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Original Research Article

Dual Fluorescence and Photoprototropic Characteristics of 2-Aminodiphenylsulphone-β-Cyclodextrin Inclusion Complex

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Abstract

The absorption and fluorescence spectral characteristics of 2-aminodiphenylsulphone (2ADPS) have been investigated in the presence of β-cyclodextrin (β-CDx) in water. Dual emission is observed upon the complexation of 2ADPS in β-CDx. The stoichiometry of the host:guest inclusion complex is found to be 2:1. Steady state and time-resolved fluorescence spectral analysis support the formation of 2:1 complex between β-CDx and 2ADPS. The large enhancement in fluorescence intensity of twisted intramolecular charge transfer (TICT) band in aqueous β-CDx solution is due to the decrease in non-radiative processes. The ground and the excited state pK_a values for the monocation-neutral equilibrium of 2ADPS in β-CDx are found to be different from the pK_a values in aqueous solution. In the presence of β-CDx, 2ADPS is found to be less basic in the ground and the excited states.

Introduction

Sulphur functionalities like sulphides, sulphoxides and sulphones are found to determine the biological properties of the parent molecule [1, 2]. Diphenylsulphide and its corresponding sulphoxide and sulphone derivatives are intermediates in the manufacture of some xenobiotics. Diphenylsulphones and their derivatives are found to be pharmaceutically and industrially important [3, 4].

Cyclodextrins are one of the most widely studied molecules which can form unique structures with organic fluorophores through weak, non-covalent bonding [5–7]. These are cyclic oligosaccharides usually consisting of 6, 7 and 8 glucose units (α-, β- or γ-CDx's respectively). They have special molecular structure with hydrophobic central cavity and a hydrophilic outer surface and so they are able to encapsulate molecules of appropriate size [7–9]. This encapsulating ability has countless applications in the fields such as drug design, water purification, food industry, analytical methods, etc [10]. These applications of CDx's come mainly from their inclusion complex formation and the alterations of physical, chemical and biological properties of guest molecules caused by the inclusion interaction. The inclusion behaviour can be investigated by spectrophotometric and fluorimetric measurements [11, 12].

In our earlier work we reported the inclusion complexation behavior of 4-aminobiphenyl in β-CDx [13]. The fluorescence and prototropic study of 2-aminodiphenylsulphone in aqueous solution revealed a different behaviour from 3,3′-diaminodiphenylsulphone and 4,4′-diaminodiphenylsulphone [14]. In this present work we have investigated the luminescence and prototropic characteristics of 2ADPS in presence of β-cyclodextrin solution.

Experimental

2-Aminodiphenylsulphone (Aldrich) and β-cyclodextrin (S.D. Fine) were used as received. The purity of 2ADPS was confirmed by the identical fluorescence emission spectrum in cyclohexane with different excitation wavelengths. Solutions in the pH range of 3–12 were prepared by adding appropriate amount of NaOH and H_3PO_4. A modified Hammett's acidity scale [15] (H_0) for the solutions below 1.5 (using H_2SO_4–H_2O mixture) was used. Owing to the poor solubility of 2ADPS in water, the stock solution was made in methanol. The concentrations of the solutions used for taking spectral measurements were of the order of 10^{-5} M in 3%

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methanol–water mixture. The 2ADPS solutions in β-CDx under high acid (6–8 M H_2SO_4) concentrations were used within one hour after the preparation in order to avoid the hydrolysis of β-CDx. It was found by UV spectra that β-CDx was stable up to 6 M H_2SO_4 for more than 5 h.

Absorption spectra were recorded using a HITACHI model spectrophotometer and fluorescence measurements were made using a JASCO FP-550 spectrofluorimeter. Fluorescence lifetime measurements were taken using a Time resolved single photon counting picosecond spectrofluorimeter (SPECTRAPHYSICS). pH values in the range of 2.0–12.0 were measured on ELICO pH meter model LI-1OT.

Results and discussion

The absorption spectral data of 2ADPS recorded at pH 6 with different concentrations of β-cyclodextrin are given in Table 1.

The absorption maximum is slowly red shifted from 316.4 to 324.8 nm with the increase in the concentration of β-CDx. The slight increase in the absorbance and the red shift are attributed to the encapsulation of 2ADPS by β-CDx and to the detergent action of β-CDx.The detergent action of β-CDx is due to its hydrophobic cavity and hydrophilic exterior surfaces formed by OH groups[5]. The absorption spectrum does not change even when recorded after 12 h.

