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Inclusion complexation of a few pyrylium salts by β-cyclodextrin studied by fluorescence, NMR and laser flash photolysis†

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Inclusion complex formation between pyrylium salts **1–6** and β-cyclodextrin (β-CD) was investigated. Because of the positive charge present in the molecule, simple pyrylium salts are hydrophilic and do not show any tendency for encapsulation in β-CD. However, by tuning the hydrophobicity of the substituents present in the 4-position, one can prepare pyrylium salts, which are sufficiently hydrophobic to undergo encapsulation in β-CD cavities. Thus, **2–5** undergo encapsulation as is evident from their NMR and fluorescence spectra in the presence of β-CD. Fluorescence quantum yields of **2–5** were enhanced in the presence of β-CD and these enhancements were used to calculate the association constants by a Benesi–Hildebrand treatment. Electron transfer to the encapsulated pyrylium salts from a water-soluble donor was studied by fluorescence quenching and laser flash photolysis. The pyranyl radicals formed within the β-CD cavity as a result of electron transfer was found to be long-lived and this is attributed to the reduced rate of back electron transfer reaction achieved due to the protection afforded to the radical by the hydrophobic β-CD cavity.

1 Introduction

Cyclodextrins (CDs) are macrocyclic sugar molecules composed of α-1,4-glycosidic linkages of 6, 7 or 8 glucose units, which are denoted α-, β- and γ-cyclodextrin, respectively.[1–3] They are torus shaped with an internal hydrophobic cavity and hydrophilic peripheries of hydroxy groups on the two receptor edges. In aqueous solution, hydrophobic substrates of proper size and shape associate with the cyclodextrin cavity to form supramolecular host–guest complexes. The association properties of CD receptor systems have been extensively employed in developing artificial enzymes.[4–6] Cyclodextrin receptors have also been used in controlling stereospecific and stereoselective phototransformations.[7–9] Photophysical studies of a large number of compounds have also been carried out in the presence of CDs.[9–19] In this paper we report on the encapsulation studies of selected pyrylium salts in β-CD cavities. Pyrylium salts belong to a class of interesting compounds having applications such as laser dyes,[20,21] Q switches in lasers,[22,23] electrophotographic sensitizers,[24] liquid crystalline materials,[25,26] phototherapeutic agents[27] and sensitizers in photoinduced electron transfer reactions.[28,29] The pyrylium nucleus bears a positive charge and because of this, simple pyrylium salts are very hydrophilic and do not show any tendency to undergo encapsulation in CD cavities. Our aim has been to study the structural features of the pyrylium salts that affect encapsulation in β-CD cavities.

The pyrylium salts we have used for this study are shown below. A distinguishing feature of CD complexation is the finite size of the CD cavities which imposes size and shape selectivity for the molecules they encapsulate. In order to see whether the pyrylium salts can be encapsulated into the β-CD cavity, we have calculated the molecular dimensions of the pyrylium salts by AM1 and the values obtained are given below along with the structures.[30] β-CD has an internal diameter of 6.5 Å and a height of 7.9 Å. This suggests that the aromatic rings in **1–4** can be incorporated in a very facile manner in β-CD, whereas **5** and **6** can be incorporated only partially. Our studies have shown that in order to undergo binding with β-CD, suitable sizes as well as presence of hydrophobic groups are required. We have probed the inclusion complex formation using absorption, emission and NMR spectroscopy. We have shown that pyrylium salts encapsulated in β-CD cavities can participate in photoinduced electron transfer reactions with a donor molecule present in the aqueous phase. The pyranyl radicals formed inside the β-CD cavity as a result of electron transfer were found to be long lived compared to those in the absence of β-CD.

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2 Experimental

2.1 Materials

Synthesis of pyrylium salts **1–6** are reported elsewhere.[31,32] β-CD was purchased from Aldrich and was used as such. Sodium naphthalene-2-sulfonate was prepared according to a reported procedure[33] and was recrystallized before use. Doubly distilled water was used.

