Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information Section

Interplay of Exciton – Excimer Dynamics in 9,10-Diphenylanthracene Nanoaggregate and Thin Film Revealed by Time Resolved Spectroscopic Studies

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Table S1: *Details of crystal parameters as reported earlier[1-3]*

System	a	b	c	beta
Anthracene	8.56 Å	6.04 Å	11.16 Å	124°
9,10-DPA	10.7 Å	13.57 Å	12.29 Å	90.65°

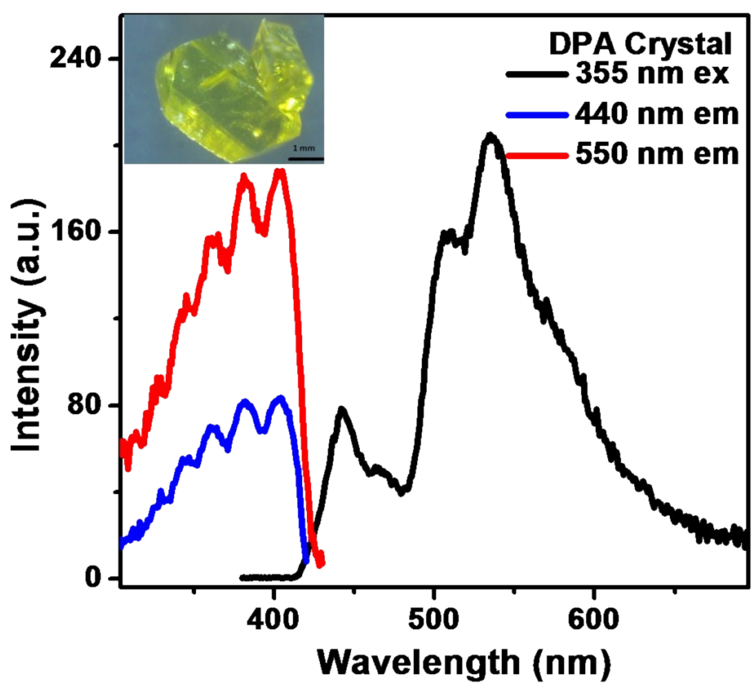

Figure S1: *Emission spectrum recorded after excitation with 360 nm light and excitation spectrum recoded for 440 nm and 550 nm emission for DPA crystal sample .Inset: Image of* *solution grown DPA crystal. Weaker emission oat 440 nm originates from excitonic statesand strong emission at 550 nm originates from excimer state.Identical excitation spectra recorded at 440 nm and 550 nm suggest that both emission bands from the same initial state. Time resolved emission studies, as shown below(Figure S2), confirms that exciton state relaxes to excimer state*

