

Supporting Information

Quantifying triplet formation in conjugated polymer / non-fullerene acceptor blends

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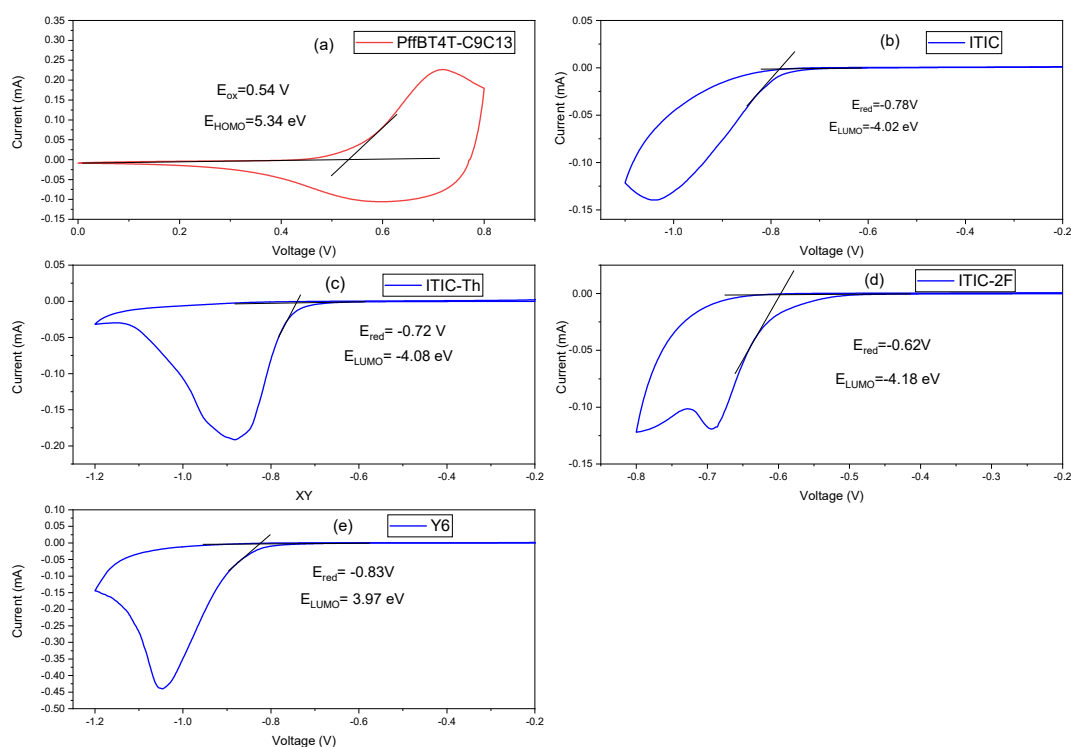


Figure S1. Cyclic voltammogram for PffBT4T-C9C13, ITIC-Th, ITIC, ITIC-2F and Y6/Y6 Films in 0.1 M Bu₄NPF₆ acetonitrile solution with scan rate at 20 mV s⁻¹ on ITO substrate.

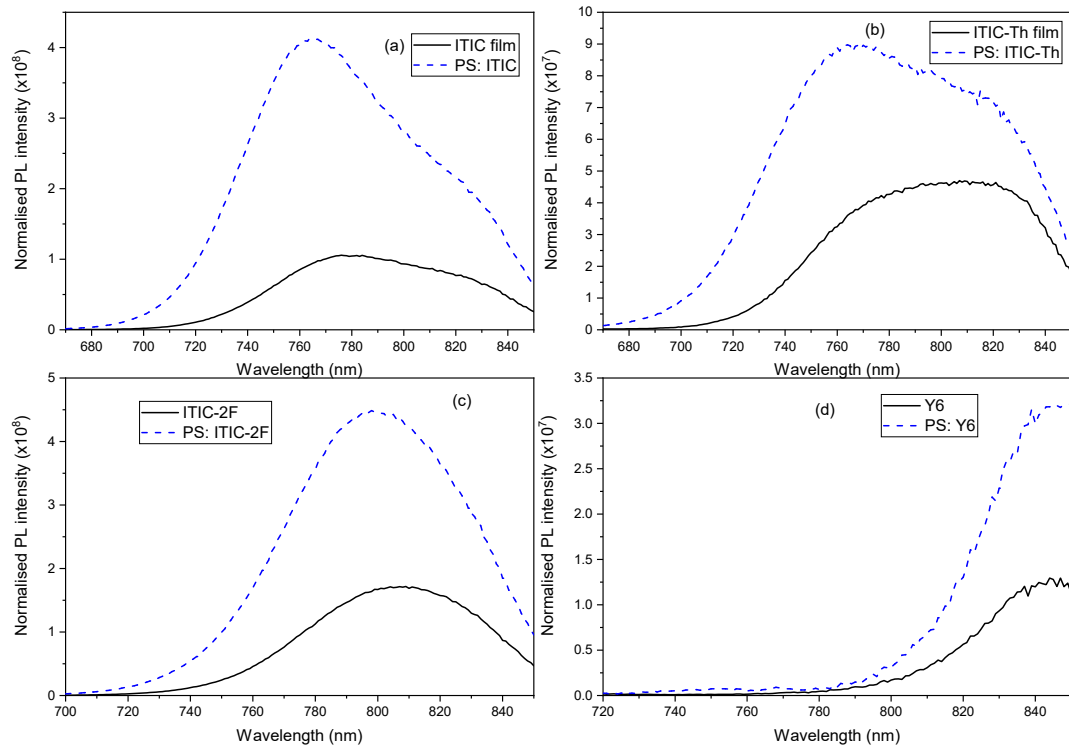


Figure S2. Normalised (per absorption) photoluminescence emission for (a) ITIC and PS:ITIC film, (b) ITIC-Th and PS:ITIC-Th film, (c) ITIC-2F and PS:ITIC-2F film (d) Y6 and PS:Y6 film. All films were excited at 650 nm.