2.2 Measurements

The absorption spectra were recorded on a Shimadzu UV-2100 or a GBC double beam UV-VIS spectrometer. Fluorescence spectra were recorded on a SPEX Fluorolog F 112X spectrofluorimeter with a right-angled geometry. Quantum yields of fluorescence were measured by the relative method using optically dilute solutions. Quinine sulfate in 0.5 M sulfuric acid ($\Phi_F = 0.54$)[34] was used as reference. Fluorescence lifetimes were determined using Edinburgh Instruments FL900CD single photon counting system. NMR spectra were recorded on a 300 MHz Bruker Avance DPX spectrometer. Laser flash photolysis experiments were carried out by employing an Applied Photophysics Model LKS-20 Laser Kinetic Spectrometer using GCR-12 Quanta Ray Nd : YAG

laser. The analyzing and detecting laser beams were at right angles to each other. The laser energy was 60 mJ at 355 nm.

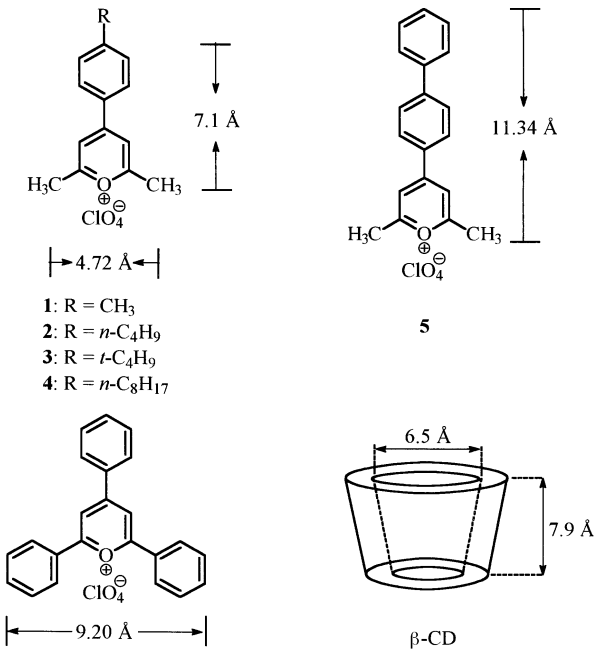
3 Results

Photophysical studies of pyrylium salts incorporated in CDs have not been reported in the literature. We have observed that some of the pyrylium salts **1**–**6** can be incorporated into β-CD cavities. Complexation studies with β-CD, however, have to be done in water, where some pyrylium salts are reported to be unstable. Because of their instability in water, photophysical studies of pyrylium derivatives have rarely been attempted in water. Gird and Balaban have, however, shown that pyrylium salts are stable in buffer solutions in the pH range 0.5–3.5.[35] We have observed that both the pyrylium salts and β-CD are stable in a sodium acetate–acetic acid buffer of pH 3.5 at room temperature for several days. Hence all the photophysical studies reported here were carried out in this buffer solution.

3.1 Absorption and emission studies

Absorption spectra of **1** and **6** in aqueous buffer solutions were unaffected by the addition of millimolar quantities of β-CD, indicating that these substrates have no interaction with β-CD. Absorption spectra of other derivatives, however, were slightly blue shifted in the presence of β-CD. Fig. 1 shows the absorption spectra of **3** in the presence of various concentrations of β-CD. Absorption changes observed in all cases were small and hence were not used for quantitative determination of the association constant.

The fluorescence spectra of **1**–**6** in aqueous buffer solutions were very similar to those in acetonitrile solution.[36] The fluorescence quantum yields and lifetimes were somewhat lower in the buffer solution. Addition of small quantities of β-CD did not lead to any change in the fluorescence spectra of **1** and **6**. The fluorescence intensities and lifetimes also remain unaffected. The fact that the absorption and emission properties of **1** and **6** are unaffected by β-CD can be taken as conclusive evidence for the absence of inclusion complex formation in these two cases. Hence these compounds were excluded from the remaining studies reported here.



Scheme 1

Table 1 Fluorescence maxima (λ_{max}), quantum yields (Φ_F), lifetimes (τ_F) and association constants (K) for pyrylium salts **2**–**5** in the presence of β-CD. Values given in parentheses are those in the absence of β-CD

Compound	$\lambda_{max,\,em}$/nm	Φ_F	τ_F/ns	K/mol^{-1} dm^3
2	410	0.072	1.4	4070
	(436)	(0.040)	(1.5)	
3	410	0.11	1.8	18400
	(436)	(0.078)	(2.0)	
4	421	0.11	1.6	15000
	(436)	(0.063)	(2.0)	
5	496	0.11	0.8	2700
	(510)	(0.025)	(0.2)	

