Excited-State Intramolecular Charge Transfer in 9-Aminoacridine Derivative

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A new fluorochromic dye was obtained from the reaction of 9-aminoacridine with ethyl-2-cyano-3-ethoxyacrylate. It displays complex fluorescence that is ascribed to normal emission from the acridine chromophore in addition to excited-state intramolecular charge transfer (ESICT) formed upon light excitation. The analysis of the fluorescence decays in different solvents reveals two short-lived components in the range of 80−450 ps and 0.7−3.2 ns, ascribed to the formation and decay of the intramolecular charge transfer (ICT) state, in addition to a third component of about 9.0 ns, which is related to the normal emission from the acridine singlet excited state, probably in an enol-imine tautomeric form. The ICT emission is readily quenched by water addition to polar solvents, and this effect is ascribed to changes in the keto-amine/enol-imine equilibrium of this fluorochromic dye.

Introduction

9-Aminoacridine (9AA) is a fluorescent dye of the family of nitrogen heterocyclic bases.[1] This compound and its derivatives have been extensively studied due to their applications in biological fields, owing to their ability to interact strongly with biomolecules such as DNA and proteins,[2−5] and in material science, understanding its photophysical and photochemical properties in different media.[6]

Dual fluorescence is an interesting photophysical effect that occurs in many molecular systems. The most studied dual fluorescence system is that one characterized by emission from a locally excited (LE) singlet state and from excited-state intramolecular charge transfer (ESICT). This effect can be modulated by changes in the molecular structure, solvent interaction, viscosity, and pressure.[7−15] The first observation of dual fluorescence was reported in 1955 in the study of 4-(dimethylamino)benzonitrile (DMABN).[8] In addition, several new compounds that exhibit dual fluorescence have been reported, such as 1-*tert*-butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6),[9] 4-(*N*-phenylamino)benzoic acid (PhABA),[12] derivatives of tetrahydropyrene,[13] and fluorazene (FPP).[15] Some of these intramolecular charge transfer (ICT) molecules have been employed in biology and in analytical chemistry as special fluorochromes.[16−18] Also, the use of ICT systems in the design of optoelectronic devices on a small size scale is nowadays an important issue in material science.[19]

Another type of dual fluorescence much studied has its origin from an excited singlet state coupled with excited-state intramolecular proton transfer (ESIPT).[20−25] This class of chemical compounds has also fascinating photophysical properties with several applications in biology[23] and in spectroscopy.[20,22,24−25] Finally, there are molecules reported recently in the literature that display both ESICT and ESIPT processes.[26−35] For instance, amino salicylates, benzalinides, 4-(dimethylamino)-1*H*-pyrrolo-[2,3-*b*]pyridine (DPP),[33] and 2-hydroxy-4-(di-*p*-tolylamino)-benzaldehyde[35] and its 4-*N*,*N*-dimethylamino derivatives are some of the compounds with both ESICT and ESIPT processes.

In this work, an acridine derivative (9AA-ethyl-2-cyanoacrylate (9AAECA); see the molecular structure in Figure 1) is studied as a new fluorochromic compound that displays a complex excited-state behavior recognized as a combination of intramolecular charge transfer (ESICT) and keto-amine/enol-imine equilibrium, which provides this system a special spectroscopic character with strong solvatochromic effects.

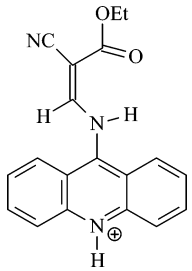

Figure 1. Molecular structure of 9-aminoacridine derivative (9AAECA cation form).