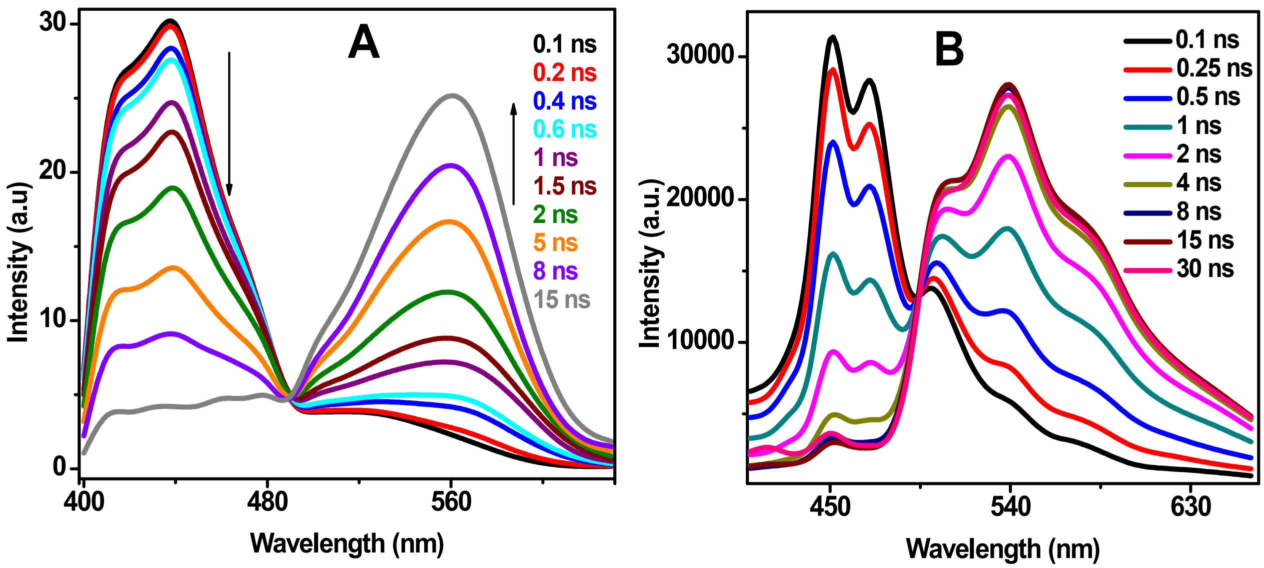

Figure S2: *TRANES spectra observed for (A) DPA NA-2 and (B) DPA crystal*

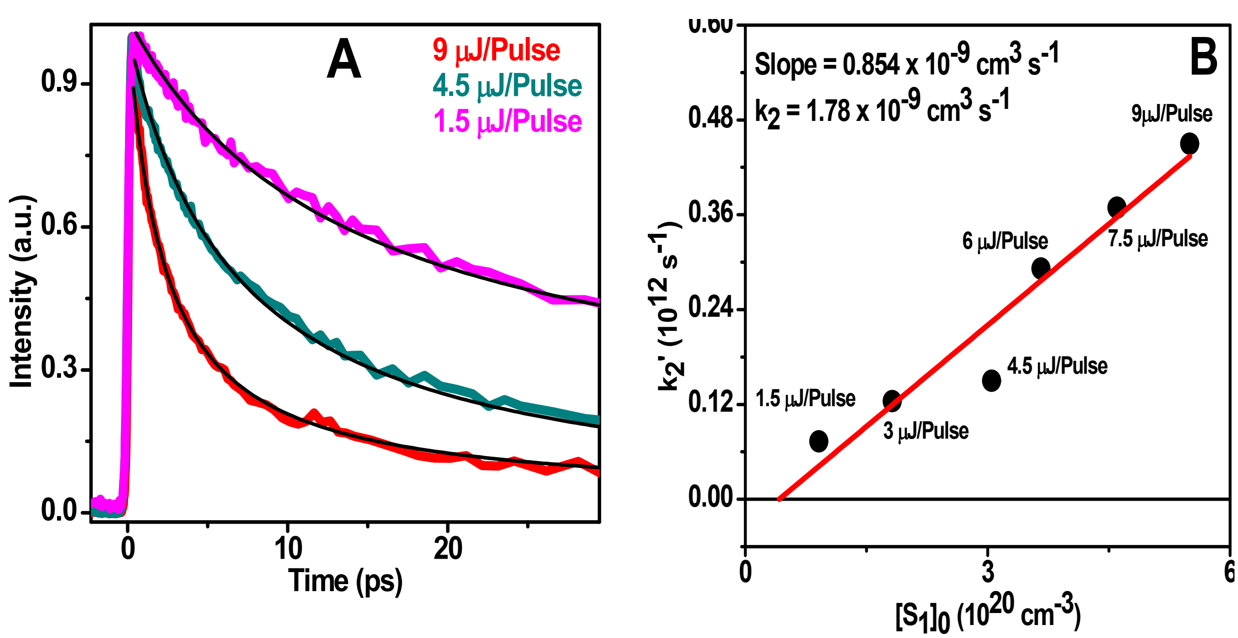

Figure S3: *(A)Temporal profiles recorded at 430 nm for different excitation energy with 390 nm light for 9,10-DPA thin film and in (B) k_2' vs. $[S_1]_0$ plot for 9,10-DPA thin film sample. The excitation energy per pulse associated with each data point are provided.*

Table S2: *Fitting parameters for temporal profiles recorded at 430 nm for different excitation energies with DPA NA-1 sample.*

Pulse/Energy	I_0	Residual	k_2	k_1
11	449.5	86.6	0.17	0.003 ± 0.0003
9	428.73	99.42	0.12	
7	411	110.02	0.09	
4.5	416	92.45	0.055	

Table S3: *Fitting parameters for temporal profiles recorded at 430 nm for different excitation energies with DPA TF sample.*

Pulse/Energy	I_0	Residual	k_2	k_1
9	1	0.031	0.45	0.0027 ± 0.0003
7.5	1	0.054	0.37	
6	1	0.065	0.292	
4.5	1	0.012	0.15	
3	1	0.015	0.124	
1.5	1	0.19	0.0732	

Other parameters required for exciton density calculation: Abs=0.41 Thickness =100 nm, Beam dia=0.5 mm

Calculation S1:Calculation of exciton density ($[S_1]_0$)in fluorescence upconversion experiment.

A representative procedure of exciton density estimation is shown for excitation energy 11 μJ/pulse.

The excitation pulse energy=11 μJ at λ_{ex}=390 nm corresponds to number of photon per pulse = 2.16×10^{13}

Absorbance of the sample was 0.22 i.e. 40 % of incident photon are absorbed or 0.86×10^{13} number of photon are absorbed per pulse.

The volume of excitation region $=\pi r^2 d=19.63 \times 10^{-5}$ cm^3 corresponding to beam diameter (2r) = 0.5 mm, path length (d) =1 mm

Average volume of each aggregate=$\pi R^2 h$ = 1.54 × 10^7 nm^3 [R=275 nm, h= 65 nm obtained from AFM expeiment]

Number of DPA molecule present per aggregate =4.97 × 10^7 considering volume of each DPA molecule to be about 0.31 nm^3 estimated from molecular volume calculation following Edward et. Al.[4]

Number of DPA molecule present in excitation region=Concentration x volume (in lit.) × 6.023 × 10^{23} = 2 × 10^{-4} × 19.63 × 10^{-8}× 6.023 × 10^{23} =23.6× 10^{12} [Sample Concentration =0.2 mM]

Total number of aggregate present in the excitation region= 23.6 × 10^{12}/ 4.97 ×10^7 =4.76 × 10^5

Number of photons absorbed by each particle of the nanoaggregate = 0.86 × 10^{13}/ 4.76 ×10^5 = 1.81 × 10^7

Exciton density ($[S_1]_0$) = 1.81 × 10^7/ 1.54 ×10^7 nm^3 =1.17 × 10^{21} cm^{-3}

Calculation S2:Calculation of Annihilation radius for DPA NA

The exciton density at threshold of annihilation = 0.59 x 10^{20} cm^{-3}as obtained fromX-axis intercept of k_2' vs $[S_1]_0$ plot (figure 6B in main text)

At annihilation threshold condition, two excitons are expected to be separated by a distance of 2 × annihilation radius (R_a) (assuming homogeneous distribution of excitons inside nanoaggregate)

If we assume homogeneous generation of excitons inside the nanoaggregate, then per exciton available volume = 1 cm^3 / 0.59 × 10^{20} = 16.9 nm^3

$$\frac{4\pi {R_a}^3}{3} = 16.9\ nm^3$$

R_a = 1.6 nm

References

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