Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information for:

Spectroscopically tracking charge separation in polymer:fullerene blends with three phase morphology

J. K. Gallaher,[a,b] Shyamal K. K. Prasad, [a,b] M. A. Uddin,[c] T. Kim,[d] J. Y. Kim,[d] H.Y. Woo,*[c] and J. M. Hodgkiss*[a,b]

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Device characteristics

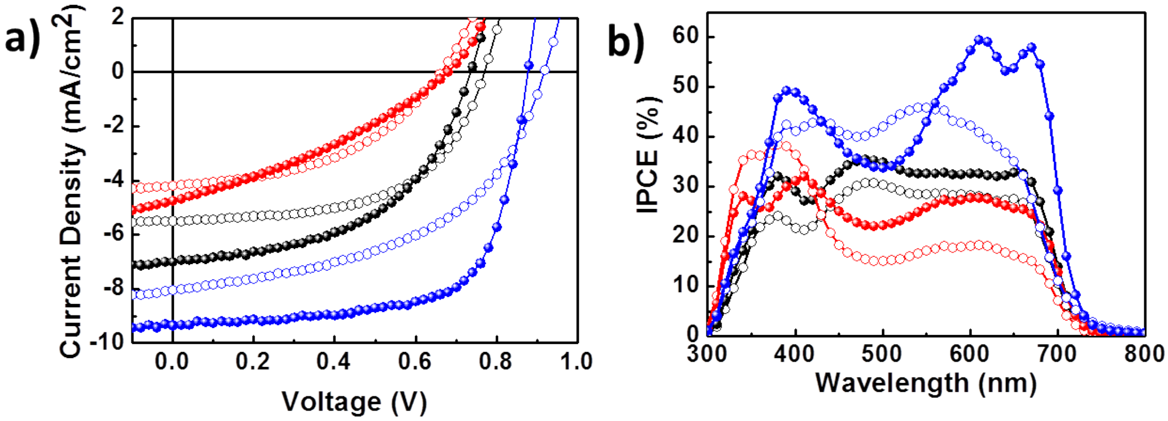

Fig. S 1 – Photovoltaic device characteristics for PTTBT:PCBM (black), PDTBT:PCBM (red) and PTBT:PCBM (blue) devices. (a) *J*-*V* and (b) IPCE curves with (solid) and without processing additive (open).

2D-GIXRD

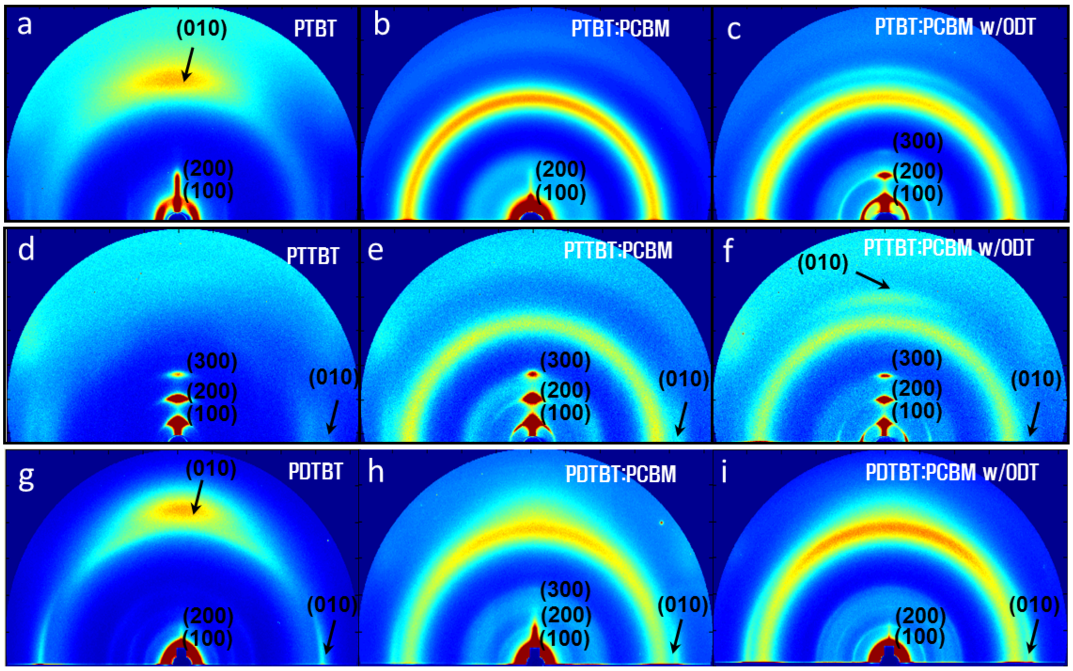

Fig. S 2 - 2D-GIXRD images of pristine and blended films with/without ODT for PTTBT, PDTBT and PTBT.

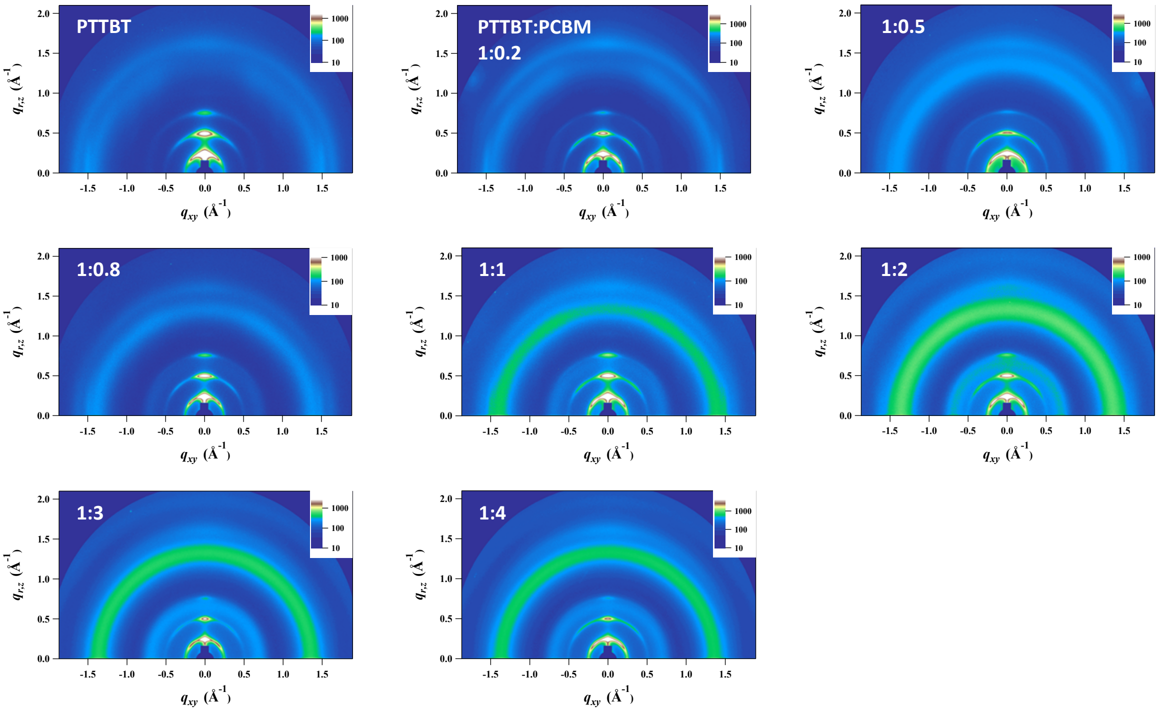

Fig. S 3. 2D-GIWAXS images of pristine PTTBT and PTTBT:PCBM (without ODT) with changing blend ratio

