

Photophysical Properties of Coumarin-152 and Coumarin-481 Dyes: Unusual Behavior in Nonpolar and in Higher Polarity Solvents

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Received: July 1, 2002; In Final Form: March 27, 2003

Solvent polarity and temperature effect on the photophysical properties of two 1,2-benzopyrone dyes, namely, coumarin-152 (C152) and coumarin-481 (C481), have been investigated using steady-state and time-resolved fluorescence measurements. In nonpolar (NP) solvents (e.g., hexane, cyclohexane, methylcyclohexane, 2-methylpentane, and 3-methylpentane), the Stokes' shifts ($\Delta\bar{\nu}$) and fluorescence lifetimes (τ_f) for both the dyes are unexpectedly lower. Excluding NP solvents, for all other solvents the $\Delta\bar{\nu}$ correlates linearly with the solvent polarity function, $\Delta f = \{(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)\}$, and the slopes of these plots indicate that the fluorescent states for both the dyes in these solvents are of intramolecular charge transfer (ICT) character. The unusually lower $\Delta\bar{\nu}$ and τ_f values in NP solvents have been rationalized considering nonpolar structures for the fluorescent states of the dyes in these solvents. The fluorescence quantum yields (Φ_f) and τ_f values of the two dyes also show an unusual reduction in higher polarity solvents ($\Delta f > \sim 0.2$). Furthermore, unlike in all other solvents, in solvents with $\Delta f > \sim 0.2$, the Φ_f and τ_f values are strongly temperature-dependent. These results indicated the involvement of a new activation-controlled nonradiative deexcitation channel in higher polarity solvents, assigned to the involvement of the nonfluorescent twisted intramolecular charge transfer (TICT) state. Though the activation barrier (ΔE_a) for such processes usually decreases with solvent polarity, for the present systems the ΔE_a is seen to increase with Δf . This unusual behavior has been rationalized assuming that the ΔE_a arises because of the potential energy (PE) crossing of the TICT and ground states rather than that of the ICT and TICT states as is usually the case for most TICT molecules. On increasing Δf , since the highly polar TICT state not only gets better stabilization but also its PE surface becomes more steeper than the ICT state, the ΔE_a effectively increases with solvent polarity.

1. Introduction

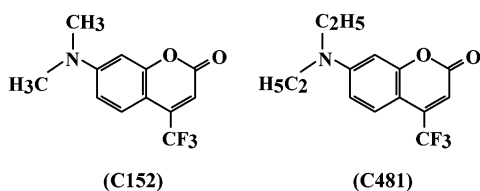
Derivatives of 1,2-benzopyrone, commonly known as the coumarin dyes, are the well-known laser dyes for the blue-green region.^{1–7} Among these dyes, the ones having different amino groups at 7-position (commonly known as 7-aminocoumarins) are of special significance in relation to their different applications.^{1–12} The fluorescence quantum yield (Φ_f) of these dyes is usually very high, often close to unity.^{1–12} Though in some of these dyes the internal conversion (IC) process contributes marginally to deexcite the fluorescent state, the contribution of intersystem crossing (ISC) process is mostly negligible.^{8–12} These dyes undergo substantial changes in their dipole moments on excitation,^{1–12} causing large Stokes' shifts between their absorption and fluorescence spectra.^{1–12} These Stokes' shifts are again very sensitive to the solvent polarities.^{1–12} Because of these properties, the 7-aminocoumarin dyes have widely been used as probes in a variety of investigations, namely, in the study of solvatochromic properties,^{8–12} determination of polarities in microenvironments,^{13,14} investigation of photoinduced electron-transfer dynamics,^{15–18} measurements of solvent relaxation times (τ_s),^{19–25} and so forth.

Photophysical properties of coumarin dyes have been the subject of extensive investigation for the last several years.^{1–12,26–29} Though a number of 7-aminocoumarin dyes are reported to display some unusual behavior, the reason of these

observations are either not adequately addressed or not properly understood in the earlier studies. Recently, we have investigated the detailed photophysical properties of a 7-aminocoumarin dye, namely, coumarin-151 (C151; 7-amino-4-trifluoromethyl-1,2-benzopyrone) in different solvents.³⁰ It has been observed that C151 displays unusual photophysical behavior in nonpolar solvents in comparison to those in all other solvents.³⁰ From a detailed solvent polarity and temperature-dependent studies, as well as from the picosecond laser flash photolysis and pulse radiolysis results, it has been inferred that C151 exists in different structural forms in nonpolar and other solvents.³⁰ In the literature, it is reported that the coumarin dyes with 7-dialkylamino groups (e.g., 7-*N,N*-dimethylamino-4-trifluoromethyl-1,2-benzopyrone; coumarin-152; C152; and 7-*N,N*-diethylamino-4-trifluoromethyl-1,2-benzopyrone; coumarin-481; C481) behave unusually in higher polarity solvents, showing drastic reduction in their Φ_f and fluorescence lifetimes (τ_f) values.^{8–12} Though the involvement of twisted intramolecular charge transfer (TICT) states has been invoked to explain these results in higher polarity solvents, detailed analysis for different decay channels of the excited states is lacking.^{8–12} In the present work, solvent polarity and temperature effect on the photophysical properties of C152 and C481 dyes have been investigated in detail to understand the complete deexcitation mechanism of the excited dyes in different solvents. Chemical structures of C152 and C481 dyes are shown in Chart 1.

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CHART 1



2. Materials and Methods

Laser-grade C152 and C481 dyes were obtained from Exciton and used without further purification. The organic solvents used were of spectroscopic grade from Spectrochem India. Dielectric constants (ϵ) and refractive indices (n) of pure solvents were taken from literature³¹ and those of the mixed solvents (ϵ_{MS} , n_{MS} , respectively) were estimated from the volume fractions (f) of the cosolvents using eqs 1 and 2, respectively.^{32–37}

$$\epsilon_{MS} = f_A \epsilon_A + f_B \epsilon_B \quad (1)$$

$$n_{MS}^2 = f_A n_A^2 + f_B n_B^2 \quad (2)$$

where the subscripts A and B represent the respective cosolvents. Following Lippert and Mataga, the polarity parameter (Δf) for different solvents were estimated using eq 3.^{38–41}

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (3)$$

Absorption spectra of the dyes were recorded using a Shimadzu model UV-160A spectrophotometer. Steady-state fluorescence measurements were recorded after correction for the wavelength-dependent instrument responses using a Hitachi spectrofluorimeter model F-4010. The Φ_f values were measured in a comparative method,^{42,43} using $\Phi_f = 0.19$ for C151 dye in hexane as the reference.^{8,30} Fluorescence lifetimes were measured using a time-correlated single-photon-counting (TCSPC) spectrometer,^{44,45} model 199, from Edinburgh Instrument, U.K. The details of this instrument have been given elsewhere.^{46,47} Briefly, a thyatron-triggered hydrogen discharge lamp (30 kHz) having a pulse width of ~ 1.2 ns (at fwhm) was used as the excitation source. Observed fluorescence decays were analyzed following reconvolution procedure,^{44,45} using a proper instrument response function. For all the cases, the observed decays were seen to fit well with a single-exponential function as

$$I(t) = B \exp(-t/\tau_f) \quad (4)$$

where τ_f is the fluorescence lifetime and B is the preexponential factor. The reduced chi-square (χ^2) values for all the analysis were within 1.00–1.15 and the distribution of the weighted residuals were random among the data channels.^{44,45} All the present measurements were carried out in aerated solutions, keeping the samples in a 1 cm \times 1 cm quartz cell. The optical density of the solutions at the excitation wavelength was kept at about 0.3, which corresponds to the dye concentrations of about $(1.5\text{--}1.7) \times 10^{-5}$ mol dm⁻³.

