Electronic Supplementary Information

Global and Target Analysis of Relaxation Processes of Collapsed State of P3HT Polymer Nanoparticles

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Calculation of concentration of Au NP

We have used 500 µl of 10 mM $HAuCl_4,3H_2O$ solution for preparation of Au NPs which corresponds to 1.97 mg $HAuCl_4,3H_2O$ i.e. 0.985 mg Au. We have found that diameter of each Au NP was ≈5 nm which means the volume of each Au NP is $4/3 \times \Pi \times (5/2 \times 10^{-7})^3$ cm^{-3}. Now, the total volume of the prepared Au NP solution was 20 mL. So, no. of Au NP in 20 mL solution will be, {mass of Au present/ (volume of each particle × density of Au)}. Since the density of Au is 19.32 gcm^{-3}, total no of Au NP in 20 mL solution is $\{0.985 \times 10^{-3}/ (4/3 \times \Pi \times (5/2 \times 10^{-7})^3 \times 19.32)$ which is equal to 7.8×10^{14}. So, in 1000 mL there is $(7.8 \times 10^{14} \times 1000/20) = 3.89 \times 10^{16}$ no. of Au NP. Now, 1 mole corresponds to 6.023×10^{23} no. of particles. Therefore, in 1000 mL stock solution there is $(3.89 \times 10^{16} /6.023 \times 10^{23}) = 64 \times 10^{-9}$ moles Au NP. So, the molar concentration of Au NP stock solution is 64×10^{-9} M i.e 64 nM. Now, we have added 75, 125 and 250 µl of this stock solution for preparing the composites and the final volume of each set was 3 mL which means final concentration of Au NP in the composite systems are 1.5 nM, 2.5 nM and 5 nM.

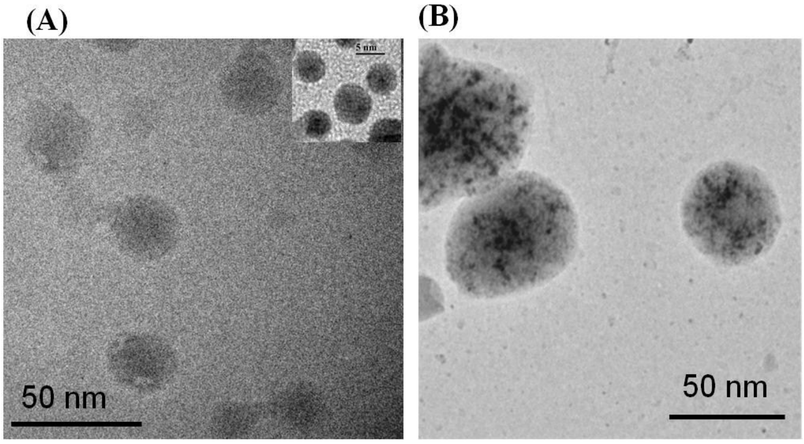

Fig. S1: TEM images of (A) P3HT PNP (inset show image of prepared Au NP) and (B) P3HT PNP/Au NP heterostructures

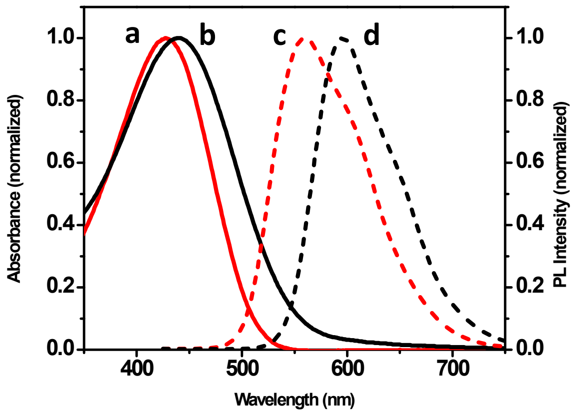

Fig. S2: UV-Vis absorption spectra and PL spectra respectively of P3HT in THF (a,c) and P3HT PNP (b,d)