Fluorescence properties of **2**–**5** were affected by the presence of β-CD. In Table 1 we have indicated the fluorescence properties of these substrates in the buffer solution in the absence and presence of excess β-CD. As is evident from Table 1, the presence of β-CD leads to a 2–6 fold enhancement in the fluorescence quantum yields along with a blue shift in the emission maxima and this can be taken as evidence for the formation of inclusion complexes in these cases. Fluorescence enhancements in these cases can be analyzed by the Benesi–Hildebrand equation for 1 : 1 complex formation between pyrylium salts and β-CD.[37] According to this equation,

$$1/(\Phi_F^0 - \Phi_F) = 1/(\Phi_F - \Phi_{complex}) + 1/(\Phi_F - \Phi_{complex})K[\beta\text{-CD}] \quad (1)$$

where, Φ_F^0 is the fluorescence quantum yield in the absence of β-CD, Φ_F is the observed fluorescence quantum yield in the presence of β-CD, $\Phi_{complex}$ is the fluorescence quantum yield of the pyrylium salt-β-CD complex and K is the association constant for the 1 : 1 complex. Values of $1/(\Phi_F^0 - \Phi_F)$ were plotted against 1/[β-CD] for pyrylium salts **2**–**5** and linear plots were obtained in all cases (Fig. 2). This suggested that the inclusion complexes formed in these cases have 1 : 1 stoichiometry. K values determined from these plots are presented in Table 1. Notice that K values obtained for **3** and **4** are very large.

Although pyrylium salts **2**–**5** formed inclusion complexes with β-CD, the nature of these complexes was not the same in all cases. This is evident from the fluorescence profiles of the substrates in the presence of β-CD. Fluorescence profiles of **2** and **3** in the presence of β-CD were similar. Fluorescence spectra of **3** in the presence of different concentrations of β-CD are shown in Fig. 3. In this case, the enhancement was associated with the appearance of some structure, a blue shift of 26 nm for the emission maximum and a narrowing of the spectral band. The fluorescence spectrum in the presence of

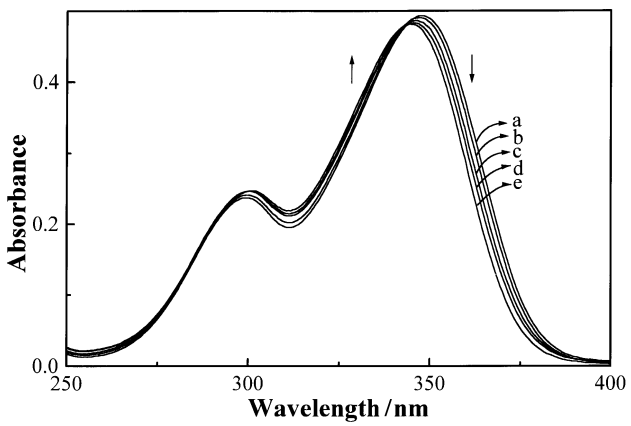


Fig. 1 Absorption spectra of **3** (2×10^{-5} mol dm^{-3}) in the presence of various concentrations of β-CD. [β-CD] were: (a) 0, (b) 5×10^{-5}, (c) 1×10^{-4}, (d) 5×10^{-4} and (e) 1×10^{-3} mol dm^{-3}.