3. Results and Discussion

3.1. Solvent Polarity Effect on Absorption and Fluorescence Spectra. Absorption and fluorescence spectra of C152 and C481 dyes are strongly dependent on the solvent polarities. Table 1 lists the absorption ($\lambda_{\text{abs}}^{\text{max}}$) and fluorescence ($\lambda_{\text{fl}}^{\text{max}}$) maxima (in nm) of the two dyes in different solvents along with the solvent polarity function, Δf . Figure 1A and B shows the

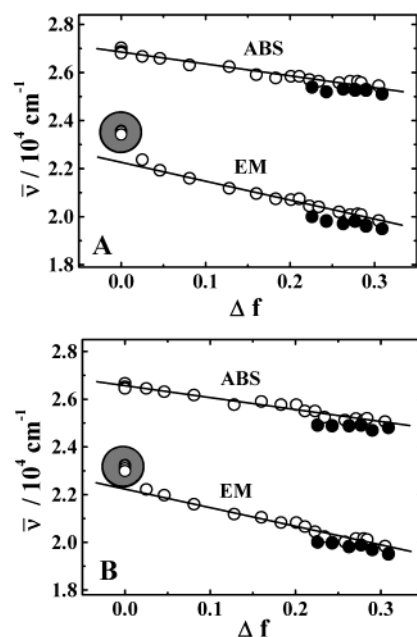


Figure 1. Plot of absorption and fluorescence maxima ($\bar{\nu}_{\text{abs}}$ and $\bar{\nu}_{\text{fl}}$, respectively, in cm^{-1}) of (A) C152 and (B) C481 against the solvent polarity function, Δf (cf. eq 3). As indicated by the large shaded circles, the $\bar{\nu}_{\text{fl}}$ values in NP solvents are unusually higher in comparison to those in other solvents. The solid circles in the plots represent the data points for the alcoholic solvents.

absorption ($\bar{\nu}_{\text{abs}}$) and emission ($\bar{\nu}_{\text{fl}}$) maxima (in cm^{-1}) versus Δf for C152 and C481 dyes, respectively. For both the dyes, the $\bar{\nu}_{\text{abs}}$ versus Δf plots are reasonably linear for all the solvents studied. The marginal deviations in the data points for alcoholic solvents (solid circles) are assigned to solute–solvent hydrogen-bonding interaction, which causes an extra red shift in the observed spectra.^{48–50} The $\bar{\nu}_{\text{fl}}$ versus Δf plots for both the dyes also have reasonably good linearity for the majority of the solvents. For the nonpolar solvents (e.g., hexane, cyclohexane, methylcyclohexane, 2-methylpentane, and 3-methylpentane; henceforth we will refer to them as the NP solvents), however, the $\bar{\nu}_{\text{fl}}$ values are unusually higher and do not correlate with those in other solvents.

For most of the molecules, their longer wavelength absorption and the fluorescence bands in different solvents arise because of transitions between the same two ground and excited electronic states.^{42,43} For these systems, the Stokes' shifts ($\Delta\bar{\nu} = \bar{\nu}_{\text{abs}} - \bar{\nu}_{\text{fl}}$) are expected to correlate linearly with Δf , following Lippert and Mataga relationship (eq 5).^{30,35–40,42,43}

$$\Delta\bar{\nu} = \Delta\bar{\nu}_0 + \frac{2\Delta\mu^2}{hcr^3} \Delta f \quad (5)$$

where $\Delta\mu = (\mu_e - \mu_g)$, μ_e and μ_g being the excited and ground-state dipole moments, respectively, h is the Planck's constant, c is the velocity of light, and r is the Onsager radius of interaction. Table 1 lists the $\Delta\bar{\nu}$ values for C152 and C481 dyes in different solvents. Figure 2A and B shows the respective $\Delta\bar{\nu}$ versus Δf plots for the two dyes. It is seen from Figure 2 that, though the $\Delta\bar{\nu}$ versus Δf plots are reasonably linear for almost all the solvents, for the NP solvents the $\Delta\bar{\nu}$ values are unusually lower. These results thus indicate that the fluorescent states of the two dyes in NP solvents must be of different nature than in other solvents.

Excluding NP solvents, in all other solvents the linear $\Delta\bar{\nu}$ versus Δf plots indicate that the nature of the fluorescent states remain the same for both the dyes.^{42,43} Thus, using eq 5 the μ_e

TABLE 1: Absorption and Fluorescence Maxima and the Stokes' Shifts for C152 and C481 Dyes in Different Solvents

solvents ^a	Δf	C152			C481		
		$\lambda_{\text{abs}}^{\text{max}}/\text{nm}$	$\lambda_{\text{em}}^{\text{max}}/\text{nm}$	$\Delta\bar{\nu}/\text{cm}^{-1}$	$\lambda_{\text{abs}}^{\text{max}}/\text{nm}$	$\lambda_{\text{em}}^{\text{max}}/\text{nm}$	$\Delta\bar{\nu}/\text{cm}^{-1}$
HX	0	371	426	3479	375	431	3465
2MP	0	370	424	3442	375	430	3411
3MP	0	370	425	3498	375	431	3465
CHX	0	372	427	3463	377	433	3431
MCHX	0	373	427	3390	378	435	3467
3MP ₉₅ EA ₀₅	0.025	375	447	4295	378	450	4233
3MP ₉₀ EA ₁₀	0.046	376	456	4666	380	455	4337
3MP ₈₀ EA ₂₀	0.081	380	463	4718	382	463	4580
3MP ₆₀ EA ₄₀	0.128	381	472	5060	388	472	4587
3MP ₄₀ EA ₆₀	0.16	386	477	4942	386	475	4854
3MP ₂₀ EA ₈₀	0.183	388	482	5026	388	480	4940
EA	0.201	387	483	5136	388	480	4940
EA ₉₈ ACN ₀₂	0.211	387	482	5093	392	484	4849
EA ₉₅ ACN ₀₅	0.223	389	489	5257	392	489	5061
OcOH	0.226	394	500	5381	401	499	4898
EA ₉₀ ACN ₁₀	0.234	390	490	5233	396	494	5009
HxOH	0.243	397	504	5348	402	501	4916
EA ₈₀ ACN ₂₀	0.258	391	495	5373	398	500	4923
BuOH	0.263	395	507	5592	402	504	5034
EA ₇₀ ACN ₃₀	0.271	390	498	5561	397	496	5028
<i>i</i> PrOH	0.277	396	504	5411	401	503	5056
EA ₆₀ ACN ₄₀	0.28	390	497	5520	398	496	4964
ACT	0.284	391	498	5495	397	497	5079
EtOH	0.290	396	509	5606	405	508	5006
ACN	0.305	393	504	5604	399	504	5221
MeOH	0.309	398	513	5632	403	512	5283