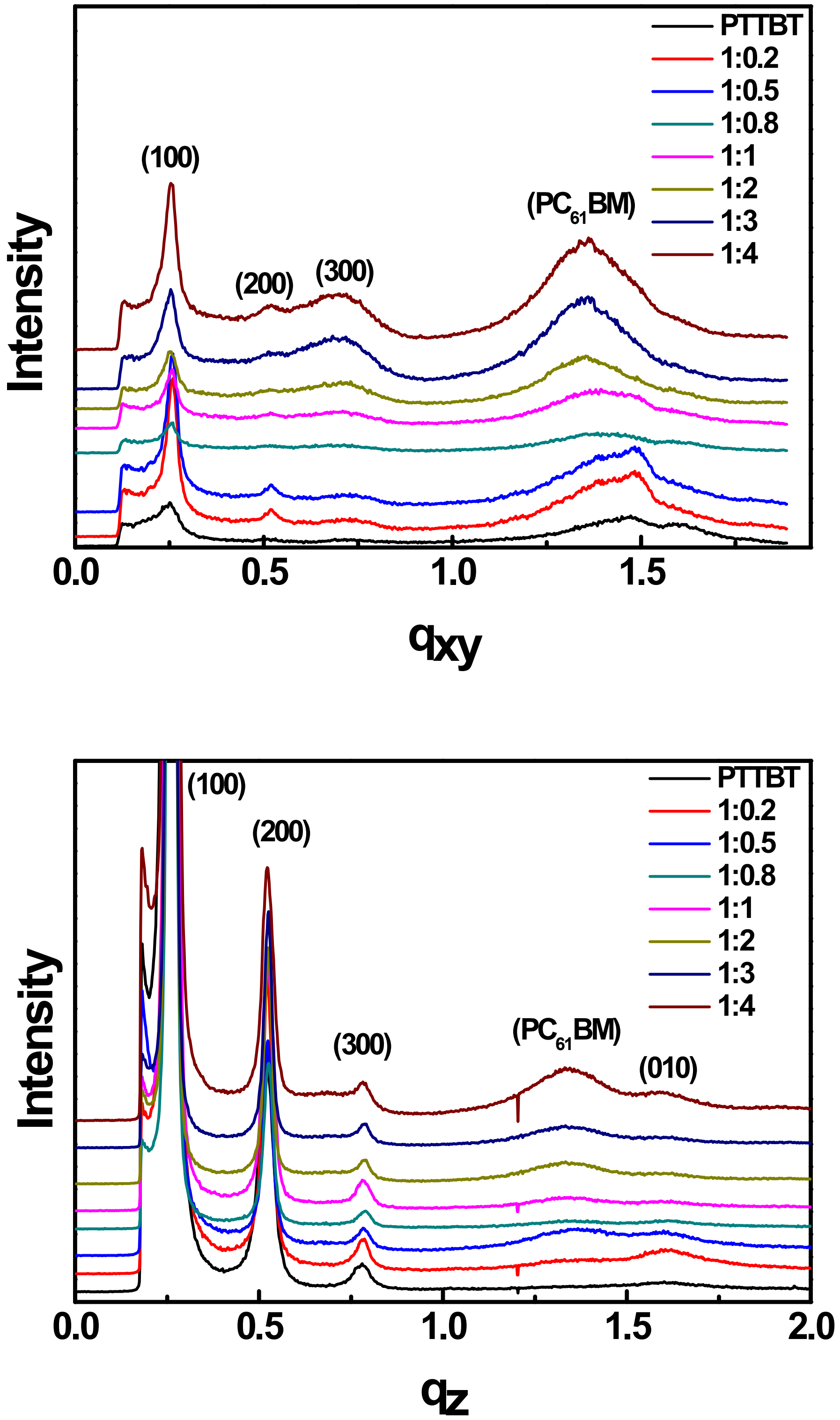

Fig S 4. In-plane (top) and out-of-plane (bottom) GIWAXS line-cuts for pristine and blended PTTBT, from the 2D images in Fig S3.

Intensity dependent – Annihilation effects

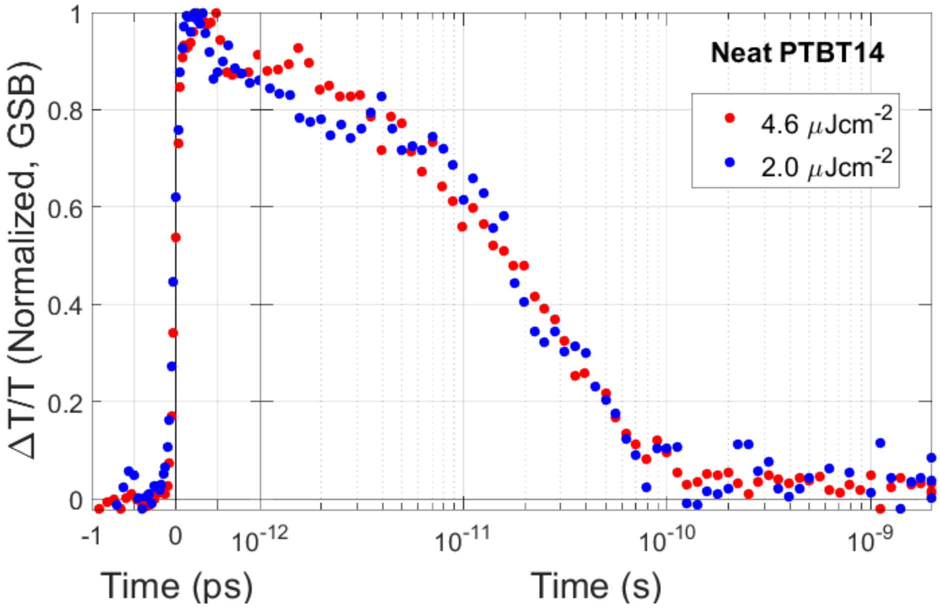

Fig. S 5 - Decay kinetics of neat PTBT14 at 2 different fluence, this is reminiscent of the data collected for all samples.

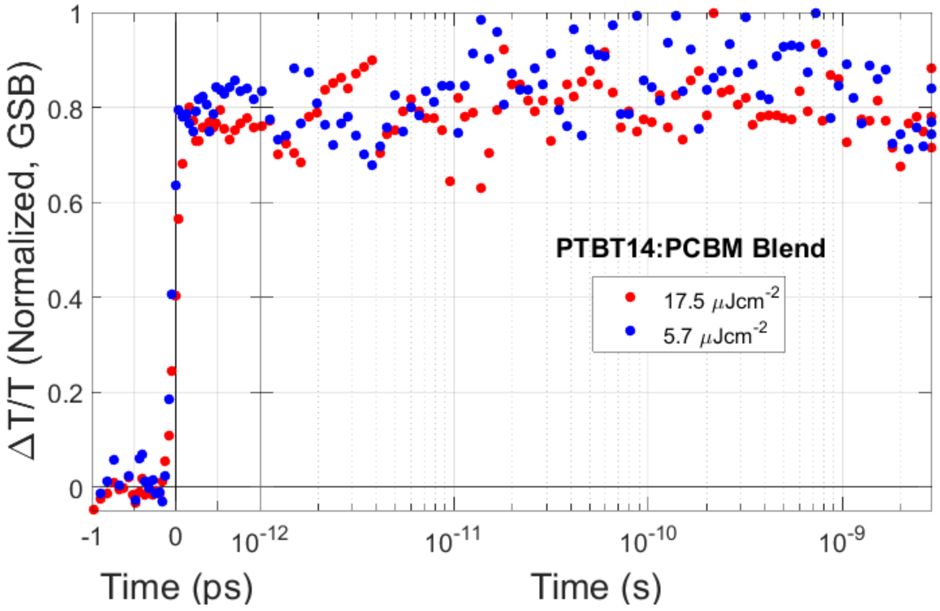

Fig. S 6 Decay kinetics of neat PTBT:PCBM at 2 different fluence, this is reminiscent of the data collected for all samples.

