

# Inclusion as a driving force for the intramolecular charge transfer (ICT) fluorescence of *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) in $\alpha$ -cyclodextrin ( $\alpha$ -CD) aqueous solution

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Received: 28 September 2007 / Accepted: 26 February 2008 / Published online: 18 March 2008  
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**Abstract** A 1:1 inclusion complex between *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) molecule and  $\alpha$ -cyclodextrin ( $\alpha$ -CD) in aqueous solution is formed with a stabilization constant of ca.  $45.65 \pm 3.59 \text{ M}^{-1}$  at 25 °C. The formation of the complex is accompanied by enhancement of the long wavelength fluorescence at 510 nm (attributed to intramolecular charge transfer (ICT) due to twisting) relative to the normal fluorescence at 420 nm. In water, the long-wavelength fluorescence is hidden under the red tail of the normal fluorescence band due to quenching by non-radiative transition. Inclusion by CD reduces quenching and thus constitutes a driving force for DPABME to emit at longer wavelength via ICT process.

**Keywords** Guest–host inclusion · Intramolecular charge transfer · Fluorescence · *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) · Cyclodextrins

## Introduction

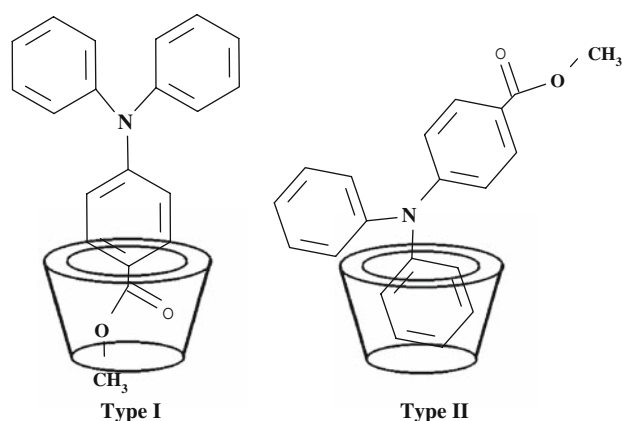
Fluorescence of organic molecules is used to probe micro-polarity and microviscosity of various cyclodextrins (CDs) in aqueous solutions [1–6]. CDs are oligosaccharides having a shape of a two open ends truncated cone, which varies in

size from 5.2 Å, 6.6 Å to 8.4 Å in  $\alpha$ -CD,  $\beta$ -CD and  $\gamma$ -CD, respectively [6]. The intensity, shape and wavelength of the fluorescence of certain probes in CD are highly dependent on their relative sizes and positioning (guest–host) inside the CD cavities [1–6]. As an example, Al-Hassan et al. [1–3], found that *p*-*N,N*-dimethylaminobenzonitrile (DMABN), a twisted intramolecular charge transfer (TICT) fluorescent probe [7], forms 1:1 as well as 1:2 inclusion complexes with  $\alpha$ -CD and 1:1 as well as 2:2 inclusion complexes with  $\beta$ -CD in aqueous solutions. These types of inclusion complexes were confirmed recently [8, 9] by using circular dichroism, transient triplet absorption and by theoretical calculations using MonteCarlo (DMC) calculations. In general, the number of compounds emitting from TICT excited state, like DMABN, are increasing in literature [7]. Since the ICT state results from the motion of one part of the molecule, donor, with respect to the acceptor [7], the use of CD to probe this motion due to inclusion is highly appreciated.

In the present study, we are investigating the role of  $\alpha$ -CD on the fluorescence of *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) (Scheme 1) in aqueous solutions. Previous investigators [10] made a fluorescence study on similar probes, namely *N*-(4-cyanophenyl)carbazole (CPC) [10] and hexadecyl 4-biphenylamino benzoate (HBAB) [11] in various solvents. Rettig and Zander [10] found CPC to emit either from a LE state, (called normal fluorescence or b-band),  $\lambda_f = 350 \text{ nm}$ , when present in non-polar hydrocarbon solvent or from a twisted state, called anomalous fluorescence or TICT-band,  $\lambda_f = 485 \text{ nm}$  when present in polar acetonitrile solvent. In polar acetonitrile, they suggested that CPC is pre-twisted around the carbazole-benzonitrile bond in the ground state and considered it to resemble with 3,5-dimethyl-*N,N*-dimethyl-*p*-aminobenzonitrile (3,5D-DMABN) [12]. Philips and

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**Scheme 1** The proposed 1:1 inclusion complexes (Types I and II) between *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) and  $\alpha$ -cyclodextrin ( $\alpha$ -CD)

co-workers [13], however, attributed the long emission in CPC to specific solute-solvent interaction and not to TICT state using supersonic jet experiment. On the other hand, Chen et al. [11] attributed the fluorescence of HBAB in various polar and non-polar solvents to result from TICT, ICT and LE states. Moreover, they considered triphenylamine as the donor and the hexadecyl ester group as the acceptor and suggested that twisting occurs around the phenyl-carbonyl bond. Their reasoning [11] has no experimental or theoretical support when TICT proposal [7] is used.

