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Supporting Information

Effect of Nanoscale Confinement on Ultrafast Dynamics of Singlet Fission in TIPS-Pentacene

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[SI-I]: Dynamic light scattering (DLS) measurements:

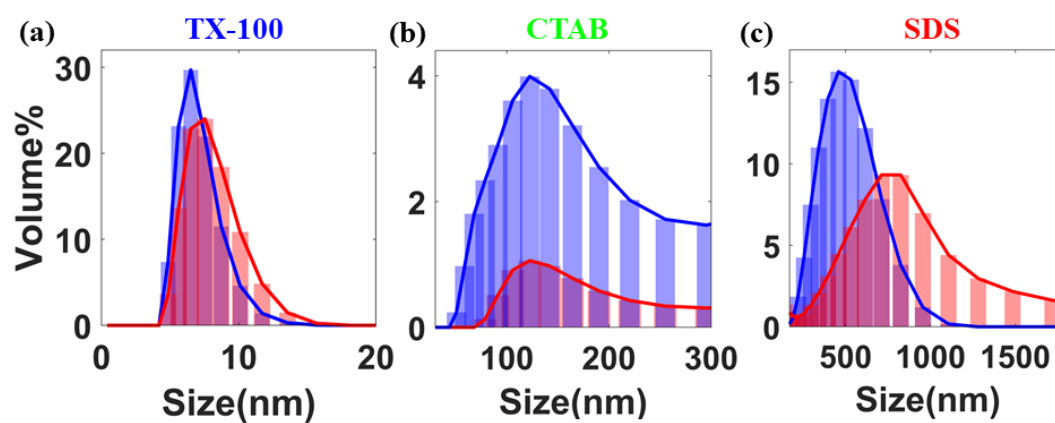


Figure S1. Plots of size distribution of (a) TX-100, (b) CTAB and (c) SDS micellar nanostructures without (blue) and with (red) TIPS-Pn dye encapsulation.

[SI-II]: Normalized absorption and emission spectra:

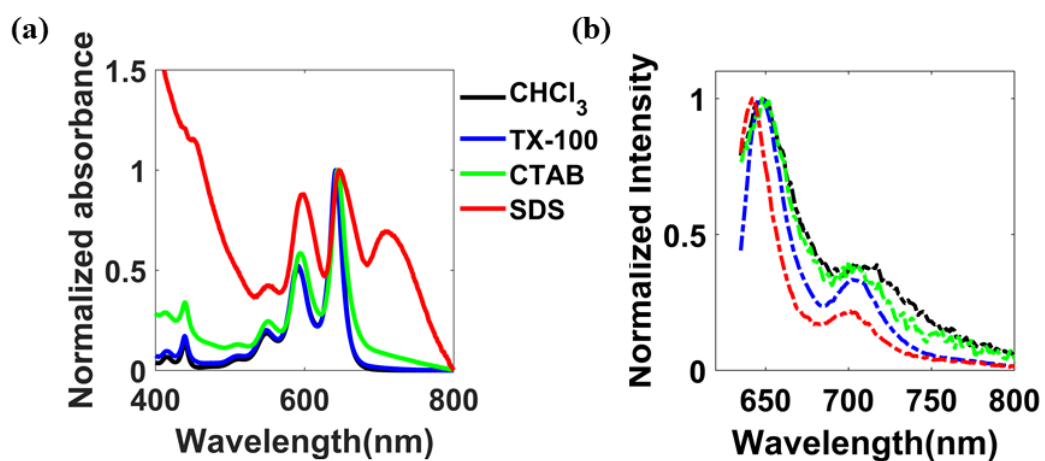


Figure S2. Plots for normalized (a) absorption, and (b) emission spectra of TIPS-Pn in bulk CHCl_3 (black) and in TX-100 (blue), CTAB (green), SDS (red) micellar NPs.