Polymer:fullerene + ODT TA data

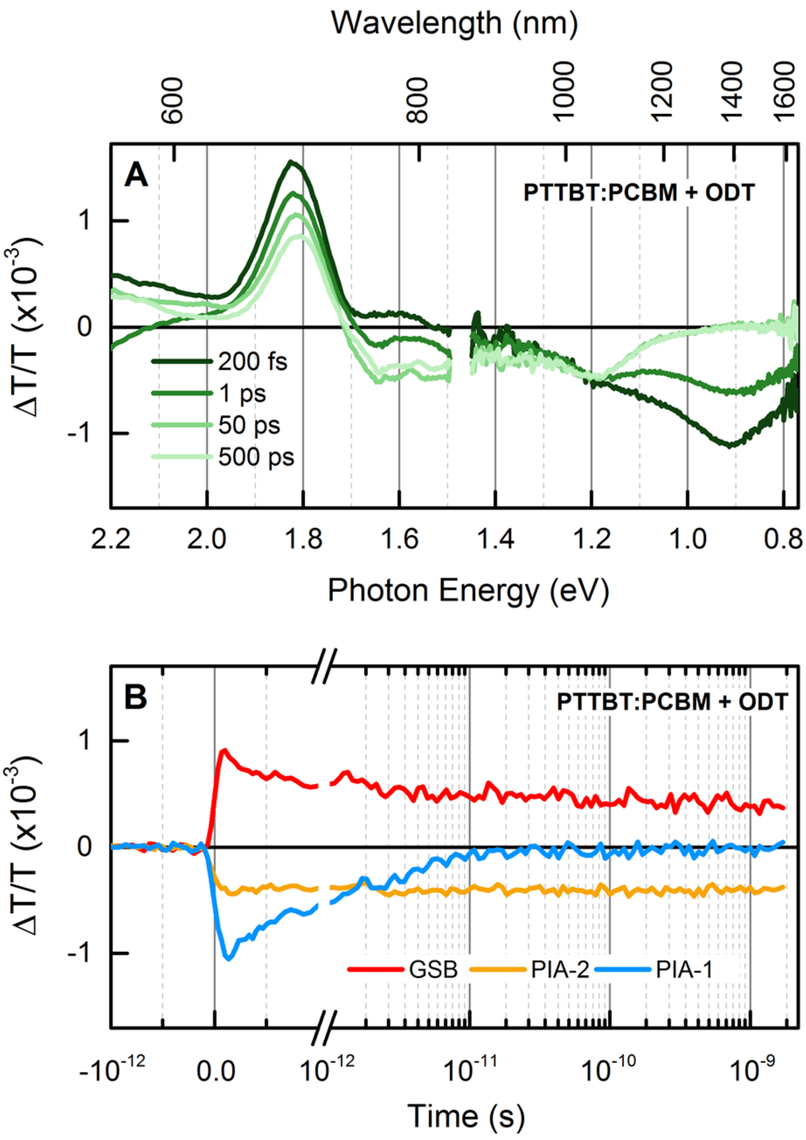

Fig. S 7 - TA spectra (A) and kinetics (B) of PTTBT:PCBM + ODT. Excitation wavelengths was 532 nm.

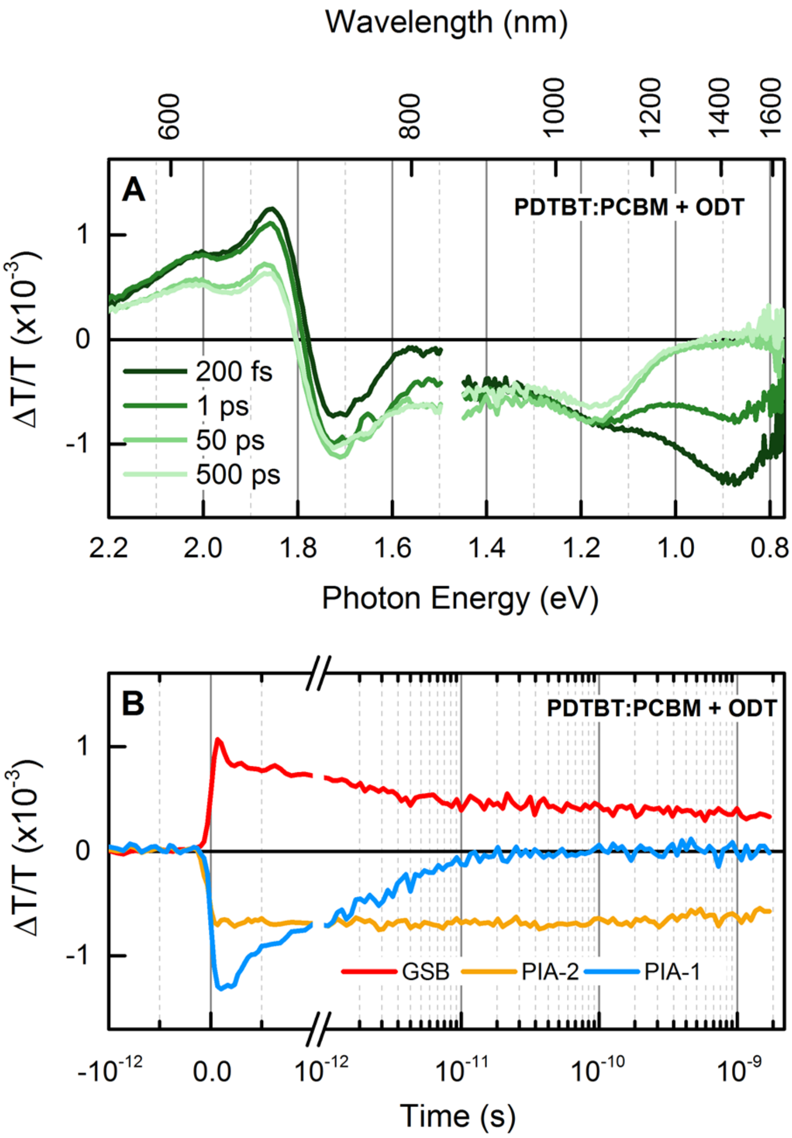

Fig. S 8 - TA spectra (A) and kinetics (B) of PDTBT:PCBM + ODT. Excitation wavelengths was 532 nm.

Charge recombination intensity dependence

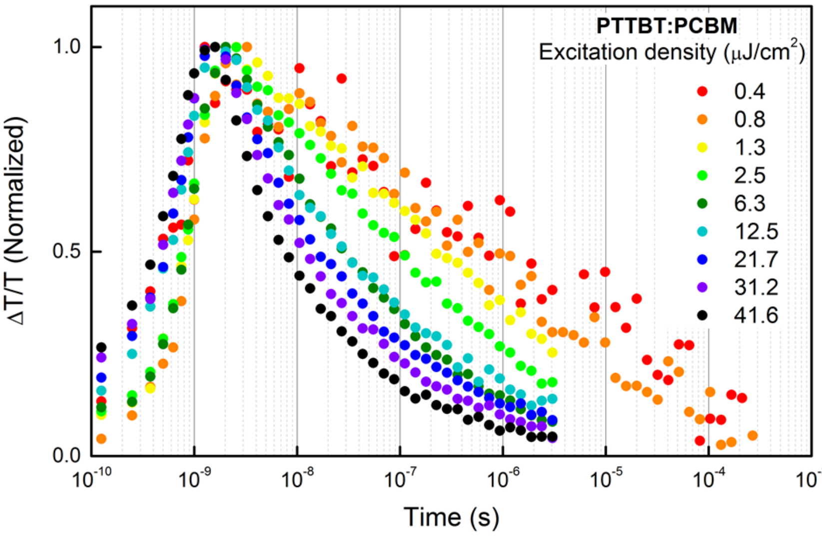

Fig. S 9 - Intensity dependent recombination for PTTBT:PCBM at the fluences indicated.

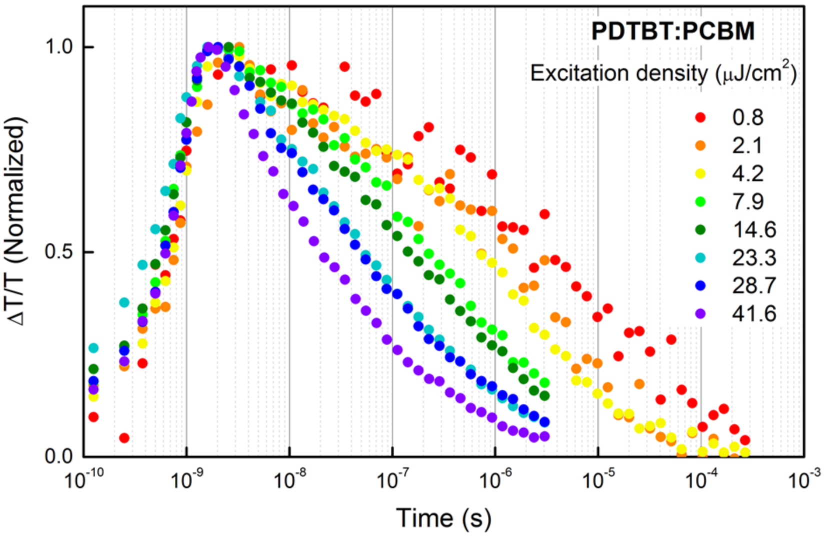

Fig. S 10 - Intensity dependent recombination for PDTBT:PCBM at the fluences indicated.