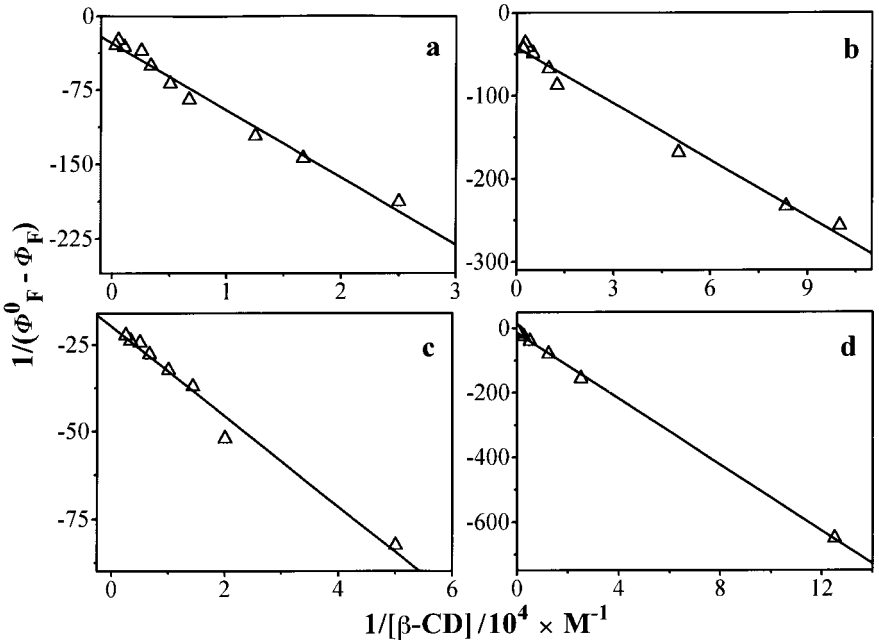


Fig. 2 Plots of $1/(\Phi^0_F - \Phi_F)$ *vs.* 1/[β-CD] for the fluorescence yield enhancement of (a) **2**, (b) **3**, (c) **4** and (d) **5**. Fluorophore concentration was 4×10^{-6} mol dm^{-3} in all cases.

excess β-CD is very similar to the spectrum of **3** in dichloromethane. This clearly suggested that **3** is associated within the hydrophobic cavity of β-CD. An important feature in these cases is the presence of an isoemissive point, which may be due to the equilibrium between free and bound forms of **3**.

The fluorescence spectra of **5** in the presence of different β-CD concentrations are shown in Fig. 4. In this case, although a six-fold enhancement of fluorescence was observed, a relatively large concentration of β-CD was needed for achieving complete complexation. The shift in the emission maximum was very gradual and no isoemissive point was observed. The fluorescence profiles of **4** in the presence of β-CD showed an intermediate behaviour. The spectrum in the presence of excess β-CD was similar to that of **4** in dichloromethane solution, but the shift in the emission maximum was only 15 nm and there was no isoemissive point.

Fluorescence decays of **2**–**5** were single exponential in the buffer solution. In the presence of excess β-CD, the decay profiles deviated slightly from exponential behaviour. We have however, fitted these decays to single exponential functions ($\chi^2 < 2$) and the values obtained are given in Table 1. Notice that for **2**–**4** the fluorescence lifetimes are shorter in the presence of β-CD. The trend is reversed in the case of **5**.

3.2 NMR studies

Additional evidence for the formation of inclusion complexes in the case of **2**–**4** was obtained from changes in the chemical shift and line shapes of β-CD NMR proton signals in the presence of these substrates. These experiments could not be done in the case of **5** because this compound was not very stable in neutral D_2O for long periods of time. The ^{1}H NMR spectrum of β-CD in D_2O is shown in Fig. 5a and the peak assignments are reported elsewhere.[38,39] The H-3 and H-5 protons are located in the interior of the β-CD cavity. Therefore it is most likely that these protons shift as a result of proximal or direct interaction with the guest molecule. The H-6 proton is located at the smaller rim of the cavity and is also normally affected by the presence of guest molecules. The H-2 and H-4 protons located at the exterior of the β-CD torus are relatively unaffected by the guest molecules.[39]

Incorporation of pyrylium salts **2**–**4** leads to differences in the chemical shifts of all β-CD protons. The observed chemical shift differences are indicated in Table 2. Notice that in all three cases chemical shifts of the H-3, H-5 and H-6 protons are affected in the presence of β-CD. Chemical shifts of the H-2 and H-4 protons are less affected. Chemical shifts of the

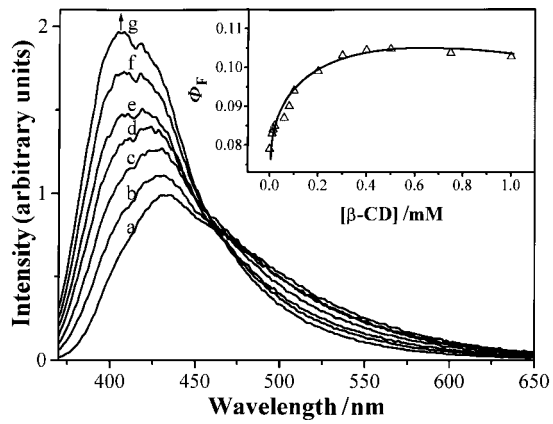


Fig. 3 Effect of β-CD on the emission spectrum of 4×10^{-6} mol dm^{-3} **3**. [β-CD] were: (a) 0, (b) 2×10^{-5}, (c) 4×10^{-5}, (d) 6×10^{-5}, (e) 2×10^{-4}, (f) 3×10^{-4} and (g) 5×10^{-4} mol dm^{-3}. Inset shows a plot of fluorescence quantum yield *vs.* [β-CD].