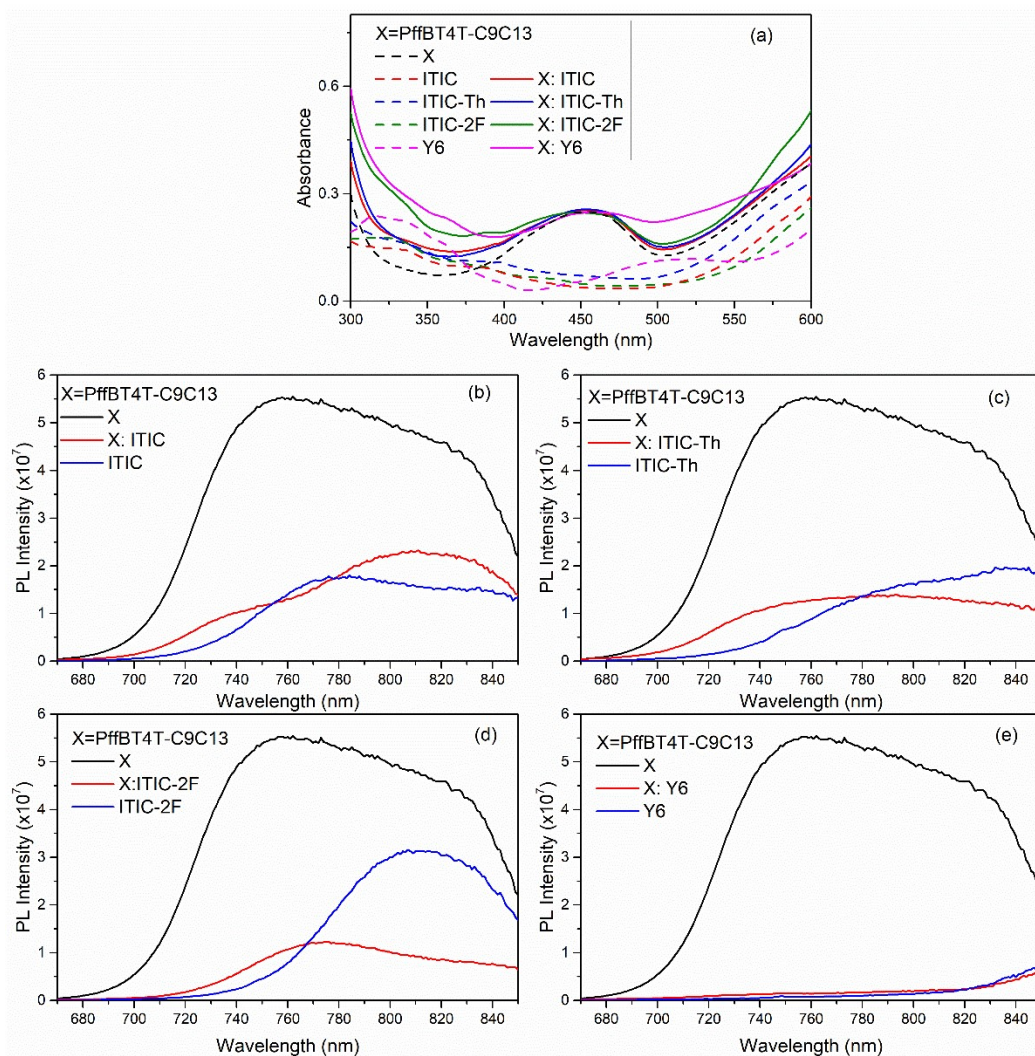


Figure S3. (a) Zoom of the 455 nm absorbance peak of PffBT4T-C9C13 used to estimate PL quenching yield, showing the minimal NFA absorbance. Photoluminescence emission spectra of (b) PffBT4T-C9C13: ITIC film, (c) PffBT4T-C9C13: ITIC-Th film, (d) PffBT4T-C9C13:ITIC-2F film, and (e) PffBT4T-C9C13:Y6 film, compared to the pristine components, with 455 nm excitation wavelength.

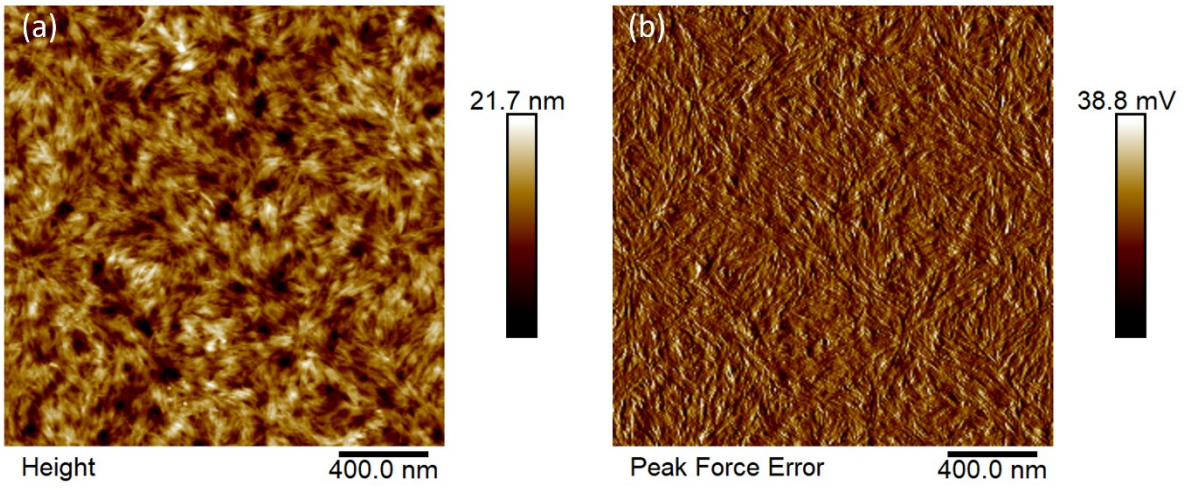


Figure S4. AFM (a) height and (b) topography images for PffBT4T-C9C13 film.