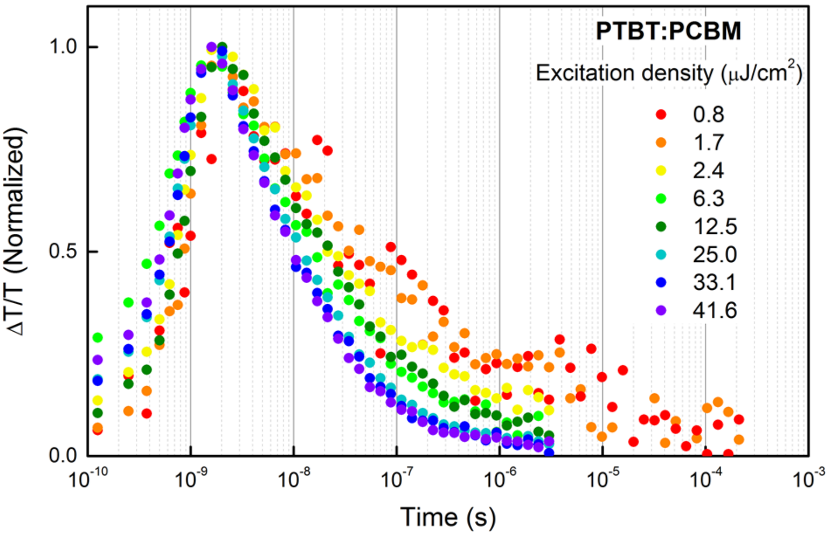

Fig. S 11 - Intensity dependent recombination for PTBT:PCBM at the fluences indicated.

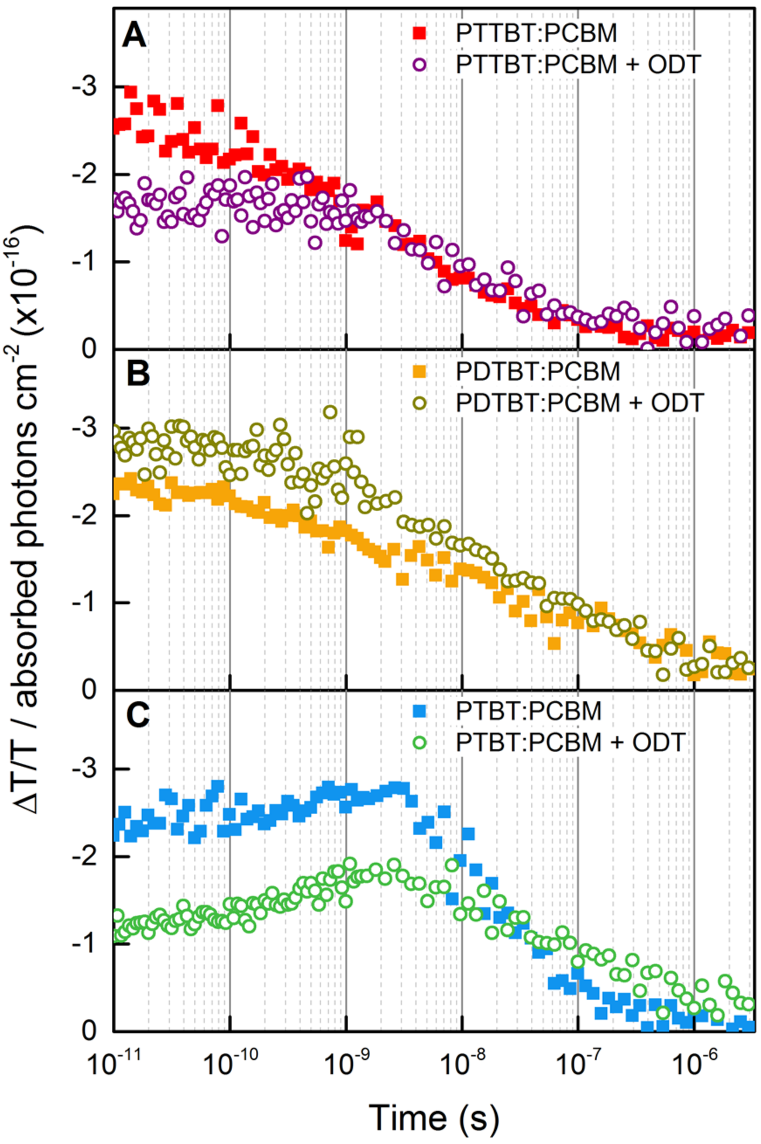

Fig. S 12 - Transient absorption recombination kinetics integrated over the 0.9 – 1.4 eV region for each polymer:PCBM processed with and without ODT additive. Each kinetic trace is normalised by absorbed photon flux (photons/cm^2) to account for differences in optical density at the excitation wavelength (532 nm) of each sample. All kinetic decays were collected with an excitation fluence of approximately 5 μJ cm^{-2} allows comparison of intensity dependent decay dynamics. Spectral overlap of polarons with excitons is avoided by excluding the dynamics before 10 ps, at which time excitons have decayed.

Spectral shift analysis

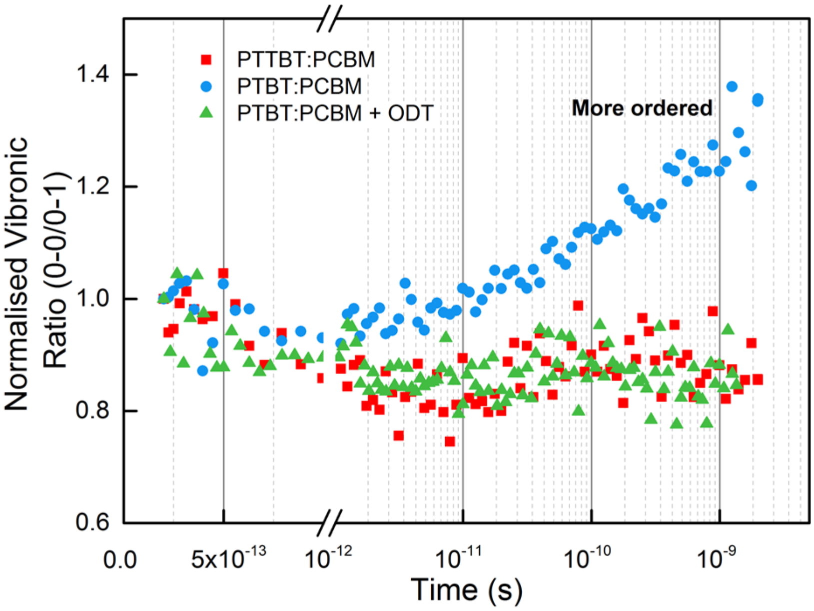

Fig. S 13 - Vibronic ratio (0-0/0-1) extracted from TA data for PTTBT:PCBM, and PTBT:PCBM with and without ODT as indicated

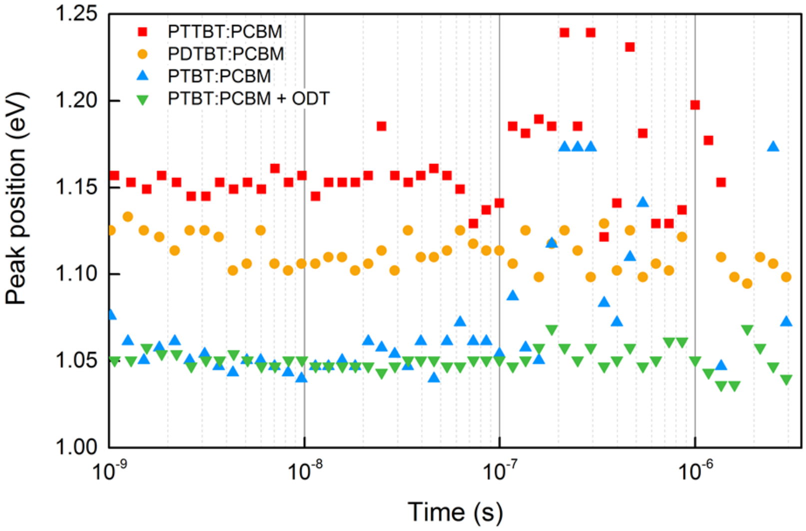

Fig. S 14 - Polaron peak position as a function of time during recombination.

