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Photo-induced interaction of hydrophobic and hydrophilic dye molecules at nanometer distances

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Abstract

This study investigated the possible efficient photo-induced interaction of hydrophobic and hydrophilic dyes that were separated by several special micro-environments. The three coumarin dyes as hydrophobic dyes and Rose Bengal B Na^+ salt (RB) as a hydrophilic dye were chosen as the energy donor and the acceptor in this report. The two kinds of dye molecules can be separated fully in anionic, neutral and cationic micelles, and mixed surfactant vesicles, while energy can be still transferred efficiently from the coumarin dyes to RB. The results showed that the quenched fluorescence of the coumarin dyes by RB does not follow the Stern–Volmer equation, but agrees well with the Perrin formulation, indicating that the energy transfer takes place through Förster's dipole–dipole interaction. The calculated results from Förster's theory reveal that the energy donor and acceptor can interact strongly even if they are separated on the average by about 4–5 nm in these micro-environments.

Keywords: Hydrophobic and hydrophilic dyes; Photo-induced interaction; Energy transfer; Micro-environments; Nanometer; Quenched fluorescence

1. Introduction

Energy transfer processes have attracted considerable attention, since they have wide application in energy conversion processes, dye lasers, solar cells and in photochemical synthesis. One important kind of non-radiative photo-induced energy transfer from the excited state of a donor (D) to an acceptor (A) is a result of a dipole–dipole interaction. Based on Förster's theory [1], the rate and efficiency of energy transfer depends on a number of factors including: (1) the extent of the overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, (2) the relative orientation of the donor and acceptor transition dipoles, and (3) the distance between these molecules. Thus, the energy transfer processes will depend not only on the characteristics of the donor–acceptor pair but also on its immediate environment. Photo-induced energy transfer processes have been extensively investigated in various media [2–5], such as in a Nafion membrane [2–5], and have appeared to be a powerful tool for obtaining information about micro-environments. Therefore, this has greatly stimulated studies illustrating the effects of many constrained and

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organized media on such processes. Media that could support a higher local concentration and thus improve energy transfer efficiency have been noted, such as polyelectrolytes [6].

Micelles and vesicles as simplified models of cell membranes have been used model systems for in vitro investigation [7]. The studies of the physical and chemical processes in highly organized micelles and vesicles are the basis of comprehending complicated mimetic membranes. Therefore, papers on energy transfer processes in these micro-environments have been published [8–13], while most such research has mainly been on improving the efficiency of energy transfer.

In this work, we synthesized three hydrophobic coumarin dyes and used them as energy donors, while hydrophilic dye RB acted as the energy acceptor. The hydrophobic and hydrophilic dye molecules can be separated fully in the micelles and the mixed surfactant vesicles. How energy transfer worked and some other relevant properties have been studied in detail.

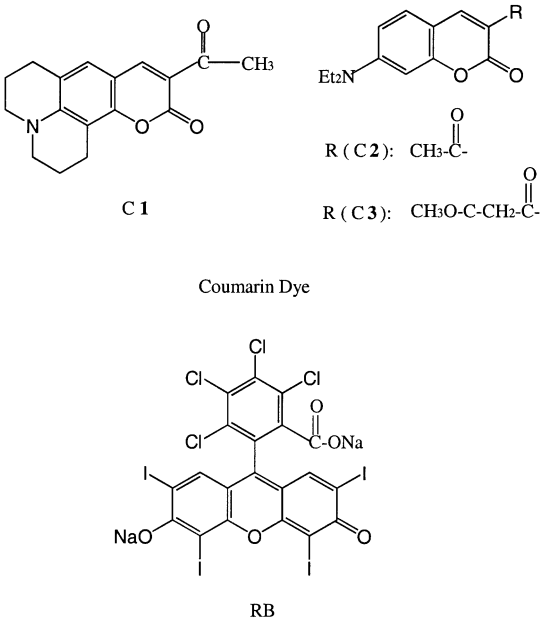

Fig. 1. The structures of coumarin dye and RB.

2. Experiment

2.1. Materials

The coumarin dyes (C **1**, C **2**, C **3**) were synthesized according to [14] and recrystallized before use four times from a mixture of ethanol and acetonitrile. Their structures (Fig. 1) were characterized by NMR and MS. RB was purchased from Sigma Corporation (Fig. 1) and used as received. Dodecyl sulfate, sodium salt (SDS), cetyltrimethylammonium (CTAB) and Triton-X100 (TX-100) were purchased from Aldrich and used as received. The other two surfactants, octyltrimethylammonium bromide (OTAB) and sodium laurate (SL) were also Aldrich products, and were recrystallized twice from ethanol–ether before use. Double distilled water was used throughout this work.

