

Multiple fluorescence emission from hexyl *p*-*N,N*-dihexylaminobenzoate aggregates in water–dioxane binary mixtures: tuning of excited-state photophysics in self-assembly

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Abstract

The fluorescence and absorption spectra of three-long-alkyl-chain containing ester, hexyl *p*-*N,N*-dihexylaminobenzoate (HDHAB), a molecule capable of excited state intramolecular charge transfer (ICT), in water–dioxane binary solvent mixtures were recorded as a function of water volume fraction (Φ). It is clearly shown by the spectral variations that HDHAB molecules start to aggregate in the binary solvent at ca. $\Phi = 0.5$. Absorption spectra indicate that the aggregates are in J-form. It is observed that before aggregation HDHAB emits dual fluorescence typical of the presence of excited state ICT reaction, with ICT emission band red-shifting in position and decreasing in intensity with increasing Φ , while upon aggregation the low-energy emission shows a sudden blue-shift and the fluorescence spectrum is dominated by a band peaked at ca. 435 nm, together with two shoulders at ca. 350 and 400 nm, respectively. The 435 nm band is assigned to the emission from ICT state, while the 400 nm shoulder to excimer, and 350 nm shoulder to locally excited (LE) state. The results show that the ICT reaction in HDHAB aggregates is the dominant excited state reaction, differing from what is observed in cetyl *p*-*N,N*-dimethylaminobenzoate aggregates in similar solvents in which the excimer formation was a dominant excited state process. A tuning of the excited-state photophysics in self-assembly is thus shown. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Aggregate; Hexyl *p*-*N,N*-Dihexylaminobenzoate; Dual fluorescence; Excimer; Intramolecular charge transfer (ICT); Multiple emission

1. Introduction

It is well established that, in supramolecular and self-assembly, the relative mutual orientation

and the microenvironment of forming molecules are dramatically different from those in bulk phase [1–4]. Thus an appreciable change in the excited photophysics and photochemistry upon formation of a supramolecular assembly can be expected and this turns out to be true [1–11]

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Following this line one may alternatively expect that by using supramolecular assembly formation tuning of the excited-state photoprocesses can be performed. Herein described is our attempt to do this tuning by using a new kind of supramolecular assembly that is formed by aggregation of long-alkyl-chain containing organic molecules in water-organic solvent mixtures [5–11].

In the present work a three-long-chain containing fluorophore, hexyl *p*-*N,N*-dihexylaminobenzoate (HDHAB, Scheme 1), was synthesized and its aggregation and photophysics in water–dioxane mixtures studied by fluorescence and absorption spectroscopy. HDHAB was designed as it is capable of forming both intramolecular charge transfer (ICT) state [10–18] and excimer[9] in the photoinduced excited state.¹ Thus the directly populated locally excited (LE) state of HDHAB has at least two decay channels, i.e. to ICT state and to excimer.

Since the ICT state has a dipole moment much higher than that of the ground state and a molecular configuration change occurs during ICT reaction, it is understandable that the formation and emission of ICT state will be heavily affected by the environment around the fluorophore. Meanwhile the excimer formation is a diffusion-controlled process requiring a strict geometric arrangement of forming species [19], the formation and emission of excimer will be subject to environmental properties as well. Both processes

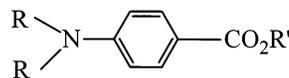
¹ *p*-*N,N*-Dimethylaminobenzonitrile (DMABN) and ethyl *p*-*N,N*-dimethylaminobenzoate (EDMAB) showing dual fluorescence has been well documented. The origin of the 'abnormal' low energy emission is still a subject of controversial discussion. Two points have been reached, one is that the state responsible for this emission is an intramolecular charge transfer (ICT) state and a molecular configuration change occurs upon charge transfer from the electron donor to acceptor. The object that is still under discussion is the nature of configurational change. Two main models have been proposed, one, the TICT (Twisted Intramolecular Charge Transfer) model by Grabowski [12–14] stated that a twisting of the donor group by 90° occurred in the ICT process to afford a perpendicular configuration in the final ICT state, and the other by Zachariasse [15–18] indicated that the nitrogen inversion is a promotion mode for the ICT reaction and the ICT state is planar. In this paper we thus simply take ICT to stand for the state responsible for that long wavelength emission

could be monitored by fluorescence spectra. Thus HDHAB is a good candidate for the present study. The absorption spectra of HDHAB were also recorded for identifying the geometric arrangement of forming molecules in the aggregates, following Kasha exciton theory [20–22].

