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Effect of donor orientation on ultrafast intermolecular electron transfer in coumarin-amine systems

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Effect of donor amine orientation on nondiffusive ultrafast intermolecular electron transfer (ET) reactions in coumarin-amine systems has been investigated using femtosecond fluorescence upconversion measurements. Intermolecular ET from different aromatic and aliphatic amines used as donor solvents to the excited coumarin-151 (C151) acceptor occurs with ultrafast rates such that the shortest fluorescence lifetime component (τ_1) is the measure of the fastest ET rate ($\tau_1 = \tau_{ET}^{fast} = (k_{ET}^{fast})^{-1}$), assigned to the C151-amine contact pairs in which amine donors are properly oriented with respect to C151 to maximize the acceptor-donor electronic coupling (V_{el}). It is interestingly observed that as the amine solvents are diluted by suitable diluents (either keeping solvent dielectric constant similar or with increasing dielectric constant), the τ_1 remains almost in the similar range as long as the amine dilution does not cross a certain critical limit, which in terms of the amine mole fraction (x_A) is found to be ~0.4 for aromatic amines and ~0.8 for aliphatic amines. Beyond these dilutions in the two respective cases of the amine systems, the τ_1 values are seen to increase very sharply. The large difference in the critical x_A values involving aromatic and aliphatic amine donors has been rationalized in terms of the largely different orientational restrictions for the ET reactions as imposed by the aliphatic (n-type) and aromatic (π-type) nature of the amine donors [A. K. Satpati *et al.*, J. Mol. Struct. **878**, 84 (2008)]. Since the highest occupied molecular orbital (HOMO) of the n-type aliphatic amines is mostly centralized at the amino nitrogen, only some specific orientations of these amines with respect to the close-contact acceptor dye [also of π-character; A. K. Satpati *et al.*, J. Mol. Struct. **878**, 84 (2008) and E. W. Castner *et al.*, J. Phys. Chem. A **104**, 2869 (2000)] can give suitable V_{el} and thus ultrafast ET reaction. In contrary, the HOMO of the π-type aromatic amines is largely distributed throughout the whole molecule and thus most of the orientations of these amines can give significant V_{el} for ultrafast ET reactions with close-contact C151 dyes. © *2008 American Institute of Physics.* [DOI: 10.1063/1.2975192]

I. INTRODUCTION

Electron transfer (ET) is one of the most fundamental reactions occurring in chemistry and biology.[1–5] Though it is realized that the ET parameters such as the reaction free energy (ΔG^0), the electronic coupling between the reactant and product states (V_{el}), the solvent (λ_s) and intramolecular (λ_i) reorganization energies, the solvent relaxation dynamics (τ_s) around the reactants, etc., play very significant roles in determining the dynamics of the ET reactions,[1–19] the main challenge in understanding the ET reactions in detail is to resolve the effects of each of these parameters on the observed ET dynamics. This is so because different ET parameters play their role in the ET dynamics in a very complex manner. Thus, understanding the role of different ET parameters in controlling the rates of ET reactions is one of the most intriguing aspects of the ET studies. The curiosity of understanding different ET parameters that control the ET reactions has attracted large number of experimental and theoretical studies on this subject area for many years.[6–19]

Fluorescence quenching studies under diffusive conditions (dilute solutions of the reactants) is the most widely used methodology to investigate the kinetics of bimolecular ET reactions in homogeneous media.[2–5,20–30] In these studies, the concentrations of both the reactants are kept much lower than the concentration of the solvent molecules in the medium. Moreover, the concentration of the fluorophore (either donor or acceptor) is also kept much lower than that of the quencher (either acceptor or donor in the respective cases) so that the kinetics of the reactions can be analyzed suitably assuming pseudo-first-order condition. In these experiments, the reduction in the fluorescence intensity or fluorescence lifetime with varying quencher concentrations can be correlated following a suitable diffusional kinetic scheme and accordingly the effective rate constant for the ET reaction can be estimated.[2–5,20–30] In these studies, since ET takes place under diffusive condition, the bimolecular rate constant for the effective reaction can have its limiting maximum value similar to that of the bimolecular diffusional rate constant k_d. Thus, under diffusive conditions, the true ET rate constants (k_{ET}) cannot be estimated when k_{ET} becomes larger than k_d.[2–5,20–30] A judicial approach that has been adopted by many research groups to avoid the limitations imposed by

the translational diffusion of the reactants on the ET rates was to use the quenchers directly as the solvents such that the fluorophores can always be in contact with large number of quencher molecules and thus translational diffusion of the reactants does not become the prerequisite for the formation of the encounter complexes.[13,31–43] Under this situation, an excited fluorophore can simply undergo ET reaction with one of the close-contact quencher molecules that results the maximum acceptor-donor electronic coupling, without involving any translational diffusion of the reactants. Accordingly, the observed fluorescence lifetimes (τ) of the fluorophore can directly be considered as the ET rate ($\tau_{ET} = (k_{ET})^{-1}$).[13,31–42] One of the most interesting findings from these studies is the unusually fast ET rates, often faster than the solvent relaxation (orientational) rates.[13,17,31–42] In the present work we have studied such ET reactions with solvent as a donor or with very high donor concentrations, using the dye coumarin-151 (C151) as the electron acceptor and aliphatic and aromatic amines as the electron donors, to understand the orientational effect of the reactants, especially of the amine donors, on the ultrafast ET reactions. In the present work C151 is used as the electron acceptor because among different coumarin dyes, C151 was seen to undergo the fastest ET in amine solvents.[13,31–36] Furthermore, since C151 is a π-type acceptor [highest occupied molecular orbital (HOMO) is of π-character],[17,44,45] any orientational effect that is observed for the ultrafast ET involving C151 acceptor and aliphatic and aromatic amine donors could effectively be ascribed to the nature of the amine donors involved. Though orientation of the reactants is expected to modulate the ET dynamics quite substantially, not much of attention has been given on this aspect in literature on ultrafast ET dynamics. In the present study, we have used the femtosecond fluorescence upconversion measurements in different C151-amine systems under the conditions of either solvent as a donor or with very high donor concentrations to reveal the effect of relative orientation of reactants on the ultrafast ET dynamics. Chemical structure of C151 dye and those of the aromatic and aliphatic amine donors used in this study are shown in Chart 1.
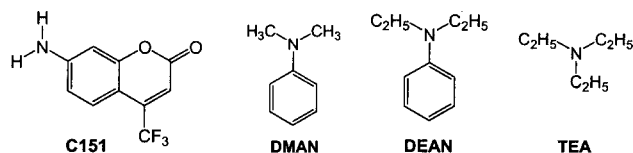
II. MATERIALS AND METHODS

Laser grade C151 dye was obtained from Exciton, Ohio, USA and used as received. The aromatic amines, namely, N,N-dimethylaniline (DMAN) and N,N-diethylaniline (DEAN), were obtained from Spectrochem, India and purified by vacuum distillation before use. The aliphatic amine, namely, triethylamine (TEA), was obtained from Spectrochem, India and purified by distillation under normal pressure. All spectroscopic grade organic solvents (cyclohexane, ethyl acetate, and acetonitrile) used in the present study were obtained from Spectrochem, India and used as received.