2.2. Methods

2.2.1. Coumarin dyes were solubilized in micelles

The solutions of the coumarin dyes in aqueous detergents were prepared by placing the appropriate amount of choroform stock solutions (the concentration is 1.0×10^{-5} mol/l for all coumarin dyes) in a dry volumetric flask, evaporating the solvent with flushing nitrogen, and redissolving the residue in the detergent stock solution (the concentration of detergents is 1.0×10^{-2}, 6.8×10^{-4} and 2.6×10^{-4} mol/l for SDS, CTAB and TX-100, respectively) with 5 h sonication. Thus, the anionic SDS, neutral TX-100 and cationic CTAB micelles, solubilizing coumarin dyes (1.0×10^{-5} mol/l) were prepared.

2.2.2. Coumarin dyes were solubilized in mixed surfactants vesicles

The solutions of the coumarin dyes in aqueous detergents were prepared by placing the appropriate amount of choroform stock solutions (the concentration is 1.0×10^{-5} mol/l for all coumarin dyes) in a dry volumetric flask, evaporating the solvent with flushing nitrogen, and redissolving the residue in the solution of 0.082 M SL, and 0.082 M OTAB at pH 9.2 and then the mixed solution was sonicated for about 0.5 h at 50 °C. The vesicle samples were successfully prepared. Vesicles were negatively stained with a 2% (w/w)

uranyl acetate solution and examined on a Hitachi H-600 electron microscope to verify its formation.

2.2.3. RB was introduced into micelles and vesicles

High concentration (5.0×10^{-2} mol/l) aqueous RB solution was prepared, and suitable amount of RB was introduced into micelles and vesicles with syringe according to its concentration.

Fluorescence quantum yields were determined using 9,10-biphenylanthracene in cyclohexane ($\phi=0.90$) as a standard.

2.3. Equipment

The absorption and fluorescence spectra were recorded with a Hitachi 330 UV–visible spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, equipped with a differential spectrum correction unit, respectively. The fluorescence quantum yield determination was carried out on a Perkin-Elmer LS-5 fluorescence spectrophotometer equipped with a data processing unit for calculating the integrated intensities. The fluorescence lifetimes were determined on a Horbia NAES-1100 time-correlated single photon counting unit. The lifetimes were calculated from the decay curves using the least-squares method.

3. Results and discussion

3.1. Separation of the coumarin dyes and RB in the micro-enviroments

The absorption and emission of the maxima of the coumarin dyes in 1,4-dioxane and chloroform are shown in Table 1. The maximum absorption and the maximum emission shift to a longer wavelength with an increase in solvent polarity. The results suggest clearly that these compounds are characterized by intra-molecule charge transfer. Therefore, their structures show zwitterionic properties, and should have considerable polarity in the excited state [15]. It would be predicted that all are solubilized in the hydrocarbon region of the micelles, close to polar head for the static electric effect in ionic micelles since they display zwitterionic character. Because C 1 displays a little greater charge transfer, it could be nearer to the polar head in ionic micelles. When they are solubilized in the mixed surfactant vesicles, they all should locate in the bilayer for their hydrophobic group effect. We obtained similar results when pyrene was solubilized in mixed surfactant vesicles [16].

Table 1
The absorption and emission maxima (nm) of coumarin dyes in 1,4-dioxane and chloroform

Medium	C **1**		C **2**		C **3**	
	$\lambda_{a,max}$	$\lambda_{f,max}$	$\lambda_{a,max}$	$\lambda_{f,max}$	$\lambda_{a,max}$	$\lambda_{f,max}$
1,4-Dioxane	437	471	422	459	432	459
$CHCl_3$	451	491	432	464	443	470

Table 2 shows that the media also strongly affect the fluorescence lifetime and fluorescence quantum yields of the compounds. The spectroscopic properties of the compounds in the micelles and the vesicles are similar to those when water acts as medium, indicating that the compounds are affected by water molecules in the micro-environments. This can be understood from the structure properties of the media. Water molecules can penetrate into the micelles, even reaching the hydrocarbon region. For the mixed surfactant vesicles, the outer and inner regions are both aqueous.

