Supporting information

Photophysics of 7-(Diethylamino)coumarin-3-carboxylic Acid in Cationic Micelles: Effect of Chain Length and Head Group of the Surfactants and Urea

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1. Method to calculate solvation time: In order to study the solvation dynamics, we have constructed the time resolved emission spectra (TRES), according to the procedure described by Maroncelli and Fleming.[1] The spectrum at any time (t) is represented as S(λ;t), and describe as follows:

$$S(\lambda;t) = D(t;\lambda)\frac{s_0(\lambda)}{\int_0^\infty D(t;\lambda)dt} \quad \text{(S1)}$$

where, D (t;λ) is the representative of fitted decay. Thus S(λ;t) can be easily obtained from the fitted decay [D(t;λ)], by the relative normalisation of the steady state emission spectrum. All TRES are fitted by using the log-normal function:

$$I(\nu) = I_0 \exp\left[-\ln 2\left(\frac{\ln\left[1+2b\left(\nu-\nu_p\right)/\Delta\right]}{b}\right)^2\right] \quad \text{(S2)}$$

where ν_p, I_0, Δ, and b are the peak frequency, peak height, width parameter and asymmetric parameter, respectively. To get the solvent relaxation time we have deduced the solvent response function [C(t)]:

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad \text{(S3)}$$

where ν(t), ν(0), ν(∞) are the emission maxima frequencies, at the time t, at the time t = 0, and at t = ∞. The decay of C(t) with time can be fitted by the exponential function:

$$C(t) = \sum_{i=0}^{n} b_i e^{\frac{-t}{\tau_i}} \quad \text{(S4)}$$

where b_i stand for the amplitude, and τ_i stand for the solvent relaxation time constant. The average solvation time can be expressed using the equation (6):

$$\langle \tau_{solv} \rangle = \sum_{i=1}^{n} b_i \tau_i \quad \text{(S5)}$$

2. Two-step model and wobbling-in-cone model: The biexponential anisotropy decays of 7-DCCA in these micellar media is mainly due to several motions. To explain the biexponential nature of the anisotropy decay of 7-DCCA in these micellar medium two-step model and wobbling-in-cone model was used.[2-6] These models tell us that the probe molecule located at the micellar surface undergoes slow restricted translational motion along the micellar surface, and a fast wobbling motion inside an imaginary cone. According to the two-step model the slow and the fast motion can be separated, and the total correlation function is the product of the two functions corresponding to the fast motion within the micelles and the slow motion of the micelle.[7] The components of rotational relaxation time can be given by the following equations:

$$\frac{1}{\tau_{slow}} = \frac{1}{\tau_M} + \frac{1}{\tau_L} \quad \text{(S6)}$$

where τ_M is the rotational relaxation time of the entire micelle and τ_L represents the time for lateral diffusion of the probe molecule along the curved micellar surface. The fast component of the rotational relaxation time can be given by the following relation:

$$\frac{1}{\tau_{fast}} = \frac{1}{\tau_W} + \frac{1}{\tau_{slow}} \quad \text{(S7)}$$

where, τ_w represents the reorientation time of the dye molecule to execute the wobbling motion by a semicone angle of an imaginary cone. Now the rotational relaxation time of entire micelle τ_M can be represented by the following equation:

$$\tau_M = \frac{4\pi\eta r_h^3}{3KT} \tag{S8}$$

where r_h represents the hydrodynamic radius of the micelles. These values have been taken from the literature.[8]

Another parameter useful for understanding the position of the probe molecule is the order parameter *S*. The pre exponential factor β and *S* are related to each other by the following relation:

$$\beta = S^2 \tag{S9}$$

The order parameter describes the equilibrium orientational distribution of the probe in the micellar medium and follows the relation $0 \leq S^2 \leq 1$. When the motion is completely restricted $S = 1$ and when completely unrestricted $S = 0$.

We have calculated the semi cone angle θ and wobbling diffusion coefficient D_w by using equations (14) and (15)[2]

$$\theta^\circ = \cos^{-1}\left\{\left(\frac{1}{2}\right)\left[\left(1+8|S|\right)^{1/2} - 1\right]\right\} \tag{S10}$$

$$D_w\tau_w\left(1-S^2\right) = -x_0^2\left(1+x_0\right)^2\left\{\ln\left[\frac{\left(1+x_0\right)}{2}\right] + \frac{\left(1-x_0\right)}{2}\right\} / \left[2\left(1-x_0\right)\right] + \left(1-x_0\right)\left(6+8x_0-x_0^2-12x_0^3-7x_0^4\right) / 24 \tag{S11}$$