Spectral fitting

Fitting was achieved using a combination of two algorithms. Firstly, for fitting of the near-IR probe region >10 ps (after exciton decay) we used soft-modelling, namely, evolving factor analysis and model-free multivariate curve resolution alternating least squares (MCR-ALS) algorithm.[1,2] The number of components required was guided by performing singular value decomposition and the constraint of non-negative concentration profiles was enforced. Secondly, fitting was performed for the time involving exciton decay (-1ps to 1 ns) for all polymer:fullerene blends. This was achieved by expanding the spectral basis set obtained using MCR-ALS to include a spectral component to account for the exciton contribution. Due to the short lifetime of the exciton in the polymer:fullerene blends, MCR-ALS would often not provide ample weighting to extract the exciton signature. To this end, we used a spectral slice from the TA surface of neat polymer as the third component whereby the excitation is solely the polymer exciton. The polymer:fullerne blend data from sub-picosecond to nanosecond was fit with every combination of neat polymer spectra using linear non-negative least squares (NNLSQ) and the minimum residual (using residual sum of square) was chosen as the optimum spectral basis set. These fitting procedures were performed for all polymer:fullerene blends. The details of the fits, i.e., spectral basis sets, relative component weightings, and residual surfaces, are presented below.

2-Phase morphology blends (PTTBT:PCBM and PDTBT:PCBM)

PTTBT:PCBM blend

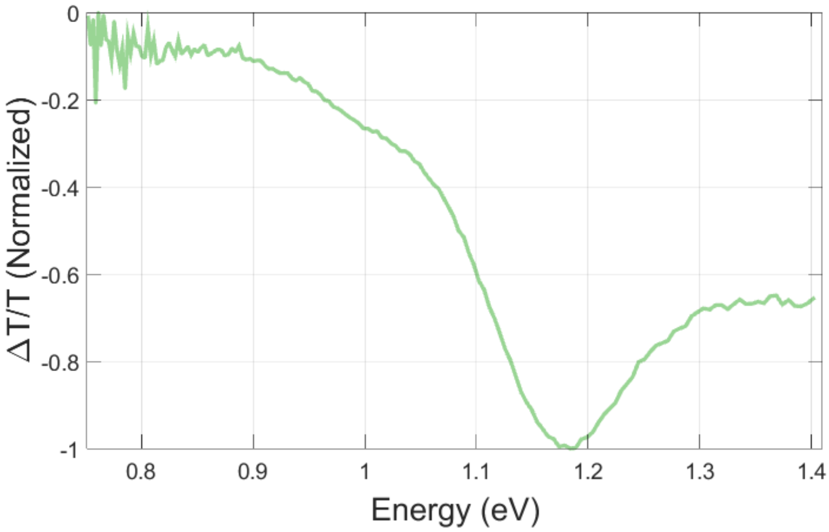

Fig. S 15 - Spectral component obtained from MCR-ALS for PTTBT:PCBM (>10 ps)

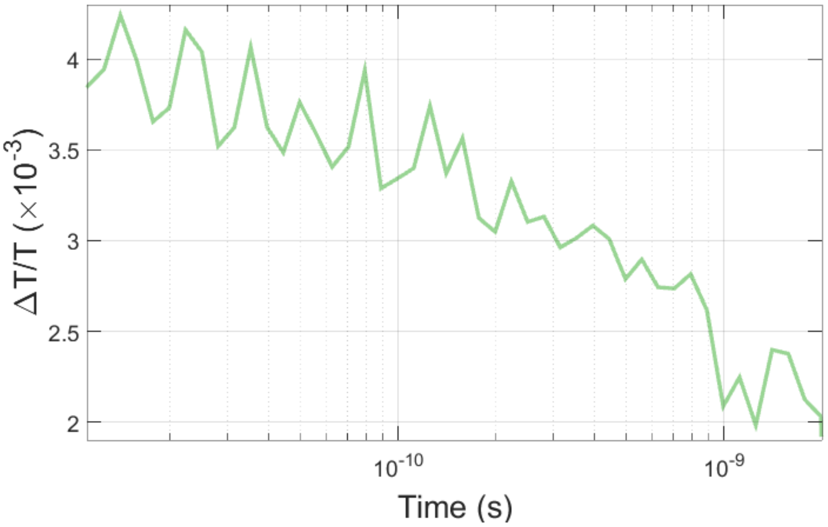

Fig. S 16 – Component weighting of the spectrum shown in Fig. S 13 using MCR-ALS fitting for PTTBT:PCBM (>10 ps)

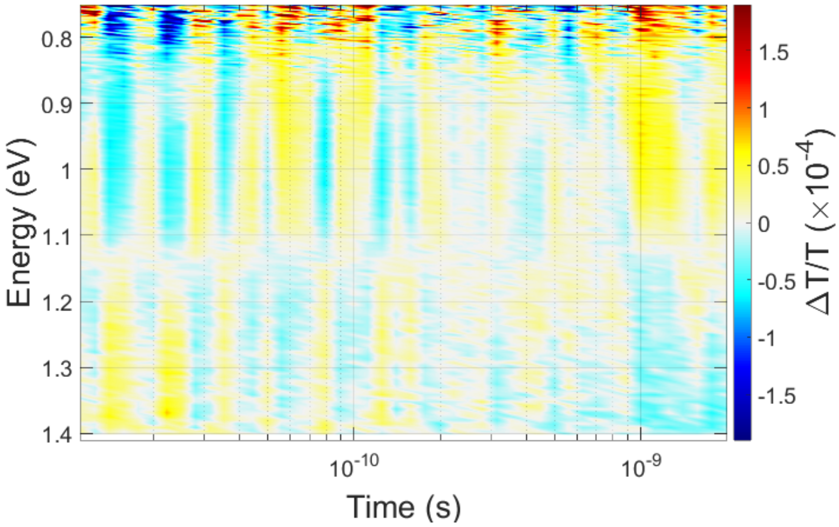

Fig. S 17 - Residual surface obtained from MCR-ALS for PTTBT:PCBM (>10 ps).

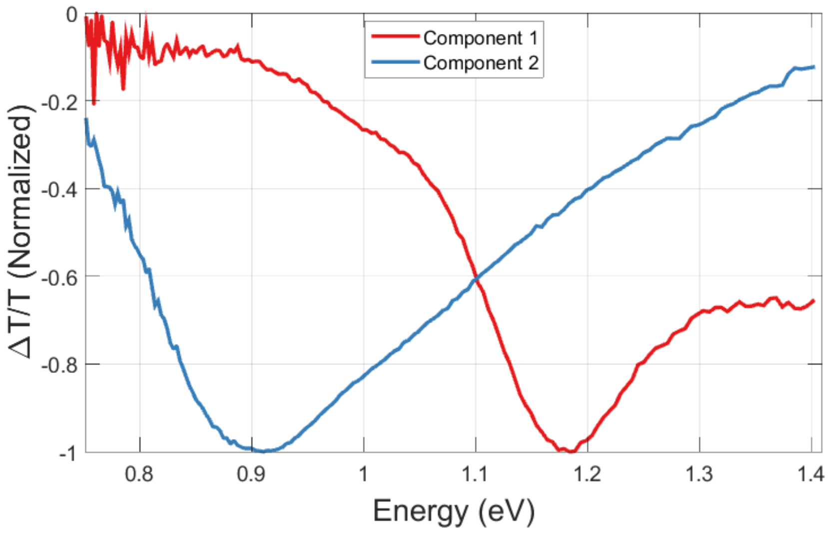

Fig. S 18 - Spectral basis set used for NNLSQ fitting of PTTBT:PCBM (-1ps to 1 ns timescales). Component 1 (polaron) is from MCR-ALS as shown in Fig. S 13. Component 2 (exciton) is obtained from neat PTTBT with the routine described above.

