Electronic Supporting Information

Photoinduced charge generation rates in soluble P3HT:PCBM nano-aggregates predict the solventdependent film morphology

Palas Roy, Ajay Jha, and Jyotishman Dasgupta*

Department of Chemical Sciences, 1 Homi Bhabha Road,

Tata Institute of Fundamental Research, Mumbai 400005, India.

*E-mail:<u>dasgupta@tifr.res.in</u>

Contents

	Page Page
1. Materials and Methods	S2-S10
2. Supplementary figures: (Fig. S1 – Fig. S22)	
Steady-state absorption spectra of P3HT in different solvents	S 11

Steady-state absorption spectra of PSH1 in different solvents	511
Steady-state absorption spectra of P3HT:PCBM in different solvents	S12
DLS of PCBM in different solvents	S13
Power dependent TA of P3HT for annihilation measurement	S14
Quenching of fluorescence of P3HT by PCBM in different solvents	S15
TCSPC of P3HT and P3HT:PCBM in different solvents	S16
Absorption spectrum of chemically oxidised P3HT by FeCl ₃	S17
3D Representation of TA spectra using toluene as solvent	S18
3D Representation of TA spectra using chlorobenzene as solvent	S19
3D Representation of TA spectra using chloroform as solvent	S20
$\Delta\Delta A$ spectra in TL at different time delays	S21
$\Delta\Delta A$ spectra in CLB at different time delays	S22
$\Delta\Delta A$ spectra in CHCl ₃ at different time delays	S23
Concentration and power dependent TA of neat P3HT solution	S24
ESA of P3HT:PCBM solution under repeated scan	S25
ESA of only PCBM solution	S26
Time series of $\Delta\Delta A$ vs wavelength in CLB and CHCl ₃	S27
Normalization coefficients to construct $\Delta\Delta A$ spectra	S28
Triplet state absorption and its rise time	S29
TEM of only P3HT casted from different solvents	S30
TEM of P3HT and P3HT:PCBM casted from toluene	S31
SRS of PCBM at different concentrations in toluene	S32
Pump power dependence to the ESA of P3HT	S33

3. References

S34

1. Materials and Methods:

Chemicals. Poly(3-hexylthiophene-2,5-diyl) (P3HT) ($M_n = 54-75 \text{ kg mol}^{-1}$, regioregular) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) purchased from Sigma Aldrich, USA were used. Chloroform (CHCl₃) (AR grade), chlorobenzene (CLB) (AR grade) and toluene (TL) (HPLC grade) were purchased from SD Fine-Chem Pvt. Ltd., India.

Sample Preparation. For preparing pristine P3HT samples, 1 mg of the polymer was added to 4 ml of respective solvents. In order to make 1:20 w/w P3HT:PCBM mixture, 1 mg of polymer and 20 mg of PCBM were added to 4 ml of the respective solvents. All these solutions were firstly argon purged and then sealed. Subsequently these samples were heated for 2 hrs at 333 K and then brought at room temperature. For all steady-state and time-resolved measurements we used the above described sample preparation protocol.

Steady-state absorption and emission measurements. The steady-state absorption measurements were carried out in JASCO V-670 spectrophotometer using a cuvette with path length of 0.2 mm. Solution of P3HT was chemically oxidized using ferric chloride as an oxidizing agent, and the absorption spectrum was recorded (see Supporting Information Fig. S7).

All steady-state emission spectra were measured in a Horiba Jobin-Yvon SPEX Fluorolog-3 spectrofluorometer using a quartz cuvette with pathlength of 1 cm. Fluorescence spectra were corrected for the spectral sensitivity of photomultiplier. The slit widths were adjusted to keep the detection in the linear range.

Transmission electron microscopy. Pristine P3HT solutions (0.25 mg/mL) in different solvents were placed on carbon-coated 100 mesh copper grids. The grid was placed on a filter paper in order to absorb surrounding solvents rapidly. The grids were dried under vacuum

desiccator for 1 day. The samples were examined with transmission electron microscope LIBRA 120, EFTEM, Carl Zeiss, Germany.