The spectroscopic properties of RB in various media are presented in Table 3. The absorption and emission maxima show a negative solvent polar effect, blue shifting with increasing polarity of the media. The fluorescence quantum yields increase in the micelles with respect to those in water, suggesting that microviscosity plays a role in the decay process of the excited state of RB. The fluorescence lifetime of RB in the micelles is longer than that in the water medium, which can be attributed to an increase of structural rigidity in the micelles and thus a reduction of collisional interactions with dissolved oxygen in the bulk solution.

Because of its excellent hydrophilic properties, RB will be solubilized in a Gouy–Chapman layer of the micelles where water molecules reside, and it will prefer locating in the outer aqueous solution of the vesicles when it is added to the vesicles gradually. Thus, the coumarin dyes and RB can be

Table 2
The fluorescence quantum yields and the fluorescence lifetimes of coumarins dyes in water and micelles, and vesicles

Medium	C **1**		C **2**		C **3**	
	τ (ns)	ϕ	τ (ns)	ϕ	τ (ns)	ϕ
H_2O	3.47	0.151	0.392	0.0249	0.592	0.0551
SDS micelles	4.36	0.0806	0.681	0.0479	2.413	0.0479
CTAB micelles	4.33	–	1.118	0.0647	2.309	0.0647
TX-100 micelles	4.72	0.225	0.964	0.241	1.109	0.210
Vesicles	–	0.168	0.337	0.031	0.305	0.044

Table 3
The spectroscopic properties of RB in various media

Medium	$\lambda_{a,max}$ (nm)	$\lambda_{f,max}$ (nm)	τ (ns)	ϕ
H_2O	543	568	0.344	0.010
H_2O/ethanol (v/v = 1/1)	546	572	–	–
SDS micelles	548	573	0.407	0.012
CTAB micelles	557	577	0.989	0.058
TX-100 micelles	561	581	0.865	0.029

separated when they are solubilized in the micelles and vesicles.

3.2. Photo-induced interaction of the coumarin dyes and RB in the microenvironments

Considerable overlaps can be obtained from the fluorescence emissions of the coumarin dyes and the absorption of RB. For instance, Fig. 2 shows the emission of C **2** and the absorption of RB in TX-100 micelles, which suggest that photo-induced energy transfer can take place between them. When RB was added into the micelles and mixed surfactant vesicles solubilizing coumarin dyes, and then the mixture was excited at 380 nm (RB has no any absorption at 380 nm), the fluorescence intensities of the coumarin dyes decreased and the fluorescence intensity of RB increased gradually. An example is presented in Fig. 3, the energy was almost completely transferred from C 2 to RB when the concentration of RB at a higher concentration (3×10^{-4} mol/l) in TX-100 micelles.

The energy transfer efficiency from the relative florescence quantum yields of the donor in the presence and absence of the acceptor is given by:

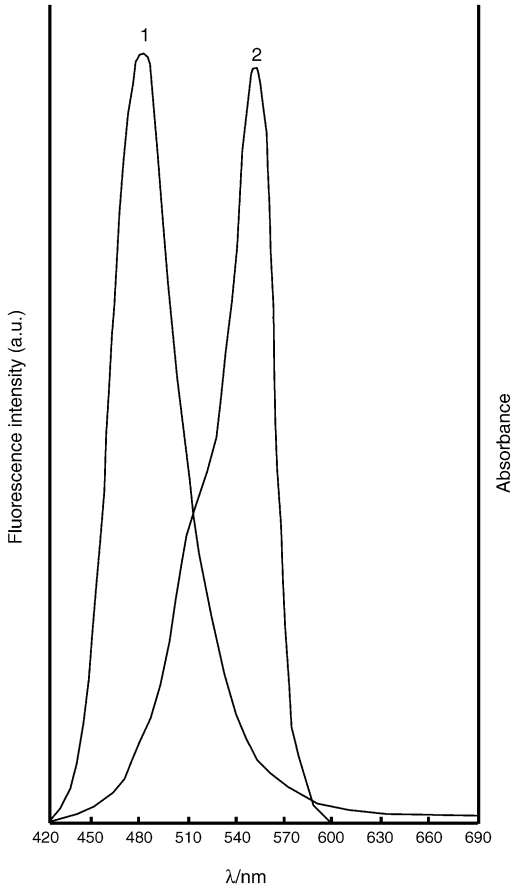

Fig. 2. The fluorescence spectrum of C **2** (1, excited at 380 nm) and absorption spectrum of RB (2) in TX-100 micelles.