Figure 1 represents the fluorescence spectra of 2ADPS with different amounts of β-CDx at pH 6. The wavelength 290 nm is used for excitation as there is no significant change in absorption at this wavelength. The fluorescence spectrum of 2ADPS in the absence of β-CDx has a single maximum at 440 nm. In aqueous β-CDx solution the fluorescence is intensified and blue shifted with the increase in β-CDx concentration up to 0.0024 M after which there is no shift and enhancement of fluorescence. A new fluorescence maximum at 334 nm is observed in the presence of β-CDx. This increases with the increase in the concentration of β-CDx. This dual emission is observed only in β-CDx. The blue shift in longer wavelength emission and the enhancement of fluorescence intensity reveal that there is inclusion of fluorophore in the non-polar cavity of β-CDx. The dual emission of 2ADPS may be due to two emitting states in

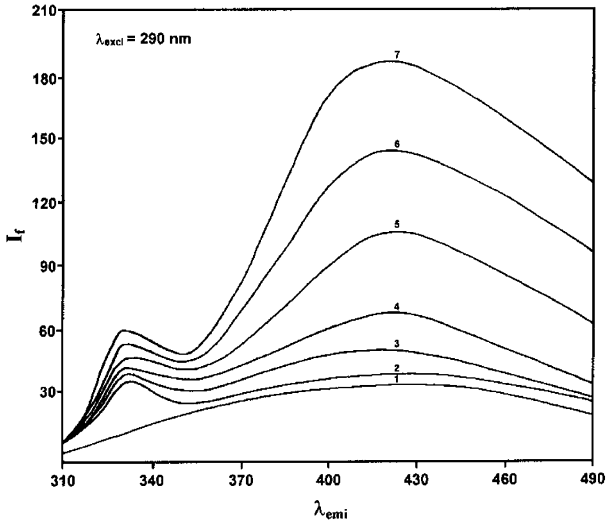

Figure 1. Fluorescence emission spectra of 2ADPS at different concentrations of β-CDx (at pH 6). (1). 0 M β-CDx, (2). 0.0004 M β-CDx, (3). 0.0008 M β-CDx, (4). 0.0012 M β-CDx, (5). 0.0016 M β-CDx, (6). 0.002 M β-CDx, (7). 0.0024 M β-CDx.

β-CDx solution. To analyse the dual emission, fluorescence spectra in cyclohexane, methanol and glucose solutions are compared with that of 2ADPS in β-CDx (Figure 2). In cyclohexane only one peak at 365 nm is obtained whereas in methanol and glucose only the longer wavelength maximum is observed. Aminodiphenylsulphones are reported to undergo twisted intramolecular charge transfer in the excited singlet state [16, 17] and it has been found that these molecules yield two emitting states in polar solvents. The two emitting states are locally excited (LE) and twisted intramolecular charge transfer (TICT) states. In our previous work we observed the dual emission for 3DADPS and 4DADPS but not for 2ADPS. The absence of dual fluorescence for 2ADPS was reported to be due to the intramolecular hydrogen bonding between $-SO_2-$ and $-NH_2$ groups [14]. Since TICT states are more stabilised in polar solvents emission from TICT state is always red shifted. In 2ADPS the intramolecular hydrogen bonding is stronger in cyclohexane and twisting is restricted. Hence in cyclohexane emission from LE state at 365 nm is observed. In water intermolecular hydrogen bonding disrupts intramolecular hydrogen bonding and the TICT emission at 440 nm becomes very strong. Thus the LE emission is not observed. A similar spectrum is also

Table 1. Absorption and fluorescence spectral data of 2ADPS

Concentration of β-CDx M	Absorption maximum λ_{abs} nm (log ε)	Fluorescence maximum λ_{flu} nm (Excitation wavelength = 290 nm)
0	272.4 (3.82), 316.4 (3.87)	440
0.0004	273.6 (3.83), 319.6 (3.88)	334, 437
0.0008	273.8 (3.86), 323.0 (3.91)	334, 430
0.0012	273.8 (3.88), 324.2 (3.90)	334, 428
0.0016	273.8 (3.90), 324.8 (3.94)	334, 428
0.0020	274.2 (3.91), 324.8 (3.95)	334, 427
0.0024	274.6 (3.93), 324.8 (3.97)	334, 427

