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Dual luminescence of dimethylaminobenzaldehyde in aqueous β-cyclodextrin: non-polar and TICT emissions

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Abstract

Absorption as well as steady-state and time-resolved emission studies of p-dimethylaminobenzaldehyde (DMABA) in aqueous β-cyclodextrin (βCD) solutions have been reported. Dual fluorescence corresponding to the non-polar (NP) and twisted intramolecular charge transfer (TICT) has been observed. Two types of ground state DMABA–βCD complexes are proposed. The twisted intramolecular charge transfer (TICT) emission is severely suppressed for the complex where the fluorophore is totally encapsulated but it is enhanced due to the reduced polarity imposed by the βCD-microenvironment for the complex where DMABA is only partially enclosed.

Keywords: Dual luminescence; Dimethylaminobenzaldehyde; β-Cyclodextrin; Non-polar emission; TICT emission

1. Introduction

Cyclodextrins are interesting microvessels capable of embedding appropriately sized fluorophores and thus providing restriction in space and a reduced polarity in the near vicinity of the chromophore [1–8]. This space restriction and lowering of micropolarity are shown to influence a number of photophysical/photochemical processes [5–8] including the twisted intramolecular charge transfer [9–13]. The TICT phenomenon, though discovered only in the early 1970s, has received immense attention and has been the subject of several recent studies [9–21]. Since TICT involves the rotation of a group around a bond (the ring–NMe_2 bond for commonly studied systems) which will be restricted in a rigidly packed environment, CDs of different core size are expected to influence the TICT emission differently. Again, the reduced polarity of the CD-microenvironment as compared to water has some influence on the luminescence properties. Thus, the overall effect is likely to be rather complex and is likely to depend on the cavity size of the cyclodextrin. In a recent study [13], we have shown that DMABA is only partially enclosed within αCD (diameter approx. 4.5 Å) and the twisting of the dimethylamino group is not restricted. Moreover, compared to the non-polar (NP) emission the TICT emission was found to be enhanced tremendously on complexation with αCD. This was ascribed to the lowering of polarity of the CD-microenvironment as this would lead to a lowering of the non-radiative decays from the TICT state to the low-lying states. We are now interested in studying the phenomenon in βCD (diameter approx. 6.5 Å) where the cavity is, perhaps, just large enough to enclose the entire fluorophore. If the fluorophore is tightly packed within the βCD cavity, the TICT emission is expected to be suppressed severely. But the following sections will report that both NP and TICT emissions are enhanced on complexation with βCD, although the rate of enhancement of the TICT compared to the NP yield is much less than was found in the case of αCD complexation [13]. The observation has been explained in the light of our earlier proposition [10], that two types of fluorophore–βCD complexes are formed in the ground state.

2. Experimental details

DMABA (Aldrich) was purified by vacuum sublimation followed by recrystallisation from 90% ethanol. The purity of the compound was checked using spectroscopic methods as well as TLC where it gave only a single spot. βCD was obtained from Aldrich and was used as received. Triply distilled water was used for

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the preparation of solutions. Although degassing of the solutions did not produce any difference in the basic observation, the reports are for deaerated solutions and the degassing was done with bubbling dry nitrogen.

A Shimadzu MPS 2000 absorption spectrophotometer and Spex Fluorolog were used to record the absorption and emission spectra respectively. For the time-resolved experiments the time-correlated single-photon counting technique was adopted [22] and a nitrogen flashlamp of nanosecond duration (Edinburgh Instruments, 199 fluorescence spectrometer) was used as the excitation source.

3. Results and discussion

The absorption spectra of aqueous solutions of DMABA as a function of βCD are shown in Fig. 1. With the addition of βCD the absorbance gradually increases with a slight blue shift of the absorption maxima. No isosbestic point could be noticed which rules out the possibility of a single equilibrium involving one-to-one complexation between the fluorophore and the βCD. Cyclodextrin complexes differing from 1:1 stoichiometry have been reported by several groups [5,7,10,23]. Two possibilities are proposed for this deviation. Firstly, more than one guest molecule can be accommodated within a single CD cavity. Secondly, due to the space restriction, more than one type of complex, each having 1:1 stoichiometry, may be formed. The following discussion proposes two distinct complexes, similar to those for dimethylaminobenzonitrile–β-cyclodextrin (DMABN–βCD) [10], one with DMABA completely enclosed within the βCD cavity and the other with part of the fluorophore projecting out of the cavity. The slight increase in absorbance is, presumably, due to the detergent action of CD and is attributed to the additional dissolution of DMABA adsorbed on the surface of the walls of the container [5,7,10].

