

Photophysics of 1-hydroxy- and 1-methoxy-9-fluorenone II. Non-radiative deactivation

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Received 26 January 2004; received in revised form 24 May 2004; accepted 5 July 2004

Available online 24 August 2004

Abstract

Absorption, fluorescence, fluorescence excitation spectra and time dependence fluorimetric studies of 1-hydroxy-9-fluorenone (1-HFu) and 1-methoxy-9-fluorenone (1-MFu) have been studied in different solvents and binary solvent mixtures. Fluorescence quantum yields (ϕ_f) of both the molecules increase in polar/aprotic solvents. In protic solvents ϕ_f of 1-HFu decreases with increase in their polarity, whereas in case of 1-MFu it increases up to ethanol and then decreases in methanol and water. Importance of inter- and intramolecular hydrogen bonding (IHB) has been studied by using binary mixtures of solvents, like trifluoroethanol (TFE)–cyclohexane and acetonitrile–water mixtures.

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Keywords: 1-Hydroxy-9-fluorenone; 1-Methoxy-9-fluorenone; Non-radiative deactivation; Excited-state dipole moment; Spectroscopic states

1. Introduction

It is well established that photophysical and photochemical characteristics of molecules, in which the excited states of different character are closely spaced, can be altered by the substituents in aromatic ring and solvent polarity. This change in properties could be either due to reversal of low-lying excited states or increase in the participation of one electronic state into other, caused by change in solvent property or by electron-donating/withdrawing substituent. Results of these studies help in understanding the microscopic mechanisms of relaxation processes, fluorescence behavior of the excited molecules and theories regarding radiationless processes [1,2].

9-Fluorenone (9-Fu) is one of these kinds of molecules, whose photophysical properties are very sensitive to microenvironments [3–13]. Literature survey has shown that different derivatives of 9-Fu studied contains the substituent at 2-position, with few exceptions where amino group is present at 1-, 3- and 4-position [14–18] also. These results have

shown that (i) S_1 and S_2 states in 9-Fu are of $n-\pi^*$ and $\pi-\pi^*$, respectively, in character. Due to this, 9-Fu exhibits weak fluorescence. Fluorescence intensity increases with increase in polarity and decreases with increase in the proton donor capacity of solvents and (ii) in non-polar solvents, intersystem crossing is the major pathway from excited singlet state when electron-withdrawing group is attached to the fluorene moiety, whereas an electron-donating group increases the rate of internal conversion. Biczok et al.'s [13,18] results have established that: (i) internal conversion is the main path of deactivation between the excited singlet (S_1) state and the ground-state (S_0) for 2-, 3- and 4-amino-9-fluorenone (2-AFu, 3-AFu and 4-AFu). Rate constant of internal conversion can be nicely correlated to the energy gap law, and intersystem crossing (ISC) rate is very slow for these molecules. (ii) In case of 1-amino-9-fluorenone (1-AFu) ISC was found to be the dominant process for S_1 in all the solvents. The short fluorescence decay time of 1-AFu does not originate from IHB induced interconversion but it is due to the fast triplet formation.

Present work involves the spectroscopic study of 1-HFu and 1-MFu. Former molecule involves IHB, whereas latter does not. Time-dependent fluorescence spectroscopy coupled

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with steady-state spectrofluorimetric studies have been carried out to find out the nature of emitting state and to see the importance of IHB and intermolecular hydrogen bonding of polar/protic nature of the solvent in the relaxation phenomenon of 1-HFu and 1-MFu.

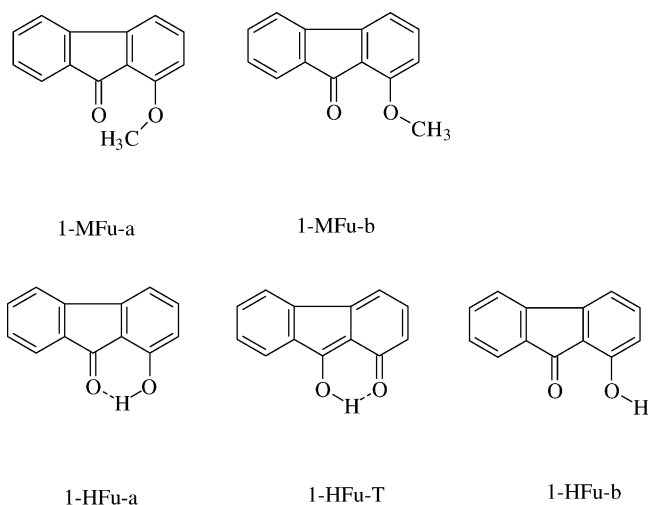
2. Materials and methods

1-HFu was procured from Aldrich Chemical Company, UK, whereas 1-MFu was prepared from 1-HFu using methyl iodide in basic medium [19]. Both these compounds were purified by repeated crystallization from ethanol. Obtaining identical fluorescence and fluorescence excitation spectra with different excitation and emission wavelengths, respectively, in any one particular solvent checked the purity of both the compounds. All the solvents, except ethanol, were either of spectroscopic grade or HPLC grade from E. Merck and were used as such. Commercial ethanol was purified as described in literature [20]. Triply distilled water was used for the preparation of aqueous solutions.

Procedure used to prepare the solutions, adjustment of pH and instruments used to record absorption, fluorescence excitation and fluorescence spectra, as well as, to measure excited-state lifetimes were the same as mentioned in our recent papers [21,22]. Fluorescence quantum yields (ϕ_f) have been measured from solutions having absorbance less than 0.1, using quinine sulphate in 1N H₂SO₄ as reference ($\phi_f = 0.55$) [23]. Concentration of 1-HFu and 1-MFu was kept at 2×10^{-5} M.