Experimental Section

Synthesis of the 9-Aminoacridine Derivative. The derivation of 9AA with a vinylene group was obtained from reaction with ethyl-2-cyano-3-ethoxyacrylate, using experimental conditions similar to those reported in the literature.[36] A 1.2 mmol sample of ethyl-2-cyano-3ethoxyacrylate (Acros Organics) was added to 1.0 mmol of 9-aminoacridine (free base prepared from 9-aminoacridine hydrochloride (Aldrich Co.) treated with ammonium hydroxide solution, and dried at low pressure in a desiccator); both were dissolved in ethanol. The system was gently heated under reflux for 6 h, cooled, and solvent evaporated under low pressure. The crude compound was purified through flash chromatography using a concentration gradient of hexane/ethyl acetate, affording a yield of 35% of a red solid after treating the main fraction eluted, identified by UV−visible absorption analysis. Signals in addition to that of the acridine moiety were as follows. FTIR (cm^{-1}): 3230 (R_2N-H), 2205 (CN), 1666 (C═O), 1631 (C═C), 1233 (C−O−C). ^1H NMR (in $CDCl_3$): 1.65 (R_2NH), 4.47−4.53 (q), 1.45−1.50 (t) of OCH_2CH_3. The cationic form of the dye was confirmed by the ^1H NMR (in $CDCl_3$) signal at 12.3 ppm of the protonated N heterocyclic. The mass spectrum (LC−MS) resulted in m/z =

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318.2, which confirms the product formation. Solvents for spectroscopic measurements were distilled and dried with 4 Å molecular sieves before use.

Instrumentation. The FTIR and ^{1}H NMR spectra were obtained using Bomem MB 102 and Bruker DRX 400 spectrometers, respectively. LC−MS mass spectrum was performed in a Micromass UK Ltd. Platform LC, using an electron spray interface with a voltage of 10 V. Absorption measurements were performed on a Cary 5G Varian spectrophotometer, and the corrected steady-state fluorescence spectra were recorded on a Hitachi spectrofluorimeter at 298 K. The samples were conditioned in a 1 × 1 cm quartz cuvette, thermostated by circulating fluid through a jacketed cuvette holder, and in air-equilibrated condition. Fluorescence quantum yields (ϕ_{em}) were calculated using quinine sulfate in 1 N H_2SO_4 ($\phi_{em} = 0.546$) as standard. Fluorescence decays in solution were measured by a time-correlated single photon counting technique using a CD-900 Edinburgh spectrometer equipped with Glan-Thompson polarizers, and a Peltier cooled PMT (Hamamatsu R955) or a Hamamatsu R3809U-50 MCP as photon detectors. The light pulse was provided by frequency doubling the 200 fs laser pulse of a Mira 900 Ti:sapphire laser pumped by a Verdi 5 W Coherent. The laser pulsed frequency was reduced by using a Conoptics pulse picker system. The fluorescence decays were analyzed by a reconvolution procedure with multiexponential models and using global methods.

Results and Discussion

Steady-State Measurements. The absorption and emission spectra of 9AAECA were studied in different organic solvents. The absorption and emission behaviors of this dye in CCl_4 (apolar solvent), in 1-methyl-2-pyrrolidone (aprotic solvent), and in 2-propanol (protic solvent) are shown in Figure 2.

The absorption spectra of 9AAECA in different solvents show a common strong absorption at about 350 nm, but low-energy bands are very distinct. These transitions are not present in the precursor dye 9AA, and are related to the effect of the ethyl-2′-cyanoacrylate substitute. The broad low-energy band shifts to red with increase of the solvent polarity (weak absorption with a shoulder at 400 nm in CCl_4, strong absorption at $\lambda_{max} = 450$ nm in 1-methyl-2-pyrrolidone and in 2- propanol with $\lambda_{max} = 470$ nm). Contrasting with its precursor 9AA, which displays a structured absorption spectrum in the region of 400 nm with weak dependency on solvent polarity, the spectral absorption behavior of 9AAECA indicates some degree of charge-transfer character, similar to what was observed with other acridine derivatives reported in the literature.[37]

The fluorescence of 9AAECA is also solvent dependent. The broad emission band in CCl_4 centered on $\lambda = 491.4$ nm is red shifted to 522 nm in polar solvents. In aprotic polar solvents such as 1-methyl-2-pyrrolidone (1M2P) and dimethyl sulfoxide (DMSO), the emission intensity is dominated by ICT character. In 2-propanol, however, in addition to the strong emission at 522 nm, there is a weak emission contribution from the LE state emission appearing at about 450 nm, only when excitation is performed at 400 nm (see Figure 2B). The excitation spectra (Figure 2C) with emission monitoring at 550 nm show maxima at 433 and 460 nm for 9AAECA in 2-propanol and 1M2P, respectively. In 1M2P solution, the excitation spectrum almost coincides with the low-energy absorption band, but for 2-propanol solution, the excitation spectrum is blue shifted about 37 nm compared with its absorption spectrum.