where $x_0 = \cos\theta^o$

3. Determination of binding constant: To find out the binding constant between dye and micelles we have used the following equation:[9]

$$I_t = I_0 + \left(I_t - I_0\right)\frac{K[M]}{1+K[M]} \tag{S12}$$

where I_∞, I_0, I_t are the fluorescence intensities, when complete binding of dye with the micelle has occurred, in the absence of surfactant and at any intermediate micellar

concentration, respectively. Fluorescence intensity at emission maximum of 7-DCCA at respective micelles was taken. The variation of fluorescence intensity with surfactant concentration is shown in Figure 3. Here, [M] is the micellar concentration and it is expressed as follows:

$$[M] = \frac{(S - CMC)}{N} \quad \text{(S13)}$$

where, S is the surfactant concentration, CMC is the critical micellar concentration and N stand for the aggregation number. The CMC values of DTAB, MTAB, CTAB and CDAB micelles are 15.60 mM, 5 mM, 0.8 mM, 0.79 mM respectively.[8] The aggregation number of DTAB, MTAB, CDAB and CTAB are reported in the literature.[10-11] Equation S12 was used to fit the data, to find out the binding constant (Figure 3).

Table S1: The two-steps and wobbling-in-a-cone model parameters for 7-DCCA in micellar media.

System	τ_{fast} (ns)	τ_{slow} (ns)	τ_W (ns)	τ_M (ns)	τ_L (ns)	r_h (nm)	D_L (10^{-6} cm^2 s^{-1})	$\theta = \cos^{-1}\{(1/2)[(1+8S)^{1/2}-1]\}$	D_w (s^{-1})
7-DCCA in DTAB	0.17	0.890	0.210	7.63	1.000	1.96	6.40	38.3	9.25×10^8
7-DCCA in TTAB	0.24	1.122	0.305	13.40	1.224	2.36	7.58	24.4	1.68×10^8
7-DCCA in CTAB	0.24	1.230	0.300	25.10	1.290	2.91	10.94	37.6	6.33×10^8
7-DCCA in CDAB	0.26	1.240	0.330	21.20	1.320	2.75	9.55	39.8	6.00×10^8

