

for alanine production is very difficult from this simple experimental results. However, we can propose the reaction scheme as in Figure 7.

The imino acid, which is produced from thermal equilibrium between lactic acid and ammonia, is reduced by excited electrons on the conduction band of CdS or on Pt to produce alanine. These excited electrons are also consumed to reduced water, *i.e.* for hydrogen production. The difference in the selectivity of alanine production would be explained as follows. In the case of CdS(B), the electron energy must be lost to some extent by the trapping in the surface sub-band gap levels. If we assume that these surface trapped electrons can reduce the imino acid but not water, the high selectivity of alanine production of CdS(A) would be explained. On the other hand, in the case of CdS(A), the energy of excited electrons are not lost and they are used promptly to reduced water. Therefore in this case, electrons would be consumed much more to reduce water than to reduce the imino acid. Although this assumption can explain the difference in the selectivity between CdS(A) and CdS(B) in the same hexagonal form, the further investigation would be needed to clarify the mechanism. These studies are now in progress by using single crystal electrode of CdS.

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## Micellar Effects on Intramolecular Charge Transfer Emission from Biphenylcarboxylic Acids

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The intramolecular charge transfer (ICT) phenomena of the photoexcited 2-biphenylcarboxylic acid (2BPCA) and 4-biphenylcarboxylic acid (4BPCA) have been investigated in some surfactant micellar solutions. The ICT emission of 4BPCA and 2BPCA in aqueous solution at sufficiently low pH (1-3) has been observed to be markedly quenched and blue-shifted upon addition of a cationic surfactant, cetyltrimethylammonium chloride (CTAC) in contrast to little change in anionic sodium dodecyl sulfate (SDS) and neutral Brij 35. An anionic emission band has been observed to be enhanced at expense of the ICT emission as a function of the concentration of CTAC. These results with the micellar effects on the fluorescence decay kinetics of 4BPCA suggest that formation of the ICT state of the excited acids is inhibited by CTAC-induced proton transfer as well as the decrease in the polarity and/or hydrogen-bonding ability of the micellar microenvironment entrapping the acids.

### Introduction

The intramolecular charge transfer (ICT) emission is currently the most attractive topics in the investigation of solvation dynamics.<sup>1-3</sup> It has been observed that the excited-state ICT processes in many molecules are accompanied by solvent relaxation and their rates are controlled exclusively by polarity of the medium.<sup>4-6</sup> The rate of the excited-state ICT process is also controlled by the molecular geometry both

in the ground and the excited states, which is greatly affected by the specific solvent-solute interaction.<sup>2,7-9</sup> Because of these characteristics, the ICT emission is commonly used to probe the microenvironments, including microscopic polarity of complex biological systems.<sup>10,11</sup> However, there have not been systematic investigations of the ICT emission in the simple biomimetic systems such as surfactant micelles or cyclodextrins, although preliminary reports are available for the effects of cyclodextrins on the ICT emission from dimethylamino benzonitrile.<sup>12,13</sup>

The surfactant micelles, one of microheterogeneous structures, have been attracting much attention as good membrane mimetic media.<sup>14</sup> The micelles provide such a wide va-

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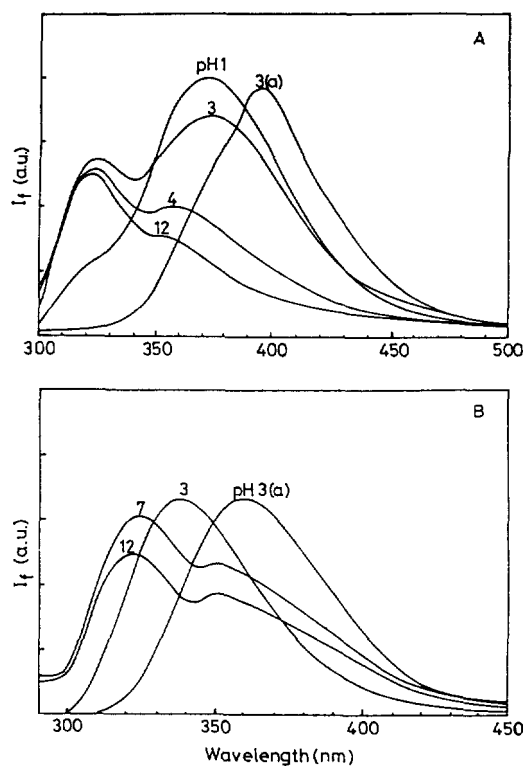
riety of polarity and restricted environment that they markedly influence a number of photophysical and photochemical properties including the excited-state geometry.<sup>15-17</sup> They are also known to affect the acid-base equilibria of some acids or bases.<sup>18</sup> Thus it would be interesting to see how the surfactant micellar systems affect the ICT emission.

