

PHOTOINDUCED INTRAMOLECULAR CHARGE TRANSFER IN SELF-ASSEMBLY. 1. AGGREGATION AND DUAL FLUORESCENCE OF ETHYL P-DIDECYLAMINOBEZOATE IN DIOXANE-WATER BINARY SOLVENT

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Abstract: Aggregation of ethyl p-didecylaminobenzoate (EDDAB) in dioxane-water binary mixture was shown to occur at water volume fraction of 0.47 and a strong intramolecular charge transfer emission was observed in the aggregate.

Aggregation of long-alkyl-chain containing molecules in organo-aqueous mixture and its effect on the photophysics and photochemistry of aggregating molecules have been well documented [1, 2]. The photophysics of photoinduced intramolecular charge transfer (ICT) state of p-dimethylaminobenzonitrile (DMABN) and p-dimethylaminobenzoic acid ester (DMABE) is strongly affected by the environmental properties because of the large dipole moment of ICT state and molecular conformation change in ICT state formation [3, 4]. Thus the coupling of the aforementioned two phenomena should be of interest. Tung et al [5] have reported the aggregation of cetyl p-dimethylaminobenzoate in dioxane-water mixture and no ICT emission but excimer emission was observed in the aggregate. This was attributed to the nonpolar environment in the aggregate in which the ICT process is not able to compete with excimer formation.

It has recently been shown that the ICT rate constant of DMABN or DMABE is increased when the methyl substituents at amino group are replaced by longer alkyl chains [6, 7]. Research on the Langmuir-Blodgett membrane of amine indicated that the amine with two long alkyl chains provided larger free volume for the neighbouring group than that with one alkyl chain [8]. It is well known that excimer formation has an exact geometric requirement with the two fluorophores in a sandwich configuration separated by 0.3 – 0.4 nm. Based on the fact that excimer formation can occur in the aggregate of cetyl p-dimethylaminobenzoate [5] which, on geometric consideration, is similar to that with one alkyl chain substituted at amino group, one may assume that the geometric condition in the aggregate of DMABE derivative with two alkyl chains at amino group would not be optimal for or even

fail to meet the requirements for excimer formation. As a consequence, one can expect that in the aggregate of the derivative of DMABE with two long alkyl chains at amino group the ICT emission would be observed because of the higher ICT rate and the difficulty in excimer formation. In the present letter, we will show that this is indeed the case in the aggregate of ethyl *p*-didecylaminobenzoate (EDDAB) in dioxane-water binary mixture.

In pure dioxane, EDDAB and its dimethylamino derivative, ethyl *p*-dimethylamino-benzoate (EDMAB), emit dual fluorescence, typical of the presence of an excited state ICT reaction. The short wavelength band is due to the locally excited (LE) state while that at longer wavelength due to the ICT state [3, 4]. In dioxane-water binary solvent, the ICT emission of EDDAB and EDMAB changes with increasing water volume fraction (ϕ). Figure 1 shows the wavenumbers of ICT emission of

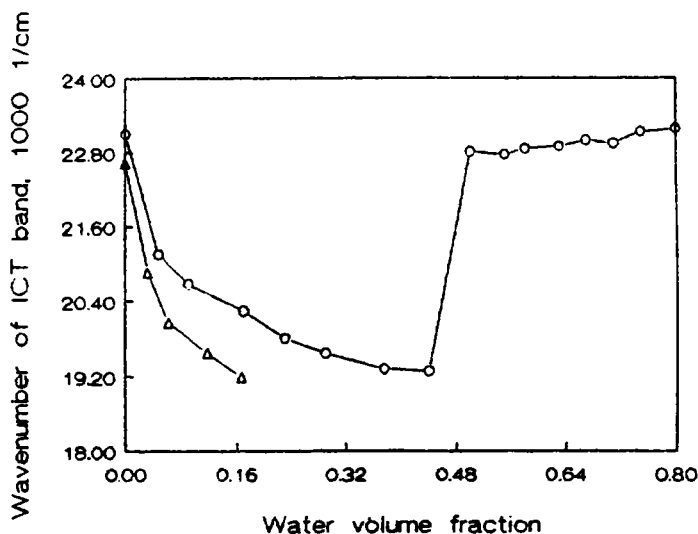


Figure 1 Wavenumber of ICT band of EDDAB (\circ) and EDMAB (Δ) as a function of water volume fraction in dioxane-water binary mixture