^a Abbreviations for the solvents are HX (hexane), 2MP (2-methyl pentane), 3MP (3-methyl pentane), CHX (cyclohexane), MCHX (methyl cyclohexane), EA (ethyl acetate), OcOH (octanol), HxOH (hexanol), BuOH (butanol), *i*PrOH (2-propanol), ACT (acetone), EtOH (ethanol), ACN (acetonitrile), MeOH (methanol), 3MP₉₅E₅ (95% 3MP and 5% EA, v/v), 3MP₉₀E₁₀ (90% 3MP and 10% EA, v/v), 3MP₈₀E₂₀ (80% 3MP and 20% EA, v/v), 3MP₆₀E₄₀ (60% 3MP and 40% EA, v/v), 3MP₄₀E₆₀ (40% 3MP and 60% EA, v/v), 3MP₂₀E₈₀ (20% 3MP and 80% EA, v/v), EA₉₈ACN₀₂ (98% EA and 2% ACN), EA₉₅ACN₀₅ (95% EA and 5% ACN), EA₉₀ACN₁₀ (90% EA and 10% ACN), EA₈₀ACN₂₀ (80% EA and 20% ACN), EA₇₀ACN₃₀ (70% EA and 30% ACN), EA₆₀ACN₄₀ (60% EA and 40% ACN).

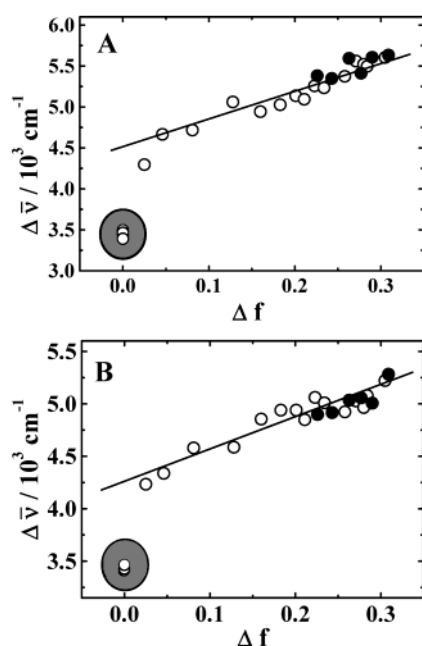


Figure 2. Plot of Stokes' shifts ($\Delta\bar{\nu}$ in cm^{-1}) for (A) C152 and (B) C481 against the solvent polarity function, Δf (cf. eq 3). As indicated by large shaded circles, the $\Delta\bar{\nu}$ values in NP solvents are unusually lower in comparison to those in other solvents. The solid circles in the plots represent the data points for the alcoholic solvents.

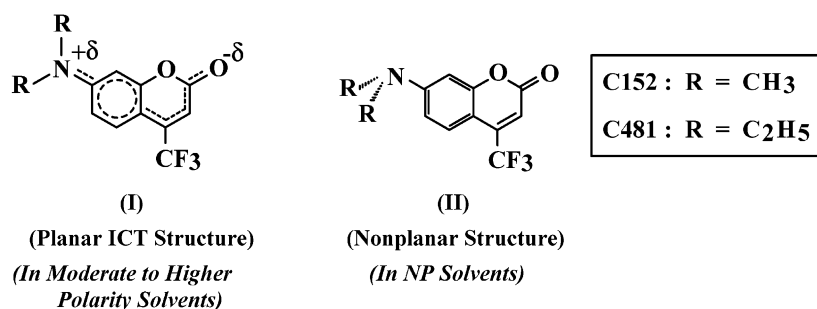
values of the two dyes were estimated from the slopes of these plots, considering r to be equal to the radii of the dyes (3.62 and 3.82 Å, respectively, for C152 and C481, as estimated using Edwards' volume addition method)⁵¹ and μ_g to be equal to 6.27 and 6.48 D, respectively, for C152 and C481.⁸ The μ_e values

of C152 and C481 thus were estimated to be about 10.4 and 10.7 D, respectively, indicating the polar nature of the fluorescent states. We assign these states to be of intramolecular charge transfer (ICT) character, with structure similar to structure I shown in Chart 2.³⁰ In the earlier works, a similar ICT character was assigned to the fluorescent states of these molecules.^{8–12}

The observation that the $\Delta\bar{\nu}$ values for both the dyes in NP solvents are unusually lower indicates that in these solvents the fluorescent states of these dyes must be much less polar than in the other solvents. At this point, it is interesting to compare present results with those obtained for C151 dye in our earlier work.³⁰ In C151, there is a simple NH_2 group at the 7-position of the 1,2-benzopyrone moiety instead of the 7-*N,N*-dialkylamino groups present in C152 and C481 dyes. With C151 also, it was observed that the $\Delta\bar{\nu}$ values in NP solvents are abnormally lower in comparison to those in other solvents. From detailed solvent polarity and temperature-dependent studies, it was inferred that in NP solvents the dye C151 exists in a nonpolar structure with its 7- NH_2 group having a pyramidal configuration and consequently out of resonance with the benzopyrone moiety. Thus, drawing an analogy with the C151 dye, we infer that C152 and C481 dyes also exist in the similar nonpolar structures in NP solvents, as schematically shown by structure II in Chart 2.

