ARTICLES

Hydrogen Bonding Properties of Coumarin 151, 500, and 35: The Effect of Substitution at the 7-Amino Position

K. Das,* B. Jain, and H. S. Patel

Bio-Medical Applications Section, Center For Advanced Technology, Indore, M.P. India 452013

Received: October 4, 2005; In Final Form: December 7, 2005

The steady-state spectral properties (absorption and emission) of three structurally similar Coumarin dyes, C151, C500, and C35 were investigated in 13 different solvents. A Kamlet−Taft (KT) analysis of the spectral peak frequencies reveals that, in addition to polarity, hydrogen bonding between the carbonyl oxygen and a protic solvent in the excited state imparts maximum stabilization for C151 and minimum for C35, while that for C500 lies in between. The spectral properties of the three dyes in two solvents, chloroform and THF, which have similar polarity in the KT scale but have only hydrogen-bond donor (chloroform) and hydrogen-bond acceptor (THF) properties, are seen to be sensitive to the substitution pattern at the 7-amino position. In addition, a slow emission spectral relaxation is observed for C151 and C500 having a time constant of ∼500 ps in chloroform. For C35 this was too fast to be detected by the time resolution of our setup. The exact reason for this slow spectral relaxation in chloroform is unclear at present, and further studies are needed to understand clearly the structural effects on the hydrogen bonding dynamics of these dyes.

Introduction

The 7-amino coumarins form an important class of dyes from the point of studying the diverse nature of solute−solvent interaction.[1] These dyes are known to undergo electron transfer from the amino to the carbonyl group under optical excitation. They are also capable of forming hydrogen bond (HB) with protic solvents in the ground and in the excited state. The nature of HB between these dyes and a generalized solvent is illustrated in Figure 1 by taking C151 as an example. Three types of HB are possible which include participation of the amino nitrogen (type A), carbonyl oxygen (type B), and amino hydrogens (type C) with hydrogen-bonding solvents. It was observed earlier that due to the formation of these HBs the photophysics of the dyes gets complex.[1−2] Consequently, quite a few works have been done in order to understand better the nature of the specific HB interaction between them and polar protic solvents. Maroncelli and co-workers have examined the case of specific solvent attachment between C102 and trifluoroethanol and also specific HB interactions between various Coumarin dyes in 1-propanol.[3−4] Topp and co-workers have studied the fluorescence depolarization rates of C35, C151, and C153 in linear alcohols and found evidence for HB (type C) between C151 and the solvents in the excited state.[5] Various groups have studied the preferential solvation of C153 and C102 in a binary mixture of nonpolar and polar aprotic solvents and compared that with the binary mixture of a nonpolar and polar protic solvent. The effect of specific HB (generally type B) on the solvation statics and dynamics has thus been investigated.[6−9] The dissociation and reformation of the HB (type B) between Coumarin dyes and neat protic solvents has also been studied by fluorescence and vibrational spectroscopies. Gustavsson and co-workers have studied the spectral statics and dynamics of C151, C35, and C153 in different solvents. Fluorescence upconversion with 200 fs of time resolution revealed a 10−20-ps relaxation in methanol, which they suggest to be reformation of the HB (type B) in the excited state between the carbonyl oxygen and the solvent.[10] The influence of HB in the solvation dynamics of C102 has also been measured by time-resolved vibrational spectroscopy by monitoring the carbonyl stretching vibration. The breakage of the HB between C102 and aniline (type B) in the excited state is completed within 250 fs, and the reformation of the same has been found to take place within 30 ps. The longer reformation time of the HB has been ascribed due to nondiffusive and diffusive structural reorganization of the solvent.[11] Nibbering and co-workers have applied the same technique to study the HB dissociation dynamics of C102 in chloroform and with phenol complexes;[12] however, they have

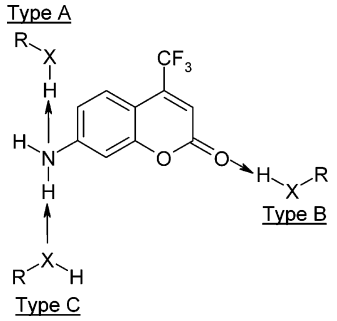

Figure 1. Illustration of different types of HB possible between the dyes and solvent taking C151 as an example. The solvent is depicted as R−X−H, where X is the electronegative atom (e.g., oxygen).

* To whom correspondence should be addressed. Phone: 091 0731 248 8431. Fax: 091 0731 248 8430. E-mail: kaustuv@cat.ernet.in.