Dynamic light scattering measurements. Hydrodynamic radius of only P3HT and P3HT:20PCBM in different solvents were performed using a DAWN 8+, eight angle light scattering instrument (Wyatt Technology, Santa Barbara, CA) at room temperature (298 K).

Time-resolved emission measurements using TCSPC. Time-resolved fluorescence measurements were performed using a pico-second time-correlated single photon counting (TCSPC) technique. The output 1 ps laser pulse of 917 nm at 8 MHz repetition rate from a Ti:Sapphire oscillator, pumped by a Nd-YAG laser (Millenia X, Spectra Physics), was frequency doubled to generate 458 nm laser pulse to excite the polymer. Fluorescence decay traces at 575 nm were collected by the use of a microchannel plate photomultiplier (model R2809; Hamamatsu Corp.) coupled to a time-correlated single photon-counting setup. The instrument response functions (IRF) at 458 nm were obtained using a dilute colloidal suspension of dried nondairy coffee whitener. The FWHM of the IRF was ~90 ps. A 530 nm long pass filter was used for the fluorescence measurements. To eliminate the contribution from the decay of anisotropy, the emission was monitored at the magic angle (54.7°).

Pump-probe measurements. The detailed description of the pump-probe set up has been mentioned elsewhere.⁴² Briefly, fundamental output from the oscillator (Coherent Micra-5 modelocked Ti:Sapphire Laser system) of 80 MHz repetition rate with bandwidth of ~100 nm and power of 5 nJ/pulse, is amplified using regenerative amplifier Coherent Legend Elite[®]. The output of the amplifier is ~4 mJ/pulse, with a repetition rate of 1 kHz and ~30 fs pulse width. Part of this amplified pulse was used to generate the 475 nm pump pulse using an optical parametric amplifier (Coherent OPeraASolo[®], Ultrafast Optical Parametric Amplifier system). Pump pulse energy was attenuated to 64 μ J/cm² in order to minimize the photo-

damage. The white-light probe continuum was generated using a 2 mm thick sapphire crystal, while the NIR regimes (850-1300 nm) of the probe continuum is separated using a 850 nm long pass filter. After passing through the sample, probe is finally dispersed by Helios[®] spectrograph onto an imaging element (297 pixels). Polarization of the pump pulse is kept at magic angle (54.7°) for all the measurements to remove any effect of rotational diffusion. The actinic pump and probe pulses were focused and overlapped on the sample inside a flow cuvette with 0.5 mm glass window. The instrument response function, IRF with 475 nm excitation pump and NIR probe was determined to be ~90 fs using optical Kerr-effect arrangement with a pair of polarizer (in pump path) and analyzer (in the probe path). All pump-probe measurements were done in the flowing condition with the liquid driven by a peristaltic pump. The flow rate was maintained in order to refurnish fresh sample before every shot.

Stimulated Raman Scattering. Stimulated Raman Scattering (SRS) can be used to get fluorescence background free coherent Raman signal. Here a combination of narrow bandwidth (~20 cm⁻¹) Raman pump centered at 816 nm (measured using Ocean optics spectrometer) along with a broadband femtosecond NIR (850-1300 nm) probe pulse stimulates the coherent Raman scattering process from the sample. The femtosecond NIR probe pulse was generated after focusing the fundamental onto a sapphire crystal, and was compressed subsequently using a home-built two-prism compressor set up. The narrow bandwidth Raman pump pulse was generated from the broadband femtosecond fundamental pulse using a grating filter configuration that was previously reported.⁴³ Both Raman pump and probe pulses are overlapped in time and space on the sample to get SRS signal. The spectral resolution was limited by the Raman pump pulse which was set at ~2 ps. All measurements were carried out in a cuvette with constant stirring of the sample using a small magnetic stir bar. The Raman pump power was fixed at 2 mW for optimal signals. The transmitted probe beam from the sample was dispersed using Acton SP 2300 spectrograph and spectra were recorded with a computer-controlled Pixis[®] 100F CCD detector (Princeton Instruments, Roper Scientific). Shot-to-shot detection of the pump-on versus pump-off spectra using lock-in detection provided fast accumulation of data with minimum spectral variations. Each spectrum was accumulated for 10s and identical experimental conditions were maintained for all samples. The detector was calibrated using the CCD-detected stimulated Raman spectrum of cyclohexane collected under identical conditions.

