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Complexation and proton dissociation behavior of 7-hydroxy-4-methylcoumarin and related compounds in the presence of β-cyclodextrin

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Abstract

The pH effects on the 1:1 complexation behavior of β-cyclodextrin (β-CDx) with the title compounds have been investigated by measuring ultraviolet (UV) absorption, circular dichroism (CD), fluorescence and ^{1}H nuclear magnetic resonance (NMR) spectra and fluorescence lifetimes of the β-CDx inclusion complexes formed. Steric effects of substituent attached at the four position of a guest molecule on the stability of the inclusion complex as well as on the induced CD spectral intensity demonstrated that the guest is included into the β-CDx cavity so as to locate this substituent around the rim of the cavity at low and even at high pH (where a tautomer anion is exclusively produced). The ^{1}H NMR data were consistent with the intracavity immersion of a given guest molecule from the secondary hydroxy group side and, additionally, substantiated the structure of the β-CDx inclusion complex generated at low pH. Through an analysis of the pH-dependent UV absorption and fluorescence spectra of 7-hydroxycoumarine derivatives, it was found that the proton dissociation abilities of these guests undergo negligible effects of the β-CDx inclusion in both the ground-state and the excited singlet-state. This finding strongly suggested that both the quinoid-type carbonyl and oxido groups in the tautomer anion guest are exposed to the bulk aqueous phase to interact with the surrounding water molecules.

Keywords: 7-Hydroxycoumarin derivatives; β-Cyclodextrin; Proton dissociation; Substituent effects; pH effects

1. Introduction

β-Cyclodextrin (β-CDx) is a water-soluble oligosaccharide composed of seven D-(+)-glucopyranose units having inner-cavity diameters of 6.0 (top) and 6.5 Å (bottom) and a depth of 7.9 Å [1]. The hydrophobic internal cavity of β-CDx has an excellent ability to incorporate hydrophobic aromatic molecules in aqueous solution, provided that the sizes of the host's internal cavity and the entering guest molecule are suitable for complexation. This ability has made it possible to utilize β-CDx (in addition to α-CDx and γ-CDx) for many applications [1–3]. The great difference between "in-cavity" and "out-of-cavity" environments may be responsible for the alteration in the physical and spectroscopic properties of guest molecules included into the host cavity.

On the other hand, the complicated pH-dependent fluorescence behavior of 7-hydroxycoumarin (7HC) and its derivatives has attracted considerable attention from spectroscopic point of view, and many efforts have been devoted to unraveling the structure of the excited singlet-state species that are responsible for the multiple fluorescence [4–15]. In a previous study, we analyzed the effects of added tertiary amines on the spectroscopic behavior of 7HC and 7-hydroxy-4-methylcoumarin (7H4MC) 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 [16]. It was also found that depending on both the solvent property and the amine basicity, 7HC exists in the form of a hydrogen-bonded complex, a 7HC anion, or in the form of a tautomer anion. Thus, we may expect that the CDx cavity of hydrophobic environment affects the proton dissociation ability of 7HC and its derivatives as well as the structure adopted by these guests under acidic and basic conditions.

Since, the discovery of the ground-state 7HC tautomer ion pair by us could shed a new light on the mechanism of proton transfer of the hydroxycoumarine derivatives in the ground and excited singlet-states, it is of great value to

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investigate the complexation behavior of these derivatives with CDx. For this purpose we chose 7H4MC, potassium (7-hydroxycoumarin-4-yl)acetate (7HC4AK), 7-HC and 7-methoxy-4-methylcoumarin (7M4MC) as guests and β-CDx as a host, and analyzed spectroscopic behavior of these guest molecules in the presence and absence of β-CDx.

2. Experimental details

2.1. Measurements

Ultraviolet (UV) absorption and fluorescence spectra were recorded on a Shimadzu UV-2200 spectrophotometer and a Hitachi F-4500 spectrofluorimeter, respectively. As excitation wavelengths for recording fluorescence spectra and decay curves, we chose, in most cases, isosbestic points obtained from the UV absorption spectral changes for each guest molecule. Infrared (IR) and nuclear magnetic resonance (NMR) spectra were taken with a Hitachi 270-30 infrared spectrometer and a JEOL JNM-A500 spectrometer, respectively. Chemical shifts of NMR signals were determined using 3-trimethylsilyl[2,2,3,3-$^2H_4$]propionate as an external standard or tetramethylsilane as an internal standard. Induced circular dichroism (ICD) spectra were recorded on a JASCO J-600 spectrodichrometer. Fluorescence lifetimes were measured under nitrogen with a time-correlated single photon counting apparatus (Horiba NAES-700; cut-off wavelength = 420 nm).

