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Cationic micellar effects on the proton transfer reactions of *N*-substituted 2-(7-hydroxycoumarin-4-yl)acetamides and related compound in the ground and excited singlet states

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Abstract

A spectroscopic investigation was undertaken to determine cationic micellar effects on the ground-state and excited singlet-state proton transfer reactions of the title compounds with and without triethylamine (TEA). It was found that the presence of hexadecyltrimethylammonium chloride (HTAC) micelles containing TEA apparently lowers the equilibrium constant for the formation of tautomer anions having hydrophobic alkyl or aryl side chains (owing to a decrease of the effective concentration of TEA in the micellar phase) but exerted only a minor effect on the tautomerization of 7-hydroxy-4-methylcoumarin. The latter finding was explained in terms of the adsorption of this guest on the cationic head group with the hydroxy group directed toward the bulk aqueous phase. Analysis of HTAC micellar effects on the fluorescence spectra and lifetimes of the guests and their tautomer anions in the absence of TEA revealed that the orientation of our bichromophoric guest molecules in the micellar phase is subject to dramatic electronic effects of aryl substituents attached at the 4-position of the hydroxycoumarin ring.

Keywords: 7-Hydroxycoumarin derivatives; Hexadecyltrimethylammonium chloride; Proton transfer; Micellar effects; Substituent effects

1. Introduction

Most important property of compartmentalized liquids such as micelles is that they have an ability to concentrate guest molecules into relatively small effective volumes and then to promote the re-encounter of such molecules [1–5]. This property also makes micelles a good device for inducing efficient electrostatic interactions between the micelle head groups and the guest molecules, as well as strong hydrophobic interactions of these molecules with the micelle side chains. Although much attention has been given to the elucidation of the mechanism of micelle-catalyzed reactions [1,5], there is only a limited study of micellar effects on the proton transfer reactions of hydroxy-substituted guest molecules in the excited state [6–19].

On the other hand, the complicated pH-dependent fluorescence behavior of 7-hydroxycoumarin and its derivatives has attracted considerable attention from spectroscopic point of view, and efforts have been made to unravel the structures of the excited singlet-state species that are responsible for the multiple fluorescence [20–32]. In a previous study we analyzed the effects of added tertiary amines on the spectroscopic behavior of 7-hydroxycoumarin in non-aqueous solvents, and found that protic polar solvents such as methanol greatly accelerate the production of the ground-state tautomer ion pair through the strong hydrogen-bonding solvation of this ion pair [33]. It was also found that depending on both the solvent property and the amine basicity, 7-hydroxycoumarin exists in the form of a hydrogen-bonded complex, a hydroxycoumarin anion, or a hydroxycoumarin tautomer anion. Thus, we may expect that the head group of cationic micelles promotes the formation of the tautomer anion through an electrostatic interaction. It is also possible to predict that the introduction of a hydrophobic alkyl or an aryl group into the hydroxycoumarin chromophore affects the ability (with which a given tautomer anion forms), as well as the location and orientation of this guest anion in the cationic micellar phase, in the absence and presence of a tertiary amine.

Since the polarity and proton-donating ability of solvents exert their dramatic effects on the UV absorption and fluorescence behavior of 7-hydroxycoumarin tautomer anion [33], this anion must be an excellent probe for inspecting the interaction with supramolecules such as micelles of inhomogeneous environments [1–5]. In order to explore the location

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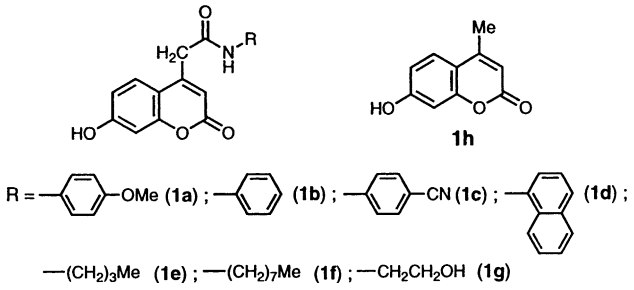
and orientation of bichromophoric 7-hydroxycoumarin derivatives in the micellar phase through analysis of cationic micellar effects on the proton dissociation behavior of these derivatives in the ground and excited singlet states, we synthesized 2-(7-hydroxycoumarin-4-yl)acetamide derivatives (**1a**–**g**), hoping to gain information useful for the design of a novel solar energy conversion and storage supramolecular system. In the present study we employed 7-hydroxy-4-methylcoumarin (**1h**), hexadecyltrimethylammonium chloride (HTAC) micelle and triethylamine (TEA) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a reference guest, a cationic micelle host and a tertiary amine, respectively.



2. Results and discussion

2.1. Micellar effects on the UV absorption spectra

In order to make sure that the hydroxycoumarin guest **1** is solubilized into the micellar phase, we examined a relationship between the HTAC detergent concentration and the absorbance at 370 nm where the tautomer anion shows a characteristic absorption [33] (data not shown). For example, the absorbance of **1a** (2.5×10^{-5} mol dm^{-3}) at 370 nm undergoes only a very small effect of added HTAC in its low concentration range ([HTAC] $< 1.0 \times 10^{-3}$ mol dm^{-3}), whereas the 370 nm absorption increases as the detergent concentration is increased ([HTAC] $> 1.5 \times 10^{-3}$ mol dm^{-3}) and then remains nearly constant in the high concentration range ([HTAC] $> 5.0 \times 10^{-3}$ mol dm^{-3}). The finding that the critical micelle concentration (CMC) of 1.4×10^{-3} mol dm^{-3} estimated from an analysis of the dependence of the absorbance at 370 nm on the HTAC concentration is in excellent agreement with the literature CMC value (1.4×10^{-3} mol dm^{-3} [34,35]) confirms that the guest **1a** is incorporated into the HTAC micellar phase to form a detectable amount of the tautomer anion which should be stabilized mainly by electrostatic interaction with the cationic head groups and hydrogen-bonding solvation by water molecules existing at the micellar surface [1,5]. The same CMC values were obtained for the other guest molecules **1b**–**h** ($1.3–1.4 \times 10^{-3}$ mol dm^{-3}). Any guest molecules (2.5×10^{-5} mol dm^{-3}) exhibit only a weak absorption at 370 nm and the tautomer anion absorption at this wavelength becomes an almost constant at about [HTAC] = 5.0×10^{-3} mol dm^{-3}. This fact allows us to evaluate the concentration of tautomer anions formed in the HTAC micellar phase by the use of their molar absorption coefficients determined independently in aqueous micellar solutions containing TEA (Table 1). The results given in Table 1 reveal that the concentration is almost the same irrespective of the hydrophobicity of the substituent, suggesting that there are not much differences in the magnitude of electrostatic and hydrogen-bonding interactions at the micellar interface among the guest tautomer anions in the ground-state.

