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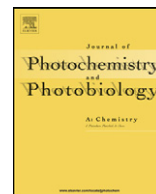22 PUBLICATIONS   66 CITATIONS

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Photophysical properties of an environment sensitive fluorophore 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole and its excited state interaction with N,N-dimethylaniline: A spectroscopic investigation

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ABSTRACT

Photophysical properties of a fluorophore 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole (KTHC-67) have been studied in a number of organic solvents. The profile of the fluorescence spectrum and the wavelength at which fluorescence intensity maximizes are found to vary with the nature of the solvent. The photophysics of KTHC-67 is much more influenced by the hydrogen bond donor and acceptor abilities of the solvents rather than their polarity of the solvent. Excited state interactions of KTHC-67 with N,N-dimethylaniline (DMA) have also been investigated in three homogeneous solvents, acetonitrile (ACN), dimethyl sulphoxide (DMSO) and ethanol (EtOH). Photoinduced electron transfer from DMA to KTHC-67 is evident from the subsequent changes in the fluorescence intensity, fluorescence lifetime and transient absorbance of KTHC-67 in presence of DMA.

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1. Introduction

1-Keto-1,2,3,4-tetrahydrocabazoles (Fig. 1) were synthesized as a precursor for obtaining naturally occurring carbazole alkaloids and carbazoloquinones [1]. In a recent communication Saha et al. reported that methoxy derivatives of 1-keto-1,2,3,4-tetrahydrocabazoles show significant fluorescence emission [2]. Fluorescence spectroscopic techniques are utilized in a wide range of applications due to their high sensitivity [3–13]. In the present report, we have carried out photophysical investigations on 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole (Fig. 1), abbreviated as KTHC-67. The position of the fluorescence emission maximum of KTHC-67 is found to be sensitive to the nature of the solvent. A bathochromic shift of the emission maximum is observed when the dielectric constant of the solvent has been increased or when a protic solvent has been used. Such solvent sensitivity makes it

useful to probe the immediate microenvironment. As the molecule is quite sensitive towards protic solvent, it may be specifically utilized to sense the presence of intermolecular hydrogen bonding. Moreover the molecule has appreciable quantum yield which may be exploited in its use as a biomarker. However considering its wavelengths of excitation and emission that will interfere with the related optical properties of ubiquitous biomolecules in living systems we have some future plans to modify the molecule to suite the purpose. Keeping in mind its possible future use, we have also studied its interaction with simple organic donor N, N-dimethylaniline (DMA) to understand the type of reactions it is likely to participate in. The aforesaid intramolecular charge transfer may compete with the intermolecular charge transfer between DMA and the KTHC-67. There is no ground state interaction between KTHC-67 and DMA. The interaction exists only in the excited state which is reflected in the quenching of fluorescence quantum yield and lifetime of KTHC-67 in presence of DMA. The nature of interaction is found to be influenced by the type of the solvent used. Investigation of the transient intermediates by Laser Flash Photolysis experiments reveals that electron transfer from DMA to KTHC-67 is the probable cause for the interaction.

1-Keto-1,2,3,4-tetrahydrocarbazole

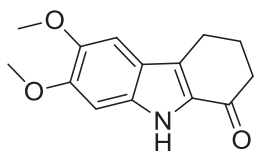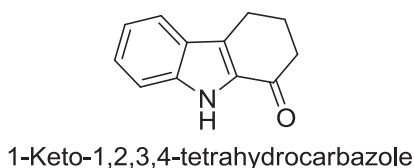1-Keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole

Fig. 1. Structures of 1-keto-1,2,3,4-tetrahydrocarbazole and 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole.

2. Experimental

2.1. Materials

Synthesis and crystallization of 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole (KTHC-67) have been performed as described elsewhere [24]. GC grade N,N-dimethylaniline (DMA) has been purchased from Sisco Research Laboratories Pvt. Ltd. and used after proper distillation. UV spectroscopic grade acetonitrile (ACN), dichloromethane (DCM), ethanol (EtOH), methanol (MeOH), benzene (BZ), 1,4-dioxane (DOX) and dimethyl sulphoxide (DMSO) have been purchased from Spectrochem Pvt. Ltd. and used without further purification. All the solvents have been checked using absorption and fluorescence techniques to ensure the absence of impurities in the wavelength ranges of interest. Anthracene has been purchased from Sigma–Aldrich and used after proper recrystallization. Water from Millipore water purification system has been used.

2.2. Spectral methods

Jasco V-650 spectrophotometer and Horiba Jobin-Yvon Fluoromax-3 have been used for absorbance and fluorescence measurements respectively. Fluorescence lifetimes have been measured using a time-correlated single-photon-counting (TCSPC) spectrophotometer (Horiba Jobin-Yvon Single Photon Counting Controller Fluorohub). The sample has been excited at 340 nm using LED. The calculations have been performed using deconvolution technique, which is based upon a convolution integral, using the software supplied by Horiba Jobin-Yvon. Nanosecond

laser flash photolysis set-up from Applied Photophysics has been used for the measurement of transient absorption spectra. The sample has been excited at 355 nm (FWHM = 8 ns) using Nd-YAG laser (Lab series, Model Lab 150, Spectra Physics). The analyzing light is from a 150 W pulsed xenon lamp. The laser and the analyzing beams cross at right angles and pass through a quartz cell containing sample solution. A monochromator (equipped with an IP28 photomultiplier) has been used to analyze transient absorption. Signals from the photomultiplier have been recorded as a function of time on a Tektronix oscilloscope (TDS 3054B, 500 MHz, 5 Gs/s) and the data have been transferred to a computer using the TEKVISA software. The samples have been de-aerated for 20 min by passing pure argon gas prior to each experiment. No degradation of the samples has been noticed throughout the experiment. All the data have been analyzed, fitted and plotted by the software Origin® 8.0 Pro. All experiments have been carried out using quartz cuvettes of 1 cm^2 cross-sections purchased from Hellma Analytics.