These contradictory interpretations motivated us to investigate the role of solvent and CD on the fluorescence of DPABME, a similar probe to CPC and HBAB. In hydrocarbons and acetonitrile [14], we found that DPABME's fluorescence is similar to those obtained by Rettig and Zander [10]. In various alcohols [14] we found that its fluorescence resembles those obtained by Chen et al. [11]. In water, however, the fluorescence was observed at shorter wavelength, as compared to acetonitrile and longer than that observed in hydrocarbon. This added another motivation to investigate its fluorescence in  $\alpha$ -CD aqueous solutions. We have observed that the long fluorescence is hidden under the long tail of the short fluorescent band and is enhanced upon inclusion with  $\alpha$ -CD. Our results are explained in terms of the TICT model used for DMABN and related compounds. The results obtained and the interpretation presented herein might help in understanding the photophysical properties of DPABME, which will have impact on their use as organic electroluminescence (OEL) probes in industry [11, 15].

## Experimental

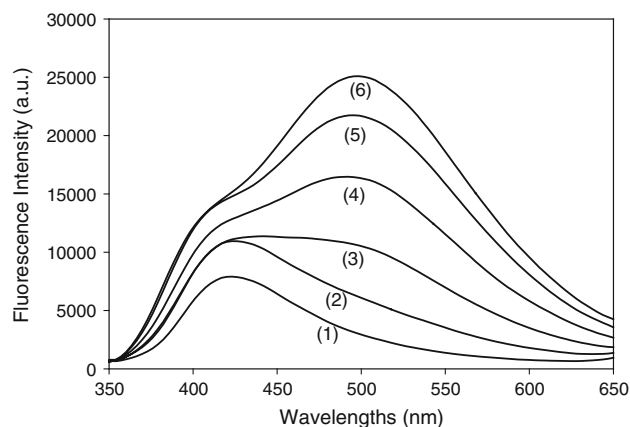
$\alpha$ -Cyclodextrin ( $\alpha$ -CD) (Wako Pure Products) was kindly supplied by Professor T. Azumi (Tohoku University,

Sendai) and used without further purification. *p*-(*N,N*-diphenylamino)benzoic acid methyl ester (DPABME) has been reported [16]. Water used was doubly distilled and all solutions of DPABME were made in pure water, with  $[DPABME] = 1 \times 10^{-5}$  M, unless otherwise specified. The absorption spectra were collected using a Labomed Double PC UV-Vis spectrophotometer, while the fluorescence spectra were measured using Edinburgh FS-900CDT fluorometer with excitation and emission bandwidth of  $4 \text{ nm} \pm 0.5$ ; the full description of the particular instrument is reported elsewhere [17]. The time-resolved data were measured using time correlated single photon counting (TCSPC) apparatus: Edinburgh Instrument Model 199 [17]. The sample was excited with a flash lamp filled with  $N_2$  at 1.5 bar operated at 8 kv of  $\sim 3 \text{ ns} \pm 0.5$  duration (half-width) with low-level light signals of repetition rate at  $\sim 20 \text{ kHz}$ . The excitation and emission bandwidth was  $10 \text{ nm} \pm 1$ .

## Results and discussion

The absorption spectra were measured for  $1 \times 10^{-5}$  M of DPABME in aqueous solutions in the absence and presence of  $\alpha$ -CD. The absorbance at maximum  $\sim 331 \text{ nm}$  shifts slightly to longer wavelength upon increase of the concentration of  $\alpha$ -CD. Such spectral changes might indicate the formation of inclusion complexes [3] between DPABME and  $\alpha$ -CD cavities.

