ELECTRONIC SUPPLEMENTARY INFORMATION

Charge Generation and Morphology in P3HT:PCBM Nanoparticles Prepared by Mini-emulsion and Reprecipitation Methods

*Kyra N. Schwarz, Sam B. Farley, Trevor A. Smith, Kenneth P. Ghiggino**

School of Chemistry, University of Melbourne, Victoria, 3010, Australia

Email: ghiggino@unimelb.edu.au

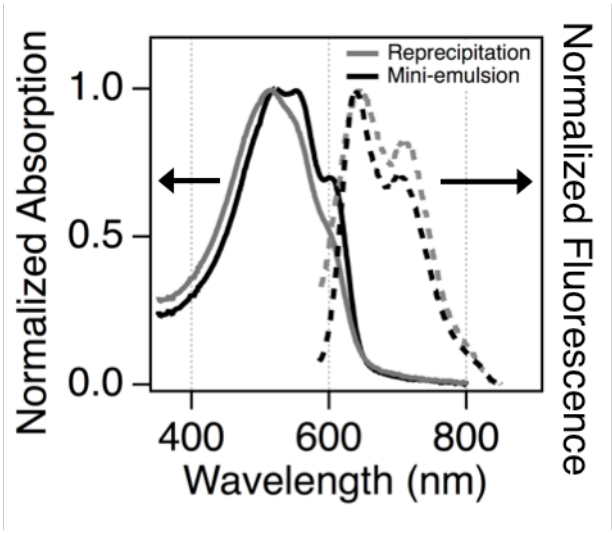

Fig. S1. Normalized absorption (solid lines) and fluorescence spectra (dashed lines) of suspensions in water of P3HT nanoparticles prepared using the reprecipitation (grey) and mini-emulsion (black) methods

An established analytical model of weakly interacting H-aggregates (excitonic coupling) by Spano allows for a quantitative analysis of the polymer aggregate species.[1] This modified Franck-Condon fit describes absorbance, A, as a function of photon energy, E, to determine the relative intensities of the individual vibronic transitions, *m* (Equation S1):

$$A \propto \sum_{m=0} \left(\frac{e^{-S}S^m}{m!}\right)\left(1 - \frac{We^{-S}}{2E_p}\sum_{n\neq m}\frac{S^n}{n!(n-m)}\right)^2 \Gamma\left(E - E_{0-0} - mE_p\right) \qquad \text{(S1)}$$

where S is the Huang-Rhys factor, W is the free exciton bandwidth, n is the vibrational quantum number, $E_{0\text{-}0}$ is the 0-0 transition energy, E_p is the energy of the main intramolecular vibration**,** and Γ describes the Gaussian line shape. In this work, the same linewidth, σ, was used for each transition. The free fitting parameters were σ, $E_{0\text{-}0,}$ and W, and it was assumed that the Huang–Rhys factor was unity and the coupling to the electronic transition is dominated by the C=C symmetric stretch at 0.179 eV.[2,3]

