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Influence of cyclodextrin complexation on the emission of thioflavin T and its off-on control

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Abstract

The effect of cyclodextrin (CD) complexation on the emission of thioflavin T is studied at room temperature. Formation of 2:1 (TFT^+:γ-CD) inclusion complex at lower concentration and 2:2 inclusion complex at higher concentration of γ-CD is observed. The formation of 2:1 inclusion complex caused a decrease in the emission intensity and an increase in the emission intensity with a red shift in the emission band due to the formation of emittive dimer by the 2:2 inclusion complex. The observed dimer emission in the presence of γ-CD underwent "off–on" switching in the presence of an acid. In the acid medium, the TFT^+ molecule underwent protonation and the protonated dye molecule ($TFTH^{2+}$) cannot form dimer in the cavity of γ-CD because of the electrostatic repulsion. 3D emission spectral studies were carried out for the γ-CD inclusion complex of TFT^+. Enhancement in the emission intensity of TFT^+ was noticed in the presence of β-CD and hydroxypropyl–β-CD (HPCD). The dimer emission of TFT^+ was not observed in the presence of β-CD and HPCD. The stoichiometries of the inclusion complexes were found to be 1:1 and 1:2 (TFT^+:β-CD) in the case of β-CD and 1:1 in the case of HPCD. Formation constants were calculated for the inclusion complexes of TFT^+ with different CDs. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Thioflavin T; Cyclodextrin; Dimer emission; "Off–on" control

1. Introduction

The use of cyclodextrins (CDs) as an organized medium for controlling the chemical [1–4] and photochemical [5–9] reactions received much attention in the past few years. These CDs are naturally occurring cyclic oligomers comprised of glucopyranose units [1]. Since these molecules have a unique molecular architecture that is shaped like a truncated cone with a hollow, hydrophobic cavity, guest molecules of proper size can be accommodated into the cavity of CDs to form inclusion complexes [1–9]. There is an interest in manipulating the complexation as this is the key to applying CD in the fields as diverse as pharmacology, analytical chemistry, organic synthesis, photochemistry and photophysics [1–10]. In particular, these host–guest systems are considered as good models for studying protein–ligand interactions and enzymatic analysis.

Considerable attention has been focused on the use of CDs in luminescence applications [11–24]. It is observed that many probe molecules exhibit enhanced luminescence upon complexation with CDs. The enhanced luminescence of the probe molecule is due to the protection of the probe molecule inside the cavity from external quenchers and also due to increased local viscosity in the CD cavity with concomitant reduction of oxygen quenching [11]. The quenching of the fluorescence is also observed when the guest molecule is included into the cavity of CDs [25]. Aggregation and deaggregation of monomer and dimer dye molecules in the presence of CDs have also been observed [26,27]. The CDs, in particular γ-CD, is known to increase the formation of dimer and excimer by the inclusion of multiple guest molecules into its cavity [28]. The excimer emission of different molecules like pyrene, naphthalene, oxazole and their derivatives have been observed in the presence of CDs [22,23].

Thioflavin T, 3,6-dimethyl-2-(4-dimethylaminophenyl)-benzothiazolium cation (TFT^+) (Scheme 1), is a benzothiazolium dye and it has been used for staining amyloid and paraamyloid tissues [28]. The temperature dependent spectral properties of TFT^+ in solution and the formation of ground state dimer at low temperatures (300–77 K) have been studied [29]. The interaction of TFT^+ with DNA and clays have also been reported [30,31]. In the present investigation, we report the γ-CD induced dimer emission of TFT^+ and its "off–on" control in the presence of an acid. The influence of β-CD and hydroxypropyl–β-CD (HPCD)

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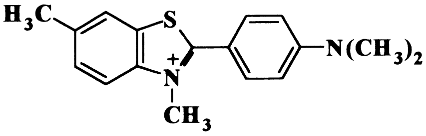

Scheme 1. Structure of thioflavin T (TFT^+).

complexation on the spectral properties of TFT^+ is also described.

2. Experimental

TFT^+ (Aldrich) was thrice recrystallized from methanol and characterized by absorption spectrum [29]. α-CD, β-CD, γ-CD and HPCD (Aldrich) were used as received. All other chemicals used in this investigations are of analytical grade. All the measurements were carried out at room temperature (25°C). Water used in this investigation was doubly distilled over alkaline potassium permanganate in an all-glass apparatus. Absorption spectra were recorded using JASCO UV-vis spectrophotometer. Fluorescence measurements were performed using Hitachi F4500 spectrofluorometer. The excitation and emission slits were set at 5 nm for all the measurements. The excitation wavelength for the protonated and unprotonated TFT^+ molecules are 310 and 330 nm, respectively. To prepare samples for complexation studies, 1 ml of the aqueous stock solution of TFT^+ (2.6×10^{-4} M) was diluted to 10 ml containing appropriate amount of β-CD/γ-CD. The molecular dimensions of the TFT^+ molecule were measured by simulating the molecular model using Biosym–InsightII molecular modeling software in a silicon graphics computer system.