Table 1
Molar absorption coefficients (ε) and concentration of tautomer anions (TA) formed in the presence of HTAC micelle hosts at room temperature

Guests	ε at 370 nm (dm^3 mol^{-1} cm^{-1})[a]	[TA] (10^{-6} mol dm^{-3})
1a	15400	1.4
1b	16900	1.2
1c	17200	1.5
1d	17100	1.5
1e	17200	0.9
1f	19800	1.3
1g	21300	0.8
1h	20400	1.1

[a] [Guest] $= 1.0 \times 10^{-5}$ mol dm^{-3} [HTAC] $= 5.0 \times 10^{-3}$ mol dm^{-3} [TEA] $= 5.0–10.0 \times 10^{-4}$ mol dm^{-3}. No absorbance of TA at 370 nm was changed in this range of TEA concentration.

2.2. Micellar effects on the proton dissociation ability in the presence of TEA

In a previous study we showed that the protic solvent, methanol, containing TEA promotes the formation of the 7-hydroxycoumarin-derived tautomer ion pair even in the ground-state, through the strong hydrogen-bonding solvation of this ion pair [33]. Thus, an analysis of protic solvent and HTAC micellar effects on the equilibrium constant (K) for the formation of the tautomer ion pair in the ground-state is considered to provide information regarding hydrophilicity around the tautomer ion pair probe generated in the micelle cage. As typically shown in Fig. 1, the presence of TEA induced UV absorption spectral changes of **1a** accompanied by the appearance of isosbestic points and the 370 nm absorption, confirming the exclusive formation of the corresponding tautomer anion. The changes in the absorbance (ΔA at 370 nm) as a function of the TEA concentration ($[\mathrm{TEA}]_0 \gg [\mathbf{1}]_0$, where $[\mathrm{TEA}]_0$ and $[\mathbf{1}]_0$ refer to the initial concentrations of TEA and **1**, respectively) can be related to the K according to Eq. (1), which is frequently utilized as the Benesi–Hildebrand expression [36]; $\Delta\varepsilon$ is the difference in molar absorption coefficient between the tautomer anion and **1** at a given wavelength. Good linear relationships between ΔA^{-1} and $[\mathrm{TEA}]_0^{-1}$ are observed (Fig. 2) and the ratio of intercept to slope in these linear plots gives the equilibrium constant K (Table 2).

$$\frac{[1]_0}{\Delta A} = (\Delta\varepsilon K)^{-1}[\mathrm{TEA}]_0^{-1} + (\Delta\varepsilon)^{-1} \quad \textbf{(1)}$$

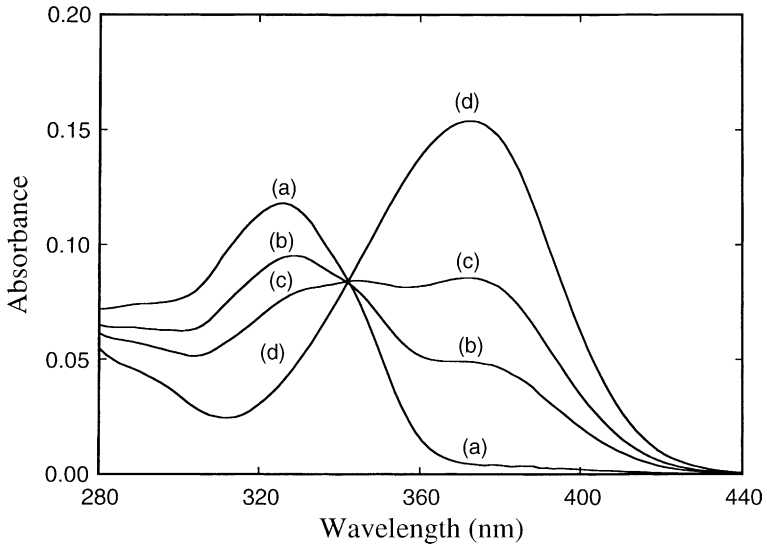


Fig. 1. UV absorption spectral changes caused by the reaction between **1a** (1.0×10^{-5} mol dm^{-3}) and TEA (curve a, [TEA] = 0; curve b, [TEA] = 3.0×10^{-5}; curve c, [TEA] = 4.0×10^{-5}; curve d, [TEA] = 4.0×10^{-4} mol dm^{-3}) in the presence of HTAC ([HTAC] = 1.0×10^{-2} mol dm^{-3}) at room temperature.

Analysis of substituent and solvent effects on the K value reveals that this value undergoes only a small electronic effect of the substituent in methanol and water whereas an alteration in solvent from methanol to water increases the K by about two orders of magnitude. The former finding indicates that a methylene group (attached at the 4-position) greatly suppresses the transmission of an electronic effect to the coumarin ring. This is well reflected in the negligible substituent effects on the pK_a values for our guests, determined from the pH dependence of their UV absorption spectra in 5 vol.% methanol–water containing 0.1 mol dm^{-3} potassium chloride (pH = 5.0–11.0, Table 2). The latter finding reveals greater hydrogen-bonding solvation and ionizing abilities of water, as compared to methanol. Interestingly, the presence of HTAC micelles ([HTAC] = 1.5×10^{-2} mol dm^{-3}) reduced the K value by a factor of ca. 3–8 but it exerts only a minor effect on the tautomerization reaction of 7-hydroxy-4-methylcoumarin (**1h**). Taking into consideration the electrostatic interaction of the cationic head group with TEA and the ester carbonyl in the coumarin ring, we are led to propose Scheme 1 in which the TEA-induced tautomerization of **1a**–**g** occurs near this head group producing the tautomer anion with the hydrophobic side chain directed toward the micellar interior. Recently, Aramendia and his co-workers reported that approximately 70% of TEA in aqueous solution distributes in the HTAC micellar phase at