3. Semi-empirical quantum mechanical calculations

Different species of 1-HFu and 1-MFu considered are given in Scheme 1. The electronic structure calculations were carried out on each species using GAUSSIAN98 program [24].



Scheme 1.

Geometry optimization was performed on each species of 1-HFu and 1-MFu in S₀ state using DFT [25,26] B3LYP with 6-31 G** basis set [24,27]. Geometry of these stationary points on S₁ state was calculated using configurations interaction singles (CIS) [24,28]. Time-dependent (TD) [29,30] DFT B3LYP with 6-31 G** basis set was also used to calculate the excited-state energies at the calculated stationary point geometry in S₀ and S₁ states. Relevant data are compiled in Table 2.

4. Results

4.1. Absorption and fluorescence spectra

In order to understand the results of this paper, spectral characteristics of 1-MFu and 1-HFu in different solvents discussed in the preceding paper [35] are summarized here. Absorption band maxima ($\lambda_{\max}^{\text{ab}}$) of all the bands are red shifted and ϵ_{\max} increases with increase in the solvents polarity and their protic nature of the solvents. Only one small Stokes shifted fluorescence band, nearly at the same wavelength, is observed in both the molecules. Fluorescence band maxima ($\lambda_{\max}^{\text{f}}$) are large red-shifted under the same environments. $\lambda_{\max}^{\text{f}}$ and Φ_f are invariant to the excitation wavelength (λ_{exc}). Fluorescence excitation spectra recorded in each solvent and monitored at different emission wavelengths resemble with each other, as well as, with absorption spectrum. It suggests that there is only one species in S₀ state and emission is observed from the most relaxed excited state.

4.2. Lifetimes of the excited state

Excited-state lifetimes of 1-MFu and 1-HFu were measured in different solvents by using $\lambda_{\text{exc}} = 354$ nm, whereas the λ_{em} were the fluorescence band maxima in respective solvents. Fluorescence intensity in each case followed a single exponential decay with $\chi^2 = 1 \pm 0.1$ and good autocorrelation functions. Fig. 1 represents a typical fluorescence decay profile of 1-HFu in acetonitrile. Values of the radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated from the lifetimes (τ) and ϕ_f using the following relations.

$$k_r = \frac{\phi_f}{\tau}, \quad k_{\text{nr}} = \left(\frac{1}{\tau}\right) - k_r$$

Values of k_r , k_{nr} , τ and ϕ_f are compiled in Table 1. In case of 1-MFu, we could only determine the value of k_{nr} in acetonitrile, as in other polar/aprotic solvents, ϕ_f is too small to measure the lifetimes. k_{nr} for 1-HFu decreases with increase in polarity of the solvents and increases with increase in proton donor capacity of the solvents. Values of k_{nr} obtained in polar/protic solvents for 1-HFu and 1-MFu are nearly similar, whereas the value of k_{nr} for 1MFu in acetonitrile is nearly

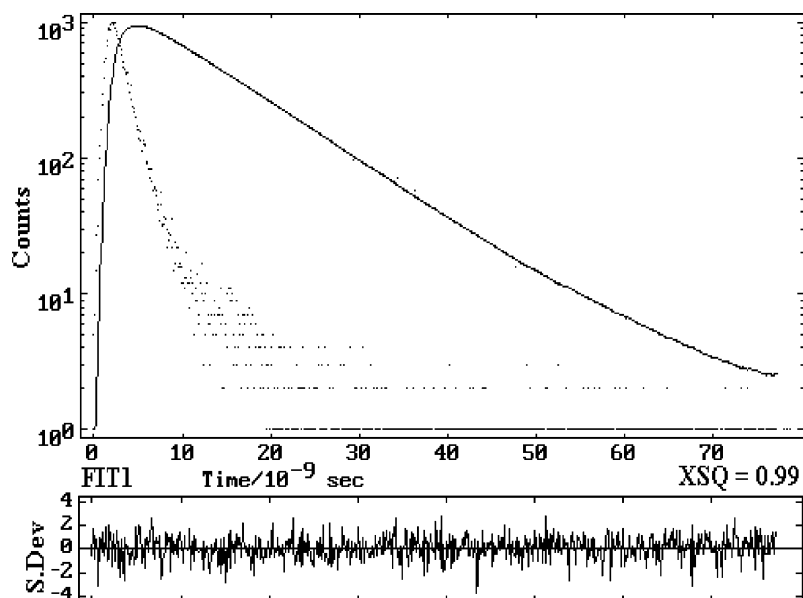


Fig. 1. Fluorescence decay profile of 1-HFu in acetonitrile. $\lambda_{\text{exc}} = 354 \text{ nm}$, $\lambda_{\text{em}} = 496 \text{ nm}$, $[1\text{-HFu}] = 1 \times 10^{-3} \text{ M}$.

five times greater than that for 1-HFu.