3. Results and discussion

3.1. Absorption and emission spectra of TFT^+ in aqueous solution

The absorption spectrum of TFT^+ in aqueous solution shows an absorption band at 412 nm [29]. The absorbance at 412 nm increased with the increase in the concentration of TFT^+ and the absorption band was not shifted even at very high concentration. Shirra [29] reported that the TFT^+ molecules form ground state dimer at low temperature (300–77 K) and the dimer shows absorption bands at 364 and 460 nm. The TFT^+ molecules undergo protonation in acidic solution ($pK_a=1.6$) and an absorption band was observed at 310 nm for the protonated TFT^+ molecule ($TFTH^{2+}$) (Fig. 1).

$$TFT^+ + H^+ \rightleftarrows TFTH^{2+} \qquad (1)$$

The emission spectrum recorded for the TFT^+ in aqueous solution shows an emission band at 450 nm. At higher concentrations of TFT^+ ($>1.8\times10^{-3}$ M), the dye molecule shows a very weak emission band at 584 nm. The excitation spectrum recorded at low concentration of dye shows only one excitation band at 330 nm. However, at higher concentration, two weak excitation bands at 330 and 480 nm were observed. The weak emission band observed at higher concentration of the dye can be due to the formation of an emittive dimer. It is interesting to note that, unlike other dye molecules [32], the protonated TFT^+ dye molecule is fluorescent and it shows an emission band at the same wavelength (450 nm) as the unprotonated dye molecule.

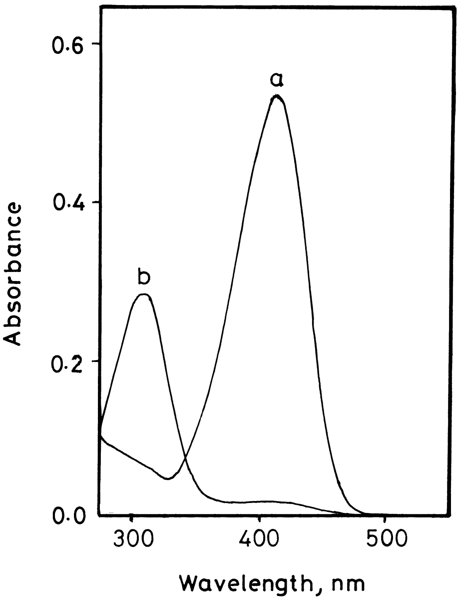

Fig. 1. Absorption spectra of TFT^+ (2.1×10^{-5} M): (a) in aqueous solution and (b) in the presence of 0.5 M HCl.

3.2. Emission of thioflavin T in aqueous γ-CD solution

The absorption spectra of TFT^+ in the absence and presence of γ-CD were recorded and showed a small increase in the absorbance at 412 nm due to the formation of inclusion complex. It has been observed that the TFT^+ molecules undergo dimerization in the ground state at low temperature and shows absorption bands at 364 and 460 nm [29]. In the present investigation, we could not observe such absorption band for dimer even at higher concentrations of TFT^+ in the absence and presence of γ-CD at room temperature.

The emission spectra of TFT^+ in aqueous solution in the absence and presence of different concentrations of γ-CD are shown in Fig. 2. An observable decrease in the emission intensity with a small red shift in the emission band was observed in the presence of lower concentrations of γ-CD ($\leq1\times10^{-3}$ M). An isoemissive point at 500 nm was observed at lower concentrations of γ-CD. Further increase in the concentrations of γ-CD lead to an increase in the emission intensity with a large red shift in the emission band. At higher concentrations ($\geq2\times10^{-2}$ M) of γ-CD, the emis-

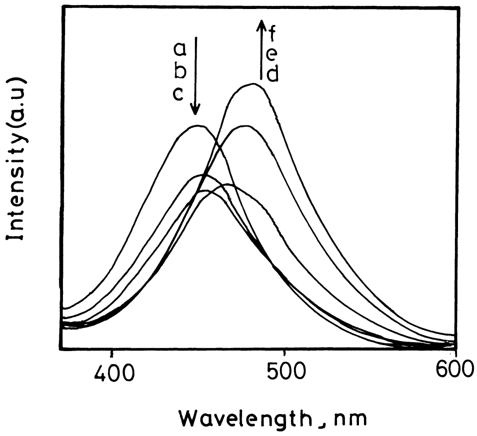

Fig. 2. Emission spectra of TFT^+ (2.65×10^{-5} M) at different concentrations of γ-CD. [γ-CD]: (a) 0.0, (b) 7.7×10^{-4}, (c) 1.5×10^{-3}, (d) 8.28×10^{-3}, (e) 1.7×10^{-2} and (f) 2.1×10^{-2} M. Excitation is at 330 nm.