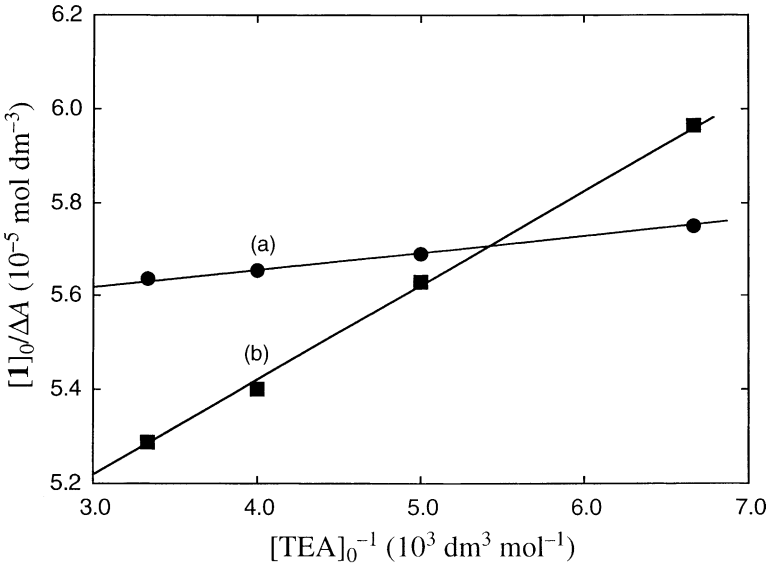


Fig. 2. Benesi–Hildebrand plots for the formation of **1a** (1.0×10^{-5} mol dm^{-3})-derived tautomer anion in 5 vol.% MeOH–H_2O containing TEA in the absence (a) and presence (b) of HTAC ([HTAC] = 1.0×10^{-2} mol dm^{-3}) at room temperature.

Table 2
Equilibrium constants (K) for the formation of tautomer anions derived from the reactions of guests **1** (1.0×10^{-5} mol dm^{-3}) with TEA in MeOH, 5 vol.% MeOH–H_2O and HTAC micelles at room temperature

Guests	K (10^4 dm^3 mol^{-1})			pK_a[c]
	MeOH	H_2O[a]	HTAC micelles[a,b]	
1a	0.071	10	2.0	9.5
1b	0.069	30	7.0	9.4
1c	0.090	10	2.0	9.5
1d	0.079	10	4.0	9.6
1e	0.080	40	6.0	9.7
1f	0.076	30	4.0	9.6
1g	0.12	40	7.0	9.4
1h	0.067	24	18	9.4

[a] Contains 5 vol.% MeOH.
[b] [HTAC] = 1.5×10^{-2} mol dm^{-3}.
[c] Determined in 5 vol.% MeOH–H_2O containing 0.1 mol dm^{-3} KCl.

Table 3
Protic solvent and micellar effects on the UV absorption maxima (λ_{max}) of tautomer anions obtained by the reactions of guests **1** (2.5×10^{-5} mol dm^{-3}) with DBU (2.0×10^{-2} mol dm^{-3}) at room temperature

Guests	λ_{max} (nm)					
	H_2O[a]	MeOH	EtOH	PrOH	BuOH	HTAC micelles[a,b]
1a	370	371	378	380	380	372
1b	370	371	378	380	380	372
1c	370	371	378	380	381	374
1d	371	370	378	380	380	372
1e	371	371	378	380	380	373
1f	371	371	378	380	380	373
1g	370	371	378	380	380	372
1h	360	364	371	373	374	374

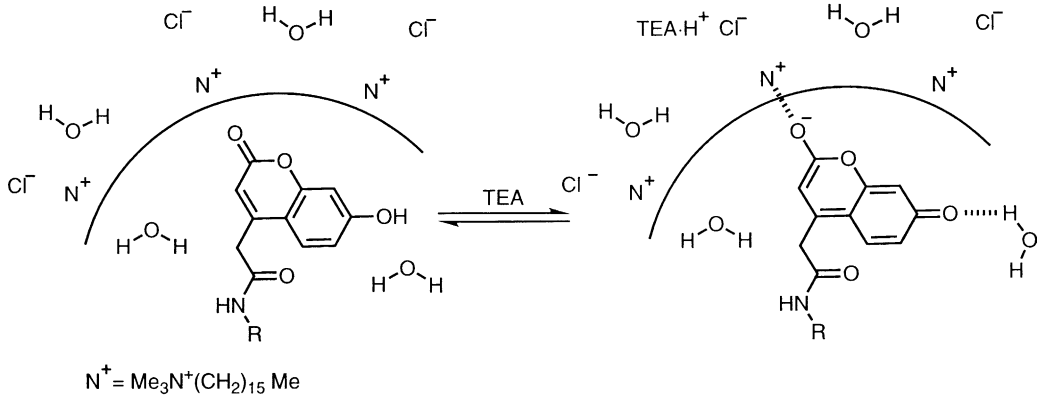
[a] Contains 5 vol.% MeOH.
[b] [HTAC] = 1.5×10^{-2} mol dm^{-3}.

room temperature [37]. In addition, the electrostatic interaction of the cationic head group with TEA decreases the effective concentration of this amine in the micelle cage. Thus, it is very likely that the drop in the TEA concentration in the micellar phase is the major reason for the decreased K values. The hydrogen-bonding solvation and ionizing abilities of water existing near the head group is considered to be comparable to those of bulk water. On the other hand, the finding of negligible micellar effects on the extent of tautomerization for **1h** forces us to propose that this guest exists at the micellar interface with the hydroxy group (at the 7-position) directed toward the aqueous phase. The methyl substituent at the 4-position may not have sufficient hydrophobicity to penetrate the coumarin ring into the micellar phase.

UV absorption spectral data of the tautomer anions, collected in Table 3, confirm that less hydrophilic protic solvents have a tendency to shift the absorption maximum to longer wavelengths, whereas its maximum wavelength in water and methanol is very close to each other except for **1h**. Thus, the appearance of the tautomer anion absorption in HTAC micelles at somewhat longer wavelengths (1–2 nm) substantiates the existence of a given tautomer anion in less hydrophilic environment. The electrostatic interaction between the cationic head groups and the tautomer anion may exclude water molecules (which solvate the head groups) to render the environment around the anion less hydrophilic [1,2]. Surprisingly, on changing the environment around the **1h**-derived tautomer anion from water to HTAC micelles, the first absorption band is red-shifted by 14 nm. This finding is consistent with the more decreased hydrophilicity of the solubilization site for the **1h**-derived tautomer anion, as compared to that for the other guest anions. Taking into account that the solubilizate having the hydrophobic coumarin ring is adsorbed on the micelle head groups, the pronounced red shift of the tautomer absorption may be interpreted in terms of the adsorption accompanied by the exclusion of more water molecules. The relative stability of the tautomer anions in bulk aqueous and micellar phases should remain almost constant through the electrostatic interaction between the cationic head groups and the tautomer anion in the latter phase.