2. Experimental

HDHAB was synthesized by refluxing *p*-aminobenzoic acid in hexyl bromide in the presence of anhydrous sodium carbonate. The solvent was removed by distillation in vacuum. The product was separated and purified on silica gel column eluted by petroleum ether (b.p. 60–90°C)-ethyl acetate binary solvent. Methyl *p*-*N,N*-dimethylaminobenzoate (MDMAB, Scheme 1) was prepared as described previously [23,24]. *p*-*N,N*-Dimethylaminobenzonitrile (DMABN) was purchased from Aldrich and purified by twice recrystallizing from absolute ethyl alcohol and one sublimation in vacuum. AR grade 1,4-dioxane was further purified by passing it through an alkaline Al₂O₃ column. Water was twice deionized with an electric conductivity of lower than 1 μS cm⁻¹.

Fluorescence spectra were recorded on a Shimadzu RF-5000 fluorescence spectrophotometer using an 150 W xenon lamp as excitation source. The excitation wavelength was fixed at 280 nm and spectral scan rate selected as medium. The slits for both excitation and emission monochromators were 5 nm. Absorption spectra were recorded on a Shimadzu UV-240 absorption spectrophotometer by using an 1-cm quartz cell. Solvents without chromophore were employed as blanks. All experiments were performed at ambient temperature (25 ± 2°C).



R = R' = CH₃, **MDMAB**

R = R' = n-C₆H₁₃, **HDHAB**

R = CH₃, R' = n-C₁₆H₃₃, **CDMAB**

Scheme 1. The molecular formula of ICT esters.

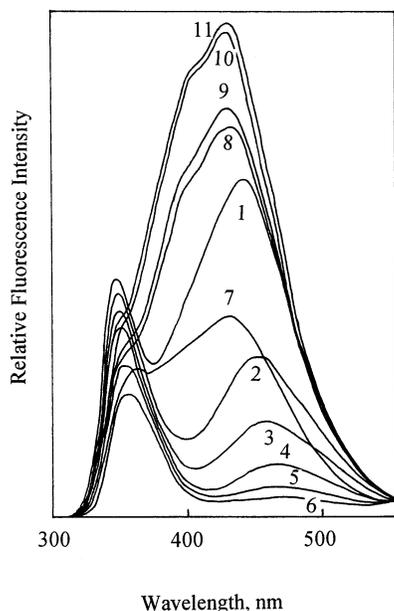


Fig. 1. Fluorescence spectra of HDHAB in water–dioxane binary solvents $[\text{HDHAB}] = 5.0 \times 10^{-5} \text{ mol l}^{-1}$, $\Phi = 0(1)$, $0.05(2)$, $0.1(3)$, $0.2(4)$, $0.3(5)$, $0.4(6)$, $0.5(7)$, $0.6(8)$, $0.7(9)$, $0.8(10)$, $0.9(11)$, respectively.

3. Results and discussion

Fig. 1 presents the fluorescence spectra of HDHAB in water–dioxane binary solvents as a function of water volume fraction, Φ . In pure dioxane and in a medium with a Φ of lower than 0.5, a dual fluorescence emission which is typical of the presence of excited state ICT reaction [10–18] can be seen from this figure, of which the long-wavelength fluorescence band is due to the ICT state and the short-wavelength band at 350 nm is due to the LE state. The ICT band shifts to the red and decreases in intensity with increasing Φ , which is clearly an indication of increasing bulk phase polarity, since the ICT state has a dipole moment much higher than that of the ground state [12–18]. Meanwhile the intensity of ICT band decreases faster than the LE band (Fig. 2, curve a') which is in agreement with the conclusion that ICT state has a higher dipole moment than LE state too [12–18]. In solutions at Φ above 0.5, however, the long-wavelength band observed at Φ below 0.5 suddenly shifts to blue,