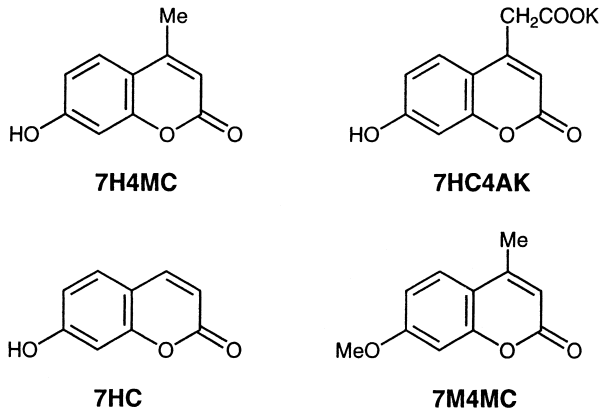
The pH of a solution was adjusted by adding 0.1 mol dm^{-3} HCl or 0.1 mol dm^{-3} KOH to the solution containing 0.1 mol dm^{-3} KCl. As a cosolvent, 2% methanol by volume was used in order to exactly hold the guest concentration constant. Before spectroscopic measurements, the solution was allowed to stand for at least 1 h at room temperature (24 ± 1°C).

2.2. Materials and solvents

7HC4AK was prepared in 56% yield by treatment of (7-hydroxycoumarin-4-yl)acetic acid (1.57 g, 71 mmol; Aldrich) with KOH (0.43 g, 78 mmol) in methanol (5 ml). A precipitate formed was collected and washed with a small amount of cold methanol. IR (KBr) ν: 3394, 1704, 1548, 1143 cm^{-1}. ^{1}H NMR (DMSO-d$_6$) δ: 3.17 (2H, s), 5.64 (1H, s), 6.14 (1H, d, J = 2.1 Hz), 6.35 (1H, dd, J = 2.1, 8.9 Hz), 7.27 (1H, d, J = 8.9 Hz).

7-HC, 7H4MC and 7M4MC (Aldrich) were purified by repeated recrystallization from ethanol. β-CDx (Aldrich) was used without further purification. All other chemicals employed were obtained from commercial sources and were of the highest grade available.

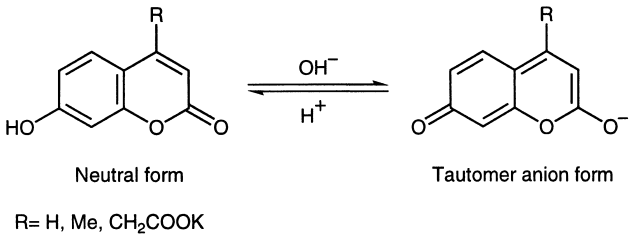
Water was purified by distillation, followed by passage through a Millipore Milli-Q system. Methanol was purified according to the standard method [17].



3. Results and discussion

3.1. UV absorption and ICD spectra

As already described in the introduction, it is expected that 7-hydroxycoumarin derivatives employed in this study form tautomer ion pairs exclusively, (which show their UV absorption around 370 nm), upon proton dissociation in water of an excellent hydrogen-bonding solvation ability (Scheme 1). From the pH dependence of the UV absorption spectrum of 7H4MC typically shown in Fig. 1, we see that on increasing pH there appears the 360 nm absorption band which is characteristic of a tautomer anion, and that the pH titration curve allows us to estimate the pK_a value of 7H4MC as 9.4 (inset of Fig. 1). In addition, essentially the same titration curve was obtained even in the presence of β-CDx (inset of Fig. 1), strongly suggesting that the inclusion of 7H4MC into the host cavity affects the proton dissociation ability of this guest to a negligible extent. 7HC4AK and 7HC also exhibited the same pH-dependent UV spectral changes with and without β-CDx and gave the same pK_a value (9.4 ± 0.1) within experimental error. Since, the ring-opening reaction of the coumarin skeleton at pH 2.0 and 10.5 takes place, if any, to only a very small extent during measurement, it is possible to estimate stoichiometric ratio and equilibrium constant for the formation of the β-CDx inclusion complexes with the guests existing in the neutral (pH 2.0) or predominantly the tautomer ion pair (pH 10.5) form.



Scheme 1.