$$E = 1 - \phi_{DA}/\phi_D \quad (1)$$

where ϕ_{DA}, ϕ_D are the florescence quantum yields of the donor in the presence and absence of the

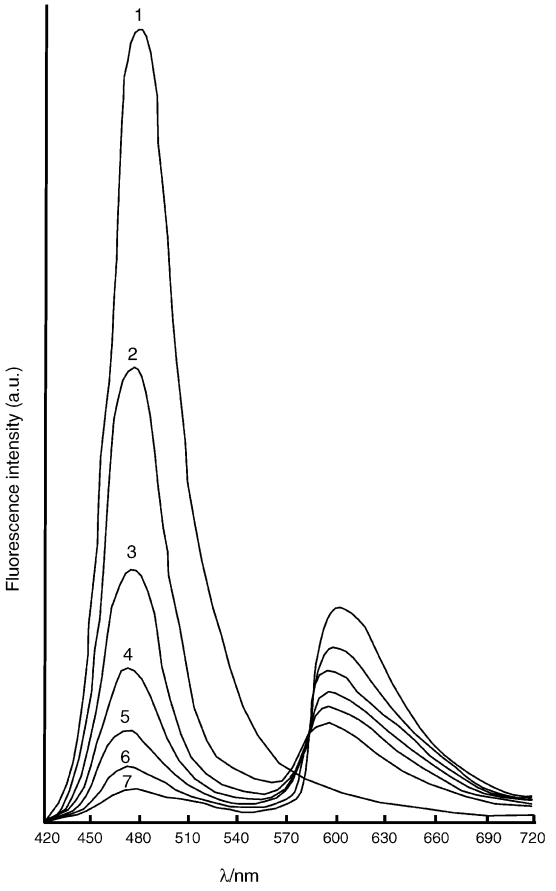

Fig. 3. The fluorescence spectra of C **2** when the RB was added gradually in TX-100 micelles, excited at 380 nm, [c2] = 2×10^{-6} mol/l. The concentration of RB is: 1, 0 mol/l, 2, 5×10^{-5} mol/l,3, 1×10^{-4} mol/l, 4, 1.5×10−4 mol/l, 5; 2×10^{-4} mol/l, 6; 2.5×10^{-4} mol/l, 7; 3×10^{-4} mol/l.

acceptor respectively. Thus, it is an interesting result that, in the same medium, the energy transfer efficiency depended only on the concentration of the acceptor (Table 4).

Another notable result is that the photoinduced energy transfer between the coumarin dyes and RB in the micelles and vesicles did not follow the Stern–Volmer formula [17] (cf. Fig. 4):

$$I_0/I = 1 + K_q \bullet \tau \bullet [Q] \tag{2}$$

while agreeing well with the Perrin formulation [18–20] (Fig. 5a–c):

Table 4
The comparison of photo-induced energy transfer efficiency from C **2** to RB in TX-100 micelles when the concentration of donor is different

[RB]×10^{-5} (mol/l)		5	10	15	20	25	30
E	[a]	44.8	69.9	84.1	89.5	93.7	96.5
	[b]	44.9	69.8	84.1	89.6	93.4	96.8

[a] [C **2**] = 2×10^{-6} (mol/l).
[b] [C **2**] = 2×10^{-5} (mol/l).

$$\ln I_0/I = \ln\ \phi_{DA}/\phi_D = V \bullet N \bullet [Q] \tag{3}$$

where I, I_0 are the fluorescence intensity of the donor in the presence and absence of the acceptor respectively, τ is the fluorescence lifetime of the donor, K_q is the quenching constant, ϕ_D, ϕ_{DA} are the same as in Eq. (1), V is the volume of the active sphere of quenching (in cm^3), N is Avogadro's number, and $[Q]$ is the concentration of quencher in mol/l. Therefore, we can draw the conclusion that the mechanism of photoinduced energy transfer from the coumarin dyes to RB in micelles and vesicles is most likely Förster's dipole–dipole interaction. Because the micelles and vesicles prevent the solute molecules from moving, and the hydrophobic and hydrophilic dye molecules locate at different positions in the micelles and vesicles, the photo-induced interaction process via the diffusion of the donor and the acceptor—dynamic quenching—can be excluded in the micelles and vesicles. It seem that molecules are separated by a long rigid group, and could act through the bridge bond.