4.3. Solvatochromism

Large changes observed in $\lambda_{\text{max}}^{\text{f}}$ of both 1-HFu and 1-MFu with increase in solvent polarity suggests an increase in dipole moment of both the molecules in the S_1 state. Changes in dipole moments upon excitation can be estimated using Lippert–Matga [31,32] analysis of absorption and fluorescence spectra. Lippert–Matga plot was constructed (Fig. 2) for 1-MFu and 1-HFu using following equation:

$$\bar{\nu}_{\text{ss}} = \bar{\nu}_{\text{max}}^{\text{ab}} - \bar{\nu}_{\text{max}}^{\text{f}} = \text{const} + \left[\frac{2(\mu_{\text{e}} - \mu_{\text{g}})^2}{hca^3} \right] f(D, n)$$

where $f(D, n) = (D - 1)/(2D + 1) - (n^2 - 1)/(2n^2 + 1)$ indicates the orientation polarizability and depicts polarity parameter of the solvent, n is the refractive index, D the bulk dielectric

constant, μ_{e} and μ_{g} are dipole moments of the species in S_0 and S_1 states, respectively, h the Planck's constant, c the velocity of light and a the Onsager's cavity radius. Stoke's shifts were calculated either by taking middle wavelength (MW) absorption band maximum (as long wavelength, LW, absorption band maximum is not well defined) or by taking LW fluorescence excitation band maximum obtained by simulation of the LW fluorescence excitation spectra. Results obtained from both the plots are within the error limits. Although in many fluorophores, a linear relation is observed between the Stoke's shift and polarity parameters in both polar aprotic and polar protic solvents [33], but in case of 1-HFu and 1-MFu, the steady-state Stoke's shifts can be best approximated by a linear function if the solvents are divided into two groups, aprotic and protic ones. However, for both molecules the slopes of the lines correlating the protic and aprotic solvents are quite similar. These results suggest that specific solute solvent interactions (hydrogen bonding) occur in protic solvents and influence the Stoke's shift. This is supported by the linear relation observed in the plot between Stoke's

Table 1

Excited-state lifetimes (τ , ns), fluorescence quantum yields (ϕ_{f}), rate constants for radiative (k_{r} , 10^7 s^{-1}) and non-radiative (k_{nr} , 10^8 s^{-1}) of 1-HFu and 1-MFu in different solvents

Solvents	1-HFu				1-MFu			
	τ	ϕ_{f}	k_{r}	k_{nr}	τ	ϕ_{f}	k_{r}	k_{nr}
Cyclohexane	1.24	0.0129	1.04	7.96	–	–	–	–
Ether	2.39	0.022	0.92	4.09	–	–	–	–
Dioxane	3.38	0.0284	0.84	2.87	–	–	–	–
Ethyl acetate	5.48	0.0383	0.7	1.76	–	–	–	–
Acetonitrile	9.67	0.053	0.55	0.98	2.1	0.0073	0.35	4.73
<i>n</i> -Butanol	5.22	0.022	0.42	1.88	7.27	0.023	0.32	1.34
2-Propanol	5.50	0.024	0.44	1.78	8.52	0.029	0.34	1.14
<i>n</i> -Propanol	4.82	0.021	0.44	2.02	6.93	0.021	0.30	1.41
Ethanol	4.85	0.0197	0.41	2.02	5.98	0.020	0.34	1.64
Methanol	3.61	0.012	0.33	2.74	3.92	0.011	0.29	2.52
Cyclohexane (+0.139 M TFE)	4.49	0.020	0.47	2.18	4.17	0.0198	0.48	2.35

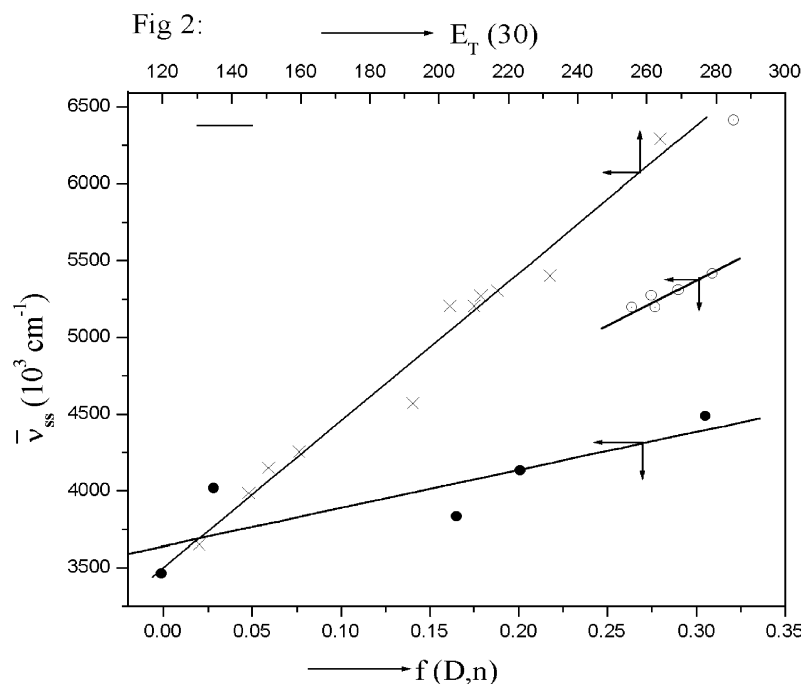


Fig. 2. Plot of Stokes' shifts vs. Lippert's parameter and $E_T(30)$ parameters: (●●●) polar aprotic; (○○○) polar rotic; (×××) $E_T(30)$ parameter.

shifts versus $E_T(30)$ parameter (Fig. 2). μ_e was found to be 7.82 D for 1-MFu, obtained from the slope of Lippert's plot and taking μ_g (calculated with the help of AM1 calculations) and a as 0.4 nm. Increase in dipole moment of 1-MFu suggests involvement of a charge transfer character in S_1 state. Similar results were also observed for 1-HFu and value of μ_e obtained is 7.92 D.

