Synergistic dynamics of photoionization and photoinduced electron transfer probed by laser flash photolysis and ultrafast fluorescence spectroscopy

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Abstract

Photoionization (PI) and photoinduced electron transfer (PET) dynamics of coumarin 450 (C450) in micelles were investigated in the time domains of micro to femtoseconds using steady-state and time-resolved absorption and fluorescence spectroscopy. The PI of C450 occurs inside the micelles leads to the formation of C450 cation radical (CR) and hydrated electron, which is characterized by the respective transient absorption. The PI of C450 is monophotonic in nature and the yield is dependent on the charge of the micelles. The observation of amine CR in the transient absorption confirms the PET from amine to the excited state of C450 in micelles, which results in the quenching of both fluorescence intensity and lifetime. The decrease in femtosecond fluorescent decay of C450 and the absence of transient C450 radical anion in the presence of amine implies that the concerted ultrafast PET promoted PI and PET to the C450 CR–electron pair. The decrease in the time constant for the formation of relaxed state in the presence of amines is due to the ultrafast PET to the C450 CR–electron pair, which prevents the formation of a relaxed state through recombination at a longer time scale. In the present investigation, the recombination dynamics of the CR–electron pair is justified as one of the origins of the slow solvation in micelles. The influence of amine concentration on the decay of C450 CR indicates ET reaction between C450 CR and amine, which is further confirmed by the bleach recovery of C450 ground state in the presence of amine.

Pushing the limits of flash photolysis to unravel the secrets of biological electron and proton transfer - a topical issue in honour of Klaus Brettel.

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Graphic abstract

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1 Introduction

The photoinduced excited-state processes of small organic molecules play a significant role in several fields including chemistry, biology, etc. to unravel many physicochemical processes in nature [1–6]. Among the photoinduced processes, the dynamics of electron transfer (ET) and photoionization (PI) are greatly influenced by the microheterogeneity of soft matter and its environments. Many biological processes are composed of complex reactions, such as DNA repair, stimulating sensory proteins, etc., that are mainly governed by electron transfer [7–13]. The ET reaction denotes the movement of an electron from donor atom/molecule to acceptor which generally occurs in a fast time scale. The efficiency of transferring electrons may be influenced by several factors especially the microenvironment of the molecules around them [13]. Thus, the dynamic of ET turns out to be an essential aspect to determine the mechanism of mimic biological processes, the dynamics involved in complex systems can be resolved from a known simple system. As similar to ET, photoionization is a significant process that generates transient radical ions and hydrated electron pairs in the aqueous medium [14–18]. In many biological and chemical processes, the dynamic of hydrated electrons such that the rate of generation and recombination provide information about the surrounding environment [18–20]. The hydrated electrons yield can be calculated from the competing processes, such as recombination and solvation

of the initially formed radical ion–electron pair. In a biological environment, the suppression of charge recombination processes by the surrounding environment results in a higher photoionization yield. The higher efficiency of photoionization can be achieved in organized media due to the efficient charge separation process by compartmentalization of photoionization products [18, 21, 22].

Micelles are self-assembled organized media that are formed by amphiphilic molecules at a specific concentration in an aqueous solution. The micellar system exhibits core–shell morphology in which the core of the micelle is composed of hydrophobic tails components, whereas hydrophilic headgroups components are present in the micellar shell (Stern/palisade layer). This heterogeneity feature of micelles resembles the biological microenvironments, thus the study of photoinduced processes in micelles remains to be a thriving research field in photochemistry [6, 18, 21]. The photoionization is promoted by micellar charge through the efficient separation of the electron by coulombic forces. Earlier scientific results imply that the yield of photoionization is higher in the micellar environment through efficient charge separation [18, 22].

Similarly, the dynamics of ET rely on the features of micelles, for instance, the amphiphilic nature of micelles facilitates a short distance between the donor and acceptor molecules leads to ultrafast ET. Previously, many groups have studied the PET process in various micellar systems to understanding the ET dynamics [17, 23–28]. It was reported

that the ultrafast ET dynamic was greatly influenced by the solvation process, because both processes occur in the time domain of pico- to femtoseconds thereby competing with each other [23, 25]. The solvation dynamics of water molecules present in the organized assemblies such as micelles were reported to be ~100–1000 times slower than the bulk water. The origin of the slow dynamics displayed by the water molecules in micelles and other organized assemblies was extensively studied for the past two decades and still needs to be explored. In addition to the influence of solvation dynamics, the photoionization process may influence the ET dynamics. Thus, it is of great importance to unveil the remaining important facets involved in the reaction mechanism behind these photoinduced and excited-state processes.

