Supporting Information

Panchromatic Polymer-polymer Ternary Solar Cells Enhanced by Förster Resonance Energy Transfer and Solvent Vapor Annealing

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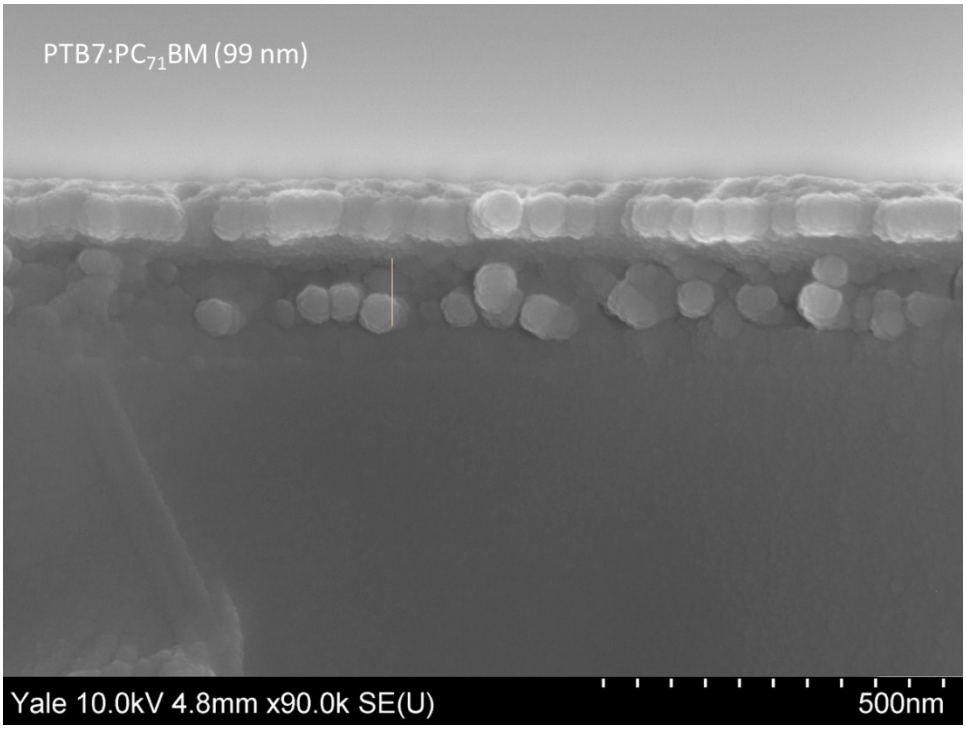
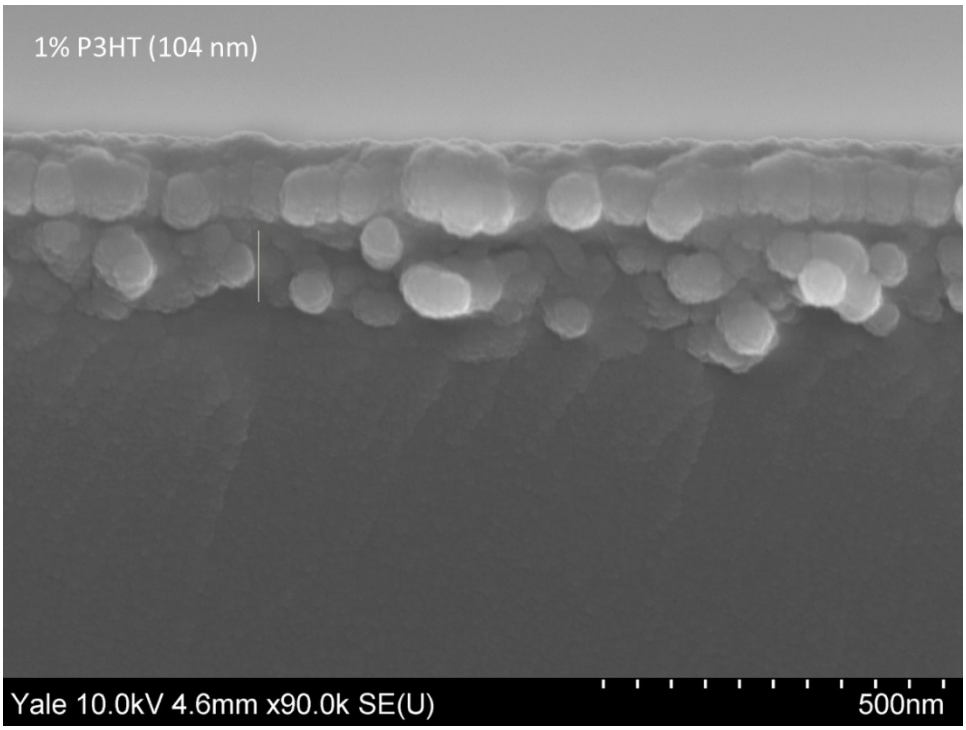
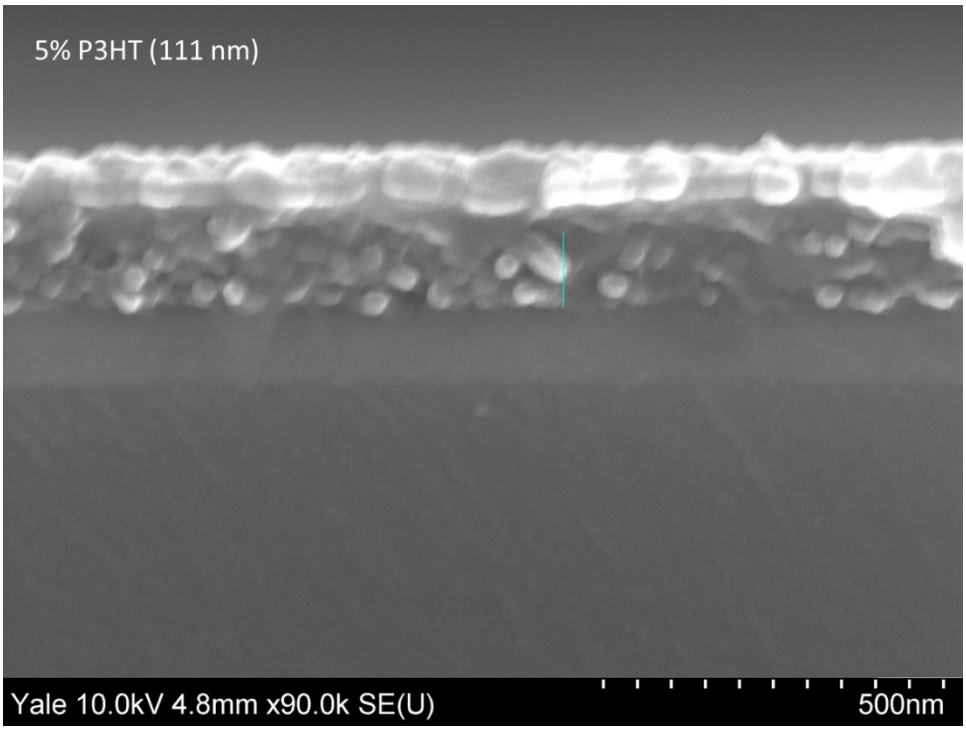
S1 | Summary of estimated film thicknesses of active layers and hole-mobility calculations