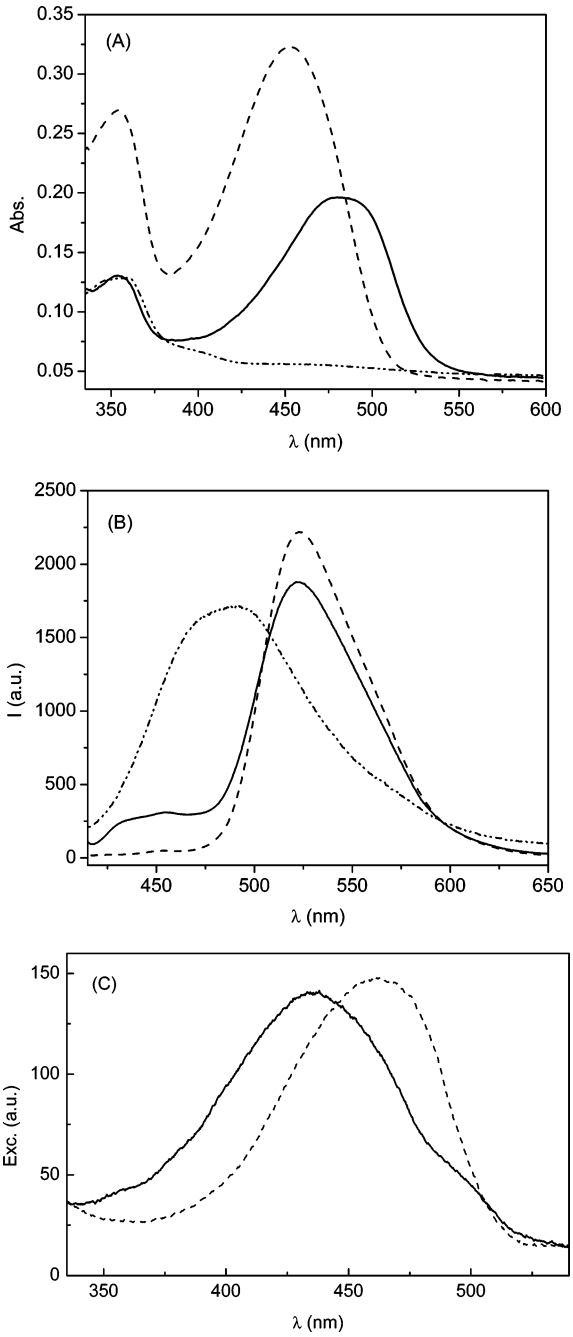

Figure 2. Electronic spectra of absorption (A), emission (excitation at 400 nm) (B), and excitation (emission at 550 nm) (C) of 9AAECA in organic solvents. (− •• −) CCl_4; (—) 2- propanol; (---) 1-methyl-2-pyrrolidone.

The emission quantum yield of the red emission of 9AAECA varies from 0.02 in ethanol up to 0.25 in 1-methyl-2-pyrrolidone. These results add additional clues to the ICT character of this dye in the excited state. The photoinduced ICT process in 9AAECA may result from the presence of the strong electron-withdrawing groups of the vinylic derivative (the CN and C═O groups) and an electron-donor group (NH). However, the presence of the acrylate group could generate keto−enol tautomerization (formally a keto-amine/enol-imine tautomerization), and in this case it will implicate the transfer of the amine proton of the NH to the carbonyl oxygen with formation of an enol form. In such a situation, the observed red emission band should be ascribed to ESICT coupled with keto-amine/enol-imine equilibrium. This assumption will be discussed in more detail with time-resolved fluorescence data analysis (vide

