Electronic Supplementary Information for:

Layer by layer solution processed organic solar cells based on small molecule donor and polymer acceptor

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Calculation of DIB-SQ weight content from XPS

$$\text{DIB-SQ weight content} = \frac{\text{DIB-SQ weight}}{\text{DIB-SQ weight} + \text{PPDIDTT weight}} = \frac{n_{SQ}M_{SQ}}{n_{SQ}M_{SQ} + n_P M_P} = \frac{1}{1 + \frac{n_P M_P}{n_{SQ}M_{SQ}}}$$

$$\frac{N}{S} = \frac{2n_P + 2n_{SQ}}{3n_P}$$

$$\Downarrow$$

$$\frac{n_{SQ}}{n_P} = 1.5\frac{N}{S} - 1$$

$$\text{DIB-SQ weight content} = \frac{1}{\left(\frac{M_P}{M_{SQ}\left(1.5\frac{N}{S} - 1\right)}\right) + 1}$$

Where M_P is the molecular weight of repeated unit of PPDIDTT (1288); M_{SQ} is the molecular weight of DIB-SQ (554); n_p is the mole number of repeated unit of PPDIDTT; n_{SQ} is the mole number of DIB-SQ; $\frac{N}{S}$ is the atom ratio of N/S. A DIB-SQ molecule has two N atoms while a repeated unit of PPDIDTT has two N atoms and three S atoms.

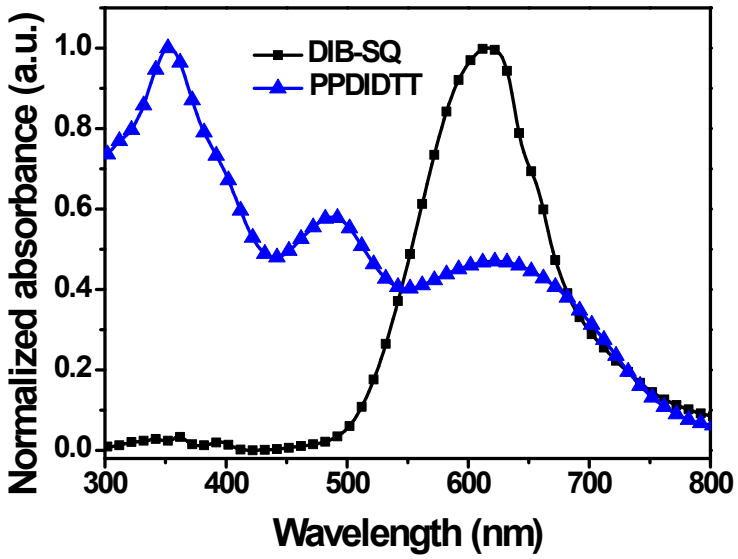


Fig. S1 UV-vis spectra of DIB-SQ and PPDIDTT films.

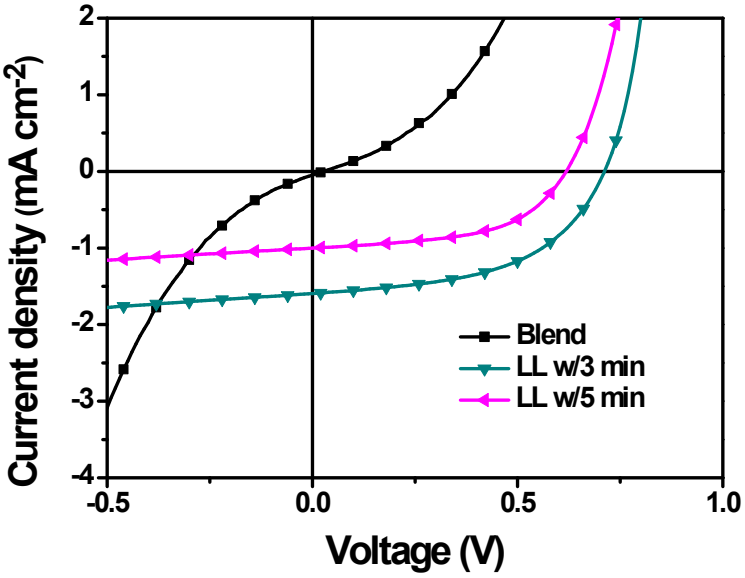


Fig. S2 *J*–*V* characteristics of DIB-SQ/ PPDIDTT blend devices and LL devices after thermal annealing at 100 °C for 3 min and 5 min.