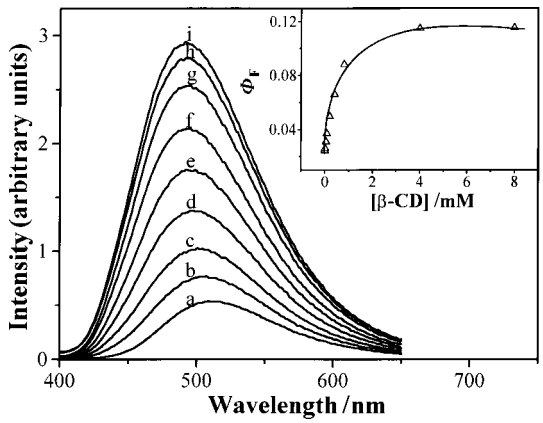


Fig. 4 Effect of β-CD on the emission spectrum of 4×10^{-6} mol dm^{-3} **5**. [β-CD] were: (a) 0, (b) 8×10^{-6}, (c) 4×10^{-5}, (d) 8×10^{-5}, (e) 2×10^{-4}, (f) 4×10^{-4}, (g) 8×10^{-4}, (h) 4×10^{-3} and (i) 8×10^{-3} mol dm^{-3}. Inset shows a plot of fluorescence quantum yield *vs.* [β-CD].

Table 2 Induced ^{1}H NMR (300 MHz, D_2O) chemical shifts ($\Delta\nu$/Hz) of β-cyclodextrin and pyrylium salt (**2**–**4**) protons upon complex formation[a]

	$\Delta\nu$/Hz		
Protons	**2**	**3**	**4**
Pyrylium			
2,6-Me	9	15	0
H^a	26	27	26.5
H^b	25.8	35	34.0
H^c	−21	−11.4	−4.4
β-Cyclodextrin			
H-2	−1	−11.9	−12.5
H-3	−18.5	−29.2	−26
H-4	−1.7	−11.4	−15
H-5	21.8	−28	−23
H-6	−9.1	−12.9	−22.4

[a] For proton assignments see Fig. 5.

protons of the pyrylium salts are also affected by encapsulation. ^{1}H NMR spectra of **3** in the presence and absence of β-CD are shown in Fig. 5b and 5c, respectively. The *t*-butyl protons showed a dramatic down field shift of 0.13 ppm in the presence of β-CD. The methyl protons at the 2- and 6-positions showed a relatively smaller shift. Other protons in the pyrylium ring were also affected to a different extent. Similar chemical shift differences were noticed in the case of **2** and **4**. A noticeable difference was that the methyl protons at the 2- and 6-positions in **4** were unaffected by encapsulation in β-CD.

3.3 Electron transfer studies

CDs have been used as molecular receptors to control electron transfer reactions in organized assemblies.[40–47] Pyrylium salts are good electron acceptors in their excited states. In order to study the effect of encapsulation on the electron transfer properties of pyrylium salts, we have undertaken a study of the electron transfer property of pyrylium salt–β-CD complexes using fluorescence quenching and laser flash photolysis techniques. The water-soluble molecule, sodium naphthalene-2-sulfonate (2-NS) was used as the electron donor in these studies. Lin and Schuster have earlier shown that 2-NS quenches the fluorescence of several pyrylium salts in polar solvents by an electron transfer mechanism.[48] Absorption and emission properties of 2-NS were unaffected by the addition of β-CD indicating that this molecule shows no affinity for encapsulation in β-CD under our experimental conditions. Thus, in the quenching reactions studied in the presence of excess β-CD, we can safely assume that the pyrylium salt is present inside and the quencher is present outside the β-CD cavity.