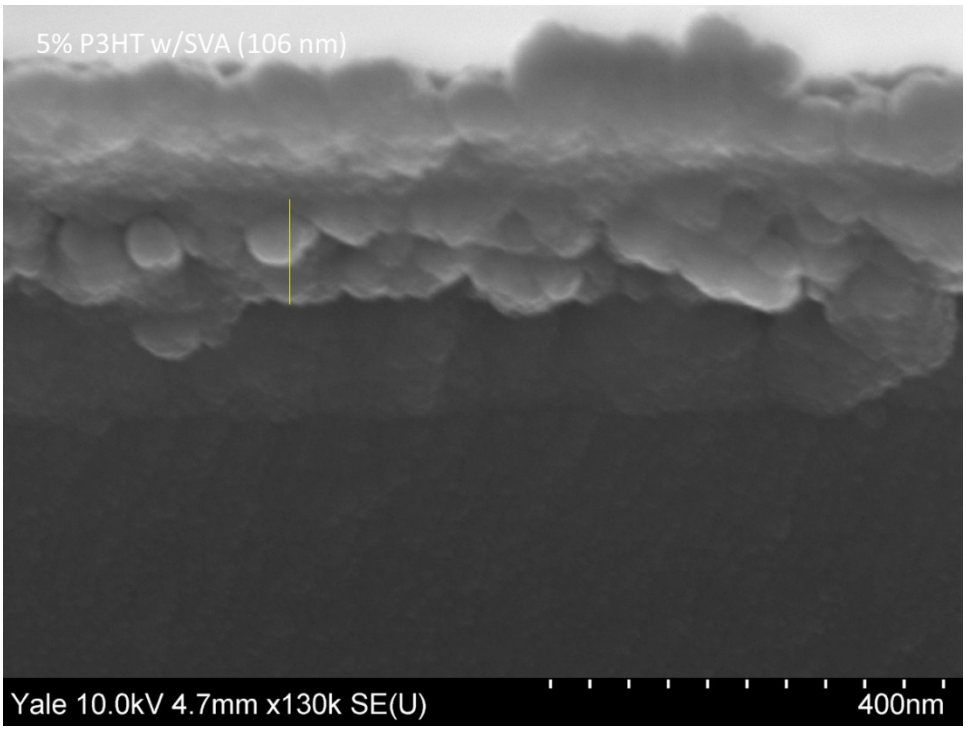
S1a. Cross-sectional SEM (X-SEM) images and summary of film thickness