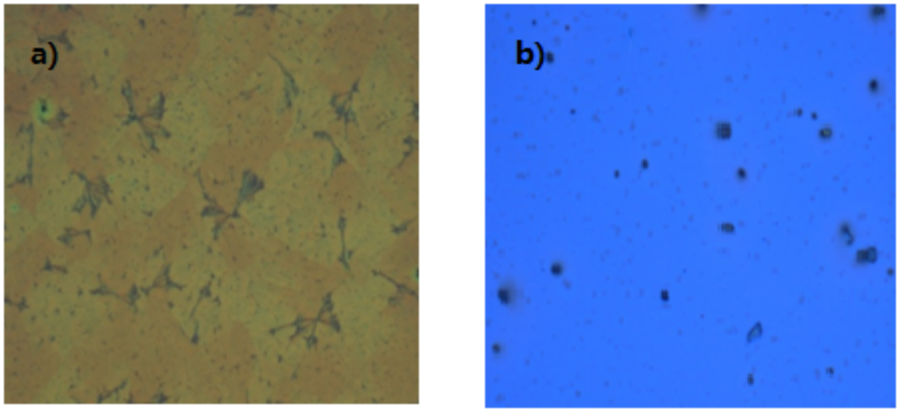
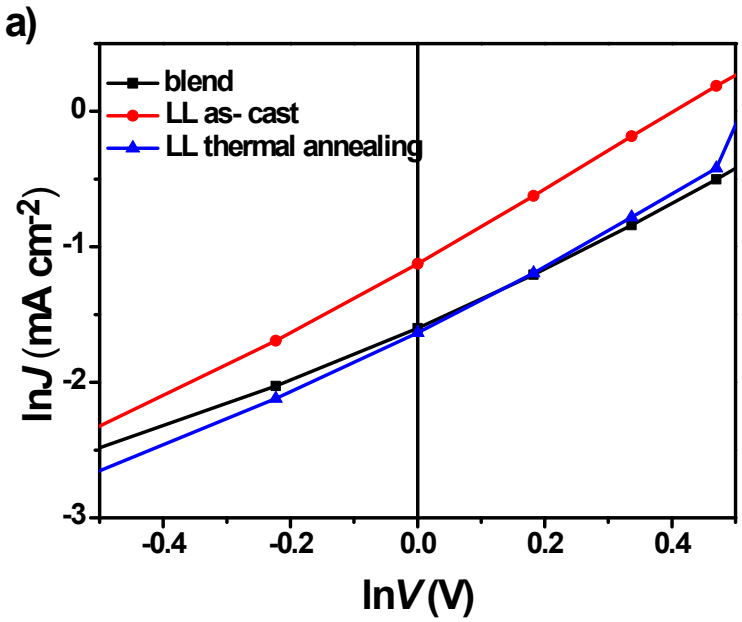


Fig. S3 Optical microscope images of a) DIB-SQ film (250 μm × 250 μm) and b) DIB-SQ /PPDIDTT (2:1) blend film (250 μm × 250 μm) on silica glass substrates.



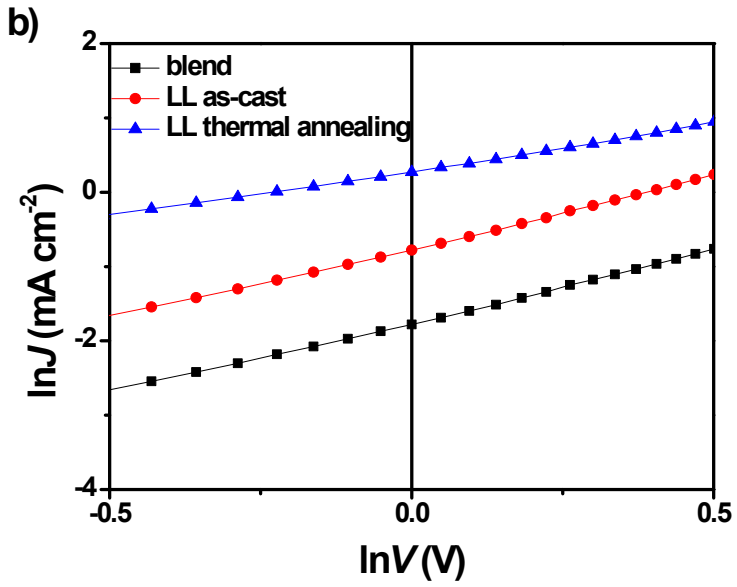


Fig. S4 *J*–*V* characteristics under dark for a) hole-only and b) electron-only devices based on DIB-SQ/PPDIDTT blend and LL films with or without thermal annealing at 100 °C for 1 min.