3.2. Solvent Polarity Effect on Fluorescence Quantum Yields and Lifetimes. The Φ_f values of C152 and C481 were estimated in different solvents at room temperature and are listed in Table 2. Figure 3A and B shows the Φ_f versus Δf plots for C152 and C481 dyes, respectively. The interesting point from these plots is that the Φ_f values drastically reduce in higher polarity solvents, having $\Delta f > \sim 0.2$. In the lower to medium solvent polarity region ($\Delta f < \sim 0.2$), however, Φ_f reduces only marginally with Δf following apparently a linear correlation. As discussed in section 3.1, the $\Delta\bar{\nu}$ versus Δf plots (cf. Figure

CHART 2


TABLE 2: Fluorescence Quantum Yields (Φ_f), Lifetimes (τ_f), and Radiative (k_f) and Nonradiative (k_{nr}) Decay Rate Constants for C152 and C481 Dyes in Different Solvents

solvents ^a	Δf	C152				C481			
		Φ_f	τ_f/ns	$k_f/10^7 \text{ s}^{-1}$	$k_{nr}/10^7 \text{ s}^{-1}$	Φ_f	τ_f/ns	$k_f/10^7 \text{ s}^{-1}$	$k_{nr}/10^7 \text{ s}^{-1}$
HX	0	1.00	3.48	28.74	0	1.00	3.52	28.41	0
2MP	0	1.00	3.53	28.33	0	1.00	3.74	26.73	0
3MP	0	0.98	3.52	27.84	0.57	1.00	3.70	27.02	0
CHX	0	0.97	3.51	27.64	0.85	1.00	3.69	27.10	0
MCHX	0	1.00	3.52	28.41	0	1.00	3.68	27.17	0
3MP ₉₅ EA ₀₅	0.025	0.98	4.16	23.56	0.48	0.99	4.13	23.95	0.24
3MP ₉₀ EA ₁₀	0.046	0.98	4.45	22.02	0.45	0.93	4.41	21.09	1.59
3MP ₈₀ EA ₂₀	0.081	0.90	4.67	19.27	2.14	0.89	4.48	19.87	2.46
3MP ₆₀ EA ₄₀	0.128	0.81	4.72	17.16	4.03	0.84	4.64	18.10	3.45
3MP ₄₀ EA ₆₀	0.16	0.80	4.73	16.91	4.23	0.81	4.50	18.00	4.22
3MP ₂₀ EA ₈₀	0.183	0.79	4.77	16.56	4.40	0.75	4.40	17.05	5.68
EA	0.201	0.71	4.7	15.11	6.17	0.69	3.90	17.69	7.95
EA ₉₈ ACN ₀₂	0.211	0.69	4.59	15.03	6.76	0.55	3.60	15.28	12.50
EA ₉₅ ACN ₀₅	0.223	0.68	4.45	15.28	7.19	0.50	3.55	14.08	14.08
OcOH	0.226	0.48	3.86	12.44	13.47	0.42	2.74	15.33	21.17
EA ₉₀ ACN ₁₀	0.234	0.57	4.11	13.87	10.46	0.41	2.97	13.80	19.86
HxOH	0.243	0.42	3.59	11.70	16.15	0.32	2.23	14.35	30.50
EA ₈₀ ACN ₂₀	0.258	0.45	3.65	12.33	15.07	0.31	2.21	14.03	31.22
BuOH	0.263	0.29	2.89	10.03	24.57	0.23	1.61	14.28	47.83
EA ₇₀ ACN ₃₀	0.271	0.41	3.22	12.73	18.32	0.23	1.80	13.00	42.56
iPrOH	0.277	0.28	2.79	10.03	25.81	0.20	1.37	14.60	58.39
EA ₆₀ ACN ₄₀	0.28	0.39	2.83	13.78	21.56	0.20	1.53	13.07	52.29
ACT	0.284	0.30	2.49	12.07	28.15	0.17	1.25	13.60	66.40
EtOH	0.290	0.19	1.63	11.66	49.69	0.08	0.71	11.27	129.58
ACN	0.305	0.22	1.92	11.46	40.63	0.08	0.66	12.42	139.09
MeOH	0.309	0.09	0.88	10.23	103.41	0.05	0.34	13.24	280.88

^a Abbreviations for the solvents are given in the footnote of Table 1.

2A and B) indicated that both the dyes exist in ICT structure in all these solvents excluding the NP solvents. Thus, the drastic reduction in the Φ_f values above $\Delta f \sim 0.2$ clearly indicates that in the higher polarity solvents the dye-excited states undergo a fast nonradiative deexcitation process, which is absent in lower to medium polarity solvents.

As indicated in section 3.1, in NP solvents both C152 and C481 dyes exist in nonpolar structures (cf. Chart 2), as was also inferred earlier for C151 dye.³⁰ Thus, following the fact that the Φ_f values of C151 in NP solvents are very small,³⁰ it was expected that the Φ_f values for C152 and C481 in NP solvents should also be much lower.³⁰ The apparently higher Φ_f values for C152 and C481 dyes in NP solvents are difficult to rationalize at this state without having a detailed knowledge of the τ_f , and more specifically, the radiative (k_f) and nonradiative (k_{nr}) rate constants for the dye-excited states in different solvents.

The τ_f values of C152 and C481 dyes in different solvents were measured at room temperature and are listed in Table 2. Figure 3C and D shows the τ_f versus Δf plots for the two respective dyes. It is seen that the τ_f values in lower to the medium polarity solvents (excluding NP solvents) increase only marginally with Δf following an apparently linear correlation, whereas in higher polarity solvents ($\Delta f > \sim 0.2$) the τ_f values

decrease very sharply with Δf . In NP solvents, the τ_f values are also seen to be quite lower and do not correlate with those in other solvents of lower to medium polarities. Since no specific solute–solvent interaction is expected in NP solvents, the unexpectedly lower τ_f values in these solvents support the assumption that the dye-excited states exist in different structural forms in NP and other solvents. The drastic reduction in the τ_f (and also Φ_f) values in higher polarity solvents ($\Delta f > \sim 0.2$) indicate that in these solvents there is a new nonradiative deexcitation channel operating for the fluorescent states of these dyes.

To understand the detailed deexcitation mechanism, the k_f and k_{nr} values were estimated in different solvents using eqs 6 and 7.^{35,36,42,43}

$$\Phi_f = \frac{k_f}{k_f + k_{nr}} \quad (6)$$

$$\tau_f = \frac{1}{k_f + k_{nr}} \quad (7)$$

The k_f and k_{nr} values thus obtained for the two dyes in different solvents are listed in Table 2. Figure 4A and B shows the k_f versus Δf plots and Figure 4C and D shows the k_{nr} versus Δf plots for C152 and C481 dyes, respectively. It is seen from

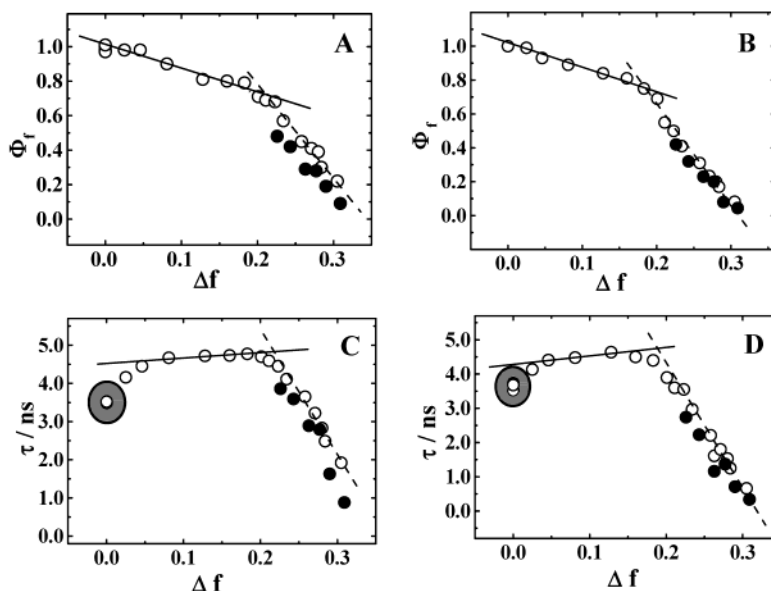


Figure 3. Variations in the Φ_f [(A) for C152 and (B) for C481] and τ_f [(C) for C152 and (D) for C481] values of the two dyes with the solvent polarity function, Δf (cf. eq 3). The solid circles in the plots represent the data points for the alcoholic solvents. The unusually lower τ_f values in NP solvents have been indicated by large shaded circles in Figure C and D.