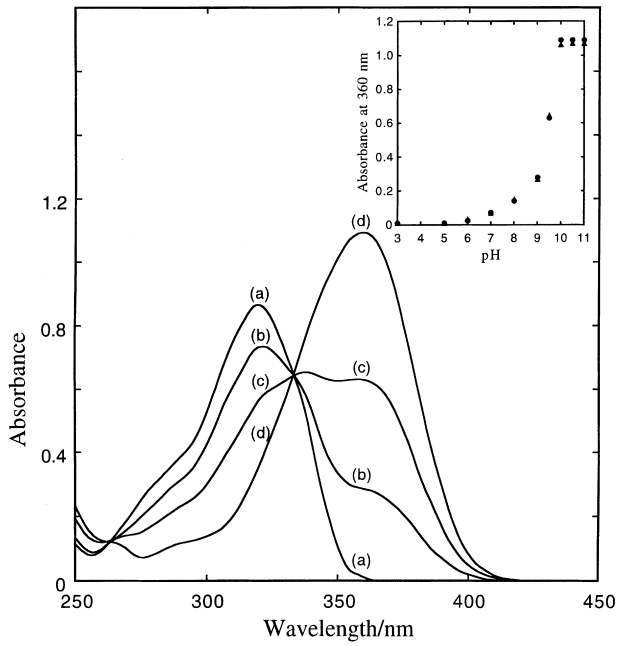


Fig. 1. pH dependence of the UV absorption spectrum of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing KCl (0.1 mol dm^{-3}) at 24 ± 1°C. pH: (a) 5.0; (b) 9.0; (c) 9.5; (d) 10.5. Inset: spectrophotometric titration curves for 7H4MC in the absence (●) and presence (▲) of β-CDx (1.0×10^{-2} mol dm^{-3}).

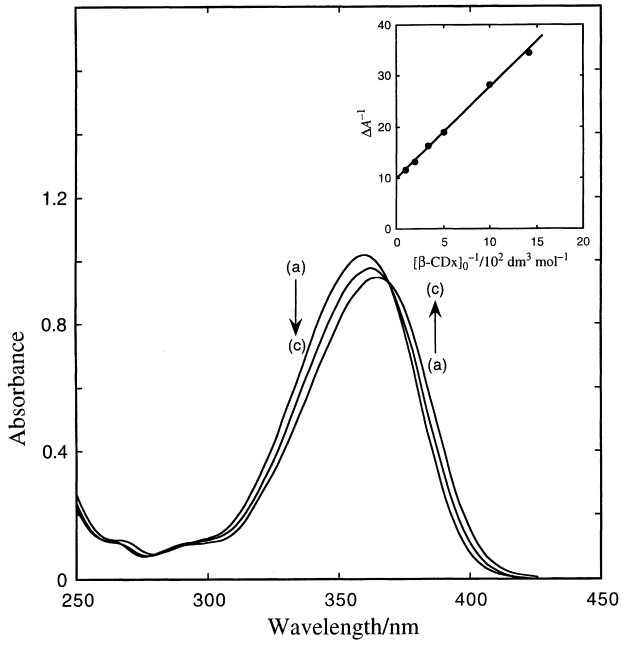


Fig. 3. UV absorption spectral changes of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing β-CDx and KCl (0.1 mol dm^{-3}) at 24 ± 1°C, pH 10.5. $[\beta\text{-CDx}]_0$ (mol dm^{-3}): (a) 0; (b) 2.0×10^{-3}; (c) 1.0×10^{-2}. Inset: Benesi–Hildebrand plot of ΔA^{-1} vs. $[\beta\text{-CDx}]_0^{-1}$ for the β-CDx complexation with 7H4MC at pH 10.5.

In Figs. 2 and 3, are typically shown UV absorption spectra of 7H4MC in the presence and absence of β-CDx at pH 2.0 and 10.5, respectively, along with the Benesi–Hildebrand plots (insets of Figs. 2 and 3) obtained at each pH value. With a progressive increase in the β-CDx concentration ($0.050–1.0 \times 10^{-2}$ mol dm^{-3}) at pH 2.0, the first absorption band at 320 nm is very slightly red-sifted (about 0.5 nm) with a decrease in its intensity, accompanied by an isosbestic point at 268 nm. At pH 10.5 a more remarkable spectral change of the 360 nm band originating from a tautomer anion was observed with an isosbestic point at 368 nm. In addition, a good linear relationship was obtained between the reciprocal of the changes in absorbance at a given wavelength (ΔA^{-1}) and the reciprocal of the initial concentration of β-CDx ($[\beta\text{-CDx}]_0^{-1}$). These observations indicate the formation of a 1:1 inclusion complex of β-CDx with both the host molecules, which must be in less hydrophilic environment [16,18]. Because similar UV absorption spectral changes and linear plots were observed in the presence of the β-CDx host for any guests examined, equilibrium constants (K) for the formation of the inclusion complexes were determined from the ratio of intercept to slope in the linear Benesi–Hildebrand plots and are collected in Table 1.