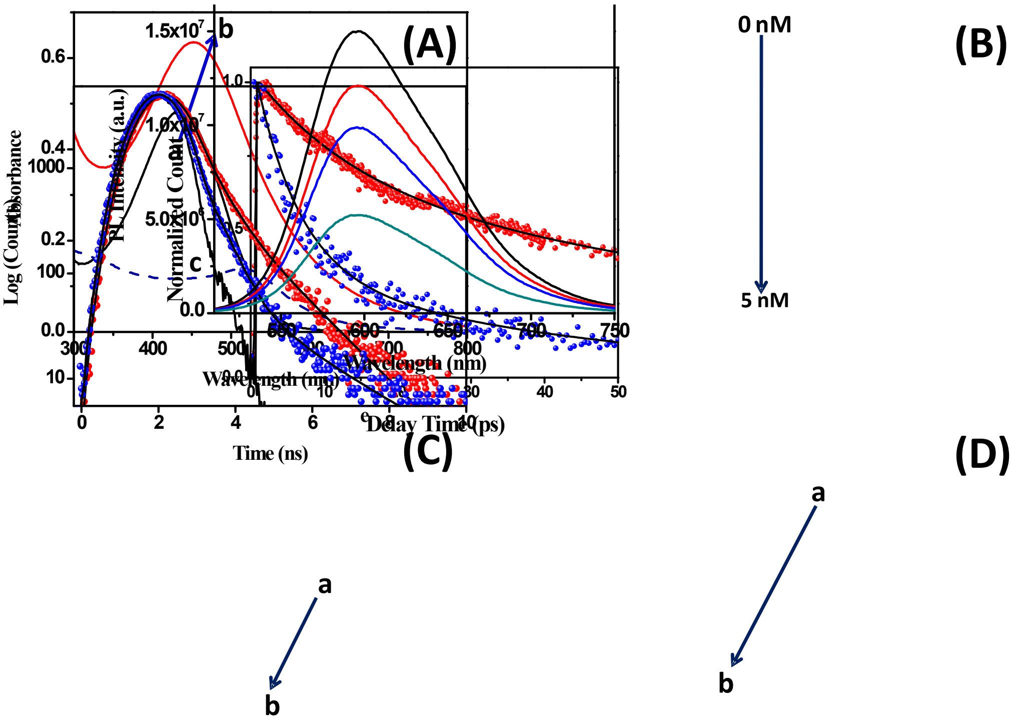

Fig. S3: (A) UV-Vis spectra of (a) P3HT PNP, (b) P3HT PNP/Au NP heterostructure and (c) 5 nM Au NP; (B) PL spectra of P3HT PNP and P3HT PNP/Au NP heterostructure with increasing concentration of Au NP from 0 to 5 nM; (C) TCSPC and (D) Fluorescence Upconversion decay curves of (a) P3HT PNP and (b) P3HT PNP/Au NP heterostructure

Time-correlated single photon counting (TCSPC) instrumentation:

The data was analyzed by following equation:

$$P(t) = b + \sum_{i}^{n} \alpha_i \exp(-\frac{t}{\tau_i})$$

Here, n is the number of emissive species, b is the baseline correction ("DC" offset), and α_i and τ_i are the pre-exponential factor and the excited-state fluorescence decay time associated with the i^{th} component. The average decay time, ⟨τ⟩, was calculated from the following equation.

$$< \tau >= \sum_{i=1}^{n} \beta_i \tau_i$$

Where $\beta_i = \alpha_i / \sum \alpha_i$ and it is the contribution of the decay component. α_i and τ_i are the pre-exponential factors and excited-state fluorescence lifetimes associated with the i^{th} component, respectively. This value should be called an amplitude-weighted lifetime.