4.4. Binary solvents

Absorption spectra of 1-MFu and 1-HFu have been studied in binary solvent mixtures like cyclohexane/TFE (up to 0.14 M) and acetonitrile/water mixture. Slight red-shift in all the three absorption band maxima, increase ε_{\max} and loss of vibrational structure of MW and LW absorption bands were observed with the addition of protic solvent. Although no clear isosbestic point in the MW and LW absorption band system is observed in case of cyclohexane/TFE system, a nice clear isosbestic points (344 and 340 nm for 1-MFu and 1-HFu, respectively) are observed in case of acetonitrile/water system. This suggests the formation of hydrogen-bonded complex of solute molecules with water in S_0 state. A large decrease in FWHM is observed in the absorption spectrum of 1-MFu (from 5540 to 4930 cm^{-1}) when TFE is added to cyclohexane, where as in case of 1-HFu it is only from 5800 to 5490 cm^{-1} . In case of acetonitrile/water system, changes observed in FWHM for both 1-MFu and 1-HFu are very small, i.e. 150 cm^{-1} for 1-MFu and $\sim 80 \text{ cm}^{-1}$ for 1-HFu.

The association constants (K) for the formation of 1:1 hydrogen bonded complex were calculated from the effects of added water to acetonitrile on absorption spectrum of 1-HFu

and 1-MFu solutions, using the relationship [34]:

$$\frac{A_0}{A - A_0} = \left\{ \frac{\varepsilon_M}{\varepsilon_M - \varepsilon_C} \right\} \left\{ 1 + \frac{1}{KC_0} \right\}$$

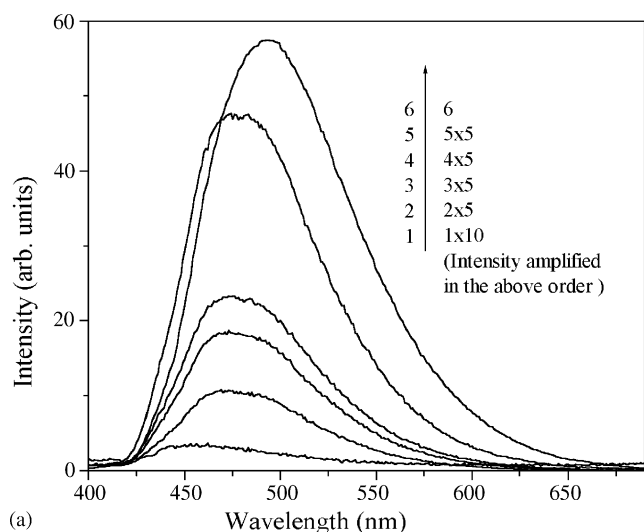
where A_0 and A are the absorbance in the absence and presence of water in acetonitrile, respectively, ε_M and ε_C respectively denote the molar extinction coefficients of the free and complex molecule, C_0 the concentration of water and is much greater than that of respective fluorenone. A linear relationship is observed between $A_0/(A - A_0)$ versus $1/C_0$ with regression coefficient of 0.97 and 0.99, respectively, for 1-HFu and 1-MFu. Values of K obtained for 1-HFu and 1-MFu are 0.28 and 0.18, respectively. Values of K obtained are very small.

We have also measured the association constants of water with 1-HFu from the measured fluorescence intensity at a selected wavelength using the expression [34]:

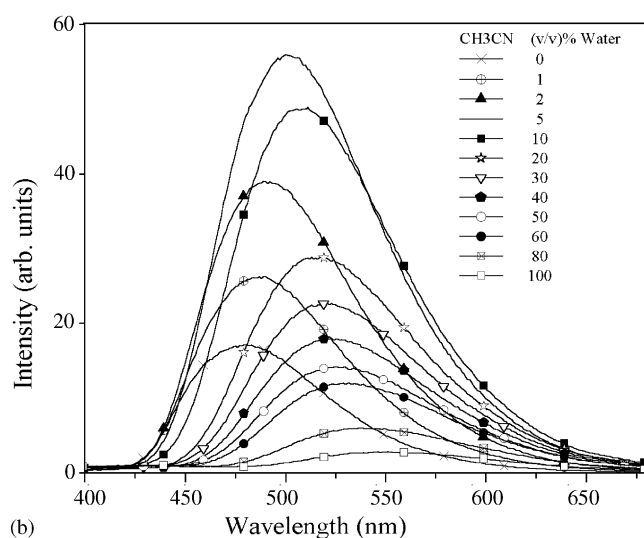
$$\frac{F_0}{F - F_0} = \left\{ \frac{\Phi_M \varepsilon_M}{\Phi_C \varepsilon_C - \Phi_M \varepsilon_M} \right\} \left\{ \frac{1}{KC_0 + 1} \right\}$$

where F_0 and F denote the measured fluorescence intensity without and with the addition of water, Φ_M and Φ_C are the fluorescence quantum yields of 1-HFu in pure acetonitrile and water, respectively. Value of K obtained from the linear plot of $F_0/(F - F_0)$ versus $1/C_0$ is 0.38. The agreement between the values of K deduced from absorption data and fluorescence data is not bad.

Decrease in the fluorescence intensity of 1-HFu with addition of water in acetonitrile has been correlated with Stern–Volmer plot. The plot (not shown) is linear up to $[\text{H}_2\text{O}] < 20 \text{ M}$ and Stern–Volmer constant (K_{S-V}) obtained from the linear plot is found to be 0.35 M^{-1} . We could not measure the



(a)

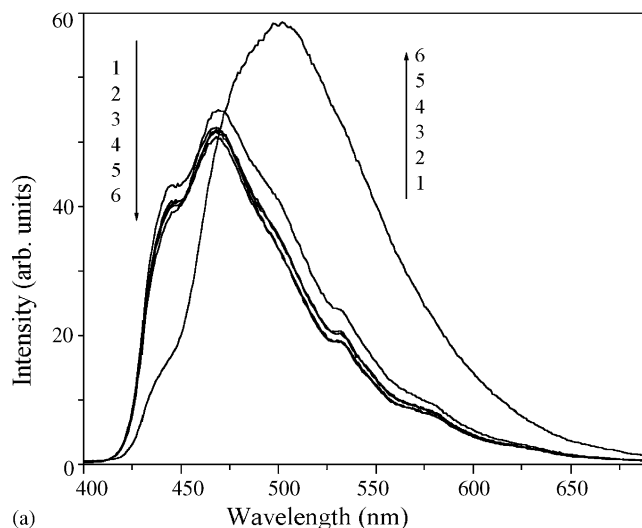


(b)