In the present study, we have attempted to search the micellar effects on the photophysical properties focusing on the photoexcited ICT processes of two biphenylcarboxylic acids, 2-biphenylcarboxylic acid (2BPCA) and 4-biphenyl carboxylic acid (4BPCA) which have been previously found to be a new type of ICT molecules.<sup>19</sup> The pH effects on the ICT emission of the acids in the micellar solutions have been also observed. Our results show that the photoexcited ICT state is quenched by the surfactant-induced proton transfer as well as the decrease in the polarity and/or the hydrogen bonding ability of the micellar microenvironment of the acids.

### Experimental

2BPCA and 4BPCA were purchased from Aldrich Chemical Co. and purified by repeated recrystallization with ethanol. The melting points of 2BPCA and 4BPCA are in good agreements with the values in the reference 19 (114°C and 226°C, respectively). As the surfactants, sodium dodecyl sulfate (SDS), cetyltrimethylammonium chloride (CTAC) and Brij 35 were purchased from Merck Co. and used as received. The surfactant stock solutions of various concentrations were prepared in different pH-buffer solutions. When the sample solutions containing surfactants were prepared, one milliliter of a buffer solution containing 2BPCA or 4BPCA ( $2.0 \times 10^{-4}$  M) was added to 9 ml of a surfactant stock solution so that the concentration of the acids remains constant through the verification of the surfactant concentration. The buffer solutions were prepared by mixing GR grade acid or base with its salt; KCl-HCl (pH 2), HAc-NaAc (pH 3-5),  $\text{KH}_2\text{PO}_4$ - $\text{Na}_2\text{PO}_4$  (pH 6-8),  $\text{NH}_4\text{Cl}$ - $\text{NH}_4\text{OH}$  (pH 9-10),  $\text{NaH}_2\text{PO}_4$ - $\text{NaOH}$  (pH 11-12). Water was triply distilled in the presence of acidic dichromate and alkaline permanganate. All the sample solutions were degassed before the spectral measurements by means of freeze-pump-thaw (3-4 cycles down to  $10^{-4}$  torr) technique.

Fluorescence spectra were measured on a scanning SLM-AMINCO 4800 spectrofluorometer which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter. The optical density at an excitation wavelength was held constant when different solutions were compared. The fluorescence lifetime of BPCA's in micellar solutions were measured by the time correlated single photon counting (TCSPC) method. The excitation laser source is a frequency doubled mode-locked  $\text{Nd}^{3+}$ : YAG laser (Coherent; Antrares 76-S) pumping a dual jet dye laser (Coherent; Model 701-1). The cavity dumped beam from the dye laser has 1 ps pulse width at 7.6 MHz dumping rate, and the tunability of 560-620 nm when Rhodamine 6G for gain dye and DODCI for the saturable absorber were used. To excite samples, the dye laser pulse was frequency-doubled by BBO crystal. The temporal instrument response function was measured by detection of the scattered laser pulse of ca. 1 ps duration from quartz crystal and typically it had a 100 ps FWHM when Hamamatsu photomultiplier tube (R928) was used.