3. Results and discussion

3.1. Spectral characteristics of KTHC-67

Fig. 2(a) shows the absorption spectra of KTHC-67 in acetonitrile (ACN), dichloromethane (DCM), ethanol (EtOH), methanol (MeOH), benzene (BZ), 1,4-dioxane (DOX) and dimethyl sulphoxide (DMSO). Spectral position undergoes no significant shift in these solvents.

Fig. 2(b) shows the fluorescence spectra of KTHC-67 in the same solvents. Although the absorption maxima of KTHC-67 in various solvents fall in the range of 330–340 nm, the excitation wavelength for all the fluorescence experiments has been set at 350 nm, to avoid the contribution of large DMA absorption at the excitation wavelength in later experiments [14]. Quantum yields of KTHC-67 in the solvents are listed in Table 1.

The positions of the emission maximum in the solvents are expected to vary in accordance to its empirical polarity parameters $E_T(30)$ [15,16]. More the $E_T(30)$ value of the solvent more will be the emission maximum shifted towards the red end of the spectrum. The relative quantum yield in different solvents depends in a complex manner on its viscosity, dielectric constant as well as hydrogen bond donor and acceptor abilities. The various parameters of the solvents are listed in Table 2.

Various compositions of water-1,4-dioxane mixtures have been chosen for further investigation of the influence of surrounding medium on the photophysics of KTHC-67. This particular mixed solvent system is used for its known empirical polarity parameters $E_T(30)$ [19]. It has been observed that emission maximum of
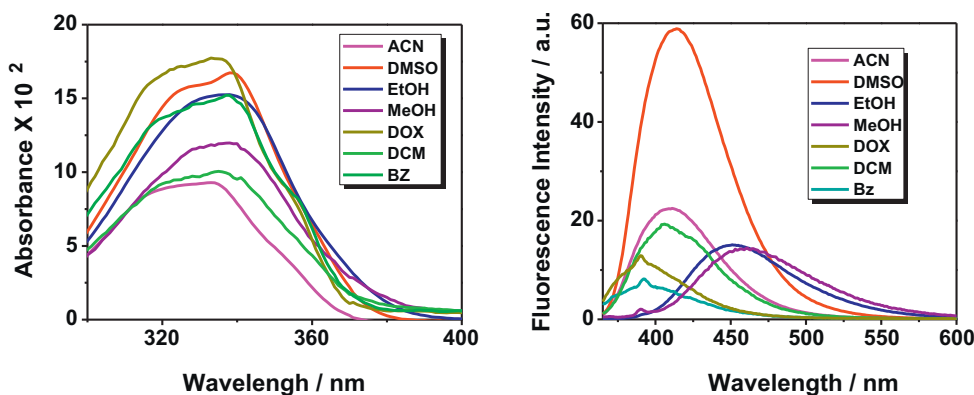

Fig. 2. (a) Absorption and (b) fluorescence spectra of KTHC-67 [10^{-6} M] in ACN, DMSO, EtOH, MeOH, DOX, DCM and BZ. For fluorescence measurements KTHC-67 has been excited at 350 nm.

Table 1
Quantum yields of KTHC-67 [10^{-6} M] in different solvents. Anthracene has been taken as the reference compound for the determination of quantum yield [7].

Solvent	ACN	DCM	EtOH	MeOH	BZ	DOX	DMSO
Quantum yield	0.079	0.112	0.115	0.119	0.041	0.061	0.327

Table 2
Solvent parameters.

Solvent	ACN	DCM	EtOH	MeOH	BZ	DOX	DMSO
Dielectric constant (20 °C) [17]	37.5	9.1	22.4	32.6	2.28	2.21	46.6
Absolute viscosity/cP (25 °C) [17]	0.38	0.44	1.08	0.6	0.65	1.3	2.0
Refractive index (25 °C) [17]	1.342	1.4211	1.359	1.326	1.498	1.420	1.476
π^{*a} [18]	0.75	0.82	0.54	0.60	0.59	0.55	1.00
α^{b} [18]	0.19	0.30	0.83	0.93	0.00	0.00	0.00
β^{c} [18]	0.31	0.00	0.77	0.62	0.10	0.37	0.76
$E_T(30)^{d}$ [16]	46.0	41.1	51.9	55.5	34.5	36.0	45.0

[a] π^* is the polarity or polarizability effects of the solvent.
[b] α is the hydrogen bond donor (HBD) acidity of the solvent.
[c] β is the hydrogen bond acceptor (HBA) basicity of the solvent.
[d] $E_T(30)$ is the Dimroth–Reichardt empirical polarity parameter of the solvent.

KTHC-67 undergoes bathochromic shift on increasing the percentage of water in the solvent mixture as shown in Fig. 3(a). This is because with increasing percentage of water, the extent of intermolecular H-bonding and dielectric constant of the solvent mixture increases. Fluorescence energies (E_F) of KTHC-67 varies in a similar manner with the empirical polarity parameters, $E_T(30)$ of pure solvents and 1,4-dioxane-water solvent mixtures respectively as shown in Fig. 3(b). Relative integrated fluorescence intensity of KTHC-67 in 1,4-dioxane-water solvent mixtures follows a typical trend by reaching maximum at certain composition (Fig. 3(c)). Absorption spectra of KTHC-67 in these 1,4-dioxane-water solvent mixtures do not vary significantly which is very similar to the observations obtained in pure solvents (Fig. 3(d)).