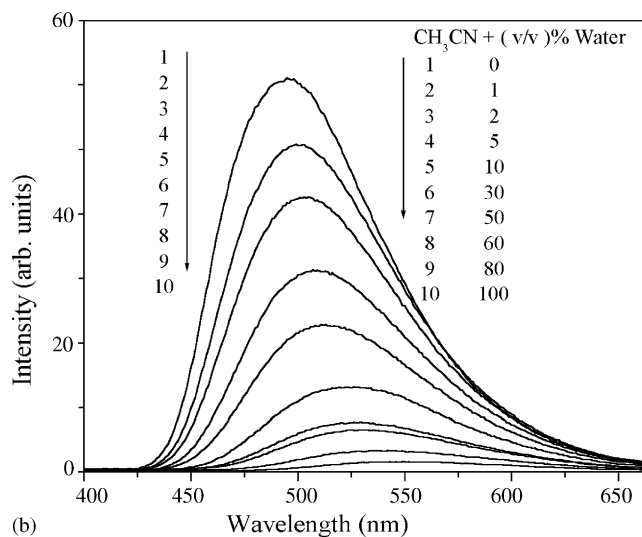
Fig. 3. (a) Fluorescence spectrum of 1-MFu in cyclohexane as a function of the amount of TFE added: 1, cyclohexane; 2, 1.12 mM TFE; 3, 2.2 mM TFE; 4, 3.1 mM TFE; 5, 5.85 mM TFE; 6, 139 M TFE. (b) Fluorescence spectrum of 1-MFu in acetonitrile as a function of the amount of water added: 1, 0% H₂O; 2, 1% H₂O; 3, 2% H₂O; 4, 5% H₂O; 5, 10% H₂O; 6, 20% H₂O; 7, 30% H₂O; 8, 40% H₂O; 9, 50% H₂O; 10, 60% H₂O; 11, 80% H₂O; 12, H₂O. [1-MFu] = 2×10^{-5} M.

lifetime of 1-HFu in water to ascertain the nature of fluorescence quenching (whether static or dynamic) because of very poor fluorescence quantum yield. But the agreement between the values of K_{S-V} and association constant (K) suggests that the fluorescence quenching could be of static in nature.

Effect of TFE addition to cyclohexane (Fig. 3a) is more pronounced on the fluorescence spectrum than on the absorption one. With the addition of TFE (up to 0.14 M) to cyclohexane, λ_{\max}^f of 1-MFu was red shifted, and ϕ_f increases by a factor of ~ 300 -fold. FWHM of fluorescence spectrum does not change much in this range of TFE used. This suggests the formation of hydrogen-bonded complex between 1-MFu and TFE. Similar study in acetonitrile/water mixture (Fig. 3b) of



(a)



(b)

Fig. 4. (a) Fluorescence spectrum of 1-HFu in cyclohexane as a function of the amount of TFE added: 1, cyclohexane; 2, 1.12 mM TFE; 3, 2.2 mM TFE; 4, 3.1 mM TFE; 5, 5.85 mM TFE; 6, 139 M TFE. (b) Fluorescence spectrum of 1-HFu in acetonitrile as a function of the amount of water added: 1, 0% H₂O; 2, 1% H₂O; 3, 2% H₂O; 4, 5% H₂O; 5, 10% H₂O; 6, 20% H₂O; 7, 30% H₂O; 8, 40% H₂O; 9, 50% H₂O; 10, 60% H₂O; 11, 80% H₂O; 12, H₂O. [1-HFu] = 2×10^{-5} M.

1-MFu indicates that λ_{\max}^f and FWHM keep on increasing with addition of water to acetonitrile, whereas ϕ_f first increases by a factor of ~ 3.6 with the addition of 2.8 M water and then decreases in water by a factor of ~ 2 . This behavior is different from that observed in 9-Fu when ethanol is added to acetonitrile or cyclohexane [11]. Similar studies in case of 1-HFu (Fig. 4) reveals that changes observed in λ_{\max}^f and FWHM are similar to those observed in 1-MFu. ϕ_f of 1-HFu increases only by a factor of 1.5 in 0.14 M TFE in cyclohexane, but ϕ_f of 1-MFu and 1-HFu at the extreme concentration of TFE in cyclohexane are the same. On the other hand, ϕ_f of 1-HFu continuously decreases and λ_{\max}^f was red-shifted with the increase of water to acetonitrile. Unlike that of 1-MFu,

FWHM of the fluorescence band of 1-HFu nearly remains invariant under the similar conditions.

5. Discussion

5.1. Assignment of the emitting state

It has been concluded in the preceding paper [35] that $n-\pi^*$ and $\pi-\pi^*$ are the S_1 and S_2 states of 1-MFu-b and 1-HFu-b, respectively. $\pi-\pi^*$ and $n-\pi^*$ are the S_1 and S_2 states for 1-MFu-a and 1-HFu-a. Based on the absorption and fluorescence characteristics, it has also been shown that 1-HFu-a is the only species for 1-HFu, whereas both the rotamers of 1-MFu can be present in S_0 and S_1 states (Scheme 1). Lippert–Matga's plot has shown that a large increase in dipole moment ($\Delta\mu = 5.77$ D) is observed for 1-MFu when excited to S_1 state. This indicates that the lowest excited state in these rotamers involve charge transfer between the OCH_3 group and carbonyl moiety. These results combined with steady-state Stokes shift results suggest that 1-MFu-b is either absent or $\pi\pi^*$ is the S_1 state.