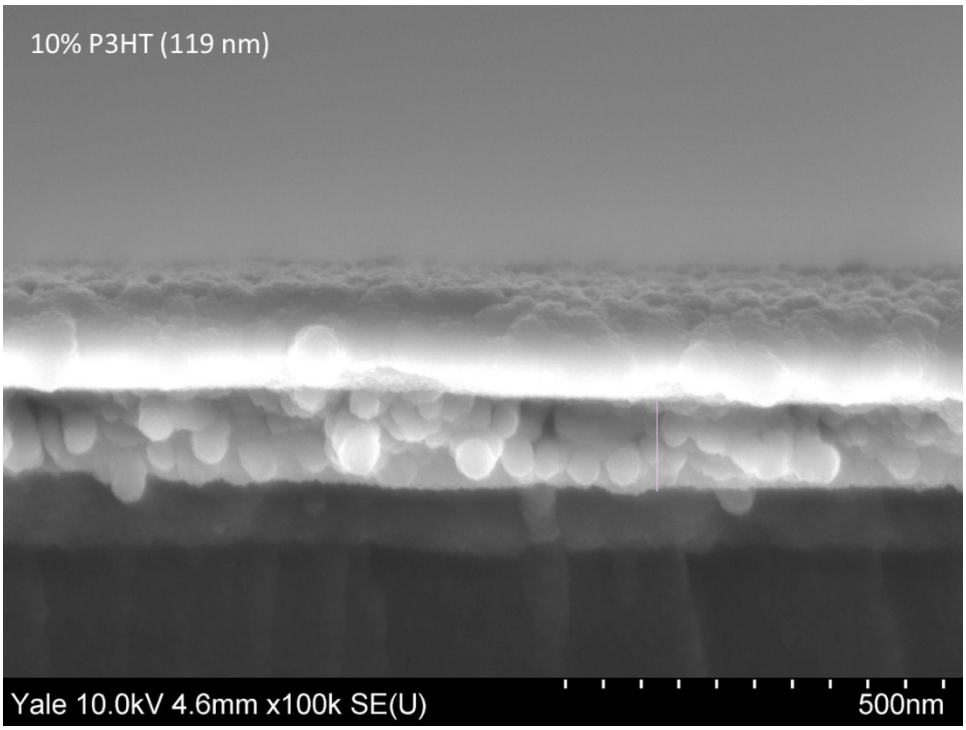
Films	Thickness (nm)
Binary PTB7:$PC_{71}BM$	99
Ternary w/ 1% P3HT	104
Ternary w/ 5% P3HT	111
Ternary w/ 5% P3HT (solvent annealed)	106
Ternary w/ 10% P3HT (solvent annealed)	119