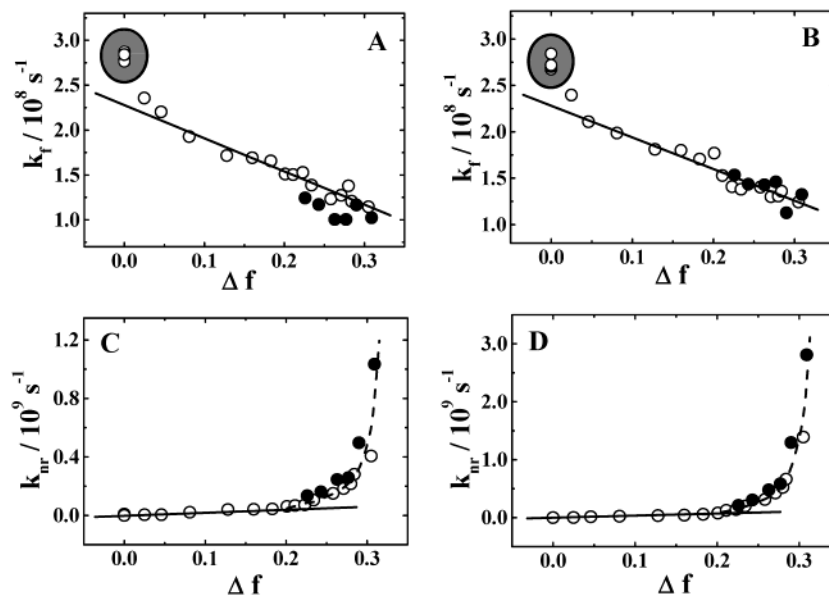


Figure 4. Plots of the radiative (k_f) and nonradiative (k_{nr}) decay rate constants for C152 (plots A and C, respectively) and C481 (plots B and D, respectively) dyes against the solvent polarity function, Δf (cf. eq 3). As indicated by large shaded circles, the k_f values in NP solvents are unusually higher in comparison to those in other solvents. The solid circles in the plots represent the data points for the alcoholic solvents.

Figure 4A and B that excluding the NP solvents, for the rest of the solvents the k_f versus Δf plots follow an apparently linear correlation. Though there is no well-defined correlation given in the literature between k_f and Δf , the apparent linearity observed experimentally indicates that the nature of the fluorescent states remains similar for all the solvents of lower to higher polarity excluding the NP solvents. As seen from Figure 4A and B, in NP solvents the k_f values are substantially higher. These results are thus in support of our assumption that the fluorescent states of the dyes in NP solvents are of different nature than in the other solvents (cf. Chart 2).

It is seen from Table 2 that the k_{nr} values for both the dyes are just negligible in NP solvents. In other lower polarity solvents ($\Delta f < \sim 0.1$), the k_{nr} values are much lower in comparison to the corresponding k_f values. Since in NP and other lower polarity solvents the k_{nr} values are exceptionally small compared to the k_f values, the Φ_f values in all these

solvents are very high and are almost in the same range. Thus, the higher Φ_f values for C152 and C481 dyes in NP solvents in comparison to those of C151 reported earlier³⁰ appear to be due to high k_f and negligible k_{nr} values. Because of the same reason, the Φ_f values of C152 and C481 dyes in NP solvents apparently correlate with those in other lower to medium polarity solvents, as indicated by Figure 3A and B, though the dye-excited states are supposed to be of different structural forms in NP and other solvents.

As indicated by Figure 4C and D, the k_{nr} versus Δf plots are apparently linear for the lower to medium polarity solvents ($\Delta f < \sim 0.2$). For the higher polarity solvents ($\Delta f > \sim 0.2$), however, the k_{nr} values are seen to increase almost exponentially with Δf . These results thus clearly indicate that in higher polarity solvents a fast nonradiative deexcitation channel operates for both the dyes, which is absent in lower to medium polarity solvents.

TABLE 3: The Transition Dipole Moments for Absorption (M_{abs}) and Fluorescence (M_{fl}) for C152 and C481 Dyes in Different Solvents

solvents ^a	Δf	C152		C481	
		M_{abs}/D	M_{fl}/D	M_{abs}/D	M_{fl}/D
HX	0	4.70	5.44	4.91	5.51
3MP	0	4.78	5.59	4.96	5.40
MCHX	0	4.82	5.37	4.85	5.35
3MP ₈₀ EA ₂₀	0.081	4.69	5.15	4.76	5.23
3MP ₄₀ EA ₆₀	0.16	4.79	5.05	4.87	5.21
EA	0.201	4.83	4.97	5.00	5.20
EA ₈₀ ACN ₂₀	0.258	4.82	4.84	4.95	4.99
ACN	0.305	4.95	4.95	5.06	4.96

^a Abbreviations for the solvents are given in the footnote of Table 1.

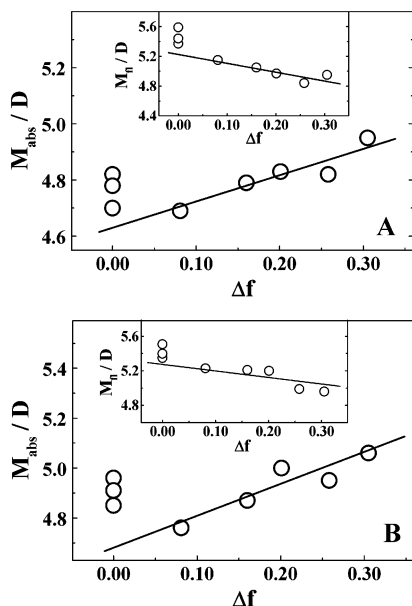


Figure 5. Plots of the M_{abs} for C152 and C481 dyes (plots A and B, respectively) against the solvent polarity function Δf (cf. eq 3). The M_{fl} versus Δf plots for C152 and C481 dyes are shown in the insets of Figure 5A and B, respectively.