2.3. Micellar effects on the fluorescence spectra and lifetimes

It has been found that water molecules are involved in the rate-limiting step for the tautomerization of 7-hydroxy-



Scheme 1.

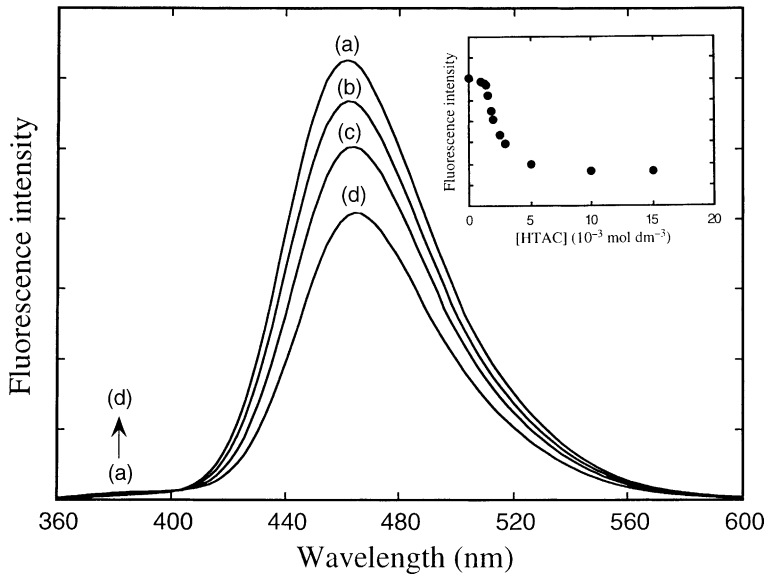


Fig. 3. HTAC micellar effects on the fluorescence spectrum of **1a** (2.5×10^{-5} mol dm^{-3}) in 5 vol.% MeOH–H_2O at room temperature. Excitation wavelength is 340 nm. [HTAC] = 0 (curve a), 1.8×10^{-3} (curve b), 3.0×10^{-3} (curve c) and 1.5×10^{-2} mol dm^{-3} (curve d). Inset: dependence of the fluorescence intensity of **1a** at 462 nm on the HTAC concentration.

coumarin derivatives in the excited singlet-state and then greatly accelerate this phototautomerization through the hydrogen-bonding solvation of both the starting hydroxycoumarins and their tautomer anions [38]. In the preceding section we demonstrated that 7-hydroxycoumarins having hydrophobic aryl (**1a–d**) and alkyl (**1e–g**) side chains are solubilized into the HTAC micellar phase. Since in the absence of TEA more than 94% hydroxycoumarin guests are present in undissociated forms within the micellar phase, we are allowed to expect that the location and orientation of these bichromophoric guest molecules in the micelle host are reflected in the dependence of their fluorescence intensities and lifetimes on the HTAC concentration.

As typically shown in Figs. 3 and 4, both the guests **1a** and **1c** having the methoxyphenyl and cyanophenyl substituents, respectively, exhibit only tautomer fluorescences of nearly equal intensity at 462 nm, when HTAC micelles are absent. Intriguingly, the fluorescence intensity of the tautomer anion derived from **1a** is lowered with a 4 nm red shift of this emission maximum as well as with a very slight increase in

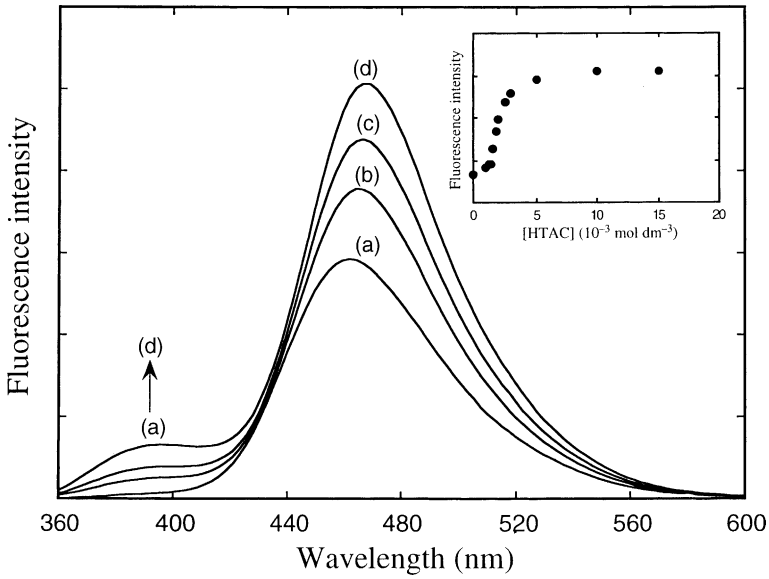
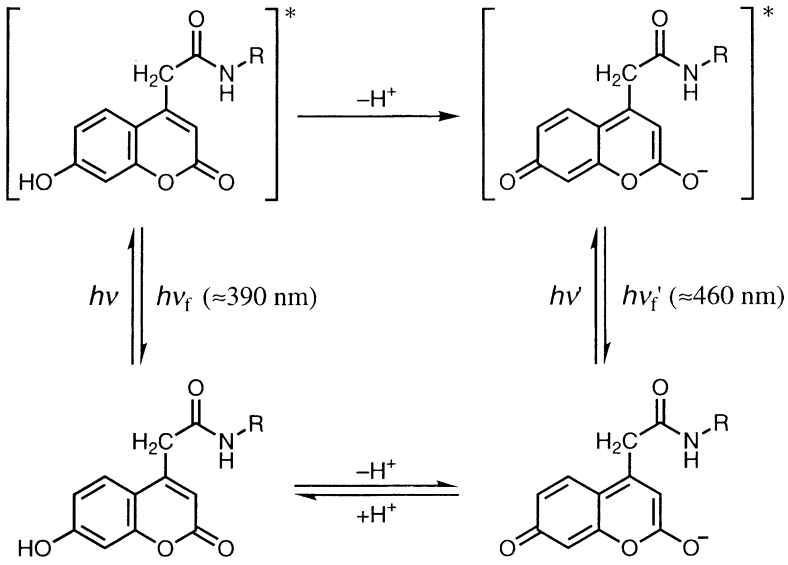


Fig. 4. HTAC micellar effects on the fluorescence spectrum of **1c** (2.5×10^{-5} mol dm^{-3}) in 5 vol.% MeOH–H_2O at room temperature. Excitation wavelength is 340 nm. [HTAC] = 0 (curve a), 1.8×10^{-3} (curve b), 2.5×10^{-3} (curve c) and 1.0×10^{-2} mol dm^{-3} (curve d). Inset: dependence of the fluorescence intensity of **1c** at 462 nm on the HTAC concentration.