The ground and excited state dipole moments of KTHC-67 have been determined by the employment of quantum-mechanical second-order perturbation method and taking into account the Onsagar model of reaction field for a polarizable dipole moment. This leads to the following two equations for the difference and
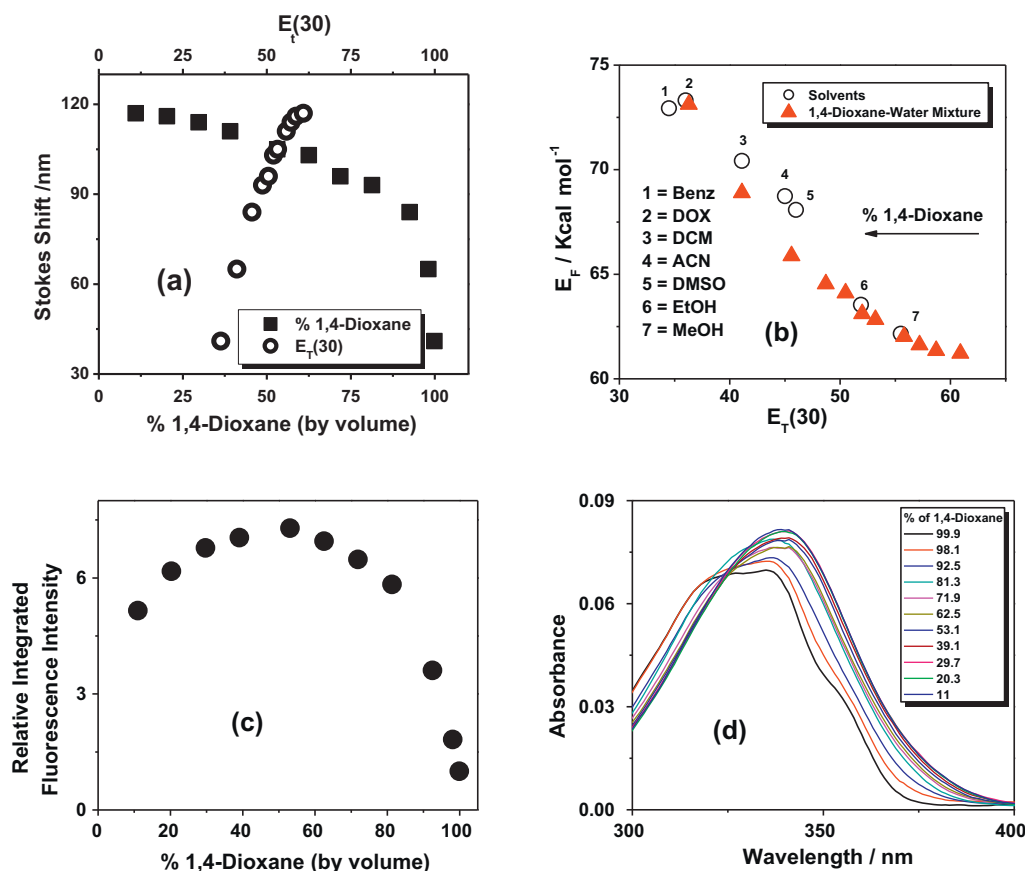

Fig. 3. (a) Dependence of Stokes shift on the volume percentage of 1,4-dioxane in water-1,4-dioxane solvent mixtures and on the values of empirical polarity parameters, $E_T(30)$ of the solvent mixtures. (b) Dependence of fluorescence energies (E_F) of KTHC-67 on the $E_T(30)$ values of pure solvents and 1,4-dioxane-water solvent mixtures. (c) Relative integrated fluorescence intensity of KTHC-67 in various compositions of water-1,4-dioxane solvent mixtures. (d) Dependence of absorbance of KTHC-67 on the compositions of water-1,4-dioxane solvent mixtures. KTHC-67 concentration in each case has been 2.5×10^{-6} M.
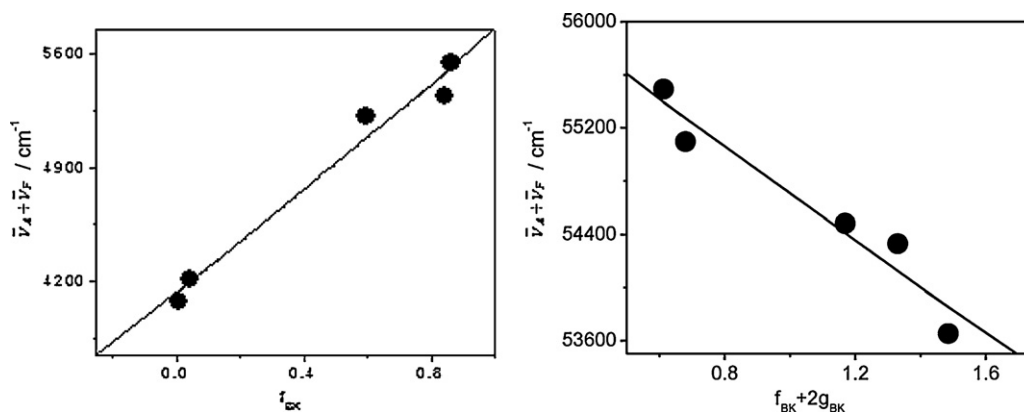
Fig. 4. (a) Plot of $\bar{\nu}_A - \bar{\nu}_F$ versus $f_{BK}(\varepsilon, n)$. (b) Plot of $\bar{\nu}_A + \bar{\nu}_F$ versus $f_{BK}(\varepsilon, n) + 2g_{BK}(n)$.