The corresponding fluorescence spectra of ( $1 \times 10^{-5}$  M) DPABME show dramatic changes as compared to those in water, as shown in Fig. 1. In water, only one-fluorescence band with maximum  $\sim 420 \text{ nm}$  is observed, with a long tail extended beyond  $500 \text{ nm}$ . The second fluorescence band ( $510 \text{ nm}$ ) started to show up, along with the normal fluorescence band, and undergoes enhancement with the



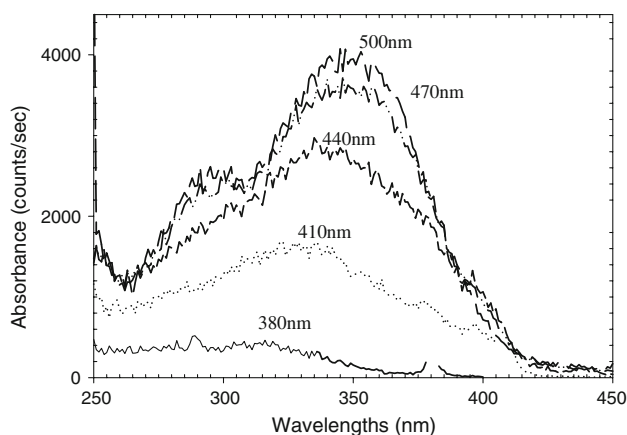
**Fig. 1** Fluorescence spectra of DPABME at 298 K ( $\lambda_{\text{ex}} = 335 \text{ nm}$ ) after 1 h from the addition of: (1) 0; (2) 2.5; (3) 4.7; (4) 6.7; (5) 8.6 and (6) 10.3 mM concentration of  $\alpha$ -CD in aqueous solutions

addition of  $\alpha$ -CD due to possible inclusion. Figure 1 also shows the quantum yield of the long fluorescence to increase 20 times by increasing the concentration of  $\alpha$ -CD to  $\sim 10$  mM.

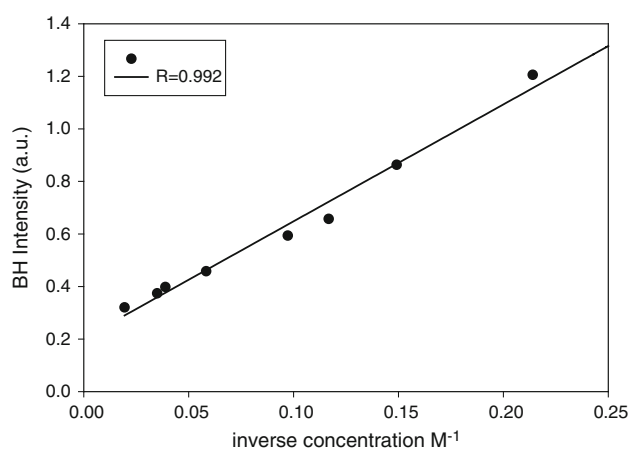
The corresponding excitation spectra are shown in Fig. 2 and indicate the formation of one type inclusion complexes between DPABME and  $\alpha$ -CD. This is unlike DMABN, which forms two types of inclusion complexes with  $\alpha$ -CD (see Fig. 5 in reference [2]) as evidenced by its different excitation spectra and TICT fluorescence (see Figs. 1 and 2 in reference [2]). It should be emphasized that two possible inclusion complexes (types I and II) are expected to form between DPABME and  $\alpha$ -CD, as illustrated by Scheme 1. However, only type I enables the two phenyl groups of the donor (*-N*-diphenyl amine) to be in resonance and in different plan with respect to the acceptor (*-methylbenzoate*), which encourages us to assume that type I inclusion complex overcomes that of type II (Scheme 1). Additionally, the formation of one type of inclusion complex is supported by the excitation-wavelength independent of DPABME's fluorescence in  $\alpha$ -CD. Finally,  $^1\text{H-NMR}$  data should also support the above argument with respect to complex formation and orientation of insertion of DPABME into the  $\alpha$ -CD cavity, however, the low solubility of DPABME in  $\text{D}_2\text{O}$  and the consequences of its low sensitivity to NMR prevented us from drawing any conclusion from the NMR results.

The stationary fluorescence data at 510 nm were analyzed using Benesi-Hilderbrand plots [18] as shown in Fig. 3 ( $K_a = 45.65 \pm 3.587 \text{ M}^{-1}$ ). The linear plot ( $R = 0.992$ ) indicates the presence of 1:1 inclusion complexes between DPABME and  $\alpha$ -CD in aqueous solutions.

The enhancement of the second fluorescence band (510 nm) in  $\alpha$ -CD is explained in terms of ICT model assuming that DPABME acts as a TICT probe when one part of the molecule behaves as a donor (diphenylamine)



**Fig. 2** The excitation spectra of DPABME ( $1 \times 10^{-5} \text{ M}$ ) in the presence of 10 mM of  $\alpha$ -CD at different emission wavelengths at 25 °C



**Fig. 3** Benesi-Hildebrand (BH) plot for 1:1 stoichiometry ( $R = 0.992$ ) and the association constant,  $K_a = 45.65 \pm 3.59 \text{ M}^{-1}$  at 25 °C

and the other part as an acceptor (methyl benzoate). This is consistent with the interpretation of Rettig and Zander [10], who considered carbazole as the donor and benzonitrile as the acceptor in explaining the long fluorescence from TICT state of CPC in acetonitrile. In acetonitrile solvent, both CPC and DPABME have similar emission and the locally excited state apparently is nonemissive. In alcohols, however, both bands (normal b-band and TICT) are present but the b-band (emission from locally excited state) appears as a shoulder at the blue edge of the emission spectrum of DPABME and is enhanced upon red-edge excitation [19].