Table S1: TCSPC decay fitting parameters of P3HT PNP and P3HT PNP/Au NP heterostructure

Sample	**τ_1 (a_1) (ns)**	**τ_2 (a_2) (ns)**	**τ_3 (a_3) (ns)**	**$\tau_{avg.}$ (ns)**
P3HT PNP	0.335 (0.93)	1.1 (0.07)	-	0.388
P3HT/Au NP Heterostructure	0.23 (0.83)	0.597 (0.15)	1.2 (0.02)	0.304

Table S2: Fluorescence upconversion decay fitting parameters of P3HT PNP and P3HT PNP/Au NP heterostructure

Sample	**τ_1 (a_1) ps**	**τ_2 (a_2) ps**
P3HT PNP	15 (0.31)	380 (0.69)
P3HT/Au NP Heterostructure	8 (0.73)	275 (0.27)

Table S3: Fitting parameters of bleach recovery kinetics of P3HT PNP and P3HT PNP/Au NP heterostructure obtained from TAS

Sample	**τ_1^g (a_1) (fs)**	**τ_1^r (a_2) (ps)**	**τ_2^r (a_3) (ps)**	**τ_3^r (a_3) (ps)**	**τ_4^r (a_4) (ps)**
P3HT in THF	<100 (100%)	2.4 (48%)	490 (37%)		>8000 (15%)
P3HT in PNP	<100 (100%)	0.554 (56%)	4.73 (20%)	445 (14%)	>8000 (10%)
P3HT/Au NP Heterostructure	<100 (100%)	0.2 (70%)	3.2 (12%)	295 (10%)	>8000 (8%)

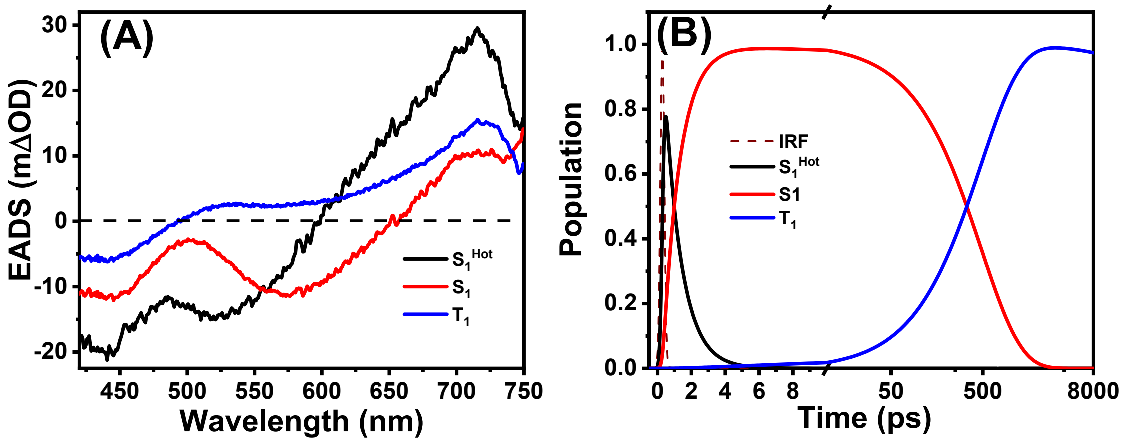

Fig. S4: Obtained evolution-associated difference spectra (EADS) of the corresponding states of P3HT in THF after exciting at 400 nm.

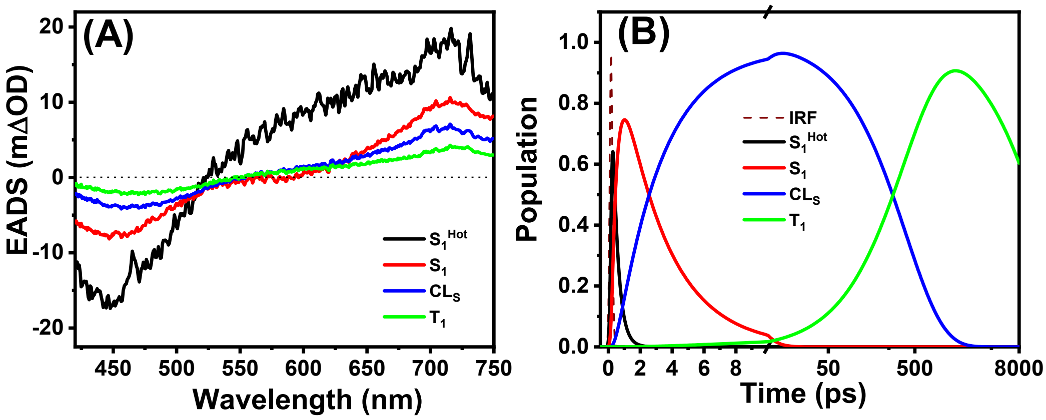

Fig. S5: Obtained evolution-associated difference spectra (EADS) of the corresponding states of P3HT PNP after exciting at 400 nm.