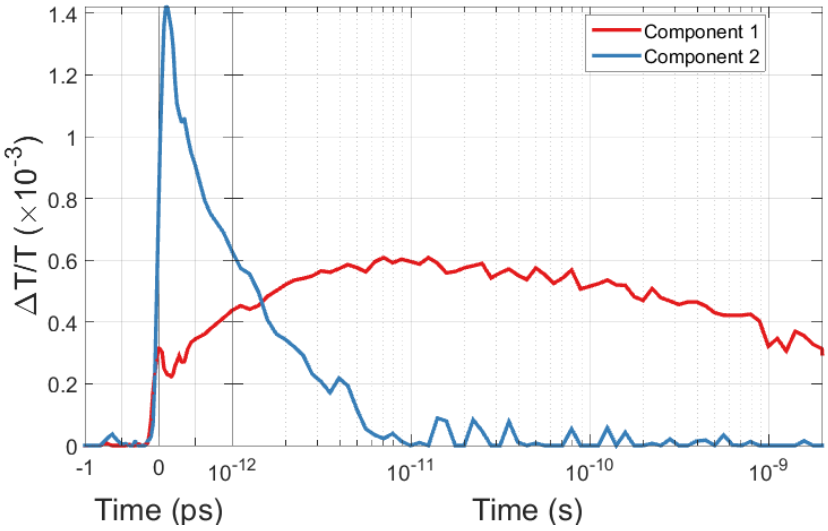

Fig. S 19 – Component weightings from NNLSQ of PTTBT:PCBM (-1ps to 1 ns timescales) using the spectral basis set presented in Fig. S 16.

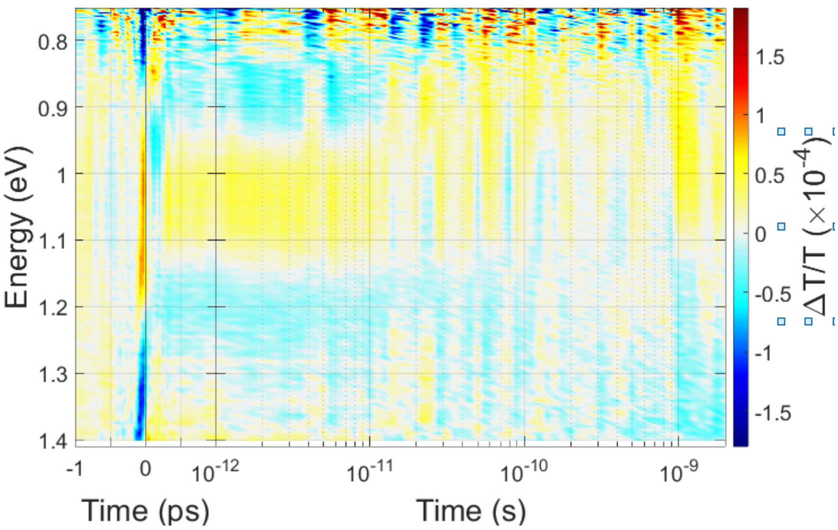

Fig. S 20 - Residual surface from NNLSQ of PTTBT:PCBM (-1ps to 1 ns timescales) using the spectral basis set presented in Fig. S 16.

PDTBT:PCBM blend

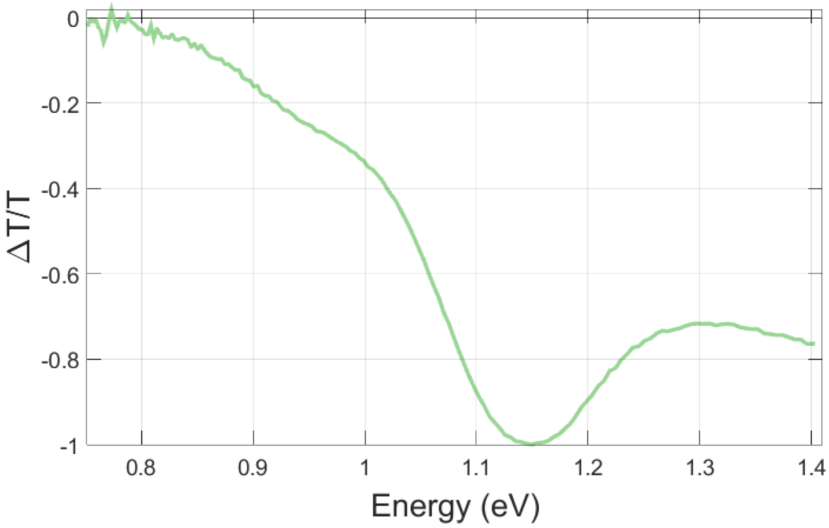

Fig. S 21 - Spectral component obtained from MCR-ALS for PDTBT:PCBM (>10 ps)

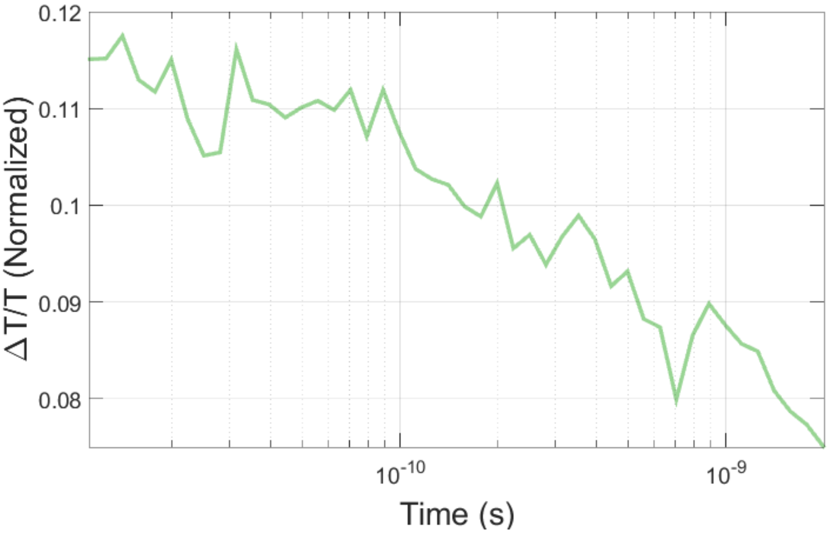

Fig. S 22 - Component weighting of the spectrum shown in Fig. S 19 using MCR-ALS fitting for PDTBT:PCBM (>10 ps)

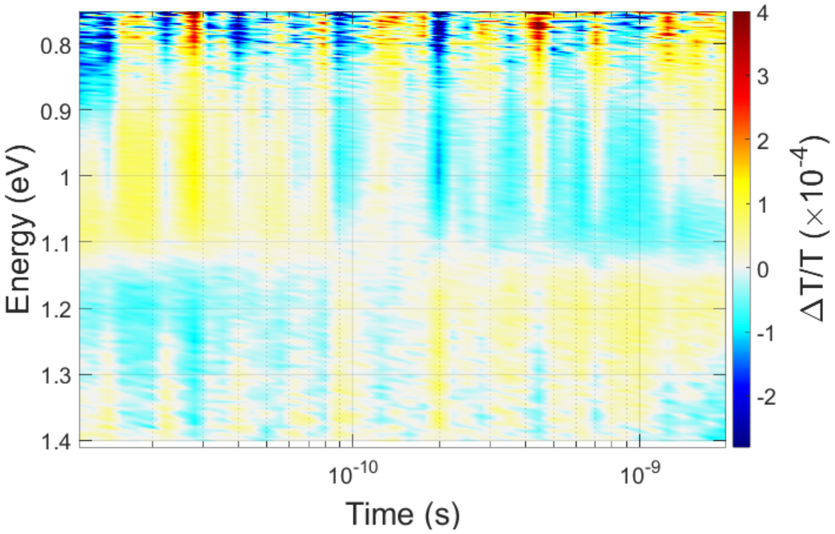

Fig. S 23 - Residual surface obtained from MCR-ALS for PDTBT:PCBM (>10 ps).

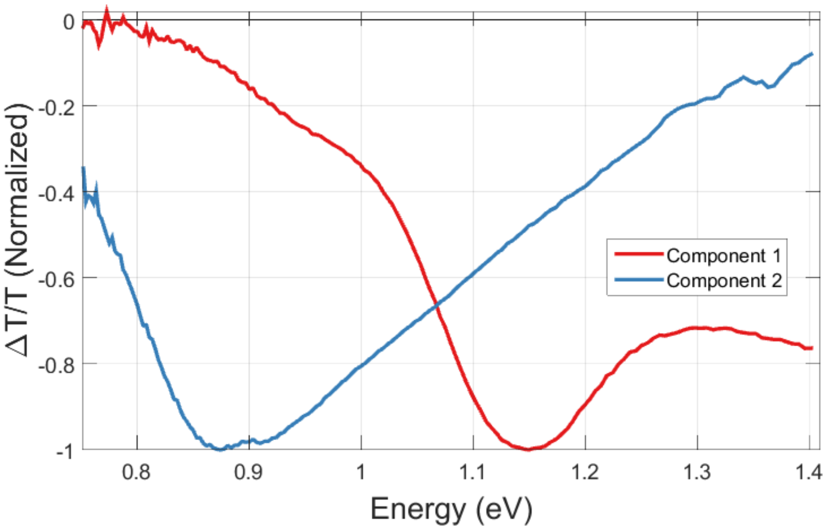

Fig. S 24 - Spectral basis set used for NNLSQ fitting of PDTBT:PCBM (-1ps to 1 ns timescales). Component 1 (polaron) is from MCR-ALS as shown in Fig. S 19. Component 2 (exciton) is obtained from neat PDTBT with the routine described above.