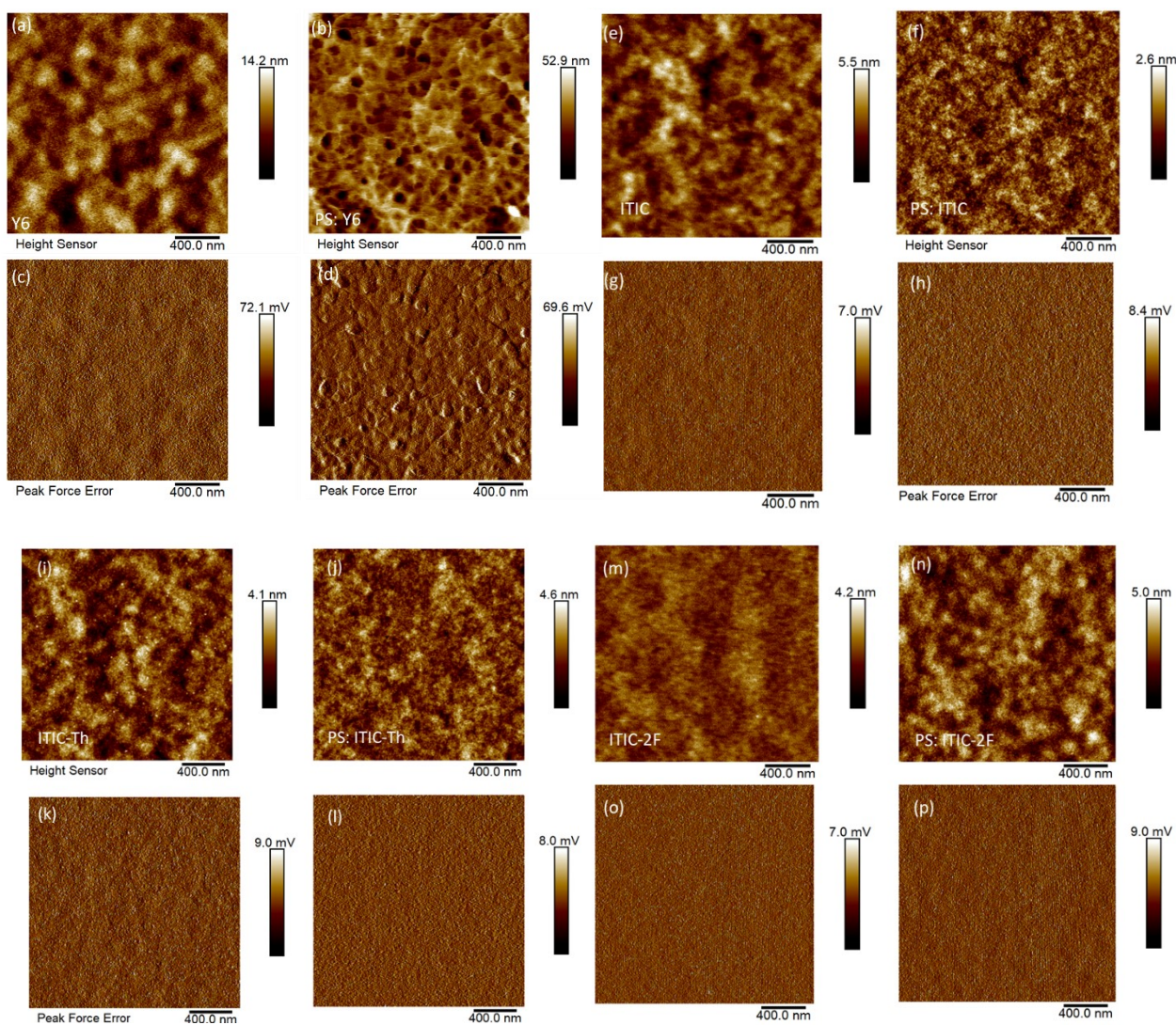


Figure S5. AFM images of phase and topography for (a and c) Y6, (b and d) PS:Y6 (1:1.2); (e and g) ITIC, (f and h) PS:ITIC (1:1.2); (i and k) ITIC-Th, (j and l) PS:ITIC-Th (1:1.2); (m and o) ITIC-2F, (n and p) PS:ITIC-2F (1:1.2). Scale bars are 400 nm. Comparing the Y6 and Y6:PS film, an increased roughness from 1.8 nm for Y6 to 5.2 nm for PS:Y6 was found, and an increase in grain size was induced with addition of polystyrene. In contrast, all the ITIC series' films are very smooth, with R_q values of less than 1 nm.

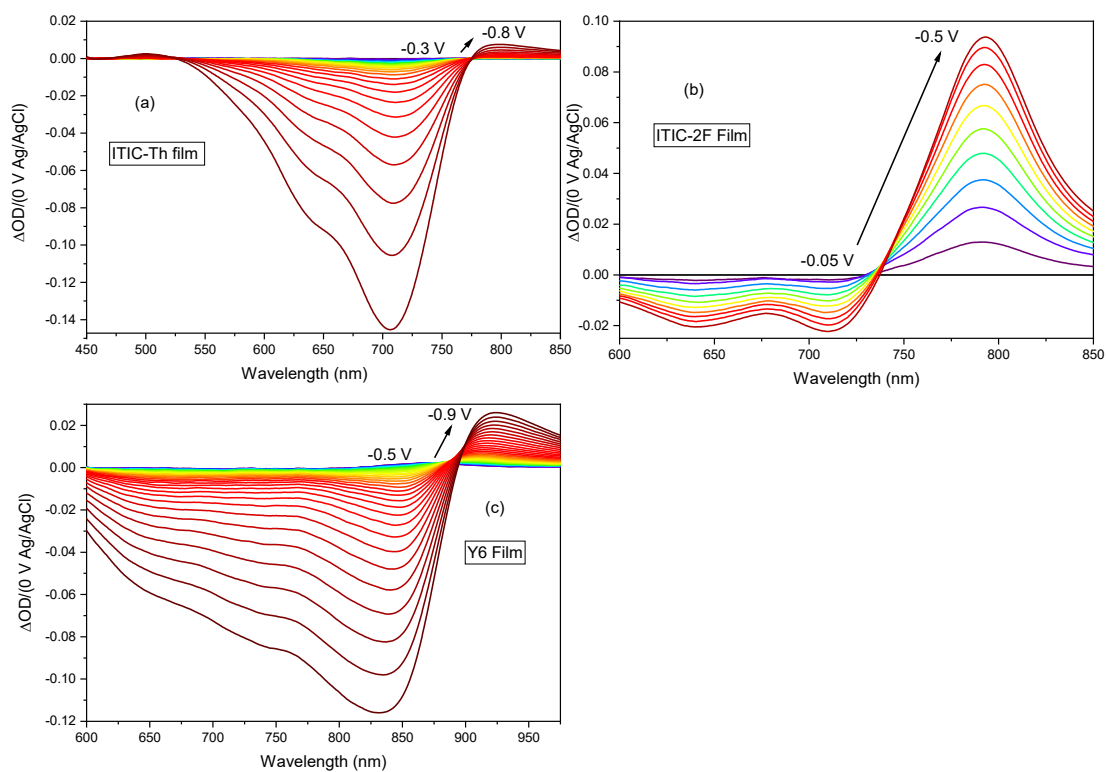


Figure S6. Spectroelectrochromic spectra for pristine (a) ITIC-Th, (b) ITIC-2F, and (c) Y6 films. Ag/AgNO₃ was used as a reference electrode and Pt mesh as counter electrode and 0.1 M TBAP in acetonitrile as the electrolyte.

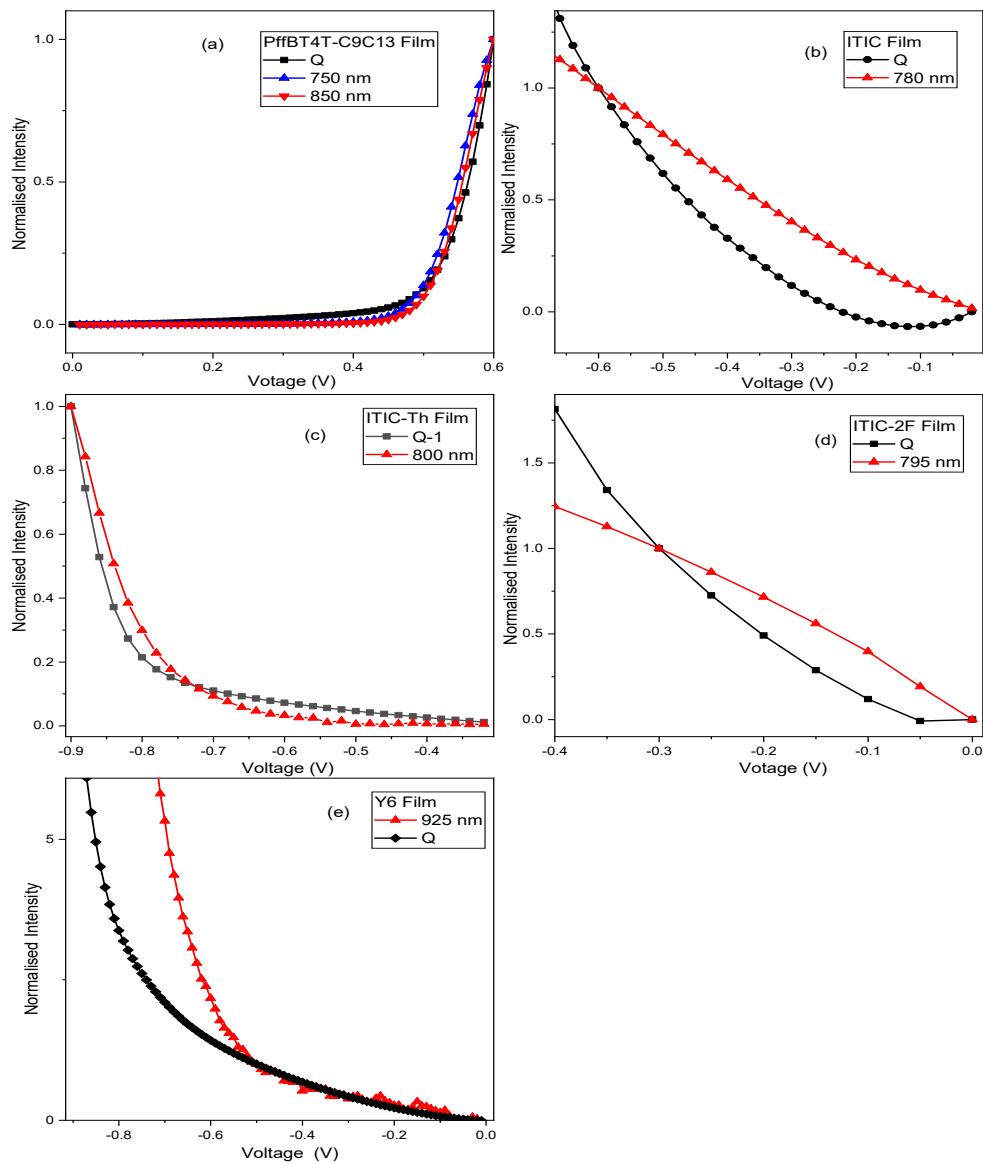


Figure S7. Normalised intensity to show the correlation between number of charges generated (Q , acquired via integration of the JV curve) and the NFA anion peak amplitude variation with applied voltage.