5.2. Non-radiative decay rate constant

Photophysics of 1-MFu and 1-HFu is as complex as that of 9-Fu or its derivatives [7–13]. λ_{\max}^f of 1-MFu and 1-HFu is regularly red-shifted, whereas ϕ_f of both the molecules increases with increase of solvent polarity and then decreases with increase in the protic nature of solvents. There are three competitive processes from S_1 state: fluorescence, intersystem crossing and internal conversion. Among these processes, intersystem crossing depends up on the $n-\pi^*$ and $\pi-\pi^*$ character in both S_m and T_n states, where m and n stands for the higher singlet and triplet states other than the first one. It has been shown that spin-orbit coupling between $^1(n-\pi^*) \rightarrow ^3(\pi-\pi^*)$ in molecules having non-bonding electrons is a dominant factor for governing the competition [36].

Variation of ϕ_f in different solvents can be correlated with the effect of solvents on k_{nr} . We have not been able to measure the lifetimes of 1-MFu in polar/aprotic solvents, except acetonitrile, due to its very poor ϕ_f . Even though the geometries of both the molecules (i.e. 1-HFu involves IHB and 1-MFu does not) are different, the trends observed in ϕ_f of both the molecules in different solvents, suggest that effect of solvents on the excited-state dynamics can be explained in general by the similar mechanism. In the following section, we have tried to focus on the dependence of k_{nr} on the solvent properties and structure of the molecules.

In many cases, relative rate constants are expressed in terms of energy gap law [37,38]:

$$k_{nr} \propto \exp(-\beta \Delta E)$$

where ΔE is the energy gap between the S_0 and S_1 states and β is a constant. Value of ΔE has been calculated by taking the intersection point of fluorescence and fluorescence exci-

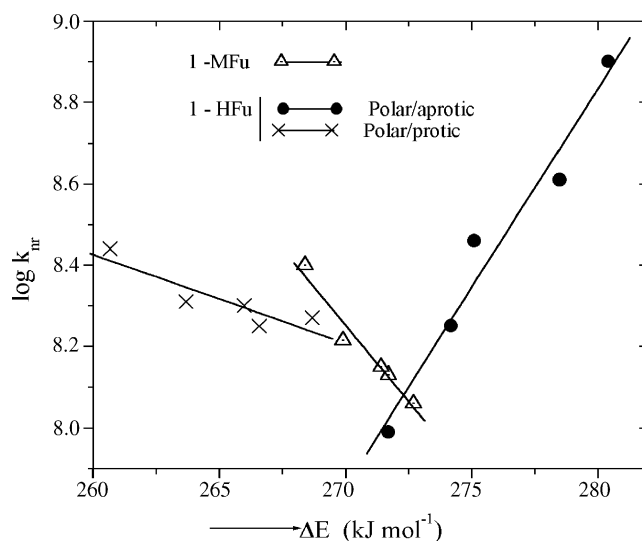


Fig. 5. Plot of $\log k_{nr}$ as a function of energy gap law, ΔE , between S_1 and S_0 states: (●●●) polar aprotic solvents, 1-HFu; (××) polar protic solvents, 1-HFu; (△△) polar protic solvents, 1-MFu.

tation spectra in each solvent. This relation is generally true when the major deactivation pathway involves internal conversion through the highest vibrational frequency mode of S_0 state. Results of Fig. 5 and Table 1 show that k_{nr} decreases with decrease in the energy gap in polar aprotic solvents and increases with decrease in the energy gap in polar protic solvents. In other words, energy gap law is followed in protic solvents and not in aprotic ones. A similar behavior is also observed in 1-AFu [14]. This clearly suggests that internal conversion does not play as the major role in non-radiative deactivation pathway in these molecules, especially in non-polar and polar aprotic solvents. In order to explain the above differences, other mechanisms, which do affect the k_{nr} , may also be looked into. It is noticed that both bulk dielectric effects and specific interactions between solvents and solutes (hydrogen bonding) can affect the non-radiative coupling between S_0 and S_1 states and give rise to deviations from the energy gap law.

To examine the effects of bulk solvent dielectric constant on k_{nr} , we have used the π^* scale, suggested by Taft and co-workers [39]. Fig. 6 depicts the plot of $\log k_{nr}$ as a function of π^* for 1-HFu and 1-MFu. Plot in case of polar/aprotic solvents for 1-HFu indicates that value of k_{nr} decreases with increase in the bulk dielectric constant of the solvents. Although similar data could not be obtained for 1-MFu (as mentioned earlier) in polar/aprotic solvents, but the trend observed in ϕ_f of 1-MFu in these solvents suggests that k_{nr} for 1-MFu will also follow a similar behavior as noted for 1-HFu. On the other hand, in polar/protic solvents, values of k_{nr} for 1-MFu and 1-HFu increase with increase of π^* scale. Value of k_{nr} for 1-HFu in polar/aprotic solvents (e.g. acetonitrile) is smaller than that observed in polar/protic solvents having the same dielectric constant. This suggests that besides the bulk dielectric constant of the solvents hydrogen bond capacity of the