In the present study, steady-state (SS) fluorescence measurements were carried out using a Hitachi model F-4010 (Japan) spectrofluorimeter. Ultrafast fluorescence decays were measured using a femtosecond fluorescence upconversion setup (FOG 100, CDP Inc., Russia) based on diode pumped solid state (DPSS) laser pumped 50 fs titanium:sapphire laser (CDP Inc., Russia). In these measurements, samples were excited with the second harmonic light ($\sim$400 nm) of the titanium:sapphire laser and fluorescence from the samples was upconverted by mixing it with the fundamental light pulse (gate pulse; $\sim$800 nm, horizontally polarized) of the laser in a 0.5 mm type I beta barium borate (BBO) crystal. All the measurements were carried out with magic angle polarization of the excitation pulse (using a Berek variable compensator) with respect to the gate pulse to avoid the interference of the rotational relaxation of the fluorophore on the measured fluorescence decays. Optical delay between the excitation and gate pulses was varied using a delay rail (6.6 fs per steps) in the path of the gate pulses. The upconverted signal was measured with a photon counter after passing through a proper bandpass filter and a double monochromator. In all these measurements the samples were taken in a rotating cell (0.4 mm path length) to have a better heat dissipation and thus to avoid the photodegradation of the dye. For each of the decays, at least five repetitive scans were taken to average the data points and also to see the reproducibility of the decays measured. For all the systems considered in the present work for discussion and comparison, the fluorescence decays collected in the repetitive scans showed very good reproducibility, suggesting that there is no significant photodegradation of dye during the upconversion measurements. To check this further, the absorption spectra of the samples were recorded before and after the fluorescence upconversion measurements and were found to be quite similar (absorbance changes less than 5%).

All measured emission decays were fitted with a multi-exponential function using the standard convolute-and-compare nonlinear least squares procedure.[46] In this method, the model exponential function was convoluted with the instrument response function (IRF) and compared with the experimental data, until a satisfactory fit is obtained. The IRF was measured through the cross correlation of the excitation and the fundamental gate pulse. The IRF was found to have Gaussian intensity profile with full width at half maximum of 220 fs.

In the present study all coumarin samples were excited with 400 nm laser pulses. Until otherwise stated, the emission decays of the sample were monitored at 450 nm. At the monitoring wavelength of the fluorescence decays, the contribution of the scattering light (Raman scattering) from the medium was checked by placing a sample cell filled with solvent only. The contribution of such scattering at the monitoring wavelength was negligible. Thus the measured decays at the monitoring wavelength were free from any contribution due to IRF.

III. RESULTS AND DISCUSSION

Fluorescence decays of C151 dye in DMAN and TEA solvents are shown in Figs. 1(a) and 1(b), respectively. For
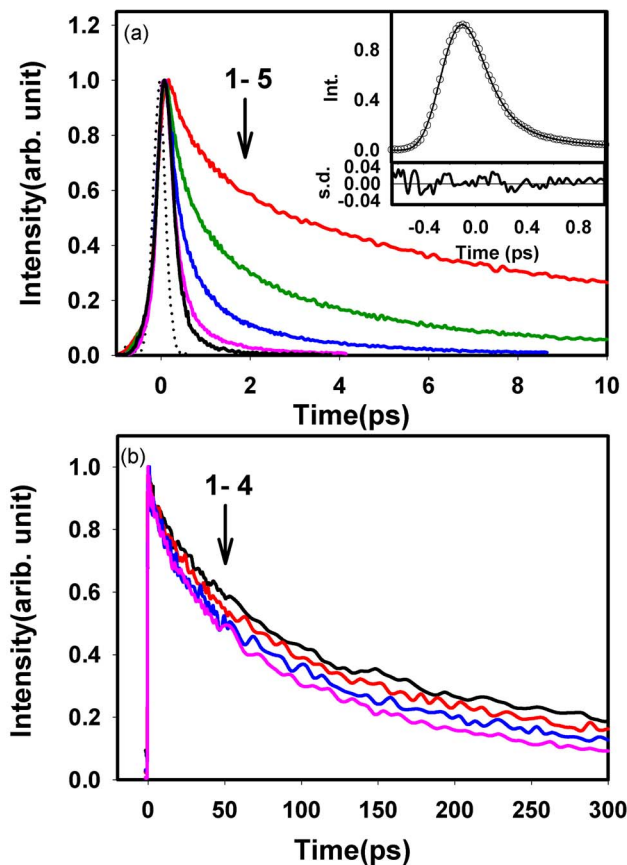
FIG. 1. (Color online) Fluorescence transient decays for C151 dye at different mole fractions of (a) DMAN [$x_A(1-5)$=0.209, 0.443, 0.649, 0.877, and 1] and (b) TEA [$x_A(1-4)$=0.205, 0.443, 0.755, and 1]. The diluents were the appropriate cyclohexane-ethyl acetate solvent mixtures. The dotted line in (a) indicates the IRF. Inset demonstrates the quality of the fitting along with the residual for the C151-DMAN system with x_A=1: (○) experimental data point; (—) fitted data.

TABLE I. Fluorescence decay parameters of C151 dye in different amine solvents and at different dilutions of the amines using cyclohexane-ethyl acetate mixed solvent as the diluents. The redox potentials of the acceptors and donors are listed as follows. The oxidation potentials of DMAN, DEAN, and TEA are 0.76, 0.72, and 1.05 V, respectively, and the reduction potential of C151 dye is −1.57 V. All these values are in acetonitrile solution against saturated calomel electrode (Refs. 27 and 66).

C151 in DMAN				
x_A of DMAN	a_1	τ_1 (ps)[a]	a_2	τ_2 (ps)[a]
1	0.98	0.23	0.02	1.07
0.877	0.93	0.22	0.07	1.13
0.755	0.88	0.24	0.12	1.42
0.649	0.87	0.25	0.13	2.24
0.443	0.56	0.27	0.44	2.05
0.209	0.52	0.74	0.48	19.1

C151 in DEAN				
x_A of DEAN	a_1	τ_1 (ps)[a]	a_2	τ_2 (ps)[a]
1	0.94	0.19	0.06	0.72
0.848	0.92	0.20	0.08	0.95
0.713	0.88	0.25	0.12	1.04
0.591	0.86	0.27	0.14	1.40
0.383	0.61	0.30	0.39	2.37
0.172	0.52	0.75	0.48	13.3

C151 in TEA					
x_A of TEA	a_1	τ_1 (ps)[a]	a_2	τ_2 (ps)[a]	a_3	τ_3 (ps)[a]
1	0.08	12.8	0.34	63.7	0.58	233.0
0.874	0.11	12.9	0.48	91.1	0.41	301.0
0.755	0.08	13.4	0.32	95.6	0.60	315.0
0.643	0.13	20.1	0.43	108.0	0.44	340.0
0.436	0.17	33.3	0.40	173.0	0.43	368.0
0.205	0.05	54.2	0.27	207.0	0.68	455.0

