Supporting information

1. TEM thickness maps

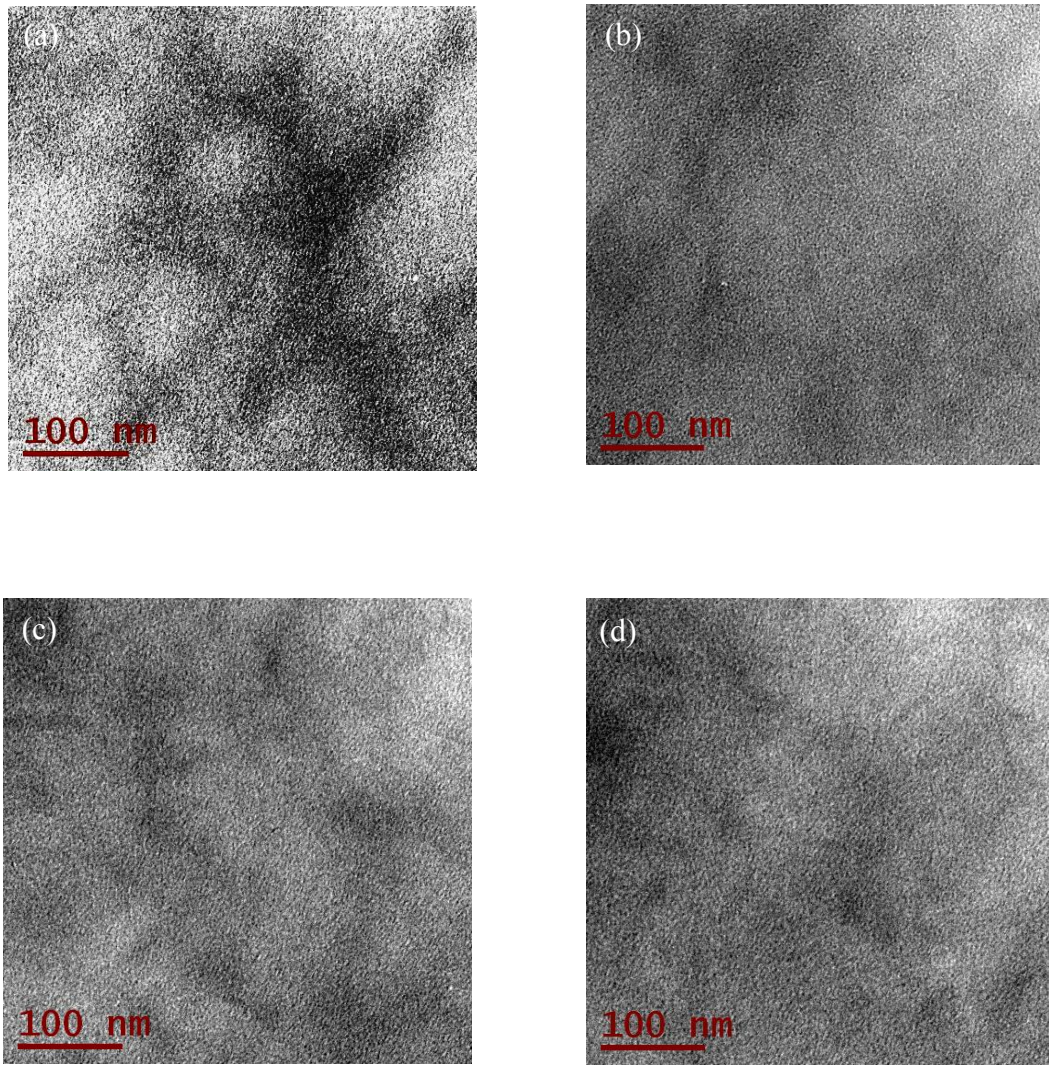

Figure S1 TEM thickness maps for (a) pristine, (b) DIO, (c) CN, and (d) ODT processed PDPP3T:$PC_{60}BM$ thin films. The

2. Calculation of charge carrier lifetime, charge carrier density, bimolecular recombination order and coefficient

Charge carrier lifetime and density and bimolecular recombination orders and coefficients were calculated as per previous reports[1, 2]

Voltage decay in transient photovoltage (TPV) acquired by using 1 MΩ input impedance of oscilloscope is given by

$$\Delta V = V_{oc} + \Delta V_o \exp^{(-t/\tau)} \quad \text{.....(I)}$$

Where τ is recombination time and V_{oc} is open circuit voltage

Current decay in transient photocurrent (TPC) acquired across a 20Ω resistor connected to 1MΩ input impedance of oscilloscope is given by

$$\Delta I = \Delta I_o \exp^{(-t/\tau)} \quad \text{.....(II)}$$

where $\Delta I_o = \Delta V_o/R$ and R is the 20 Ω resistance used to put device in short circuit condition

The charge carrier density is calculated by using following expressions. The total charges that are generated during TPC can be calculated by integrating the current.

$$\Delta Q = \int I \, dt \quad \text{.....(II)}$$

The differential capacitance is calculated using TPC in conjugation with TPV as follows

$$dc = \frac{\Delta Q}{\Delta V_\circ} \quad \text{.....(III)}$$

where ΔQ is obtained from TPC analysis while $\Delta V_\circ$ is the amplitude of TPV transient under different illumination condition

The charge carrier density under certain illumination condition is given by

$$n = \frac{1}{Aed} \int_0^{V_{oc}} c \, dV \quad \text{.....(IV)}$$

where e is elementary charge, A and *d* are the area and thickness of the device, respectively.

The apparent recombination order (λ+1) is inferred from the slope of log-log plot of the small perturbation lifetime (t) vs charge carrier density which gives - λ as

$$t \propto n^{-\lambda} \text{.....(V)}$$

where n is charge carrier concentration.

The recombination coefficient K is given by

$$k(n) = -\frac{n^{\lambda-1}}{(\lambda+1)\tau_{\Delta n_0} n_0^{\lambda}} \text{ .....(VI)}$$

where τ, $_{\Delta n0}$, n_o *and* λ are determined experimentally.

References

1. A. Maurano, C. G. Shuttle, R. Hamilton, A. M. Ballantyne, J. Nelson, W. Zhang, M. Heeney and J. R. Durrant, *J. Phys. Chem. C*, 2011, **115**, 5947-5957.
2. D. Spoltore, W. D. Oosterbaan, S. Khelifi, J. N. Clifford, A. Viterisi, E. Palomares, M. Burgelman, L. Lutsen, D. Vanderzande and J. Manca, *Adv. Energy Mater.*, 2013, **3**, 466-471.