sion band was observed at 481 nm. The emission spectra recorded at higher concentrations of γ-CD deviated from the isoemissive point (500 nm) observed at lower concentrations of γ-CD. It indicates that the equilibrium involves two different stoichiometries. The decrease in the emission intensity at lower concentrations of γ-CD is ascribed to the self-quenching of the TFT^+ fluorescence by the inclusion of two TFT^+ molecules into the cavity of γ-CD (2:1 TFT^+: γ-CD inclusion complex). Since the internal cavity diameter of γ-CD (9.2 Å) is large enough to accommodate two TFT^+ molecules in its cavity, the inclusion of two dye molecules into the cavity of γ-CD is feasible. The observed increase in the emission intensity and the appearance of a new band at 481 nm at higher concentrations of γ-CD are attributed to the formation of emittive dimer by the 2:2 (TFT^+: γ-CD) inclusion complex (reactions (2) and (3)).

$$2TFT^+ + \gamma\text{-CD} \rightleftarrows (TFT^+)_2 - \gamma\text{-CD} \quad (2)$$

$$(TFT^+)_2 - \gamma\text{-CD} + \gamma\text{-CD} \rightleftarrows \gamma\text{-CD} - (TFT^+)_2 - \gamma\text{-CD} \quad (3)$$

The TFT^+ molecule can be regarded approximately as a rectangular volume of dimensions 16.5×7.0×5 Å. Since the depth of the cavity is only 7.8 Å, the whole molecule cannot be included into the cavity of γ-CD. In such case, part of the molecule is projected out of the cavity and this allows the encapsulation of the projected part of the TFT^+ by another γ-CD.

The observed red shifted emission in the presence of γ-CD was due to the formation of emittive dimer by the stepwise formation of 2:2 inclusion complex (reactions (2) and (3)). At lower concentration the emission intensity decreased due to the formation of 2:1 inclusion complex and at higher concentration the emission intensity increased due to the formation of 2:2 inclusion complex. When one CD molecule encapsulate two dye molecules, part of the dye molecules will be exposed to the homogeneous solution. However, when two CD molecules encapsulate the dye molecules they are completely isolated from the homogeneous solution and the dye molecules can experience a restricted microenvironment. The red shifted dimer emission was not observed in the presence of β-CD and it will be discussed latter.

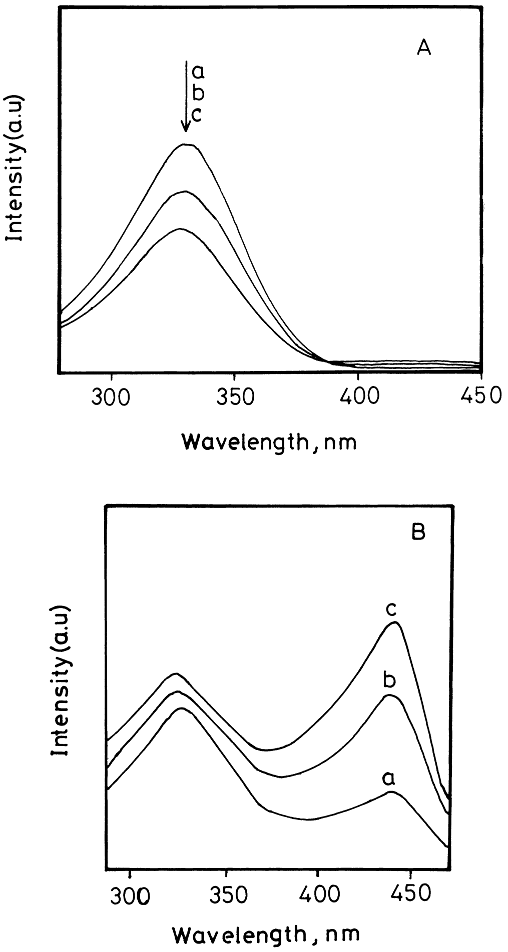

Fig. 3. Excitation spectra of TFT^+ (2.65×10^{-5} M) in the presence of different concentrations of γ-CD. (A) at lower concentrations: (a) 0.0, (b) 7.7×10^{-4} and (c) 1.5×10^{-3} M (emission is at 450 nm). (B) at higher concentrations: (a) 8.28×10^{-3}, (b) 1.7×10^{-2} and (c) 2.1×10^{-2} M (emission is at 481 nm).