[a]Errors in decay times were within 10%–15%. Error bars are also indicated in the figures.

the purpose of comparison, the decays in Fig. 1 are shown after normalization at their peak counts. The actual decays for these systems and their fits are shown in the supporting information. Observed decay for C151 dye in DEAN solvent was very similar to that in DMAN solvent. As indicated from Fig. 1, the fluorescence decays are nonsingle exponential in nature in all the cases. Note that similar nonsingle exponential nature of the fluorescence decays has also been reported earlier by different research groups for ultrafast ET reactions in donor amine solvents.[13,17,31–36,43] It is seen that for C151-DMAN and C151-DEAN systems a biexponential analysis gives reasonably good fit to the observed decays, with the shorter component (~200 fs) contributing the maximum (94%–98%) and the longer component (~1 ps) contributing only marginally (2%–6%). For the C151-TEA system, however, it is seen that the decay fits better to a triexponential function. The fluorescence lifetime components (τ_1, τ_2, etc.) and their relative contributions (a_1, a_2, etc.) as obtained for the dye in different amine solvents are listed in Table I. As seen from Table I, all the fluorescence lifetime components for C151 in all the amines used are much lower in comparison to the 4−5 ns fluorescence lifetimes of the dye in other noninteracting solvents.[47–50] These results thus suggest that in amine solvents the ET from a suitable amine molecule to

adjacent excited C151 dye occurs with an extremely fast rate. Since the shortest fluorescence lifetime components (τ_1) in the present systems are several orders of magnitude lower than the fluorescence lifetime of the dye in noninteracting solvents, we can assume that these shortest lifetime components are the direct measure of the fastest ET time ($\tau_1 = 1/k_{ET}^{fast}$) in the present systems.[13,31–35] Note here that in the present study, we also tried to measure the fluorescence decays of the dye in another aliphatic amine solvent, namely, tripropylamine (TPrA). However, the repetitive scans collected for the fluorescence decays of C151 in TPrA do not show the reproducibility rather the peak count undergoes a gradual reduction in each consecutive scan. This observation suggests that the dye C151 undergoes a significant photodegradation in TPrA during the upconversion measurements. Thus, in the present study, we do not use the fluorescence decays observed in the C151-TPrA system for any further analysis and comparison. Note, however, that the qualitative nature of the fluorescence transients observed for the C151-TPrA system was quite similar to that of the C151-TEA system.

The nonexponential nature of the fluorescence decay of C151 dye in neat amine solvents, as shown in Fig. 1, was

explained by different groups adopting different kinetic models and interaction mechanisms.[13,17,31–36,43] Yoshihara and co-workers[13,31–35] correlated these nonexponential decays adopting the concept of two-dimensional ET (2DET) theory,[51–53] where ET occurs along the intramolecular coordinate of the reactants under a nonequilibrium distribution of the reactants with respect to the solvent polarization coordinate. Such a situation arises because in most of these systems the ET reaction occurs much faster than the diffusive motion of the solvent molecules around the reacting acceptor-donor pairs. According to Castner *et al.*,[17] the nonexponentiality in the ultrafast ET reactions for the chromophoric dyes in donor amine solvents is due to the dynamic variation of the electron-coupling matrix element (V_{el}), as arises due to the orientational redistribution of the near-neighbor donor amines during the ET time. Tachiya and co-workers introduced the concept of two types of interactions, namely, the charge transfer complex formation between the close-contact acceptor-donor pairs and the photoinduced charge separation (CS) between the acceptors and donors that are not in direct contact, to explain the nonexponential behavior of the observed decays.[38,39,54] Kuzmin *et al.* treated the nonexponential behavior of the ultrafast ET dynamics in donor amine solvents or in solutions with very high donor concentrations considering the continuous distribution of ET rate constants, as arises due to the statistical distribution of donors relative to the acceptors and the consequent distribution of the electronic coupling matrix element and distances between the reactant molecules.[43] In one of the studies Rubtsov *et al.* showed that the observed fluorescence decays for the oxazine-1 (OX-1) dyes dissolved in amine solvents are significantly changed on changing the monitoring wavelength.[36] Based on these results, and considering that such wavelength dependent changes in the fluorescence decays cannot arise due to the influence of the solvent relaxation in amine solvents, they suggested that the interacting acceptor-donor pairs with different intermolecular separations are actually responsible for the observed nonexponentiality in the fluorescence decays for these systems. As suggested by these authors[36] and also as it follows from the work of Kuzmin *et al.*[43] the shortest lifetime component in these systems is due to the ultrafast ET in the close-contact acceptor-donor pairs. Accordingly, the other slower lifetime components in these systems arise due to other acceptor-donor pairs with varying intermolecular separations. From molecular dynamic simulations, Castner *et al.*[17] estimated that in neat amine solvents there are about 13–16 amine molecules in the first solvation shell of an acceptor dye. A similar estimate for the number of nearest neighbor amine molecules around a dye in amine solvents is also predicted by Morandeira *et al.* from simple geometrical considerations.[40] Thus, following the picture introduced by Rubtsov *et al.*,[36] we can assume that the fastest fluorescence decay component as measured in the present systems actually corresponds to the fastest ET reactions between the close-contact acceptor-donor pairs. At the close contact, quite good number of donor amines can be suitably oriented with respect to the acceptor dye to give the maximum V_{el} and thus the fastest ET reaction. Note that this simplified picture, as we adopt here to represent the fastest

ET in different coumarin-amine systems, can easily be incorporated into any of the kinetic models discussed in literature in relation to the nonexponential behavior of the ultrafast ET reactions in similar systems.[13,17,31–41] In relation to the present discussion, we mainly focus on the fastest fluorescence decay component in different coumarin-amine systems, which is expected to give us a clear picture of the orientational effects of the amine donors on ultrafast ET reactions, excluding any significant interference from the lateral diffusion of the reactants.

As mentioned earlier, Rubtsov *et al.*[36] showed in oxazine-1-DMAN system that the emission decay and accordingly the ET rate depend on the monitoring wavelength. This result has been explained on the basis of the heterogeneity in the solvent structure around the probe. To check whether in the present cases of coumarin-amine systems the observed ultrafast ET component is properly detected or not, we also recorded the fluorescence decays for some of the systems at different emission wavelengths. Unlike the results of Rubtsov *et al.*,[36] we have seen that the decays are not that strongly dependent on the monitoring wavelengths, especially for the fastest ET systems (see supporting information). Moreover, the fast decay time constants (τ_{fast}) in these decays are seen to remain almost in the similar range for all the measuring wavelengths (see supporting information). The longer decay constants are, however, seen to change to some extent with the measuring wavelength. The reason for the significant differences between our results and that from Rubtsov *et al.*[36] is not very clear to us. However, one of the possible reasons that we could think may be related to the cationic nature of the OX-1 dye in comparison to the neutral C151 molecule (see supporting information). Thus, in the case of OX-1, it is expected that the dye will undergo a stronger ion-dipole interaction (potential energy varies with $1/r^2$ and typical energy $\sim$15 kJ mol^{-1})[55] with the surrounding solvent (DMAN) molecules in comparison to a relatively weaker dipole-dipole interaction (potential energy varies with $1/r^6$ and typical energy $\sim$0.6 kJ mol^{-1})[55] between C151 dye and surrounding DMAN molecules. It is thus expected that for OX-1-DMAN system the ion-dipole interaction will cause some alignment of the donor solvent molecules around the dye depending on its charge centers. Such an alignment is not likely in the C151-DMAN system due to weaker dipole-dipole interaction. Note that for both OX-1-DMAN and C151-DMAN systems, the other interactions, like the π-π interactions, are expected to play an almost similar role because the aromatic π-clouds (see supporting information) in both OX-1 and C151 should be quite similarly polarizable. Thus, we feel that the differences in the behavior of OX-1-DMAN and C151-DMAN systems could be mainly due to the differences in the strengths of the ion-dipole and dipole-dipole interactions present between the dye and the surrounding solvent molecules in the two respective cases.