[SI-III]: Time-resolved fluorescence analysis:

TIPS-Pn in CHCl₃, TX-100, CTAB, and SDS nanoparticles are excited by 630 nm laser diode and lifetime (at magic angle, 54.7°) and anisotropy (at 0° and 90° emission polarization) decays are collected at emission maxima. The lifetime and anisotropy decays are fitted using DAS 6 analysis software as follows:

The lifetime of a multicomponent fluorescence decay is fitted in an exponential equation as:

$$I(t) = A + \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

and

where A represents the background term, τ_i the lifetime of each decay component with corresponding amplitudes α_i . The fitting parameters of each sample are shown in [Table S1](#).

Similar, to lifetime the time-resolved fluorescence anisotropy decay can be fitted as:

$$r(t) = A + \sum_{i=1}^n I_i \exp(-t/\tau_i) \quad (2)$$

and

where A represents the residual anisotropy at a longer time than rotational time, I_i the time constant of each component of depolarized fluorescence contributed by either energy migration or rotational diffusion with corresponding amplitudes I_i . The fitting parameters for the anisotropy decay of each sample are shown in [Table S2](#).

Ideally, the initial anisotropy must be estimated using extremely viscous medium (for example, glycerol). However, due to insolubility of TIPS-Pn in viscous medium, the initial anisotropy couldn't be measured. The assignment of the anisotropy decay times in terms of diffusional reorientation and energy hopping is discussed in detail in our previous work [1, 2] which we summarize here:

After photoexcitation, the probability of emitting photon from initially excited molecule in a identical multichromophoric system, can be shown as [3]:

$$P_i(t) = \sum_{j=1}^n \alpha_{ij} \exp(-t/\tau_j) \quad (3)$$

where, γ represents energy transfer rate within homo-chromophores. The time-resolved anisotropy for the depolarization created by energy transfer process is given as:

$$(4)$$

where, A_0 represents the static anisotropy of first excited molecule. After inclusion of rotational time of molecule, the total anisotropy can be shown as:

$$(5)$$

Here, τ_1 , τ_2 , and τ_3 ; therefore, after following the condition $\phi_1 < \phi_2$, eq.

(5) is reduced to:

$$(6)$$

This represents the total anisotropy decay containing both the components.

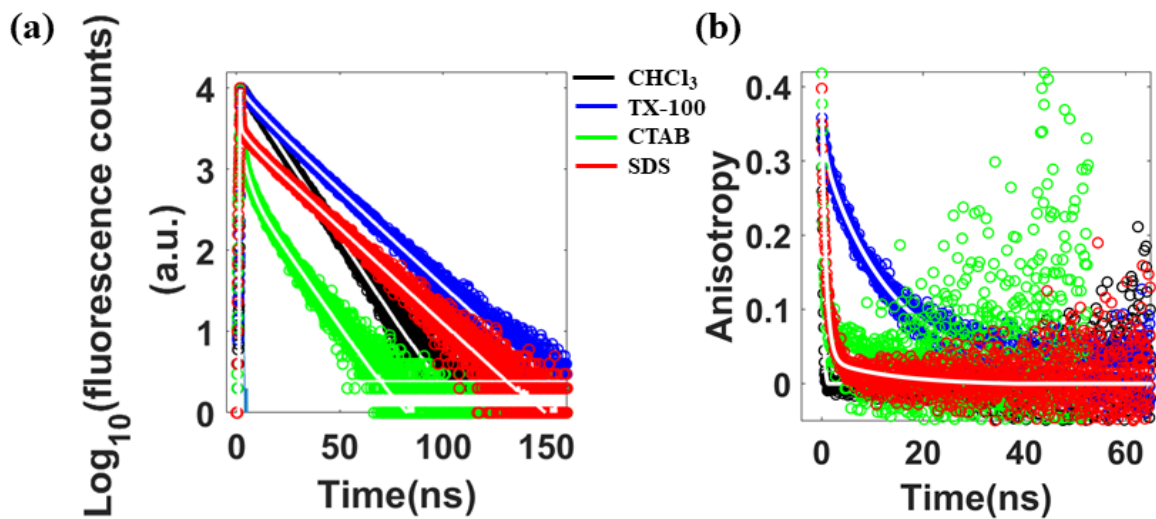


Figure S3. Time traces of (a) fluorescence lifetime, and (b) time-resolved fluorescence anisotropy of TIPS-Pn dye in bulk CHCl_3 (black), and in TX-100 (blue), CTAB (green), SDS (red) micellar nanostructures.