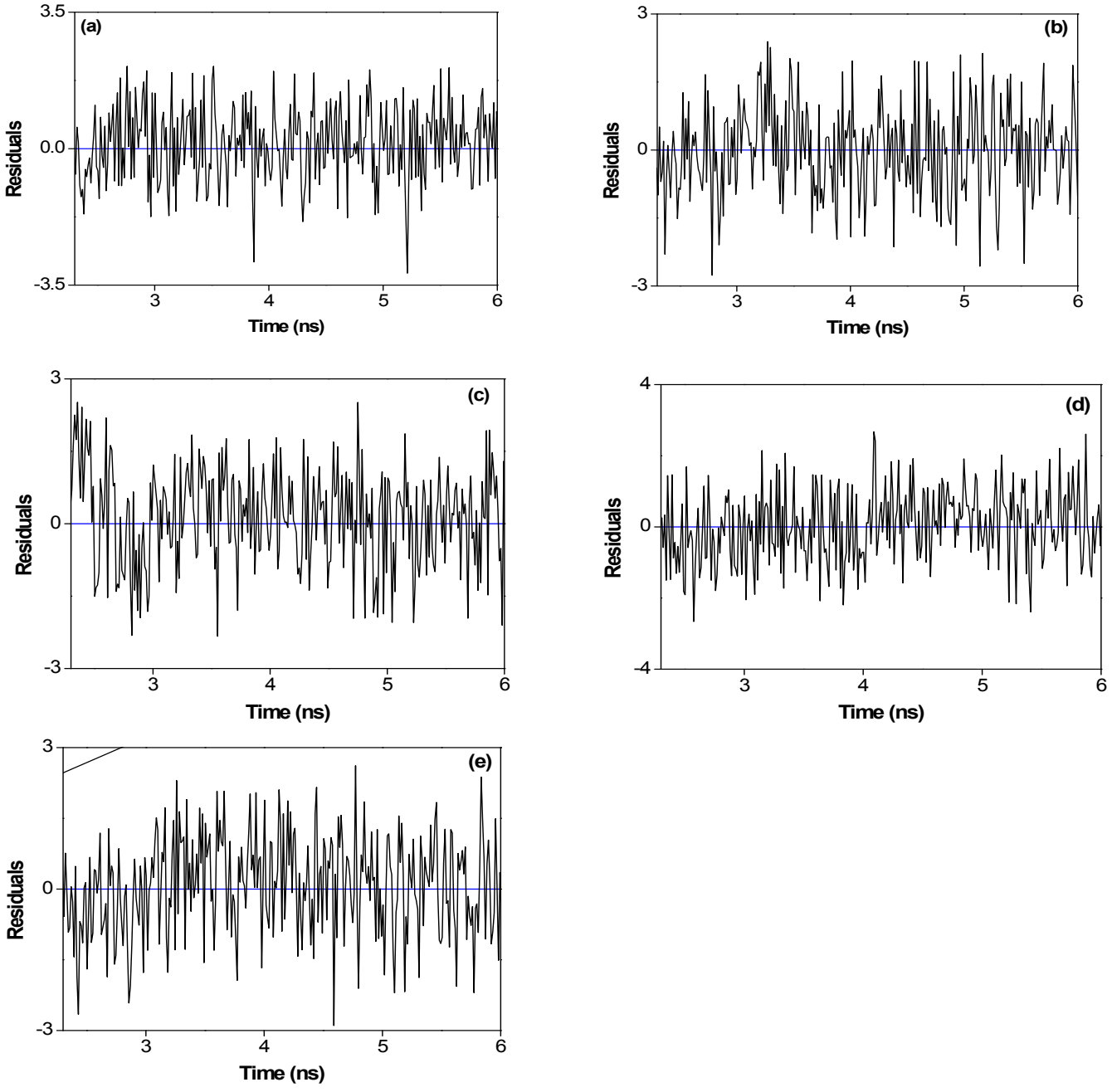

Fig. S1: Residual for the fitted fluorescence lifetime decay of (a) 7-DCCA in water, (b) in DTAB micellar medium, (c) in DTAB micellar medium in presence of 7 (M) urea, (d) in TTAB micellar medium and (e) in TTAB micellar medium in presence of 7 (M) urea.