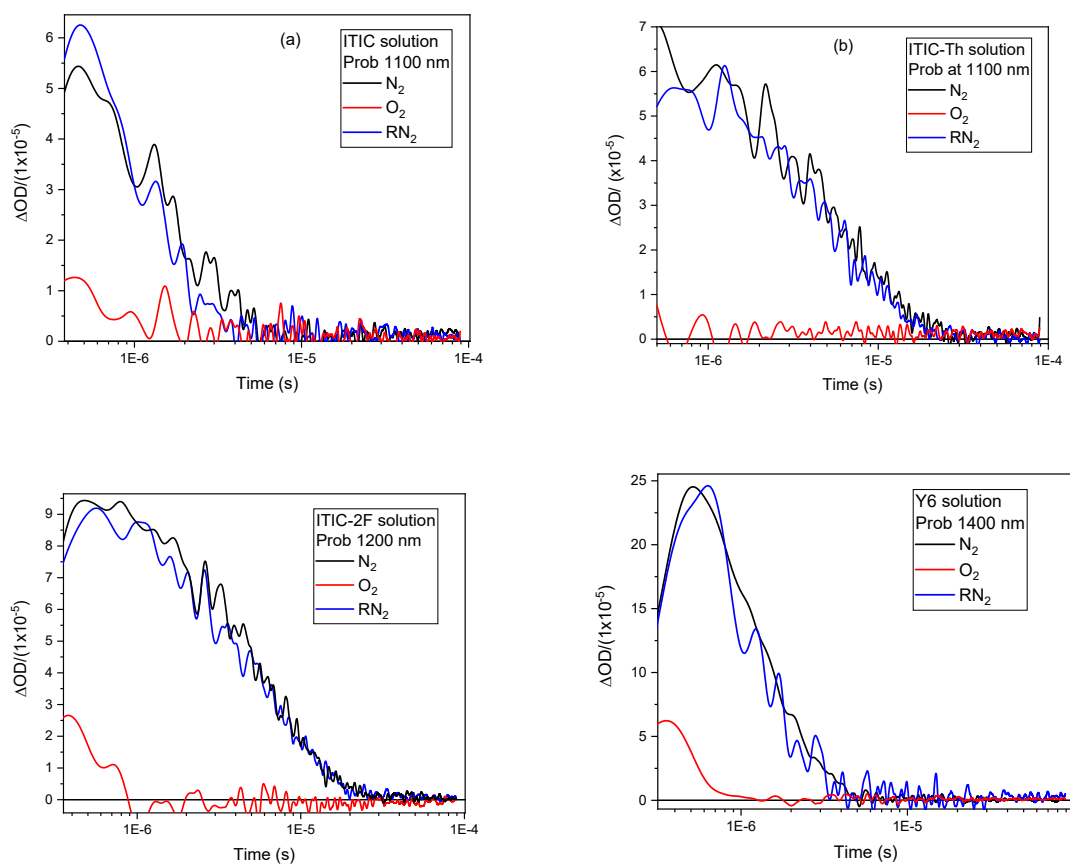


Figure S8. Oxygen dependence decay dynamics for the NFA solutions (a) ITIC (b) ITIC-Th (c) ITIC-2F (d) Y6.

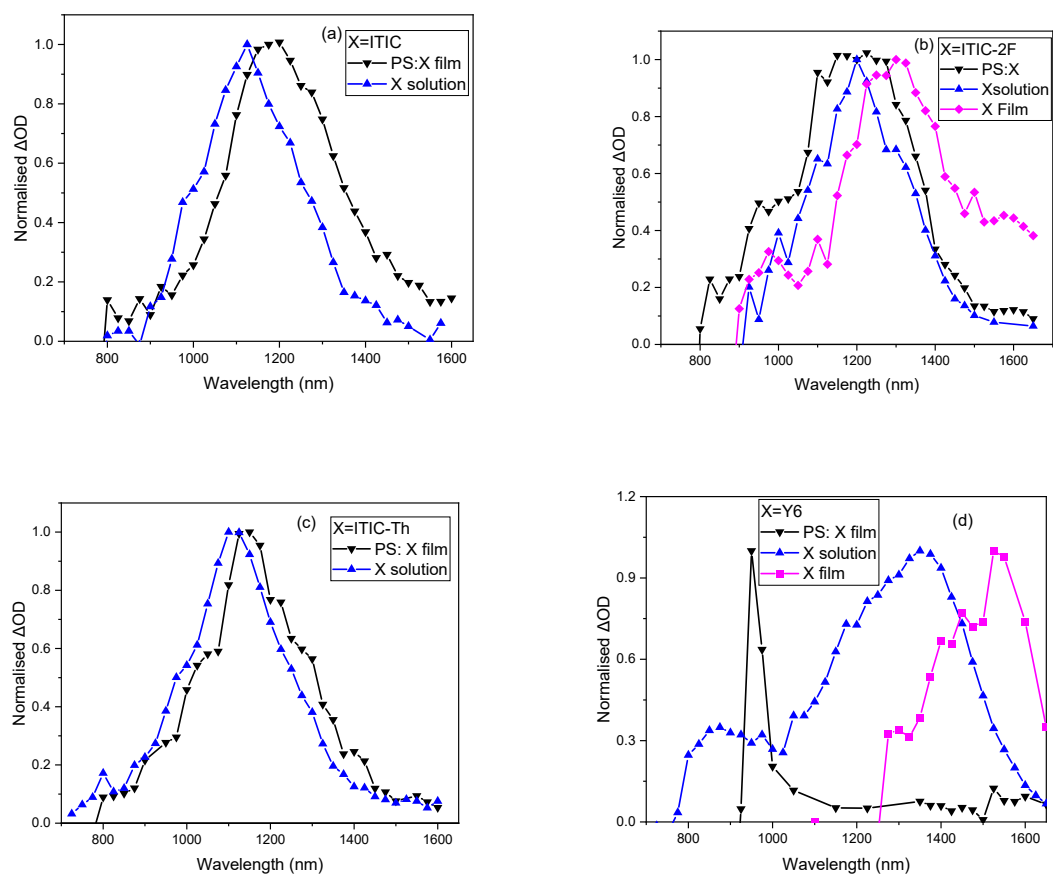


Figure S9. Normalised TA spectra comparison for pristine NFAs solution with PS:NFA films (a) ITIC (b) ITIC-Th (c) ITIC-2F (d) Y6.