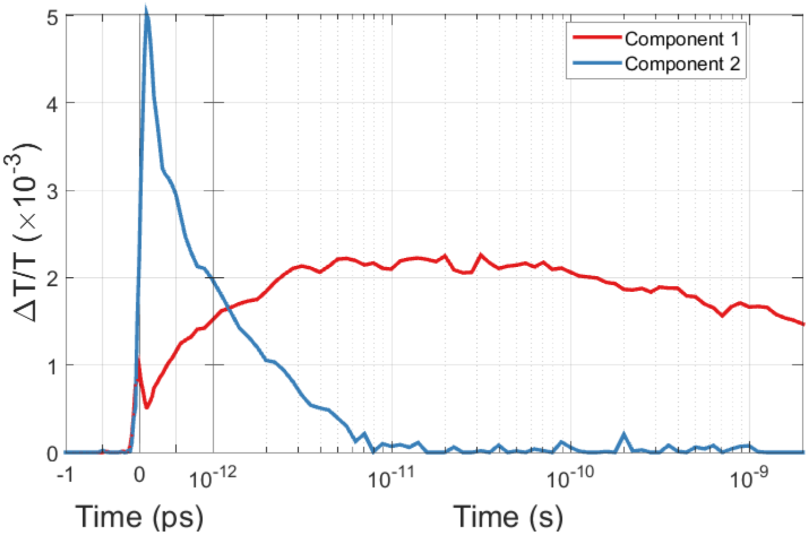

Fig. S 25 - Component weightings from NNLSQ of PDTBT:PCBM (-1ps to 1 ns timescales) using the spectral basis set presented in Fig. S 22.

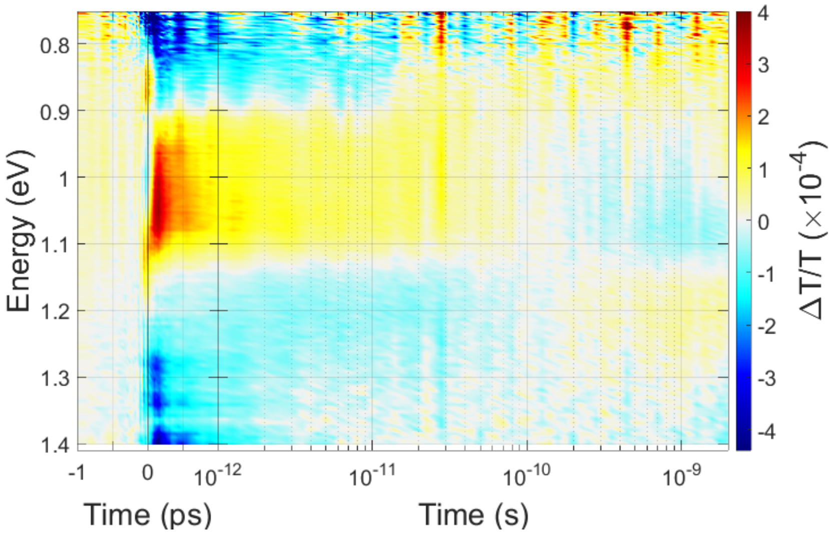

Fig. S 26 - Residual surface from NNLSQ of PDTBT:PCBM (-1ps to 1 ns timescales) using the spectral basis set presented in Fig. S 22.

3-phase morphology blends (PTBT:PCBM with and without ODT)

The TA surface (>10 ps, NIR probe) of PTBT:PCBM was concatenated in the probe photon energy dimension with PTBT:PCBM + ODT before performing the fitting procedures. The spectral basis set and relative weighting from MCR-ALS are presented in the manuscript with the residual surfaces presented here.

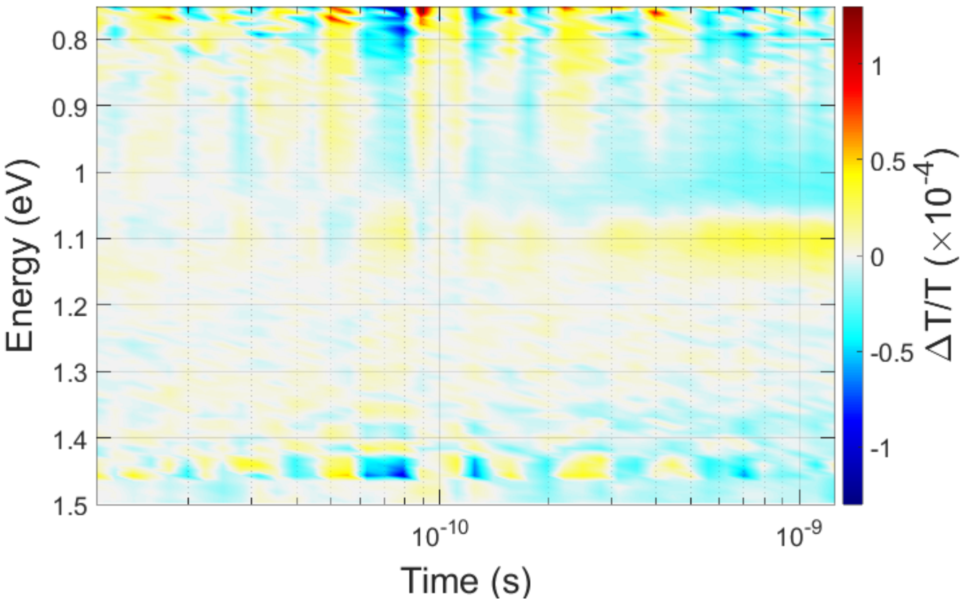

Fig. S 27 – Residual surface after MCR-ALS fitting using the two shape components reported in the text for PTBT:PCBM (>10 ps).

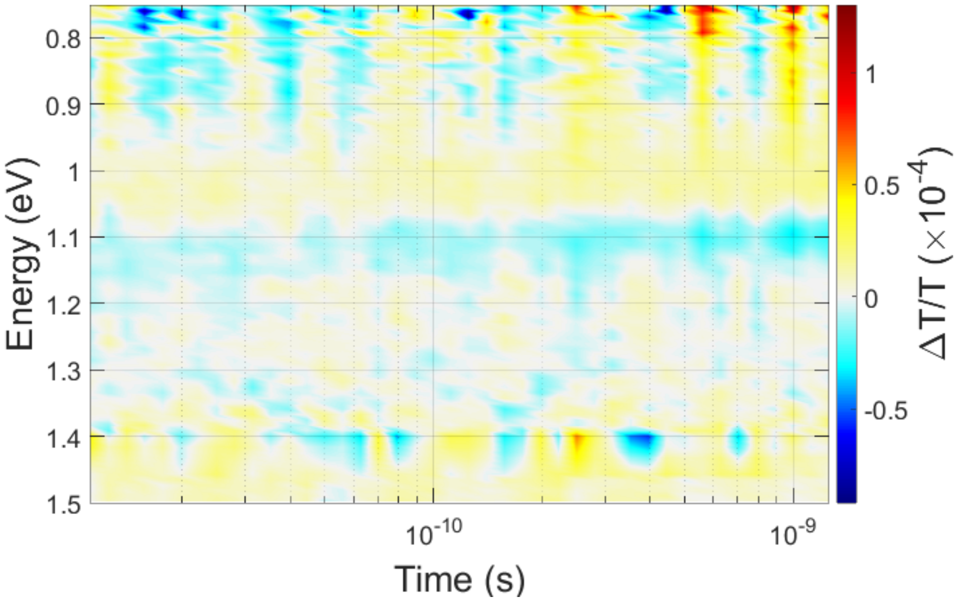

Fig. S 28 - Residual surface after MCR-ALS fitting using the two shape components reported in the text for PTBT:PCBM + ODT (>10 ps).