Fig. 2 records the emission spectra of a series of DMABA solutions at various βCD concentrations and reflects a remarkable change in the emission properties of both NP and TICT states upon complexation. The TICT yield in pure aqueous medium is extremely poor. This has been ascribed to lowering of the energy of the TICT state through stabilisation in the highly polar environment resulting in a rapid non-radiative decay of the TICT state to the low lying states [9,10,13]. With the addition of βCD, both the non-polar (NP) and the TICT yields increase. The rate of enhancement of the TICT emission is, however, greater than that for the other band. This can be seen more clearly from looking at the normalised emission spectra (normalised, arbitrarily, at 425 nm) given in Fig. 3. While the NP emission yield in a 8 mM βCD solution is increased to double that in an aqueous medium, the TICT emission is

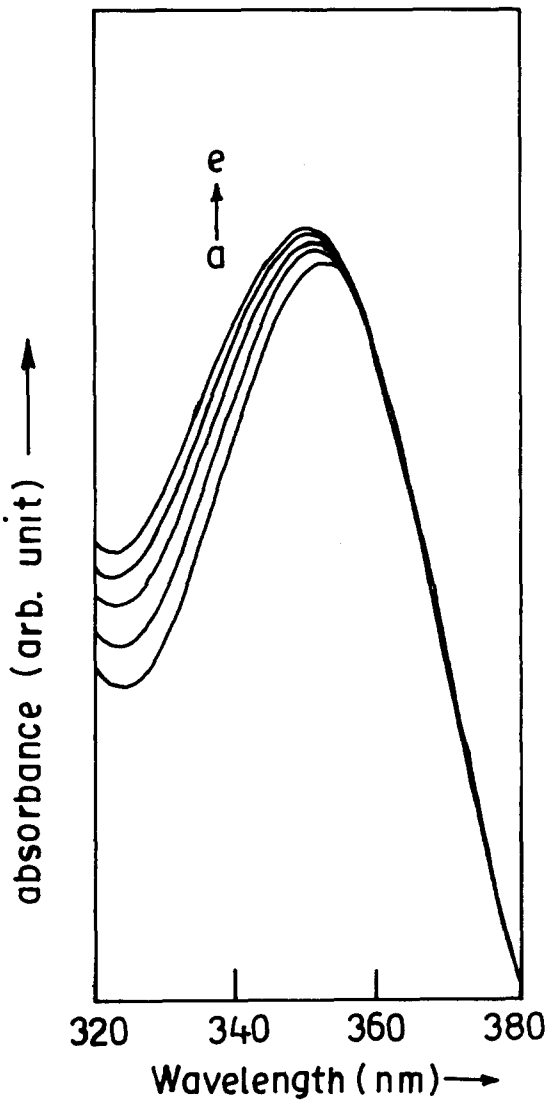

Fig. 1. Absorption spectra of 1×10^{-5} M aqueous solution of DMABA containing (a) 0 mM, (b) 1 mM, (c) 2 mM, (d) 5 mM and (e) 8 mM of βCD.

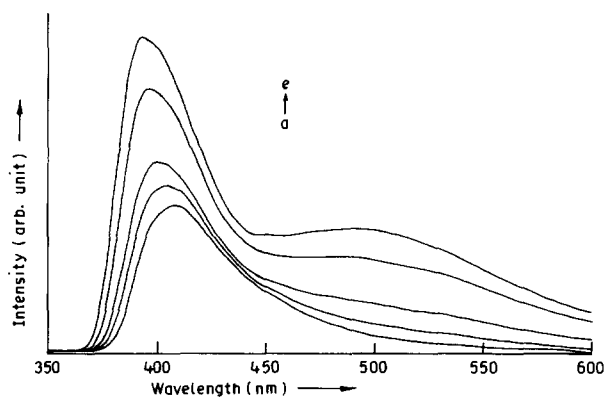

Fig. 2. Emission spectra of 1×10^{-5} M aqueous solution of DMABA containing βCD concentrations of (a) 0 mM, (b) 1 mM, (c) 2 mM, (d) 5 mM and (e) 8 mM.