In order to further confirm the observed emission of the TFT^+–γ-CD inclusion complex, the excitation and 3D emission spectral studies have been performed. The excitation spectra recorded at different concentrations of γ-CD are shown in Fig. 3. In the absence and at lower concentrations of γ-CD only one excitation band was observed at 330 nm. However, at higher concentrations of γ-CD an additional excitation band was observed at 440 nm and is ascribed to the formation of the emissive dimer. Excitation of the molecule at 440 nm shows a very intense emission at 481 nm due to the dimer of TFT^+ (Fig. 4). The spectra recorded at lower concentrations of γ-CD show an isosbestic point at 388 nm (Fig. 3(A)). The excitation spectra recorded at higher concentrations deviate from the isosbestic points. The 3D emission contours recorded for TFT^+ in the absence and presence of γ-CD are shown in Figs. 5 and 6 and the corresponding excitation and emission spectra are also

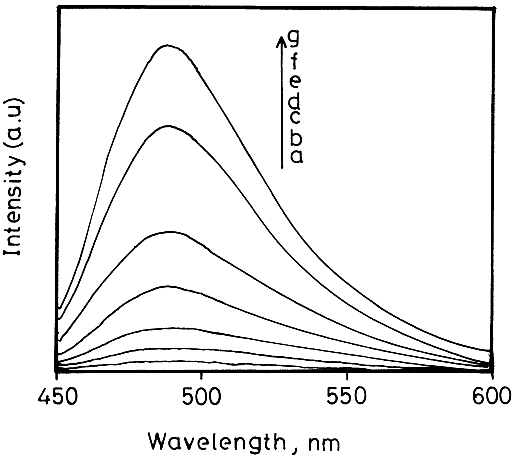

Fig. 4. Emission spectra of TFT^+ (2.65×10^{-5} M) in the presence of different concentrations of γ-CD. [γ-CD]: (a) 0.0, (b) 7.7×10^{-4}, (c) 1.5×10^{-3}, (d) 8.28×10^{-3}, (e) 1.7×10^{-2} and (f) 2.1×10^{-2} M. Excitation is at 440 nm.

shown. In the absence of γ-CD, TFT^+ molecule shows only one contour as shown in Fig. 5. The excitation spectrum shows only one band as discussed earlier. The contour intensity decreased at lower concentrations of γ-CD and a new contour was observed upon increasing the concentrations of γ-CD. At higher concentrations of γ-CD, two contours were observed as shown in Fig. 6 and the corresponding excitation spectrum shows two excitation bands at 330 and 443 nm due to the monomer TFT^+ and the dimer, respectively. The new contour observed at higher concentrations of γ-CD is due to the formation of 2:2 inclusion complex. These results confirm that the formation of 2:1 inclusion complex at lower concentrations of γ-CD leads to the self-quenching of the TFT^+ fluorescence and the formation of 2:2 inclusion complex at higher concentrations of γ-CD leads to the red shift and enhancement in the emission band. In the absence of γ-CD, the 3D spectrum of TFT^+ at higher concentration (1.8×10^{-3} M) showed a very weak emission band at 548 nm and it was not observed at lower concentrations of TFT^+ in the absence of γ-CD. However, in the presence of γ-CD a very intense dimer emission was observed even at lower concentration of TFT^+ (2.6×10^{-5} M). This means that the γ-CD complexation induces the formation of emittive dimer TFT^+. Since the TFT^+ molecule is in the planar configuration [29], two dye molecules can be included into the cavity of γ-CD in a sandwich manner with an anti-conformation because of the positive charge density in the thiazole ring. The observed dimer emission in the presence of γ-CD is due to the formation of 2:2 inclusion complex (reactions (2) and (3)). This 2:2 inclusion complex was not formed by the association of two 1:1 inclusion complex as it has been observed for pyrene in the presence of γ-CD [21]. In the presence of β-CD we have not observed the dimer emission because it cannot include two dye molecules in its cavity (vide infra).

It is very interesting to note that the observed emission of γ-CD inclusion complex of TFT^+ undergoes "off–on" switch in the presence and absence of an acid. The emission of TFT^+ observed at 481 nm in the presence of γ-CD was not observed in acidic solution and it was observed only in neutral aqueous solution. The emission spectra recorded at different concentrations of γ-CD in aqueous acidic solution (0.2 M HCl) show a small increase in the emission intensity and the emission intensity did not occur in the initial stage upon the addition of γ-CD as observed in the aqueous solution. It shows that the inclusion of two dye molecules into the cavity of γ-CD was not occurred in the presence of acid. Since the TFT^+ molecules undergoes protonation in the presence of acid, the inclusion of two protonated TFT^+ molecules into the cavity of γ-CD was not possible due to the electrostatic repulsion between the two dye molecules. These results confirm that the emission observed in aqueous γ-CD solution is due to the formation of 2:2 inclusion