As ET reaction causes a change in the oxidation states of the reactants, the solvent molecules around the reactants undergo a significant reorganization during the ET reaction. It is well documented in literature that the dynamics of the solvent reorganization has profound influence on the ET dynamics.[51,56] However, the effect of solvent reorganization

on the ET reaction depends on the relative rates of these two processes and nicely been explained in the two-dimensional model of the ET reaction.[51,56] In a solvent with very fast relaxation, the solvent molecules reorient very quickly and thus ET takes place from the equilibrated solvent configuration of the reactants. In a solvent with slow response, however, ET reaction can preferentially take place along the nuclear coordinate under a nonequilibrium solvent configuration for the reactants. For the intermediate situation, where solvent relaxation and the ET rate are quite comparable, the ET can take place at different solvent configurations. In common solvents with very fast solvent relaxation dynamics, e.g., water, acetonitrile, etc.,[57,58] ET mostly occurs with a rate slower or comparable to the solvent relaxation process.[1–19,51,52,56] In amine solvents, however, the major part of the solvent relaxation process (i.e., the reorientational relaxation) is reported to be significantly slow.[13,31,33,59] For DMAN, the average solvation time (for reorientational relaxation) has been reported to be ~16 ps by Yoshihara and co-workers.[31,59,60] Considering this average solvation time, the ultrafast ET component observed for C151 dye in DMAN solvent seems to be significantly faster than solvent relaxation. Thus, for the present ET systems, it is expected that the solvent reorientational relaxation will be incomplete during the ET reaction and accordingly the ET in the present systems should occur under a nonequilibrium solvent configuration for the reactants, a situation clearly envisaged in two-dimensional ET model.[31–35,51,61] Note at this point, however, that for amine solvents, Smith et al.[62] suggested from Kerr measurements that along with the major picosecond reorientational relaxation components (as reported by Yoshihara and co-workers)[31,60] there is also a small contribution (10%–20%) from an ultrafast component (~200 fs) arising from the librational motion of the solvent molecules. They arrived at this inference by connecting the pure liquid dynamics (obtained from Kerr measurements) to the solvation dynamics (estimated from dynamic Stokes' shift measurements) using a power-law relationship proposed by Maroncelli et al.[63] As suggested later by Castner and Maroncelli,[64] such a power-law relationship often does not give any satisfactory correlation between the results from Kerr measurements and dynamic Stokes' shift measurements. Thus, for the present systems, it seems to be difficult to comment on the actual contribution of the librational motion on the overall solvent relaxation dynamics, especially because in the dynamic Stokes' shift measurements in DMAN solvent, as reported by Yoshihara and co-workers,[31,59,60] the ultrafast solvation component attributable to the solvent librational motion could not be resolved. Since it is expected that the solvent molecules will always have some librational motion, whatever its contribution to the overall solvation dynamics, it should always have some effect on the observed ET dynamics via the modulation of the electronic coupling matrix element, V_{el}. We expect that for the present systems, the librational motion of the amine molecules around the acceptor dye mainly causes a modulation in the dye-amine electronic coupling than contributing much on the overall solvent relaxation around the reacting donor-acceptor pairs. It is indicated from the computational results reported by Castner et

al.[17] that the librational motion of the solvent donors in the dye-donor solvent systems can cause a large fluctuation in V_{el} and accordingly can modulate the ultrafast ET dynamics. Certainly the ultrafast ET component observed in the present systems has an effect within itself arising due to the ultrafast librational motions and the consequent fluctuations in V_{el}.

In literature, the examples for ET reactions in nonpolar solvents are very limited because they require very high driving force for such reactions to take place. Murata and Tachiya[54] showed that even in a nonpolar solvent, the criteria of the equal energy of the reactant and the product states, which is a prerequisite for a reaction to take place, can be achieved by changing the distance between the reactants. These authors have nicely demonstrated that even in the absence of solvent polarization, the ET between the donor and acceptor can take place in a nonpolar solvent if the V_{el} is made sufficiently large. It has been proposed that such a high V_{el} can be achieved in a nonpolar solvent through proper orientation of the reactants.[54] Logically the same is also the situation for the ET systems studied in the present work. Thus, following the concept of Murata and Tachiya,[54] we infer that in the present cases, where amine is used as the solvent, the solvent reorganizational polarization does not play any important role for the ET reaction to take place. For the present systems, the ET reaction is mainly governed by the high V_{el} values for the properly oriented amine and coumarin pairs. Such a concept is also in agreement with the molecular dynamics simulation results of Castner et al.[17] These authors showed that in an amine solvent a coumarin molecule is surrounded by ~13–16 amine molecules in the first solvation shell and among these amine molecules a few can have orientations such that V_{el} can have a value as high as 200–800 cm^{-1} and accordingly can give adiabatic ET reaction with ultrafast rate.[17]

It is clearly indicated from Table I that the fastest ET component (~200 fs) for C151 dye in the aromatic amine solvents, DMAN and DEAN, is much faster than that (~13 ps) of the dye in aliphatic amine solvent, TEA. Though the differences in the ET parameters such as V_{el}, λ_s, and λ_i can have their specific roles to determine the ET rates in different systems, yet the large differences in these fastest ET rates observed between the C151-aromatic and C151-aliphatic amine systems are assumed to be mainly due to the differences in the free energy changes (ΔG^0) for the ET reactions in these systems. Since the oxidation potentials of DMAN and DEAN are quite similar (see Table I),[27–30,32,33] both C151-DMAN and C151-DEAN systems render quite similar ΔG^0 values and accordingly the fastest ET components for both of these systems are almost in the similar range ($\tau_1 \sim 190–230$ fs). For TEA, however, since its oxidation potential is much higher (by about 0.3 V) compared to those of DMAN and DEAN,[27–30,65,66] the ΔG^0 for C151-TEA system should also be about 0.3 eV less negative than those of the C151-DMAN and C151-DEAN systems. Accordingly, the fastest decay component is significantly slower ($\tau_1 \sim 13$ ps) for the C151-TEA system compared to those of C151-DMAN and C151-DEAN systems. In addition to this ΔG^0 effect, a relatively lower V_{el} involving aliphatic amine donor compared to aromatic amine, as suggested by Castner

et al.[17] and Shirota *et al.*,[33] can also have an additional effect to cause the ultrafast ET reaction comparatively slower for the former donor than the latter.