Laser flash photolysis (LFP) is a broadly used technique for investigating fundamental photoprocesses, such as ET kinetics, the formation of short-lived excited states, formation of radical ions and their subsequent recombination, and transient species formed during photoionization [29–31]. The intense laser pulse generates a short-lived transient species of a sample that leads to changes in the absorption characteristics. In a flash photolysis spectrometer, the resultant absorption changes due to laser pulse excitation can be monitored as a function of time by applying a probe beam through the sample. Transient absorption studies can be performed with time resolutions from picoseconds to seconds which facilitates the detection of photoinduced reaction dynamics. In this work, the excited-state dynamics of coumarin 450 (C450, Scheme 1) were investigated by a combination of laser flash photolysis with steady-state and time-resolved fluorescence spectroscopy to gain more insight into the dynamics of photoinduced processes. In general, coumarin dyes are utilized as a fluorescent probe to investigating several physiochemical processes and the properties of microenvironments in heterogeneous media [23, 25, 27, 32–35]. Previously, we have investigated the photoionization and solvation dynamics of coumarin 307 (C307) in micelles in which the radical-ion pair recombination dynamics were probed using time-dependent Stokes shift in combination with time-resolved transient absorption studies [18]. In the present study, the synergistic dynamics of photoionization and photoinduced electron transfer of C450 were investigated to probe the impact of photoionization on the dynamics of the electron transfer process. In general, the photophysical and

Scheme 1 Structure of C450

photochemical properties of coumarin dyes are dependent on the substituent at the 4th and 7th positions of the dye. The main difference between the C307 and C450 is a substituent at the 4th position such that C307 has an electron-withdrawing group (CF_3), whereas in the case of C450, the electron-donating group (CH_3) present at the 4th position. It is anticipated that the presence of either electron-withdrawing or donating group might influence the photoionization and electron transfer processes of coumarin. The radiative and non-radiative processes are mainly influenced by the substituents, because the stronger electron-withdrawing trifluoromethyl group at the 4th position causes an increase in the radiative process and a decrease in the non-radiative ISC process. Thus, the photoionization efficiency may be governed by the substituent at the 4th position of coumarin dye. Moreover, the extent of fluorescence quenching also depends on the substituent group at the 4th and 7th positions of the coumarin dyes.

Three diverse kinds of micelles including anionic micelles (sodium dodecyl sulfate, SDS), cationic micelles (cetyltrimethylammonium bromide, CTAB), and neutral micelles (Triton X-100, TX-100) were used in the present investigation. The LFP technique was applied to examine the photoionization process of C450 in all micelles. The steady-state and time-resolved fluorescence measurements were performed to demonstrate the PET process between C450 and aromatic amines. The C450 dye was served as an electron acceptor, while the aromatic amines, namely, aniline (AN), *N*-methylaniline (MAN), and *N,N'*-dimethylaniline (DMAN), were used as an electron donor. The ultrafast ET dynamics were investigated using a femtosecond upconversion technique, while the evidence for the excited-state ET process and respective mechanism were verified by the nanosecond transient absorption measurements.

2 Experimental section

2.1 Materials

Laser grade C450 dye was purchased from Exciton. Surfactants (SDS, CTAB, and TX-100) were purchased from Sigma-Aldrich and SRL chemicals. Aromatic amines were purchased from SRL chemicals. Milli-Q water was used to prepare micellar solutions. The C450 dye was dissolved in all micellar solutions with a concentration of ~10 μM . The concentration of each micellar solution was fixed to be 0.06 M which is higher than the critical micellar concentration (CMC). The CMC of SDS, CTAB, and TX-100 surfactant is 8.3, 0.80, and 0.24 mM, respectively [18, 36].

2.2 Methods

The absorption and fluorescence spectra were monitored with an Agilent 8453 UV–visible diode array and Fluoromax-4 (Horiba Jobin Yvon) spectrometer, respectively. Nanosecond laser flash photolysis (Applied photophysics, U.K.) was utilized to perform transient absorption experiments. The third harmonic (355 nm, pulse width-8 ns, pulse energy-150 mJ) output from the Q-switched Nd:YAG laser (LAB 150, Quanta-Ray, Spectra-Physics, USA) was applied to excite the sample. The white light from a 150 W xenon lamp was used to probe the transient species produced by the laser excitation. The xenon lamp output was pulsed through the arc lamp pulser (Applied photophysics, U.K) during the transient measurements. The transmitted light from the sample was passed through a Czerny–Turner monochromator and the intensity was monitored by a photomultiplier tube (R-928, Hamamatsu) with a 5-stage photomultiplier base (Applied Photophysics). The transient signals were captured with an Agilent Infinium digital storage oscilloscope (500 MHz) followed by transferring data to the computer. The samples were purged with argon or N₂O gas for 45 min before irradiation of laser.

The time-correlated single-photon counting (TCSPC) technique was utilized to acquire fluorescence lifetime decays using a femtosecond laser (750 nm, Tsunami, Spectra-Physics). The flexible harmonic generator was applied to generate second harmonics laser (375 nm) output as an excitation source. The ultrafast fluorescence dynamics were examined with a femtosecond upconversion system (FOG 100, CDP, Russia). The samples were irradiated by a second harmonic laser pulse (~380 nm) from a mode-locked Ti–sapphire laser. The detailed information for TCSPC and femtosecond upconversion setup is given in the supporting information.