At this stage, it is interesting to calculate and compare the transition dipole moments for absorption (M_{abs}) and fluorescence (M_{fl}) for the present dyes in NP and other solvents. The M_{abs} and M_{fl} values for C152 and C481 dyes in some selective NP and other solvents were calculated using the following relations.^{42,43}

$$M_{\text{abs}}^2 = \frac{3h}{8\pi^3 N_0 \nu_{\text{abs}}^{\text{max}}} \cdot \frac{2303c}{n} \int \epsilon_{\nu} d\nu \quad (8)$$

$$M_{\text{fl}}^2 = \frac{3c^3 h k_f}{64\pi^4 n^3} \cdot \frac{\int (F_{\nu}/\nu^3) d\nu}{\int F_{\nu} d\nu} \quad (9)$$

where h is the Planck's constant, N_0 is the Avogadro's number, c is the velocity of light in a vacuum, $\nu_{\text{abs}}^{\text{max}}$ is the absorption maxima, ϵ_{ν} is the molar extinction coefficient at ν , k_f is radiative rate constant, F_{ν} is the fluorescence intensity at ν , and n is the refractive index of the solvent. The M_{abs} and M_{fl} values thus estimated for C152 and C481 dyes are listed in Table 3. Figure 5A and B shows the M_{abs} versus Δf plots for the two respective dyes. The M_{fl} versus Δf plots for the two dyes are shown in the insets of Figure 5A and B, respectively. It is seen from Figure 5 that both M_{abs} and M_{fl} values for the two dyes in NP solvents are unexpectedly higher and do not correlate with those in other solvents. These results are thus in agreement with our assump-

tion that in NP solvents the fluorescent states of the two dyes exist in different structural form than in other solvents. As seen from Table 3, the M_{fl} values appear to be somewhat higher than the M_{abs} values for the majority of the solvents. The exact reason for this is not very clear to us. We tentatively feel that there is a large difference in the nuclear coordinates of the potential energy (PE) surfaces in the ground and excited states, which causes a variation in the transition probabilities for the absorption and fluorescence processes for these dyes.

3.3. Temperature Effect on Fluorescence Quantum Yields and Lifetimes. The steady-state (SS) fluorescence properties of C152 and C481 dyes are temperature-independent in NP and other lower to medium polarity ($\Delta f < \sim 0.2$) solvents. In higher polarity solvents ($\Delta f > \sim 0.2$), however, the Φ_f values gradually decrease with temperature. Figure 6A and B shows typical temperature-dependent fluorescence spectra of C152 and C481 dyes, respectively, in ACN solution. The Φ_f versus T (absolute temperature) plots for the two respective dyes in ACN solution are shown in Figure 6C and D. Similar results were also obtained in other higher polarity ($\Delta f > \sim 0.2$) solvents, though the extent of the effect increased with Δf . Since for the lower to medium polarity solvents k_f dominates over k_{nr} , and since Φ_f is independent of temperature in these solvents, it is indicative that k_f is in fact temperature-independent, which is also the case for most fluorescent molecules.^{31,32,38,39} Thus, considering k_f to be temperature-independent, the temperature-dependent Φ_f values in higher polarity solvents were analyzed using modified Arrhenius' eq 10.⁵²

$$\frac{1}{\Phi_f} = 1 + \frac{k_{\text{nr}}}{k_f} = 1 + \left(\frac{1}{k_f}\right) k_{\text{nr}}^0 \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (10)$$

where k_{nr}^0 is the preexponential factor and ΔE_a is the activation barrier for the nonradiative channel. Following eq 10, linear $\ln\{(1/\Phi_f) - 1\}$ versus $1/T$ plots were obtained for the two dyes in different solvents having $\Delta f > \sim 0.2$. Such typical plots in ACN solutions are shown in the insets of Figure 6C and D for the two respective dyes. The ΔE_a values estimated from the slopes of such plots are listed in Table 4. It is seen from Table 4 that the ΔE_a values for both the dyes gradually increase with an increase in Δf .

As already mentioned, the Φ_f in NP solvents are independent of temperature. It is thus indicated that in NP solvents there is no activation-controlled deexcitation channel for the excited dyes. It is interesting at this point to compare these results with those obtained earlier for C151 in NP solvents.³⁰ For C151, the Φ_f values in NP solvents were strongly temperature-dependent, and the observed temperature effect was inferred to be arising through the flip-flop motion of the 7-NH₂ group of the dye with a nonplanar structure.³⁰ Since C152 and C481 dyes are also supposed to exist in the similar nonpolar structures in NP solvents (cf. Chart 2), the temperature independence of Φ_f for the present dyes in NP solvents apparently seems to be somewhat puzzling. If, however, it is considered that the 7-dialkylamino groups in the present dyes are much heavier than the 7-NH₂ group in C151, it is possible that the flip-flop motions of the former groups are very slow compared to that of the latter. Thus, such a motion cannot introduce any competitive deexcitation channel for the excited C152 and C481 dyes, as was otherwise observed for C151.³⁰

Like the Φ_f values, the τ_f values of the two dyes were also temperature-independent in NP and other lower to medium polarity solvents ($\Delta f < \sim 0.2$) but strongly temperature-dependent in higher polarity solvents ($\Delta f > \sim 0.2$). Figure 7A

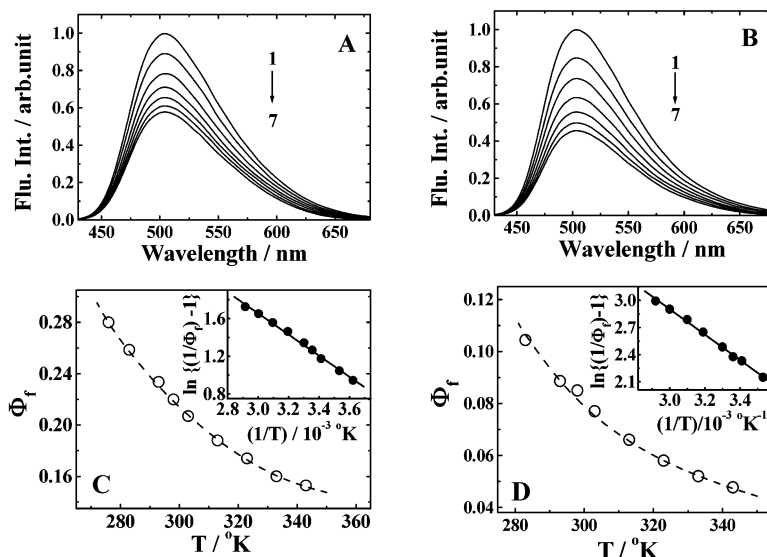


Figure 6. Steady-state fluorescence characteristics of C152 and C481 dyes in acetonitrile solution at different temperatures. Figure A and B shows the fluorescence spectra for C152 and C481 dyes, respectively, at temperatures of 10, 20, 30, 40, 50, 60, and 70 °C (spectra 1–7, respectively). Figure C and D shows the changes in the Φ_f values with absolute temperature (T) for C152 and C481 dyes, respectively, in acetonitrile solutions. Insets of Figure C and D show the corresponding Arrhenius plots obtained in accordance with eq 10.