So, in the following, based on:

$$V = 4/3 \bullet \pi \bullet R^3 \tag{4}$$

the radius R of the quenching sphere can be obtained. Only if the distance r between the donor and the acceptor lies in the R can the photo-induced energy transfer occur. If $r > R$, such an interaction would not be observed. Table 5 shows how big R is. Even if the donor and acceptor are separated by a long distance (14–20 nm), the photo-induced interaction between the coumarin dyes and RB could proceed. We found that for all

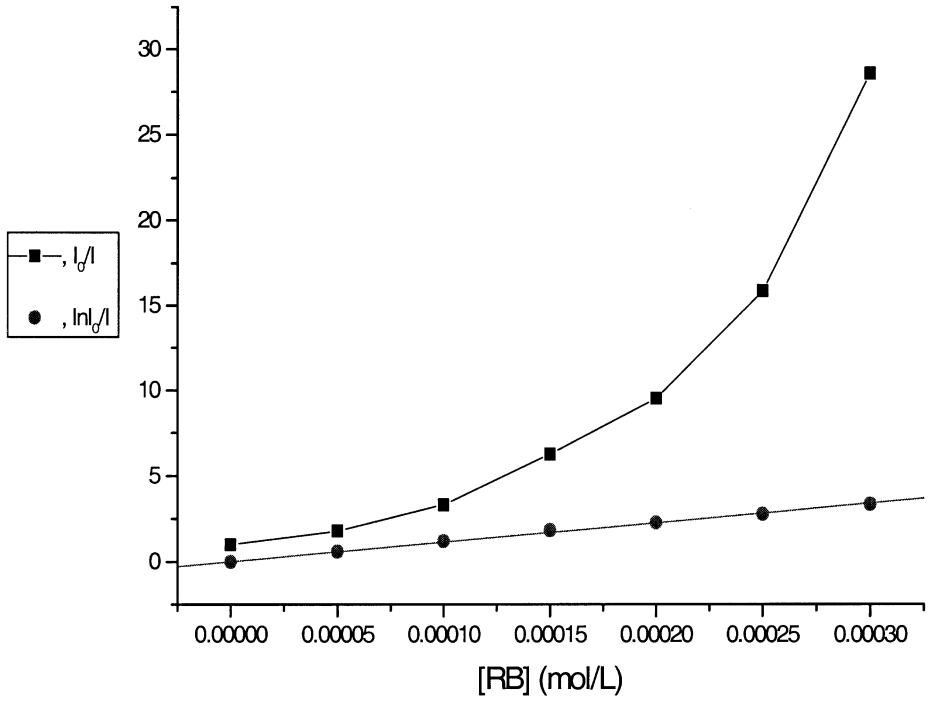

Fig. 4. The plot (straight line) for Perrin equation of C **2** quenched by RB in TX-100 micelles.

the energy transfer pairs, the energy transfer efficiency in the vesicles was lower than that in the micelles, and thus the R is smaller in the vesicles than in the micelles. This is likely because of reduced diffusion in the vesicles due to its higher thermo-stability and semi-rigid bilayer membrane.

In order to understand further photo-induced interaction of the coumarin dyes and RB in the micelles and vesicles, we determined the distance r between them according to Förster's theory. Nnumerial integration was used to give a spectral overlap integral J ($mol^{-1}\bullet cm^6$):

$$J = \int_0^\infty F_D(\lambda) \bullet \varepsilon_A(\lambda) \bullet \lambda^4 \bullet d\lambda \quad (5)$$

in which $F_D(\lambda)$ is the donor florescence intensity at λ and $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at λ. Thus, the critical energy transfer distance, R_0, defined as the distance at which the rate of energy transfer and inherent rate of deactivation of excited molecules are equal, was calculated from the spectral properties using the following equation:

$$R_0^6 = 9000 \ln(10) \bullet \kappa^2 \bullet \phi_D \bullet J/128 \bullet \pi 5 \bullet \eta 4 \bullet N \quad (6)$$

where J is the spectral overlap integral ($mol^{-1}\bullet cm^6$), κ^2 (0.0476) is the orientation factor, ϕ_D is fluorescence quantum yield of the donor in the absence of the acceptor, η (1.334) is the refractive index of the medium, and N is Avogadro's number. The donor–acceptor distance r can be obtained from the energy transfer efficiency E and R_0, using the following relation:

$$E = R_0^6/r^6 + R_0^6 \quad (7)$$

The values of R_0 and r for the different donor–acceptor pairs in various media have been calculated and listed in Table 6. The results show clearly that the distances between the coumarin dyes and RB lie within the quenched radius, and thus we did find that photo-induced interaction between them takes place efficiently. The value of the critical energy transfer distance R_0 falls within