10.1021/jp0556411 CCC: $33.50
Published on Web 01/07/2006

not observed the reformation of the HB between the dye and the solvent on a time scale of several picoseconds, as described earlier.[10−11]

For a better understanding of how the spectral properties of the dyes depend on solvents, the solvent itself needs to be characterized separately based on its polarity and HB ability. The classification of solvents with respect to their polarity and hydrogen bonding ability is done in Kamlet−Taft (KT) analysis.[13−14] In KT analysis, the solvents capable of HB have been further classified as hydrogen-bond acceptors (HBA) and hydrogen-bond donors (HBD). The HBA property of a solvent depends on its ability to accept a hydrogen from a solute to form a HB (type C in Figure 1), and the HBD property depends on its ability to donate a hydrogen to form a HB with a solute (types A and B in Figure 1). The dependence of the absorption and the emission peak frequency of a probe/solute in a solvent is given by the equation

$$\upsilon = \upsilon_0 + p\pi^* + a\alpha + b\beta \qquad (1)$$

where υ denotes the spectral peak frequency in a particular solvent, π^* denotes the polarity, α and β denotes the HBD and HBA properties of that solvent, and υ_0 denotes the peak frequency in absence of any solvent. The value of the coefficients *p*, *a*, and *b* (obtained from analyzing the spectral parameters in a series of solvents) gives an idea about the effect of polarity and HB on the spectral properties of a solute. It should be mentioned here such an analysis may not be perfect; there is always the possibility of a "solvent bias" due to limited choice of solvents. Nevertheless such an analysis provides useful information about the influence of the solvent parameters on the solute's spectral properties. The protic solvents (generally alcohols and nitriles) used to understand the nature of HB interaction in the earlier studies[4−12] have both HBA and HBD properties in the KT scale. Since the HB interaction between Coumarin dyes and protic solvents is a complex issue to resolve, it prompted us to study this interaction by choosing solvents, which have, according to KT scale, either HBD or HBA properties. THF and $CHCl_3$ were chosen, which on the KT scale have only either HBD ($CHCl_3$) or HBA (THF) properties, while having similar polarity. Three Coumarin dyes are chosen C151, C500, and C35, which are structurally very similar except for the substitution at the 7-amino position (Figure 2) are varied from hydrogen to ethyl. The organization of the paper is as follows. The dependence of the spectral peak frequency (absorption and emission) with solvent polarity and HB property was studied by doing a KT analysis. Next, the steady state and time-resolved spectral properties were examined in THF and $CHCl_3$ and compared to those in the nonpolar solvent hexane. Finally, the most important findings of this study, observation of a slower spectral relaxation of C151 and C500 in $CHCl_3$, were reported and the nature of the slower spectral relaxation is discussed.

Experimental Section

The three Coumarins (C151, C500, and C35) from Exciton Inc. were used as received. All the solvents were distilled prior to use. For all absorption and fluorescence measurements the optical density of the dyes (1 cm optical path) were kept typically 0.1 at the maximum, which corresponds to micromolar concentrations of the dyes. The spectra recorded were corrected from experimental and instrumental artifacts. For KT analysis, the absorption and emission band maxima (recorded in 13 solvents) were obtained by fitting the spectra to a log-normal function[15]

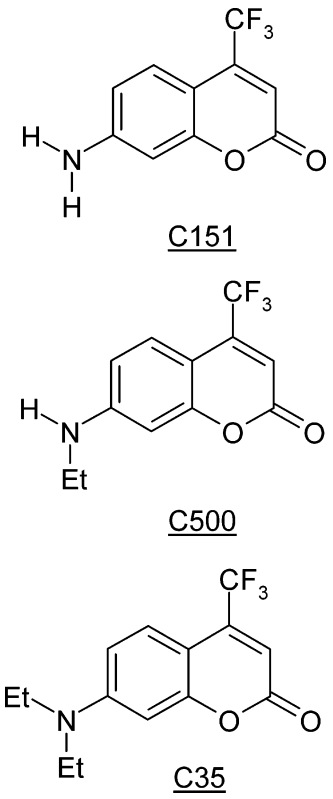

Figure 2. Chemical structures of the three Coumarin dyes used in this study

$$g(\nu) = g_0 \exp\left\{-\ln(2)\left(\frac{\ln[1 + 2b(\nu - \nu_p)/\Delta]}{b}\right)^2\right\} \text{ for } \alpha > 1$$

$$g(\nu) = 0 \text{ for } \alpha \le 1$$

where $\alpha = 2b(\nu - \nu_p)/\Delta$. This function is widely used to fit the spectra of various chromophores, which are generally asymmetric in shape. The parameters g_0, ν_p, Δ, and *b* are the peak height, peak frequency, width, and asymmetry parameter, respectively. The laser system used for the time-resolved experiments consisted of a Coherent Mira 900F femtosecond laser system, the output of which was pulse picked (Coherent 9200 pulse picker) at a rate of 3.8 MHz, and then frequency doubled in an Ultrafast harmonic generation system (Inrad 5−050). The fluorescence decays were recorded using a time-correlated single photon counting (TCSPC) system from Edinburgh instruments (Lifespec-Red). This system has an instrument response function (IRF) of 180 ps as described earlier.[16] All the dyes were excited by vertically polarized light at 360 nm, and the emission was detected at magic angle through a monochromator. To obtain time-dependent spectra in chloroform, fluorescence decays were taken at 5−10-nm intervals with a resolution of 4 nm, having 10K counts in the peak channel. The decays were analyzed with the software supplied by the manufacturer. The spectrum $S(\lambda,t)$ at a given time *t*, was constructed as follows[15]