Scheme 2.

emission intensity for the undissociated guest, on increasing the HTAC concentration (Fig. 3). In contrast, the increased concentration of the detergent results in an enhancement of both the **1c** and its tautomer emission intensities with a 6 nm red shift in the latter emission maximum (Fig. 4), being indicative of a large difference in the orientation of the coumarin and aromatic rings between **1a** and **1c**. The concentration dependence of emission intensity at 462–468 nm allowed us to estimate the CMC as 1.4×10^{-3} (**1a**) and 1.3×10^{-3} (**1c**) mol dm^{-3}, being consistent with the literature CMC value (insets of Figs. 3 and 4). The same values were obtained also for the other guest molecules. Because the tautomer anion cannot revert to the excited singlet-state undissociated form during its lifetime [33], we are led to propose Scheme 2 for the tautomerization reaction in the HTAC micelles. An analysis of Figs. 3 and 4 confirms that on increasing the HTAC concentration, the fluorescence intensity of the undissociated form has a tendency to enhance to much more extent, as compared to that of the tautomer anion form. This tendency suggests that the micellar phase near the head groups somewhat inhibits the tautomerization in the excited singlet-state.

The dependence of the fluorescence intensity of **1c** on the HTAC concentration is very similar to that of **1h** though the extent of the latter dependence is less pronounced (Fig. 5), allowing us to propose that the ester carbonyl group in **1c**

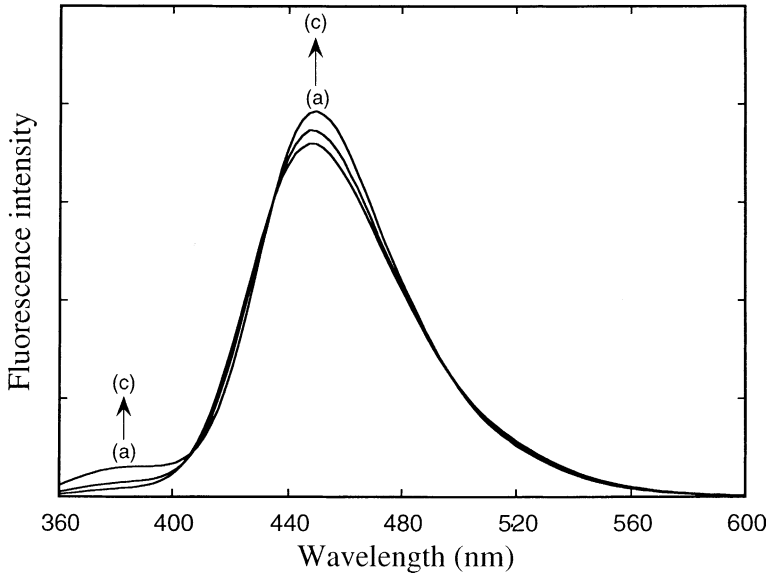
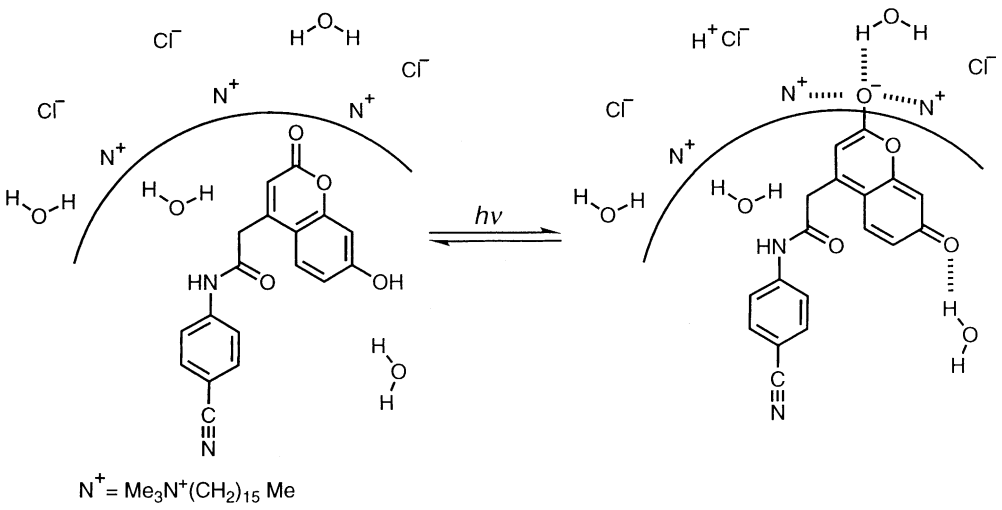


Fig. 5. HTAC micellar effects on the fluorescence spectrum of **1h** (2.5×10^{-5} mol dm^{-3}) in 5 vol.% MeOH–H_2O at room temperature. Excitation wavelength is 340 nm. [HTAC] = 0 (curve a), 5.0×10^{-3} (curve b) and 1.5×10^{-2} mol dm^{-3} (curve c).



Scheme 3.

is buried into the cationic head groups with the hydrophobic cyanophenyl moiety directed toward the micellar interior (Scheme 3). Thus, a certain amount of water molecules (by which the head group is solvated) are excluded to render the environment around the guest less hydrophilic. Because the fluorescence intensity of **1c** (2.5×10^{-5} mol dm^{-3}) at 390 nm is increased in the order of 5 vol.% MeOH–H_2O ($\lambda_{ex} = 340$ nm; relative intensity $\ll 1.00$) $\ll$ MeOH (1.00) $<$ EtOH (1.01) $<$ PrOH (1.21) $<$ BuOH (1.21), the decreased hydrophilicity results in an enhancement of the fluorescence intensity of the undissociated guest molecule, as observed. The fact that the emission intensity of the **1c**-derived tautomer anion increases with an increase in the HTAC concentration implies that a strong electrostatic interaction between the cationic head groups and the tautomer anion in relatively hydrophobic environment is responsible for the acceleration of the tautomer anion emission (Scheme 3). The emission behavior of the guests **1e–g** in the presence of the HTAC micelle host is similar to that of **1c** though the extent of an increase in emission intensity is smaller than that for the latter, thus confirming that the ester carbonyl oxygen in the former guest molecules is less deeply buried into the cationic head groups with the hydrophobic butyl, octyl and hydroxyethyl side chains directed toward the micellar interior. Large dipole moments of the cyano phenyl (4.18 D in the ground-state [39]) and 7-hydroxycoumarin (4.94 D in the ground-state and 7.99 D in the excited singlet-state [40]) moieties might strengthen the electrostatic interaction described above.