1% P3HT (104 nm)
Yale 10.0kV 4.6mm x90.0k SE(U)
500nm


5% P3HT (111 nm)
Yale 10.0kV 4.8mm x90.0k SE(U)
500nm


5% P3HT w/SVA (106 nm)
Yale 10.0kV 4.7mm x130k SE(U)
400nm


10% P3HT (119 nm)
Yale 10.0kV 4.6mm x100k SE(U)
500nm

S1b. Calculations of hole mobility with thickness estimation from X-SEM

Frenkel effect on excitonic solar cells was accounted by space-charge current equation formulated by Murgatroyd[1, 2].

$$J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3}\exp\left[\frac{0.891}{kT}\left(\frac{e^3V}{\pi\varepsilon_r\varepsilon_0 L}\right)^{\frac{1}{2}}\right] \quad (1)$$

The J-V curves under dark are plotted into semi-natural logarithm manner in figure 5c

The film thickness, L, gauging from cross-sectional scanning electron microscopy (X-SEM) imaging, is summarized in table above. The relative permittivity, ε_r, is assumed to be 4 for all films, while ε0, is substituted by the vacuum permittivity constant in equation (1). Slopes and intercepts obtained from the best linear fits are tabulated in the following

Sample	Slope	Intercept	μ0 ($cm^2V^{-1}s^{-1}$)	E0 (kV/cm)	μ ($cm^2V^{-1}s^{-1}$) @V=1.0V
PTB7:PC71BM	0.00288	-35.755	9.917E-04	95.50	2.76E-03
S. Anneal 5%	0.00283	-34.34	4.082E-03	98.90	1.12E-02
w/ 5% P3HT	0.00247	-34.627	3.064E-03	129.83	7.37E-03

S2 | Estimation of Förster Radius and Energy Transfer Rate.

Förster distance, R_0, at which the energy-transfer efficiency is at 50% is estimated using the following equation[3].

