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Where Does the Fluorescing Moiety Reside in a Carbon Dot? - Investigations Based on Fluorescence Anisotropy Decay and Resonance Energy Transfer Dynamics

Ananya Das[†], Debjit Roy[†], Chayan K. De[†], Prasun K. Mandal*[†‡]

[†]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, West-Bengal, 741246, India.

[‡]Centre for Advanced Functional Materials, Indian Institute of Science Education and Research (IISER) Kolkata Mohanpur, West-Bengal, 741246, India.

*e-mail: prasunchem@iiserkol.ac.in

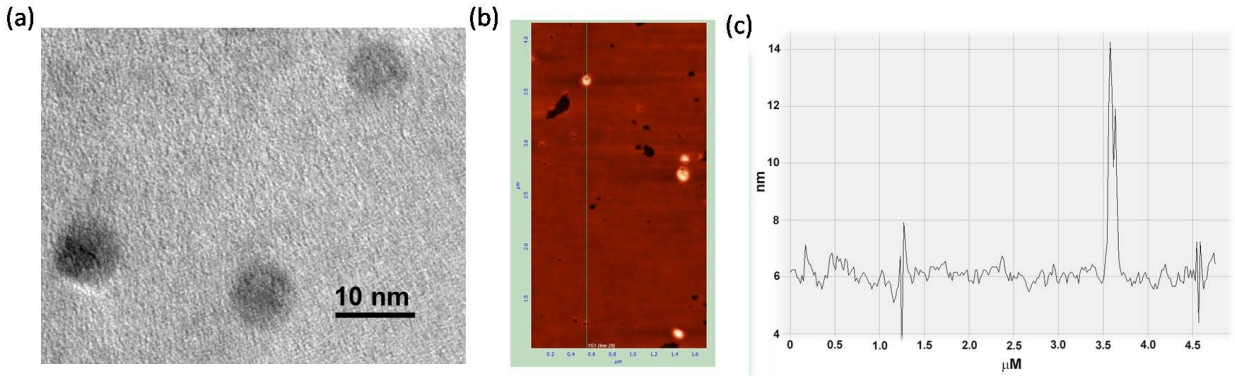


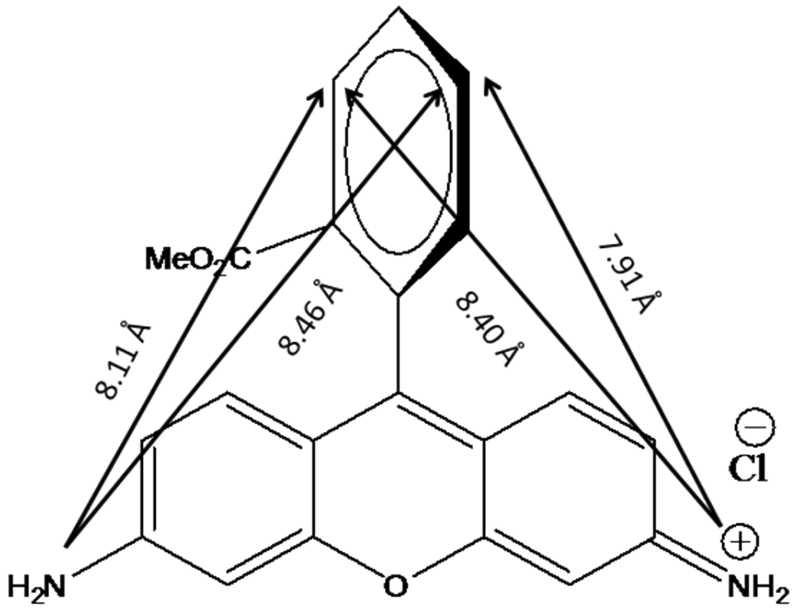
Fig. S1. TEM image of CD (a), AFM image of CD (b) and the corresponding size from AFM (c).