$$S(\lambda,t) = D(t,\lambda)\frac{S_0(\lambda)}{\int_0^\infty D(t,\lambda)\,\mathrm{d}t}$$

where $D(t,\lambda)$ is the fitted decay at wavelength λ and $S_0(\lambda)$ is

TABLE 1: KT Parameters (Taken from Refs 13 and 14) and Absorption and Emission Peak Frequencies (Obtained by Log-Normal Fitting of the Spectra) of the Three Dyes in 13 Different Solvents

solvent	π^*	a	b	C151 abs (cm^{-1})	C151 em (cm^{-1})	C500 abs (cm^{-1})	C500 em (cm^{-1})	C35 abs (cm^{-1})	C35 em (cm^{-1})
1-BuOH	0.47	0.79	0.88	26115	20671	25441	20181	24832	19745
2-PrOH	0.48	0.76	0.95	26008	20886	25306	20433	24954	19921
Dioxane	0.55	0	0.37	27489	22273	26481	21493	25535	21040
EtOH	0.54	0.83	0.77	26236	20720	25443	20147	24889	19381
MeOH	0.6	0.93	0.62	26534	20524	25577	19901	24966	19604
MeCN	0.75	0.19	0.31	27299	21554	26105	20675	25070	19938
DMF	0.88	0	0.69	26179	20943	25475	20354	24842	19791
DMSO	1	0	0.76	25916	20594	25258	20090	24584	19475
water	1.09	1.17	0.18	27390	20062	25768	19569	24426	18842
hexane	−0.08	0	0	28720	24846	27317	24144	25980	23481
CCl_4	0.28	0	0	28428	24361	27107	23597	25653	22853
$CHCl_3$	0.58	0.44	0	27822	22570	26319	21729	24931	21238
THF	0.58	0	0.55	26886	22179	26016	21528	25273	20986

the steady-state fluorescence spectrum. From the time-resolved spectra the peak frequencies were obtained by fitting the experimental data points with the log-normal function as described above. By use of the peak frequencies the solvation correlation function $C(t)$ defined as[15]

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

(where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ denote the peak frequencies at zero time, at time t, and at infinite time) were constructed and its time-dependent decay analyzed to get the characteristic solvation time.

Results and Discussion

Kamlet−Taft Analysis of the Steady-State Spectra. The effects of solvent polarity and HB on the photophysics of these dyes have been the subjects of numerous investigations.[1−12,15,17−20] The peak frequencies of absorption and emission of the three dyes (obtained by fitting the spectrum to the log-normal function described in the Experimental Section) in 13 solvents along with the solvent KT parameters[13,14] are shown in Table 1. To understand separately the effect of solvent polarity and solvent HB property on the spectral peak frequencies of these dyes, the frequencies are fitted according to eq 1 as described earlier. The resulting fits for the three dyes are shown in Figure 3 where the calculated frequencies (absorption/emission) are plotted against the observed ones. The values of the coefficients p, a, and b along with the regression coefficient (R) for the fits are presented in Table 2. For C35 absorption, the fit as well as the R value is somewhat poorer in quality compared to the other data sets. The figures in parentheses in Table 2 is the relative percentage of the coefficients p, a, and b, which gives an idea about the contribution of polarity and HBD and HBA properties of the solvent on the spectral properties of the solute. As we go down the series, from C151 to C35, we see the following trends (from Table 2).

Solvent polarity: In the ground state, the contribution of polarity parameter p increases as we go from C151 to C35 (see the relative percentages in Table 2). This trend is expected because as the degree of alkylation in the 7-amino group is increased the donor property of the amino group increases making the ground state more polar. This is also supported by dipole moment values obtained theoretically.[17] In the excited state the contribution of p remains more or less similar for all the three dyes. Thus in going from ground state to the excited state the solvent polarity imparts maximum stabilization for C151 and minimum for C35, while that for C500 lies in between.

Solvent HBD: Contribution of the a coefficient increases quite significantly as we go from C151 to C35 in the ground state (see the relative percentages in Table 2). In fact the contribution of a for C151 is very little in the ground state. This suggests that hydrogen bonding between the carbonyl oxygen or the lone pair of amino nitrogen with solvent (HB types A and B in Figure 1, respectively) is not significant for C151. In the excited state the contribution of a remains similar for all three dyes (20%). This means that the stabilization offered (in going from ground to excited state), by the HBD property of a solvent is maximum for C151, decreases for C500 and for C35 it is in fact, minimum.

Solvent HBA: The contribution of the b coefficient decreases quite considerably as we go from C151 to C35 in the ground state (see the relative percentages in Table 2). This trend is also expected because the hydrogen bonds formed in this case will include the amino hydrogens (HB type C in Figure 1), and their numbers reduce as we go from C151 to C35. In the excited state, this coefficient remains more or less similar for all the three dyes and its value decreases compared to that of the ground state (except for C35). For C35, which do not have any amino hydrogens, the b value is expected to be zero both in ground and excited state.