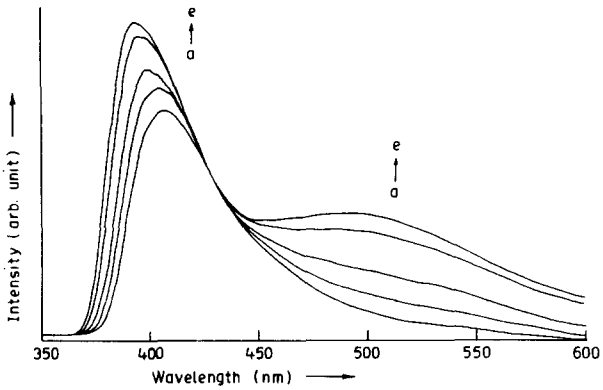

Fig. 3. Normalised emission spectra of 1×10^{-5} M aqueous solution of DMABA in βCD concentrations (a) 0 mM, (b) 1 mM, (c) 2 mM, d) 5 mM and (e) 8 mM (the normalisation was done at 425 nm arbitrarily).

enhanced to approx. 6×. The relative fluorescence enhancement, RFE (ratio of the enhancement of emission yield of TICT band to that of the NP band in presence of βCD) in other words, is about 3 with 8 mM βCD solution.

To ascertain if there is any parental relationship between the NP and TICT emissions, the excitation spectra corresponding to the two emissions (monitored at 400 nm and 500 nm respectively) were examined. We noticed a clear hypsochromic shift of the lowest energy band of the NP excitation spectrum (353 nm) as compared to that monitored at the TICT emission 359 nm) (Fig. 4). This small but distinct difference between the two excitation spectra indicates that the wo emissions are essentially due to two different sets of DMABA–βCD complexes having absorption maxima at 353 nm and 359 nm respectively. One can argue hat the differential enhancement in the two band ntensities may result from the difference in concenrations of the two ground state complexes as a function of [βCD] (because of different complexation constants) and thus from a variation of the OD's of these two orms at the excitation wavelength. Although we observed a small and gradual shift in the absorption spectra of DMABA with the addition of βCD, the change in OD was too small, particularly, at 356 nm $\lambda_{excitation}$ for emission studies and the midway between he two excitation maxima corresponding to the two emissions), to have any appreciable influence on the elative fluorescence yield of the NP and TICT bands and, hence, this was ignored.

Steady-state study thus indicates that the NP and TICT emissions in presence of βCD are due to two different sets of ground state DMABA–βCD complexes. This is further supported from our time-resolved study. Although both the emitting species are short lived, eliable lifetime values could be extracted through deconvolution. The decays become longer for both the species as we go on adding βCD (Table 1). Although

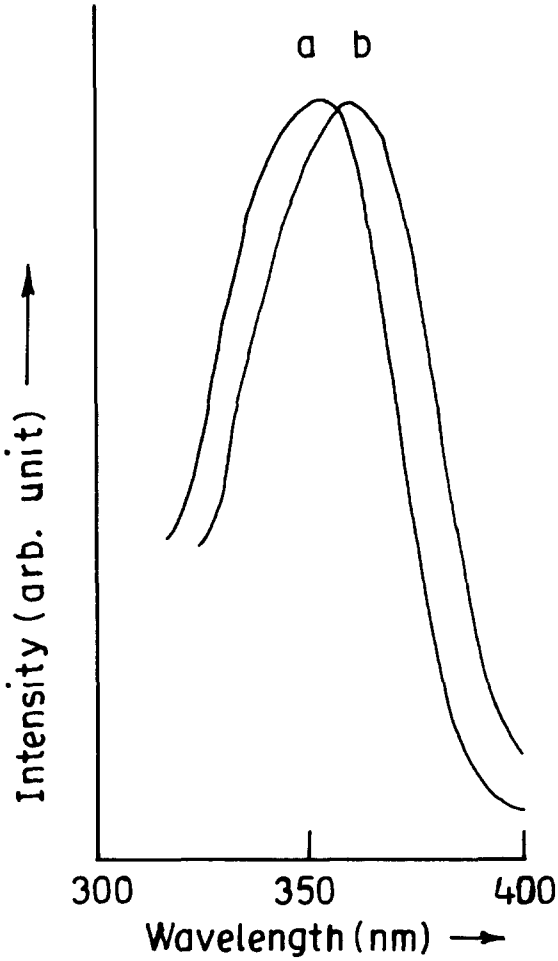

Fig. 4. Normalised excitation spectra of aqueous solution of DMABA containing 8 mM βCD monitored at (a) 400 nm and (b) 500 nm.