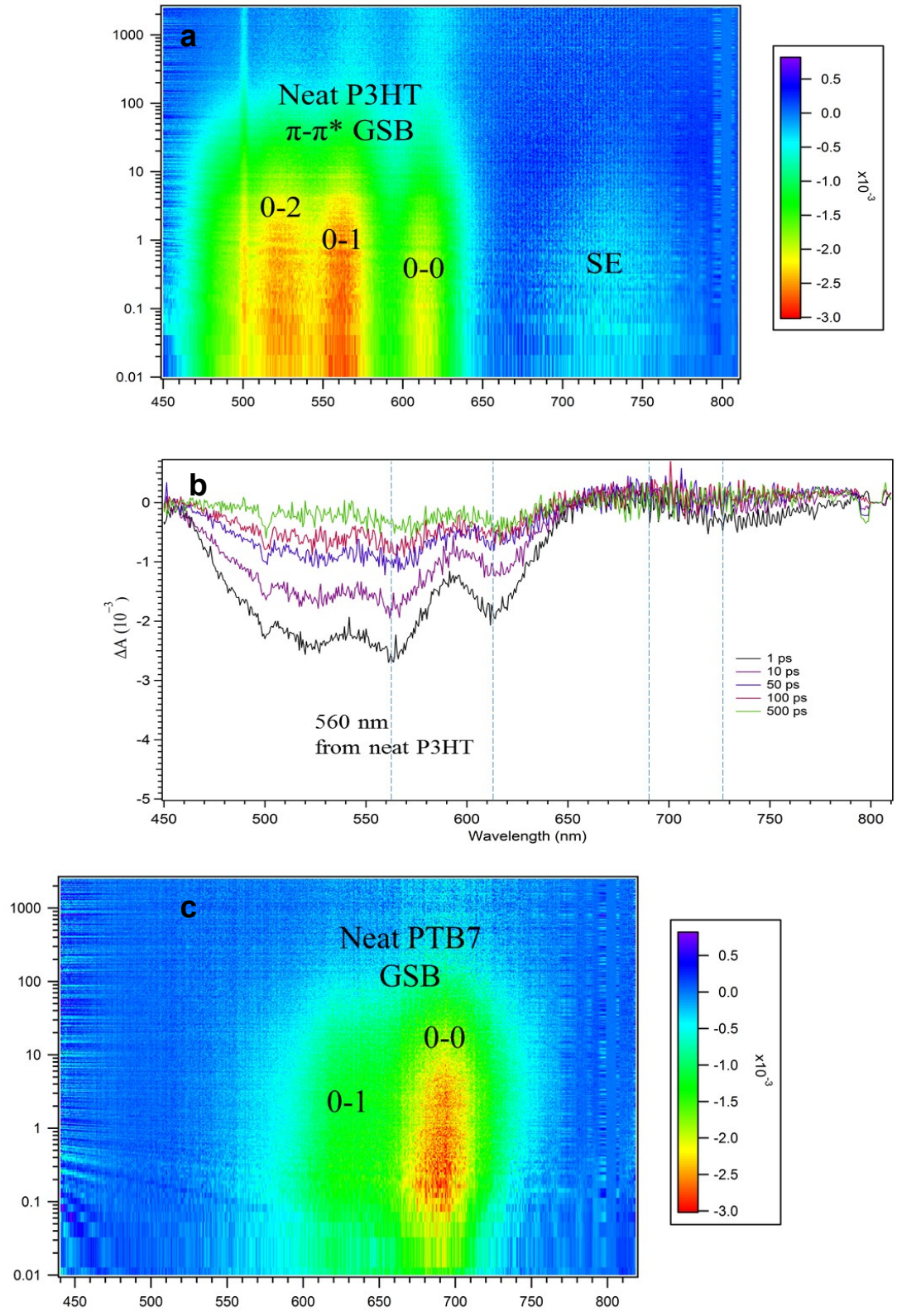
$$R_0 = (0.211)\left(\kappa^2 n^{-4} Q_D J(\lambda)\right)^{\frac{1}{6}} \quad \text{(in } nm\text{)} \quad (2)$$

