Supplementary Material (ESI) for Journal of Materials Chemistry

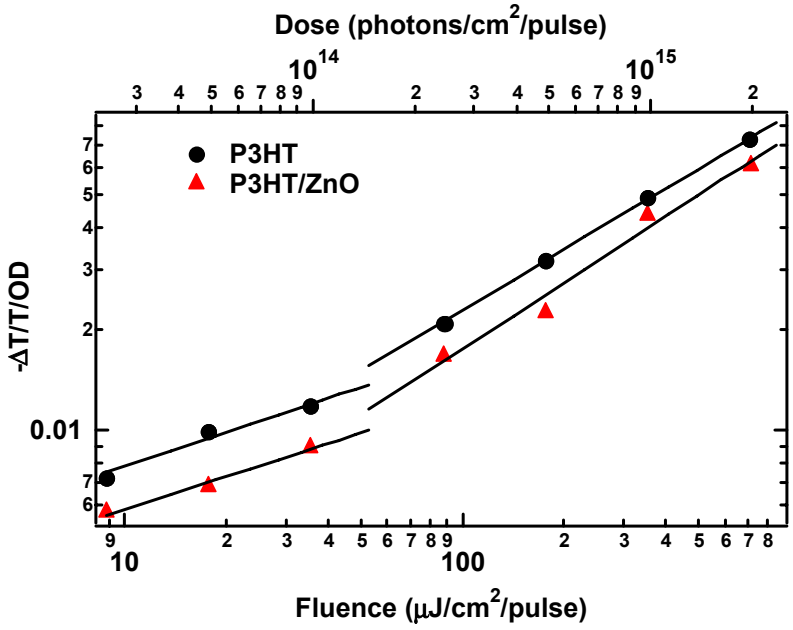
Impact of interfacial polymer morphology on photoexcitation dynamics and device performance in P3HT/ZnO heterojunctions

Matthew T. Lloyd, Rohit P. Prasankumar, Michael B. Sinclair, Alex C. Mayer, Dana C. Olson, and Julia W. P. Hsu

Supporting Information

Pump fluence dependence

P3HT on glass and P3HT/ZnO composite samples were subjected to increased excitation intensity as shown in Fig. S1. The pump and probe wavelengths were 550 nm and 3031 nm (probing the P_1 polaron), respectively. The maximum TPA signal (normalized by the optical density of the polymer layer at 550 nm) followed a power law dependence on pump fluence. Below 35 μJ/cm^2/pulse the absorption showed a low dependence on pump fluence with an exponent of approximately 0.32 for both samples. Above this fluence, the dependence on pump fluence increased yielding exponents of 0.60 and 0.65 for pristine P3HT and P3HT/ZnO, respectively. A similar dependence (exponents of 0.60 – 0.63) has also been reported for P3HT in near-steady-state photoinduced absorption measurements.[1] While a square root dependence on pump intensity is known to originate from bimolecular recombination, a contribution from both geminate and bimolecular recombination is likely to account for exponents of >0.5 at higher pump fluences.[2] Unless otherwise noted, a pump fluence of 18 μJ/cm^2/pulse was used for all subsequent TPA measurements in this study.



Supplementary Material (ESI) for Journal of Materials Chemistry

Fig. S1. Maximum TPA signal for P3HT on glass (black) and P3HT/ZnO composites (red) as a function of pump fluence. The TPA signal has been normalized by the sample optical density at the pump wavelength (550 nm). The samples were measured at room temperature under dynamic vacuum (<10^{-4} Torr).

TPA curve fitting

Fits to the measured TPA data were carried out a triple decay form of Eq. 1, which was found to minimize the error over the 0 - 500 ps time frame.[5]

$$\alpha_0 + \sum_i \frac{\alpha_i}{2} e^{\frac{-t}{\tau_i}} [1 - erf(\frac{-4t\tau_i + \sigma^2}{2.83\sigma\tau_i})] \qquad (1)$$

The function is convolved with the pump pulse, and returns values for the effective rise time σ, and the decay time constants τ_i with their corresponding pre-factors, α_i. The weighted average lifetime <τ> was calculated by summing the products of the individual decay constants and their respective pre-factor. Table S1 shows fitting parameters extracted from the data in Figure 4 with an iterative, least-squares algorithm using Igro Pro (WaveMetrics) software.