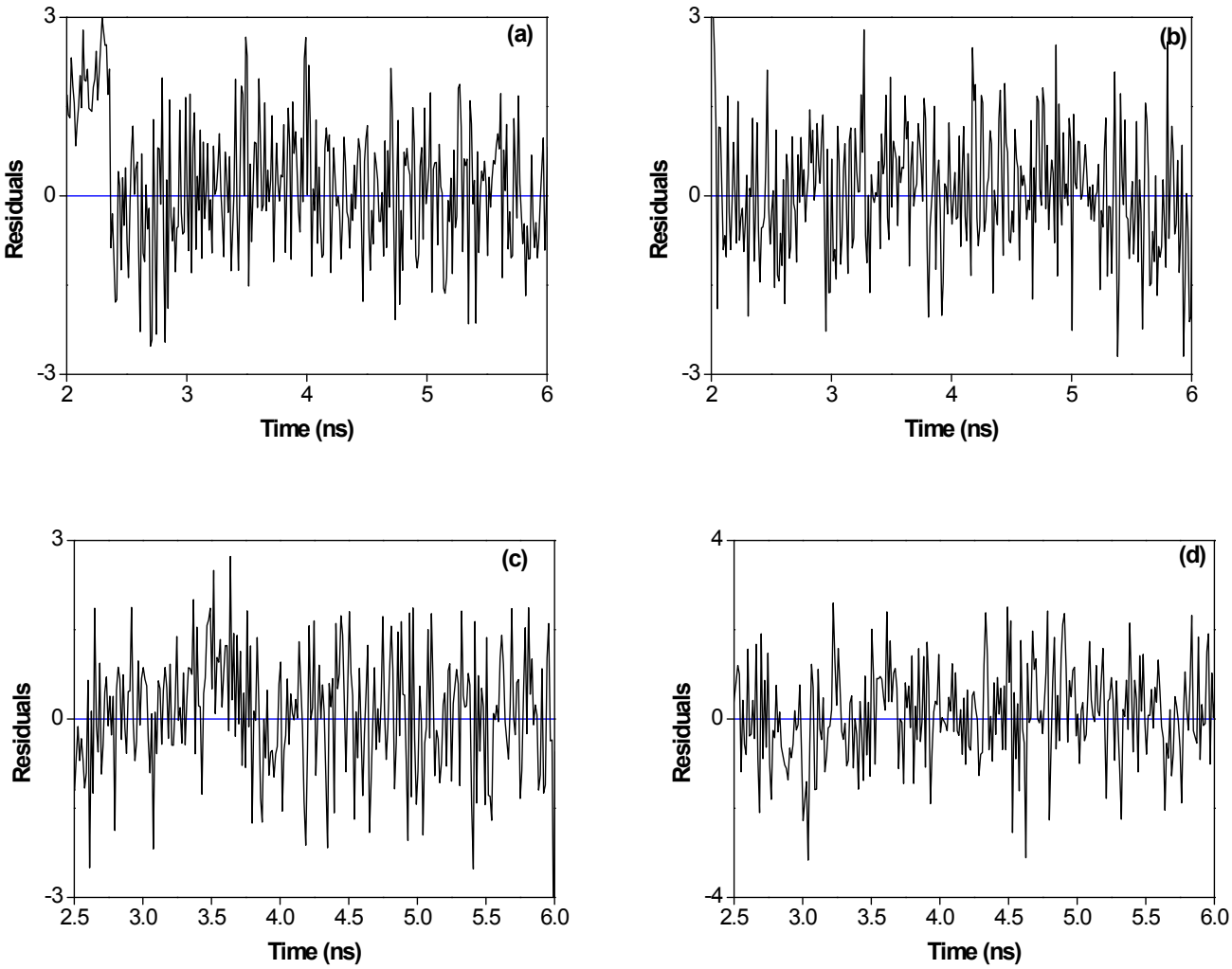

Fig. S2: Residual for the fitted fluorescence lifetime decay of (a) 7-DCCA in CTAB micellar medium, (b) in CTAB micellar medium in presence of 7 (M) urea, (c) in CDAB micellar medium and (e) in CDAB micellar medium in presence of 7 (M) urea.

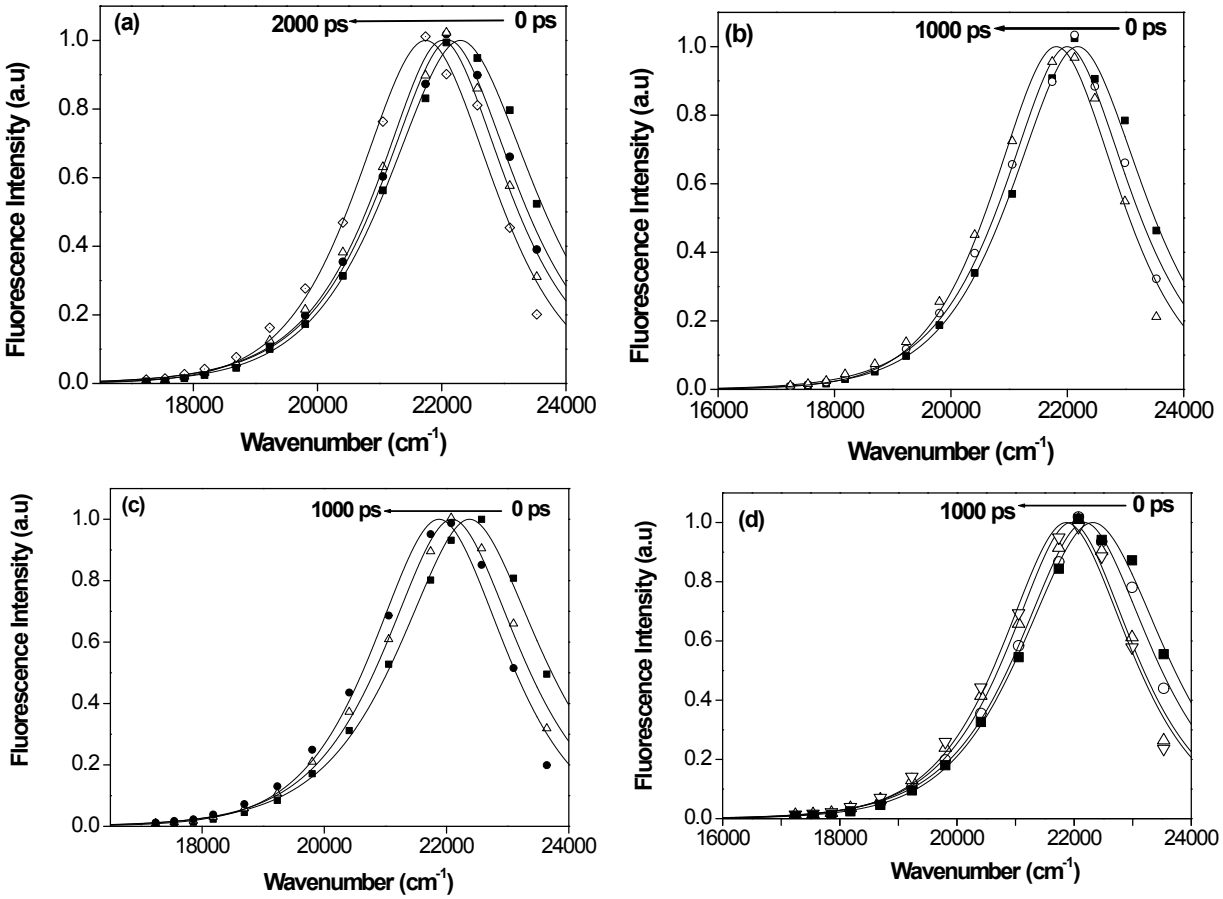

Fig. S3: Time resolved emission spectra (TRES) of 7-DCCA in (a) DTAB (b) TTAB (c) CTAB and (d) CDAB micellar media.