To get better insight of these ultrafast ET reactions, especially the orientational effects of the amine donors, we have measured the fluorescence decays of C151 dye in solutions where amine mole fraction (x_A) is gradually reduced by a suitable diluent. In the first part of these experiments, an appropriate mixture of cyclohexane and ethyl acetate was used as the diluent such that the dielectric constant of this solvent mixture is similar to that of the amine solvent concerned. The dielectric constants of these cyclohexane-ethyl acetate mixed solvents (ε_{MS}) were estimated by using the following relation:[67–72]

$$\varepsilon_{MS} = \sum_i f_i \varepsilon_i, \qquad (1)$$

where f_i and ε_i represent the volume fraction and dielectric constant of the ith cosolvents. In these experiments, the purpose of choosing the diluents with dielectric constant similar to that of the concerned amine solvent is to avoid the effect of solvent polarity on different ET parameters, especially λ_s and ΔG^0, so that the changes in the ET rates can simply be correlated in terms of the changing number density of the amines around the excited dyes. Note that in the present experiments, the C151 solutions in the amine solvents were diluted by the respective diluents only up to that extent such that even in the most diluted condition the amine content in the solution is significantly high, ~25% by volume and ~0.2 by amine mole fraction x_A. Since in the neat amine solvents the acceptor dyes are supposed to be surrounded by about 13–16 amine molecules in the first solvation shell,[17,40] even in the most diluted amine solutions used in the present study there are expected to be at least three or more amine molecules in the vicinity of the acceptor dyes. Accordingly, we can assume that even up to the highest dilution of the amines used, the condition of nondiffusive ET reaction (no translational diffusion of the reactants) is reasonably valid, at least for the observed ultrafast ET component.

In the second part of these experiments, acetonitrile was used as the diluent to substantiate the results obtained in the first part of this study. In this case, as the effective solvent polarity increases gradually with the dilution of the amine solvents by acetonitrile, there will be a consequent change in the ET parameters such as λ_s and ΔG^0. However, as the ultrafast ET component in the present systems is reported to occur much faster than the solvent relaxation process,[13,31–42] we expect that these ET results should also be quite similar to those in the earlier cases where the diluents are having the similar dielectric constants as that of the concerned amine solvents used.

Figures 1(a) and 1(b) show the fluorescence decays of C151 dye observed in solutions at different dilutions of DMAN and TEA solvents, respectively, where appropriate cyclohexane-ethyl acetate solvent mixtures are used as the diluents to keep the dielectric constant of the solution the same. The results at different dilutions of the DEAN solvent by suitable cyclohexane-ethyl acetate solvent mixtures were quite similar to those of the respective dilutions of DMAN

TABLE II. Fluorescence decay parameters of C151 dye in DMAN at different dilutions using acetonitrile solvent as the diluent.

x_A of DMAN	a_1	τ_1 (ps)[a]	a_2	τ_2 (ps)[a]
1	0.95	0.18	0.05	0.71
0.877	0.91	0.19	0.09	1.00
0.755	0.86	0.19	0.04	1.09
0.649	0.82	0.19	0.18	1.41
0.443	0.76	0.20	0.24	2.41
0.209	0.56	0.39	0.44	5.79

[a]Error in decay time varies from 10% to 15%. Error bars are also indicated in the figures.

solvent. As indicated from the visual inspection of Figs. 1(a) and 1(b), the longer components of the decays gradually become slower as the dilution of the amines increases. The fastest component of the fluorescence decays in these systems, however, is indicated to remain almost in the similar range, until the amine mole fraction (x_A) in the solution reduces to a certain limit, even though the relative contribution of this fastest component is seen to reduce gradually with the dilution of the amine solvents. Similar to the case of C151 dye in neat amine solutions, in the present cases of diluted amine solutions, the fluorescence decays were also analyzed by using either a biexponential function (for DMAN and DEAN) or a triexponential (for TEA) function. Table I lists the fluorescence lifetime components (τ_1, τ_2, etc.) and their relative amplitudes (a_1, a_2, etc.) in all these cases of diluted amine solutions. Following a similar line, measurements were also carried out on the dye-amine systems using polar solvent acetonitrile as the diluents and the results are presented in Table II. As seen from Tables I and II, the τ_1 component of the fluorescence lifetime of the dye remains almost in the similar range, as long as the x_A values are about 0.4 or more for DMAN. At much higher amine dilution ($x_A < \sim 0.4$), however, the τ_1 values seem to increase very sharply, without correlating with the values observed at $x_A > \sim 0.4$.

Figure 2(a) shows the changes in the τ_1 component ($\tau_1 = 1/k_{ET}^{fast}$) for the C151-DMAN system as a function of the dilution of the amine by the appropriate cyclohexane-ethyl acetate solvent mixtures. It is seen that as the x_A value of the amine is decreased in the solution, there is no significant change in the τ_1 value for the dye as long as the x_A value of the amine is not reduced below about 0.4. At $x_A < 0.4$, however, the τ_1 value suddenly increases very largely in comparison to the trend observed in the region of $x_A > \sim 0.4$. For the C151-DEAN system, the variation in τ_1 is shown in Fig. 2(b). It is to be noticed that the variation of τ_1 with the x_A value of DEAN is quite similar to that of the C151-DMAN system. Thus, the presence of the fastest ET component of ~200–250 fs remains almost in the similar range for the region of $x_A > \sim 0.4$ for DEAN. At $x_A < 0.4$, however, the τ_1 component increases suddenly. From the present results we can thus infer that for C151-DMAN and C151-DEAN systems, unless the x_A value of the amines is reduced to about 0.4, there are still a measurable fraction of the close-contact C151-DMAN and C151-DEAN pairs in the solution that have suitable acceptor-donor orientations to provide large V_{el}
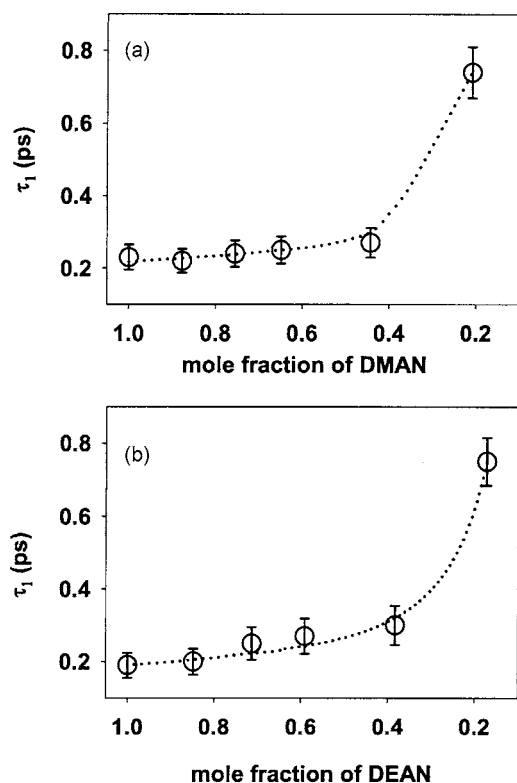
FIG. 2. Changes in the fastest fluorescence decay time (τ_1) for C151 dye at different mole fractions of (a) DMAN and (b) DEAN. The solution was diluted with appropriate cyclohexane-ethyl acetate solvent mixtures.