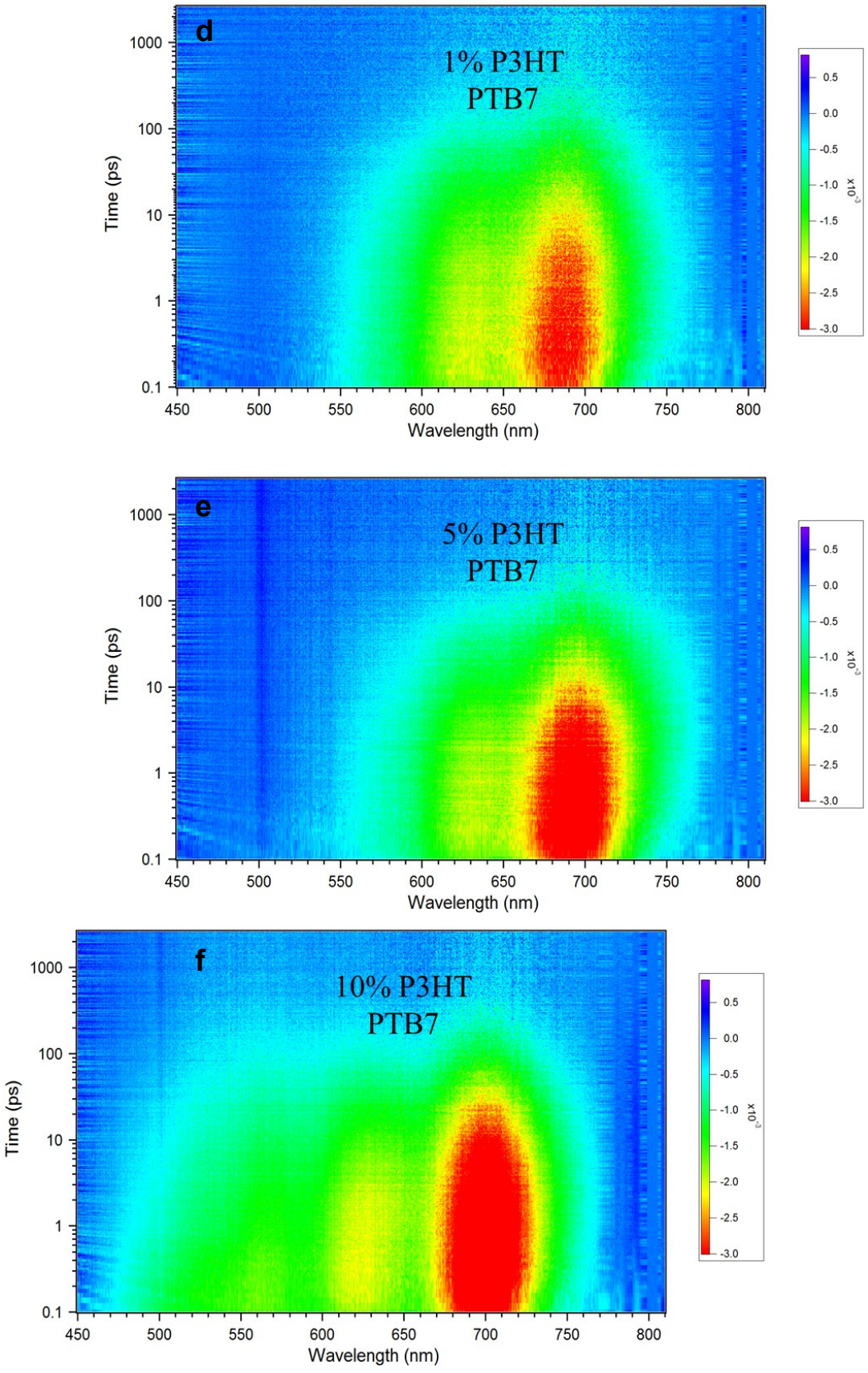
where $J(\lambda) = \dfrac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda}$

κ is the orientation factor between the donor and acceptor dipoles; Q_D is the average donor fluorescence quantum yield in the absence of the acceptor; n is the medium refractive index; N_A is the Avogadro constant, or 6.022×10^{23} mol^{-1}; $J(\lambda)$ represents the overlap integral, characterized by normalized spectrum overlap between donor molecule's $F_D(\lambda)$, fluorescence intensity in arbitrary unit and $\varepsilon_A(\lambda)$, acceptor's absorption coefficient in M^{-1}cm^{-1} scaled by λ, wavelength (in cm) to the fourth power.