Kinetics data fitting procedure. The kinetic analyses of TCSPC and transient absorption measurements were carried out using IGOR pro 5 wavemetrics software with programs written to deconvolve the time-constants from the measured IRF. The procedure yields decay time constants and their respective amplitudes. The equation employed for fitting is given below:

$$y(t) = w_{1} \left[\left(w_{2}e^{\frac{[k_{0}^{2}-4bk_{0}(t-w_{9})]}{4b}} \right) \operatorname{normdist} \left(\frac{2b(t-w_{9})-k_{0}}{\sqrt{2b}} \right) \right. \\ \left. + \left(w_{4}e^{\frac{[k_{1}^{2}-4bk_{1}(t-w_{9})]}{4b}} \right) \operatorname{normdist} \left(\frac{2b(t-w_{9})-k_{1}}{\sqrt{2b}} \right) \right. \\ \left. + \left(w_{6}e^{\frac{[k_{2}^{2}-4bk_{2}(t-w_{9})]}{4b}} \right) \operatorname{normdist} \left(\frac{2b(t-w_{9})-k_{2}}{\sqrt{2b}} \right) \right. \\ \left. + \left([-1-(w_{4}-w_{6})]e^{\frac{[k_{3}^{2}-4bk_{3}(t-w_{9})]}{4b}} \right) \operatorname{normdist} \left(\frac{2b(t-w_{9})-k_{3}}{\sqrt{2b}} \right) \right] \right]$$

... [1]

Where,

$$b = \frac{4\ln 2}{w_0^2} k_0 = \frac{1}{w_3} k_1 = \frac{1}{w_5} \quad k_2 = \frac{1}{w_8}$$

 w_0 = instrument response function, IRF.

 $w_1 = scaling factor.$

 w_2 , w_4 , w_6 = amplitudes of the first, second, third exponentials.

 w_3 , w_5 , w_7 , w_8 = Four time constants.

 $w_9 = \text{zero time.}$

The transient absorption data treatment involves time correction to account for the chirp of the probe pulse before proceeding to kinetic analysis.

Normalisation of transient spectra to construct $\Delta\Delta A$. Transient absorption measurement of only P3HT and its 1:20 mixture with PCBM were taken in different solvents (see Fig. S8, S9 and S10) on the same day with identical experimental conditions. In order to capture only the polaron feature we constructed $\Delta\Delta A$ spectra at different time delays. Our preliminary assumption is that in the transient absorption spectra of the mixture there is contribution from both the free and bound polymer, and the bound polymer gives the signature of polaron. To eliminate the contribution of free exciton spectra from the mixture, we normalised the pristine P3HT spectra with respect to P3HT/20PCBM spectra at different time delays by looking at the excitonic feature on the red edge (the normalisation coefficients are plotted as a function of pump-probe time delay in Fig. S18). Difference between these two spectra has been used to construct $\Delta\Delta A$ spectra which represent only the polaron signature arising from the bound polymer population. This procedure was repeated for different time traces in three different solvents as shown in Fig. S11, S12 and S13. It permits independent verification of assignment. This investigation is supported by the study on P3HT/PCBM nano-particle papers published by Tak Kee and co-workers¹ and by Guo et al.²

Calculation of singlet exciton molar absorptivity. Steady state absorption spectra of P3HT in solution (0.25 mg/ml) were taken in a 0.2mm cuvette because sample concentration was high enough. Molar extinction coefficient of P3HT in different solvents can be given by,

$$\varepsilon_{485} = \frac{A}{[P3HT].l}$$

$$= \frac{0.29}{\frac{0.25}{65000} mol \ L^{-1} \ X \ 0.02 cm} = 3.77 \ X \ 10^{6} \ L \ mol^{-1} \ cm^{-1} \ (in \ CLB)$$

$$= 3.575 \ X \ 10^{6} \ L \ mol^{-1} \ cm^{-1} \ (in \ CHCl_{3})$$

$$= 3.484 \ X \ 10^{6} \ L \ mol^{-1} \ cm^{-1} \ (in \ TL)$$

Fraction of light absorbed (I/I_0) during passing through the solution inside a 1 mm cuvette can be given by,