The fluorescence intensity of tautomer anion [generated quantitatively from **1a** (2.5×10^{-5} mol dm^{-3}) containing DBU (2.0×10^{-2} mol dm^{-3})] is lowered as the

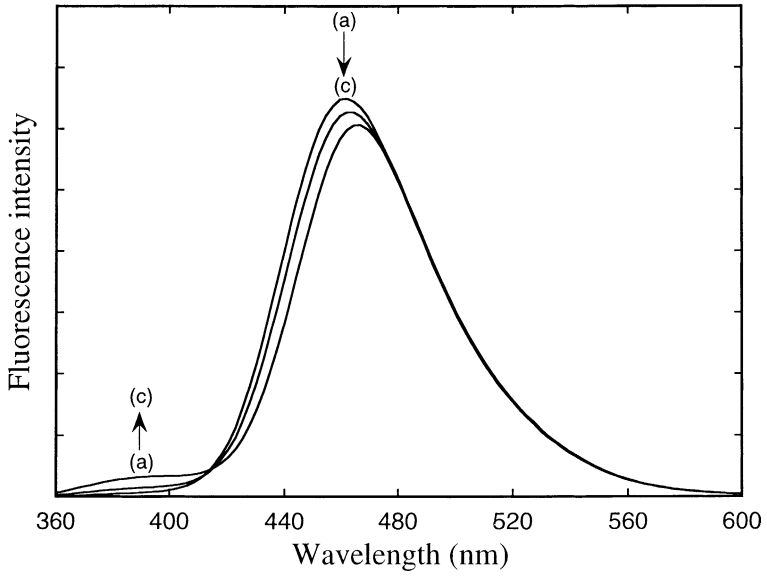


Fig. 6. HTAC micellar effects on the fluorescence spectrum of **1b** (2.5×10^{-5} mol dm^{-3}) in 5 vol.% MeOH–H_2O at room temperature. Excitation wavelength is 340 nm. [HTAC] = 0 (curve a), 2.0×10^{-3} (curve b) and 1.5×10^{-2} mol dm^{-3} (curve c).

hydrophilicity of protic solvents examined is decreased: 5 vol.% MeOH–H_2O (excitation wavelength = 340 nm; relative intensity at 454 nm = 1.00; emission maximum wavelength = 454 nm) > MeOH (0.80; 460 nm) > EtOH (0.69; 461 nm) > PrOH (0.65; 461 nm) > BuOH (0.62; 461 nm). This finding is consistent with the existence of the **1a**-derived tautomer anion in less hydrophilic environment, as already proposed. Since the methoxyphenyl group has strong electron-donating ability, an electrostatic repulsion between the methoxyphenyl and hydroxycoumarin anion moieties in the excited state is very likely to strengthen the interaction of these two moieties with the cationic head groups. For this interaction the hydrophilicity around the **1a**-derived tautomer anion is decreased to more extent to lower the fluorescence intensity of the tautomer anion, as observed. In Fig. 6 is typically shown micellar effects on the fluorescence behavior of **1b** bearing the phenyl substituent. The presence of HTAC micelles resulted in a gradual increase of the 390 nm emission accompanying a similar degree of decrease in the tautomer emission. Almost the same emission behavior was observed for **1d** in the presence of the micelles. From a comparison of the emission behavior for **1b** with that for **1a** and **1c**, we see that the former guest exhibits a behavior characteristic of both the latter guests. Therefore, we are led to conclude that the aromatic ring of **1b** and **1d** in the excited singlet-state is distributed in the micellar phase with this ring directed toward both the head group and the hydrocarbon core.

The previous study showed that the β-cyclodextrin cavity with a less hydrophilic environment lengthens the fluorescence lifetime of the **1h**-derived tautomer anion by 0.6–0.9 ns [41], thus allowing us to predict longer emission lifetimes of our guest-derived tautomer anions generated in the micellar phase than in the aqueous one. In Table 4 are collected the fluorescence lifetimes of the tautomer anions, determined in the absence and presence of HTAC micelles. When the guest molecules are solubilized into the HTAC micelle host, the environment near the micellar interface makes the fluorescence lifetimes of tautomer anions (except for the **1c**-derived tautomer) longer by 0.3–0.8 ns. This finding is consistent with our prediction and, hence, provide additional evidence for the existence of the excited singlet-state guests, **1a**, **1b** and **1d**–**h**, in less hydrophilic environment, although the lifetime is not very sensitive to both the location and orientation of a given guest tautomer anion in the micelles. Interestingly, the fluorescence lifetime of the **1c**-derived tautomer anion generated in water is shorter by ca. 3 ns, as compared to that of the other tautomers. Taking into account the strong electron-withdrawing ability of the cyano group,

Table 4
HTAC micellar effects on the fluorescence lifetimes (τ) of tautomer anions of guests **1** (1.0×10^{-5} mol dm^{-3}), formed in the excited singlet-state at room temperature

Guests	τ (ns)	
	5 vol.% MeOH–H_2O	HTAC micelles[a,b]
1a	5.4	6.2
1b	5.9	6.4
1c	2.7	5.8
1d	5.8	6.3
1e	6.0	6.3
1f	6.0	6.3
1g	5.6	5.9
1h	5.2	5.5

[a] [HTAC] = 1.5×10^{-2} mol dm^{-3}.
[b] Contains 5 vol.% MeOH.