Thus results of the KT analysis reveals that the effect of polarity and HBD and HBA properties of solvent differs considerably for the three dyes in the ground state; in the excited state these are all comparable. The trends observed are mostly explainable considering the nature of the substitution on the 7-amino position, except, the ground-state a value for C151 and the b values for C35 as discussed above. Despite the presence of a carbonyl group in C151 the a value is considerably low indicating that, according to KT analysis, HB type A and B are not favorable in the ground state. Gustavsson and co-workers have done a detailed KT analysis of the steady-state stokes shift of C151, C35, and C153 in different solvents earlier.[10] In their analysis they have used a "simplified" log-normal function and have observed that some solvents such as dioxane (used in this study), formamide, and ethylene glycol have to be omitted from the KT analysis because of some specific solute−solvent interaction (other than HB) between the dyes and the solvents. They have observed that for C151 and C35 there is a stabilization of the dye in the excited state by accepting hydrogen bonds from the solvent. However in our case we find this to be true only for C151. We should also note that as described earlier the b parameter for C35 is not zero in our case. It is possible that our limited choice of 13 solvents can affect the analysis. An attempt to fit the spectral peak frequencies of C35 by deliberately fixing the solvent b parameter to zero in eq 1 resulted in a worse fit. There may also be a possibility of other

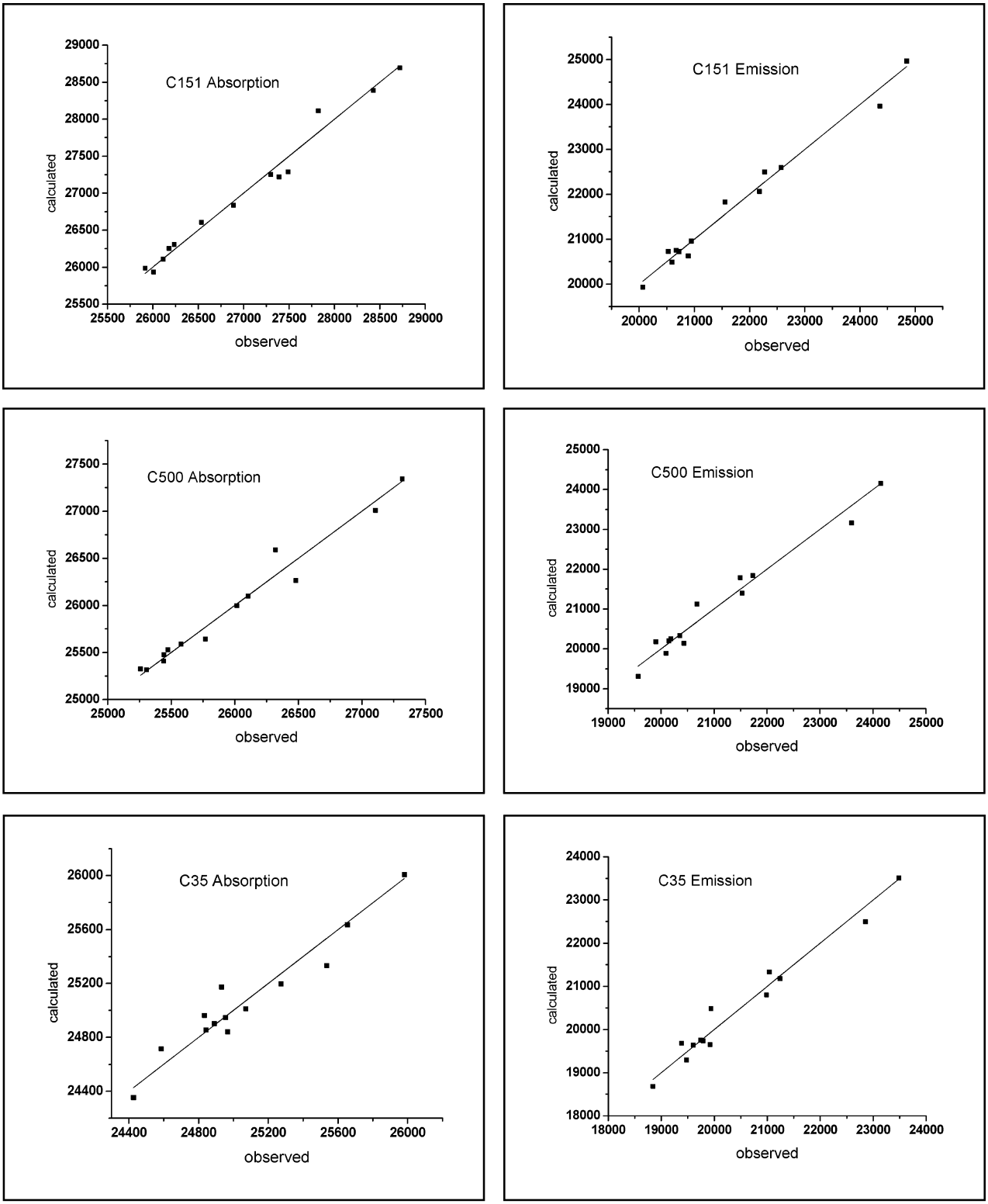

Figure 3. Plot of the calculated (KT analysis) and experimentally observed (after log-normal fitting) spectral peak frequencies (absorption and emission) of the three dyes in 13 different solvents. The solid line represents the ideal case, i.e., when the calculated values match exactly with the observed values.