Table S1. Rotational correlation time of CD in solvents of different viscosity

Solvent	Viscosity At 25°C (cP)	λ_{em} (nm)	τ_{rot} (ns)	χ^2
Ethylene glycol	16.8	440	1.28	1.03
		500	1.32	1.08
		550	1.35	1.01
Propylene glycol	42	440	3.97	1.05
		500	4.11	1.03
		550	4.21	1.08
Glycerol	1412	440	27.92	1.11
		500	29.46	1.08
		550	35.31	1.11

Details of geometry optimization:

The geometry of the molecule has been optimized by density function theory (DFT) using Gaussian 09 software. [1] All the calculations were performed using a B3LYP functional and a 6-31G basis set for all the atoms. Default criteria for geometry optimization were used in each case.



Rhodamine123

Average diameter of Rh123 = (8.11+8.46+8.40+7.91)/4 Å=8.22 Å=~0.8 nm

Table S2. Förster parameters for RET

Solvent	Concentration (μM)	λ_{ex} (nm)	λ_{em} (nm)	J(λ) (M^{-1} cm^{-1} nm^4)	R_0 (Å)	τ_D (ns)	τ_{RET} (ns)	Donor-acceptor distance (Å)	Average Donor-acceptor distance (nm)
Water	50	377	620	1.37×10^{15}	49.98	14.6	5.37	42.31	4.24
	100						5.52	42.50	
	150						5.46	42.42	
	200						5.37	42.31	

Donor acceptor distance (r_{DA}) using Förster formulation has been calculated using the following relation:

$$r_{DA} = R_0 \left(\frac{1}{(\tau_D / \tau_{RET})}\right)^{\frac{1}{6}}$$

where, R_0 is Förster radius, τ_D is donor lifetime in absence of acceptor, τ_{RET} is resonance energy transfer time or rise time.

We have performed several control experiments in order to nullify the fact that the risetime is from other processes like exciplex formation or solvation etc. If exciplex is formed a new emission band may appear. We have not observed any new band other than the donor and acceptor emission. Nonetheless we have performed several control experiments. In the steady state we have recorded emission spectrum of both donor and acceptor in absence of each other and maintaining the high concentration (same concentrations that we have used in RET experiment) of both donor and acceptor separately. No new emission band was observed in case of either donor or acceptor. No shift of the emission maximum has been observed. We have also performed time resolved fluorescence decay of both donor and acceptor in absence of each other and maintaining the high concentration (same concentrations that we have used in RET experiment) of both donor and acceptor separately. We did not observed any rise time in either of donor or acceptor decay. These plots have been shown below. Thus, based on four different control experiments, the possibility of exciplex formation can be excluded with high degree of certainty.

Whether spectroscopic properties of the CDs are dependent on concentration or not we have performed a few control experiments. In order to exclude the concentration dependent artifact from the donor itself we have performed both steady state and time resolved experiments with different concentration of CDs. We have chosen two different concentration, where one is at least 10 times higher than the other. However with increase of concentration there was no significant change in the steady state spectroscopic properties (say emission maxima). The excited state decay remains single exponential for low concentration as well as for high concentration. The lifetime remains similar ($\tau = 15.2 \pm 0.6$ ns). There is very little concentration quenching that has been observed with the high concentration. With the same high concentration solution we have performed RET experiment. The excited state quenching of donor has been observed in presences of acceptor. CD decay time in presence of 200 μM Rh123 $\tau = 12.5$ ns, thus, about 20% faster decay has been observed for donor in presence of acceptor. Thus, the donor quenching in presence of acceptor is definitely not an artifact, but due to quenching because of the presence of acceptor. We could also confirm that self-quenching of donor is not interfering in RET process between donor and acceptor. Time resolved SV plot also confirm that there is dynamic quenching component. Quite importantly, we did not observe any rise time in donor decay when the concentration of donor is quite high and please note that the same concentration has been used for RET measurements. We have also performed a control experiment in order to check whether there is any concentration dependent risetime in case of acceptor. As has been shown below there is no risetime in acceptor decay (in absence of donor) even when the concentration of acceptor is 200 μM. Please note this is the same high concentration with which the RET exeperiments have been performed. The results of these several control experiments have been depicted in Fig. S2, Fig. S3, Fig. S4, Fig. S5, Fig. S6.

Thus, we can conclude that only RET is happening between CD (donor) and Rh123 (acceptor) and no other process such as exciplex etc. is operating.