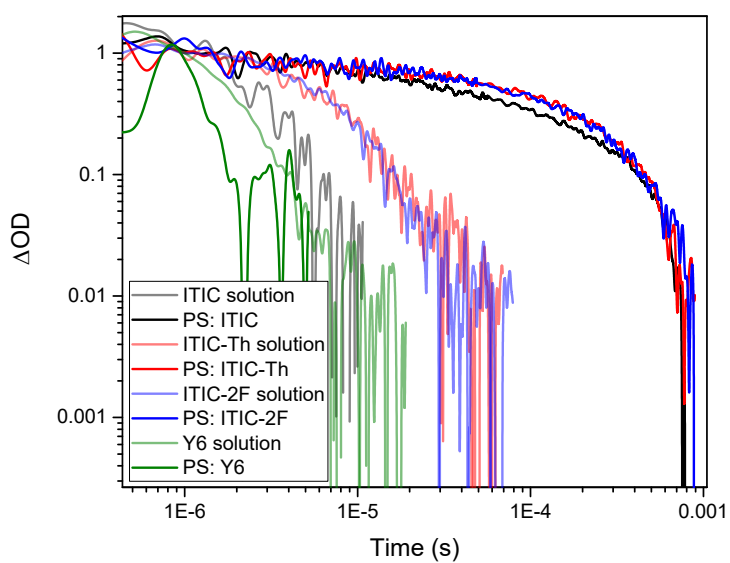


Figure S10. Normalised decay dynamics comparison for pristine NFA solutions and PS:NFA films.

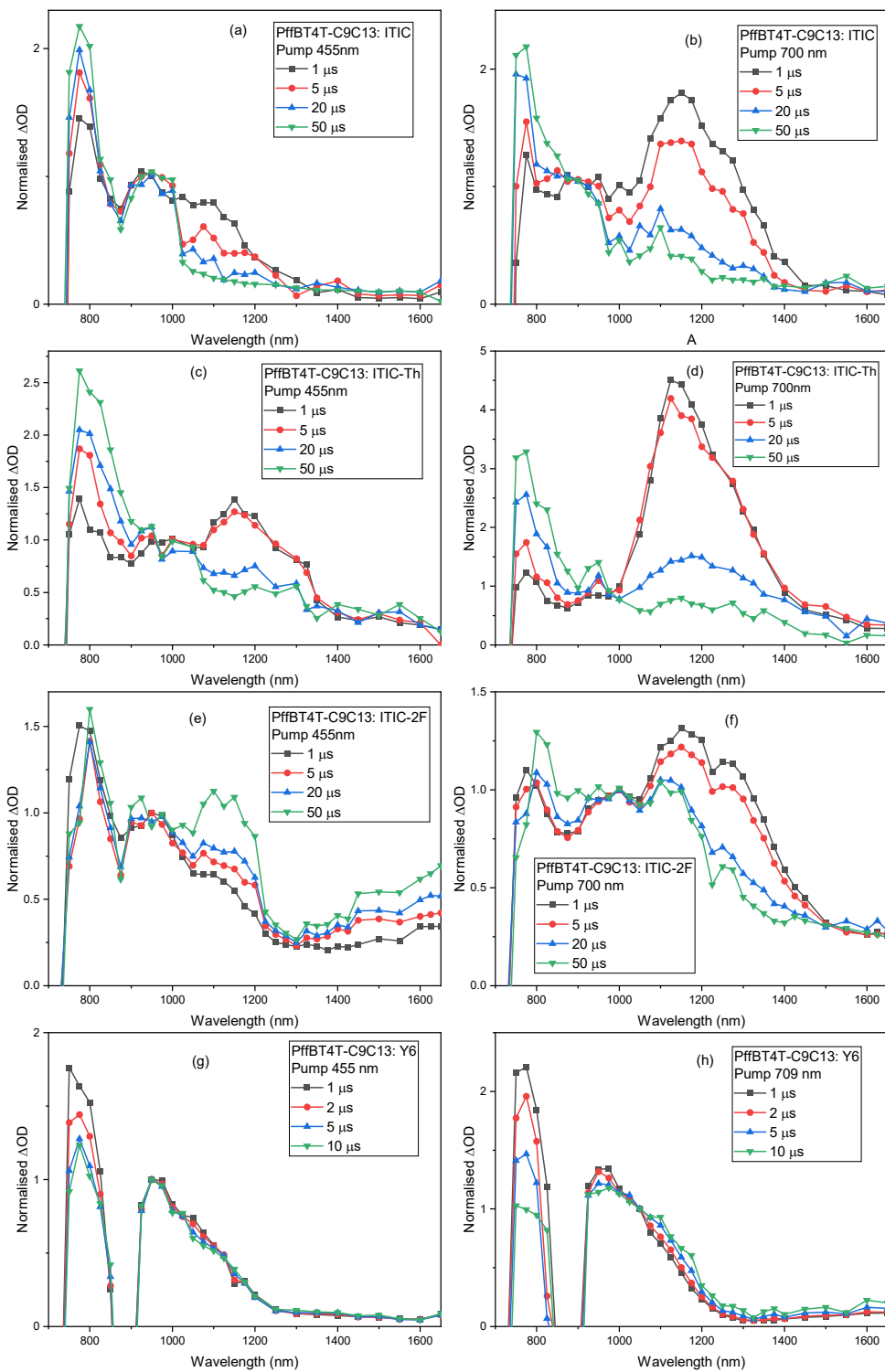


Figure S11. Time evolution of the TA spectra of (a) PffBT4T-C9C13: ITIC blend films with excitation wavelength 455 nm and excitation energy $22 \mu\text{J cm}^{-2}$ at different time scales (b) PffBT4T-C9C13: ITIC blend films with excitation wavelength 700 nm and excitation energy $18 \mu\text{J cm}^{-2}$ at different time scales

(c) PffBT4T-C9C13: ITIC-2F blend films with excitation wavelength 455 nm and excitation energy $10 \mu\text{J cm}^{-2}$ at different time scales (d) PffBT4T-C9C13: ITIC-2F blend films with excitation wavelength 700 nm and excitation energy $8 \mu\text{J cm}^{-2}$ at different time scales (e) PffBT4T-C9C13: ITIC-Th blend films with excitation wavelength 455 nm and excitation energy $23 \mu\text{J cm}^{-2}$ at different time scales (f) PffBT4T-C9C13: ITIC-Th blend films with excitation wavelength 700 nm and excitation energy $21 \mu\text{J cm}^{-2}$ at different time scales.(g) PffBT4T-C9C13: Y6 blend films with excitation wavelength 455 nm and excitation energy $13 \mu\text{J cm}^{-2}$ at different time scales (h) PffBT4T-C9C13: Y6 blend films with excitation wavelength 709 nm and excitation energy $11 \mu\text{J cm}^{-2}$ at different time scales. The weight ratio for all of the PffBT4T-C9C13/acceptors' blend film is 1:1.2.