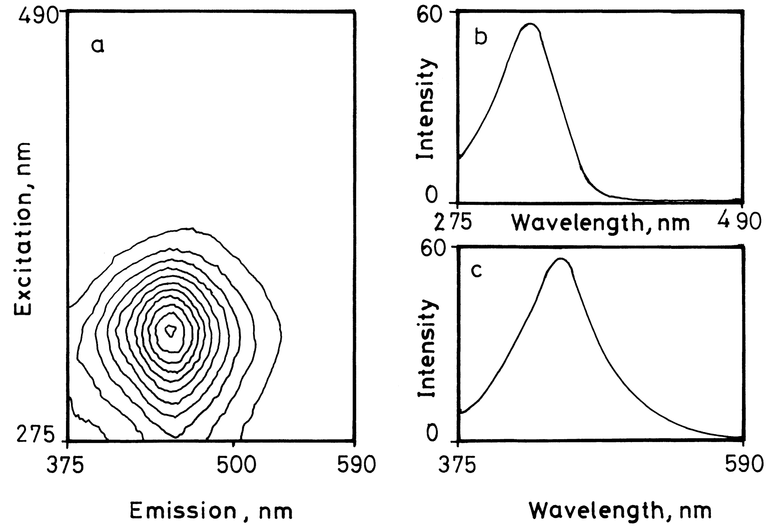

Fig. 5. 3D emission spectra of TFT^+ (2.65×10^{-5} M) in the absence of γ-CD: (a) contour plot, (b) corresponding excitation spectra and (c) emission spectra.

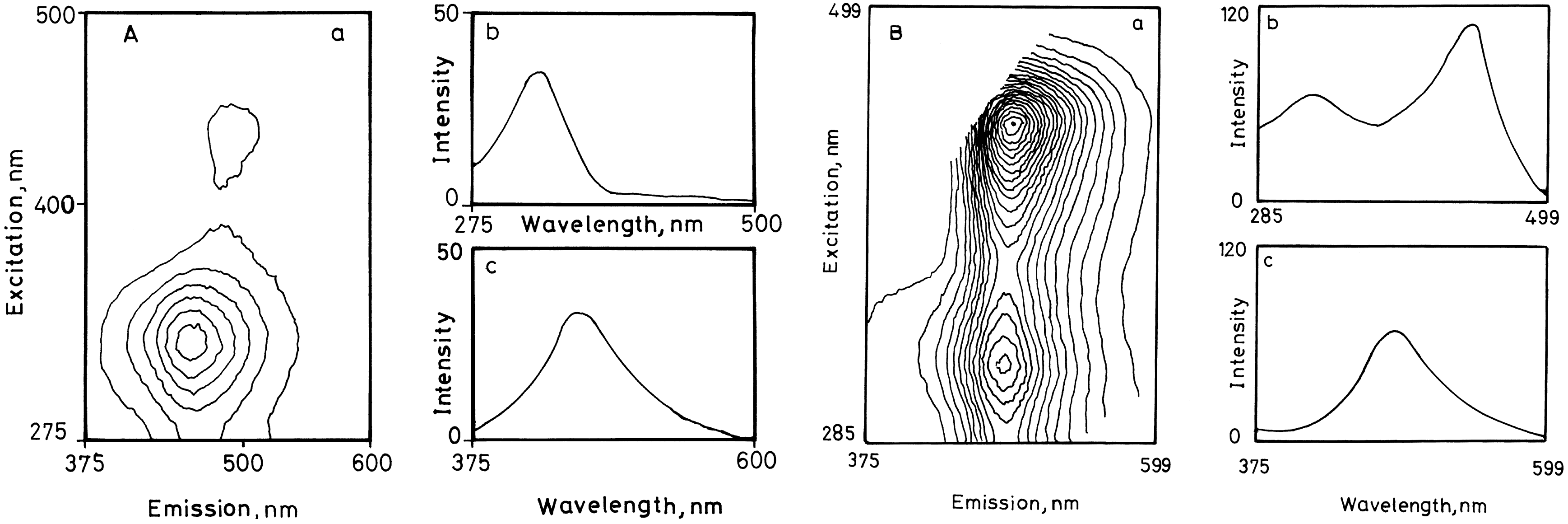

Fig. 6. 3D emission spectra of TFT$^+$ (2.65×10^{-5} M) in the presence of: (A) 2.5×10^{-3} M and (B) 1.8×10^{-2} M of γ-CD. (a) Contour plot, (b) corresponding excitation spectra and (c) emission spectra.