3 Results and discussion

3.1 Steady-state absorption and fluorescence studies

To understand the location of C450 in micelles, the absorption and emission spectra of C450 were recorded in different micelles and solvents, and the resultant spectra are shown in Fig. 1 and the respective peak maxima and Stokes shifts are given in Table S1. The absorption spectra of C450 show the longer wavelength absorption peak at ~365 nm in polar solvents and micelles, whereas the absorption is blue-shifted in hexane (343 nm). This longer wavelength absorption peak is due to the charge transfer from the amino group to the carbonyl group that occurs intramolecularly within C450 (Scheme S1) [18, 23]. On increasing the solvent polarity, the absorption and emission maxima of C450 were shifted to the longer wavelength region. Similarly, the Stokes shifts were found to be higher in polar solvents compared to that of non-polar solvents. For instance, the Stokes shift of C450 in hexane and water was observed to be 3180 and 5397 cm⁻¹, respectively. Though the methanol is less polar than acetonitrile, the Stokes shift of C450 in methanol shows a higher value compared to that of acetonitrile. The obtained high Stokes shift in methanol is due to the hydrogen bonding interaction between the C450 (amino or carbonyl group) and methanol [18, 37]. It clearly implies that the absorption and emission behavior of C450 was strongly influenced by both the polarity and hydrogen bonding ability of the solvents.

The micelles allow three different locations (bulk aqueous phase, Stern/palisade layer, and nonpolar hydrocarbon core) for the probe to reside and the polarity inside the micelles is less than the water. In all micellar solutions, the Stokes shift of C450 was found to be ~4700 cm⁻¹ which is similar to the value observed in methanol (4646 cm⁻¹). The C450 in all micelles shows a lower Stokes shift value when compared to water (5397 cm⁻¹), while it shows much higher value than in hexane (3180 cm⁻¹). These findings confirm that the C450 dyes

Fig. 1 Normalized absorption and fluorescence spectra of C450 in various micelles and solvents

are favorably located in the Stern/palisade layer of the micelles rather than in the aqueous phase and micellar core region. Moreover, as observed in methanol, the weak hydrogen bonding interaction might possible between the dyes with water molecules present in the Stern/palisade layer of the micelles. The absorption maximum of C450 in all the micelles shows a redshift as compared to water which further supports the hydrogen bonding interaction. The presence of an electron-donating methyl group at the 4th position of C450 stabilizes the ground state through hydrogen bonding interaction with water. The magnitude of the redshift is more in SDS and CTAB micelles when compared to TX-100. It indicates that the ground state of C450 is more stabilized in ionic micelles by water molecules and the probe stays in the Stern/palisade layer of the micelles [18].

3.2 Time-resolved nanosecond transient absorption studies of C450

The nanosecond laser flash photolysis measurement was performed to investigate the characteristics of the excited-state processes, such as photoionization, triplet states in micelles. The transient absorption spectra of C450 in SDS, CTAB, and TX-100 micelles under argon and N_2O saturated conditions were recorded by exciting at 355 nm and the resultant spectra along with the transient decays are presented in Fig. 2. The C450 in all micellar systems shows broad absorption in the wavelength range 450–750 nm with a peak maximum at ~610 and 710 nm (Fig. 2a, c, e). In the presence of electron scavenger (N_2O), the transient absorption peak at 710 nm disappears in all the micelles which confirms that the transient absorption peak at 710 nm is due to the hydrated electron [18, 38]. The hydrated electron decay at

Fig. 2 Transient absorption spectrum of C450 in (a) SDS, (c) CTAB, and (e) TX-100 micelles recorded at 1 μ s after the laser flash under argon and N_2O saturated condition (λ_{ex} = 355 nm). The transient decay monitored at 610 and 710 nm under argon saturated condition (b) SDS, d) CTAB, and f) TX-100 micelles)

710 nm follows the pseudo-first-order rate equation and the lifetime of the hydrated electron was calculated from the rate constant. The lifetime of the hydrated electron was found to be 5.5, 1.8, and 3.9 μs in SDS, CTAB, and TX-100 micelles, respectively. The observation of hydrated electrons indicates photoionization of C450 occurs upon excitation, which leads to the formation of a C450 radical cation and hydrated electron (Scheme S1) [18, 38].

Since the hydrated electron absorbs in the wavelength range of 500–750 nm, the absorbance of a transient peak at 610 nm was effectively scavenged by N_2O which leads to a decrease in the transient absorption in all the micelles. The transient absorption decay monitored at 610 nm has two decay components (short-lived and long-lived) in all micelles under argon saturated conditions and was not affected in the presence of N_2O (Fig. 2b, d, f). Previously, Dhenadhyalan et al. reported photoionization of C307 in micelles results in the formation of coumarin cation radical and hydrated electron with a peak maximum of 600 and 710 nm, respectively [18]. Based on that, the transient peak observed at 610 nm for C450 in all micelles is assigned to the radical cation of C450 [18, 38, 39]. The lifetime of a short-lived component at 610 nm was estimated to be 7.1, 2.6, and 6.2 μs , while the long-lived component exhibited 139, 94, and 77 μs lifetime in SDS, CTAB, and TX-100 micelles, respectively. The bi-exponential behavior indicates that the short-lived component originated from the radical ion–electron pair in which the radical cation still in contact with a hydrated electron, whereas the long-lived component belongs to the well-separated radical cation from the radical ion–electron pair.