for example, from 485 to 435 nm at $\Phi = 0.6$, and its intensity is enhanced so strongly that the band at 435 nm dominates the spectrum (Fig. 2). Meanwhile a shoulder at ca. 400 nm emerges. This discontinuity in spectral variations can be more clearly seen in Fig. 2, in which the maximum position in wave number of the long-wavelength band and the intensity ratio of the long-wavelength band to the LE band, I_a/I_b , are plotted versus Φ . From the breaks in curves a and a', aggregation of HDHAB at $\Phi = 0.5$ can be identified. In principle, two reasons can be considered for this discontinuity in spectral variations; one is the discontinuity in polarity variation and the other is the change in existing form of HDHAB molecules, namely from monomer to aggregate, as expected from the behavior of long alkyl chain containing organic molecules in organo-aqueous media [5–8].

The polarities of water–dioxane binary solvents of different Φ were examined by the dual fluorescence of well-known ICT fluorophore, *p*-*N,N*-dimethylaminobenzonitrile (DMABN), whose ICT emission can be observed in the whole range of water–dioxane mixtures of varying Φ . The ICT emission maximum position in wave number, ν_a , which can act as an index for solvent polarity, and the intensity ratio of ICT band to LE band, I_a/I_b , were measured and the data presented in Fig. 3. This figure shows that, at Φ beyond 0.1, both ν_a and I_a/I_b vary smoothly with increasing Φ , indicating a continuous changing in the polarities of water–dioxane binary mixtures around $\Phi = 0.5$. The I_a/I_b ratio increases at lower than 0.1. A similar observation was reported for *p*-*N,N*-dimethylaminobenzaldehyde (DMABA) and was discussed in terms of DMABA– H_2O hydrogen bonding [25]. Hence the aggregation of HDHAB in water–dioxane solutions with Φ higher than 0.5 is concluded to be responsible for the discontinuity in the spectral variations of HDHAB observed in water–dioxane binary solvent at $\Phi = 0.5$ [5–10]. The fact that an HDHAB derivative, methyl *p*-*N,N*-dimethylaminobenzoate (MDMAB, Scheme 1), without a long alkyl chain, does not show similar jump in spectral parameters supports this conclusion.

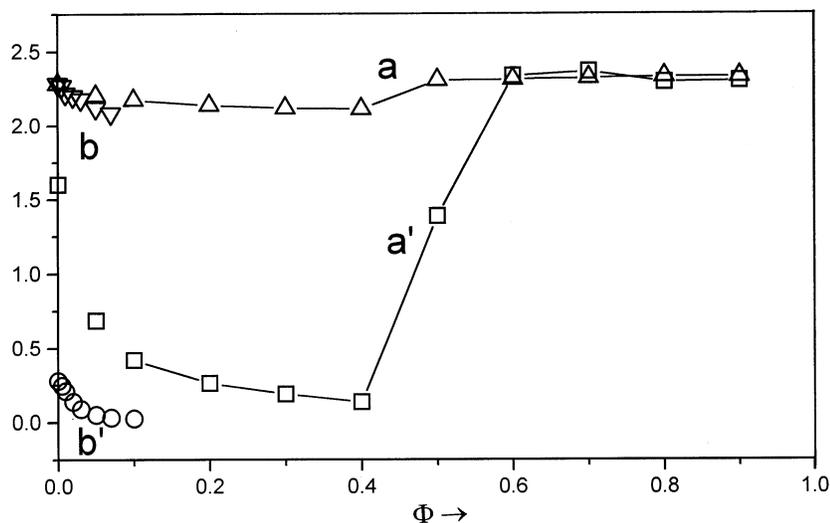


Fig. 2. The wave number ($1 \times 10^4 \text{ cm}^{-1}$, a, b) of low energy emission band and I_a/I_b (a' , b') of HDHAB (a, a') and of MDMAB (b, b') as a function of water volume fraction, Φ .