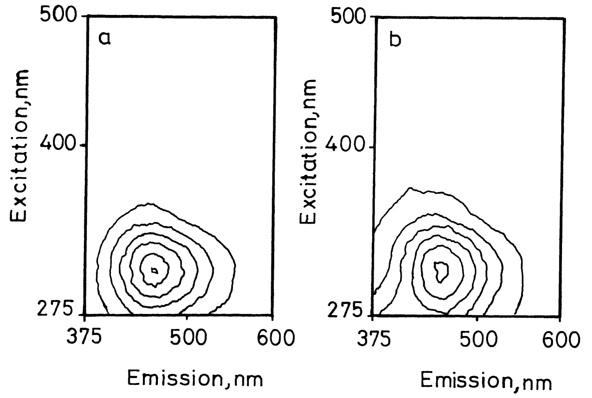

Fig. 7. 3D emission spectra of TFT$^+$ (2.65×10^{-5} M) in the presence of 0.2 M of HCl. (a) [γ-CD]: 0 and (b) [γ-CD]: 1.8×10^{-2} M.

complex. The "off–on" switch observed in the presence and absence of acid was further confirmed by recording the 3D spectra. Fig. 7 shows the 3D emission spectra recorded for the acidic (0.2 M HCl) solution of TFT$^+$ in the absence and presence of γ-CD. Only one contour corresponding to the protonated dye was observed in the absence and presence of γ-CD. However, the addition of γ-CD to an aqueous solution of TFT$^+$ shows two contours (Fig. 6) as described earlier. Thus the emission of γ-CD inclusion complex of TFT$^+$ undergoes "off–on" switch in the presence and absence of acid.

The formation constants for the inclusion of TFT$^+$ into the cavity of CDs were calculated by Benesi–Hildebrand equation using linear and nonlinear regression analysis (Eqs. (4) and (5)) [10]. The decrease in the emission intensity has been used to calculate the formation constant.

$$1/(I - I_0) = [1/K_1(I_1 - I_0)].[1/[\mathrm{CD}]] + 1/(I_1 - I_0), \qquad (4)$$

$$I = \frac{I_0 + I_1 K_f[\mathrm{CD}]}{1 + K_f[\mathrm{CD}]}, \qquad (5)$$

where I_0 and I_1 denotes the fluorescence intensity in pure water and in the complex, respectively, and I is the fluorescence intensity at a given CD concentration. The calculated formation constant values are given in Table 1.

3.3. Spectral properties of TFT$^+$ in the presence of β-CD

The absorption spectra of TFT$^+$ in the presence of β-CD did not show significant change in the absorption spectrum. A very small increase in the absorbance at 412 nm was observed due to the inclusion of TFT$^+$ into the cavity of β-CD. However, the emission spectra in the presence of β-CD show a significant enhancement in the emission intensity and a small blue shift (2–3 nm) in the emission band (Fig. 8) at higher concentration of β-CD. An enhancement in the fluorescence intensity of the guest molecules by the CD encapsulation has been reported and these effects have been attributed to a decrease in the rotational freedom of the guest molecule and the removal of water molecules from the CD cavity which can quench the excited state molecule [5]. The enhancement in the emission intensity is due to the inclusion of the TFT$^+$ into the cavity of β-CD. The reduced polarity and restricted microenvironment provided by the β-CD cavity increase the emission intensity of TFT$^+$.

Table 1
The formation constants for the inclusion of TFT$^+$ in to the cavity of CDs

CD	Stoichiometry	K_f [a]
γ-CD	1:2	960
β-CD	1:1	4890
β-CD	2:1	395
HPCD	1:1	4106

[a] Average of three experimental values; error limit: 10–15%.

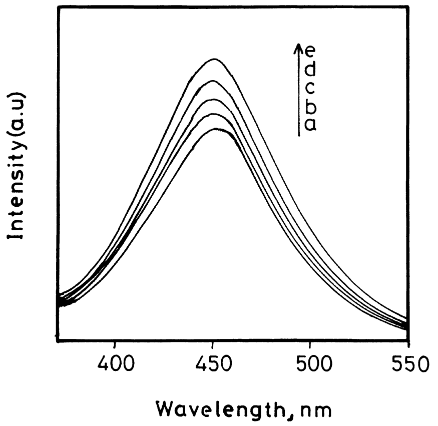

Fig. 8. Emission spectra of TFT$^+$ (2.65×10^{-5} M) in the presence of different concentrations of β-CD. [β-CD]: (a) 0.0, (b) 5.2×10^{-4}, (c) 1.057×10^{-3}, (d) 2.6×10^{-3} and (e) 5.2×10^{-3} M.