sum of the absorption and fluorescence shifts in various solvents [20–23]:

$$\bar{\nu}_A - \bar{\nu}_F = m_1 . f_{BK}(\varepsilon, n) + const \tag{1}$$

$$\bar{\nu}_A + \bar{\nu}_F = -m_2 . [f_{BK}(\varepsilon, n) + 2g_{BK}(n)] + const \tag{2}$$

where

$$m_1 = \frac{2(\mu_e - \mu_g)^2}{hca^3} \tag{3}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \tag{4}$$

For a spherical cavity with an Onsager radius a, the solvent polarity parameters are

$$f_{BK}(\varepsilon, n) = \frac{\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}}{\left(1 - \frac{2\alpha}{a^3} \cdot \frac{\varepsilon - 1}{2\varepsilon + 1}\right)\left(1 - \frac{2\alpha}{a^3} \cdot \frac{n^2 - 1}{2n^2 + 1}\right)^2} \tag{5}$$

$$g_{BK}(n) = \frac{\frac{n^2 - 1}{2n^2 + 1}\left(1 - \frac{\alpha}{a^3} \cdot \frac{n^2 - 1}{2n^2 + 1}\right)}{\left(1 - \frac{2\alpha}{a^3} \cdot \frac{n^2 - 1}{2n^2 + 1}\right)^2} \tag{6}$$

where ε denotes the electric permittivity and n is the refractive index.

For an isotropic polarizability of the solute, the condition $2\alpha/a^3 = 1$ is frequently satisfied and the simplified form of relations (5) and (6) become

$$f_{BK}(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right) \tag{7}$$

$$g_{BK}(n) = \frac{3}{2}\frac{n^4 - 1}{(n^2 + 2)^2} \tag{8}$$

After calculating $f_{BK}(\varepsilon, n)$ and $g_{BK}(n)$ for all the solvents except for the protic solvents [4] from relations (7) and (8), $\bar{\nu}_A - \bar{\nu}_F$ has been plotted against $f_{BK}(\varepsilon, n)$ (Fig. 4(a)) and $\bar{\nu}_A + \bar{\nu}_F$ has been plotted against $[f_{BK}(\varepsilon, n) + 2g_{BK}(n)]$ (Fig. 4(b)) and according to relations (1) and (2) m_1 and m_2 have been found from the respective slopes. For a special case where the ground and excited-state dipole moments (μ_g and μ_e) are parallel [23–25], the relations (3) and (4) yield

$$\mu_g = \frac{1}{2}(m_2 - m_1)\left(\frac{hca^3}{2m_1}\right)^{1/2} \tag{9}$$

$$\mu_e = \frac{1}{2}(m_1 + m_2)\left(\frac{hca^3}{2m_1}\right)^{1/2} \tag{10}$$

$$\mu_e = \mu_g \frac{m_1 + m_2}{m_2 - m_1}, (m_2 > m_1) \tag{11}$$

Using the values of m_1 and m_2 obtained from Fig. 4 and using relations (9) and (10), the values for the ground and excited dipole moments have been calculated as $0.149D$ and $3.346D$ respectively. The solvent polarity sensitivity of KTHC-67 in aprotic solvents thus can be explained by its $3.197D$ higher dipole moment in the excited state.

To further quantify the individual contributions of different modes of solute–solvent interactions that control the solvent induced shifts of the emission maxima of KTHC-67, a multi-parameter approach, known as solvatochromic comparison method (SCM) proposed by Kamlet and Taft has been used [18,26–31]. This approach separates the polarity/polarizability effects of the solvent (π^*), its HBD (hydrogen bond donor) acidity (α) and its HBA (hydrogen bond acceptor) basicity (β) on the spectral properties of the fluorophore. According to SCM, the emission frequencies can be correlated using the following multiple linear regression analysis approach.

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* + a\alpha + b\beta \tag{12}$$

Here, the coefficients s, a and b measure the relative sensitivities of the fluorophore to the said solvent properties. $\bar{\nu}_0$ is the emission frequency of the reference solvent.

The values obtained for KTHC-67 using benzene as the reference solvent are

$$\bar{\nu} = 25510.2 - 531.2\pi^* - 2531.1\alpha - 1461.1\beta \tag{13}$$

Emission frequencies are expressed in cm^{-1}. The negative sign of the coefficients is representative of the bathochromic shift of the emission maximum of KTHC-67 with increase of the solvent polarity, its H-bond donor and acceptor ability. The relative magnitudes of s, a and b indicate that HBD acidity of the solvent plays a major role on the photophysics of KTHC-67 while HBA basicity of the solvent plays an intermediate role. Solvent polarity/polarizability is found to be least significant in controlling the emission behaviour of KTHC-67. This again explains the relative positions of the emission maximum of KTHC-67 in different types of solvents as shown in Fig. 2(b).

