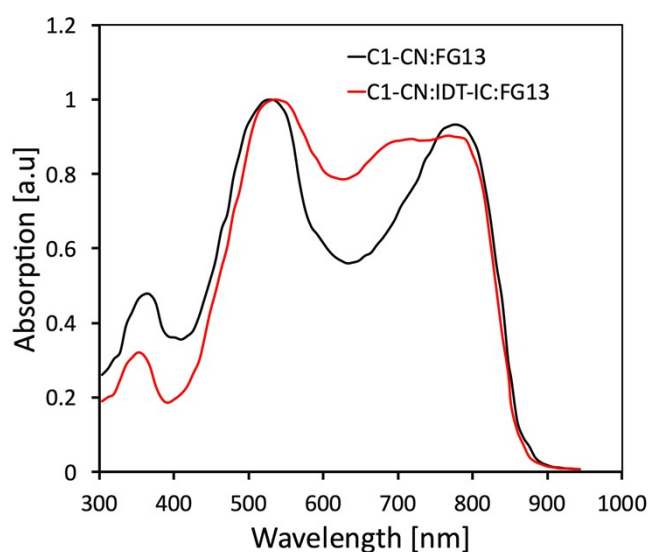


Figure S3. Thin film absorption spectra of binary C1-CN:F13 and ternary C1-CN:IDT-IC:F13.

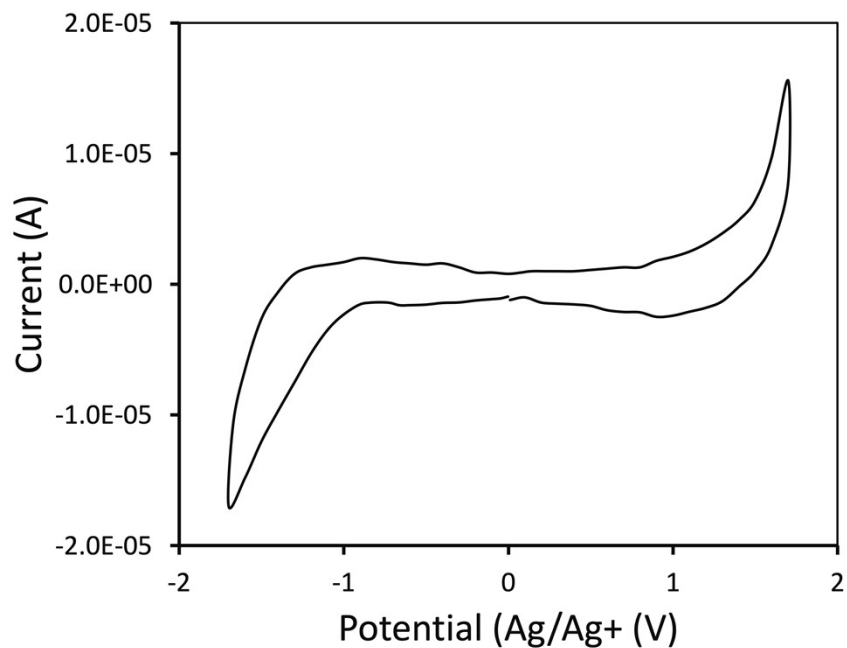


Figure S4. Cyclic voltammetry curves for mixed IDT-IC:F13 (0.3:0.9 w/w) films

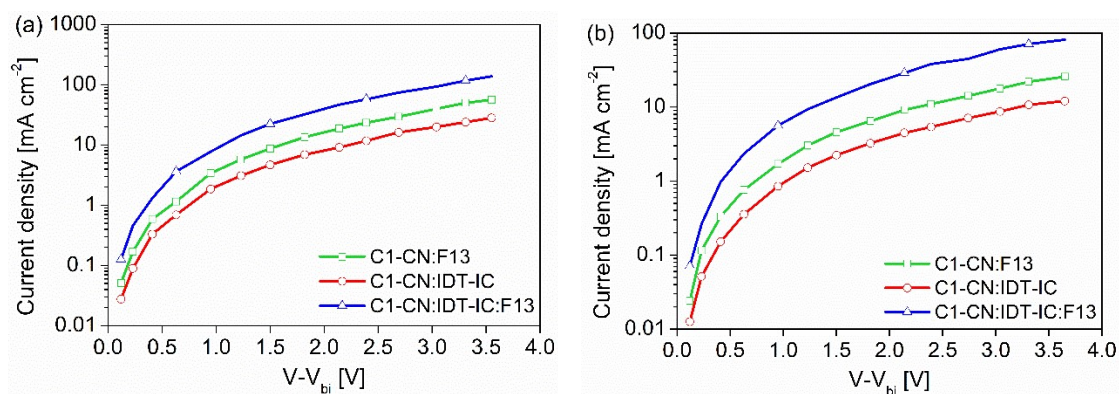


Figure S5. Dark J-V characteristics and their fitting with SCLC model for (a) hole only and (b) electron only devices for binary and ternary blends.

Table S1. Photovoltaic parameters of the OSCs based C1-CN:IDT-IC with different weight ratios using chloroform solvent.

| C1-CN:IDT-IC wt. ratio | J_{SC} [mA/cm ²] | V_{OC} [V] | FF | PCE [%] |
|------------------------|--------------------------------|--------------|-------------|-------------|
| 1:0.4 | 7.04 | 0.92 | 0.53 | 3.43 |
| 1:0.8 | 7.88 | 0.92 | 0.54 | 3.91 |
| 1:1.2 | 8.38 | 0.91 | 0.55 | 4.19 |
| 1:1.4 | 7.86 | 0.92 | 0.53 | 3.83 |

Table S2. Photovoltaic parameters of the OSCs based C1-CN:F13 with different weight ratios using chloroform solvent.

| C1-CN:F13 wt. ratio | J_{SC} [mA/cm ²] | V_{OC} [V] | FF | PCE [%] |
|---------------------|--------------------------------|--------------|-------------|--------------|
| 1:0.4 | 16.86 | 1.03 | 0.58 | 10.07 |
| 1:0.8 | 18.12 | 1.01 | 0.60 | 10.98 |
| 1:1.2 | 18.74 | 1.02 | 0.61 | 11.66 |
| 1:1.4 | 18.23 | 1.03 | 0.59 | 11.08 |

Table S3. Photovoltaic parameters of the ternary OSCs based C1-CN:IDT-IC:F13 with different weight ratios of IDT-IC and F13 using chloroform solvent.

| IDT-IC:F13 wt. ratio | J_{SC} [mA/cm ²] | V_{OC} [V] | FF | PCE [%] |
|----------------------|--------------------------------|--------------|-------------|--------------|
| 0.1:1.1 | 19.08 | 1.01 | 0.63 | 12.14 |
| 0.2:1.0 | 19.97 | 0.98 | 0.64 | 12.52 |
| 0.3:0.9 | 20.72 | 0.97 | 0.67 | 13.46 |
| 0.4:0.8 | 20.04 | 0.94 | 0.65 | 12.24 |