The photoionization efficiency of C450 in micelles was calculated using the molar extinction coefficient at 710 nm ($18,000 \text{ M}^{-1} \text{ cm}^{-1}$) [38], the absorbance of a hydrated electron (at 200 ns) at the 150 mJ excitation pulse energy and the concentration of C450 in the ground state. The photoionization efficiency was evaluated using the following equation [18, 40]:

$$PI(\%) = \frac{\Delta A_{710} \times 100}{\epsilon_{710} \times [C450]}$$

The photoionization efficiency of C450 was estimated to be 91, 13, and 62% in SDS, CTAB, and TX-100 micelles, respectively. This finding reveals that the efficiency of photoionization depends on the nature of the Stern/palisade layer in terms of separation and recombination of the radical-ion and hydrate electron pairs. In anionic SDS micelles, the formed hydrated electrons in the negatively charged Stern layer are readily expelled into the aqueous phase due to the electrostatic repulsion and leave the coumarin radical cation inside the Stern layer by electrostatic attraction. This effective separation between radical cation and hydrated electron

pairs could enhance the photoionization efficiency in SDS micelles. Furthermore, the effective separation between radical-ion pairs was confirmed by the observed long lifetime (139 μs) of coumarin radical cation in SDS compared to that of CTAB and TX-100 micelles. In the cationic micelles (CTAB), the radical cation and hydrated electron pairs undergo fast recombination due to less favorable separation. The hydrated electron and radical cation are located in the positively charged Stern layer of CTAB micelles owing to electrostatic attraction and hydrophobicity of the coumarin cation radical. In the non-ionic TX-100 micelles, there are no electrostatic effects in the palisade layer, and the products of the photoionization can be freely diffused in a large thickness. Consequently, the photoionization efficiency of C450 in micelles follows the order of $\text{SDS} > \text{TX-100} > \text{CTAB}$.

To confirm whether the photoionization process of C450 in micelles is mono-photon or multi-photon, the transient decay of the hydrated electron was recorded by varying the laser pulse energy [41]. The plot of hydrated electron absorbance at 710 nm against the laser pulse energy is found to be linear in all the micelles (Figure S1) and the value of the slope is close to unity (Table S2). It confirms that the photoionization of C450 in the micellar medium is mono-photon [18, 41].

3.3 Fluorescence quenching studies of C450 by amines in micelles

Steady-state absorption and fluorescence spectra of C450 in the presence of aromatic amines (AN, MAN, and DMAN) were recorded in SDS, CTAB, and TX-100 micelles. The resultant absorption spectra in each micelle show that the longer wavelength absorption peak of C450 at $\sim 370 \text{ nm}$ was not affected even in the presence of higher concentrations of amines (Figure S2). This finding confirms that there is no ground-state interaction between the C450 and amines. On the other hand, the fluorescence intensity of C450 at $\sim 448 \text{ nm}$ was found to gradually decrease with increasing concentrations of amine (Fig. 3a–c) due to the strong interaction of C450 with amines in the excited state. There is no change in the spectral shape of the emission spectra was observed in all micellar systems which ruled out the formation of exciplex [24]. The amine molecules tend to locate in the Stern/palisade layer [42, 43] as similar to C450 dyes. It is well known, the coumarin dyes and aromatic amines act as excellent electron acceptors and electron donors, respectively [23, 43]. Thus, the observed quenching of fluorescence intensity is ascribed to the photoinduced electron transfer (PET) from the amine to the excited C450.

The Stern–Volmer (S–V) analysis for the steady-state quenching of C450 fluorescence by amines was carried out to determine the bimolecular quenching rate constants using the following equation [44]:

Fig. 3 a–c Fluorescence spectra of C450 with the addition of different concentrations of DMAN in different micelles. d–f Stern–Volmer plots of C450-amine systems in different micelles. (a, d) SDS, (b, e) CTAB, and (c, f) TX-100

$$\frac{I_0}{I} = 1 + K_{SV}[Q]_{eff} = 1 + k_q\tau_0[Q]_{eff}$$

where I and I_0 are the fluorescence intensity of C450 in the presence and absence of amine, respectively. K_{SV} and k_q are the Stern Volmer constant and bimolecular quenching rate constant, τ_0 is the fluorescence lifetime of C450 without amine, and $[Q]_{eff}$ is an effective concentration of amine in the micellar phase (supporting information). Here, the effective quencher concentration was used instead of the total amine concentration, because the concentration of amines in the micellar Stern/palisade layer will be higher than the total amine concentration used in the solution [23, 24].

The resultant S–V plots exhibit linearity at initial concentrations, whereas a positive deviation from the linearity was observed at higher amine concentrations in each micellar system (Fig. 3d–f). The upward curvature indicates the presence of transient quenching due to the proximity

of C450-amine pairs [44–46]. The bimolecular quenching rate constants were determined from the linear plot at initial concentrations of amine and the resultant values are listed in Table 1.