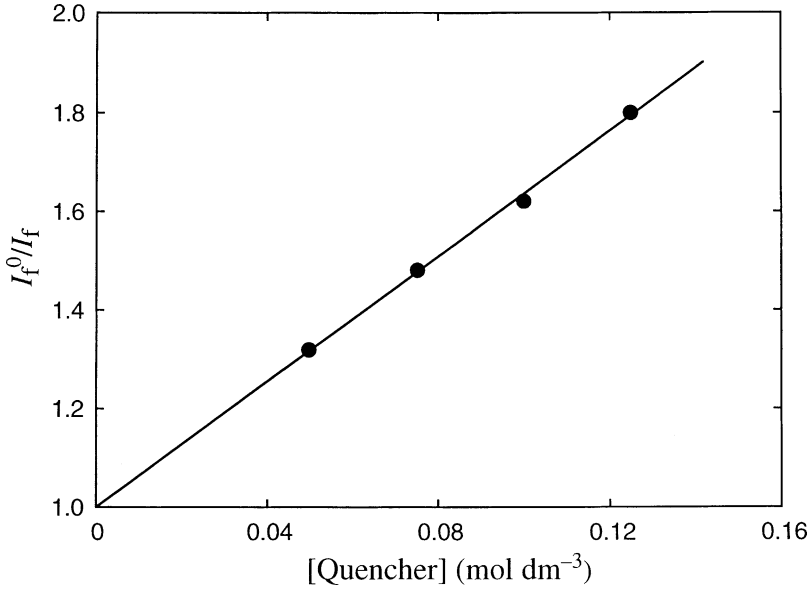


Fig. 7. Stern–Volmer plot for the fluorescence quenching of **1h**-derived tautomer anion by *p*-cyanoacetanilide (quencher) in 75 vol.% MeOH–H_2O containing TEA (2.0×10^{-2} mol dm^{-3}) at room temperature. Excitation wavelength is 340 nm. [***1***h] = 2.5×10^{-4} mol dm^{-3}. I_f and I_f^0 refer to the fluorescence intensities of the tautomer anion with and without the quencher.

it is reasonable to interpret this shortened lifetime in terms of the contribution of an intramolecular charge transfer-type emission quenching process. This interpretation is substantiated by the occurrence of intermolecular quenching of the **1h**-derived tautomer fluorescence by *p*-cyanoacetanilide (quenching constant = 6.3 $dm^3\,mol^{-1}$; rate constant for the emission quenching = $1.2 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$), as shown in Fig. 7. Since there is not so much difference in emission lifetime among the tautomer anions generated in the micelle host, the conformation of **1c**-derived tautomer anion (given in Scheme 3) are considered to greatly suppress the above-mentioned emission quenching process.

3. Experimental details

3.1. Measurements

Ultraviolet (UV) absorption and fluorescence spectra were recorded on a Hitachi Model UV-3300 spectrophotometer and a Hitachi Model F-4500 spectrofluorimeter, respectively. Fluorescence lifetimes were measured under N_2 at room temperature with a time-correlated single-photon counting apparatus (Horiba NAES-700; excitation wavelength = 340 nm; cut-off wavelength = 380 nm), which was equipped with a flash lamp filled with dihydrogen. Analysis of the fluorescence decay curves was accomplished according to the previously described procedure [41,42]. Typically, 1×10^4 counts were sampled in the peak channel. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL Model JNM-A500 spectrometer. Chemical shifts (in ppm) were determined using tetramethylsilane as an internal standard. Infrared (IR) spectra were taken with a Hitachi Model 270-30 infrared spectrometer. Elemental analyses were performed on a Perkin-Elmer PE2400 series II CHNS/O analyzer.

The micellar solution prepared was allowed to stand for at least 1 h at room temperature (24 ± 2 °C). For estimating the pK_a values of 7-hydroxycoumarin guests **1a**–**h** (1.0×10^{-5} mol dm^{-3}), the pH of a given solution was adjusted by adding a 0.1 mol dm^{-3} HCl or a 0.1 mol dm^{-3} KOH solution to water containing 0.1 mol dm^{-3} KCl. As a co-solvent, 5 vol.% methanol was employed in order to exactly hold the guest concentration constant.

3.2. Materials and solvents

TEA and DBU were fractionally distilled from sodium hydroxide at atmospheric and reduced pressures, respectively. Water was purified by distillation, followed by passage through a Millipore Milli-Q system. The pH of water was adjusted to 5.0 by adding 0.1 mol dm^{-3} HCl solution. Methanol was purified according to the standard method [43]. Ethanol, propanol and butanol were of spectroscopic grade and used without further purification. Commercially available HTAC and 7-hydroxy-4-methylcoumarin (**1h**) were purified by repeated recrystallization from methanol–acetone and ethanol, respectively. All other chemicals used were obtained from commercial sources and were of the highest grade available.

N-Substituted (7-hydroxycoumarin-4-yl)acetamide derivatives (**1a**–**g**) were prepared according to the following procedure. 1-Ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (13.1 g, 68.3 mmol) was slowly added to a DMF solution (50 ml) containing (7-hydroxycoumarin-4-yl) acetic acid (5.0 g, 22.7 mmol), *N*-hydroxysuccinimide (2.65 g, 23 mmol) and alkyl or aryl amine (27.4 mmol) with stirring at 0 °C. After 2 h, the reaction mixture was warmed to room temperature and then stirring was continued for additional 3 h. After the mixture was poured into water (500 ml), the pH of the solution was adjusted to 4–5 by using a 1 mol dm^{-3} HCl solution. The solid separated out was filtered with suction and washed repeatedly with water. The crude product was recrystallized three times from ethanol or ethanol–hexane. Physical and spectroscopic properties of **1a**–**g** are as follows.

3.2.1. *N-(4-Methoxyphenyl)-2-(7-hydroxycoumarin-4-yl)acetamide (**1a**)*

mp 237.0–238.0 °C. IR (KBr) ν: 3214, 3140, 1701, 1605, 1272 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 3.70 (3H, s), 3.84 (2H, s), 6.22 (1H, s), 6.72 (1H, d, J = 2.4 Hz), 6.80 (1H, dd, J = 2.4, 8.6 Hz), 6.87 (2H, d, J = 9.2 Hz), 7.46 (2H, d, J = 9.2 Hz), 7.65 (1H, d, J = 8.6 Hz), 10.14 (1H, s), 10.58 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 39.5, 55.2, 102.4, 111.6, 111.9, 113.0, 113.9 (2C), 120.9 (2C), 126.8, 131.9, 151.1, 155.1, 155.5, 160.3, 161.2, 166.1. Analysis: calculated for $C_{18}H_{15}NO_5$: C, 66.46%; H, 4.65%; N, 4.31%; found: C, 66.16%; H, 4.79%; N, 4.62%.