The relative values of the ground and excited state dipole moments of KTHC-67 as well the individual contributions of different modes of solute–solvent interactions that control the solvent induced shifts of the emission maxima of the compounds indicate that its photophysics is more sensitive to the presence of H-bond donating solvent than to the solvent dielectric constant. This special sensitivity can be attributed to the H-bonding of the carbonyl group of KTHC-67 with the H-bond donating solvent. The more is
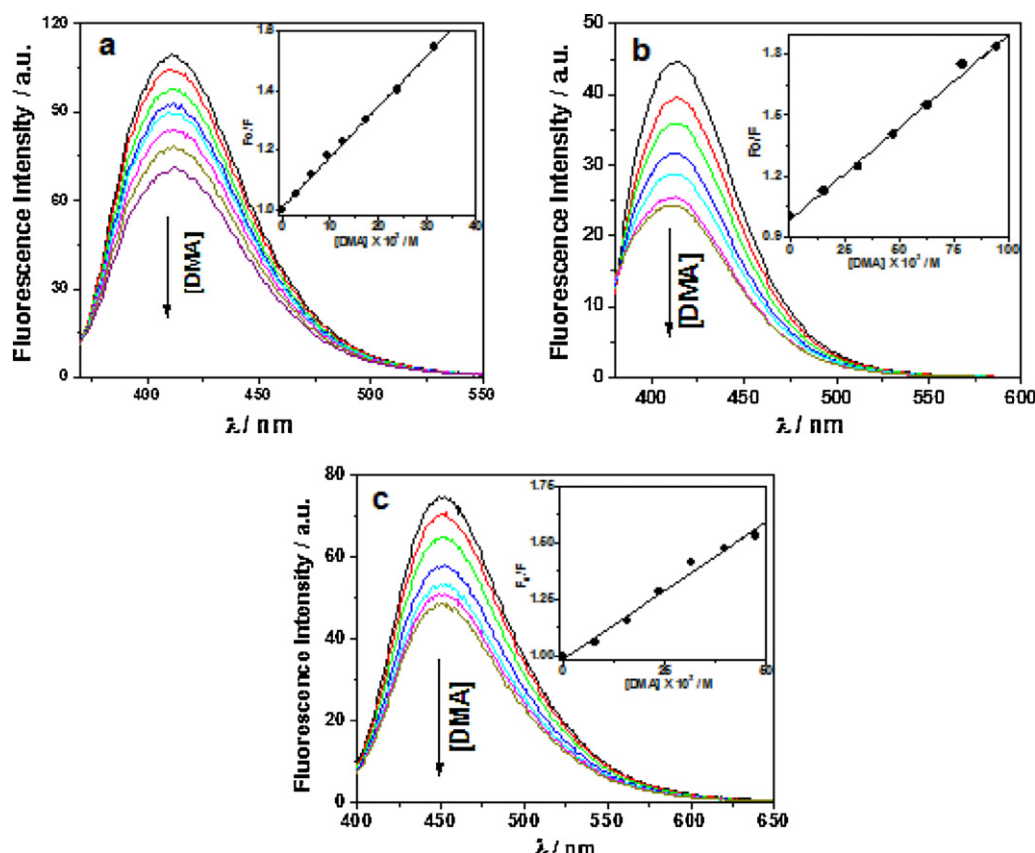
Fig. 5. Quenching of KTHC-67 with DMA in (a) ACN, (b) DMSO and (c) EtOH with concentrations of KTHC-67 as 2.142×10^{-6} M, 5.715×10^{-6} M and 2.958×10^{-6} M respectively. Each inset represents the corresponding Stern–Volmer plot. Concentration of DMA has been varied from 0 M to 0.032 M in ACN, 0 M to 0.095 M in DMSO and 0 M to 0.047 M in EtOH. KTHC-67 has been excited at 350 nm.

the strength of the H-bond the more will be the polarization of the carbonyl group and hence the sensitivity towards protic solvent.

3.2. Interaction between KTHC-67 and N,N-dimethylaniline: steady-state fluorescence measurements

On gradual addition of DMA to the solution of KTHC-67 in any of the following solvents, EtOH, ACN or DMSO, the absorption spectra of the compound do not show any significant change. This excludes the possibility of formation of ground state complex between KTHC-67 and DMA in those solvents. However the fluorescence intensity of KTHC-67 has been found to quench on gradual increase in concentration of DMA which might be due to photoinduced electron transfer (PET) from DMA to KTHC-67. The extent of steady-state fluorescence quenching has been calculated using the Stern–Volmer [32] (SV) relationship

$$\frac{F_0}{F} = 1 + K_{sv}[Q] \qquad (14)$$

In Eq. (14) F_0 and F are the fluorescence intensities in the absence and presence of the quencher (Q) and K_{sv} is the Stern–Volmer quenching constant.

Fig. 5 shows the quenching of KTHC-67 with DMA in three solvents ACN, DMSO and EtOH as well as the corresponding Stern–Volmer plots. All the spectra have been corrected for inner filter effects. The calculated values of K_{sv} are given in Table 3. The extent of quenching is less as evident from small magnitudes of K_{sv}. The most probable reason is that photoinduced electron transfer from DMA to KTHC-67 is opposed by the intramolecular charge transfer within KTHC-67.

The order of K_{sv} in different solvents depends on the extent of caging offered by the solvent by its dielectric constant, viscosity and intermolecular hydrogen bonding because quenching is a diffusion-controlled phenomenon. Since, DMSO has highest viscosity (2.0 cP) and highest dielectric constant (46.6) among the three solvents, quenching occurs to least extent. EtOH has moderate viscosity (1.08 cP) and least dielectric constant (22.4) which is supplemented by the presence of intermolecular hydrogen bonding, as a result quenching constant has intermediate value. ACN has moderate dielectric constant (37.5) and least viscosity (0.38 cP) and also is lacking any intermolecular hydrogen bonding. As a consequence quenching is maximum in ACN.