Fluorescence of **2**–**4**, both in the absence and presence of β-CD was quenched by the addition of 2-NS. Plots of fluorescence intensity *vs.* [2-NS] were linear in all cases and fitted the Stern–Volmer equation,

$$\frac{I_0}{I} = 1 + k_q\tau[\text{2-NS}] \qquad (2)$$

where, I_0 and I represent the fluorescence intensities in the absence and presence of 2-NS, k_q is the quenching rate constant and τ is the fluorescence lifetime in the absence of the quencher. In the absence of β-CD, k_q values of (2–2.5) × 10^{10} mol^{-1} dm^3 s^{-1} were obtained for **2**–**5**. This value is slightly lower than the value of 2.8 × 10^{10} mol^{-1} dm^3 s^{-1} reported in acetonitrile by Lin and Schuster.[48] In the presence of β-CD, quenching rates were reduced to about 50%. The reduction in the quenching efficiency is attributed to encapsulation and few examples are reported in the literature.[44–47] This also confirms that the 2-NS molecules are not encapsulated in the cavities along with the pyrylium salts. If this happens, the quenching rates would be larger in the presence of β-CD.[44,45]

In order to gain a better understanding of the electron transfer reaction, transient absorption spectra were recorded in the case of **3** encapsulated in β-CD. It has been shown that flash photolysis of pyrylium salt–2-NS lead to formation of pyranyl radical (λ_{max} 430–480 nm) and 2-NS radical cation (600–700 nm).[48] Laser flash photolysis of the **3**–2-NS system using the 355 nm light from a Nd : YAG laser gave the transient spectrum shown in Fig. 6. Based on literature precedents, the 420–440 nm band was assigned to the pyranyl radical and the absorptions in the 600–700 nm region was attributed to the 2-NS radical cation.[48] This clearly shows that quenching of **3** by 2-NS occurred by an electron transfer mechanism according to eqn. (3).

$$PY^* + \text{2-NS} \rightarrow PY^{\cdot} + \text{2-NS}^{\cdot +} \qquad (3)$$

The transient absorption spectrum of the **3**–2-NS system in the presence of excess β-CD was also similar (Fig. 6). This confirmed that electron transfer occurred even when the pyrylium salt is encapsulated in the CD and the quencher is present outside in the aqueous phase.

A very important result in these studies is the enhanced lifetime of the pyranyl radicals in the presence of β-CD. We have observed that the lifetimes of the radicals were enhanced approximately 20 times in the presence of β-CD. This is shown in the kinetic traces in Fig. 7, which shows the decay of

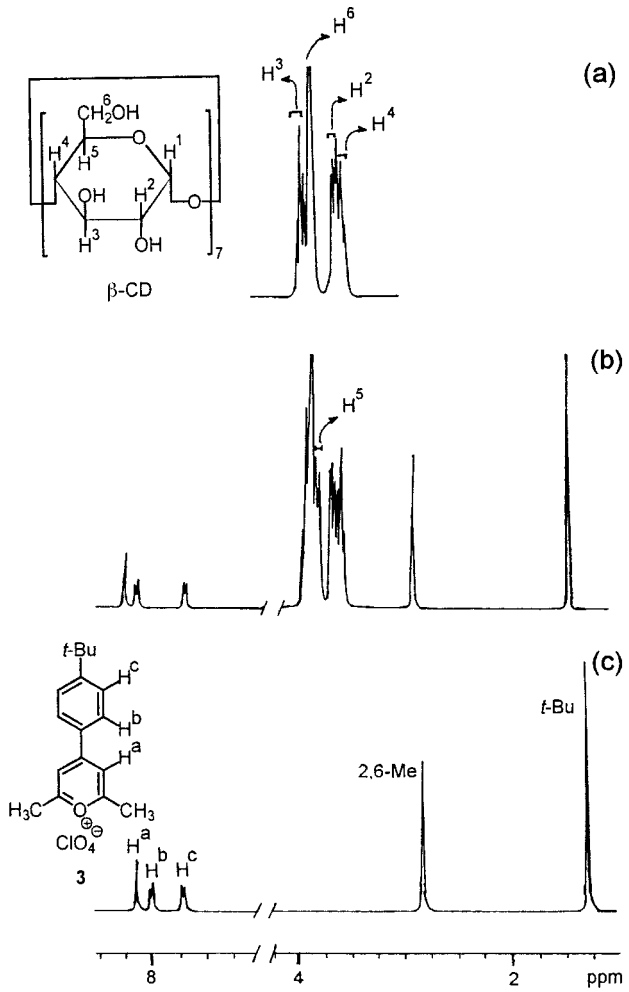


Fig. 5 Nuclear magnetic resonance spectra of (a) β-CD in D_2O, (b) a mixture of **3** (5 × 10^{-3} mol dm^{-3}) and β-CD (2 × 10^{-2} mol dm^{-3}) in D_2O and (c) **3** in D_2O. Spectra were acquired with a 300 MHz Bruker spectrometer.