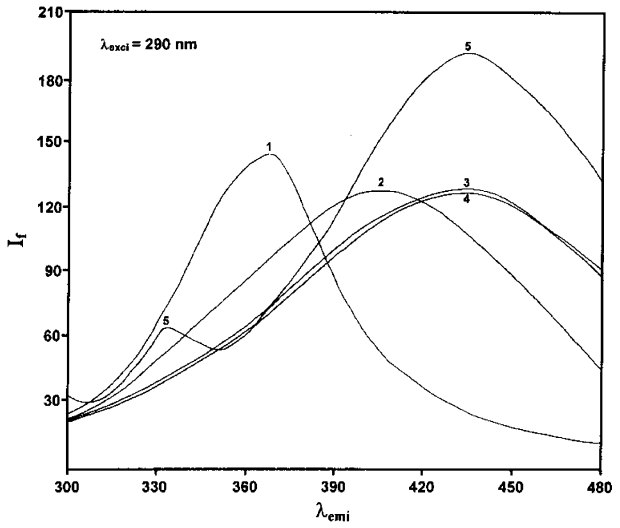

Figure 2. Fluorescence spectra of 2ADPS (2×10^{-5} M) with different solvents (λ_{exi} 290 nm.) (1. Cyclohexane, 2. Methanol, 3. Water, 4. D(+)-Glucose, 5. β-CDx).

observed in glucose solution.The disruption of intramolecular hydrogen bonding by intermolecular hydrogen bonding is less in methanol and so the fluorescence spectrum is in between water and cyclohexane. But in β-CDx the encapsulation stabilizes the LE state and LE emission starts appearing at 334 nm. The increase in fluorescence with increase in the concentration of β-CDx for both the LE (334 nm) and TICT (440 nm) emission bands is shown in Figure 3. The intensity increase is more for the longer wavelength emission. Generally, complex formation decreases the TICT emission as the twisting is restricted in the complex but in 2ADPS both LE and TICT emissions are increased by complex formation. This abnormal behavior is explained by the shape and stoichiometry of the inclusion complex in the next section.

The fluorescence excitation spectra of 2ADPS in β-CDx with the emission maxima corresponding to the LE and the TICT bands are found to resemble each other and the absorption spectra. This indicates the absence of red edge effect and the same ground state precursor for both the emissions [18].

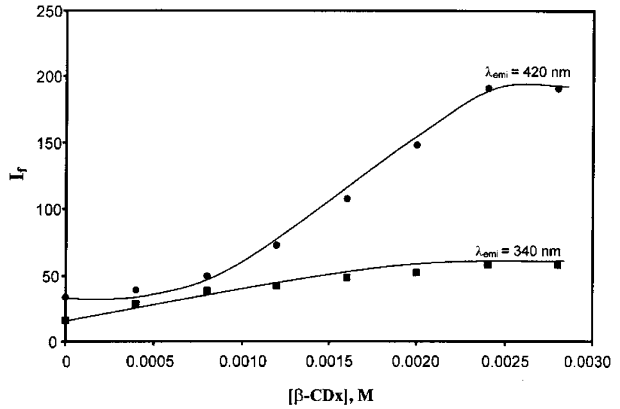

Figure 3. Fluorescence intensities of 2ADPS(2×10^{-5} M) with various concentrations of β-CDx at pH 6.

The binding constant and the stoichiometry of the inclusion complex are obtained from the Benesi–Hildebrand equation [19–21]. The change in absorbance is very small with the increase in β-CDx concentration and so the values obtained in fluorescence were used in Benesi–Hildebrand equations. The equations for 1:1 and 2:1 host:guest complexes are given below.

$$\frac{1}{I-I_0}=\frac{1}{I'-I_0}+\frac{1}{K(I'-I_0)[\beta\text{-CDx}]} \tag{1}$$

$$\frac{1}{I-I_0}=\frac{1}{I'-I_0}+\frac{1}{K(I'-I_0)[\beta\text{-CDx}]^2} \tag{2}$$