 $I/I_0 = 1\text{--}10^{\epsilon 485.[P3HT].d}$

= 0.96 (CLB)

= 0.96 (CHCl₃)

$$= 0.954 (TL)$$

The number of photons per pump pulse can be given by,

Photons/pulse= <u>
power</u> <u>
repetition rate X energy per photon</u>

= 0.24 X 10^{10} photon pulse⁻¹ (for 1µW 485nm pump)

Now, the diameter of probe beam at focus point is 100 μ m. Assuming interaction volume to be cylindrical, the volume (length of the cylinder has been calculated to be d= 0.431 mm) can be given by,

V=
$$\pi$$
. (0.005)². 0.0431 cm³ = 3.4 X 10⁻⁹ L

Then number of P3HT molecules excited,

 $[P3HT^*] = (photon/pulse)(I/I_0)(1/V)$

=
$$6.8 \times 10^{14}$$
 molecule cm⁻³ (CLB)
= 6.8×10^{14} molecule cm⁻³ (CHCl₃)
= 6.7×10^{14} molecule cm⁻³ (TL)

Thus extinction coefficient of excited state at 1220 nm can be calculated.

$$\varepsilon^*_{1220} = 1.2 \text{ X } 10^{-16} \text{ cm}^2 \text{ molecule}^{-1} \text{ (CLB)}$$

= 1.4X 10⁻¹⁶ cm² molecule⁻¹ (CHCl₃)
= 1.15 X 10⁻¹⁶ cm² molecule⁻¹ (TL)

This coefficient can be used to calculate transient number of excited molecule (n) at a given time from the experimentally obtained ΔA values. Exciton concentration can be given by,

n=
$$\frac{\Delta A}{\epsilon^{*.d}} = \frac{\Delta A}{5.17 \times 10^{-18}} \text{ cm}^{-3}(\text{CLB})$$

= $\frac{\Delta A}{6.03 \times 10^{-18}} \text{ cm}^{-3}(\text{CHCl}_3)$
= $\frac{\Delta A}{4.95 \times 10^{-18}} \text{ cm}^{-3}(\text{TL})$

Calculation of exciton diffusion coefficient of P3HT in solution. Exciton-exciton annihilation rate can be calculated from the time-independent portion of the master rate equation where the time-dependent exciton concentration (n) is given by:

$$\frac{\mathrm{dn}}{\mathrm{dt}} = \mathrm{G} - \mathrm{kn} - \gamma \mathrm{n}^2 \qquad [2]$$

where, G is the exciton generation rate, k is the exciton decay rate in the absence of annihilation and γ is the annihilation rate.³

In order to calculate the exciton diffusion length of P3HT in different solvents, singlet-singlet exciton annihilation process has been studied using transient absorption measurement. The exciton concentration (n) during annihilation process can be described by the rate equation

$$\frac{\mathrm{dn}}{\mathrm{dt}} = -\mathrm{kn} - \gamma \mathrm{n}^2 \tag{3}$$

where k is the exciton decay rate in the absence of annihilation and γ is the annihilation rate.⁶ The time dependence of γ can be measured at two different exciton densities as:

$$\gamma(t) = -\frac{K_1 - K_2}{n_1 - n_2}$$
 [4]

where K = (1/n)(dn/dt) and the subscripts 1 and 2 represents the respective values at different excitation intensities.

To see the annihilation, ESA of singlet exciton kinetics (n vs t) of P3HT solution at 1220 nm was followed with the pump of 485 nm of different power (6.4 μ J cm⁻² and 4.5 mJ cm⁻²) as shown in Fig. S4. In order to increase the time resolution and to reduce the noise associated with the differentiation of the experimental data, we first fitted the experimental kinetics with a four exponential decay function convolved with the IRF and used the fits to calculate $\gamma(t)$ using equation [4]. Fig. 7a shows the time dependent $\gamma(t)$ of P3HT in different solvents.