3.3. Interaction between KTHC-67 and N,N-dimethylaniline: fluorescence lifetime measurements

The quenching of fluorescence of KTHC-67 by DMA in different solvents can also be studied using lifetime measurements. The value of quenching constant obtained from the measurement of lifetime of KTHC-67 in the absence and presence of DMA with varied concentration would be much more accurate compared to that obtained previously from direct fluorescence quenching data because of lack of error that may arise in fluorescence intensity measurements from concentration quenching at higher

Table 3
Stern–Volmer constants for the quenching of KTHC-67 with DMA in three solvents.

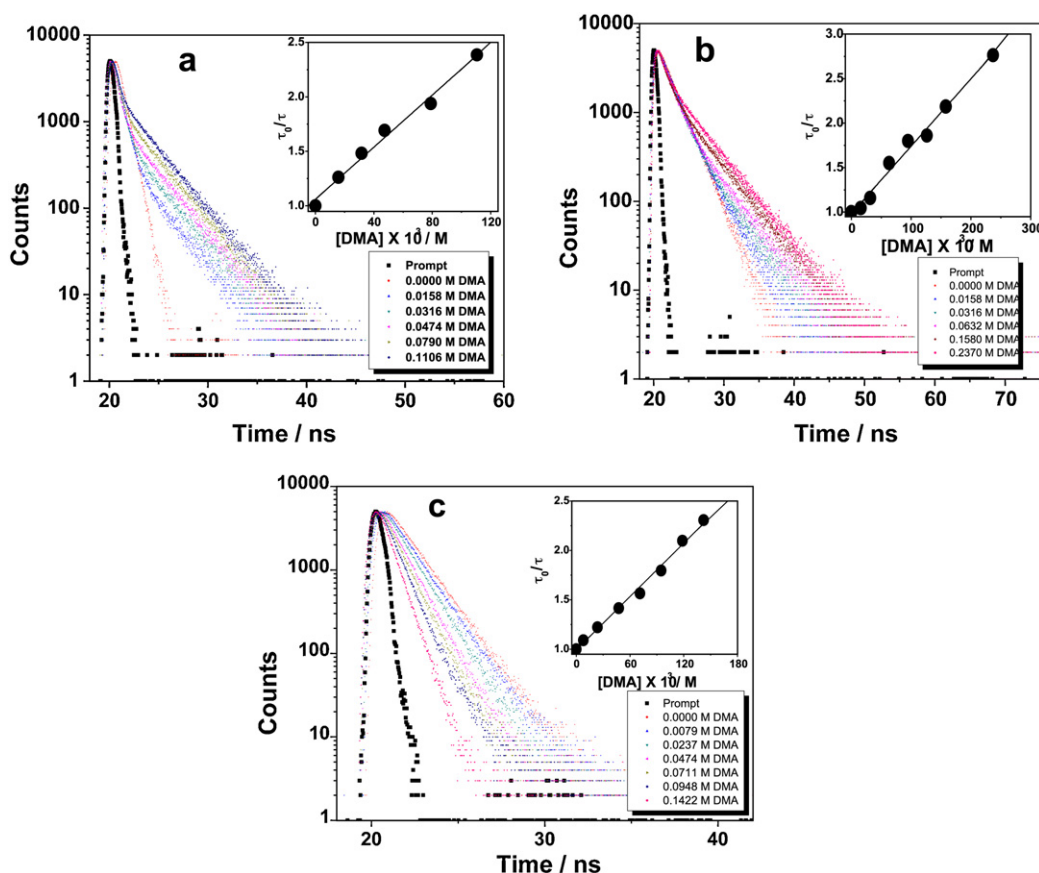| Solvent	ACN	DMSO	EtOH
K_{sv}/M	17.066	9.156	12.119

Fig. 6. Fluorescence decay profiles of KTHC-67 with DMA in (a) ACN, (b) DMSO and (c) EtOH. Concentrations of KTHC-67 in the three cases have been 2.142×10^{-6} M, 5.715×10^{-6} M and 2.958×10^{-6} M respectively. Inset in each case represents the corresponding Stern–Volmer plot. Concentrations of DMA have been varied from 0 to 0.111 M in ACN, 0 to 0.237 M in DMSO and 0 to 0.142 M in EtOH respectively. KTHC-67 has been excited with 340 nm LED.

concentrations of DMA used in this study. In fact the Stern–Volmer quenching constants obtained from lifetime measurements have been found to be lesser than that obtained from steady-state measurements, but the trend remains the same. The lifetime values for KTHC-67 have been determined using our available picosecond time-correlated single photon counting apparatus and calculated using the following expression [33].

$$I(t) = \sum_{i=1}^{n} a_i e^{-t/\tau_i} \qquad (15)$$

In Eq. (6) where $I(t)$ is the intensity of the fluorescence at time t, a_i is the pre-exponential factor for the fraction of the fluorescence intensity, τ_i is the fluorescence lifetime of the emitting species and n is the total number of emitting species. In Fig. 6, lifetime decays of KTHC-67 with increasing concentrations of DMA in three different solvents have been shown along with the Stern–Volmer plots from lifetime quenching data using the following equation.

$$\frac{\tau_0}{\tau} = 1 + K_{sv}[Q] \qquad (16)$$

Fluorescence lifetimes of KTHC-67 in the absence and presence of DMA in three solvents and the corresponding values of Stern–Volmer constants have been listed in Tables 4 and 5 respectively.