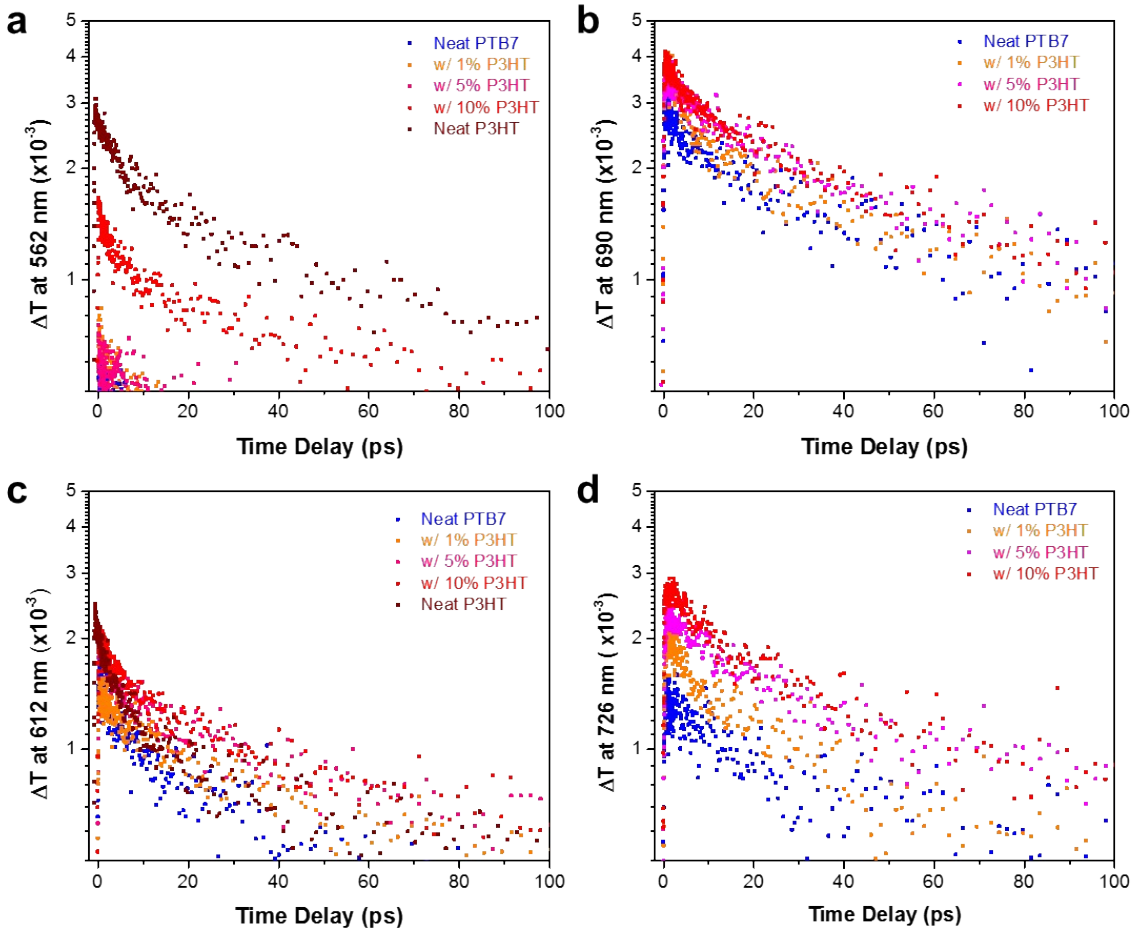
$\kappa^2 = 2/3$ (assuming random orientation), a conservative assumption compared to maximal transition of aligned dipoles where $\kappa^2 = 4$; n ~ 1.5; Q_D ~ 0.1 (for P3HT, in chloroform); $J_{DA}(\lambda) = 1.1007 \times 10^{15}$ M^{-1}cm^{3}nm^4; With these, we estimated that R_0 ~ 6.49 nm

S3 | Transient Absorption (TA). Contour plot of time-delay (in picoseconds) versus wavelength for (a) Neat P3HT and its spectral (c) Neat PTB7, as well as (d) 1 wt%, (e) 5 wt%, and (f) 10 wt% P3HT added PTB7 films. All films were pumped at 500 nm.