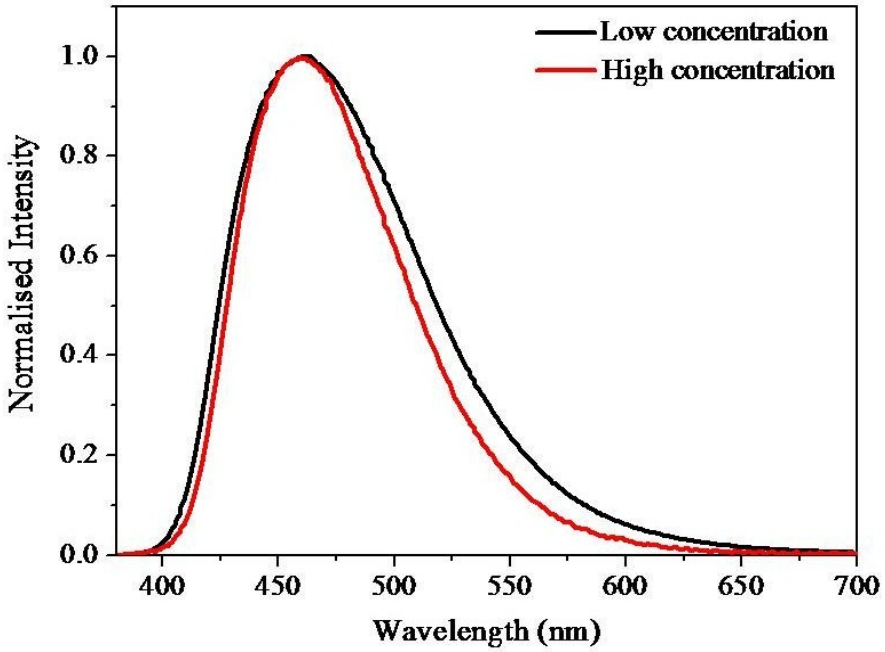


Fig. S2. Steady state emission spectra for donor (CD) at different concentrations.

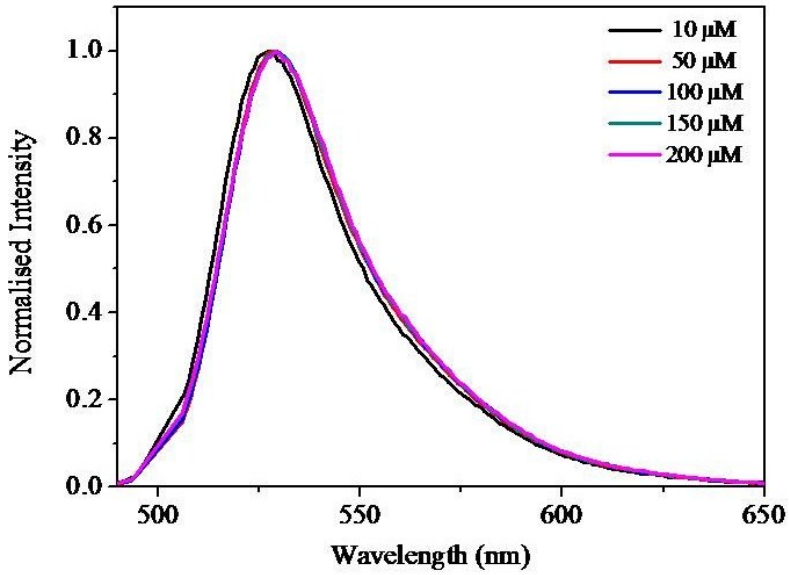


Fig. S3. Steady state emission spectra for acceptor (Rh123) at different concentrations.