specific interaction(s) (other than HB) between the solvents and C35, which the KT analysis is unable to account for. We may note here that Kohler et al. have shown earlier that, for C35, fluorescence quenching is observed at high polarity solvents irrespective of the hydrogen bonding ability of the solvent. This has been explained on the basis of the formation of a non-fluorescent TICT state in the excited state.

Spectral Properties in THF and $CHCl_3$, a Comparison with That in Hexane. We have studied the steady-state and time-resolved spectral properties of the three dyes in THF and $CHCl_3$ and compared them with that obtained in hexane. The motive behind this was to see whether there is any effect on the spectral properties of the dyes in solvents having similar polarity but capable of forming different "types" of hydrogen

TABLE 2: KT Analysis of Absorption and Emission Peak Frequencies for the Three Dyes

dye	p (π^*)[a]	b (β)[a]	a (α)[a]	ν_0[a]	R[b]
C151 abs	−843 (26%)	−2362 (73%)	−52 (1%)	28628	0.98
C151 em	−2769 (47%)	−1947 (33%)	−1228 (20%)	24744	0.98
C500 abs	−931 (36%)	−1331 (52%)	−318 (12%)	27271	0.97
C500 em	−2750 (49%)	−1699 (31%)	−1124 (20%)	23934	0.97
C35 abs	−1033 (64%)	−232 (14%)	−345 (22%)	25926	0.93
C35 em	−2814 (52%)	−1547 (28%)	−1070 (20%)	23287	0.97

[a] All the units are in cm^{-1}. The figures in parentheses indicate the relative percentage. [b] R denotes regression coefficient

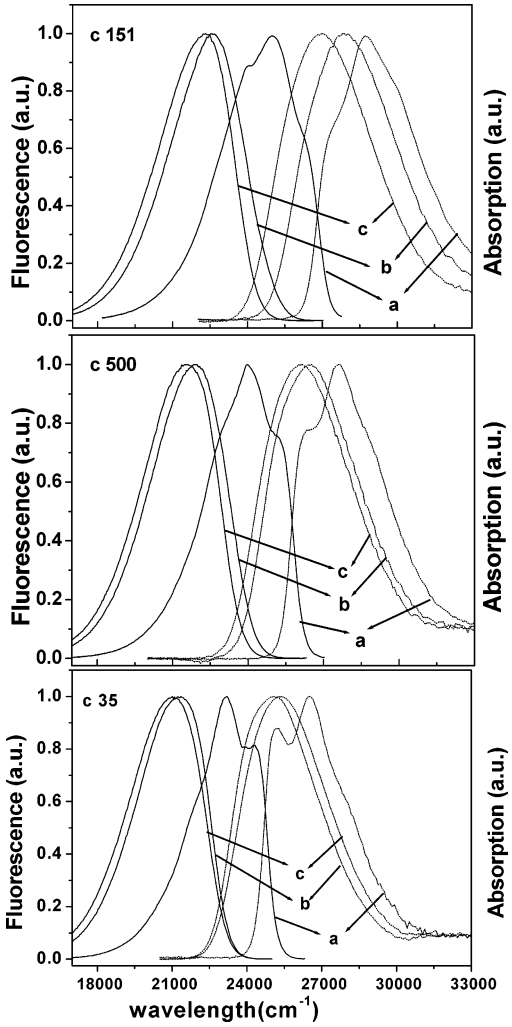

Figure 4. Peak intensity normalized absorption (dotted lines) and emission spectra (solid lines, $\lambda_{ex} = 360$ nm) of the three dyes in (a) hexane, (b) $CHCl_3$, and (c) THF.

bonds. THF, which is devoid of HBD property, will not form HB of types A and B. Since the b coefficient for C35 $\neq 0$, the effect of THF on the spectral characteristics of C35 cannot be purely due to its polarity. $CHCl_3$ is expected to contribute both polarity wise and HB wise toward the spectral characteristics for all the 3 dyes, however, being devoid of HBA property, will not form HB of type C. The peak normalized absorption and emission spectra of the three dyes in the three solvents are shown in Figure 4 and the various spectral parameters are listed in Table 3. In the nonpolar solvent hexane, all the three dyes shows structured absorption and emission. C151 is weakly fluorescent, whereas C500 and C35 are strongly fluorescent in hexane. As reported earlier, for Coumarin 151, which has no alkyl substituents at the 7-amino position, the fluorescence in