3.4 Time-resolved fluorescence quenching studies with amines

3.4.1 Picosecond time-resolved fluorescence quenching studies

To further understand the quenching mechanism, the time-resolved fluorescence measurements were carried out in each micellar system by monitoring fluorescence lifetime changes of C450 in the presence of amines. The fluorescence decay of C450 (without amine) was recorded in each micelle at their fluorescence maximum (448 nm) which exhibited a single exponential decay with a lifetime of 4.85, 4.56, and

Table 1 Quenching rate constants (k_q) of C450-amine in SDS, CTAB, and TX-100 micelles acquired from steady-state (S-S) and time-resolved (T-R) fluorescence measurements

Amines	k_q ($\times 10^9$ M $^{-1}$ s $^{-1}$)					
	SDS		CTAB		TX-100	
	S-S	T-R	S-S	T-R	S-S	T-R
AN	1.85	1.37	0.56	0.40	3.32	1.60
MAN	4.58	2.61	1.24	0.75	6.51	2.88
DMAN	4.22	2.23	1.12	0.67	4.77	2.43

4.88 ns in SDS, CTAB, and TX-100, respectively. With an increase in the concentration of amines, the fluorescence decay of C450 was drastically quenched in all micellar systems, as presented in Fig. 4. The fluorescence decays of C450 follow bi-exponential function and the fluorescence lifetime was found to gradually decrease with increasing concentrations of amine which confirms the PET between the C450 and amines.

The rate constants for time-resolved fluorescence quenching were calculated using the S–V equation [44]:

$$\frac{\tau_0}{\tau_{\text{avg}}} = 1 + K_{\text{SV}}[Q]_{\text{eff}} = 1 + k_q\tau_0[Q]_{\text{eff}}$$

where τ_0 and τ_{avg} are the fluorescence lifetime of C450 in the absence of amine and an average lifetime of C450 in the presence of amine, respectively. The resultant Stern Volmer plots display linearity even at higher concentrations of amine for each C450-amine-micellar system (Fig. 4). The linear plot reveals that the observed fluorescence quenching is due to the dynamic quenching process (Scheme S2). Because the transient quenching process due to the proximity of C450-amine pairs and takes place in ultrafast time scale (sub-picosecond). Thus, it is not possible to detect a transient quenching process with the present picosecond TCSPC setup. The rate constants calculated from the slope of the linear plot are listed in Table 1. The observed rate constant values are lower than that of the values obtained

through steady-state fluorescence measurements. It could be due to the involvement of both dynamic and transient quenching processes in steady-state measurements, whereas in the case of time-resolved measurements, the observed quenching rate constants are attributed to dynamic quenching processes only.

It is evident from Table 1, the estimated PET rate constants obtained in TX-100 are higher than those obtained in SDS and CTAB micelles. The rate constants increase in the order of TX-100 > SDS > CTAB. The bimolecular quenching rate constant in micelles is dependent on the nature of micellar headgroups, counterions, and thickness of the Stern/palisade layer. The positively charged head groups and larger size of the bromide counterions in the stern layer are responsible for the lower PET rate constant value in CTAB micelles. The strong electrostatic attraction between the electron and positive charge of the Stern layer makes the PET less favorable in CTAB as compared to SDS and TX-100 micelles. In addition, the bulky bromide counterions in CTAB micelles may increase the distance between coumarin and amine due to steric repulsion [23]. Consequently, the PET process in CTAB micelles is significantly suppressed and leads to a lower PET rate constant. In SDS micelles, the electrostatic repulsion between the negatively charged Stern layer and electron enhances the rate constant compare with that of CTAB micelles. The PET is more favorable in TX-100 micelles due to the absence of electrostatic and steric effects in the palisade layer of the

Fig. 4 a–c Fluorescence decays of C450 with the addition of different concentrations of DMAN in different micelles. d–f Stern–Volmer plots of C450-amine systems in different micelles. (a, d SDS, b, e CTAB, and c, f TX-100)

TX-100 micelles. In TX-100, due to the large thickness of the palisade layer as compared to SDS and CTAB micelles, more quencher molecules present in the palisade layer and thereby enhancing ET rates [47].

3.4.2 Femtosecond time-resolved fluorescence quenching studies

The femtosecond fluorescence up-conversion technique was employed to investigate the ultrafast photoinduced electron transfer by monitoring the fluorescence decays of C450 in the absence and presence of amines in each micelle at the blue end ($\lambda_{\text{emi}} = 410$ nm) and red end ($\lambda_{\text{emi}} = 500$ nm) of the fluorescence spectrum (Fig. 5). Upon excitation, the C450 dye is excited to an initially populated state (Franck–Condon state) and then relaxes to the first excited state (relaxed state) which represents the shorter (blue end) and longer (red end) wavelength region of the fluorescence spectrum, respectively. The acquired ultrafast fluorescence decays of C450 monitored at 410 nm (blue end) in the absence of amines in all micellar systems were fitted by tri-exponential function with components of ultrafast decay (τ_1) and fast decay (τ_2) along with nanosecond decay component (τ_3) detected in TCSPC setup (Fig. 5a–c, Table 2). The ultrafast decay component (τ_1) was found to be ~ 15 ps in SDS, whereas in the case of CTAB and TX-100, it was found to be ~ 2 ps

with a negative pre-exponential factor. The negative pre-exponential factor for the ultrafast decay component in CTAB and TX-100 micelles is presumably attributed due to the formation of a relaxed state through the recombination of C450 radical cation and solvated electron. A similar rise time has been reported for C307 through the formation of a relaxed state by the radical-ion pair recombination in TX-100 micelles [18]. Such recombination is not possible in SDS micelles due to the negative charge of the Stern layer. The absence of the rise component in the decay monitored at 410 nm in SDS micelles confirms the role of photoionization and subsequent recombination in the formation of relaxed state and solvation dynamics [23, 43, 47].