In water, the short wavelength fluorescence (430 nm) overcomes the long wavelength fluorescence (510 nm) and the TICT apparently is nonemissive. This is similar to the observations of fluorescence of 4-(*N,N*-diethylamino)benzoic acid methyl ester (DEABEE) in water [20]. DEABEE is a well-known TICT probe, which emits from LE and TICT states with intensity depending on the polarity of the solvent. In water, the TICT is also apparently nonemissive. However, the long fluorescence overcomes that of the short fluorescence upon addition of  $\alpha$ -CD. This is most probably due to the role of water that stabilizes TICT energy state and thus enhances the nonradiative deactivation according to the energy gap law [21, 22]. The size of donor in the case of DPABME is relatively large making the angle of pre-twist large enough to facilitate twisting in polar aprotic solvent and thus emission is dominant from TICT state. Since equilibrium between the LE and TICT states is determined by the height of the barrier between the two states as well as on their relative positions with respect to the ground state, their relative intensity and lifetime are also determined by those factors. In water, the height of the barrier is small and the TICT state is closer to the ground state enhancing its quick formation from the LE state as well as its quenching through nonradiative transitions.

**Table 1** Amplitudes (A), time constants ( $\tau$ ) and  $\chi^2$  of the biexponential decays monitored at 440 and 510 nm measured for aqueous solutions of DPABME in water and in  $\alpha$ -CD at 25 °C upon excitation at 337 nm

( $\alpha$ -CD)/mM	A <sub>fast</sub>	$\tau_{fast}$ /ns	A <sub>slow</sub>	$\tau_{slow}$ /ns	$\chi^2$
0	60	1.00	40	5.47	1.00
8	71	1.23	31	4.64	1.00
16	75	1.17	25	4.40	0.993
23	79	1.32	21	5.15	0.995
32	77	1.33	23	5.33	0.909

Adding  $\alpha$ -CD leads to the inclusion, most probably, from the side of the acceptor (methyl benzoate) part of the molecule being smaller than the donor (*N*-diphenylamine) part. This causes DPABME to be in a slightly less polar medium relative to water, which destabilizing thus the TICT state, increasing the energy gap with respect to the ground state and reducing the nonradiative transition. This leads to an enhancement of emission from a TICT state.

This interpretation is consistent with the fluorescence results obtained in Fig. 1 and the lifetime measurements listed in Table 1. The biexponential decay of the fluorescence at 440 nm in water and in various  $\alpha$ -CD aqueous solutions indicates the presence of two sites of emission. In water the respective lifetimes were obtained to be 1.0 and 5.5 ns. In  $\alpha$ -CD, the quantum yield of the short lifetimes was increased, whilst that of long fluorescence was decreased and the respective lifetimes become 1.3 and 5.3 ns. When the decays were taken at 510 nm, the lifetimes were closely similar to those at 440 nm indicating that our instrument using N<sub>2</sub> and H<sub>2</sub> pulses ( $\tau_f$  equals 1.5 ns after deconvolution) is unable to resolve or differentiate between the two states making us unable to draw any conclusion from the lifetime measurements.

## Conclusions

The presence of two fluorescence bands for DPABME, where the longer wavelength starts to appear upon inclusion with  $\alpha$ -CD, lead us to the conclusion that DPABME is similar to DMABN and related compounds in the sense that it emits two fluorescence bands, a normal called b-band from the locally excited state, and an anomalous one from a twisted state and called TICT band. The relative intensity or the appearance of one at the expense of the other is determined by the polarity of the medium and many other factors quoted through text. This is in contrast to the findings of previous investigators [10] who suggested that the locally excited state is inemissive for this class of molecules when present in polar medium and concluded that the longer wavelength is due to emission from twisted

conformers, already present in the ground state of the molecule. Moreover, unlike Chen et al. [11] who suggests triphenylamine is the donor and hexadecyl ester the acceptor (for the case of HBAB, a similar compound to DPABME), we consider twisting to occur between diphenylamine (donor) and methylbenzoate (acceptor) in order to be consistent with the TICT mechanism suggested for DMABN [7].

**Acknowledgment** We would like to acknowledge Yarmouk University for financial support (grant no. 2007/14).

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