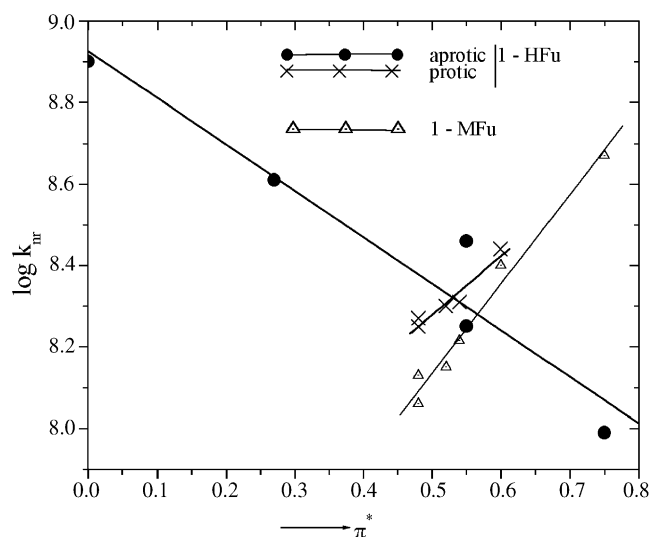


Fig. 6. Plot of $\log k_{nr}$ as a function of the polarity parameter π^* : (●●) polar aprotic solvents, 1-HFu; (××) polar protic solvents, 1-HFu; (△△) polar protic solvents, 1-MFu.

solvents also affect the radiationless decay constant. Further relative increase in the value of k_{nr} of 1-MFu with increase in polarity of protic solvents is larger than that observed for 1-HFu in the similar set of solvents. This suggests that besides the polarity of the solvents, intermolecular hydrogen bonding also influences the photophysics of the excited species.

Effect of specific hydrogen bonding interactions of the solvents on k_{nr} has been studied by plotting $\log k_{nr}$ versus bond donating strength (α) of the solvents (Fig. 7). It is clear from Fig. 7 that 1-MFu and 1-HFu followed similar trend, i.e. value of k_{nr} increases with increase in α for protic solvents and follows linear relation. We have only one polar/aprotic solvent (acetonitrile). Deviation from linearity is noticed in this case and this could be due to its poor hydrogen bond-

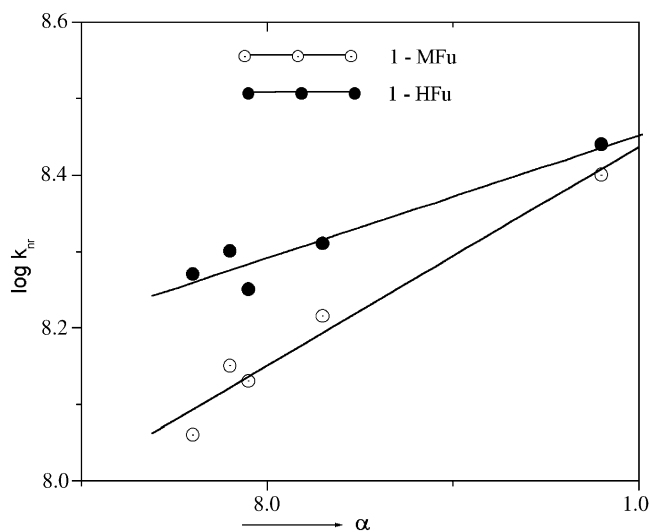


Fig. 7. Plot of $\log k_{nr}$ as a function of hydrogen-donating strength (α) of the solvents: (●●) 1-HFu; (××) 1-MFu.

donating capacity. Further similar to other parameters, the effect of hydrogen bond donating strength on k_{nr} is more for 1-MFu than that for 1-HFu.

1-MFu is an open structure molecule and has been established earlier that it can be present as 1-MFu-a rotamer. S_1 and S_2 states for 1-MFu-a are of $\pi-\pi^*$ and $n-\pi^*$ in nature, respectively, and are separated by only 660 cm^{-1} (Table 2). T_2 and T_3 are of $n-\pi^*$ and $\pi-\pi^*$ states, respectively, possessing separation gaps from S_1 as 3100 and 2800 cm^{-1} in case of 1-MFu-a rotamer. With increase in solvent polarity gap between S_1 and S_2 will increase for 1-MFu-a. In other words, participation of $n-\pi^*$ (S_2) state to $\pi-\pi^*$ (S_1) state will decrease in 1-MFu-a. Further gap between T_3 ($\pi-\pi^*$) and S_1 state will decrease for 1-MFu-a. Thus according to El-Sayed's rule [37] intersystem crossing rate will decrease with increase in polarity of solvents for 1-MFu-a. This is consistent with experimental results. In polar protic solvents, both hydrogen bonding and polarity of solvents are involved in stabilizing the $n-\pi^*$ state. Decrease of k_{nr} for 1-MFu-a up to *n*-propanol as compared to acetonitrile could be due to smaller dielectric constant and weak protic nature of *n*-propanol. With increase in hydrogen bonding strength of solvents, T_2 ($n-\pi^*$) may become higher in energy for 1-MFu-a as compared to T_3 ($\pi-\pi^*$) and thus reversal of states may be observed. So again the El-Sayed's rule will be followed. In other words, it may be concluded that intersystem crossing may play a major role in deactivating the excited rotamers of 1-MFu. This may also be supported by the results of TFE/cyclohexane, i.e. small amount of TFE will not be able to change the solvent properties of cyclohexane but will form hydrogen bonded complex with 1-MFu, because TFE is better proton donor than methanol. Although we have neglected the presence of 1-MFu-b in the system, the values of the non-radiative rate constants can also be explained on the basis of the spectral states (Table 2) present in this rotamer.