FIG. 3. Changes in the fastest fluorescence decay time (τ_1) for C151 dye at different mole fractions of DMAN. The solution was diluted with acetonitrile solvent.

and accordingly the ultrafast ET component with τ_1 in the range of $\sim$220–270 fs in the former case and $\sim$200–250 fs in the latter case. Small changes in the τ_1 value in this amine dilution region are possibly due to a change in the solvent characteristics with the amine dilutions. At $x_A < 0.4$, however, the fraction of these close-contact C151-DMAN and C151-DEAN pairs decreases to such an extent that the above ultrafast ET component becomes practically undetectable in the observed fluorescence decays and accordingly the τ_1 value of the fluorescence lifetime suddenly increases very sharply.

In the cases where the DMAN and DEAN are diluted by polar solvent acetonitrile, it is expected that the polarity of the solution will also increase gradually, causing an increase both in the solvent reorganization energy (λ_s) and the exergonicity ($-\Delta G^0$) of the ET reaction. The variations of τ_1 in these cases have been shown in Fig. 3. It is evident from this figure that even for these systems the τ_1 component remains almost in the similar range unless the x_A becomes less than $\sim$0.4. This result thus suggests that it is mainly the number of amine molecules in the first solvation shell of the acceptor dye that determines the rate of the ultrafast ET reaction than the polarity of the solution involved. As suggested by Yoshihara and co-workers,[13,31–36] the C151-DMAN and C151-DEAN systems are located near the barrierless region of the ET rate versus free energy curve. At this region, it is quite likely that ET rate will be quite insensitive to the solvent polarity,[1–5] as observed for the ultrafast ET component for the region of $x_A > \sim$0.4 for DMAN and DEAN donors. In the present context, it is important to mention the results of
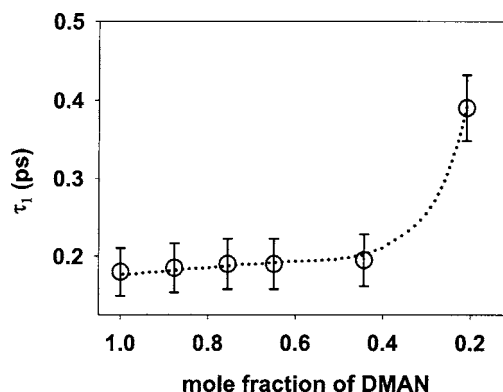
Castner et al.[17] on the coumarin-152-DMAN system with chlorobenzene as the diluent. It is indicated from their results also that beyond a DMAN dilution corresponding to $x_A \sim$0.4, there is a large increase in the τ_1 value, though the changes in τ_1 values at $x_A > \sim$0.4 are only marginal. Thus, our results are qualitatively in accordance with those observed by Castner et al.,[17] though the donor-acceptor systems as well as the diluents are different in the two cases. For C151-DMAN systems, the results from Castner et al.[17] cover only the x_A values in the range of 1.0–0.551 using toluene as the diluent. For this lower amine dilution region ($x_A < 0.551$), the results from Castner et al.[17] show only a marginal increase in τ_1 value for the dye, qualitatively very similar to that observed by us for C151-DMAN systems using cyclohexane-ethyl acetate solvent mixtures or acetonitrile as the diluents.

As solvent relaxation plays an important role on the ET dynamics, it is also necessary to discuss about the solvent relaxation processes in the binary solvents. The solvent relaxation process in most of the binary solvents is more complex than in pure solvents due to the effect of dielectric enrichment or preferential solvation.[73–84] It has been demonstrated both experimentally[73–80] and theoretically[81–84] that the solvent relaxation times follow a nonlinear relation with the composition of the binary solvents. It is generally observed that the binary solvents show relatively longer solvent relaxation times than expected from the linear combination of the individual cosolvents. As mentioned earlier, the average solvent relaxation time for DMAN is reported to be $\sim$16 ps whereas the same for the ethyl acetate is $\sim$2.7 ps.[85] As cyclohexane is a very nonpolar solvent, we do not expect any solvent polarization for cyclohexane during ET reaction. Thus, for the mixed solvent systems used for the dilution experiments, it can be safely assumed that the solvent relaxation will be much slower compared to the ultrafast ET component observed for the present systems. Accordingly, we infer that in the present cases the ET reaction takes place mainly along the nuclear coordinate with very little or no contribution from the solvent polarization, as proposed in the 2DET theory.[51,86] That the solvent relaxation in the present systems does not have any significant effect on the observed ultrafast ET rates is further substantiated by the fact that up
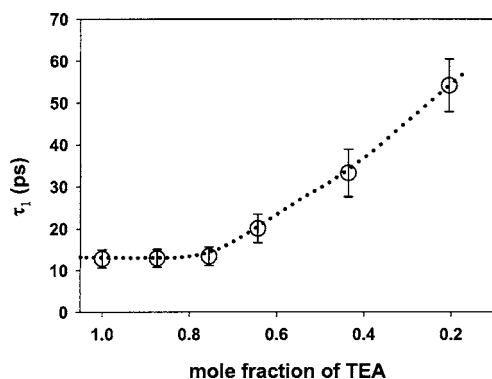
FIG. 4. Changes in the fastest fluorescence decay time (τ_1) for C151 dye at different mole fractions of TEA. The solution was diluted with appropriate cyclohexane-ethyl acetate solvent mixtures.

TABLE III. Relative area (A) under the steady-state fluorescence spectra of the C151-DMAN system at different amine dilutions, where cyclohexane-ethyl actate mixed solvents were used as the diluents. The average fluorescence lifetime $\langle \tau \rangle$ in the respective cases are also listed.

x_A of DMAN	$\langle \tau \rangle$ (ps)	Relative A
1	0.25	107
0.877	0.28	147
0.755	0.38	200
0.649	0.51	344
0.443	1.05	695
0.209	9.55	6650

to a reasonable extent of the compositions of the binary solvents ($x_A > \sim 0.4$), the fastest ET time remains almost in the similar range only with a marginal increase with the amine dilution. This observation also indicates that the spectrum of the local solvation dynamics possibly changes only marginally as long as the amine mole fraction remains more than the critical x_A values observed in the respective cases.