Table S1. Fitting parameters extracted from the TPA traces in Figure 4.

Sample	Absorption peak	α_1	α_2	α_3	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	<τ> (ps)
P3HT	P_1	0.32	0.37	0.31	1.4	12	92	33
P3HT/ZnO	P_1	0.30	0.39	0.31	1.0	8	78	28
P3HT/C16SH/ZnO	P_1	0.30	0.43	0.27	1.1	12	127	39
P3HT	PA_1	0.18	0.36	0.46	0.6	8	95	47
P3HT/ZnO	PA_1	0.17	0.33	0.50	0.3	4	64	33
P3HT/C16SH/ZnO	PA_1	0.19	0.35	0.46	0.7	10	94	47
P3HT	P_2	0.26	0.32	0.42	2.0	17	118	55
P3HT/ZnO	P_2	0.23	0.37	0.40	1.3	10	81	36
P3HT/C16SH/ZnO	P_2	0.35	0.35	0.29	3.0	30	171	61

To compare our TPA measurements with what others have measured for thin films of regioregular P3HT, we employed a triple exponential decay used by Ai *et al.* [6], given by Eq. 2.

$$\sum_i \alpha_i e^{\frac{-t}{\tau_i}} - \alpha_r e^{\frac{-t}{\tau_r}} \qquad (2)$$

We utilized a pump fluence and probe energy similar to ref. 6 to measure a TPA trace for P3HT on glass. Table S2 compares fitting parameters from literature with those we measured for the low energy polaron absorption (P_1). Although our measurements for this

sample only extended to 50 ps, the shorter decay constants (τ_1 and τ_2) and pre-factors prove to be in very good agreement.

Table S2. Comparison of measurement conditions and fitting parameters (extracted with Eq. 2) for TPA traces in this work and previously published results.

Sample	Probe energy (eV)	Pump energy (eV)	Pump fluence ($\mu J/cm^2$/pulse)	α_1	α_2	α_3	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	Reference
P3HT	0.41	2.3	360	0.65	0.25	0.10	0.4	4	56	this work
P3HT	0.25	3.1	610	0.69	0.28	0.07	0.3	4	413	ref. (6)

We used Eq. 1 to fit all our data (Figs. 4 and 5, and Table S1) because the TPA behavior in these samples has rise times and fast time constants (τ_1) on the same order as the pump pulse duration. For accurate fits near $t = 0$, it is important to include the influence of the pump pulse which is provided by Eq. 1. Moreover, as shown in Fig. S2., Eq. 1 provides superior fits to the data at t > 100 ps. Note that Eq. 1 yields longer decay constants than Eq. 2.