In ACN and DMSO, bi-exponential decay has been observed with increasing concentration of DMA but in EtOH the decay remains mono-exponential. The second component with higher lifetime in ACN and DMSO arises from the contribution of fluorescence of DMA

Table 4
Fluorescence lifetimes of KTHC-67 with DMA in ACN, DMSO and EtOH.

[DMA]/M	a_1 (a_2)	τ_1 (τ_2)/ns	χ^2
Acetonitrile			
0	0.075	0.750	1.014
0.016	0.773 (0.227)	0.595 (2.906)	1.010
0.032	0.636 (0.364)	0.506 (2.921)	1.003
0.047	0.528 (0.472)	0.443 (2.976)	1.016
0.079	0.422 (0.577)	0.387 (3.030)	1.003
0.111	0.330 (0.670)	0.314 (3.045)	1.018
Dimethyl sulphoxide			
0	0.051	2.244	0.966
0.016	0.845 (0.155)	2.144 (3.973)	1.055
0.032	0.735 (0.265)	1.936 (4.309)	1.206
0.063	0.519 (0.481)	1.446 (4.095)	1.003
0.095	0.409 (0.591)	1.247 (4.132)	1.010
0.126	0.439 (0.561)	1.206 (4.281)	1.003
0.158	0.335 (0.665)	1.026 (4.240)	1.016
0.237	0.229 (0.771)	0.812 (4.257)	1.016
Ethanol			
0	0.064	1.525	1.043
0.008	0.057	1.398	1.080
0.024	0.060	1.248	1.043
0.047	0.062	1.077	1.016
0.071	0.064	0.974	1.041
0.095	0.067	0.849	1.061
0.118	0.073	0.727	1.027
0.142	0.077	0.661	1.071

[DMA] represents the concentration of DMA that is being added. τ_1 and τ_2 represent the two different components of fluorescence lifetime of the emitting species while a_1 and a_2 represent the corresponding pre-exponential factors. χ^2 represents the goodness of fit of the lifetime data.

Table 5
Stern–Volmer constants obtained from the fluorescence lifetime measurements of KTHC-67 in presence of DMA in ACN, DMSO and EtOH.
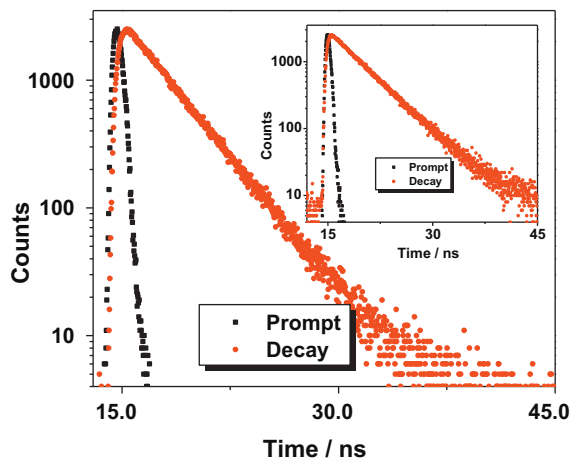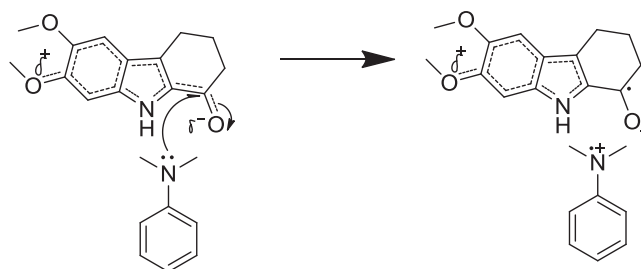
Solvent	ACN	DMSO	EtOH
K_{sv}/M	11.946	7.571	9.012

Scheme 1. Possible mode of interaction between excited KTHC-67 and DMA.

3.4. Mode of interaction between KTHC-67 and N,N-dimethylaniline: laser flash photolysis study

Transient absorption spectra of KTHC-67 with different concentrations of DMA in ACN, DMSO and EtOH have been studied using laser flash photolysis technique to determine the nature of the excited state interaction between KTHC-67 and DMA through identification of transient intermediates.

The transient absorption spectra at 1 μs time delay after laser pulse at 355 nm of 10^{-4} M KTHC-67 solution in ACN alone and in the presence of 0.053 M and 0.158 M DMA have been shown in Fig. 8(a).

In Scheme 1 the possible mechanism of interaction between DMA and KTHC-67 has been shown.

The transient absorption spectrum of KTHC-67 in the wavelength region of 360–480 nm displays a strong absorption maximum around 400–410 nm. On addition of DMA, the transient absorbance is quenched and a new hump is generated with a maximum around 440–470 nm, with an isosbestic point at 430 nm. The lifetimes of the transients also increase on addition of DMA as shown in Table 6. According to previous reports this is due to the formation of DMA radical cation, DMA+• that originates due to

Fig. 7. Lifetime decay of 0.1 M DMA solution in ACN and in DMSO (inset).