Studies with the C151-TEA system as a function of the amine dilution qualitatively show the results similar to those of the C151-DMAN and C151-DEAN systems. The τ_1 versus x_A plots for C151-TEA systems as obtained by using the cyclohexane-ethyl acetate solvent mixture as the diluent are shown in Fig. 4. It is seen from this figure that for the C151-TEA system the τ_1 value for the dye remains almost in the similar range (~ 13 ps) unless the x_A of the amine is reduced below ~ 0.8. For $x_A < 0.8$, however, the τ_1 value shows a sudden increase, an observation similar to that of C151-DMAN and C151-DEAN systems at $x_A < 0.4$. As discussed in relation to the C151-DMAN and C151-DEAN systems, the results in the C151-TEA system also clearly indicate the presence of a measurable fraction of the close-contact C151-TEA pairs with suitable TEA orientation to give maximum V_{el} (and hence the ultrafast ET component) as long as the x_A value of the amine is not reduced below about 0.8.

In the present context it is interesting to see if the fluorescence lifetimes for the present coumarin-amine systems correspond with the SS fluorescence of the dye in the solutions with respective amine dilutions. This is particularly important to find an estimate about the extent of missing ultrafast/static quenching contribution in the present ultrafast ET systems due to the limited time resolution of the present experimental setup. For this purpose, we carried out some SS measurements on the C151-DMAN system at different amine dilutions using cyclohexane-ethyl acetate solvent mixtures as the diluents. For most of the present systems, the SS fluorescence intensity was quite low and hence the spectra were largely modified due to the presence of significant Raman scattering and other background emission/scattering. The true emission spectra for these systems were thus obtained by subtracting the normalized background spectra (obtained under similar condition using only the solvent) from that of the sample used. Since for the present systems, especially at the lower amine dilution region ($x_A > \sim 0.4$), the

absolute intensity for these fluorescence spectra was unusually low compared to that of the standard fluorescence spectra for the C151 dye in a noninteracting solvent, a quantitative estimation of the quantum yield values for these systems appeared to be not justified. Thus, in the present context, we estimated the relative integrated area (A) under the SS fluorescence spectra for the present systems and compared these integrated areas directly with the average fluorescence lifetimes ($\langle \tau \rangle$) of the respective ET systems. Table III lists these A values along with the $\langle \tau \rangle$ values of the respective systems. Figure 5 shows the A versus $\langle \tau \rangle$ plot for the C151-DMAN systems at different amine dilutions. As indicated from this figure, the correlation of A with $\langle \tau \rangle$ is reasonably linear, suggesting that SS fluorescence quenching in the present systems is quite reasonably reflected in the reduction of the fluorescence lifetime values. It is thus indicated from the present results that there is no significant ultrafast/static quenching contribution missed in the present measurements.

The fact that the critical x_A value up to which the observed fluorescence decays of the dye show the presence of the ultrafast ET component is almost half the way ($x_A \sim 0.8$) for aliphatic amine compared to the aromatic amine ($x_A \sim 0.4$) donors is a striking observation. Such a large difference in these critical x_A values for the dye-aliphatic and
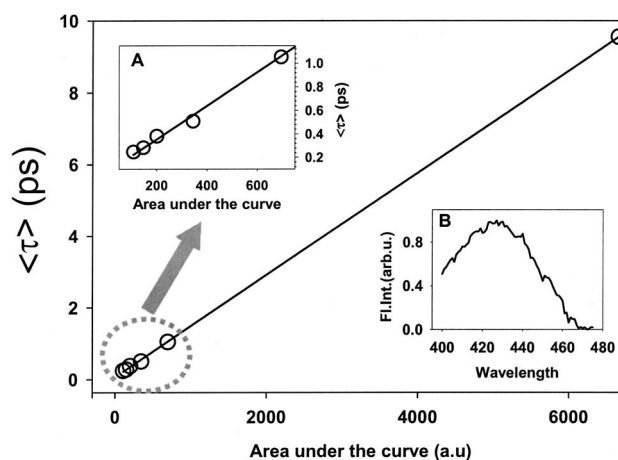

FIG. 5. The plot of the relative area (A) under the SS fluorescence spectra against the average lifetime $\langle \tau \rangle$ values for C151-DMAN systems at different amine dilutions (see Table III). The plot is linear within experimental error. Inset: (a) Expanded plot for the lower amine dilution regions as indicated by the arrow. (b) SS emission spectra for the C151-DMAN system without any amine dilution.

dye-aromatic amine systems is not expected under normal circumstances because at the same x_A value one would expect an almost similar number of amine molecules in both the cases within the first solvation shell of the acceptor dye. Thus, when in the cases of C151-DMAN and C151-DEAN systems there is a measurable fraction of the close-contact dye-amine pairs to show the presence of ultrafast ET component at $x_A \sim 0.4$, there is no reason why in the case of the C151-TEA system there should not be a similar fraction of the close-contact dye-amine pairs at the same x_A. Observed differences between different dye-amine systems, however, can be easily understood if we consider that the dye-aliphatic and dye-aromatic amine systems impose largely different extent of orientational restrictions to have the maximum acceptor-donor electronic coupling (V_{el}).[16,17,66,87] It is indicated from the present results that unlike in dye-aromatic amine systems, in dye-aliphatic amine system at least half of the possible acceptor-donor contact pairs do not have the suitable orientation to permit a reasonably high V_{el} and hence the ultrafast ET component. Thus, the differences in the critical x_A values as observed between dye-aliphatic and dye-aromatic amine systems are attributed to the much larger orientational restrictions imposed by the aliphatic amine donors toward the acceptor-donor electronic coupling for the ultrafast ET reaction to take place. The extent of ET reaction between coumarin and amine largely depends on the extent of overlap of the HOMO of the ground state amine and the lower one of the two singly occupied MOs of the excited coumarin dye, which we designate as HOMO-1 for simplification of discussion. In our earlier work from the density functional theory based quantum chemical calculations[66] and also in the work reported earlier by Castner et al. from similar quantum chemical studies,[17] it was shown that the HOMO of an aromatic amine and the HOMO-1 of the excited state coumarin dyes are of π-character, with electron cloud quite distributed throughout the whole molecule. This signifies that for most of the orientations of the aromatic amine with respect to the coumarin dye there is a possibility of reasonable overlap of the HOMO of the amine donor with the HOMO-1 of the excited coumarin acceptor. Thus, the coumarin-aromatic amine system is not expected to impose any large orientational restriction for the ET reaction, though marginal orientational effect will always be present in the system as neither the acceptor nor the donor is isotropic in nature. Contrary to aromatic amines, however, the quantum chemical calculation on the electronic structure of an aliphatic amine shows that the HOMO of such a donor is of n-type character, i.e., the electron cloud is mainly localized at the amino nitrogen atom.[66] Because of this n-type character of the HOMO, for an efficient overlap between the HOMO of the aliphatic amine and the HOMO-1 of the excited coumarin, the aliphatic amine needs to have much more specific orientations with respect to the coumarin molecule than required for an aromatic amine. Hence, a coumarin-aliphatic amine system imposes much larger orientational restriction for the ET reaction compared to the coumarin-aromatic amine system. Statistically saying, the probability of those donor-acceptor orientations that permit a reasonably high V_{el} and hence the occurrence of ultrafast ET reaction

should be quite low with aliphatic amine as a donor than an aromatic amine. Evidently, among all the close-contact dye-aliphatic amine pairs, only a small fraction can have such an orientation to show the presence of the ultrafast ET component. Accordingly coumarin-aliphatic amine systems display large orientational restriction for the ET reaction. Considering the critical $x_A \sim 0.8$ for the C151-TEA system compared to $x_A \sim 0.4$ for C151-DMAN and C151-DEAN systems, we can infer that only about 50% of the close-contact dye-aliphatic amine pairs can have the donor amines suitably oriented with respect to the acceptor dye molecules to have significant V_{el} and thus ultrafast ET component. Notably, when we consider these orientations for ultrafast ET, they naturally include all those coumarin-amine close-contact pairs that on simple librational motions ($\sim$200 fs) can attain the situation of very high V_{el} and hence can result in ultrafast ET.[17]