TABLE 4: Activation Energies (ΔE_a) for the Nonradiative Deactivation Process in the Excited Singlet State of C152 and C481 in Different Polar Solvents

solvents ^a	Δf	C152		C481	
		$\Delta E_a(\text{SS})^b/$ kcal mol ⁻¹	$\Delta E_a(\text{TR})^c/$ kcal mol ⁻¹	$\Delta E_a(\text{SS})/$ kcal mol ⁻¹	$\Delta E_a(\text{TR})/$ kcal mol ⁻¹
OcOH	0.226	1.1	0.9	2.0	2.2
HxOH	0.243	1.1	1.0	2.1	2.3
ACT	0.284	1.1	1.3	2.1	2.3
EtOH	0.290	2.1	1.9	2.8	2.6
ACN	0.305	2.2	2.1	2.8	2.9
MeOH	0.309	2.6	2.3	3.1	3.3

^a Abbreviations for the solvents are given in the footnote of Table 1.

^b Steady-state (SS) measurements. ^c Time-resolved (TR) measurements.

and B shows the τ_f versus T plots in ACN solutions for the two respective dyes. Similar results but with varying extent of the effects were also obtained in other higher polarity solvents. Assuming k_f to be temperature-independent,^{35,36,42,43} the temperature effect on τ_f in different solvents was correlated using modified Arrhenius' eq 11.⁵²

$$\frac{1}{\tau_f} = k_f + k_{nr} = k_f + k_{nr}^0 \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (11)$$

Typical linear $\ln\{(1/\tau_f) - k_f\}$ versus $1/T$ plots for C152 and C481 dyes in ACN solutions are shown in the insets of Figure 7 A and B, respectively. The ΔE_a values estimated from the slopes of such plots in different solvents are also listed in Table 4. It is seen that these ΔE_a values in different solvents are very similar to those obtained from the temperature-dependent Φ_f measurements and increase gradually with an increase in Δf .

3.4. Nonradiative Deexcitation Channel in Higher Polarity Solvents and the Prevailing Mechanism. From the temperature-dependent Φ_f and τ_f measurements, it is clearly indicated that the fluorescent states of C152 and C481 dyes undergo very fast nonradiative deexcitation in higher polarity solvents ($\Delta f > \sim 0.2$). Such a process is, however, absent in other solvents of lower to medium polarities ($\Delta f < \sim 0.2$). For most of the coumarin dyes, the ISC process does not contribute significantly in deexciting the fluorescent state, and the major nonradiative

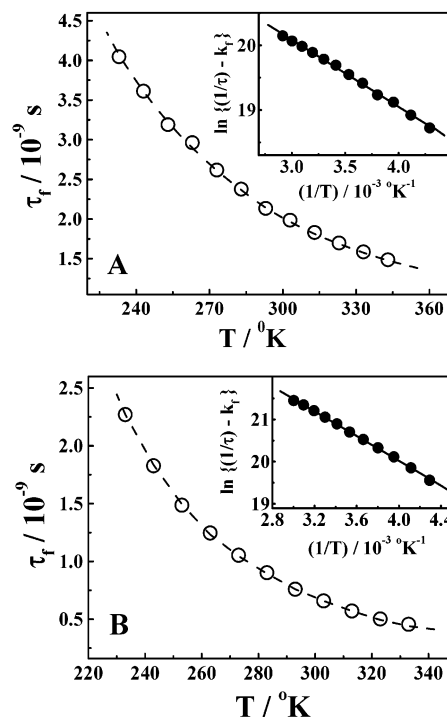


Figure 7. Temperature effect on the fluorescence lifetimes (τ_f) of (A) C152 and (B) C481 dyes in acetonitrile solutions. Insets: Show the corresponding Arrhenius plots obtained in accordance with eq 11.

channel for these dyes is the IC process.^{1–12} It is seen from Figure 4C and D that for the lower to medium polarity solvents ($\Delta f < \sim 0.2$) the k_{nr} (arising because of IC) for C152 and C481 dyes increases only marginally with Δf . Since both the dyes exist in the same ICT character in all the solvents of lower to higher polarities (cf. section 3.1), a sudden increase in IC in solvents having $\Delta f > \sim 0.2$ is highly unlikely. It is thus supposed that in the higher polarity solvents a new deexcitation channel becomes operative over and above the intrinsic IC and fluorescence processes. Considering the chemical structures of the dyes, and following Jones et al.^{9–12} and Rechthaler and Köhler,⁸ we infer that this new deexcitation channel arises because of the involvement of a nonfluorescent TICT state as an intermediate.

CHART 3

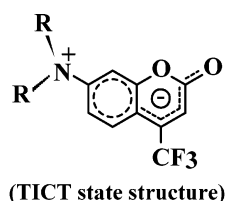
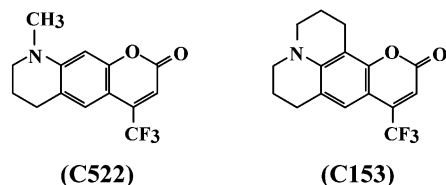


CHART 4



Schematically, the TICT state for the present dyes can be presented as in Chart 3, which is basically a zwitterionic structure and thus expected to stabilize more in higher polarity solvents.^{53–57} The feasibility of TICT state formation in 7-amino coumarins is expected to be determined by the electron-donating power of the 7-amino groups.^{53,54} In our earlier study with C151, it has been observed that with a weakly donating 7-NH₂ group there is no TICT state formation even in a strongly polar solvent.³⁰ Since the 7-*N,N*-dialkylamino groups are much stronger donors, it is possible that the TICT states in C152 and C481 dyes undergo substantial stabilization in solvents having $\Delta f > \sim 0.2$ and consequently introduce a new deexcitation channel via the ICT \rightarrow TICT \rightarrow ground-state conversion.

Since the TICT state formation requires a rotation (by 90°) of the 7-*N,N*-dialkylamino group with respect to the 1,2-benzopyrone moiety,^{55–57} it is expected that such a process can effectively be stopped if the rotation at the 7-amino groups of the dyes can be restricted. Evidence for this has been found in the present work by comparing the results of C152 and C481 with those of the other two homologous dyes, namely, C522 and C153, the chemical structures of which are shown in Chart 4. Because of the presence of *N*-cycloalkyl substituents, the TICT state formation is supposed to be not possible in C522 and C153 dyes. In fact, with these two dyes it has been observed that both the Φ_f and τ_f values correlate linearly with Δf for all the solvents studied, without showing any unusual reduction of the values even in very high polarity solvents. Further, irrespective of the solvent used, the Φ_f and τ_f values are temperature-independent for C522 and C153 dyes. Thus, comparing the results of C152 and C481 with those of C522 and C153 dyes, it is indicated that the TICT states are in fact involved in the deexcitation mechanism for the former two dyes in higher polarity solvents. It is also indicated from the present results that the TICT states of C152 and C481 dyes are nonfluorescent in nature. Though the exact reason for this is not very clear to us, it is probably related to the large geometrical differences between the TICT and the ground states, which cause the probability for the TICT to ground-state radiative transition to be extremely negligible.