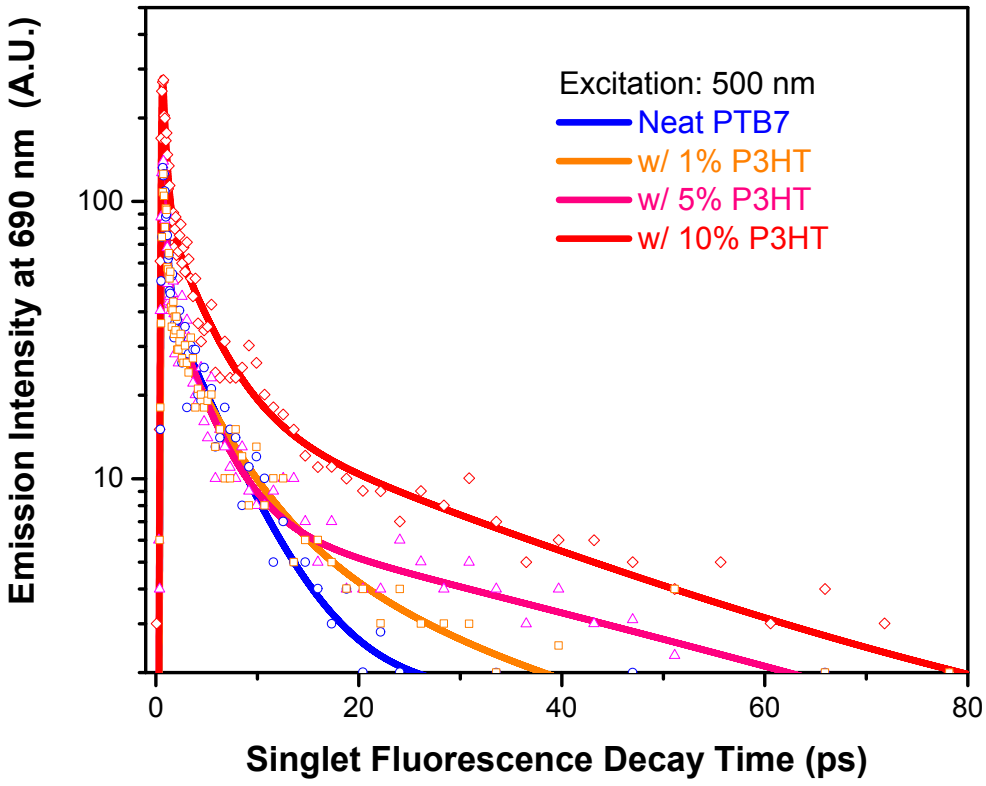



d
1% P3HT
PTB7
e
5% P3HT
PTB7
f
10% P3HT
PTB7
Time (ps)
Wavelength (nm)
1000
100
10
1
0.1
450
500
550
600
650
700
750
800
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
x10-3

S3 | Breakdown of transient absorption kinetics to separated wavelengths



S4 | Time resolved photoluminescence (TRPL) for polymer blends



The decay profiles were fitted with three exponential gaussian function[4] and the amplitude-averaged time constants are tabulated in the following.

$f(t) = y_0+(a_1*\tau_1)*\text{ExpGauss}(t-t_0,a_1,pw)+(a_2*\tau_2)*\text{ExpGauss}(t-t_0,\tau_2,pw)+(a_3*\tau_3)*\text{ExpGauss}(t-t_0,\tau_3,pw)$

	a_1	τ_1	a_2	τ_2	a_3	τ_3	$\Sigma(a_i \tau_i^2)$	$\Sigma(a_i \tau_i)$	$\langle\tau\rangle$, ps
Neat PTB7	156.2	3.166	0.316	4.580	3.731	55.735	12519.027	456.678	**27.41**
w/ 1% P3HT	118.5	2.216	0.451	5.644	4.364	56.876	15168.961	483.969	**31.34**
w/ 5% P3HT	206.9	2.309	0.433	6.426	7.812	64.529	34426.443	883.215	**38.98**
w/ 10% P3HT	283.6	2.394	0.418	4.753	13.330	77.113	80974.808	1495.579	**54.14**

Reference

1. Murgatroyd PN. Theory of space-charge-limited current enhanced by Frenkel effect. *J Phys D: Appl Phys* 1970, **3**(2)**:** 151.

2. Murgatroyd PN. On the theory of the transition from space-charge-limited current to electrode-limited current. *physica status solidi (a)* 1972, **11**(1)**:** 137-143.

3. Lakowicz JR. *Principles of Fluorescence Spectroscopy*. Springer-Verlag US, 2006.

4. Sfeir M. Visualization and Analysis of Broadband Transient Absorption Data. 2011 [cited 2014 15 December 2014]Available from: http://www.igorexchange.com/project/TADataAnalysis