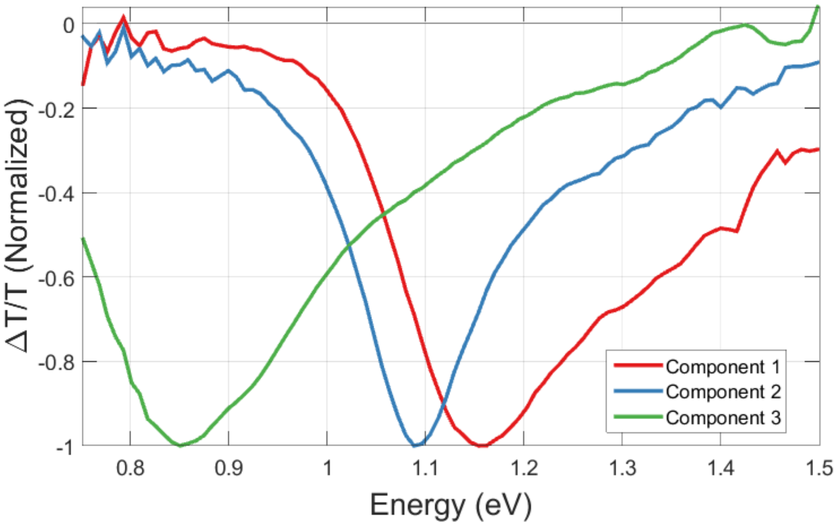

Fig. S 29- Spectral components used for non-negative linear least squares global fit of PTBT:PCBM (with and without ODT) for NIR probe photon energies over sub-picosecond to nanosecond timescales. Components 1 and 2 obtained from MCR-ALS, component 3 is a normalized component from neat polymer TA spectra.

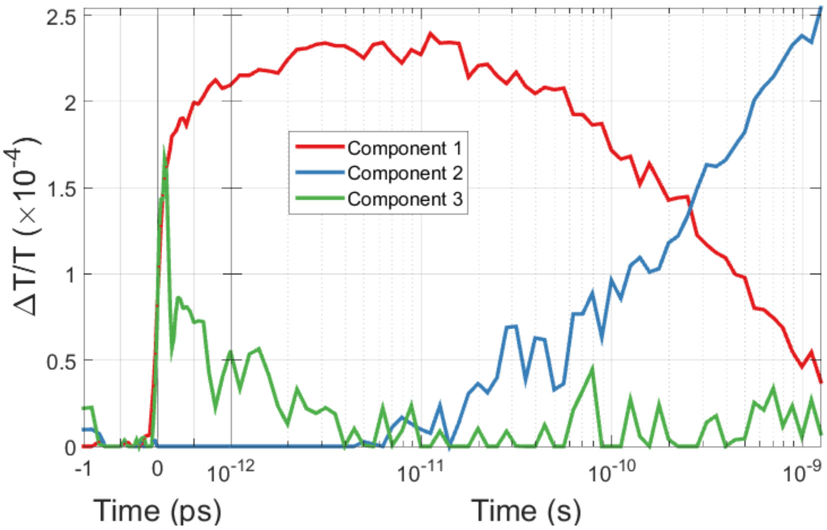

Fig. S 30 - Component weightings from a NNLSQ fit of the components in Fig. S 27 for PTBT:PCBM (-1ps to 1 ns timescales).

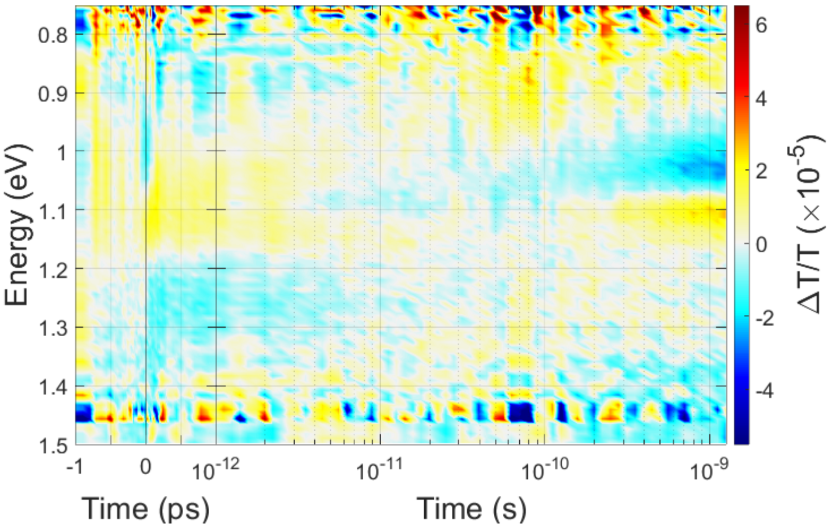

Fig. S 31 - Residuals from a NNLSQ fit of the components in Fig. S 27 for PTBT:PCBM (-1ps to 1 ns timescales).

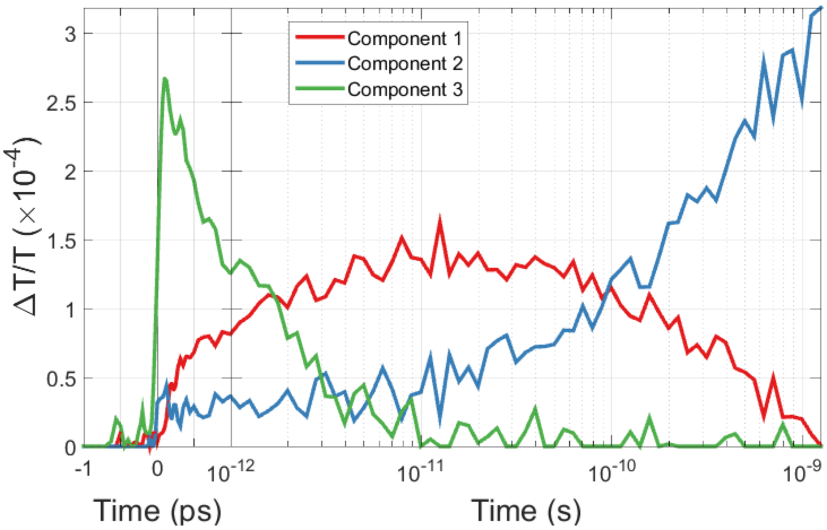

Fig. S 32 - Component weightings from a NNLSQ fit of the components in Fig. S 27 for PTBT:PCBM with ODT (-1ps to 1 ns timescales).

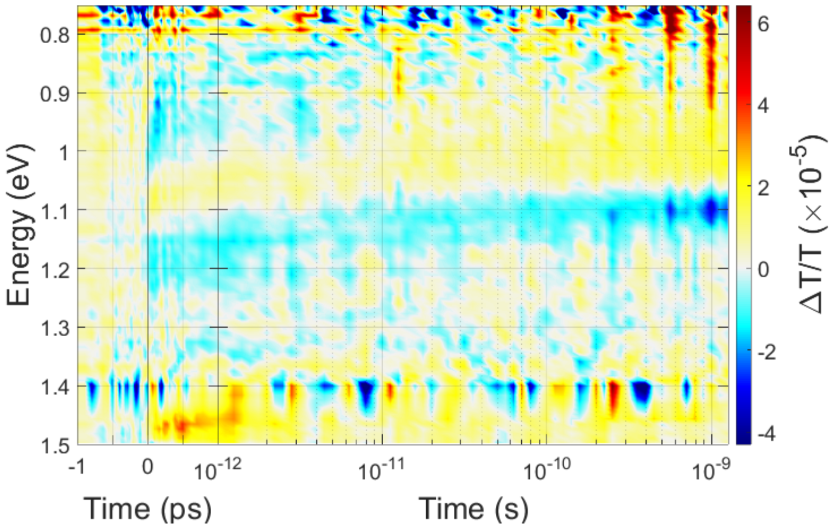

Fig. S 33 - Residuals from a NNLSQ fit of the components in Fig. S 27 for PTBT:PCBM with ODT (-1ps to 1 ns timescales).

References

1 I. A. Howard, H. Mangold, F. Etzold, D. Gehig and F. Laquai, *Ultrafast Dynamics in Molecules, Nanostructures and Interfaces*, World Scientific, 2013.

2 J. Jaumot, A. de Juan and R. Tauler, *Chemom. Intell. Lab. Syst.*, 2015, **140**, 1–12.