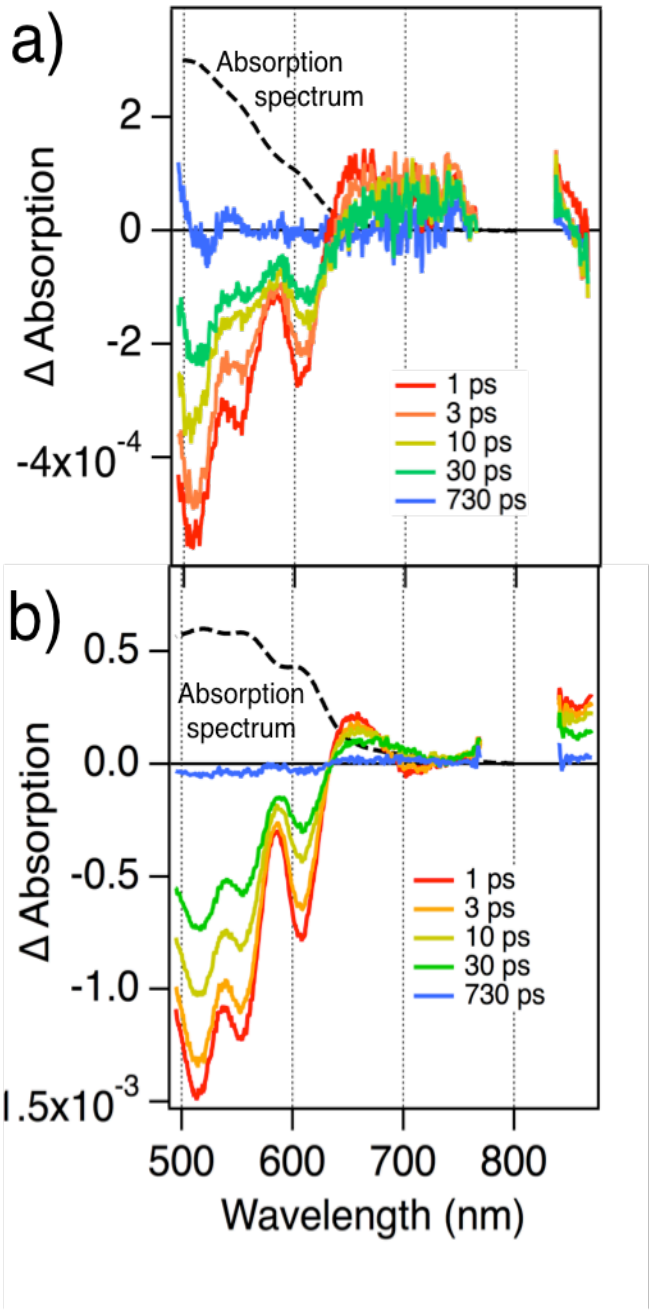

Fig. S2. P3HT nanoparticle transient absorption spectra of aggregates prepared using (a) the reprecipitation and (b) the mini-emulsion preparation methods. The steady-state absorption spectrum is shown (black dotted line) and pump fluence at 400 nm was 9.75 μJ/cm^2. Both samples display typical signatures of neat P3HT films: ground-state bleaching (480-630 nm), stimulated emission (700-750 nm) and a small amount of photo-induced absorption.

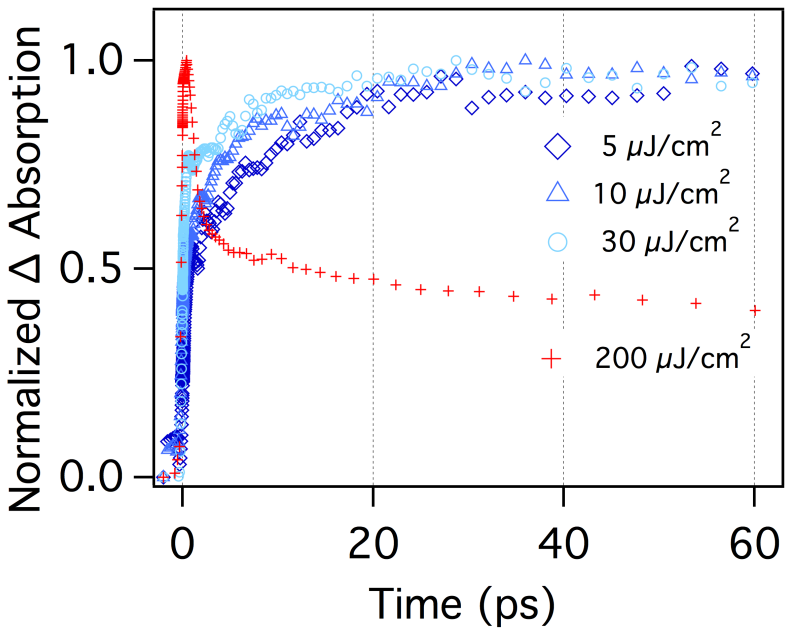

Fig. S3. Normalized transient absorption dynamics of mini-emulsion blend nanoparticle suspensions recorded at 690 nm at various pump excitation fluences. The initial rise time due to exciton diffusion in the P3HT component shows a significant dependence on pump fluence due to exciton-exciton and exciton-charge annihilation.

References

S1 F. C. Spano, *J. Chem. Phys.*, 2005, **122**, 234701.
S2 J. Clark, C. Silva, R. Friend and F. Spano, *Phys. Rev. Lett.*, 2007, **98**, 206406.
S3 S. T. Turner, P. Pingel, R. Steyrleuthner, E. J. W. Crossland, S. Ludwigs and D. Neher, *Adv. Funct. Mater.*, 2011, **21**, 4640–4652.