The fast decay component (τ_2) was found to be ~ 222 , 353, and 438 ps in SDS, CTAB, and TX-100 micelles, respectively, which is assigned to the decay of Franck–Condon (FC) excited state. The FC excited state of C450 relaxes to the ground state by the radiative transition. Photoionization and solvent relaxation processes are the important non-radiative relaxation from the FC state which competes with radiative relaxation. The lifetime of the ultrafast and fast decay components of C450 was found to decrease with an increase in the concentration of amine, which clearly reveals that the ultrafast electron transfer between the C450 excited state and amine. Interestingly, the fast decay component (τ_2) was drastically quenched

Fig. 5 Femtosecond fluorescence decays of C450 with the addition of different concentrations of DMAN in different micelles monitored at (a–c) blue-end (410 nm) and (d–f) red-end (500 nm). (a, d) SDS, (b, e) CTAB, and (c, f) TX-100

Table 2 Femtosecond fluorescence decay parameters of C450 in micelles monitored at 410 nm

Micelles	Amine	[Amine] (mM)	[Amine] _{eff} (M)	τ_1 (ps); (a ₁ %) ^{a,c}	τ_2 (ps); (a ₂ %) ^{a,c}	τ_3 (ns) ^b
SDS	AN	0	0	18.92 (11)	222.28 (89)	4.85
		3.25	0.0865	20.06 (26)	187.03 (74)	3.89
		15.02	0.4003	11.45 (55)	101.29 (45)	2.15
	MAN	3.25	0.0865	20.07 (15)	183.31 (85)	3.27
		15.02	0.4003	9.83 (30)	90.83 (70)	1.12
	DMAN	3.25	0.0865	14.77 (32)	177.00 (68)	3.09
CTAB	AN	0	0	2.73 (−0.32)	353.77 (100.32)	4.80
		3.25	0.2826	1.31 (−0.25)	334.26 (100.25)	3.71
		15.02	1.3072	0.77 (−0.23)	102.48 (100.23)	1.86
	MAN	3.25	0.2826	1.45 (−0.20)	295.36 (100.20)	3.30
		15.02	1.3072	0.68 (−0.18)	105.40 (100.18)	1.52
	DMAN	3.25	0.2826	3.11 (−0.30)	276.76 (100.30)	3.30
TX-100	AN	0	0	2.19 (−0.44)	438.49 (100.44)	4.91
		3.25	0.0195	0.82 (−0.35)	284.23 (100.35)	3.47
		15.02	0.0906	0.69 (−0.29)	101.38 (100.29)	2.52
	MAN	3.25	0.0195	0.74 (−0.29)	378.41 (100.29)	3.28
		15.02	0.0906	0.61 (−0.27)	81.25 (100.27)	2.01
	DMAN	3.25	0.0195	0.98 (−0.25)	382.93 (100.25)	3.27
		15.02	0.0906	0.92 (−0.31)	77.86 (100.31)	2.00

^aAmplitudes are listed within parentheses; amplitude contribution was calculated from the initial decay components (τ_1 and τ_2), neglecting the contribution of the long ns component

^bFrom TCSPC setup

^cError $\pm 10\%$

Table 3 Ultrafast PET rate constant (k_{et}) for the C450-amine systems in all micelles

Amines	k_{et} ($\times 10^{10} \text{ s}^{-1}$) ^a		
	SDS	CTAB	TX-100
AN	0.97	0.96	0.97
MAN	1.08	0.93	1.21
DMAN	1.49	1.16	1.26

^aError $\pm 5\%$

by amine which implies that the ultrafast electron transfer competes with the solvation and photoionization process. The rate constants (k_{et}) for the ultrafast PET were estimated using fast decay component (τ_2) in the following equation [43, 44]:

$$k_{et} = \frac{1}{\tau_2} - \frac{1}{\tau_0}$$

where τ_2 is the fast decay lifetime of C450 with amine (15 mM) and τ_0 is the fluorescence lifetime of C450 in the absence of amine (which is obtained from TCSPC). The determined ultrafast PET rate constants are in the order of $\sim 1 \times 10^{10} \text{ s}^{-1}$ in all C450-amine-micellar systems

(Table 3), which are higher than the values obtained using the TCSPC setup. The ultrafast electron transfer promotes the photoionization of C450 which is explained in the following section.