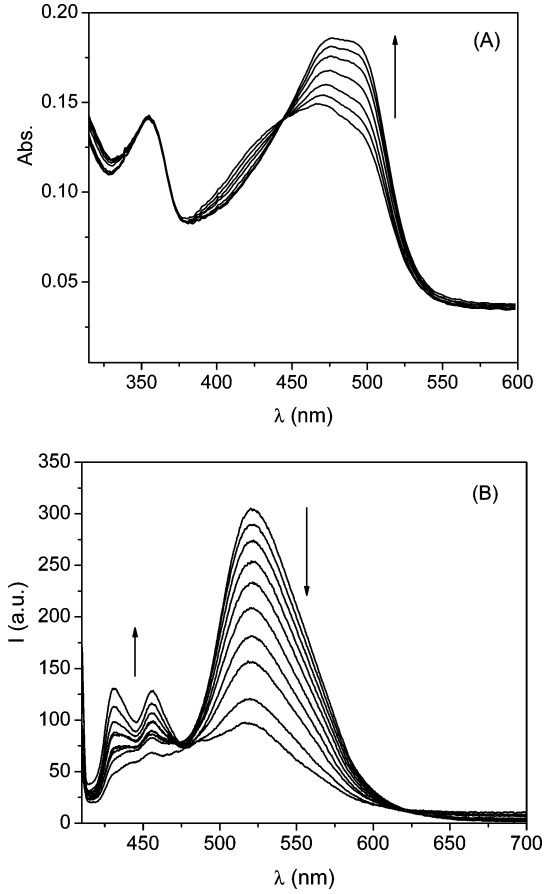

Figure 3. Absorption (A) and emission (B) spectra of 9AAECA in 2-propanol upon addition of water (0−8 vol %). $\lambda_{exc} = 400$ nm. Arrows indicate the increase of water concentration.

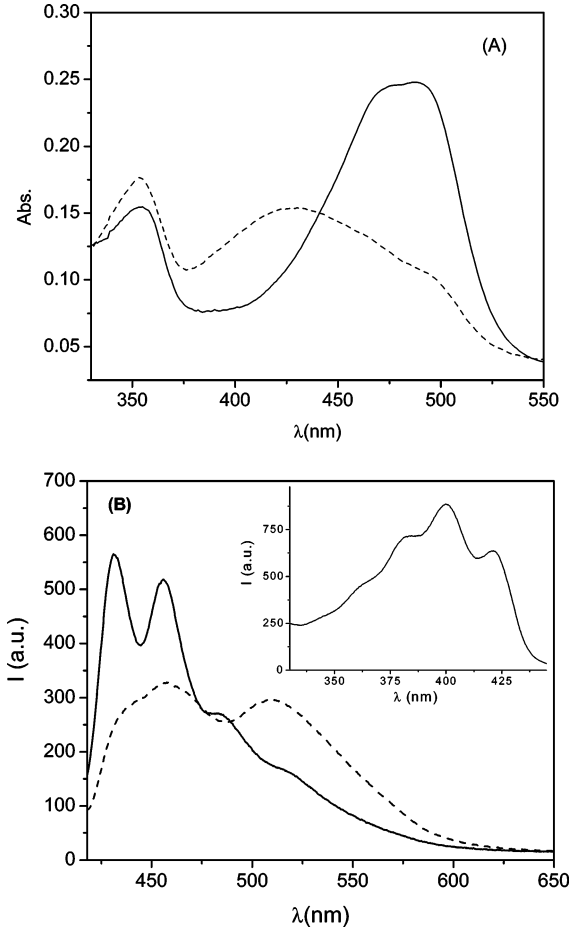

Figure 4. Absorption (A) and emission spectra of 9AAECA in methanol. (---) Dry methanol and (—) commercial methanol. Inset plot in (B) is the excitation spectrum with recording at the LE emission at 455 nm.

infra). Considering that the enol tautomer is usually more stable in apolar solvents, the previous results of absorption given in Figure 2A would indicate that the absorption at 355 nm in CCl_4 belongs to the predominant enol form in this apolar solvent. Moreover, the absence of absorption above 430 nm indicates that the ICT transition is practically forbidden for the enol-imine tautomer.

Fluorescence in a Mixture of Solvents. The fluorescence in polar solvents such as alcohols shows a clear separation between electronic states. The LE emission band is structured with vibronic peaks at about 430 and 455 nm, similar to those peaks observed for 9AA. The ICT emission band, however, is red shifted at about 80 nm, depending on the type of alcohol. Another interesting feature is the strong dependencies of absorption and emission spectra of 9AAECA on solvent composition. Addition of water to 2-propanol causes a loss of ICT character, particularly in the emission spectra (see Figure 3). The absorption spectrum is red shifted, while the emission spectrum changes only in the weight between LE and ICT emission contributions upon addition of water. The excitation spectrum with emission monitored at 555 nm has the same spectrum profile as that of 9AAECA in pure 2-propanol, but it only decreases in intensity with water addition, conserving the maximum at 433 nm (data not shown).