It is interesting to see from Table 4 that the ΔE_a for both the dyes gradually increases with an increase in Δf . Such an observation is quite unusual as in most other TICT molecules ΔE_a is seen to decrease with solvent polarity.^{58–60} In the latter systems,^{58–60} the observed ΔE_a is supposed to arise because of the ICT and TICT state potential energy (PE) crossing and the rate of the deexcitation process is determined by the ICT \rightarrow TICT conversion rate.^{58–60} If a similar situation was also

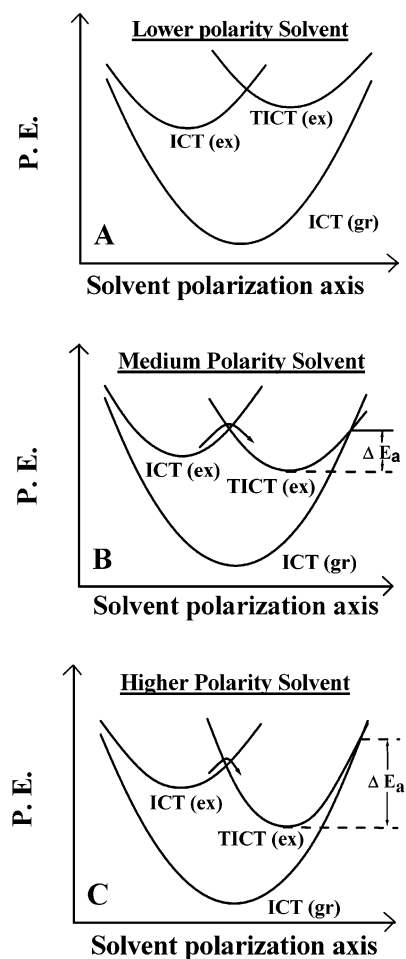


Figure 8. Conceptual potential energy (PE) diagrams showing the possible changeover of the different excited state configurations among each other with a change in the solvent polarity. The relative stabilization of different electronic states and the relative steepness of their PE surfaces with respect to the solvent polarization axis are shown only qualitatively just to indicate the expected trend.

prevailed for the present dyes, ΔE_a was expected to decrease with Δf , as the highly polar zwitterionic TICT state will be stabilizing more than the relatively less polar ICT state on increasing the solvent polarity. The increase in ΔE_a with Δf thus clearly indicates that the ICT \rightarrow TICT conversion is not the rate-determining step in the present systems. To rationalize present results, we thus propose that the TICT \rightarrow ground-state conversion is the actual activation-controlled nonradiative process in the present systems. Thus, the behavior of C152 and C481 dyes in solvents of different polarities can qualitatively be understood on the basis of the following PE diagrams shown in Figure 8. According to this figure, in the lower to the medium solvent polarity region ($\Delta f < \sim 0.2$), the TICT state is higher in energy than the ICT state and effectively there is no ICT \rightarrow TICT conversion (cf. Figure 8A). In these solvents, the fluorescent ICT states of the dyes undergo deexcitation by their intrinsic radiative (k_f) and the nonradiative (mostly IC)^{1–12} processes. On increasing $\Delta f > \sim 0.2$, the TICT structure gets more stabilized than the ICT state (cf. Figure 8B). In these solvents, thus, the ICT \rightarrow TICT conversion becomes feasible and thus a new deexcitation channel sets on through the TICT \rightarrow ground-state nonradiative transition. The fact that ΔE_a increases with Δf indicates that the ICT \rightarrow TICT conversion must be quite fast in comparison to the TICT \rightarrow ground-state conversion. With an increase in Δf further, not only the highly polar TICT state undergoes more stabilization, but also the PE

surface for this state gradually becomes more steeper (with respect to the solvent polarization axis) compared to those of the relatively less polar excited ICT and the ground states. The effects of all these are twofold. First, with increased stabilization of the TICT state, the energy gap between the TICT and the ground states reduces causing an enhancement in the deexcitation channel. Second, with the increased steepness of the TICT PE surface, the TICT and the ground states will cross gradually at higher energies with an increase in Δf (cf. Figure 8B and C). Thus, it is expected that the ΔE_a for the nonradiative deexcitation channel for the excited dyes will gradually increase with solvent polarity, as is experimentally observed for the present systems.

4. Conclusions

The photophysical properties of C152 and C481 dyes display unusual behavior both in nonpolar (NP) and in higher polarity ($\Delta f > \sim 0.2$) solvents. In the intermediate solvent polarity region ($\Delta f < \sim 0.2$; excluding the NP solvents), however, the photophysical properties of these dyes appear to be quite usual. Thus, in these solvents the Stokes shifts ($\Delta\bar{\nu}$), the fluorescence quantum yields (Φ_f), and the fluorescence lifetimes (τ_f) for both C152 and C481 dyes follow apparently linear correlation with the solvent polarity function Δf . In these solvents, it is indicated from the variations in the Stokes' shift with Δf that the fluorescent states of these dyes have the polar ICT character. In NP solvents, though, the Φ_f values are as high as those observed in other lower polarity solvents, the $\Delta\bar{\nu}$ and τ_f values are unexpectedly lower. Comparing the present results with those of C151 reported earlier,³⁰ it is inferred that in NP solvents the dye-excited states exist in a nonpolar structure, where the 7-*N,N*-dialkylamino groups of the dyes are not in resonance with the 1,2-benzopyrone moiety (cf. Chart 2). In higher polarity solvents ($\Delta f > \sim 0.2$), the Φ_f and τ_f values of both the dyes reduce drastically with an increase in Δf . Further, unlike those in the lower to medium polarity solvents ($\Delta f < \sim 0.2$), in the higher polarity solvents both Φ_f and τ_f values are strongly temperature-dependent. Considering the chemical structures of these dyes and comparing the solvent polarity and temperature-dependent results in different solvents, it is inferred that in higher polarity solvents a new activation-controlled nonradiative deexcitation channel is introduced for the fluorescent states of these molecules. It is inferred that the new deexcitation channel arises because of the involvement of the nonfluorescent TICT states. For the present systems, it is interestingly seen that the activation barrier (ΔE_a) for the new deexcitation channel gradually increases with an increase in Δf . This is an unusual observation, as in most of the TICT molecules the ΔE_a is normally seen to decrease with an increase in the solvent polarity.^{58–60} The observed results in the present systems have been rationalized on the basis of the consideration that the deexcitation of the TICT state to the ground state by a nonradiative process is the actual activation-controlled rate-determining step for the present systems. To the best of our knowledge, such an unusual solvent polarity dependence in the ΔE_a values involving TICT molecules has not so far been reported in the literature.

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