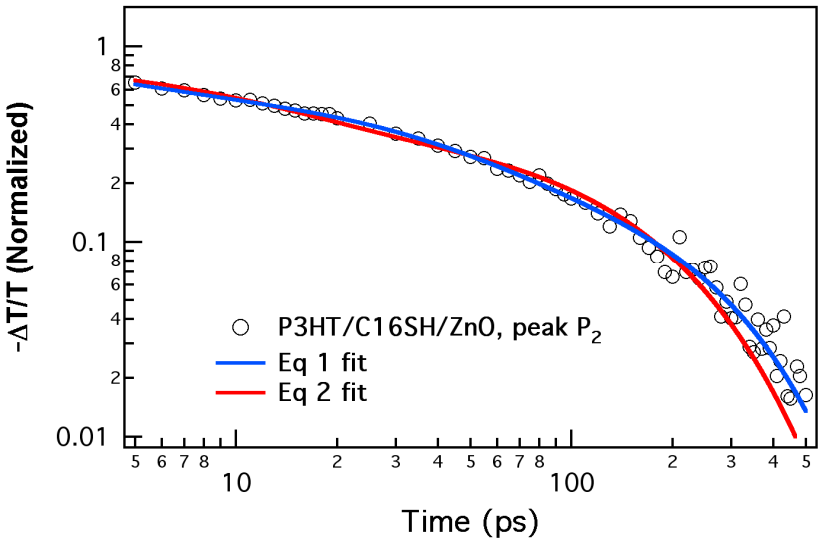


Fig. S2. Comparison of fitting functions Eq. 1 (blue) and Eq. 2 (red) illustrating better agreement with the measured data at longer times for Eq. 1.

TPA rise behavior

Fig. S3 shows the TPA signal rise time immediately after excitation, for each of the photoexcited species (P_1, PA_1, P_2). The data have been normalized to facilitate comparison between each of the samples. It is readily apparent that the rise time does not

vary significantly between either photoexcited species or between the various samples. Using Eq. 1, we were able to compare the time constant for the initial signal rise. For all the samples measured in this experiment the effective rise time measured 200±15 fs.

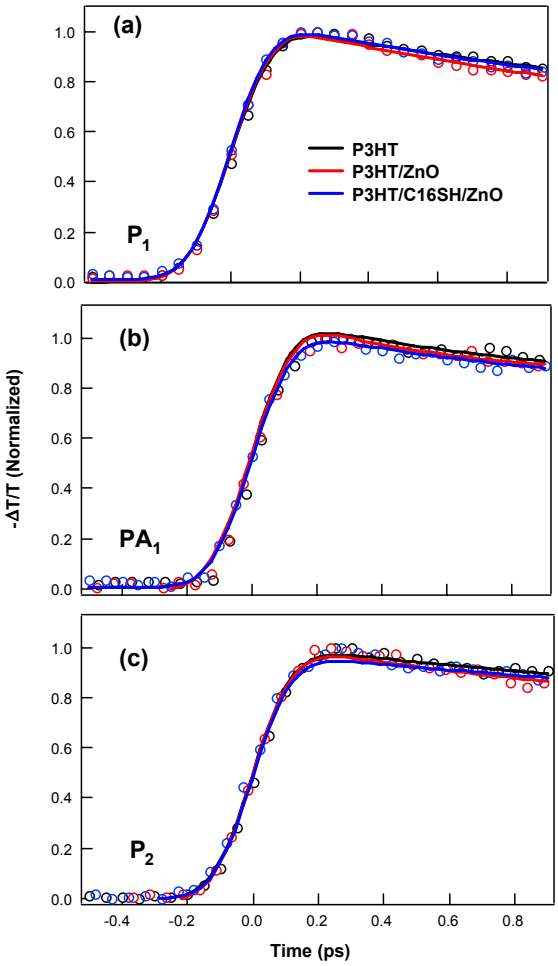


Fig. S3. Normalized TPA signal near t = 0 for (black) P3HT on glass (black), P3HT/ZnO (red), and P3HT/C16SH/ZnO (blue) composite samples for each of the photoexcited species.

References

1 P. A. van Hal, M. P. T. Christiaans, M. M. Wienk, J. M. Kroon, and R. A. J. Janssen, *J. Phys. Chem. B*, 1999, **103**, 4352.

2 G. Dellepiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, and A. Borghesi, *Phys. Rev. B*, 1993, **48**, 7850.

3 D. Olson, S. E. Shaheen, R. T. Collins, and D. S. Ginley, *J Phys Chem C*, 2007, **111**, 16670.

4 M. Lira-Cantu, K. Norrman, J. W. Andreasen, N. Casan-Pastor, and F. C. Krebs, *J Electrochem Soc*, 2007, **154**, B508.

5 J. Demsar, Thesis, University of Ljublana, 2000.

[6] X. Ai, N. Anderson, J. C. Guo, J. Kowalik, L. M. Tolbert, and T. Q. Lian, *J. Phys. Chem. B*, 2006, **110**, 25496.