The femtosecond fluorescence decays recorded at 500 nm (red end) were analyzed to verify the competing reaction between the solvation and ultrafast PET. As shown in Fig. 5d–f and Table S3, the fluorescence decays of C450 in the absence of amine exhibit a rise component in all micelles that corresponds to the formation of a relaxed excited state [23, 43, 47]. The time constant for the rise component decreases with an increase in the concentration of amine. This may be either due to the ultrafast PET that assists the formation of a relaxed state or the PET process preventing the formation of a relaxed state through recombination of cation radical and solvated electron. PET introduces an additional non-radiative decay channel in the excited state and does not assist the formation of a relaxed excited state. PET from the amine prevents the formation of a relaxed state through the recombination of cation radical and electron of C450, which is clearly shown in Fig. 5d–f. The acceleration of the formation of solvent relaxed state in the presence of amines in all the micelles is due to the ultrafast PET to

the cation radical–electron pair, which prevents the formation of a relaxed state through recombination at a longer time scale. This phenomenon is more pronounced in CTAB micelles which further confirm the efficient PET to the cation radical–electron pair. The excited-state process C450 in micelles including ultrafast PET, photoionization, formation of the relaxed state is given in Scheme 2. The present study concludes that the slow solvation processes in micelles are governed by the recombination dynamics of the cation radical–electron pair.

3.5 Time-resolved nanosecond transient absorption studies of C450: dynamics of ET with amines

The steady-state and time-resolved fluorescence results confirm that the PET occurs between C450 and amine in all micellar systems. However, it is important to further understanding the electron transfer mechanism in the presence of photoionization. Time-resolved nanosecond transient

Scheme 2 Schematic illustration of excited-state processes in the absence and presence of an amine

absorption spectra of C450 with amines were performed in SDS, CTAB, and TX-100 micelles to elucidate the mechanism of PET. The transient absorption spectra of C450 in micelles with MAN and DMAN are shown in Fig. 6. In the presence of amine, the transient absorption spectrum of C450 in SDS and TX-100 micelles shows a new transient peak at ~450 nm in addition to the hydrated electron peak at 710 nm and is assigned to the amine radical cation absorption. The absorption maximum of $MAN^{+ \bullet}$ and $DMAN^{+ \bullet}$ was observed at 450 and 470 nm, respectively, which is in good agreement with the literature [23, 48–50]. The observation of amine cation radical in the transient absorption spectrum of C450 with amine can be concluded that the PET from amine to the excited state of C450 is responsible for the fluorescence quenching.

To confirm the transient peak at 710 nm observed in SDS and TX-100 micelles due to either hydrated electron or coumarin radical anion, the transient absorption spectrum of C450 was monitored in the presence of DMAN under N_2O saturated condition (Figure S3). The resultant transient absorption spectrum exhibits a peak at 470 nm with the disappearance of a 710 nm peak. This finding confirms the presence of hydrated electrons in the presence of amines. The appearance of a hydrated electron peak implies that photoionization occurs faster than electron transfer. To confirm that the effect of amine concentration on the absorbance of a hydrated electron was examined by monitoring the transient decay at 710 nm with varying concentrations of amine (Figure S4). The absorbance and decay time of the hydrated electron were not influenced by the amines even at high concentrations (15 mM). However, the transient peaks for coumarin radical cation and radical anion were not observed in the presence of an amine. The absence of coumarin radical anion transient absorption in the presence of amines may be due to the PET-promoted photoionization. The coumarin radical cation was disappeared due to the electron transfer from amine to coumarin radical cation leading to the formation of ground-state coumarin molecule (Scheme S2).

Fig. 6 Transient absorption spectra of C450 with individual (a) MAN and (b) DMAN in micelles recorded at 1 μ s after the laser flash under argon saturated condition

The dependence of fluorescence intensity and a lifetime of C450 and independence of hydrated electron absorbance with amine concentration and absence of C450 anion radical may be due to the (i) ultrafast PET promoted photoionization (non-radiative and concerted PI and PET); (ii) decrease in the cation radical absorbance which is compensated by the increases in the hydrated electron yield in the transient absorption; (iii) decrease in the number of C450 molecules in the relaxed state by preventing the recombination through PET; and (iv) electron transfer to C450 cation radical.

3.5.1 Interaction of coumarin radical cation with amines in micelles

To study the interaction between the amine and coumarin radical cation, the decay kinetics of coumarin radical cation in micelles were measured as a function of amine concentrations. The transient absorption decays of coumarin radical cation with different concentrations of DMAN in

all micelles are shown in Fig. 7. The absorbance and decay time of coumarin radical cation was found to decrease with increasing the concentration of amines which confirms the reaction between the coumarin radical cation and amines. The rate constant for this reaction was estimated from the slope obtained by the plot of pseudo-first-order decay rate constants (k_{obs}) versus the concentration of amine according to the following equation [23, 38]:

$$k_{obs} = k_0 + k_{amine} [amine]$$

where k_0 denotes the decay rate of the coumarin radical cation in the absence of amine. The pseudo-first-order decay rate constants (k_{obs}) were calculated from the plot of $\ln(\Delta A)$ against time. The resultant k_{obs} were plotted against the concentrations of amine to determine the bimolecular quenching rate constants. The slope of the linear plot provides a rate constant, which is given in Table 4. The observed higher rate constant values with DMAN as compared to MAN indicates the strong ET interaction between C450⁺ and DMAN.