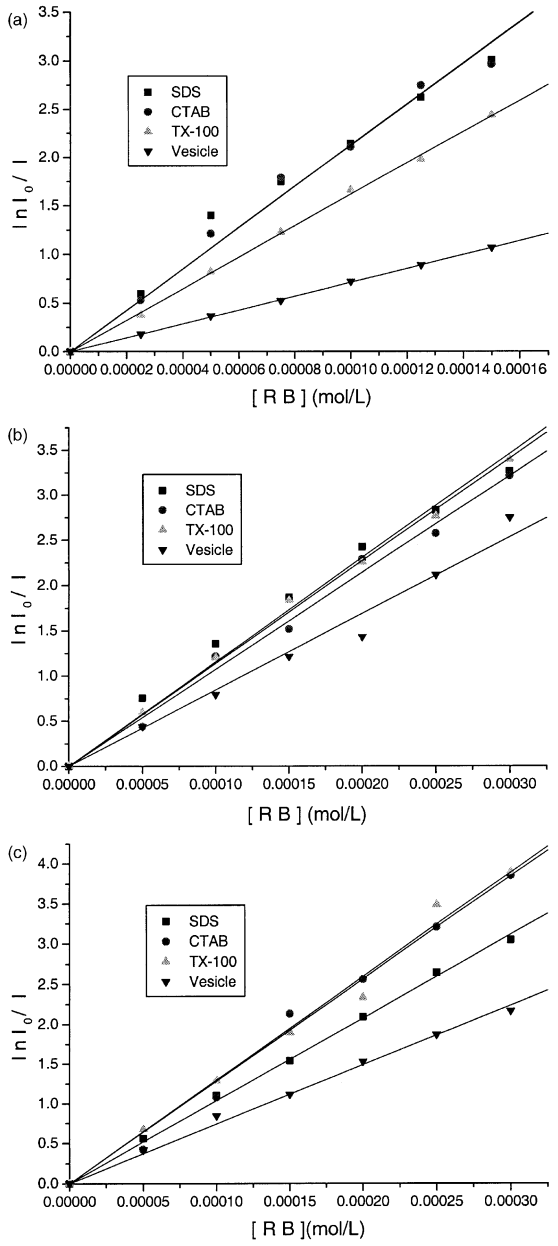

Fig. 5. The Perrin plot for quenched florescence of (a) C **1**, (b) C **2**, (c) C **3** by RB in different micro-environments.

the range of 4–5 nm, indicating that energy transfer can proceed even at great donor–acceptor distances.

We observed for a given energy transfer pair, the distance r in TX-100 micelles is bigger than in ionic micelles. Furthermore, in ionic micelles, the r is a little smaller for C**1**-RB than for the other energy transfer pairs. The results confirm our prediction that the dyes should be close to the polar head in ionic micelles, particularly in the case of C 1 given its somewhat higher polarity.

Table 5
The quenching radius R (nm) for different photo induced energy transfer pair in various media

ET pair	SDS micelles	CTAB micelles	TX-100 micelles	Vesicles
C **1**–RB	20.4	20.3	18.6	14.1
C **2**–RB	16.6	16.2	16.5	14.1
C **3**–RB	16.0	17.2	17.3	14.3

Table 6
The calculated critical energy transfer distance R_0 (nm) and the distance r (nm) for different photo-induced energy transfer pair in various media

Medium	C**1**–RB			C **2**–RB			C **3**–RB		
	E	R_0	R	E	R_0	r	E	R_0	r
SDS micelles	75.4	4.61	3.82	52.9	4.60	4.51	43.0	4.54	4.76
CTAB micelles	70.3	4.84	4.19	35.4	4.62	5.10	34.5	4.52	5.03
TX-100 micelles	55.5	5.11	4.93	44.8	5.19	5.37	49.3	5.17	5.19
Vesicles	30.0	4.50	5.18	35.5	4.32	4.77	34.5	4.46	4.97

E: the photo-induced energy transfer efficiency at [RB] = 5×10^{-5} mol/l.

4. Conclusion

We have chosen the hydrophobic and hydrophilic dye molecules that can be separated fully in micelles and vesicles to study their photoinduced interaction at nanometer distances in micelles and mixed surfactant vesicles. The results show that even at 4–5 nm separated distance, the dyes still displayed strong a photo-induced interaction, which can be explained by a static, not dynamic, mechanism.

Acknowledgements

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