TABLE 3: Emission Properties of the Three Dyes in Hexane, $CHCl_3$, and THF

system	Stokes shift (cm^{-1})	quantum yield	fluorescence lifetime (ns)[c]	radiation lifetime (ns)
C151/hexane	3874	0.19	1.1[a]	5.7
C151/$CHCl_3$	5252	0.75	4.5[a]	6.0
C151/THF	4707	0.73	4.7[b]	6.4
C500/hexane	3173	0.76	3.7[a]	4.9
C500/$CHCl_3$	4590	0.81	4.6[a]	5.7
C500/THF	4488	0.81	4.8[b]	5.9
C35/hexane	2499	0.85	3.7[b]	4.4
C35/$CHCl_3$	3673	0.62	4.9[b]	7.9
C35/THF	4287	0.62	4.7[b]	7.6

[a] Lifetimes are nonexponential. Average lifetime values are given. [b] Lifetimes are single exponential. [c] All lifetimes were recorded by excitation at 360 nm and detecting fluorescence at the peak ± 2 nm.

nonpolar solvents has been found to be quite low.[1,2,18] This has been explained on the basis of rapid internal rotation of the amino group, which opens up the nonradiative channel for relaxation. This relaxation gets reduced in polar and protic solvents by formation of the charge transferred state and/or intermolecular H-bonding with solvents. As the hydrogens of the 7-amino group are substituted by ethyl (C500 and C35), the fluorescence becomes stronger in nonpolar solvents and gets quenched in polar solvents. A detailed study has been done earlier by Kohler et al.[1] and by Pal and co-workers.[18−19]

As the polarity and the HB property of the solvents are increased the fluorescence intensity of C151 increases, C500 remains comparable and that of C35 decreases compared to that in hexane, i.e., the trend is reversed as we go from C151 to C35. Compared to hexane, the fluorescence lifetimes however increase for all of them. The radiative lifetimes also increases for all three of them, compared to that in hexane. However, we note that the formation of a nonfluorescent TICT state for C35 should increase the nonradiative rate constant rather than to an increase in the radiative lifetime. Our results, being consistent with previous reports[1,10,18−19] shows the results of the complex interplay between various photophysical processes in the excited state. Although $CHCl_3$ and THF has similar polarity according to KT scale, it is interesting to note that for C151 and C500 the absorption spectra shift to high energy in $CHCl_3$ compared to that in THF while for C35 the trend is opposite. As discussed earlier, the KT analysis shows that in the ground state, the contribution of a parameter increases and that for b parameter decreases as we go from C151 to C35, which explains the trend observed in the absorption spectra. However, it should also be noted that this blue shift in the absorption spectra of C151 and C500 in $CHCl_3$ could also result due to a destabilization of the excited state. The emission spectra, however, for all three dyes in $CHCl_3$ show a blue shift with respect to that in THF (Figure 4). In the excited state the observed blue shift in $CHCl_3$ compared to that in THF could be due to the formation of HB type B. It is also interesting to note the trend in the intramolecular contribution to the observed stokes shift (Table 3) for the three dyes. Assuming no solvent perturbation in hexane this amounts to be 3874, 3173, and 2499 cm^{-1} for C151, C500, and C35, respectively. We note that these values also contain the apparent shift due to different (nondiagonal) Franck−Condon factors when comparing absorption and emission. The fluorescence quantum yield trend in these three solvent suggest that this intramolecular contribution consists of two parts, one which decays non radiatively to the ground state (probably due to the fast rotation of the amino group as suggested earlier, maximum for C151[1,10,18−19]) and another due to intramolecular electron transfer.

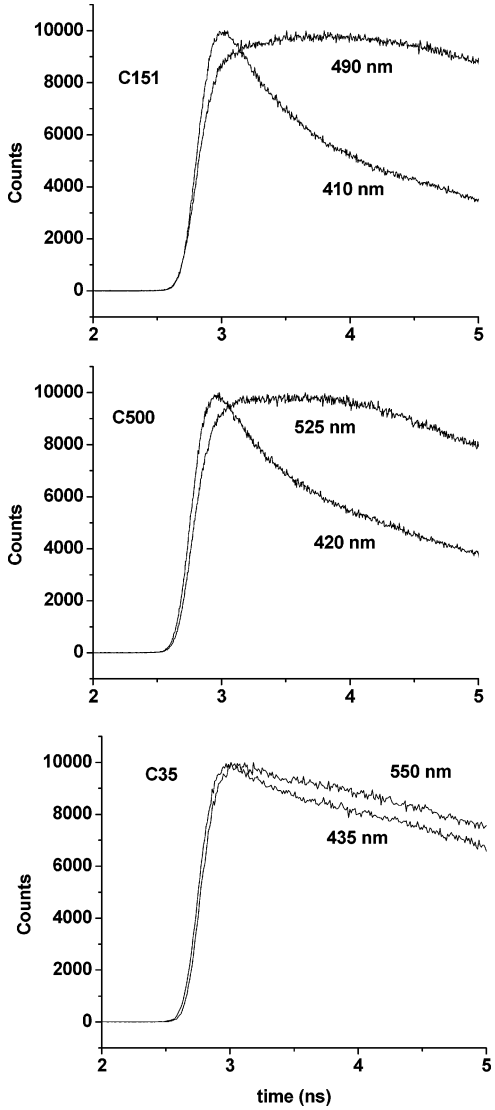

Figure 5. Fluorescence decays of the three dyes in $CHCl_3$ ($\lambda_{ex} = 360$ nm) taken at blue and at red end of the emission spectrum. The detection wavelengths (±2 nm) are indicated in each panel. *X*-axis resolution ≈ 4.90 ps.