In the equations, I_0 is the intensity of fluorescence of 2ADPS without CDx, I is the intensity with a particular concentration of β-CDx, I' is the intensity of the fully complexed form at the highest conc. of β-CDx and K is the binding constant. In this case at the highest concentration of 0.0024 M β-CDx we observed only 80.72% of the complexed form from the relative amplitude data (Table 2). Since there was no change in the amplitude and the fluorescence spectrum of complexed form with further increase in the conc. of β-CDx we have taken the I' value of 80.72% as the fluorescence intensity of the complexed form. There is no emission from the LE state initially and even after the addition of β-CDx, the increase in LE emission is not significant when compared to TICT emission. The inclusion effect on LE emission is very less. So the Benesi–Hildebrand plot has been drawn with the fluorescence intensity values at 440 nm. The Benesi–Hildebrand plots for the complexation of 2ADPS in β-CDx are shown in Figure 4. A non-linear curve is obtained when $\frac{1}{I-I_0}$ is plotted against $\frac{1}{[\beta-\text{CDx}]}$ (inset of Figure 4). A linear plot is observed for the plot of $\frac{1}{I-I_0}$ against $\frac{1}{[\beta-\text{CDx}]^2}$ (Figure 4). This suggests the formation of 2:1 host–guest inclusion complex between β-CDx and 2ADPS. The binding constant is calculated to be 1.26×10^5 M^{-2}. The formation of 2:1 complex is also confirmed by lifetime measurements. The lifetimes of 2ADPS along with their amplitude and χ^2 values with different concentrations of β-CDx are given in Table 2.

By the addition of β-CDx, the decay becomes biexponential. Single exponential fitting for 2ADPS without β-CDx and biexponential fitting for 2ADPS with all concentrations of β-CDx give best χ^2 values. The best biexponential fit from 0.0004 M β-CDx to 0.002 M β-CDx shows the existence of one inclusion complex along with the free species. The amplitude decreases for the free molecule and increases for the complexed form with the increase in concentration of β-CDx. The lifetime of the complex is longer than the lifetime of the free species. At very low concentrations (<0.0004) there may be the formation of 1:1 complex. But 1:1 complex formation was not observed by fluorescence spectral

Table 2. Time-resolved fluorescence spectral data of 2ADPS (Excitation wavelength = 278 nm, detection wavelength = 440 nm)

Concentration of β-CDx M	Lifetime (s)	Relative amplitude	χ^2	Standard deviation (s)
0	1.19×10^{-9}	100	1.08	1.99×10^{-10}
0.0004	1.21×10^{-9}	36.45	1.17	4.40×10^{-11}
	2.41×10^{-9}	63.55		1.41×10^{-10}
0.0008	1.18×10^{-9}	27.57	1.21	4.91×10^{-11}
	2.74×10^{-9}	72.43		1.55×10^{-10}
0.0016	1.16×10^{-9}	25.21	1.04	5.13×10^{-11}
	3.03×10^{-9}	74.79		1.78×10^{-10}
0.0024	1.15×10^{-9}	19.28	1.23	5.04×10^{-11}
	3.42×10^{-9}	80.72		2.01×10^{-10}

measurements. At concentrations above 0.0004 M we observed no significant change and also a triexponential decay in lifetime measurements. Hence in the concentration range from 0.0004 M to 0.0024 M only one complex with the stoichiometry of 2:1 is formed. In this case good χ^2 values are obtained only for biexponential fit (Table 2).

Effect of acidity

The absorption and the fluorescence spectra of 2ADPS with β-CDx(0.0024 M) have been studied in the H_0/pH range of −4.89 to 6. The absorption spectra at different H_0/pH are shown in Figure 5. When the pH is decreased from 6, a blue shifted absorption spectrum is obtained due to the protonation of the amino group. The spectrum does not change below H_0−4.89.

The fluorescence spectra of 2ADPS with β-CDx at different H_0/pH are presented in Figure 6. Decrease of pH from 3 causes the intensity of fluorescence to decrease up to H_0−2.28. During the increase of acidity, at H_0 −1.5, a blue shifted fluorescence spectrum starts appearing. This is due to the formation of monocation. As observed [14] in aqueous solution proton induced quenching occurs initially up to H_0−1.5.

The ground state pK_a value for the neutral-monocation equilibrium is determined using absorption spectral data and it is −1.83. This is different from the ground state pK_a value (−0.16) in aqueous solution [14]. Because of complexation in β-CDx the protonation may be difficult and requires a more acidic condition.