Isosbestic (at 447 nm) and isoemissive (at 478 nm) points are observed with the change in the solvent composition (see Figure 3). Excitation at the isosbestic point shows the same trends in emission as before: a decrease of the emission centered on 522 nm upon water addition to 2-propanol solution of 9AAECA.

The product in commercial methanol (see absorption and emission spectra in Figure 4) when excited at 400 nm exhibits also a structured band, assigned to LE emission, in addition to a weak red emission contribution that generates a shoulder at about 518 nm. This low-energy band can be ascribed to the presence of ESICT, but some degree of overlap with LE emission seems to occur. To confirm the fact that the LE emission is originated from the acridinium chromophore, an excitation spectrum monitoring the emission at the second vibronic peak of the LE emission (at 450 nm) is shown as the inset plot in Figure 4B. The excitation spectrum obtained is identical to the structured absorption of 9AA readily found in the literature. However, when the methanol is dried, the LE emission band loses in part its structure while ICT transition appears clearly as a broad emission band with a maximum at 510 nm. Addition of small amounts of water to methanol also leads to structuring of the LE band that increases in intensity in relation to the ICT band. Similar behavior was observed in ethanol and butanol solutions upon addition of water.

The quenching effect of the red emission intensity at $\lambda = 520$ nm in 2-propanol/water solvent mixtures is correlated with the water content in the alcohol. The plot of relative emission intensity as a function of water concentration is given in Figure 5. This result indicates that 9AAECA could be a probe to be used as a fluorimetric sensor for water content in organic solvents.

The observed solvent effects may be explained considering the influence of a lone pair of electrons of the 9-amino group.[12,38]

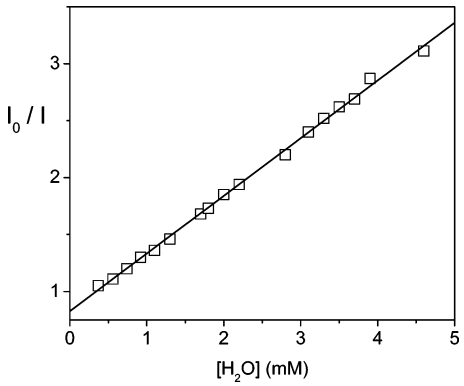

Figure 5. Stern−Volmer plot of fluorescence quenching of ICT emission of 9AAECA in 2-propanol solution as a function of water concentration. $K_{SV} = 0.51 \pm 0.03$ M^{-1}.

When a small amount of water is added to the system, hydrogen bonding with N occurs efficiently, opening a fluorescence deactivation pathway. It changes the amino conjugation effect, keeping the lone pair in resonance with the acridine ring, but inhibits the extended charge conjugation through the double bond to the carbonyl and cyano electron-withdrawing groups. On the other hand, in polar solvents with less ability to form hydrogen bonds, such as 2-propanol, this conjugation is somewhat extended to the whole molecular system, increasing the probability of ICT.

This effect of the vinylene group incorporated in the 9AA dye can be described by the resonance-assisted hydrogen bonding (RAHB) process.[39−42] It may occur in molecules containing NH and C═O groups separated by a system of conjugated double bonds (π-conjugated systems). In the case of 9AAECA (see Figure 1), the NH group is an electron donor for withdrawing groups (CN and C═O). Charge delocalization through the system of conjugated double bonds establishes intramolecular hydrogen bonding. As a consequence, a weakening of the CN and C═O bonds should be observed. IR measurements confirm this assumption, with a decrease in frequency of the CN group from $\bar{\nu} = 2228$ cm^{-1} (ethyl-2-cyano-3-ethoxyacrylate) to $\bar{\nu} = 2205$ cm^{-1} in the 9AAECA compound. For the C═O group, this decrease in frequency is more pronounced, and it occurs from $\bar{\nu} = 1713$ cm^{-1} to $\bar{\nu} = 1666$ cm^{-1}.

