Supplementary Material

Building Intermixed Donor-Acceptor Architectures for Water-Processable Organic Photovoltaics

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1. Photoluminescence and UV-Vis Spectra of NP Dispersions in Water

Figure S1. (a) Photoluminescence spectra and (b) UV-Vis absorbance spectra of RE-NP dispersion (black) and SE-NP dispersion (red).

2. Photoluminescence and UV-Vis Spectra of BHJ and Pristine Films Cast from Chloroform



Figure S2. (a) Photoluminescence spectra and (b) UV-Vis absorbance spectra of P3HT:PC₆₁BM BHJ film spin coated from chloroform (dotted line) and pristine P3HT film spin coated from chloroform (solid line). Importantly, no thermal treatment was applied to the films.

3. Exciton Dissociation Efficiency Calculation

$$PL_{c} = \frac{\int_{\lambda = 00}^{\lambda = 850} [PL(\lambda) - PL(900)] d\lambda}{\% A_{500}}$$
(1)

$$\eta_{\rm ED} = 1 - \frac{PL_c^{Blend}}{PL_c^{P3HT}} \tag{2}$$

4. Varied NP Film Thickness OPV Device Study

The nanoparticle film thickness was modified to optimise for RE-NP OPV device performance, with device characteristics presented in Table S1 and Figure S3. The nanoparticle film thickness was modified by varying spin coating speed from 1750 to 1250 RPM with a lower spin speed resulting in a greater film thickness, from 97 ± 8 to 137 ± 14 , respectively (Table 1 and Figure S3d). After thermal treatment we observed a decrease in nanoparticle film thickness, for example a film thickness of 97 ± 8 nm for a spin speed of 1750 RPM decreased to 76 ± 21

nm. We hypothesise this decrease is due to the sintering of the nanoparticles together and the filling of voids between the nanoparticles which occurs when the material T_g is passed, which is supported by SEM observation (compare Figure 2c to Figure 6c – d). While we observed a decrease in RE-NP OPV PCE with an increase in film thickness for the pre-CD TT devices, the PCE reached 1 % for all three film thickness devices following exposure to a post-CD TT of 80 °C 4 min. When looking at the device performance parameters the devices coated at a spin speed of 1750 and 1500 RPM both had a J_{SC} of 4.5 mA/cm² and a FF of 0.54, and a similar V_{oC} of 405 mV at 1750 RPM and 409 mV at 1500 RPM. For the spin coating condition of 1250 RPM we observed the V_{oC} to increase to 420 mV, this was accompanied by a small drop in J_{SC} to 4.2 mA/cm² and FF to 0.53 which counteracted the observed increase in V_{oC} leading to the parity in device PCE at 1 %.

Table S1. RE-NP OPV device characteristics of best devices for varied active layer film thickness both before and after annealing. All devices were exposed to a pre-cathode deposition thermal treatment (Pre-CD TT) of 110 °C 4 min and a post-cathode deposition thermal treatment (Post-CD TT) of 80 °C 4 min. The averages \pm standard deviation are in parentheses.

Spin Speed	Voc (mV)	\mathbf{I}_{ac} (m A /om ²)	DD	DCE $(9/2)$
(RPM)	V UU (III V)	JSC (IIIA/CIII)	FF	
Pre-CD TT				
1750	$450(439 \pm 7)$	$4.0 (4.1 \pm 0.2)$	$0.55~(0.50\pm0.03)$	$1.0~(0.9\pm0.1)$
1500	442 (441 ± 4)	$4.2 (4.0 \pm 0.2)$	$0.51~(0.50\pm0.04)$	$0.9~(0.9\pm 0.1)$
1250	428 (426 ± 6)	3.6 (3.3 ± 0.2)	$0.50~(0.48\pm0.03)$	$0.8~(0.7\pm0.1)$
Post-CD TT				
1750	405 (419 ± 19)	$4.5~(4.0\pm 0.5)$	$0.54~(0.52\pm 0.02)$	$1.0~(0.8\pm 0.1)$
1500	409 (414 ± 11)	$4.5 (4.2 \pm 0.2)$	$0.54~(0.51\pm0.03)$	$1.0~(0.9\pm0.1)$
1250	$420(428 \pm 7)$	4.2 (3.9 ± 0.3)	$0.54~(0.53\pm0.01)$	$1.0~(0.9\pm0.1)$



Figure S3. RE-NP OPV device performance with varied active layer spin speed. (a) Average power conversion efficiency (PCE) (grey closed circle) and best PCE (grey open circle) for devices pre-cathode deposition thermal treatment (Pre-CD TT), (b) average PCE (black closed circle) and best device PCE (black open circle) for devices post-cathode deposition thermal treatment (Post-CD TT), (c) current density – voltage curves for best performing OPVs, (d) film thickness vs spin speed measured as cast and following thermal treatment. Error bars in (a) and (b) represent the standard deviation in 12 replicate devices.

5. Electron Microscopy of Spherical vs Non-Spherical Nanoparticles

Correlating polymer crystallinity with particle shape.



Figure S4. (a) SEM of pristine P3HT nanoparticles, (b) TEM of 2:1 P3HT:PC₆₁BM SE-NPs, (c) TEM of 1:1 P3HT:PC₆₁BM SE-NPs, (d) TEM of TQ1:PC₇₁BM NPs, (e) SEM of pristine PC₆₁BM NPs, (f) TEM of 1:1 P3HT:PC₆₁BM RE-NPs. Scale bars are 500 nm.

6. STXM Analysis of SE-NPs



Figure S5. STXM fractional composition maps (5 x 5 μ m frame) showing the concentration of (a) P3HT and (b) PC₆₁BM with corresponding STXM mass plots (c and d) for unannealed 1:1 P3HT:PC₆₁BM SE-NPs. All scale bars are 500 nm. The colour contrast is scaled such that light colours correspond to higher component concentrations. For the mass plots (c and d) the colour scale bars indicate concentration of component in mg/cm².

7. AFM of RE-NP Film



Figure S6. AFM height maps of RE-NP film (a) as cast (no thermal treatment) (RMS roughness = 3.5 nm), (b) thermally treated at $110 \degree$ C for 4 min (RMS roughness = 2.3 nm), (c) thermally treated at $110 \degree$ C 4 min followed by 80 °C 4 min (RMS roughness = 2.8 nm). Scan area is $1 \times 1 \mu$ m. Scale bars are 200 nm.

8. SEM of Thermally Treated RE-NP Films



Figure S7. SEM images of RE-NP film thermally treated at (a) 110 °C 4 min followed by 100 °C 4 min, and (b) 110 °C 4 min followed by 120 °C 4 min. Scale bars are 200 nm.