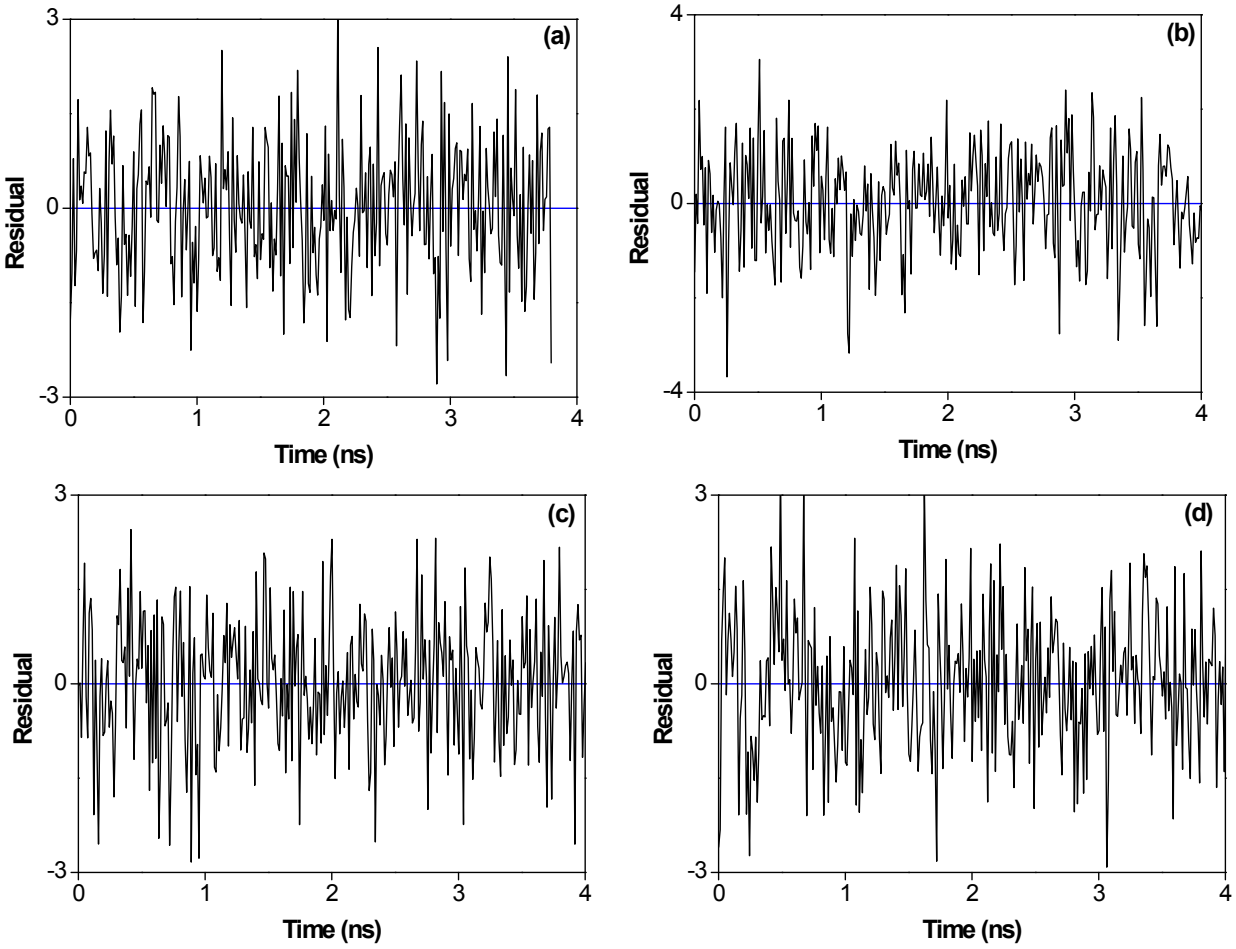

Fig. S4: Residual for the fitted fluorescence time resolved anisotropy decay for (a) 7-DCCA in DTAB micellar medium, (b) in TTAB micellar medium, (c) in CTAB micellar medium and (d) in CDAB micellar medium.

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