3.2.2. *N-Phenyl-2-(7-hydroxycoumarin-4-yl)acetamide (**1b**)*

mp 230.0–230.5 °C. IR (KBr) ν: 3280, 3140, 1707, 1608, 1269 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 3.90 (2H, s), 6.25 (1H, s), 6.74 (1H, d, J = 2.4 Hz), 6.82 (1H, dd, J = 2.4, 8.6 Hz), 7.07 (1H, dd, J = 7.3, 7.3 Hz), 7.31 (2H, dd, J = 7.3, 7.9 Hz), 7.58 (2H, d, J = 7.9 Hz), 7.66 (1H, d, J = 8.6 Hz), 10.30 (1H, s), 10.58 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 39.6, 102.3, 111.5, 111.9, 113.0, 119.2 (2C), 123.6, 126.7, 128.8 (2C), 138.8, 150.9, 155.0, 160.2, 161.2, 166.6. Analysis: calculated for $C_{17}H_{13}NO_4$: C, 69.15%; H, 4.44%; N, 4.74%; found: C, 69.23%; H, 4.15%; N, 4.88%.

3.2.3. *N-(4-Cyanophenyl)-2-(7-hydroxycoumarin-4-yl)acetamide (**1c**)*

mp 280.0–281.0 °C. IR (KBr) ν: 3264, 3116, 2220, 1696, 1600, 1230 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 3.97 (2H, s), 6.26 (1H, s), 6.75 (1H, d, J = 2.4 Hz), 6.82 (1H, dd, J = 2.4, 8.9 Hz), 7.63 (1H, d, J = 8.9 Hz), 7.77 (2H, d, J = 11.3 Hz), 7.79 (2H, d, J = 11.3 Hz), 10.61 (1H, s), 10.76 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 39.6, 102.4, 105.4, 111.5, 112.1, 113.1, 119.0, 119.3 (2C), 126.7, 133.3 (2C), 143.0,

150.4, 155.0, 160.2, 161.2, 167.5. Analysis: calculated for $C_{18}H_{12}N_2O_4$: C, 67.50%; H, 3.78%; N, 8.75%; found: C, 67.52%; H, 3.73%; N, 9.01%.

3.2.4. N-(1-Naphthyl)-2-(7-hydroxycoumarin-4-yl)acetamide (**1d**)

mp 240.0–241.0 °C. IR (KBr) ν: 3256, 3080, 1713, 1620, 1209 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ: 4.07 (2H, s), 6.32 (1H, s), 6.75 (1H, d, $J = 1.8$ Hz), 6.85 (1H, dd, $J = 1.8$, 8.5 Hz), 7.48 (1H, dd, $J = 7.9$, 7.9 Hz), 7.52–7.56 (2H, m), 7.64 (1H, d, $J = 7.9$ Hz), 7.77 (1H, d, $J = 7.9$ Hz), 7.78 (1H, d, $J = 8.5$ Hz), 7.92–7.94 (1H, m), 8.04–8.06 (1H, m), 10.27 (1H, s), 10.64 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 39.2, 102.4, 111.6, 112.1, 113.1, 122.0, 122.6, 125.6, 125.7, 126.0, 126.2, 126.8, 127.8, 128.3, 133.1, 133.8, 151.2, 155.1, 160.4, 161.3, 167.6. Analysis: calculated for $C_{21}H_{15}NO_4$: C, 73.04%; H, 4.38%; N, 4.06%; found: C, 72.74%; H, 4.10%; N, 4.39%.

3.2.5. N-Butyl-2-(7-hydroxycoumarin-4-yl)acetamide (**1e**)

mp 188.0–189.0 °C. IR (KBr) ν: 3310, 1713, 1623, 1269 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ: 0.86 (3H, t, $J = 7.3$ Hz), 1.26 (2H, tq, $J = 7.3$, 7.3 Hz), 1.38 (2H, tt, $J = 7.3$, 7.3 Hz), 3.06 (2H, dt, $J = 5.5$, 7.3 Hz), 3.62 (2H, s), 6.15 (1H, s), 6.72 (1H, d, $J = 2.4$ Hz), 6.79 (1H, dd, $J = 2.4$, 8.5 Hz), 7.60 (1H, d, $J = 8.5$ Hz), 8.15 (1H, t, $J = 5.5$ Hz), 10.56 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 13.6, 19.5, 31.1, 38.4, 39.2, 102.3, 111.5, 111.6, 112.8, 126.7, 151.3, 155.0, 160.3, 161.1, 167.4. Analysis: calculated for $C_{15}H_{17}NO_4$: C, 65.44%; H, 6.22%; N, 5.09%; found: C, 65.67%; H, 6.06%; N, 4.86%.

3.2.6. N-Octyl-2-(7-hydroxycoumarin-4-yl)acetamide (**1f**)

mp 157.0–158.0 °C. IR (KBr) ν: 3292, 1710, 1620, 1269 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ: 0.85 (3H, t, $J = 7.3$ Hz), 1.21–1.26 (10H, m), 1.38 (2H, m), 3.05 (2H, dt, $J = 5.5$, 7.3 Hz), 3.62 (2H, s), 6.16 (1H, s), 6.72 (1H, d, $J = 2.4$ Hz), 6.78 (1H, dd, $J = 2.4$, 9.2 Hz), 7.61 (1H, d, $J = 9.2$ Hz), 8.15 (1H, t, $J = 5.5$ Hz), 10.58 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 13.9, 22.1, 26.3, 28.7 (2C), 28.9, 31.2, 38.7, 39.0, 102.3, 111.5, 111.7, 112.8, 126.7, 151.3, 155.0, 160.3, 161.2, 167.4. Analysis: calculated for $C_{19}H_{25}NO_4$: C, 68.86%; H, 7.60%; N, 4.23%; found: C, 68.95%; H, 7.50%; N, 3.99%.

3.2.7. N-(2-Hydroxyethyl)-2-(7-hydroxycoumarin-4-yl)acetamide (**1g**)

mp 238.0–239.0 °C. IR (KBr) ν: 3312, 3100, 1690, 1624, 1210 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6) δ: 3.14 (2H, dt, $J = 5.5$, 6.1 Hz), 3.41 (2H, dt, $J = 5.5$, 6.1 Hz), 3.65 (2H, s), 4.72 (1H, t, $J = 5.5$ Hz), 6.17 (1H, s), 6.72 (1H, d, $J = 2.4$ Hz), 6.79 (1H, dd, $J = 2.4$, 9.2 Hz), 7.62 (1H, d, $J = 9.2$ Hz), 8.25 (1H, t, $J = 5.5$ Hz), 10.55 (1H, s). ^{13}C NMR (DMSO-d_6) δ: 38.8, 41.8, 59.7, 102.3, 111.5, 111.7, 112.9, 126.8, 151.4, 155.0, 160.3, 161.1, 167.8. Analysis: calculated for $C_{13}H_{13}NO_5$: C, 59.31%; H, 4.98%; N, 5.32%; found: C, 59.01%; H, 5.13%; N, 5.08%.

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