Fig. 9 illustrates the double reciprocal plot for the TFT$^+$–β-CD inclusion complex. The plot is not well described as a single straight line according to Eq. (4). It shows the existence of the inclusion complexes of two different stoichiometries. The initial linear portion at higher concentrations of β-CD contains K_2 for the 1:2 (TFT$^+$: β-CD) inclusion complex, while the final linear part at lower concentrations

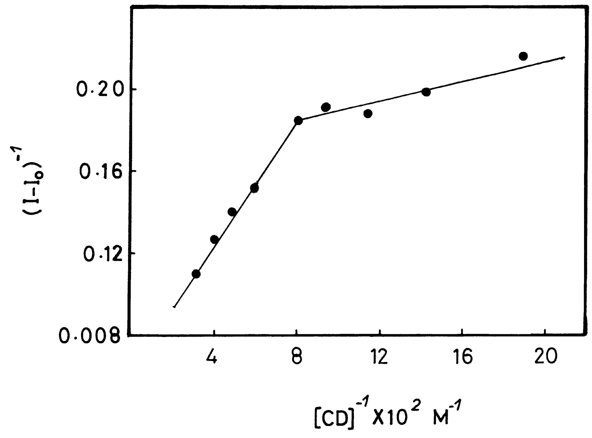

Fig. 9. The double reciprocal plot for the β-CD:TFT$^+$ system.

of β-CD contains K_1 for the 1:1 inclusion complex. Thus the equilibrium contains two inclusion complexes of stochiometry 1:1 and 1:2 and the formation constants can be evaluated from the slopes and intercepts. The formation constants were calculated by linear and nonlinear regression analysis and the values are given in Table 1. The molecular dimensions of the TFT^+ molecule allows the formation of 1:2 (TFT^+:CD) inclusion complex. The formation of 1:2 inclusion complex is feasible because the length of the TFT^+ molecule is 16.5 Å. The formation of 1:1 and 1:2 (guest: β-CD) inclusion complexes of substituted 3-H-indoles having the similar carbon skeleton of TFT^+ has been reported in the literature [10].

The absorption and emission spectral studies were also carried out for the TFT^+ molecule in the presence of HPCD and very similar results were observed as in the case of β-CD. However, the formation of 1:2 (TFT^+:CD) inclusion complex was not noticed in the presence of HPCD. The double reciprocal plot showed a single straight line showing the formation of 1:1 (TFT^+:HPCD) inclusion complex. The presence of bulky hydroxypropyl group hinders the formation of 1:2 (TFT^+:HPCD) inclusion complex. The formation constant value observed for the complexation of TFT^+ with HPCD is lower than that of the value obtained for the complexation of TFT^+ with β-CD. It shows that the complexation between TFT^+ and HPCD is relatively weak when compared to β-CD. The diminished complexing ability of HPCD relative to β-CD was due to the steric hindrance caused by the introduction of the hydroxypropyl moiety at the mouth of the CD cavity [11]. The formation constant values obtained for 1:1 and 1:2 inclusion complexes of β-CD shows that the stability of the 1:1 complex is higher than that of the 1:2 inclusion complex.

The 3D spectra recorded for the TFT^+ molecule in the absence and presence β-CD show only one contour. An increase in the contour intensity was observed in the presence of β-CD. The excitation spectra recorded in the presence and absence of β-CD show only one excitation band at 330 nm. Dimer emission was not observed for the TFT^+ in the presence of β-CD and HPCD. Since the internal cavity diameter of β-CD is small, only one TFT^+ molecule can be accommodated in its cavity. The α-CD did not show any influence on the absorption spectrum of TFT^+ and has little influence on the emission spectrum. Since the cavity diameter of α-CD is only 4.5 Å, the inclusion of TFT^+ into the cavity of α-CD is not possible and the observed very small increase in the emission intensity can be due to the inclusion of the $-N(CH_3)_2$ group of the TFT^+ molecule into the cavity of α-CD.

To further investigate the inclusion complexation of TFT^+, a series of fluorescence quenching experiments were carried out by taking iodate ion as a quencher. The Stern–Volmer quenching constant (K_{sv}) decreased with the increase in the concentration of CDs. It indicates that the TFT^+ molecule is protected from the iodate ion quenching by complexation with CDs.