EDDAB and EDMAB as a function of ϕ . At $\phi < 0.5$, the ICT band of EDDAB shifts to the red with increasing ϕ in a rate slower than that of EDMAB and, at the same time, the energy of EDDAB ICT emission is higher than that of EDMAB. From these observations it immediately follows that the ICT state of EDDAB is somewhat shielded from the bulk phase. This is in agreement with the coiling conformation of the long alkyl chain in polar solvent [1, 5]. At $\phi = 0.5$, a strong and sharply blue-shifted emission of EDDAB reappears at about 23000 cm^{-1} and a shoulder at about 28000 cm^{-1} is seen in the spectrum. With further increase in the water volume fraction, the emission maximum of EDDAB slowly shifts to the blue, while the ICT emission of EDMAB completely disappears. This difference is a clear indication of the aggregation of long chain molecule EDDAB in dioxane-water binary solvent [1, 5]. Another evidence comes from the difference in the excitation wavelength

dependence of the ICT emission of EDDAB in pure dioxane and in $\phi = 0.75$ dioxane-water mixture. In pure dioxane, the intensity ratio of ICT emission to that of LE emission of EDDAB increases with lengthening excitation wavelength. This could not be necessarily attributed to ground state aggregation [9] since the absorption spectrum and the fluorescence intensity ratio of the two bands do not change at all with the maximum absorbance of EDDAB varying from 0.556 to 1.503. In $\phi = 0.75$ binary solvent, however, fluorescence spectrum of EDDAB is independent of excitation wavelength. The excitation wavelength dependence of TICT fluorescence has also been reported for methyl *p*-dimethylaminobenzoate (MDMAB) in acetonitrile [9] and in aqueous β -cyclodextrin solution [10]. Therefore the difference in the excitation wavelength dependence of the ICT emission of EDDAB in pure dioxane and in $\phi = 0.75$ binary solvent is not due to the difference in the medium polarity but due to the different forms for EDDAB existing in $\phi = 0.75$ binary solvent than in pure dioxane.

The emission band of EDDAB aggregate in $\phi > 0.5$ dioxane-water mixture centers at above 430 nm (Figure 1). This is more than 20 nm longer than the 410 nm band that was observed in the emission spectrum of cetyl *p*-dimethylaminobenzoate (CDMAB) aggregate in the same medium [5]. The latter has been assigned to be excimer emission [5]. The fluorophore here in our case is nearly the same as that in CDMAB, the only difference could be the minor difference in the polarizability of the two fluorophores due to the slightly higher electron donating and accepting abilities of the fluorophore in our case than those in CDMAB. It has really been reported [11] that excimer emission shifts with solvent polarity due to the difference in the polarizability of the excited state and the ground state. The spectral shift is, however, not very appreciable [11]. For instance, emission of the more polarizable pyrene excimer only shifts ca.15 nm to red when solvent changes from nonpolar *n*-hexane to highly polar DMSO [11]. Coupled with the very small, if any, difference in the polarizability of the fluorophore in EDDAB of our case and that in CDMAB [5], we rule out the possibility that the 20nm red-shifted emission of EDDAB aggregate is due to excimer, but we argue that this is due to ICT state. This means that ICT state formation and emission can be observed in the aggregate of EDDAB, a DMABE derivative with two alkyl chains substituted at amino group. It is then interesting to note that the ICT emission of EDDAB aggregate shifts to blue in case that the polarity of the bulk phase increases. This is indicative of the fact that the fluorophore in aggregate is buried in a microenvironment that is more and more shielded from the bulk phase with increasing bulk phase polarity. It is then not unreasonable to conclude that the aggregate structure can be changed by changing the composition of the bulk binary solvent. From the emission wavenumber of the ICT band of EDDAB (Figure 1), it is evident that the polarity of the microenvironment of EDDAB fluorophore in aggregate form in the binary mixture is nearly the same as that in pure dioxane in which EDDAB is in monomer form. However, the LE band of EDDAB in the aggregate is only a shoulder, while a clear dual fluorescence can be observed in pure dioxane. This difference shows that the quantum yield ratio of the ICT band to LE band of EDDAB is higher in aggregate form than in monomer form in case that the ICT fluorophore experiences the same polarity.

The ICT band position of EDDAB in aggregate in $\phi = 0.75$ dioxane-water binary solvent (432.2 nm) is the same as that in pure dioxane (432.9 nm), which suggests that the polarity in the two environments is the same. The absorption maximum in $\phi = 0.75$ binary solvent (315.0 nm) is red shifted as compared to that in pure dioxane (312.5 nm). Taking account of the fact that the ICT fluorescence emission is more sensitive to medium polarity, due to the high dipole moment of ICT state, and the Kasha exciton theory [12], we conclude that the EDDAB molecules in the aggregate have a J-type arrangement, that is the molecules are aggregated in a head-to-head mode. This geometric arrangement of the fluorophores in the aggregate, which strongly differs from the required "Sandwich" geometry in excimer, makes it not possible to form an excimer.

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