Fig. 7 Transient absorption decay of C450 monitored at 610 nm with varying concentrations of DMAN in micelles monitored at 710 nm. (a) SDS, (b) CTAB, and (c) TX-100)

Table 4 Rate constants for the ET between coumarin radical cation and amines in micelles

Amines	Rate constant for ET between C450 ⁺ and amine ($\times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) ^a					
	Short-lived component			Long-lived component		
	SDS	CTAB	TX-100	SDS	CTAB	TX-100
MAN	3.85	0.82	20.48	6.85	0.15	2.82
DMAN	4.64	1.10	21.96	10.71	0.21	6.31

^aError $\pm 2\%$

3.6 Mechanism of photoionization and electron transfer processes in the excited state

The mechanism of ET reaction between C450 and amines in micelles is established through the results obtained from the steady-state and time-resolved fluorescence and transient absorption measurements. Scheme 3 illustrates the plausible mechanism of the excited-state reactions of C450 and subsequent ET with the amine. Initially, upon excitation, the photoionization of C450 results in the formation of coumarin radical cation and hydrated electron. The efficiency of the photoionization process depends on the charge of the Stern/palisade layer. The interaction between coumarin radical cation and amine in the excited state was confirmed by the formation of ground-state coumarin and amine radical cation in the presence of an amine. The fast recovery of the ground-state C450 in the presence of amine can be proved by monitoring the bleach recovery at 370 nm. Figure 8 shows the bleach recovery of C450 with varying concentrations of DMAN in CTAB micelles. In general, the depletion of ground-state molecules by laser excitation leads to the bleach at the respective absorption wavelength. The strong bleaching was observed in the absence of amine as a result of photoionization. When an amine was added, the suppression of bleaching and fast bleach recovery was observed, which confirms the regeneration of ground-state C450 due to the ET between C450 CR and amine. The femtosecond fluorescence quenching studies confirm that the ultrafast ET occurs within 100 ps which prevents back ET. The backward ET is expected to occur within 200 ps. Previously, the back ET occurred in 163 ps for C314 with the DMAN system, reported by McArthur et al. [51]. However, this ultrafast back ET could not be detected in transient absorption

Fig. 8 Ground-state bleach recovery of C450 in CTAB micelles with different concentrations of DMAN monitored at 370 nm

measurement because of limited time resolution (8 ns). The multi-exponential bleach recovery implies more than one mechanism involved in the regeneration of the ground state. Accordingly, the bleach recovery observed in transient absorption studies is ascribed due to (i) ultrafast concerted PI of C450 in the presence of amines; (ii) fast PET to C450 CR-electron pair; and (iii) slow ET between C450 CR and amine. The ultrafast ET reaction of excited C450 with amine resulted in the formation of the ground-state coumarin and amine radical cation. The steady-state fluorescence studies appear to be influenced by the respective ultrafast ET through the static quenching process. The probability of proximity between the C450 and amine pairs increases with increasing concentration of amine thereby upward curvature exhibited in the S–V plot at higher concentrations of amine.

However, the evidence for the formation of coumarin radical anion such as transient absorption peak could not

Scheme 3 Schematic representation for the photoionization and PET processes of C450 with amine

be distinguished in the ET reaction owing to the strong spectral overlap by hydrated electron and coumarin radical cation absorption. It was previously reported that the transient absorption of coumarin radical anion was observed at ~700 nm in acetonitrile using pulse radiolysis [52, 53]. Based on the overall results obtained from the steady-state and time-resolved fluorescence and transient absorption measurements, it can be concluded that several ways of PET process occurred in micelles such that ET to Franck–Condon state and relaxed excited state, and ET to coumarin radical cation after photoionization. Moreover, the photoionization process precedes ET which is not influenced by either ultrafast or dynamic ET.

4 Conclusions

Steady-state and time-resolved absorption and fluorescence techniques were applied to investigate the excited-state dynamics of C450 in the absence and presence of amines. The C450 dye was found to reside in the Stern/palisade layer of the micelles. The photoionization of C450 results in the formation of coumarin radical cation and hydrated electron in micelles. Among the studied micelles, SDS facilitates efficient charge separation yielding higher photoionization efficiency. The absence of rise component in SDS micelle and the presence of rise component in CTAB and TX-100 micelles in the femtosecond fluorescent decay of C450 monitored at the blue end of the emission spectrum concludes the role of recombination of the PI products in the formation of relaxed state. The quenching of the ultrafast and fast decay component in the presence of amines indicates the concerted PI and PET. The amine concentration-independent hydrated electron absorbance and decay rate constant confirms the concerted PI and PET. The present study demonstrates that the slow solvation processes in micelles are governed by the recombination dynamics of the radical cation–electron pair. The ET to C450 radical cation in the presence of amines was confirmed from the transient absorption studies of C450. A detailed mechanism for PET including the PI of C450 in micelles was proposed, and it is completely different from the homogeneous solution and accounts for the unique functionality of the biological system.

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Declarations

Conflict of interest There are no conflicts of interest to declare.

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