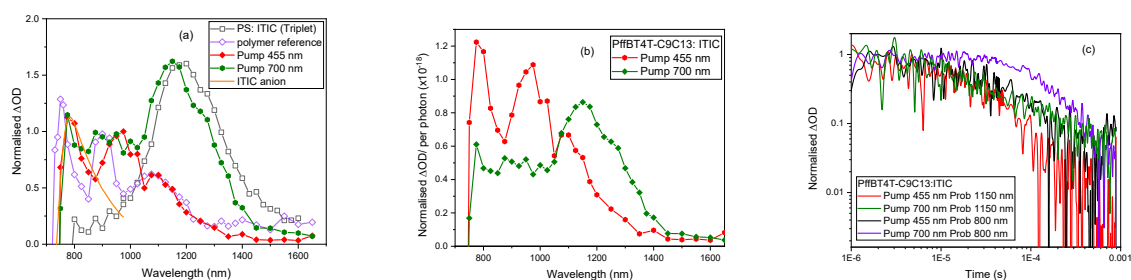


Figure S12. (a) Normalised (to 1) TA spectra for PffBT4T-C9C13: ITIC pump at 455 nm (excitation energy $22 \mu\text{J cm}^{-2}$) and 700 nm ($26 \mu\text{J cm}^{-2}$) at $1 \mu\text{s}$, PS: ITIC film ($1 \mu\text{s}$) and the annealed PffBT4T-C9C13: PC70BM film with excitation energy $5 \mu\text{J cm}^{-2}$ at $50 \mu\text{s}$. (b) Normalised (per photon) TA spectra for PffBT4T-C9C13: ITIC pump at 455 nm and 700 nm ($1 \mu\text{s}$). (c) Normalised decay dynamics of PffBT4T-C9C13: ITIC film, probing at 800, 1150 nm with excitation wavelength at 455 nm and 700 nm and excitation energy around $26 \mu\text{J cm}^{-2}$.

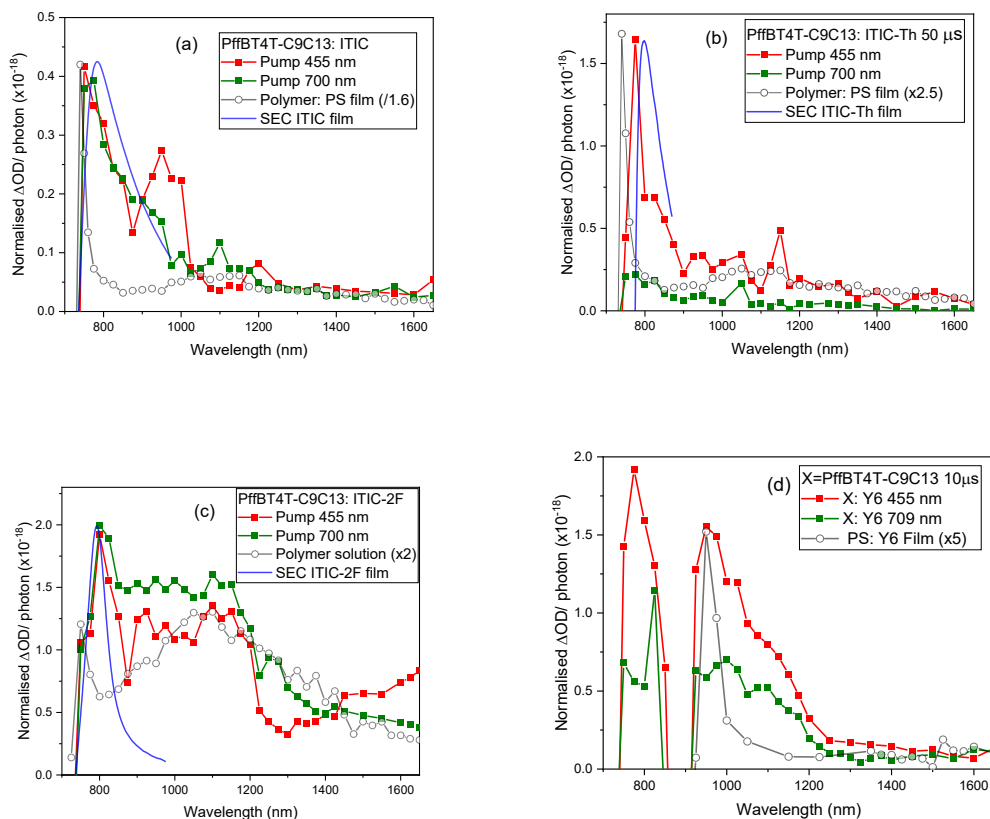


Figure S13. Normalised (per photon absorbed) TA spectra for transient absorption spectra of (a) PffBT4T-C9C13: ITIC film at 50 μs (b) PffBT4T-C9C13: ITIC-Th film and pristine PffBT4T-C9C13 film at 50 μs , (c) PffBT4T-C9C13: ITIC-2F film and PffBT4T-C9C13 solution at 50 μs , and (d) PffBT4T-C9C13: Y6 film and PS: Y6 film at 10 μs . The blend PffBT4T-C9C13: ITIC series (ITIC, ITIC-Th, ITIC-2F) are excited at both 455 nm and 700 nm. The excitation energy used for both ITIC and ITIC-Th with excitation energy 23 $\mu\text{J cm}^{-2}$, and ITIC-2F blend were around 10 $\mu\text{J cm}^{-2}$, PffBT4T-C9C13: Y6 film was excited at 455 nm and 709 nm with excitation energy around 13 $\mu\text{J cm}^{-2}$. Films PS with Y6 is excited at 709 nm with excitation energy around 30 $\mu\text{J cm}^{-2}$. The pristine PffBT4T-C9C13 film and solution are excited at 700 nm with excitation energy 72 $\mu\text{J cm}^{-2}$ and 34 $\mu\text{J cm}^{-2}$, respectively. The bracket number is the enlarge (x) or divided (/) factor. The Blue line in the above spectra are the SEC spectra for Pristine (a) ITIC (b) ITIC-Th (c) ITIC-2F (d) Y6 films.

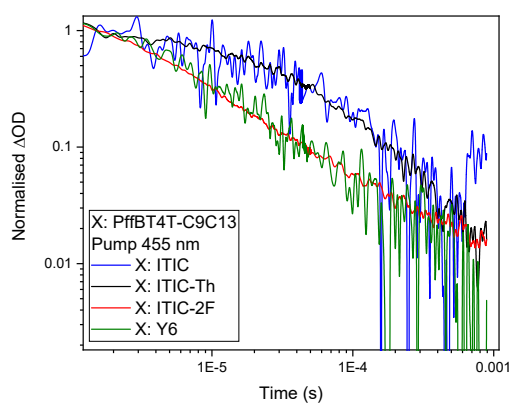
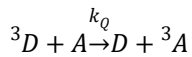


Figure S14. Normalised (to 1) decay dynamics for the polymer polaron in PffBT4T-C9C13 blended with NFAs ITIC (probe at 800 nm), ITIC-Th (probe at 775 nm), ITIC-2F (probe at 800 nm) and Y6 (probe at 800 nm) films. The excitation wavelength 455 nm is used for all the films.

Quantifying triplet populations

When quantifying the triplet formation in the blend films, the triplet molar absorption coefficient was calculated using the sensitisation method. This method involves a triplet sensitizer of known triplet molar extinction coefficient being directly excited, thereafter undergoing a triplet energy transfer to create a lower energy triplet on an acceptor of unknown triplet molar extinction coefficient. After excitation of the donor/sensitizer, the following reactions are therefore relevant:



The overall decay of the donor triplet is therefore $k_2 = k_1 + k_Q[A]$. Using microsecond transient absorption spectroscopy, the unknown triplet-triplet molar absorption coefficient can be obtained by comparison with that of the donor compound by equation 1. [1]

$$\frac{\varepsilon_T^D}{\varepsilon_T^A} = \frac{\Delta OD^D}{\Delta OD^A} \quad (1)$$

where ε_T^D is the triplet extinction coefficient for known donor compound, ε_T^A is the triplet extinction coefficient for unknown acceptor material. ΔOD^D is the maximum absorbance reached for the triplet-triplet absorption peak of the donor and ΔOD^A is the maximum absorbance of the acceptor triplet at their respective wavelength maxima.