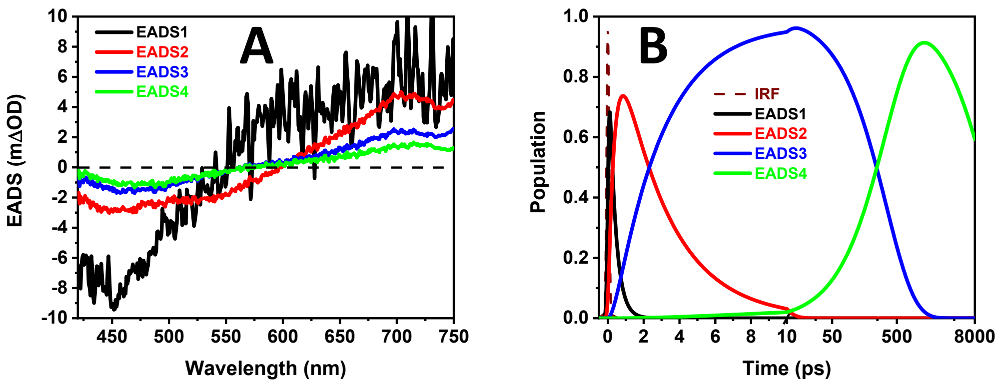

Fig. S6: Obtained evolution-associated difference spectra (EADS) of the corresponding states of P3HT/Au heterostructure after exciting at 400 nm.

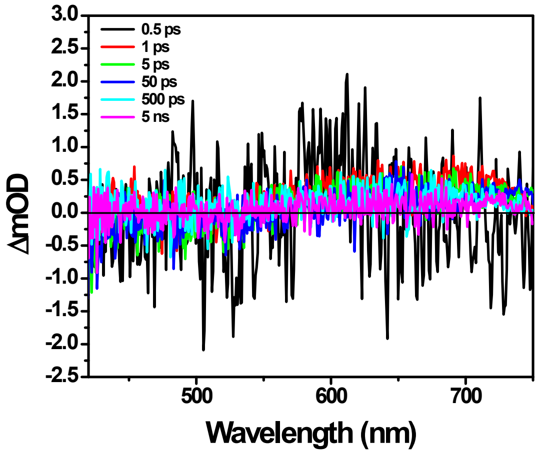

Fig. S7: TAS signal for 5 nM Au NP excited at 400 nm.

Estimated rate constants from target analysis of P3HT/Au heterostructure

The rate constant obtained for conversion of SADS 1 to SADS 2 is 6.849 ps^{-1}. This rate constant is summation of two processes: (process a) conversion from S_1^{Hot} state to the S_1 state [corresponding rate constant k_a] and (process c) the electron transfer process from the S_1^{Hot} state to Au NPs [corresponding rate constant k_c]. The value of K_a is 2.898 ps^{-1} (obtained from Fig. 4A) and the rate constant (k_c) for electron transfer from S_1^{Hot} state of PNPs to Au NPs is 3.951 ps^{-1} and the timescale associated with the process ($\tau_c = k_c^{-1}$) is 253 fs. The SADS 2 decays to ground state and SADS 3 simultaneously. The decay time of SADS 2 to ground state is 9.6 ps and the rate constant for conversion of SADS 2 to SADS 3 is 0.3125 ps^{-1}. This rate constant is also summation of two processes: (process b) population conversion from S_1 of PNP to CL_S state [corresponding rate constant k_b] and (process d) the electron transfer from CL_S state of the PNPs to the Au NPs [corresponding rate constant k_d]. The value of the rate constant k_d is found to be 0.0265 ps^{-1} and therefore the timescale associated to the electron transfer from CL_S state of the PNPs to the Au NPs is 37.7 ps^{-1}.