Spectral Relaxation Dynamics in THF and $CHCl_3$. With our TCSPC setup having an IRF of ∼180 ps, no wavelength-dependent decays were observed in the HBA solvent THF indicating that spectral relaxation is too fast to be observed. Although specific solute−solvent interaction (HB type C) has been observed for C151 in linear long chain alcohols,[5] spectral relaxation in THF is expected to be much faster than the time resolution of the TCSPC system.

In contrast, a slower spectral relaxation of these dyes in $CHCl_3$ was observed. Figure 5 describes the wavelength-dependent decays of the three dyes in the HBD solvent chloroform. A fast decay at the high-energy end and decay with a growth at the low-energy end of the emission spectra were observed for C151 and C500. For C35, decays at the blue end and at the red end are quite similar; there is no observation of growth at the red, indicating that spectral relaxation for this dye is too fast to be detected by our setup. We might add that, as our data shows, the observed "fast" relaxation for C35 might be more than just a few picoseconds, which is the typical solvent relaxation time for $CHCl_3$.[20] Our results indicate that spectral relaxation of the dyes in $CHCl_3$ is slower compared to that in THF and this relaxation is slow enough for C151 and C500 to be detected by our setup. The normalized time-resolved spectra for C151 and C500 at different times are shown in Figure 6 along with the log-normal fits. Total shifts of ∼750 and ∼670 cm^{-1} were observed for C151 and C500, respectively. The time-dependent shift of the emission peak frequency for the two dyes are used to construct the solvation correlation function $C(t)$ as described earlier. Figure 7 shows the decay of $C(t)$ with time for C151 and C500, with single-exponential fit. The decay time constant is 500 and 550 ps for C151 and C500, respectively.

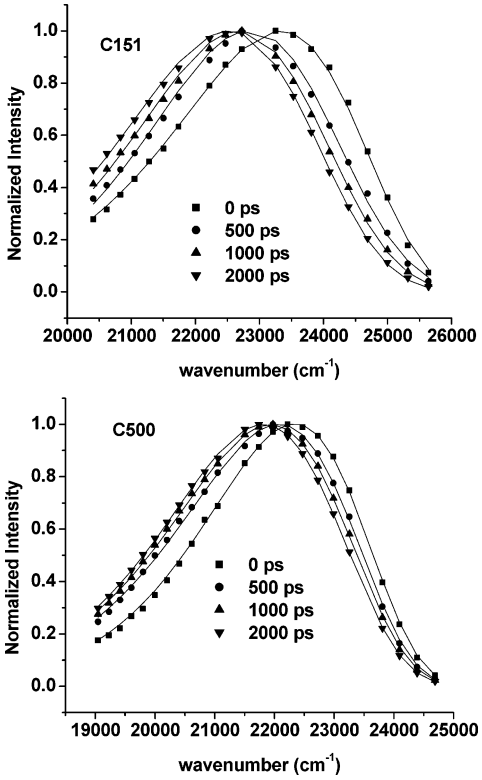

Figure 6. Normalized time-resolved emission spectra of C151 and C500 along with the log-normal fits (continuous line) showing the spectral relaxation in $CHCl_3$.

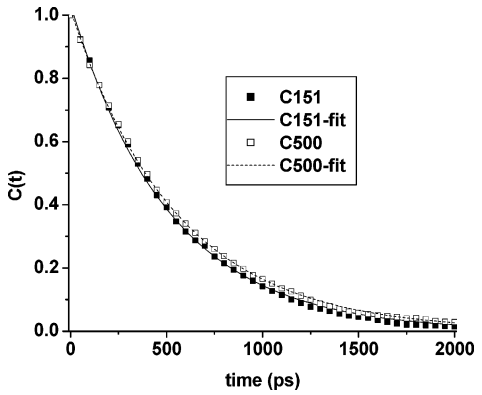

Figure 7. Decay of solvation response function $C(t)$ and single-exponential fit (continuous line) for C151 and C500 in $CHCl_3$. The time constants are 500 and 550 ps for C151 and C500, respectively.