Table S1. Best fitting parameters for lifetime decays of TIPS-Pn in CHCl₃, TX-100, CTAB and SDS nanoparticles.

Sample	A ₁	τ ₁ (ns)	α ₂	τ ₂ (ns)	α ₃	τ ₃ (ns)	τ _{av} (ns)	χ ²
CHCl ₃	-	-	-	-	1	11.21	11.21	1.305
TX100	-	-	0.21	4.76	0.79	18.01	15.22	1.145
CTAB	0.92	0.15	0.05	2.78	0.02	11.76	0.57	3.67
SDS	0.86	0.17	0.03	3.84	0.11	18.30	2.29	3.19

Table S2. Best fitting parameters for anisotropy decays of TIPS-Pn in CHCl₃, TX-100, CTAB and SDS nanoparticles.

Sample	β ₁	φ ₁ (ns)	β ₂	φ ₂ (ns)	φ _{av} (ns)	χ ²
CHCl ₃	1	0.33	-	-	0.33	1.37
TX100	0.14	0.71	0.86	12.59	11.59	1.14
CTAB	0.88	0.37	0.12	11.84	1.72	0.99
SDS	0.93	0.79	0.07	13.59	1.72	1.36

[SI-IV]: Pulse-width measurement:

Using a non-linear crystal type II β -barium borate (BBO) at the sample position (where a pump and probe beams overlap non-collinearly), the frequency-resolved optical gating (FROG) trace is obtained by spectrally dispersing the second harmonic signal on the spectrometer as shown in Figure S4(a). The autocorrelation trace at 332 nm is fitted with a Gaussian fit and the full width at half maxima (FWHM) is obtained ~ 48 fs as shown in Figure S4(b). The actual pulse width can be calculated as

(7)

Hence, the pulse-width is obtained ~ 34 fs.

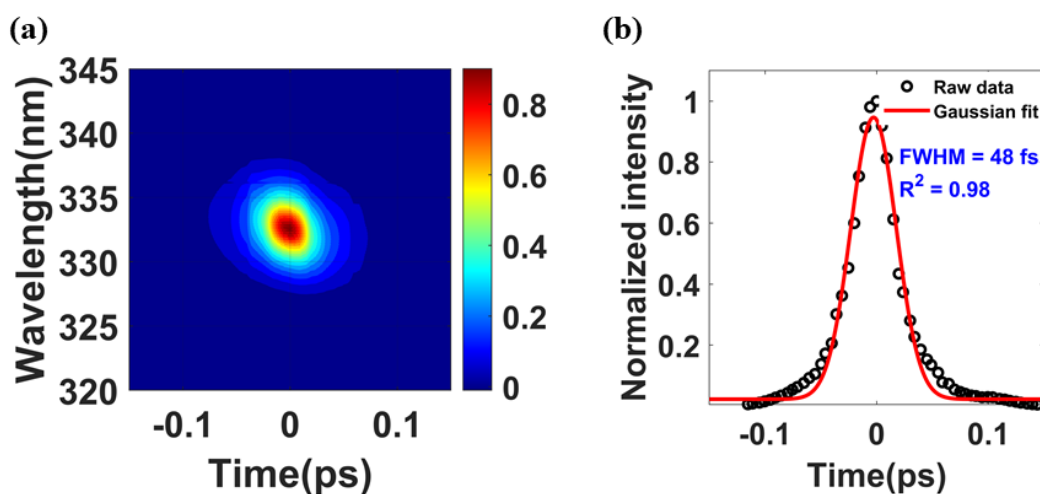


Figure S4. Plots of (a) spectrally dispersed experimental FROG trace and (b) the autocorrelation trace at 332 nm with Gaussian fitting function.