The spectroscopic results point to the presence of at least two species in dynamic equilibrium. Thus the presence of an isosbestic point observed upon addition of water to 2-propanol solution of 9AAECA (see Figure 3A) is explained by a dynamic equilibrium between the intramolecular hydrogen bonding, which ultimately leads to the enol tautomer in less polar solvent, and a solvated keto form. Addition of water not only breaks intramolecular H-bonding but also favors the keto tautomer by increasing the polarity, and these effects together cause a red shift of the absorption spectrum of the dye in solution.

Solvatochromic Measurements. The shift of the emission spectrum of 9AAECA with solvent polarity was analyzed by the Lippert−Mataga emission equation.[15,43−44]

$$\upsilon_{(\mathrm{flu})} = -\frac{2}{hca_0^3}\mu_e(\mu_e - \mu_g)\Delta f \qquad (1)$$

$$\Delta f = \frac{\epsilon - 1}{\epsilon + 1} - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right) \qquad (2)$$

In these equations, $\upsilon_{(\mathrm{flu})}$ is the maximum frequency (in wavenumbers) of the emission band, μ_e and μ_g are the excited-state and ground-state dipole moments, respectively, a_0 is the radius of the Onsager cavity, and Δf is the solvent parameter given by eq 2, which depends on the dielectric constant (ϵ) and the refractive index (n) of the solvent.

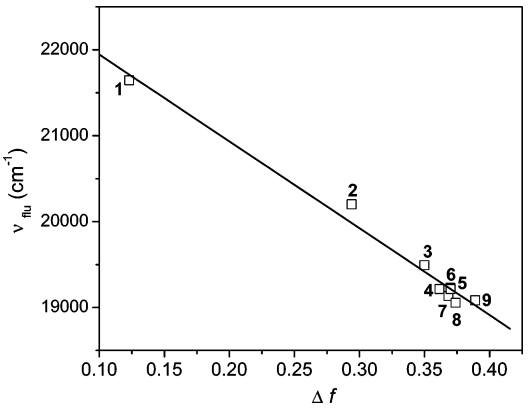

Figure 6. Plot of maximum of fluorescence band with Δf parameter. Solvents: (1) dioxane, (2) ethyl acetate, (3) *tert*-butyl alcohol, (4) butanol, (5) 1M2P, (6) 1-propanol, (7) 2-propanol, (8) DMSO, and (9) *N*,*N*-dimethylacetamide (DMA).

TABLE 1: Fluorescence Decay Times of 9AAECA in Different Solvents[a]

solvent	τ_1 (ns)	b_1	τ_2 (ps)	b_2	τ_3 (ns)	b_3
CCl_4	8.26	0.01	160	−0.53	2.95	0.48
methanol	8.40	0.02	78	−0.23	0.75	0.12
ethanol	9.04	0.02	350	−0.24	1.14	0.08
2-propanol	9.30	0.01	240	−0.47	1.56	0.67
butanol	10.20	0.01	450	−0.14	0.87	0.15
1M2P	7.65	0.01	190	−0.54	3.23	0.48
DMSO	8.70	0.02	210	−0.84	1.43	0.71

[a] Excitation wavelength at 400 nm; emission wavelength at 520 nm; $T = 298$ K. Results from global analysis of three or four decays, and $\chi^2 < 1.1$ in all fits.

Specific solute−solvent interaction like H-bonding is not implicit in the Lippert−Mataga theory. However, even with the use of several protic and aprotic solvents, a reasonable linear plot is obtained without separation of protic and aprotic solvents. From the slope of the plot of eq 1, shown in Figure 6, the excited-state dipole moments can be evaluated. Assuming the value of $\mu_g = 10$ D obtained from quantum chemical calculations (using the same method described recently in ref 45), and $a_0 = 0.65$ nm (similar to the value reported for other acridine derivatives),[37] the calculated value for the dipole moment of 9AAECA in the excited state is $\mu_e = 22 \pm 1$ D.

This value is significantly larger than the ground-state dipole moment, indicating a substantial contribution of intramolecular charge transfer in the excited state. To obtain information about this ICT dynamics, time-resolved experiments were carried out.