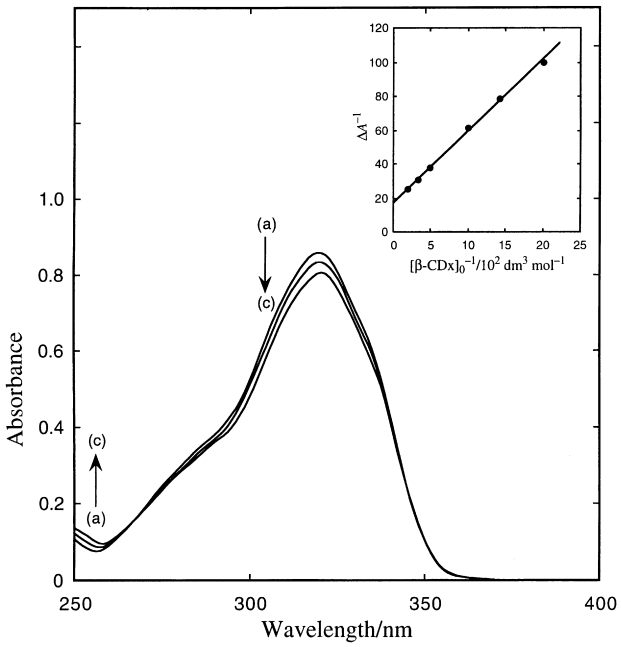


Fig. 2. UV absorption spectral changes of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing β-CDx and KCl (0.1 mol dm^{-3}) at 24 ± 1°C, pH 2.0. $[\beta\text{-CDx}]_0$ (mol dm^{-3}): (a) 0; (b) 2.0×10^{-3}; (c) 1.0×10^{-2}. Inset: Benesi–Hildebrand plot of ΔA^{-1} vs. $[\beta\text{-CDx}]_0^{-1}$ for the β-CDx complexation with 7H4MC at pH 2.0.

An inspection of Table 1 reveals that the introduction of a methyl group at the four position of the coumarin ring decreases the K value for the β-CDx–7HC complex (pH 2.0) to some extent while the CH_2COOH substituent lowers this K value by a factor of about 8. Interestingly, the stability of the β-CDx complex with 7HC anion undergoes a negligibly small methyl-substituent effect and even the CH_2COO^- group is only able to decrease the K value for this complex by a factor of 2.6. In addition, the neutral

Table 1
Equilibrium constants (K) for the association of β-CDx with 7HC, 7H4MC, 7M4MC and 7HC4AK, obtained by UV spectroscopic method at $24 \pm 1°C$[a]

Guest	K ($dm^3\,mol^{-1}$)	
	pH 2.0	pH 10.5
7HC	500	320
7H4MC	440	330
7M4MC	450	–
7HC4AK	65	120

[a] K is an average of more than three determinations.

form of 7HC and 7H4MC gives a more stable β-CDx inclusion complex, as compared to the corresponding tautomer anion form, whereas the reverse is found for the complexation with 7HC4AK. X-ray crystallographic analysis of the β-CDx–7H4MC inclusion complex has demonstrated that the 7-hydroxy group of this guest is preferentially included into the host cavity and extends to the primary hydroxy group ends of this host enabling hydrogen-bonding interactions with the neighboring water molecules [19]. In addition, taking into account that the CH_2COOH moiety in the 7HC4AK guest is very unlikely to be included into the cavity, we are led to propose the β-CDx–7H4MC complex having the 7-hydroxy group that is exposed to the bulk aqueous phase, as shown in Fig. 4. It is, thus, reasonable to interpret the decrease in the K value at pH 2.0 for 7H4MC and 7HC4AK in terms of the steric hindrance of methyl and CH_2COOH groups for the complexation with β-CDx, respectively. The very small difference in this K value between 7H4MC and 7M4MC is consistent with our interpretation described above.

On the other hand, the tautomer anion formed at high pH possesses a negative charge on the ester carbonyl oxygen of 7HC and its derivatives, so that we expect the preferential immersion of the cyclohexadienone moiety of the tautomer into the β-CDx cavity. Table 1 shows that the stability of the β-CDx–7HC complex at high pH is subject to the negligible steric effect of the methyl group and also to the much

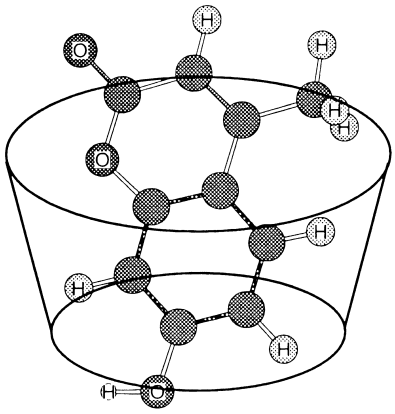


Fig. 4. Structure of the inclusion complex proposed for the β-CDx–7H4MC system at pH 2.0.