However, equation 1 is only relevant under conditions where k_Q is much greater than k_1 and k_3 . If this is not the case, then additional corrections have to be applied, as detailed in the method of Land et al. Note that Land's additional correction for 3A when it is also formed via direct excitation is negligible in our case.[1]

If decay of the acceptor triplet occurs simultaneously with its creation via energy transfer, a maximum in ΔOD will form, as observed in our results. In such cases, considering the kinetics of successive reactions enables the following equation:

$$\Delta OD_{max}^A = \Delta OD^A \left(-\frac{\ln k_2/k_3}{\frac{k_2}{k_3} - 1} \right) \quad (2)$$

Where ΔOD_{max}^A is the maximum ΔOD observed in the acceptor triplet absorbance in the presence of the donor.

Finally, a correction must also be applied for 3D decay during the energy transfer process, necessary in situations where k_1 is non-negligible. Since this is the case for ZnTPP, a correction factor of $\frac{k_2}{k_1 + k_2}$ is applied.

For this project, ZnTpp acts as the triplet sensitizer with triplet-triplet molar absorption coefficient $9500 \text{ M}^{-1} \text{ cm}^{-1}$. The TA spectra for pristine ZnTPP and the ZnTPP/NFA sensitised solutions are shown in

Figure S15, and the corresponding kinetics in Figure S16. The triplet extinction coefficients for all NFAs are calculated as shown in Table 1 (main text).

To calculate the triplet-triplet molar absorption coefficient, ITIC-2F is used as an example. Figure 15e shows the TA spectra of ZnTpp:ITIC-2F solution. The ZnTPP triplet is located below 900 nm, while the ITIC-2F triplet absorbs maximally at 1150 nm. The ITIC-2F clearly grows in over time, a hallmark of the sensitisation process. The kinetics of the ITIC-2F triplet growth and decay were probed at the maximum of 1150 nm (Figure 16c). Assuming first order behaviour such that $k_2 = 1/t_2$, the time constant of the rise (3.2×10^{-6} s) provides k_2 and the decay provides k_3 (1.5×10^{-5} s).^{[2],[3]} The ΔOD_{max} of the ITIC-2F triplet is 8.1×10^{-4} . Applying the corrections detailed above, the corrected ΔOD_{max} is 1.46

$\times 10^{-3}$. So the triplet molar extinction coefficient is $\varepsilon_T^A = \frac{\Delta OD_{max}^A \times \varepsilon_T^D}{\Delta OD^D} = \frac{1.46e-3 \times 9500}{3.4e-4} = 4.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

The triplet yield in pristine solution can be calculated using the Beer-Lamber Law $A = \varepsilon cl$, where ε is the triplet extinction coefficient, c is the concentration of solution, and l is the path length of the cuvette.

The extinction coefficient of the triplet may differ in a film sample. To address this, we utilise a correction factor methodology by considering the change in absorption cross-section, σ , for the ground state from solution to film. The molar extinction coefficients of the ground state (ε_{GS_soln}) of each NFA have been measured in chlorobenzene with three different low concentrations ($10^{-6} - 10^{-5}$ M range), where ε_{GS_soln} is established from the gradient of a plot of absorbance vs concentration. Absorption cross-section is then calculated using the known relationship:

$$\sigma_{GS_soln} = \frac{\varepsilon_{GS_soln} \ln 10}{N_A}$$

Where σ_{GS_soln} is the absorption cross-section in solution and N_A is Avogadro's number; also noting that an additional factor of 1000 is required for unit equivalence. Film absorption coefficients (α) are also converted to absorption cross section (σ_{GS_solid}) via $\sigma_{GS_solid} = \alpha/N_i$, where N_i is the number density of the initial state. N_i for the ground state can be established from the mass density and molecular weight.

The following equation is then applied to establish the correction factor for each NFA:

$$\sigma_{GS_solid} = A \sigma_{GS_soln}$$

Where A is the correction factor. The values for ε_{GS_solid} have been obtained from literature, except for ITIC-Th, for which none could be found and thus an extrapolation procedure was used. The correction factor is then applied to the ε of the NFA triplet, assuming that any change in σ of the ground state from solution to solid will occur similarly for the triplet state. The results are presented in the table below.

NFA	ε_{GS_soln} ($10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$)	σ_{GS_soln} (10^{-16} cm^2)	α in film (10^5 cm^{-1}) ^a	σ_{GS_solid} (10^{-16} cm^2)	A	³ NFA* solution ε ($\pm 0.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$)	³ NFA* film ε ($\pm 0.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$)
ITIC	1.6 ± 0.5	6.2	2.4	4.7 ± 0.5	0.76	2.7	2.1

ITIC-Th	1.9 ± 0.5	7.3	-	-		5.7	2.3^b
ITIC-2F	2.2 ± 0.5	8.4	2.5	5.2 ± 0.5	0.62	4.1	2.5
Y6	2.3 ± 0.5	8.8	2.0	4.0 ± 0.5	0.45	6.5	2.9

- From Kerremans et al. Adv. Optical Mater. 2020, 8, 2000319.
- Estimated from extrapolating along the ITIC series, observing that ε_{GS_soln} for ITIC-Th is between that of ITIC and ITIC-2F.

For triplet formation in the NFA blend films with PffBT4T-C9C13, we can then apply the estimated film triplet ε using the following equation:

$$n_T = \frac{\Delta OD \cdot A_v}{1000 \cdot \varepsilon_T \cdot d}$$

Where n_T is the triplet yield in cm^{-3} , ΔOD is corrected for absorbance, A_v is Avogadro's number, ε_T is the molar extinction coefficient of the triplet, and d is the film thickness.

