Supporting Information

A Critical Role of Additive in Binary Halogen-free Solvent Systems for Generally Processing High-efficient Organic Solar Cells

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Materials: PIDT-FQ-T Molecular weight: $M_n = 26$ kDa, PDI = 2.6; PBDTTT-C-T Molecular weight: $M_n = 22$ kDa, PDI = 2.9; P3HT Molecular weight: $M_n = 40$ kDa, PDI = 1.2; PTB7 Molecular weight: $M_n = 50$ kDa, PDI = 1.8;

SCLC Mobility measurements: Space charge limited currents have been tested in electron only devices with a configuration of ITO/Al/polymer:PCBM/Ca/Al and hole-only devices with a configuration of ITO/PEDOT:PSS/polymer:PCBM/MoO$_3$/Au. The devices were prepared following the same procedure described in the experimental section for photovoltaic devices, except that of the metal electrode. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as

$$J = \frac{9\varepsilon_0^2\mu_0 V^2}{8L^3} \exp\left(\beta \frac{V}{L}\right)$$

where $J$ is the current, $\mu_0$ is the zero-field mobility, $\varepsilon_0$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the material, $V$ is the effective voltage, and $L$ is the thickness of the active layer.

The Hansen solubility parameter ($\delta$) indicates that the miscibility of the components in a blended system is dependent on the cohesive energy densities ($E/V$), which is the energy required to infinitely separate a unit volume of any given molecule from its neighbors. There are three contributions of the energy: the dispersive forces ($\delta_D$), the dipolar intermolecular forces ($\delta_P$), and hydrogen bonding forces ($\delta_H$). This energy is directly related to the solubility parameters ($\delta$) and can be defined by equation:

$$(E/V) = \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

where $E$ is the energy change of evaporation and $V$ is the molar volume. HSPs for each solvent/solute can be represented as a point in the Cartesian coordinate system. Accordingly, the solubility of a solute in a particular solvent is estimated by using the Hansen sphere, where the HSPs of solvents are located at the center of the sphere and $R_o$ the interaction radius. The solubility of solutes can be considered as good when their HSPs fall within the range of $R_o$ of the...
solvent, and vice versa. The distance between the solute and solvent HSPs is described as \( R_a \), which can be defined by equation:

\[
R_a^2 = 4(\delta_{D1} - \delta_{D2})^2 + (\delta_{P1} - \delta_{P2})^2 + (\delta_{H1} - \delta_{H2})^2
\]  

(2)

where the subscripts 1 and 2 represent the solute and solvent, respectively.

Combining the \( R_a \) with the \( R_o \) gives the relative energy difference (RED = \( R_a / R_o \)), which provides a quantitative estimate of the solubility of the solute: highly soluble when RED is <1, partially soluble when RED = 1, and insoluble when RED is >1.

Fig. S1 Hansen solubility parameter (HSP) diagrams of PC_{71}BM and different solvents.
Fig. S2 Left, $J-V$ curve based on PIDT-FQ-T:PC$_{71}$BM device processed from CB solvent; Right, AFM tapping mode topography images of the film cast from CB solvent.

Fig. S3 Light intensity dependence of $V_{oc}$ in PIDT-FQ-T:PC$_{71}$BM devices processed from different solvents.

Fig. S4 Measured J-V characteristics under dark for a) hole-only and b) electron-only devices based on PIDT-FQ-T:PC$_{71}$BM processed from different solvents. The bias corrected for built-in Voltage $V_{bi}$, arising from difference in the work function of the contacts, and the voltage drop due to substrate series resistance, such that $V = V_{APPL} - V_{RS} - V_{bi}$. The solid lines represent the fitting curves.
Fig. S5 Left, $J-V$ curve based on P3HT:IC$_{60}$BA device processed from CB solvent; Right, AFM tapping mode topography images of the film cast from CB solvent.

Fig. S6 AFM tapping mode topography images (5 × 5 μm$^2$) of P3HT:IC$_{60}$BA blend processed from (a) CB/CN (S-Cl), (b) toluene/MN (S-Me), (c) o-xylene/DMN (S-DMe) and (d) o-xylene.
**Fig. S7** $J-V$ curves of the PBDTTT-C-T:PC$_{71}$BM devices processed from different solvents (CB+DIO, CB+CN, toluene+MN, o-xylene+DMN and o-xylene) under illumination.

**Fig. S8** $J-V$ characteristics of the PTB7:PC$_{71}$BM devices processed from different solvents (CB+DIO, CB+CN, toluene+MN, o-xylene+DMN and o-xylene) under illumination.
**Fig. S9** $J-V$ characteristics of the PIDT-FQ-T:PC$_{71}$BM and P3HT:IC$_{60}$BA devices processed from CB+DIO, under illumination.