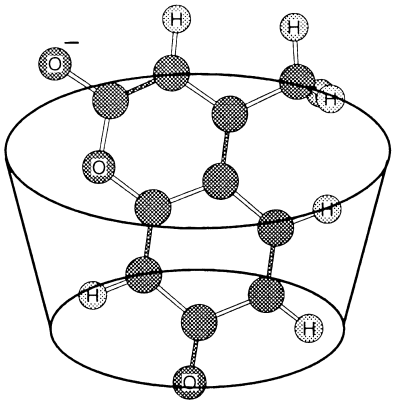


Fig. 5. Structure of the inclusion complex proposed for the β-CDx–7H4MC system at pH 10.5.

smaller steric hindrance of the CH_2COO^- group, compared with the CH_2COOH. These findings confirm that on tautomerization, the guest molecule adopts a conformation that weakens steric repulsion between the substituent and the cavity wall. It is likely that a change in the electronic-state of the coumarin ring plays a role in weakening the steric repulsion described above. The structure of the β-CDx inclusion complex with 7H4MC, where both the quinoid-type carbonyl and oxido groups are exposed to the bulk aqueous phase (Fig. 5) provides a good explanation for the negligible effect of β-CDx inclusion on the proton dissociation ability of the guest.

The coupled oscillator theory developed by Kirkwood and Tinoco [20] predicts that the guest electronic transition polarized perpendicular to the CDx cavity axis exhibits a negative ICD sign while that polarized parallel to the axis gives a positive ICD sign [21–29]. Because the first absorption transition of 7H4MC at 320 nm is considered to be polarized along the long molecular axis of the coumarin ring [30], the structure of the β-CDx inclusion complex with 7H4MC (shown in Fig. 4) allows us to predict that the 320 nm absorption gives a positive ICD band. In Figs. 6 and 7 are typically shown ICD spectra of 7H4MC in the presence of β-CDx at pH 2.0 and 10.5, respectively, together with those of 7HC4AK. As expected, 7H4MC exhibited a positive ICD band in the 260–350 nm region, providing a piece of evidence for the proposed complex structure. Interestingly, the 7H4MC-derived tautomer anion also produced a positive ICD peak at 360 nm, which corresponds to the first UV absorption band of the guest. This finding is consistent with the intracavity inclusion of the tautomer anion and then indicates that the first electronic transition of this tautomer must be polarized along the long molecular axis of the coumarin ring. It is worthwhile to note that the difference in ICD intensity between the neutral and tautomer anion forms of 7H4MC approximately conforms to that in absorbance at their absorption maximum wavelengths. On the other hand, comparison of ICD spectra of 7H4MC with those of 7HC4AK at a given pH shows that the substitution

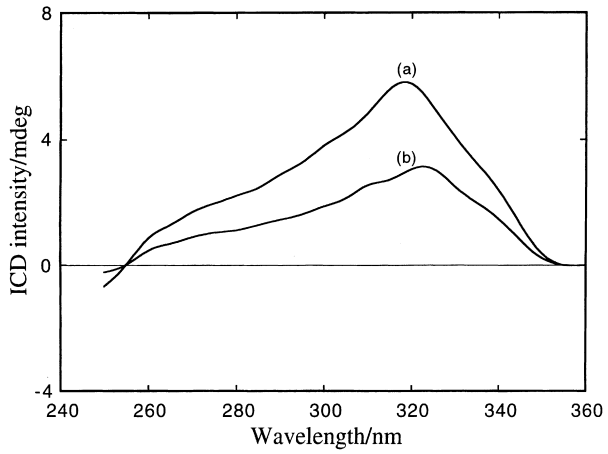


Fig. 6. ICD spectra of 7H4MC (a, 5.0×10^{-5} mol dm^{-3}) and 7HC4AK (b, 5.0×10^{-5} mol dm^{-3}) in the presence of β-CDx (1.0×10^{-2} mol dm^{-3}) at 24 ± 1°C, pH 2.0.

of a carboxylato group for the methyl hydrogen at the four position reduces the ICD intensity of the former guest by nearly half at any pH. This may reflect the smaller *K* value for the complexation with the latter guest.