It is necessary to mention that the aggregation form of HDHAB emits triple fluorescence in solutions of Φ beyond 0.5, a dominant band at 435 nm, and two shoulders at ca. 400 and 350 nm, respectively. The shoulder at ca. 350 nm can be easily assigned to LE emission as that is seen in solutions before the aggregation of HDHAB (see Fig. 1). Zhen et al [9] reported that excimer of cetyl *p*-*N,N*-dimethylaminobenzoate (CDMAB, Scheme 1) in water–dioxane mixtures at Φ higher than 0.5 emits at 410 nm. Therefore it is reasonable to attribute the shoulder at ca. 400 nm observed here to HDHAB excimer emission. The excimer emission (400 nm) in the present system is observed at slightly higher energy compared to that of CDMAB (410 nm). This could be due to the higher polarizability of HDHAB excimer than that of CDMAB excimer, leading a more sensitive response of HDHAB excimer emission to the decrease in environment polarity [26], and/or the less favorable interaction of the fluorophores in the present excimer as will be shown by the J-aggregation form later in this paper. The dominant band at 435 nm can thus be assigned to the ICT emission. It hence follows that, for the directly populated LE state of HDHAB in aggregates in the present system, there are two decay channels that can be identified from spectroscopic

evidences, i.e. LE to ICT and LE to excimer, and the ICT emission quantum yield is higher than that of excimer. It is noteworthy to compare that the LE state of the aggregates of cetyl *p*-dimethylaminobenzoate (CDMAB, Scheme 1), in which the long alkyl-chain is at the ester moiety, has only one reaction channel as LE to excimer [9]. This is quite different from the photophysics of the aggregates of HDHAB, in which, in addition to one long alkyl chain in the ester moiety, two long alkyl-chains are substituted at the amino group. Since the photophysical behavior of HDHAB and CDMAB [9] in water-poor water–dioxane mixtures, in which these two molecules are both in monomer form, are similar, this difference in the photophysics in aggregation forms of HDHAB and CDMAB clearly suggests the tuning of excited-state photophysics in supramolecular assembly.

The enhanced ICT formation and/or restricted excimer formation can account for the changed photophysical processes in HDHAB aggregates compared to those in CDMAB aggregates. It has been shown that, in organic solvents, the formation rate constant and fluorescence quantum yield of the ICT state of *p*-*N,N*-dialkylaminobenzoate ester increase with lengthening alkyl-chain [27]. It is also observed here that in water–dioxane solu-

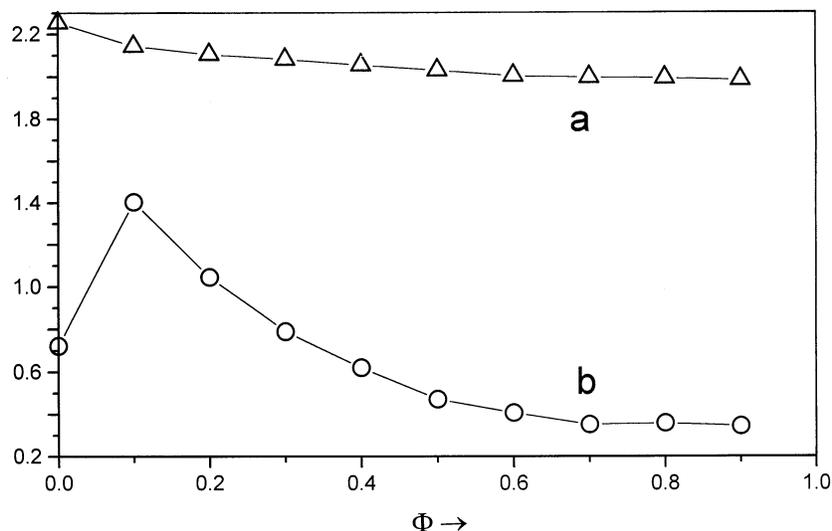


Fig. 3. Wave number ($1 \times 10^4 \text{ cm}^{-1}$, a) of the ICT emission and I_a/I_b (b) of DMABN in water–dioxane binary mixture as a function of Φ .

tions of lower Φ , the I_a/I_b ratio of HDBAR is higher than that of MDAB, see Fig. 2 curves a' and b'). From Figs. 1 and 2 it is noted that the ICT band of HDHAB in aggregates is located at a similar position to that of HDHAB monomer in pure dioxane, indicating that the fluorophores in the aggregates in water-rich solutions experience a microenvironment of low polarity close to that of dioxane and therefore are shielded from the polar bulk phase. It is thus likely that the substitution of the amino group with long hexyl groups will also enhance ICT formation in HDHAB aggregates in water-rich solutions.