The fluorimetric titration curve for the neutral form and the monocation are given in Figure 7. There is no correspondence between the decrease of fluorescence of

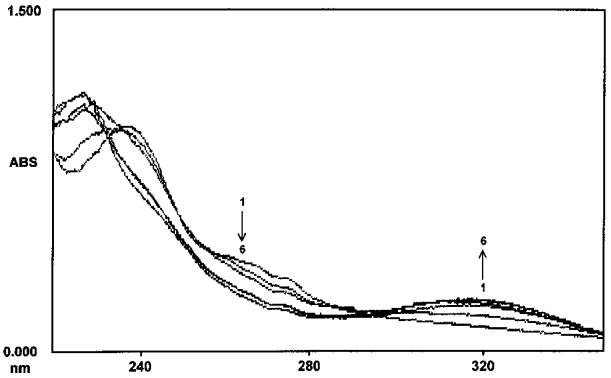

Figure 5. Absorption spectra of 2ADPS (2×10^{-5} M) with β-CDx at different H_0 values (**1**. H_0 −2.76, **2**. H_0 −2.06, **3**. H_0 −1.85, **4**. H_0 −1.38, **5**. H_0 −0.26, **6**. H_0 +0.13).

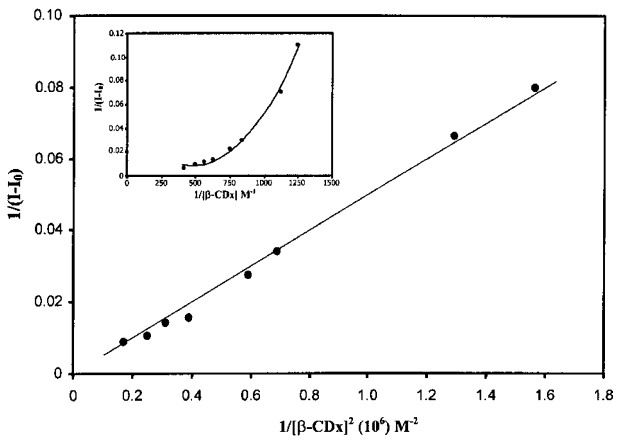

Figure 4. Benesi–Hildebrand plot for 1:2 complexation of 2ADPS (2×10^{-5} M) with β-CDx. (inset: Non-linear curve obtained for 1:1 complex formation).

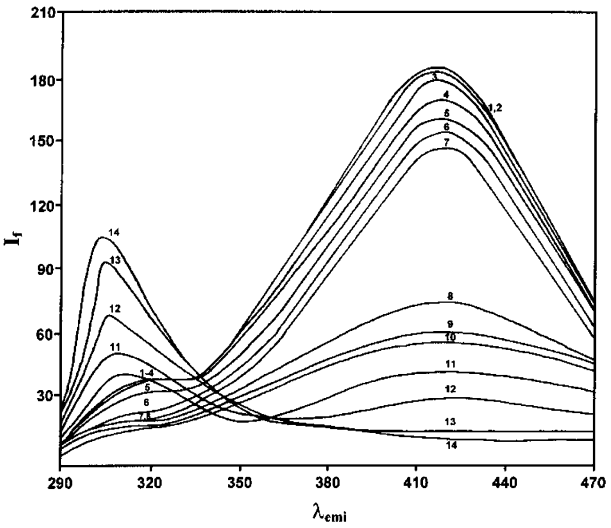

Figure 6. Fluorescence spectra of 2ADPS (2×10^{-5} M) with β-CDx at different H_0/pH values (**1**. pH 2.5, **2**. pH 2.0, **3**. pH 1.5, **4**. pH 1.0, **5**. H_0 + 0.44, **6**. H_0 + 0.13, **7**. H_0−0.26, **8**. H_0 −1.38, **9**. H_0 −1.85, **10**. H_0 −2.28, **11**. H_0 −2.76, **12**. H_0−3.32, **13**. H_0−3.87, **14**. H_0 −4.89).