Table 1
Lifetime values (τ, ns) of non-polar (at 400 nm) and TICT (at 500 nm) species of DMABA in aqueous solution containing different concentrations of βCD

βCD concentration, (mM)	0.0	2.0	8.0
τ, ns, at 400 nm, for non-polar	0.96	0.99	1.05
τ, ns, at 500 nm, for TICT	0.91	1.12	1.19

in aqueous solution of DMABA, the TICT emission decays slightly faster than the NP emission, in a solution containing βCD, the decay of the latter becomes faster than the former (Table 1). The independent mode of change in the lifetime values of the two species with the addition of βCD, rules out any parental relation between them. Conforming with the proposition of Bhattacharyya et al. for DMABN [12], the two likely ground state complexes for the present system are depicted in Fig. 5.

Thus, steady-state as well as time-resolved studies reveal that the NP and the TICT emissions of DMABA in βCD solutions originate from two unrelated ground state complexes. The absorption maximum for the complex producing NP emission is at 353 nm while that

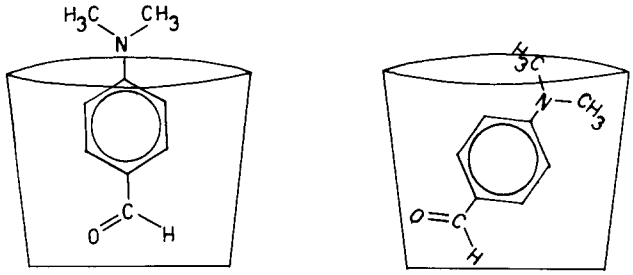

Fig. 5. DMABA–βCD complexes.

giving rise to the TICT emission is at 359 nm. We are now in a position to realise the enhancement of the two emissions, qualitatively. The blue shift of the TICT band with the addition of βCD indicates that the molecules are in a less polar microenvironment. Consequently, the TICT state is not sufficiently stabilised by solvation [10,12]. This increases the energy gap between the TICT state and the low-lying triplets and/or ground state which, in turn, reduces the rate of non-radiative transitions from the TICT. Thus, complexation of the fluorophore with βCD increases the TICT fluorescence. In our earlier communication [13], we have shown that in αCD, where only partial encapsulation of the fluorophore is possible due to the size factor, the enhancement in the nonpolar emission is inappreciable compared to the TICT emission. Thus the partially enclosed complex is supposed to be responsible for the TICT fluorescence only and makes hardly any contribution to the nonpolar emission.

The enhancement of the nonpolar emission is, however, interesting and can be rationalised as follows. It is now well known that with the lowering of the polarity of the medium the energy of the TICT state goes up resulting in an increase in the energy barrier for the NP to TICT transition [12,13,16,17]. The microenvironment within the CD cavity is essentially nonpolar and the fluorophore molecules, which are totally encapsulated within the βCD cavity, are practically incapable of producing TICT emission. Since the main non-radiative path (through TICT) is restricted the nonpolar emission is enhanced. Apparently, it seems that the steric hindrance to the twisting of the totally embedded fluorophore within the CD cavity is responsible for the lack of TICT emission. But this factor is proved to be of little significance when one finds that the TICT yield of the same DMABA is extremely low when it is positioned within the βCD cavity [24]. Here the probe finds ample space for twisting yet producing hardly any TICT, suggesting that amongst the two factors open to be operative it is the polarity factor which predominates over the steric restriction for controlling the TICT state formation.

Thus, while for the αCD complex of DMABA a part of the guest was necessarily out of the CD cavity allowing the twisting motion of the NMe_2 group about the phenyl ring; βCD, for its larger cavity size, it forms two types of inclusion complexes with the same fluorophore: one totally trapped within the core giving rise to the NP emission and the other with a part of the molecule out of the cavity, very similar to the αCD complex, enhancing the TICT emission.

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