On the other hand, it is necessary to show the geometric arrangement of fluorophores in the aggregates in order to judge whether the excimer formation is suppressed due to the geometric disfavoring or not, because excimer formation requires a subtle geometric configuration of the fluorophores, a 'Sandwich' configuration with two fluorophore molecules separated by 0.3–0.4 nm [19]. In this regard, the absorption spectra of HDHAB in water–dioxane mixtures were measured and the arrangement of the chromophores in the aggregates was analyzed according to the Kasha's exciton theory [20–22]. The absorption spectra are presented in Fig. 4. A sharp jump in

absorption spectra in binary solvents can also be seen at $\Phi = 0.5$, which is evidence of the aggregation of HDHAB molecules, as already shown in the fluorescence spectra in a similar series (see

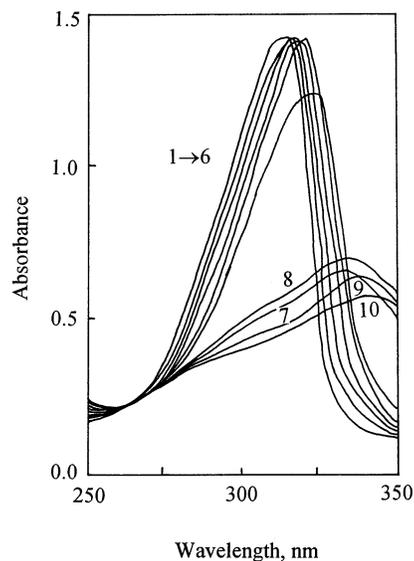


Fig. 4. Variation of HDHAB absorption spectrum with solvent composition in water–dioxane mixture HDHAB concentration is $5.0 \times 10^{-5} \text{ mol l}^{-1}$, and $\Phi = 0(1)$, 0.05(2), 0.1(3), 0.2(4), 0.3(5), 0.4(6), 0.5(7), 0.6(8), 0.7(9), 0.8(10), respectively.

Figs. 1 and 2). It is shown in Fig. 4 that, before aggregation ($\Phi < 0.5$), the absorption spectrum of HDHAB slightly shifts to red with increasing Φ , but basically it is peaked at around 310 nm. Upon aggregation at $\Phi > 0.5$ the absorption spectrum dramatically shifts to red and develops into a new band at 335 nm, while the band at 310 nm observed before aggregation is weakened and becomes a shoulder, the whole spectrum being wider. Since the chromophores in the aggregates experience a similar polarity to that in pure dioxane, as shown by the fluorescence spectra described above, the dramatic red shift of the absorption band in aggregates should indicate a J-form arrangement of the chromophores, i.e. a head-to-head arrangement [20–22]. This arrangement is far away from the excimer formation required ‘Sandwich’ configuration [19]. As a consequence, the excimer formation in HDHAB aggregates is not favored. This should account, to some extent, for the different photophysics of HDHAB aggregates from that of CDMAB aggregates in similar medium. The fact that in the present system excimer emission is still observed in aggregate form of HDHAB is suggestive of the effect of long alkyl-chain at ester moiety as what was observed in the case of CDMAB (Scheme 1)[9], although the exact reason is not yet clear to us. The observation that the geometric factor plays a role in tuning excited state photophysics points out the topological action in supramolecular assembly [1]. In conclusion it appears that both the enhancement of the ICT formation and emission, due to the lengthening of the alkyl chain substitutes at the amino group of ICT fluorophore, and the hindrance of excimer formation, due to the geometric arrangement in aggregate form, attribute to the changes in the excited-state photophysics of HDHAB aggregates compared to that of CDMAB aggregates in the same media. At this stage, we are not able to quantify to which extent each of the two factors contributes to this difference, but this quantification should deserve further efforts, since this would help perform precise control of

excited-state photoprocesses in supramolecular assembly

Acknowledgements

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