[SI-V]: Beam-profile analysis:

A beam profiling camera is used to measure the diameters of pump and probe beam at sample position. The diameter parameters $D4\sigma_x$, $D4\sigma_y$ & $D4\sigma$ are obtained $\sim 403 \mu\text{m}$, $403 \mu\text{m}$, & $345 \mu\text{m}$ for 640 nm pump and $328 \mu\text{m}$, $328 \mu\text{m}$, & $215 \mu\text{m}$ for white light probe beam, respectively. Figure S5 shows the beam profile of pump beam at 640 nm and white light probe beam.

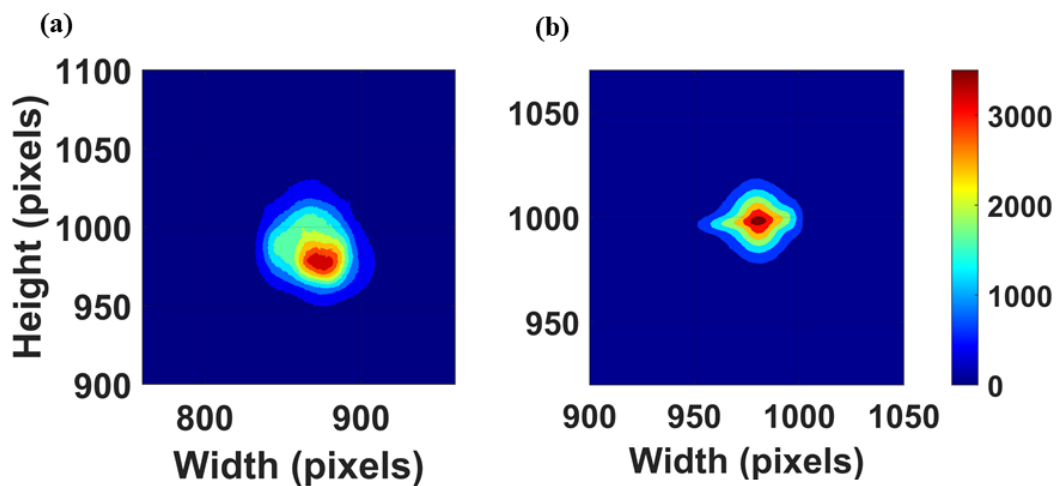


Figure S5. Contour of (a) pump (at 640 nm) and (b) white light probe beams at sample position captured by a beam profiling camera.

[SI-VI]: Concentration of triplets/singlets and SF yield:

Using steady-state extinction coefficient (ϵ_{ss}) of singlet ground state at 646 nm, the concentration of triplets at a later time (3 ns) can be calculated as (considering only triplets are present at 3 ns) [4]:

$$\text{_____} \quad (8)$$

where, _____ represents differential absorbance of 646 nm at _____ delay time and _____ represents pathlength of absorption cell. Similarly, the concentration of singlets at an early time (100 fs) can be calculated as (considering only singlets are present at 100 fs) [4]:

$$\text{_____} \quad (9)$$

Hence the singlet fission yield can be calculated using concentration of singlet and triplet states as [4]:

$$\text{_____} \quad (10)$$

The data for concentrations and SF yield is provided in Table S3.

Table S3. Concentrations of triplet and singlet states of TIPS-Pn with SF yields in various samples.

Sample	
CHCl ₃	
TX-100	
CTAB	
SDS	

[SI-VII]: Global analysis of transient absorption data:

TA data is analyzed globally using the three-component sequential kinetic model considering the whole dataset till 3.7 ns.