3.2. Fluorescence spectra and fluorescence lifetimes

In a previous study, we confirmed that the protic polar solvent, methanol, is able to form a hydrogen-bonded complex with the ester carbonyl oxygen of 7HC and related compound and thereby greatly accelerates their tautomerization in the excited singlet-state, especially in the presence of tertiary amines [16]. Since, water is also indicated to promote the phototautomerization of 7HC and its derivatives through the strong hydrogen-bonding solvation of each tautomer formed [31], it is of value to examine and compare the pH dependence of the 7H4MC fluorescence with and

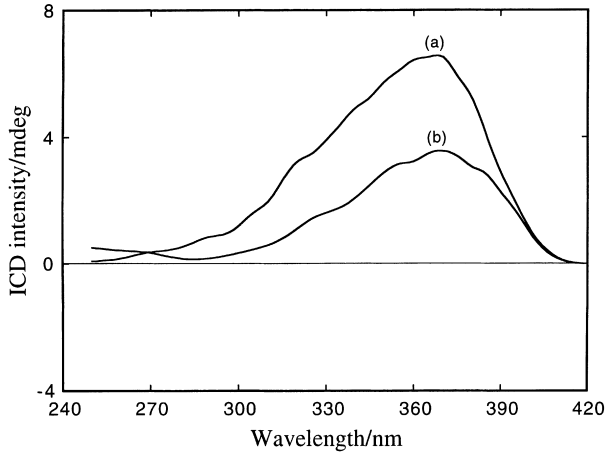


Fig. 7. ICD spectra of 7H4MC (a, 5.0×10^{-5} mol dm^{-3}) and 7HC4AK (b, 5.0×10^{-5} mol dm^{-3}) in the presence of β-CDx (1.0×10^{-2} mol dm^{-3}) at 24 ± 1°C, pH 10.5.

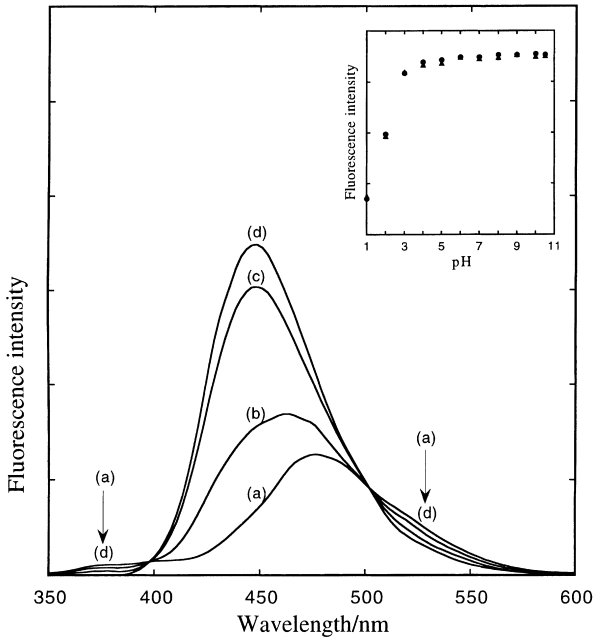
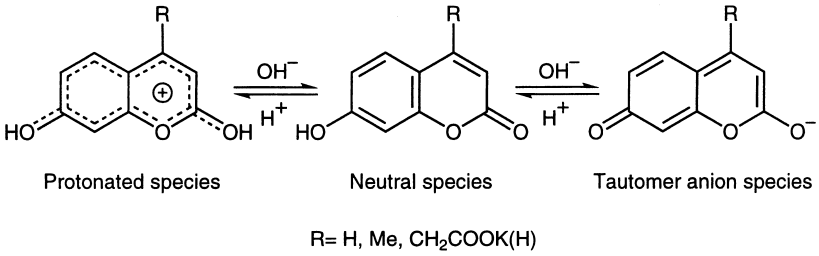


Fig. 8. pH dependence of the fluorescence spectrum of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing KCl (0.1 mol dm^{-3}) at 24 ± 1°C. Excitation wavelength (λ_{ex}): 333 nm. pH: (a) 1.0 (0.1 mol dm^{-3} HCl); (b) 2.0; (c) 3.0; (d) 10.5. Inset: spectrofluorimetric titration curves for 7H4MC in the absence (●) and presence (▲) of β-CDx (1.0×10^{-2} mol dm^{-3}).

without β-CDx. In Fig. 8, are shown pH-dependent fluorescence spectra of 7H4MC in the absence of β-CDx and their intensities at 450 nm as a function of pH (inset of Fig. 8). At low pH, 7H4MC exhibited at least three emission bands at about 380, 450 and 480 nm. On increasing pH, the 450 nm band grows rapidly at the expense of the 380 and 480 nm bands to show isoemissive points at 398 and 502 nm. On the basis of our previous results [16], the 380 and 450 nm emission bands may be assigned to neutral and tautomer anion species in the excited singlet-state, respectively (Scheme 2). In addition, the finding that the basicity of the ester carbonyl oxygen of 7HC is increased in the excited-state suggests that the 480 nm emission arises from the protonated species (Scheme 2). On the other hand, 7H4MC gave virtually the same fluorescence titration curve even in the presence of β-CDx (inset of Fig. 8). This leads us to conclude that the acidity of 7-hydroxycoumarin derivatives studied undergoes a negligible effect of the β-CDx inclusion also in the excited singlet-state.