As established earlier, 1-HFu is present as 1-HFu-a rather than 1-HFu-b (Scheme 1). Effect of polar aprotic solvents on k_{nr} can be explained as follows. Increase of solvent polarity will decrease the $n-\pi^*$ character of S_2 in S_1 ($\pi-\pi^*$) state of 1-HFu-a. On the other hand, under isolated conditions, energy of T_3 ($n-\pi^*$), which is nearly equal to that of S_1 ($\pi-\pi^*$) becomes larger than that of S_1 ($\pi-\pi^*$). In other words, endothermicity of intersystem crossing between S_1 ($\pi-\pi^*$) and T_3 ($n-\pi^*$) will increase and thus decrease the value of intersystem crossing rate with increase in solvent polarity. Although T_2 ($\pi-\pi^*$) is present below S_1 ($\pi-\pi^*$), according to El-Sayed's rule [36] intersystem crossing process will not be as effective as between the $n-\pi^*$ and $\pi-\pi^*$ states. Comparing the values of k_{nr} of 1-MFu and 1-HFu, k_{nr} is always larger for 1-MFu in any solvent, except for polar/protic ones, where these are nearly similar or smaller than of 1-HFu for each solvent. The smaller value of k_{nr} for 1-HFu in any solvent can only be attributed to the presence of IHB in 1-HFu, which decreases the value of k_{nr} . In other words, in this set of solvents, the decrease in the value of k_{nr} for both the molecules is influenced by the bulk dielec-

Table 2
Calculated properties of 1-HFu and 1-MFu in ground and excited state

Characteristics	1-MFu-a	1-MFu-b	1-HFu-a	1-HFu-b	1HFu-T
B3LYP					
E (Hartree)	−689.9548	−689.9571	−650.6651	−650.6508	−650.6425
μ_g (Da), transition energies (nm) (nature of transition)	2.05	3.44	3.49	3.85	4.2
T ₁	505 (π, π^*)	486 (π, π^*)	510 (π, π^*)	484 (π, π^*)	866 (π, π^*)
T ₂	450 (n, π^*)	481 (n, π^*)	458 (π, π^*)	478 (n, π^*)	585 (π, π^*)
T ₃	444 (π, π^*)	425 (π, π^*)	412 (n, π^*)	417 (π, π^*)	470 (n, π^*)
T ₄	368 (π, π^*)	366 (π, π^*)	373 (π, π^*)	366 (π, π^*)	359 (π, π^*)
S ₀ –S ₁	395 (π, π^*)	405 (n, π^*)	397 (π, π^*)	403 (n, π^*)	451(π, π^*)
S ₀ –S ₂	385 (n, π^*)	375 (π, π^*)	367 (n, π^*)	373 (π, π^*)	434(π, π^*)
S ₀ –S ₃	347 (π, π^*)	339 (π, π^*)	355(π, π^*)	330 (π, π^*)	431(n, π^*)

tric constant (polarity) of the solvents and thus intersystem crossing.

In polar/protic solvents, although we have established earlier that rotamer 'a' is more stable than roamer 'b' even when dipolar solvation energy was taken in to account, the equilibrium can shift to rotamer 1-HF-b when specific interactions (hydrogen bonding) with the protic solvents are considered. So both IHB and intermolecular hydrogen bonding can influence the radiationless processes, besides the dipolar interactions. Considering acetonitrile as a reference solvent, the value of k_{nr} for 1-HFu keeps on increasing with the increase in the polarity and proton-donating capacity of the solvents. Increase in the value of k_{nr} can be explained by proposing that in protic solvents equilibrium will shift to the open structure (1-HFu-b) having the similar set of singlet and triplet states as present in 1-MFu-b. Thus fluorescence quenching dynamics of 1-HFu can be explained on the same lines as done for 1-MFu. The larger value of k_{nr} for 1-HFu as compared to that for 1-MFu could be due to fact that species containing IHB in 1-HFu are still present in the system which has larger effect on the k_{nr} as compared to intermolecular hydrogen bonding. This is supported by the results of TFE/cyclohexane on the fluorescence dynamics of 1-HFu (Table 1). This behavior is similar to those observed for 1-AFu [18] in polar aprotic solvents.

We should not make the direct comparison of our results with those of Biczok et al. [18]. The reason being that they have calculated the rate constants for the individual processes, like internal conversion and intersystem crossing, whereas we have the combined results of non-radiative decay processes. In polar protic solvents, our results are different from those of 1-AFu. In case of 1-AFu, the rate constant for intersystem crossing decreases from 40×10^7 to 20×10^7 s^{−1} and that of internal conversion increases from 2.3×10^7 to 3.5×10^7 s^{−1}, whereas $k_{ISC} + k_{IC}$ decreases from 42.3×10^7 to 23.5×10^7 s^{−1} in going from acetonitrile to ethanol. In our case, the total rate for non-radiative decay increases from 9.8×10^7 to 20.2×10^7 s^{−1} under similar conditions. Further the increase in dipole moment up on excitation to S₁ state for 1-AFu is 3.5 D, whereas in case of 1-HFu it is 4.43 Da and for 1-MFu it is 5.77 D. These values are much larger than that observed for 1-AFu but match with those of 2-,

3- and 4-AFu. Thus based on their arguments the internal conversion may play the increased role in deactivation of the S₁ state. Based on our results it is very difficult to mention the importance of one over the other. Comparing the results of 1-HFu and 1-MFu, we can only say that the intramolecular hydrogen bonding plays better role in deactivation than the intermolecular hydrogen bonding.

Based on the above observations, it may be concluded that rate of non-radiative decay process in 1-MFu is influenced by intersystem crossing in polar aprotic and protic solvents. Same is true for 1-HFu in the former set of solvents, but IHB plays the major role in the deactivation of excited singlet state than the intermolecular hydrogen bonding in protic solvents.

Acknowledgment

The authors are thankful to the Department of Science and Technology, New Delhi, for the financial support to the project number SP/S1/07/2000.

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