Fluorescence Decay. With the goal to find evidence of excited-state conversion of the LE into ESICT in 9AAECA, time-resolved emission studies in nonpolar and polar (protic and aprotic) solvents were performed. In all the solvents analyzed, the complex decays are described by a triexponential decay function. The measured decay times and their respective amplitudes (preexponential factors) of this fluorochromic dye in different solvents are listed in Table 1.

The triexponential decay behavior, in both polar and nonpolar solvents, indicates a three-state dynamics, which may arise from the interplay of keto−enol equilibrium coupled with the ICT process. Although the decay time components reported in Table 1 are the eigenvalues of a three-excited-state system, the values found may be associated with major contributions of some of these species. For instance, the long-lived component τ_1 is on

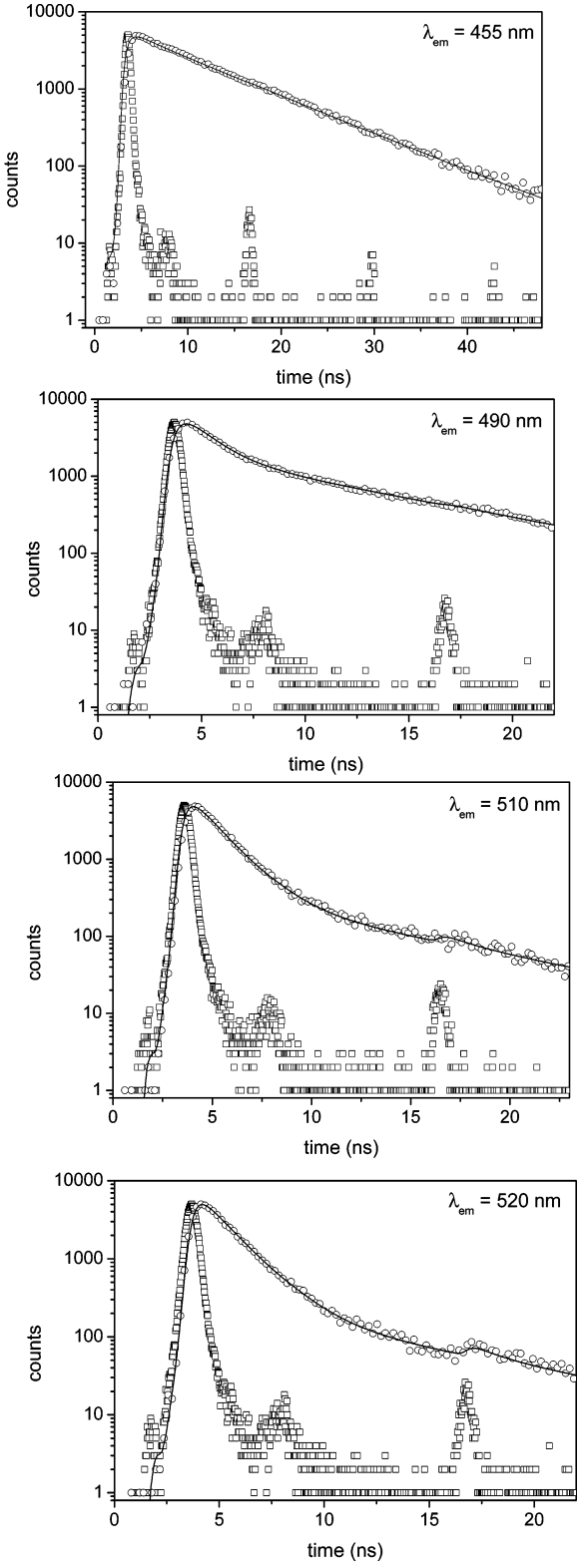

Figure 7. Fluorescence decay of 9AAECA in DMSO at different emission wavelengths. (□) Instrument response function (irf); (○) decay; (—) fitting. $\lambda_{exc} = 400$ nm; $T = 298$ K.

the same order as the lifetime of the precursor dye 9AA as previously reported in the literature,[45,46] and therefore should account mostly for the fraction of LE states of the enol tautomer. The short decay time τ_2 may be assigned largely to the formation of ESICT, and τ_3 is related to its deactivation to the ground state. This last assumption is supported by the fact that the preexponential factor b_2 listed in Table 1 is negative (a rise component), but in the model its absolute value is not too different from that of b_3.