The total stokes shift in $CHCl_3$ due to solvent polarity and HB effect can be evaluated from the difference of the stokes shift in hexane and $CHCl_3$ which are listed in Table 3. This amounts to 1378, 1417, and 1194 cm^{-1} for C151, C500, and C35, respectively. It is thus obvious that, for C151 and C500, ∼50% of the shift is too fast to be detected by our setup. Stokes shift due to solvent polarity (orientational relaxation) is expected to be much faster (typical solvent relaxation time for $CHCl_3$ is

few picoseconds[20]) and hence will be undetectable in our setup. Hence the shift observed in our spectral relaxation and its time constant is probably due to some specific interaction between $CHCl_3$ and the dyes, which seems to depend on their structural heterogeneity at the 7-amino position. The concentration of the dyes used (micromolar, see Experimental Section) is too small to effect any interaction between them, like aggregation. Specific solute−solvent interaction as that observed between C102−phenol[12] or C102−trifluoroethanol[3] may not be possible here, as $CHCl_3$ is weakly acidic. On the basis of our current findings the nature of this interaction is, at present unclear. It is possible that this "slow" spectral relaxation might be due to an HB interaction (type B) in the excited state only, but then why this is slower for C151 and C500 and faster for C35 is not clear. We hope that our finding will motivate further studies such as time-dependent monitoring of the CO stretching frequency in the excited state for a better understanding of the processes responsible for those observations.

In conclusion the absorption and emission spectral properties of three structurally similar Coumarin dyes, C151, C500, and C35, are studied in 13 different solvents. A KT analysis of the spectral peak frequencies shows that the dye−solvent hydrogen-bonding properties depends critically on the dye structure, especially substitution patterns at the 7-amino position. KT analysis further reveals that hydrogen bonding between the carbonyl oxygen and the solvent in the excited-state imparts maximum stabilization for C151 and minimum for C35, while that for C500 lies in between. The spectral properties of the three dyes in two solvents $CHCl_3$ and THF, which have similar polarity in the KT scale but have only HBD or HBA properties, respectively, are also studied. Spectral parameters in these solvents are also seen to be sensitive to the substitution pattern at the 7-amino position. The most interesting finding of this study is the observation of slow spectral relaxation of C151 and C500 in $CHCl_3$ of the order of ∼500 ps. For C35 this relaxation is too fast to be detected by our setup. The nature of this observed slow relaxation for C151 and C500 is, at present, unclear. Further studies are needed to understand clearly the structural effects on the hydrogen bonding dynamics of these dyes with solvents.

Acknowledgment. The authors wish to thank Dr. P. K. Gupta for his kind interest in this work.

References and Notes

(1) Rechthaler, K.; Köhler, G. *Chem. Phys.* **1994**, *189*, 99−116.
(2) Lopez Arbeloa, T.; Lopez Arbeloa, F.; Tapia, M. J.; Lopez Arbeola, I. *J. Phys. Chem.* **1993**, *97*, 4704−4707.
(3) Moog, R. S.; Bankert, D. L.; Maroncelli, M. *J. Phys. Chem.* **1993**, *97*, 1496−1501.
(4) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem*. **1995**, *99*, 4811−4819.
(5) Kim, T. G.; Topp, M. R. *J. Phys. Chem. A* **2004**, *108*, 7653−7659.
(6) Molotsky, T.; Huppert, D. *J. Phys. Chem. A* **2003**, *107*, 2769−2780.
(7) Molotsky, T.; Huppert, D. *J. Phys. Chem. A* 2002, *106*, 8525−8530.
(8) Krolicki, R.; Jarzeba, W.; Mostafavi, M.; Lampre, I. *J. Phys. Chem. A* **2002**, *106*, 1708−1713.
(9) Cichos, F.; Willert, A.; Rempel, U.; von Borczyskowski, C. *J. Phys. Chem. A* **1997**, *101*, 8179−8185.
(10) Gustavsson, T.; Cassara, L.; Gulbinas, V.; Gurzadyan, G.; Mialocq, J.-C., Pommeret, S.; Sorgius, M.; van der Meulen, P. *J. Phys. Chem. A* **1998**, *102*, 4229−4245.
(11) Palit, D. K.; Zhang, T.; Kumazaki, S.; Yoshihara, K. *J. Phys. Chem. A* **2003**, *107*, 10798−10804.
(12) Nibbering, E. T. J.; Fidder, H.; Pines, E. *Annu. Rev. Phys. Chem.* **2005**, *56*, 337−367.
(13) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem*. **1983**, *48*, 2877−2887.
(14) Marcus, Y.; Kamlet, M. J.; Taft, R. W. *J. Phys. Chem*. **1988**, *92*, 3613−3622.
(15) Maroncelli, M.; Fleming G. R. *J. Chem. Phys*. **1987**, *86*, 6221−6239.
(16) Das, K.; Jain, B.; Dube, A.; Gupta, P. K. *Chem. Phys. Lett*. **2005**, *401*, 185−188.
(17) McCarthy, P. K.; Blanchard, G. J. *J. Phys. Chem*. **1993**, *97*, 12205−12209.
(18) Nad, S.; Pal, H. *J. Phys. Chem. A* **2001**, *105*, 1097−1106.
(19) Nad, S.; Pal, H. *J. Phys. Chem. A* **2003**, *107*, 501−507.
(20) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem*. **1995**, *99*, 17311−17337.