excited at 340 nm (Fig. 7). There is no such contribution in decay profile of KTHC-67 in EtOH because in this solvent the emission maximum of KTHC-67 is largely red shifted compared to that in ACN and DMSO.
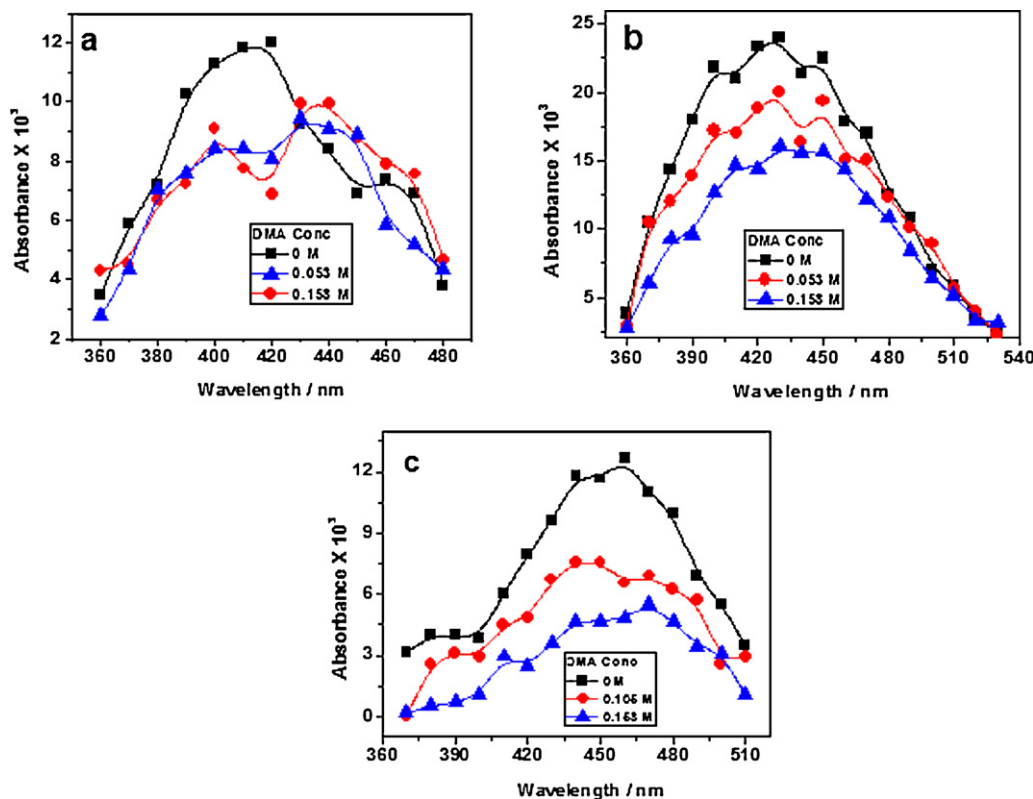

Fig. 8. Transient absorption spectra at 1 μs time delay of 10^{-4} M KTHC-67 in (a) ACN, (b) DMSO and (c) EtOH with different concentrations of DMA. DMA concentration has been varied from 0 to 0.158 M in each case. Laser excitation wavelength has been 355 nm.

Table 6
Lifetimes of the transient species for KTHC-67-DMA interaction in ACN medium at certain wavelengths.

Wavelength	400 nm	410 nm	440 nm	450 nm	460 nm	470 nm
0 mM DMA	2.59 μs	3.8 μs	2.15 μs	2.34 μs	3.09 μs	3.02 μs
62.7 mM DMA	2.21 μs	1.74 μs	3.29 μs	3.44 μs	3.84 μs	4.73 μs

Table 7
Lifetimes of the transient species for KTHC-67-DMA interaction in EtOH medium at certain wavelengths.

Wavelength	460 nm	470 nm
0 mM DMA	17.46 μs	4.02 μs
105.4 mM DMA	3.10 μs	2.22 μs

electron transfer from DMA [34–36] to the acceptor. So, the formation of this hump clearly indicates that DMA transfers electron to KTHC-67.

The transient absorption spectra at 1 μs time delay after laser pulse of 10^{-4} M KTHC-67 solution in DMSO alone and in the presence of 0.053 M and 0.158 M DMA have been shown in Fig. 8(b). No characteristic hump is observed in these spectra because of overlapping wavelength regions for the absorbance of all the transients around 420–440 nm. Photo-physics of transient intermediates has been very much solvent dependent. That is why changing the solvent from ACN to DMSO leads to bathochromic shift.

Fig. 8(c) shows the transient absorption spectra at 1 μs time delay after laser pulse of 10^{-4} M KTHC-67 solution in EtOH alone and in the presence of 0.105 M and 0.158 M DMA. Here again the positions of transient intermediates are not well defined. However the peak at 460 nm that can be attributed to transient KTHC-67 in EtOH has been found to quench with increasing concentrations of DMA with a corresponding increase in relative absorbance at 470 nm. Lifetimes of the transient species at the specified wavelengths are shown in Table 7. Similar to previous argument this change can be attributed to the formation of DMA+•. The change in the wavelength of transient absorption from 410 nm to 460 nm on changing the solvent from ACN to EtOH again shows the huge sensitivity of KTHC-67 to protic solvent.

4. Conclusions

This study reports the complete photophysical characterization of 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole (KTHC-67). Fluorescence emission of KTHC-67 is dependent on the nature of the surrounding environment and is more sensitive to the presence of protic solvents. This property makes the compound suitable as a probe for sensing its microenvironment. KTHC-67 is found to interact with DMA due to photoinduced electron transfer (PET) from DMA to KTHC-67. Our future plans are to see its photophysical behaviour in confined systems like micelles, reverse micelles, cyclodextrins. We would also like to modify the structure of KTHC-67 in order to suit the purpose of making it a potential biomarker.

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