The time dependence of $\gamma(t)$ is given by

$$\gamma(t) = 4\pi Dr \left(1 + \frac{r}{\sqrt{\pi Dt}}\right)$$
[5]

where D is time independent exciton diffusion coefficient and r is the exciton annihilation radius. Fitting the annihilation rate using equation [5] can give exciton diffusion coefficient (D) as shown in the main manuscript Fig. 7a inset. Since diffusion limited polaronic rise time is in the range of 5-20 ps (as obtained from our transient measurement as described in the main manuscript), the $\gamma(t)$ value used was in this range.

If D is diffusion coefficient of singlet exciton, then exciton diffusion length (L) at diffusion time t can be given by the equation $L = \sqrt{(2Dt)}^2$. Thus using the known value of D and t, the domain size (2L) can be approximately estimated. Based on this, we have calculated domain size of P3HT in different solvents as shown in Fig. 7b.

2. Supplementary figures:



Fig. S1 Steady-state absorption spectra of P3HT in three different solvents: chloroform, CHCl₃ (black), chlorobenzene, CLB (red) and toluene, TL (blue). Absorption spectrum of P3HT in toluene shows new features in the red edge at 516, 566 and 614 nm, due to ordered aggregate formation in this particular solvent.



Fig. S2 Steady-state absorption spectra of P3HT:PCBM in three different solvents: chloroform, CHCl₃ (black), chlorobenzene, CLB (red) and toluene, TL (blue). The green plot represents absorption spectrum of only PCBM in TL. The absorption spectrum of P3HT:PCBM in TL at the red edge is quite broad as compared to that of only P3HT in TL hinting towards the formation of different P3HT aggregate structure in presence of PCBM.



Fig. S3 DLS of only PCBM (20 wt%) in three different solvents (chlorobenzene, chloroform and toluene) showing hydrodynamic radius of <1 nm.



Fig. S4 Time dependence of exciton population decay (at 1220 nm) with different initial exciton density, n_0 (molecule cm⁻³) of pristine P3HT in chloroform measured using power dependent transient absorption (485 nm pump) measurements. The black and blue kinetics were taken under pump flux of 6.4 µJ cm⁻² and 4.5 mJ cm⁻² respectively. At high pump power, there is Singlet-singlet exciton annihilation. These kinetics were used to find out annihilation rate as described in the Methods part of Supporting information.



Fig. S5 Quenching of fluorescence of P3HT upon addition of increasing concentration of PCBM (0-20 wt%) in three different solvents: (a) toluene (TL), (b) chlorobenzene (CLB), and (c) chloroform (CHCl₃).



Fig. S6 TCSPC lifetime measurement of (a) free P3HT in CHCl₃, CLB and TL; P3HT with different concentration (0-20 wt%) of PCBM in (b) CHCl₃ and (c) CLB.



Fig. S7 Comparison of steady state absorption spectra of only P3HT polymer (in black), its mixture with excess of FeCl₃ (in red) in toluene (TL) under argon atmosphere. FeCl₃ oxidizes P3HT polymer which results into broad absorption band at ~850 nm corresponding to P3HT cation radical.



Fig. S8 The three-dimensional representative plots of the excited state absorption (ESA) profile for NIR probe wavelengths (800-1300 nm) after subjecting to excitation at 475 nm: (a) only P3HT and b) P3HT:PCBM (1:20) mixture in toluene. The intensity color code is shown on the right.



Fig. S9 The three-dimensional representative plots of the excited state absorption (ESA) profile for NIR probe wavelengths (800-1300 nm) after subjecting to excitation at 475 nm: (a) only P3HT and b) P3HT:PCBM (1:20) mixture in chlorobenzene. The intensity color code is shown on the right.



Fig. S10 The three-dimensional representative plots of the excited state absorption (ESA) profile for NIR probe wavelengths (800-1300 nm) after subjecting to excitation at 475 nm: (a) only P3HT and b) P3HT:PCBM (1:20) mixture in chloroform. The intensity color code is shown on the right.



Fig. S11 $\Delta\Delta A$ Spectra of P3HT:PCBM (1:20) mixture (in blue) in toluene at different time delays with respective ΔA spectra for pristine P3HT (in black) and P3HT:PCBM (1:20) mixture (in red).



Fig. S12 $\Delta\Delta A$ spectra of P3HT:PCBM (1:20) mixture (in blue) in chlorobenzene at different time delays with respective ΔA spectra for pristine P3HT only (in black) and P3HT:PCBM (1:20) mixture (in red).