As typically shown in Fig. 9, the complexation of 7H4MC with β-CDx at pH 2.0 resulted in a gradual increase of the guest fluorescence intensity with a blue shift (10 nm) of the emission maximum, whereas a monotonous increase in the tautomer emission intensity was observed on forming the β-CDx complex at pH 10.5 (inset of Fig. 9). The guest molecule included into the β-CDx cavity at low pH is considered to adopt the tautomer form in preference to the protonated form described above. Because the ground-state



Scheme 2.

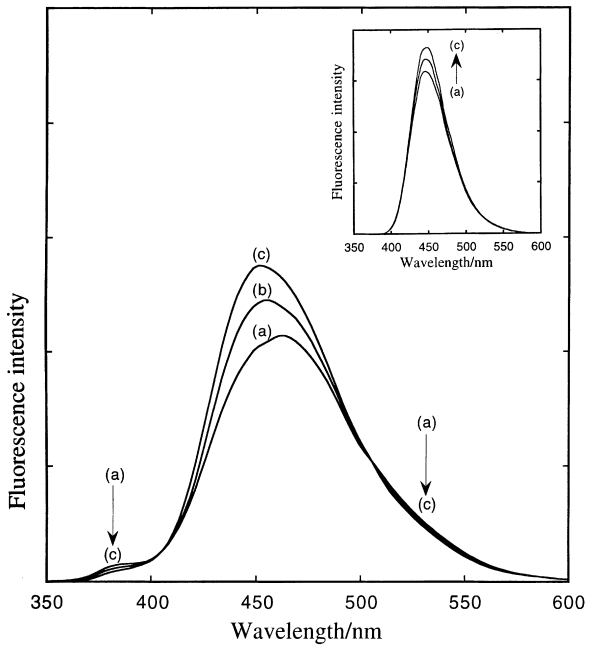


Fig. 9. Fluorescence spectral changes of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing β-CDx and KCl (0.1 mol dm^{-3}) at 24 ± 1°C, pH 2.0. λ_{ex}: 340 nm. $[\beta\text{-CDx}]_0$ (mol dm^{-3}): (a) 0; (b) 2.0×10^{-3}; (c) 1.0×10^{-2}. Inset: fluorescence spectral changes of 7H4MC (5.0×10^{-5} mol dm^{-3}) in 2 vol.% MeOH–H_2O containing β-CDx and KCl (0.1 mol dm^{-3}) at 24 ± 1°C, pH 10.5. λ_{ex}: 368 nm. $[\beta\text{-CDx}]_0$ (mol dm^{-3}): (a) 0; (b) 2.0×10^{-3}; (c) 1.0×10^{-2}.

Table 2
Fluorescence lifetimes (τ_f) of 7H4MC and 7HC4AK (5.0×10^{-5} mol dm^{-3}) in the absence and presence of β-CDx in 2 vol.% MeOH–H_2O containing KCl (0.1 mol dm^{-3}) at 24 ± 1°C

Guest	pH	[β-CDx] (mol dm^{-3})	λ_{ex}[a] (nm)	τ_f (10^{-9} s)	χ^2
7H4MC	2.0	0	340	4.3	1.08
	2.0	0.010	340	5.2	1.05
7H4MC	10.5	0	368	5.0	1.12
	10.5	0.010	368	5.6	1.26
7HC4AK	2.0	0	345	4.8	1.15
	2.0	0.010	345	5.6	1.14
7HC4AK	10.5	0	378	5.3	1.21
	10.5	0.010	378	5.8	1.05

[a] Excitation wavelength.