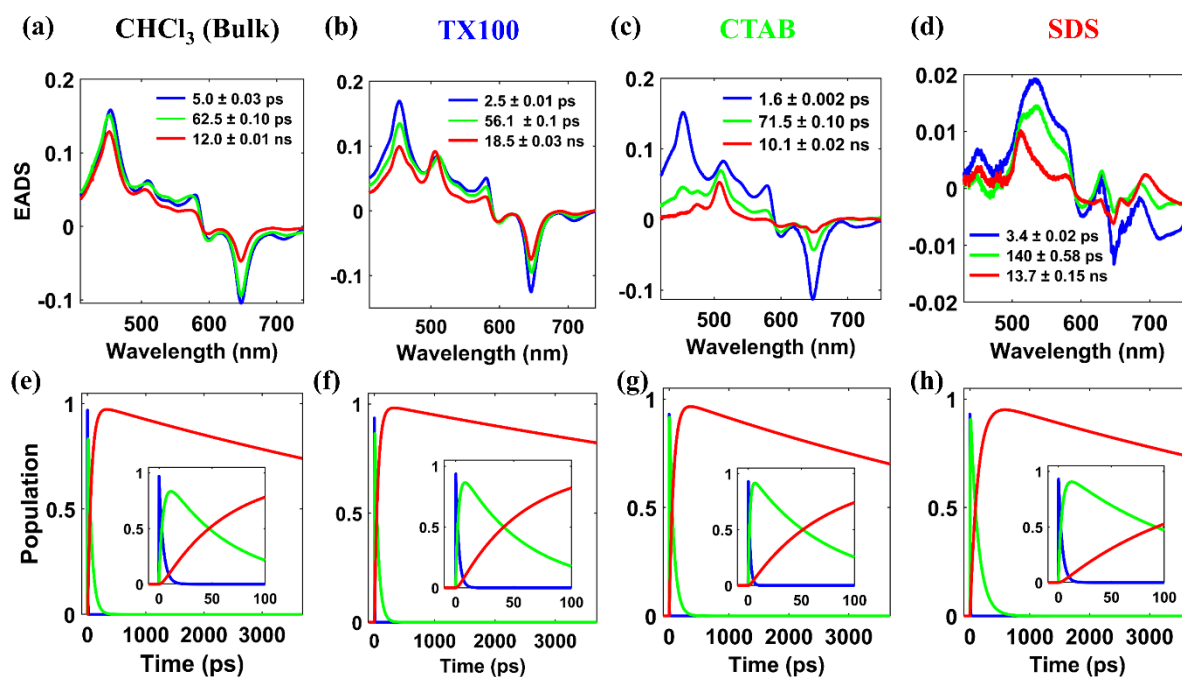


Figure S6. Plots of evolution associated decay spectra and population kinetics of TIPS-Pn in CHCl₃ (a & e), TX-100 (b & f), CTAB (c & g), and SDS (d & h) nanostructures, respectively.

Table S4. The time constants obtained from global analysis for whole dataset.

Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)
CHCl ₃	5.0 ± 0.03	62.5 ± 0.10	12.0 ± 0.01
TX-100	2.5 ± 0.01	56.1 ± 0.10	18.5 ± 0.03
CTAB	1.6 ± 0.02	71.5 ± 0.10	10.1 ± 0.02
SDS	3.4 ± 0.02	140 ± 0.58	13.7 ± 0.15

[SI-VIII]: References:

1. Y. Silori, A. K. De, *J. Photochem. Photobiol. A Chem.*, **2019**, 377, 198–206.
2. Y. Silori, A. K. De, *J. Mol. Liq.* **2019**, 298, 112093–112100.
3. S. C. Warren, A. Margineanu, M. Katan, C. Dunsby, P. M. W. French, *Int. J. Mol. Sci.* **2015**, 16, 14695–14716.
4. A. N. Stuart, P. C. Tapping, E. Schrefl, D. M. Huang and T. W. Kee, *J. Phys. Chem. C.* **2019**, 123, 5813–5825.