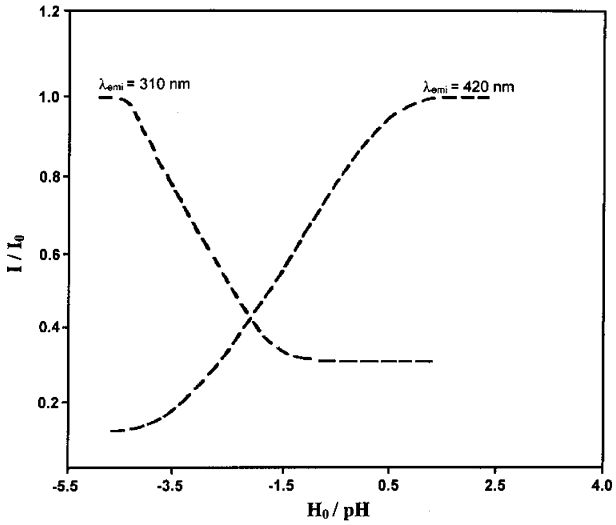

Figure 7. Fluorimetric titration curves for 2ADPS without and with β-CDx

the neutral form and the increase of monocation fluorescence. Though the fluorescence of the neutral form decreases from pH 3, monocation starts forming only from H_0−1.5. The decrease of fluorescence of the neutral form from pH 3 to H_0−3.5 by the addition of acid can only be due to two processes: (i) proton induced fluorescence quenching as observed in other aromatic amines [14, 22] (ii) protonation of the neutral form after H_0−1.5. So the decrease of fluorescence for a long range (from pH 3 to H_0−3.5) is due to both processes. In these cases the mid point of the monocation formation curve (−3.4) is taken as the excited state pK_a value [22]. This kind of behaviour is usually observed in amino compounds. In aqueous solution the excited state pKa reported by fluorimetric titration is −1.5 [14]. In the excited state also the protonation requires a more acidic condition in β-CDx than in aqueous solution. This may be due to the hydrogen bonding between the nitrogen atom of the amino group with the proton of the hydroxyl groups of the two β-CDx rims making the lone pair of amino nitrogen atom less available [23]. The ground and the excited state pK_a values of 2ADPS in β-CDx are compared with those in aqueous solution (Table 3).

Based on the photophysical and prototropic behaviour of 2ADPS in β-CDx, the possible structure of the 2:1 complex between β-CDx and 2ADPS is given in Figure 8.

This structure explains the unusual increase in the TICT emission along with the LE emission by

Table 3. Ground and excited state pK_a values of 2ADPS

Equilibrium monocation ⇌ Neutral	Ground state pK_a	Excited state pK_a
Without CDx*	−0.16	−1.5
With β-CDx	−1.83	−3.4

* From Reference 14.

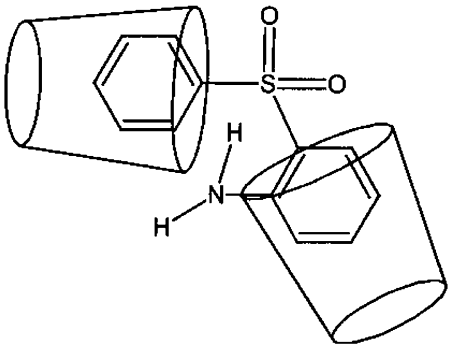

Figure 8. Schematic diagram of the inclusion complex (1:2) of 2ADPS with β-CDx.

the addition of β-CDx. In this structure one half of the molecule is inside the cavity of one β-CDx and the other half inside the other β-CDx. This structure will not affect the twisting in the compound.

By MOPAC/AM1 calculations the C–S–C angle is found to be 101.6° and the length of the molecule to be 8.695 Å. Since the molecule is bent it cannot be encapsulated in one β-CDx molecule. Both sides of the molecule are inside the non-polar hydrophobic cavity of two β-CDx molecules. Although the reduced polarity inside β-CDx should decrease the TICT emission of 2ADPS, the opposite effect is observed. This abnormal behavior can be explained as follows. In the less polar cavity of β-CDx the dipole-dipole interaction between TICT state and the environment in the β-CDx cavity will be less. This will destabilise the TICT state and consequently the energy gap between the TICT and the Frank-Condon ground state will increase. This is confirmed by the significant blue shift in TICT emission band. The increase in the energy gap reduces the non-radiative transition from the TICT state and thus the TICT emission intensity is enhanced. From the large enhancement of TICT emission in β-CDx solution and from the observation of TICT emission in solid matrices [24] it can be concluded that the restriction on molecular motion by increased viscosity in the β-CDx cavity does not affect the formation of the TICT state. A similar behaviour in the 2:1 complex of β-CDx with 2-(4′-N,N-dimethylaminophenyl)-1H-naphth[2,3-d]imidazole was reported [25].

Conclusions

Based on the above results it is found that 2:1 complex is formed between β-CDx and 2ADPS. The dual fluorescence of 2ADPS in aqueous β-CDx solution is due to the emission from LE and TICT states. The large enhancement of TICT emission relative to LE emission is explained by the less dipolar interaction of highly polar TICT state of 2ADPS with the less polar cavity of β-CDx. The fluorescence enhancement also reveals that the restriction in molecular motion does not play a major role in the photophysical properties of the molecule. The ground and excited state pK_a values indicate

that more acidic condition is required for the protonation of 2ADPS−β-CDx inclusion complex.

Acknowledgements

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