guest exists in the form of the tautomer anion at high pH, the enhanced emission intensity indicates a change in environment around this tautomer from hydrophilic to hydrophobic one, thus, leading us to predict that the β-CDx host cavity affects the fluorescence lifetime of a given guest molecule. The fluorescences of all the guests decayed according to single exponential at any pH and the lifetimes estimated are collected in Table 2. The observation of monoexponential decay of the 7H4MC fluorescence at pH 2.0 suggests a slight difference in emission lifetime between the tautomer and protonated forms. On the other hand, we may expect double exponential emission decay to be observed, particularly, for the β-CDx–7HC4AK system at low pH because the unbound guest is present in high percentage (about 60%) in the solution. However, the result obtained is not consistent with our expectation. Both the entry rate of the free guest and the exit rate of the bound guest in the excited singlet-state are very unlikely to be much faster than the decay rate of these two guest molecules. It is, thus, reasonable to assume that a small difference in fluorescence lifetime between the free and bound tautomer anion guests is responsible for the observed single exponential decay. Since the fluorescence lifetimes of 7HC-derived tautomer anion in MeOH, MeCN and 1,4-dioxane are determined to be 4.4, 5.0 and 5.4 ns, respectively [16], the finding that the presence of β-CDx lengthens each tautomer lifetime by 0.5–0.9 ns provides strong evidence for the intracavity inclusion of our guests.

3.3. ^1H NMR spectra

In order to obtain evidence in support of the structure of the β-CDx inclusion complexes with 7H4MC and 7HC4AK,

Table 3
^{1}H NMR spectral data of β-CDx (5.5×10^{-3} mol dm^{-3}), obtained in the absence and presence of 7H4MC and 7HC4AK (5.0×10^{-3} mol dm^{-3}) in D_2O containing 8 vol.% DMSO-d_6 at 24 ± 1°C

System	δ					
	1-H	2-H	3-H	4-H	5-H	6-H
β-CDx[a]	5.09	3.66	3.97	3.60	3.90	3.90
β-CDx	5.08	3.66	3.92	3.60	3.82	3.89
β-CDx–7H4MC	5.08	3.66	3.91	3.60	3.80	3.89
β-CDx–7HC4AK	5.08	3.66	3.91	3.60	3.80	3.89

[a] Data obtained in D_2O.

Table 4
^{1}H NMR spectral data of 7H4MC and 7HC4AK (5.0×10^{-3} mol dm^{-3}), obtained in the absence and presence of β-CDx (5.5×10^{-3} mol dm^{-3}) in D_2O containing 8 vol.% DMSO-d_6 at 24 ± 1°C

System	δ					
	H^3	H^5	H^6	H^8	Me	CH_2
7H4MC	6.24	7.73	6.96	6.89	2.47	
β-CDx–7H4MC	6.21	7.69	6.96	6.87	2.47	
7HC4AK	6.30	7.67	6.96	6.90		3.74
β-CDx–7HC4AK	6.27	7.67	6.96	6.90		3.74

we measured ^{1}H NMR spectra of these two guest molecules with and without β-CDx. Owing to the poor solubility of both the guests toward ^2H_2O (D_2O), we were forced to employ at least 8 vol.% of DMSO-d_6 as a cosolvent, which made the use of a buffered solution difficult. In Table 3, are tabulated the chemical shifts (δ) of β-CDx with and without each guest, and the δ values of the guests in the presence and absence of this host are collected in Table 4. We define the change in chemical shift ($\Delta\delta$ (ppm)) as the difference in chemical shifts between proton signals of the guest or β-CDx in the absence and presence of β-CDx or the guest, respectively.

Unfortunately, the addition of 8 vol.% DMSO-d_6 to a D_2O solution of β-CDx caused relatively large upfield shifts of the 3-H ($\Delta\delta = +0.05$) and 5-H ($\Delta\delta = +0.08$) signals (Table 3), allowing us to expect that the presence of this cosolvent lowers the equilibrium constant for the complexation with β-CDx and, hence, the guest is merely able to induce the small chemical shift of each proton signal for the host. Although, only limited information can be obtained from the ^{1}H NMR data, the observation of slight upfield shifts of the 3-H ($\Delta\delta = +0.01$) and 5-H ($\Delta\delta = +0.02$) signals for β-CDx in the presence of 7H4MC or 7HC4AK is consistent with the inclusion of each guest into the cavity. Additionally, a negligible shift of the 6-H signal suggests the intracavity immersion of the guest molecule from the secondary hydroxy group side.

On the other hand, β-CDx induced a distinct upfield shift of the H^3 signal ($\Delta\delta = +0.03$) for 7HC4AK without affecting the other guest proton signals (Table 4), suggesting that the CH_2COO^- group is situated near the H^3 atom to exert a shielding effect on this proton resonance. Table 4 also shows that the H^3 ($\Delta\delta = +0.03$), H^5 (+0.04) and H^8 (+0.02) signals of 7H4MC are subject to upfield shifts, although small, in the presence of β-CDx. The chemical shift changes observed for these proton signals reveal that most of the coumarin ring in a 7H4MC molecule is included into the cavity and, hence, substantiate the complex structure given in Fig. 4.

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