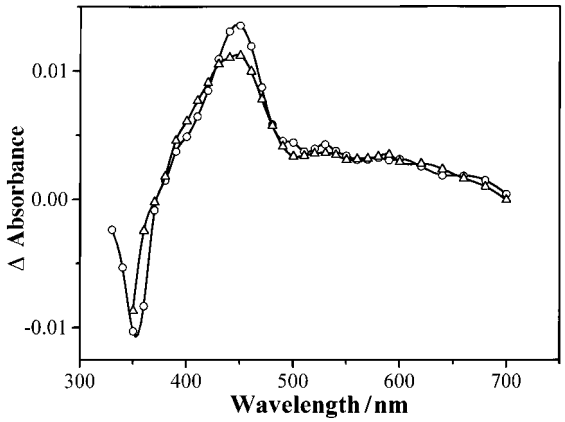


Fig. 6 Transient absorption spectra of **3** (2×10^{-5} mol dm^{-3}) with 2-NS (0.01 mol dm^{-3}) in the (○) absence and (△) presence of β-CD (2.5×10^{-3} mol dm^{-3}).

the 440 nm species in the absence and presence of β-CD. In the absence of β-CD, the transient decayed in about 20 μs time. The small residual absorption in this case is attributed to product formation. In the presence of β-CD, decay of the radical species is not complete even at 150 μs. Residual absorptions attributable to product formation is also absent in this case. This clearly showed that the pyranyl radicals are protected within the β-CD cavity for relatively long periods.

4 Discussion

It is generally accepted that the binding forces involved in the formation of β-CD inclusion complexes are: (1) hydrophobic interaction between the hydrophobic moieties of the guest molecule and the β-CD cavity; (2) release of high energy water molecules from the cavity in the complex formation process and (3) hydrogen bonding between the functional groups of the guest molecule and hydroxy groups of β-CD.[3] Regardless of the kind of binding forces involved, the geometric capability and polarity of the guest molecule are very important in determining whether the guest molecule can form an inclusion complex with β-CD.[3,9] If the guest is too small, it will pass in and out of the cavity with little or no binding at all. The stability of the inclusion complex is generally proportional to the hydrophobic character of the guest molecule. Highly hydrophilic molecules complex very weakly or not at all.

The β-CD cavity has a diameter of 6.5 Å. Except for **6**, all other pyrylium salts have widths smaller than 6.5 Å. Thus, if molecular size is the only criterion, pyrylium derivatives **1–5** should be able to complex with β-CD. Our studies have shown that **1** does not form an inclusion complex with β-CD. This indicates that complex formation in these cases is determined by other factors as well. Because of the positive charge present in the molecule, simple pyrylium salts are polar and somewhat hydrophilic in nature. Encapsulation of these salts will be possible only if the pyrylium ring is substituted with hydrophobic moieties. Since **1** does not undergo encapsulation in β-CD, we can safely assume that a phenyl or *p*-toluyl group at the 4-position of the pyrylium ring does not enhance the hydrophobicity of the molecule to the extent required for complex formation. When the 2-, 4- and 6-positions are substituted by phenyl groups as in **6**, the molecule becomes larger than the cavity and inclusion does not take place in this case because of geometric constraints. The fact that **2–5** form inclusion complexes with β-CD suggests that the aryl groups present in the 4-position of these molecules make them sufficiently hydrophobic for inclusion in the cavity.

The fluorescence profiles of **2–5** in the presence of β-CD prompted us to make certain assumptions regarding the structures of the inclusion complexes. Considering the molecular dimensions, the pyrylium salts can enter the CD cavity only along its long axis. In the case of **3**, the very high association constant suggests that the molecule is tightly bound within the cavity and the exit rate is low. The chemical shift due to the *t*-butyl protons shows a pronounced shift in the NMR suggesting that this group is held firmly within the cavity. The length of the molecule is slightly larger than the cavity height and hence the 2- and 6-methyl groups slightly project outside the cavity. In accordance with this assignment, the chemical shift of the 2- and 6-methyl groups are affected only little compared to the *t*-butyl group. In the case of **2** and **4**, the lengths of the molecules are larger than that of β-CD. Since the alkyl groups are very hydrophobic, we expect these moieties to be coiled inside the cavity and the pyrylium ring mostly exposed to the aqueous environment. Observations similar to this have been made in the encapsulation studies of alkyl-substituted viologen derivatives.[49] In the case of **5**, one of the three rings has to project outside the β-CD cavity during complex formation. Because of this, the hydrophobic stabilization is low and this resulted in low K values.