Fig. S13 $\Delta\Delta A$ spectra of P3HT:PCBM (1:20) mixture (in blue) in chloroform at different time delays with respective ΔA spectra for pristine P3HT (in black) and P3HT:PCBM (1:20) mixture (in red).



Fig. S14 ESA of only P3HT at our experimental condition (0.25mg/ml concentration of P3HT; 475nm pump with 64μ J cm⁻² flux); (a), (b) concentration dependence transient absorption (TA): The normalized TA spectra of neat polymer in different concentration show similar exciton feature; no additional band due to polaron is observed at high concentration. (c), (d) Pump power dependence TA: Power dependent TA spectra after normalization do not show any additional polaron band at our experimental conditions.



Fig. S15 The excited state absorption (ESA) of P3HT:PCBM in chlorobenzene with 475 nm pump of 64μ J cm⁻² flux and NIR probe under repeated scan (scan1: black, scan2: red) at (a) 500 fs and (b) 4 ps showing same peak position, spectral profile and same intensity i.e. no sample or morphology damage of the nano-aggregate during our measurements.



Fig. S16 Main: ESA of only PCBM in CLB at three different time scales (100 fs, 10 ps and 30 ps) after excitation using 475 nm pump. ESA of only PCBM is quite small in magnitude and does not change at the initial time scales; inset: kinetics (at 900 nm) of the ESA of PCBM in different solvents (CLB, CHCl₃ and Tl). Excitation of only PCBM using same pump wavelength and same power does not generate any peak at around 1020 nm (i.e. no spectral feature of PCBM anion radical⁴ after exciting only PCBM solution).



Fig. S17 Time series of $\Delta\Delta A$ versus wavelength for P3HT:PCBM (1:20) in (a) chloroform and (b) chlorobenzene. Both traces show appearance of broad P3HT polaron band at ~875 nm and small feature at ~1030 nm representing the anion radical of PCBM.



Fig. S18 Comparison of the normalisation coefficients at different pump-probe delays used to plot the $\Delta\Delta A$ spectra in different solvents. The decay profile shows the decay of the exciton feature to generate the polaron.



Fig. S19 (a) Transient absorption spectra of pristine P3HT in different solvents (TL, $CHCl_3$ and CLB) at 2 ns assigned to the triplet state;⁵ (b) Mono-exponential fittings showing the ~480 ps rise of the triplet state in all the three solvents measured at 705 nm.



Fig. S20 TEM of P3HT film casted from CLB, $CHCl_3$ and TL. It shows P3HT nanofibers in CLB and TL, while in $CHCl_3$ it is loosely packed disorder structure.



Fig. S21 TEM of P3HT and P3HT:20 PCBM film casted using toluene solvent.



Fig. S22 Stimulated Raman spectra of free PCBM at varying concentrations of 10 wt % to 75 wt% in toluene.



Fig. S23 Power dependence to the excited state absorption (ΔA) of P3HT in toluene. The ΔA (1100 nm) values were taken at 1 ps. The black arrow shows the 475 nm pump of power 64 μ J cm⁻² where we have done transient absorption measurements to track polaron generation kinetics. This power is in the linear regime. At high power, singlet-singlet exciton annihilation causes nonlinearity in the ΔA value.

3. References:

1. S. N. Clafton, D. M. Huang, W. R. Massey and T. W. Kee, J. Phys. Chem. B, 2013, 117, 4626-4633.

2. J. M. Guo, H. Ohkita, H. Benten and S. Ito, J. Am. Chem. Soc., 2010, 132, 6154-6164.

3. S. M. King, D. Dai, C. Rothe and A. P. Monkman, Phys. Rev. B, 2007, 76, 085204.

4. D. M. Guldi, H. Hungerbuehler and K.-D. Asmus, J. Phys. Chem., 1995, 99, 9380-9385.

5. S. Cook, A. Furube and R. Katoh, *Energy Environ. Sc.,* 2008, **1**, 294-299.

6. V. Gulbians, I. Mineviciute, D. Hertel, R. Wellander, A. Yartsev and V. Sundstrom, J. Chem. Phys., 2007, **127**, 144907.