In some of our recent studies under diffusive condition (with low reactant concentrations) in acetonitrile solution, we have observed that among different coumarin-amine systems the limiting value of the diffusion-controlled fluorescence quenching constants (k_q^{DC}) is always lower by two times or more for aliphatic amine donors compared to that with aromatic amine donors.[66,87] As observed in these studies, quenching constant k_q initially increases with reaction exergonicity $(-\Delta G^0)$ at the lower exergonicity region but eventually saturates to a diffusion-controlled limiting value of k_q^{DC} when $-\Delta G^0$ exceeds $\sim$0.4 eV. In this diffusion-controlled condition, since the k_q saturates to k_q^{DC}, the quenching rate is effectively determined by the bimolecular diffusional rate of the reactants and not by the redox characteristics of the reactants involved. Since the small changes in the size of the reactants (e.g., aliphatic and aromatic amines used) do not change the bimolecular diffusional rate constant, k_d, any significantly,[2,55] the large differences in the k_q^{DC} values involving aliphatic and aromatic amine donors cannot be rationalized in terms of the differences in the k_d values of the reactants.[66,87] Similarly, the relative magnitudes of the observed k_q^{DC} values using aliphatic and aromatic amine donors were seen not to show any correlation with the acid-base characteristics $(pK_b$ values) of the amines involved.[66,87] It was thus suggested in our earlier work that the differences in the k_q^{DC} values were mainly due to the large differences in the orientational restrictions imposed by the aliphatic and aromatic nature of the amine donors toward the ET reaction.[66,87] It was proposed that due to the n-type character of the aliphatic amines, their HOMO, which is localized to the amino nitrogen, required to be oriented directly toward the acceptor dyes in the encounter complex such that the V_{el} can become sufficient enough to give the efficient ET reaction. Under diffusive condition, since an aliphatic amine can encounter with an acceptor dye with all possible orientations in space and since only a small fraction (ρ) of these encounters can have a suitable orientation of the amine for an efficient ET reaction, the aliphatic donors inherently impose a large orientational restriction for the ET reactions in these systems. Considering this orientational restriction for the ET reaction under diffusion-controlled condition, the observed k_q^{DC}, for aliphatic amine donors should be given as k_q^{DC}

$= \rho k_d$, where ρ should be much lower than unity. For aromatic amines, since their HOMO is of π-type character and is distributed quite largely over the whole molecule,[17,66] a relatively large fraction of the amine orientations with respect to the acceptor dye are expected to give reasonably high V_{el} and hence efficient ET reaction. Thus, with aromatic amine donors, ρ will be much higher and accordingly k_q^{DC} will be more closer to the expected k_d value than in the case of aliphatic amine donor.[66,87] Note here that in our earlier studies, from a comparison of the expected k_d and experimentally observed k_q^{DC} values, rough estimates for the factor ρ for coumarin-aliphatic and coumarin-aromatic amine systems were estimated as ~ 0.34 and ~ 0.82, respectively.[66,87] It is thus indicated that relative to the dye-aromatic amine systems, at least 50% or more of the dye-aliphatic amine encounter pairs will not have a proper amine orientation to give the effective ET reaction. The observation in the present study that the critical x_A value for aliphatic amine ($x_A \sim 0.8$) is about two times higher than that of the aromatic amines ($x_A \sim 0.4$) in relation to the ultrafast ET component certainly corroborates the concept of much larger orientational restriction for the ET reaction involving aliphatic amine donors in comparison with aromatic amine donors. Note that the differences in the ET efficiency involving aliphatic and aromatic nature of the donors have also been reported and discussed earlier for many ET reactions in different perspectives.[17,33,34,88–90] We infer from the present results that the large differences in the critical x_A values involving aliphatic and aromatic amine donors for the observation of the ultrafast ET component are mainly related to the orientational restrictions arising due to the structural differences of the n- and π-type HOMOs of the aliphatic and aromatic amine donors.

IV. CONCLUSION

Femtosecond fluorescence upconversion measurements have been carried out in ET systems involving C151 acceptor and different aliphatic and aromatic amines as the donors to understand the orientational effect on ultrafast ET reactions under nondiffusive condition. Using either neat amine as the solvent donors or by diluting the amine solvents by suitable diluents of similar dielectric constant as that of the amine solvents, it is observed that up to certain dilution of the amines the fastest lifetime component (τ_1) of the dye fluorescence decay remains almost in the similar range. This τ_1 component is assigned to the fastest ET time in these systems and corresponds to the ET reactions between close-contact acceptor-donor pairs where donor amines are properly oriented with respect to the C151 acceptor such that there is maximum acceptor-donor electronic coupling (V_{el}) and hence the fastest ET reaction. It is interestingly observed that the τ_1 component of the fluorescence lifetime of the dye remains almost in the similar range up to a critical amine dilution, which in terms of amine mole fraction (x_A) in the solution is found to be $x_A \sim 0.4$ for aromatic amines but $x_A \sim 0.8$ for aliphatic amines. Such a large difference in the critical x_A values for aliphatic and aromatic amine donors is attributed to the differences in the orientational restrictions imposed by the aliphatic and aromatic nature of the amine donors. It is inferred that due to the n-type character, the HOMO of the aliphatic amines is mainly localized at the amino nitrogen. Thus the maximum V_{el} and hence the fastest ET are possible only for those acceptor-donor contact pairs where the amino nitrogen of the aliphatic amines is oriented toward the C151 dye. With π-type character, the HOMO of the aromatic amines is largely distributed throughout the whole molecule and thus majority of the amine orientations with respect to the acceptor dye can give significant V_{el} and hence the fastest ET component. With aliphatic amines as the donors since a large fraction of the close-contact acceptor-donor pairs cannot have significant V_{el}, the fastest ET component becomes unobserved in dye fluorescence decays at much lower dilution of these amines ($x_A \sim 0.8$) compared to that of the aromatic amines ($x_A \sim 0.4$). It is clearly indicated from the present results that the aliphatic and aromatic amine donors impose largely different orientational restrictions for the observation of ultrafast ET reactions under the condition of solvent as a donor or with very high donor concentrations.

SUPPORTING INFORMATION

The fits of the relevant fluorescence decays and the wavelength dependent changes in the fluorescence decays are shown in the supporting information. Supporting information for this article is available on the journal website or from the author.[91]

ACKNOWLEDGMENTS

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