4. Conclusion

The γ-CD induced dimer emission of a cationic dye (TFT^+) at room temperature and its "off–on" control in the presence of an acid is reported. The formation of 2:2 inclusion complex is responsible for the red shifted dimer emission. The excitation and 3D emission spectral data of the γ-CD inclusion complex of TFT^+ confirm the formation of emittive dimer. The new band observed in the excitation spectrum and the new contour formed at higher concentrations of γ-CD are ascribed to the formation of emittive dimer. The inclusion of two TFT^+ molecules within the two CD cavities (2:2 dye: γ-CD complex) can act as a noncovalent molecular adhesive in constructing supramolecular structure of CD. In the acid medium, the TFT^+ molecule undergoes protonation and the protonated dye is fluorescent. The emission of TFT^+–γ-CD inclusion complex undergoes "off–on" switch with acid, i.e., the dimer emission is not observed in the presence of acid. Significant enhancement in the emission intensity of TFT^+ is observed in the presence of β-CD and HPCD. The formation of the 1:1 and 1:2 inclusion complexes of TFT^+ are observed with β-CD and 1:1 inclusion complex with HPCD. Dimer emission is not observed for the TFT^+ in the presence of β-CD and HPCD. The failure to dimer emission of TFT^+ in the presence of β-CD and HPCD is attributed to the smaller CD cavity size. The complexation between TFT^+ and HPCD is weak when compared to β-CD. The α-CD does not show any influence on the absorption and emission spectral properties of TFT^+. The Stern–Volmer quenching constants (K_{sv}) calculated in the presence of CDs decrease with the increase in the concentration of CDs due to the protection of TFT^+ molecule by the CD cavity wall.

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References

[1] J. Szejtli, Cyclodextrin and Their Inclusion Complexes, Akademiai Kiado, Budapest, 1982.
[2] G. Wenze, Angew. Chem. Int. Ed. Engl. 33 (1994) 803.
[3] K.A. Connors, Chem. Rev. 97 (1997) 1325.
[4] S. Li, W.C. Purdy, Chem. Rev. 92 (1992) 11157.
[5] K. Kalyanasunderam, Photochemistry in Microheterogeneous Systems, Academic Press, London, 1987.
[6] V. Ramamurthy, D.F. Eaton, Acc. Chem. Res. 21 (1988) 300.
[7] V. Ramamurthy, R.G. Weiss, G.S. Hammond, Adv. Photochem. 18 (1993) 67.

[8] Y. Okuno, Y. Chiba, O.J. Yonemitsu, Chem. Soc., Chem. Commun. (1984) 1638.

[9] E. Adar, Y. Degani, Z. Goren, I. Willner, J. Am. Chem. Soc. 108 (1986) 4696.

[10] S. Nigam, G. Durocher, J. Phys. Chem. 100 (1996) 7135.

[11] R.P. Frankwich, K.N. Thimmaich, W.L. Hize, Anal. Chem. 63 (1991) 2924.

[12] N.J. Turro, G.S. Cox, X. Li, Photochem. Photobiol. 37 (1983) 149.

[13] S. Scypinski, L.J. Cline Love, Anal. Chem. 56 (1984) 331.

[14] G.S. Cox, N.J. Turro, N.C. Yang, M.J. Chen, J. Am. Chem. Soc. 106 (1984) 422.

[15] J.I. Clin III, W.J. Dressick, J.N. Demas, B.A. Degraff, J. Phys. Chem. 89 (1985) 94.

[16] S. Hasimoto, J.K. Thomas, J. Am. Chem. Soc. 107 (1985) 4655.

[17] S. Das, K.G. Thomas, K.J. Thomas, P.V. Kamat, M.V. George, J. Phys. Chem. 98 (1994) 9291.

[18] D. Joykrishna, E.L. Roberts, I.M. Warner, J. Phys. Chem. A 102 (1998) 301.

[19] T. Yorozu, M. Hoshino, M. Imamura, J. Phys. Chem. 86 (1982) 4426.

[20] A.P. De Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, Chem. Rev. 97 (1997) 1515.

[21] A. Ueno, I. Suzuki, T. Osa, J. Am. Chem. Soc. 111 (1989) 6391.

[22] R.A. Agbaria, D. Gill, J. Phys. Chem. 92 (1988) 1052.

[23] S. Hamai, J. Phys. Chem. 90 (1990) 2595.

[24] R.A. Agbaria, E. Roberts, I.M. Warner, J. Phys. Chem. 99 (1995) 10056.

[25] J.M. Schutte, T.T. Ndou, A. Munoz de la Pena, K.L. Greene, C.K. Williamson, I.M. Warner, J. Phys. Chem. 95 (1991) 4897.

[26] Y. Degani, I. Willner, Y. Haas, Chem. Phys. Lett. 104 (1984) 496.

[27] W.G. Herkstroeter, P.A. Matric, S. Farid, J. Am. Chem. Soc. 112 (1990) 3583.

[28] S. Waldrop, H. Puchtler, S.N. Meloan, J. Histotecnol. 7 (1984) 123.

[29] R. Shirra, Chem. Phys. Lett. 119 (1985) 463.

[30] A. Margulis, H. Rozen, S. Nir, Clays Clay Minerals 36 (1988) 270.

[31] A. Parker, T.A. Joyce, Photochem. Photobiol. 18 (1973) 467.

[32] S.A. John, R. Ramaraj, J. Appl. Polym. Sci. 65 (1997) 777.