The fluorescence lifetime measurements also suggest that the pyrylium salts are included within the β-CD cavity. Compounds **2–4** showed a marginal decrease in the τ_F value upon encapsulation. In these cases it was shown that the lifetime in polar solvents is larger due to the formation of more stable TICT states.[36] Thus, the decrease in τ_F values in the presence of β-CD can be attributed to encapsulation of **2–4** in the non-polar cavity. In the case of **5** the fluorescence lifetime increases in the presence of β-CD. In this case it was observed that the fluorescence lifetime and quantum yield decrease in polar solvents due to intramolecular electron transfer (ICT) from the biphenyl group to the pyrylium moiety. The τ_F value in this case is larger in the presence of β-CD due to a reduction in the rate of ICT within the non-polar cavity.

Electron transfer studies in the presence of β-CD provide conclusive evidence for the encapsulation of **2–5**. It is known that cyclodextrin receptors can participate in photoinduced electron transfer reactions in three complementary ways: (1) the receptor separates the donor and acceptor by selective association of one of the components, (2) the photoproduct is prevented from aggregating due to binding to the CD receptor and (3) association of the photoproduct with the CD cavity can provide protection against back electron transfer.[50] The latter aspect seems to be very important in the present case. Since the pyranyl radicals are neutral, we expect them to associate better with β-CD compared to the cationic pyrylium salt. A similar result was obtained in the encapsulation studies of viologen derivatives. It was shown in this case that dicationic viologens have no affinity for β-CD, but their neutral, two electron reduction products exhibited a great binding affinity to β-CD ($K \sim 10^4$ mol^{-1} dm^3).[51,52]

In the presence of β-CD in aqueous solution, the pyrylium salt **3** prefers to reside inside the cavity as shown in Scheme 2 with part of the pyrylium nucleus exposed to the aqueous environment and the quencher 2-NS remaining in the aqueous phase. Upon excitation, electron transfer (et) takes place

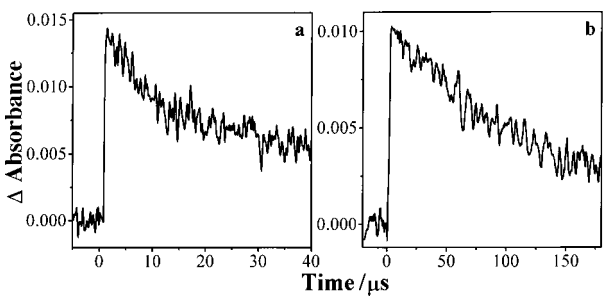
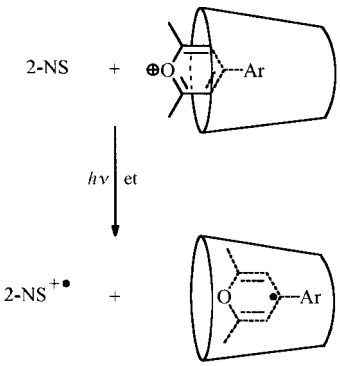


Fig. 7 Kinetic traces in the (a) absence and (b) presence of β-CD for **3**–2-NS system.



Scheme 2

according to eqn. (3). Because of the spatial separation of the donor and acceptor, the rate of electron transfer will be reduced in comparison to that in homogeneous solution. The pyranyl radical formed will move towards the interior of the cavity because of its hydrophobicity and high affinity towards the β-CD and the 2-NS radical cation would move away from the CD. This reduces the rate of back electron transfer and leads to the longer lifetime of the pyranyl radicals.

5 Conclusions

We have studied the encapsulation of pyrylium salts **1–6** in β-CD cavities by fluorescence and NMR methods. **1** and **6** did not undergo encapsulation. The fluorescence properties and NMR spectra of **2–5** are affected by β-CD indicating that these salts undergo encapsulation in the β-CD cavity. The equilibrium association constants in these cases were determined using a Benesi–Hildebrand treatment. The fluorescence profiles and NMR chemical shifts of these salts in the presence of β-CD were used to deduce useful information about the structures of the inclusion complexes in these cases. We have shown that pyrylium salts in the β-CD encapsulated state can undergo electron transfer with a quencher present in the aqueous phase. Using laser flash photolysis we have shown that the pyranyl radicals formed as a result of electron transfer within the β-CD cavity are protected from back electron transfer for long periods of time.

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