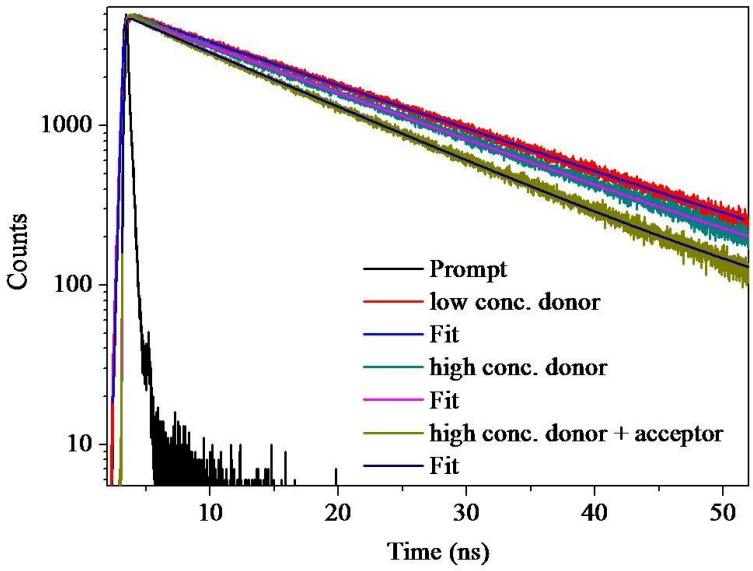


Fig. S4. Time resolved decay for CD (donor) at different concentrations.

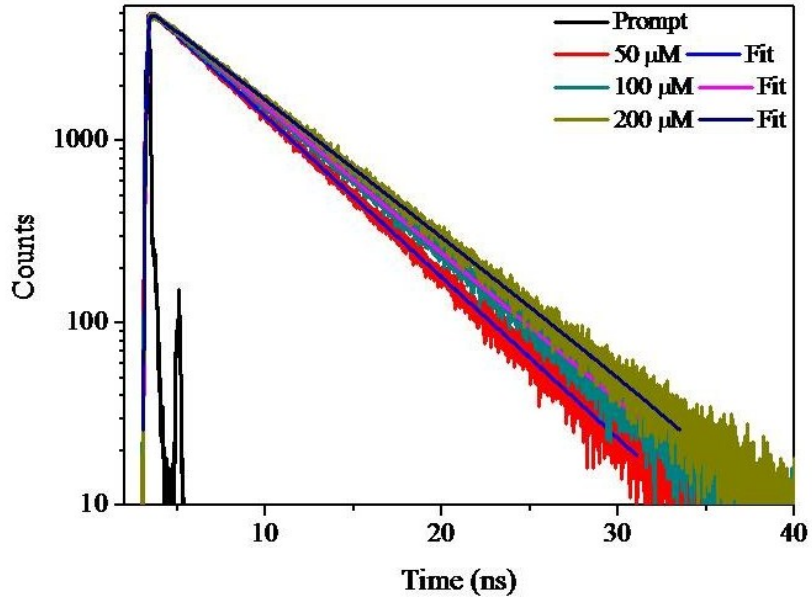


Fig. S5. Time resolved decay for Rh123(acceptor) at different concentrations.

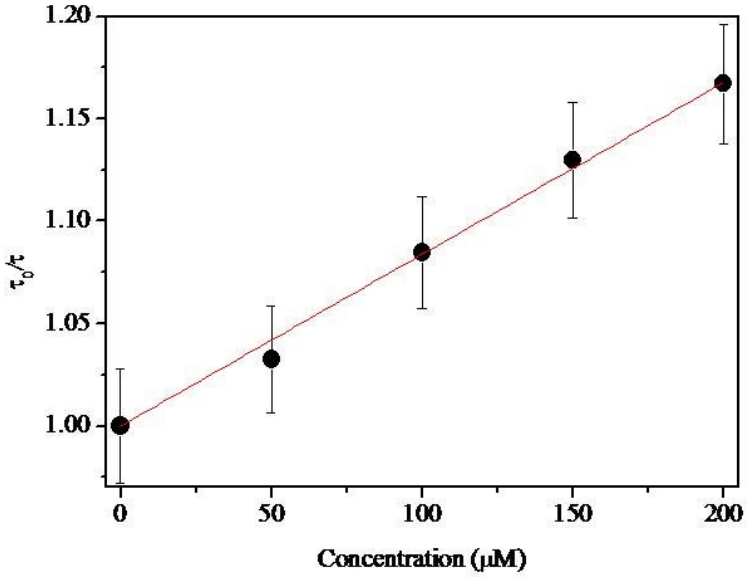


Fig. S6. Time resolved Stern –Volmer plot of CD (donor).

References

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