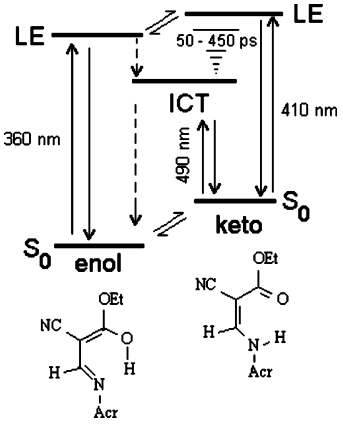

Figure 8. Typical electronic energy diagram of 9AAECA, keto−enol equilibrium, excited-state processes, and electronic absorption wavelengths (nm). Acr = acridine.

The fluorescence decay profiles of 9AAECA in DMSO as a function of the emission wavelength are shown in Figure 7. The long-lived component has a major contribution at $\lambda_{em} =$ 455 nm, decreasing in weight with increase of λ_{em}. In contrast, the weight of τ_2 starts with a low percentage at $\lambda_{em} =$ 450 nm and increases to near 50% at $\lambda_{em} = 520$ nm. Thus, in the blue region, there is a contribution of the LE emission that decreases toward the red region, where the ICT state has larger weight. The intricate point to be explained is the presence of the long-lived component τ_1. Such a decay component is related to the singlet excited state of the enol form (LE state). Its conversion to the LE excited state of the keto form should pass a high-energy barrier (thus given a slow process compared to its deactivation to ground state), because it involves a proton transfer from the OH to the imine N forming a high-energy zwitterion, which by electronic rearrangement would give the keto-amine form. For the same reason, it cannot relax quickly to a proper ICT state. A reasonable energy diagram of ground and excited electronic states and processes based on these results and considerations is illustrated in Figure 8.

The electronic energy levels of all states are solvent dependent. The very low ICT absorption band of the dye in nonpolar solvents such as CCl_4 where the enol form is the predominant species, in addition to the increase and red shift of the ICT absorption band upon addition of water to alcohols, which favor the keto form, is an indication that the main electronic absorption in the red is the ICT optical transition of the keto tautomer. However, the observed decrease of the ICT emission upon water addition has a correlation with the nonradiative deactivation through charge delocalization toward the carbonyl group and sequential proton transfer (from N−H or water), forming the enol tautomer more probably in the ground state (represented in Figure 8 by a dashed arrow).

In addition, experiments have been performed with excitation at 470 nm (that should excite only the ICT species). A single-exponential decay is observed, which proves the mechanism and the scheme of Figure 8. For instance, for 9AAECA in 1M2P, the lifetime recovered is 3.46 ns, which is very close to that component ascribed to the ICT species ($\tau_3 = 3.23$ ns) obtained by exciting at 400 nm and triexponential fitting as reported in Table 1. The same behavior was observed in DMSO: red excitation gives a single lifetime of 1.50 ns ($\tau_3 =$ 1.43 ns).

Finally, it is expected that elimination of the double bond (for instance by copolymerization of 9AAECA) should break the charge conjugation and should result in no emission from the ICT state and tautomers. Preliminary assays of the copolymer of 9AAECA with methacrylic acid showed only LE emission in methanol, and monoexponential decay with a lifetime of 13.4 ns. This lifetime value is close to the lifetimes of free 9AA (14.9 ns) and its derivative without a possible ESICT process (free acridine-9-methacrylamide, 13.1 ns, and copolymerized with methacrylic acid, 13.9 ns) in methanol, as reported recently in the literature.[45,46]

Conclusions

The complex fluorescence of 9AAECA is ascribed to emission of the acridine chromophore in the locally excited (LE) singlet state in addition to red emission from the excited-state intramolecular charge transfer (ESICT) process. The analysis of the fluorescence decays in different solvents reveals two short-lived components in the range of 80−450 ps and 0.7−3.2 ns, and a third one that is practically constant at about 9 ns. The changes of the emission bands and quantum yield with solvent are related to an intramolecular charge transfer process mediated by ground- and excited-state equilibria between enol and keto tautomers of 9AAECA.

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