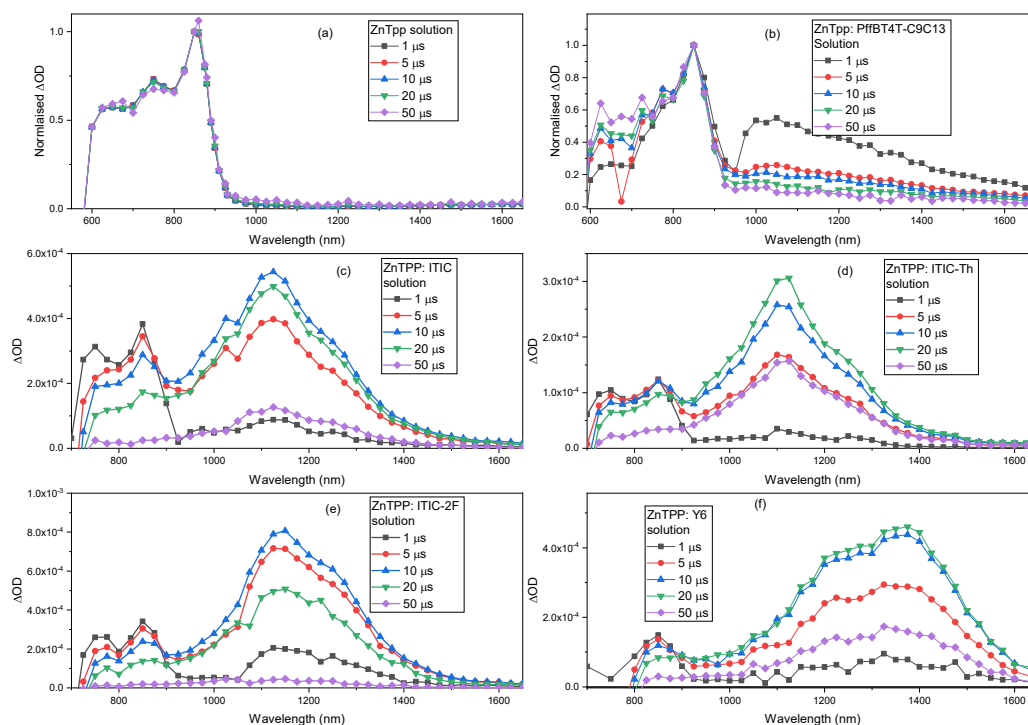


Figure S15. Normalised (to 1 at 850 nm) transient absorption spectra for (a) ZnTpp ($7 \times 10^{-6} \text{M}$) solution with an excitation energy at $30 \mu\text{J cm}^{-2}$, (b) ZnTpp: PffBT4T-C9C13 ($7 \times 10^{-6} \text{M}$: 0.05mg mL^{-1}) solution with an excitation energy at $25 \mu\text{J cm}^{-2}$. Transient absorption spectra for (c) ZnTpp:ITIC ($7 \times 10^{-6} \text{M}$: $7 \times 10^{-6} \text{M}$) solution with an excitation energy at $13 \mu\text{J cm}^{-2}$ (d) ZnTpp:ITIC-Th ($7 \times 10^{-6} \text{M}$: $7 \times 10^{-6} \text{M}$) solution with an excitation energy at $12 \mu\text{J cm}^{-2}$, (e) ZnTpp:ITIC-2F ($7 \times 10^{-6} \text{M}$: $7 \times 10^{-6} \text{M}$) solution

with an excitation energy at $12 \mu\text{J cm}^{-2}$, (f) ZnTpp:Y6 ($7 \times 10^{-6}\text{M}$: $7 \times 10^{-6}\text{M}$) solution with an excitation energy at $13 \mu\text{J cm}^{-2}$. All the spectra were obtained with an excitation wavelength at 426 nm.

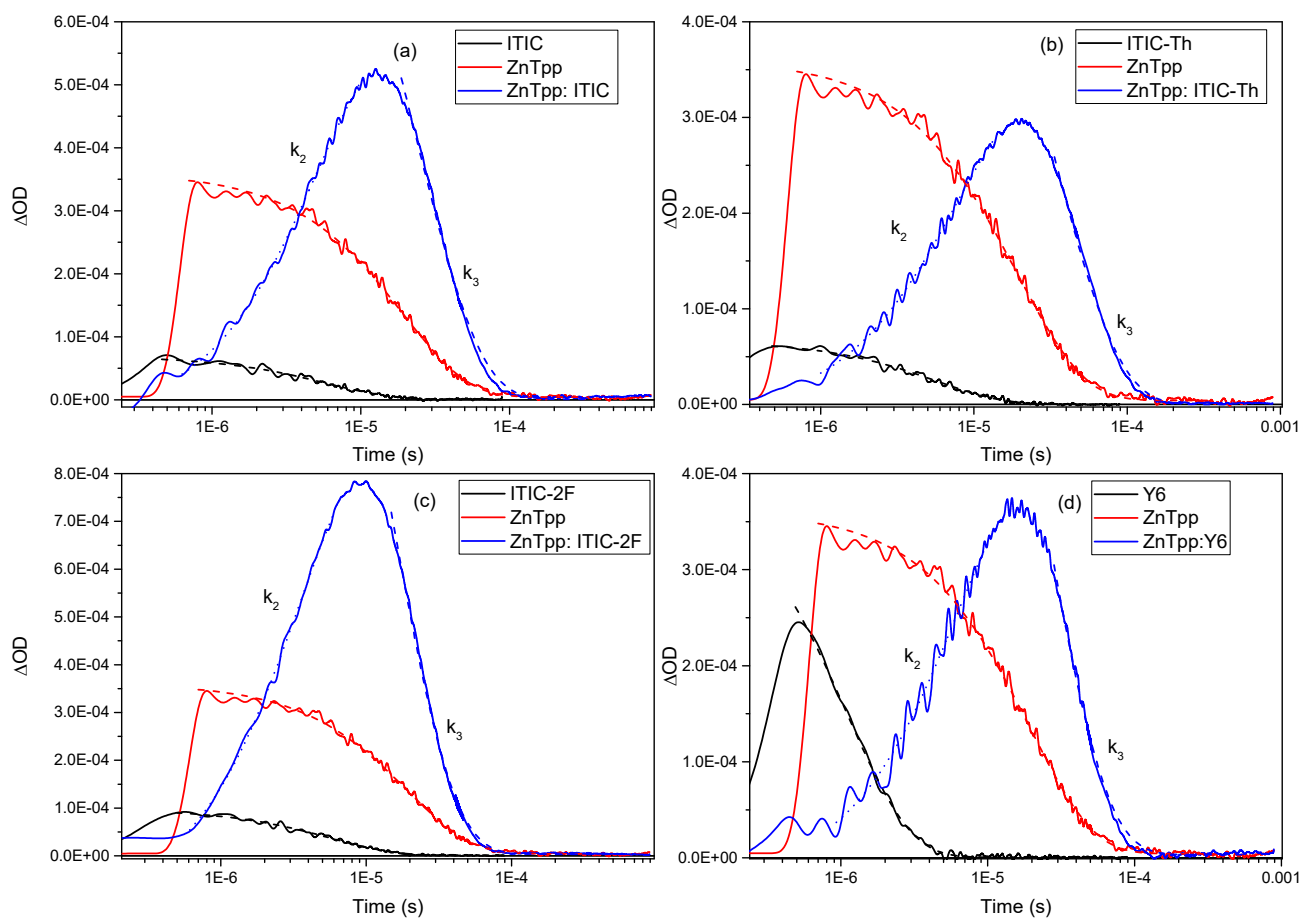


Figure S16. Decay dynamics of (a) ZnTpp: ITIC (1:1), ITIC, and ZnTpp solution, (b) ZnTpp: ITIC-2F (1:1), ITIC-2F, and ZnTpp solution, (c) ZnTpp: ITIC-Th (1:1), ITIC-Th, and ZnTpp solution and (d) ZnTpp: Y6 (1:1), Y6, and ZnTpp solution. All the solution with concentration $7 \times 10^{-6}\text{M}$ and excitation wavelength $7 \times 10^{-6}\text{M}$ and excitation wavelength 426 nm, fitted with mono-exponential decay/growth. The probe wavelength for the ZnTpp solution is 850 nm; for ZnTpp:ITIC, ITIC, ZnTpp:ITIC-Th, and ITIC-Th is 1100 nm; 1150 nm for ZnTpp:ITIC-2F and ITIC-2F; and 1400 nm for ZNTpp:Y6 and Y6. The excitation energy for all the ZnTpp:NFA solutions is around $12\text{--}14 \mu\text{J cm}^{-2}$.

References:

1. Amouyal E, Bensasson R, Land EJ 1974 *Photochem Photobiol* **20** 415–22
2. Seixas De Melo JS, Pina J, Dias FB, Maçanita AL 2013 *Appl Photochem* **9789048138** 533–85
3. Kikuchi K, Kurabayashi Y, Kokubun H, Kaizu Y, Kobayashi H 1988 *J Photochem Photobiol A Chem* **45** 261–3