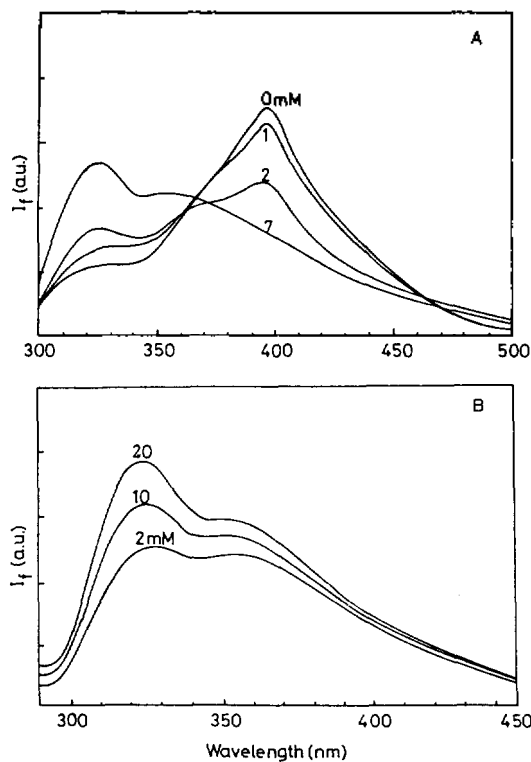


**Figure 1.** Fluorescence emission spectra of  $2 \times 10^{-5}$  M 2BPCA (A) and 4BPCA (B) in the presence of 20 mM CTAC micellar solution as a function of pH of the aqueous phase. The emission spectra were measured by excitation at 260 nm and 270 nm, respectively for 2BPCA and 4BPCA and normalized. The spectra marked with (a) represent emission spectra measured in neat aqueous solution (pH=3.0). The intensities in the fluorescence spectra of the micellar solutions are magnified by 20 times as those observed under the same condition to measure the spectrum in the aqueous solution at pH 3.0.

This allows a resolution of about 30 ps after deconvolution.<sup>20</sup>

### Results and Discussion

The fluorescence spectra of CTAC micellar solution containing  $2 \times 10^{-5}$  M 2BPCA or 4BPCA were measured as a function of bulk-phase pH and they are shown in Figure 1. In the aqueous solution at low pH (1-3), the fluorescence spectra of 2BPCA and 4BPCA show emission bands at 395 nm and 360 nm, respectively, which have been attributed to the excited-state intramolecular charge transfer (ICT) state of the neutral species having the benzene as a donor and the benzoic acid as an acceptor.<sup>19</sup> However, upon addition of CTAC the ICT emission bands of 2BPCA and 4BPCA are blue-shifted to 365 nm and 350 nm, respectively, being markedly quenched. The blue shifted emission bands were observed in alcohol solution as previously reported.<sup>19</sup> These observations indicate that the CTAC micelles provide both acids with less polar environments than water and quench the ICT state, being consistent with the reports that the ICT state is stabilized by the medium polarity.<sup>4-6</sup> Thus, the blue-shifted emission should be the normal emission originated from the initially excited state of the neutral species.



**Figure 2.** Fluorescence emission spectra of  $2 \times 10^{-5}$  M aqueous solution of 2BPCA (A) and 4BPCA (B) with different concentrations of CTAC. The solution pH was kept constant to be 5.0 or 7.0. The excitation wavelengths were 260 nm and 270 nm, respectively for 2BPCA and 4BPCA.

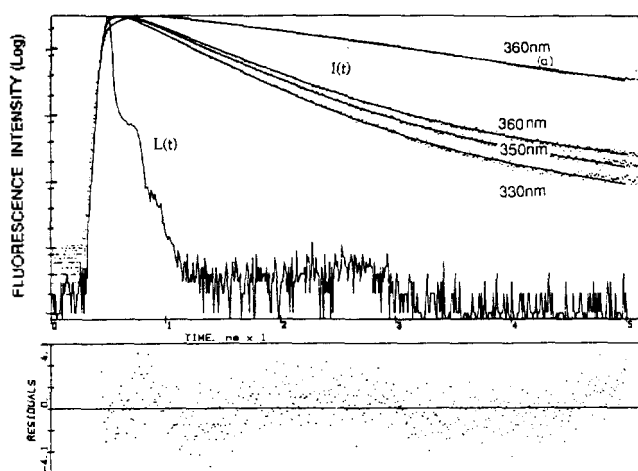
It is also noteworthy that a new emission band appears at around 325 nm in addition to the normal emission. As the pH of the solution further increases the new emission is enhanced, followed by the decrease of the ICT emission bands. Such pH dependences of the fluorescence spectra of both acids in the micellar solution look similar to those observed in aqueous solution in the absence of the micelles,<sup>19</sup> indicating that the 325 nm emission is attributed to the anionic species of the acids. These results suggest that the ICT process might be affected by the CTAC micellar environment *via* control of proton transfer of the acids as well as lowering micropolarity of the microenvironment of the acids. To support this conclusion, we measured the fluorescence of the acids as a function of CTAC concentration, keeping the pH of the solution constant. As shown in Figure 2A, the ICT emission of 2BPCA in the aqueous solution at pH=5 decreases upon addition of CTAC, being accompanied by increase of both the anionic emission (325 nm) and the nonpolar emission (360 nm). The anionic emission as well as the nonpolar emission of 4BPCA in the aqueous solution at pH=7.0 is also observed to be relatively enhanced as the concentration of CTAC increases as compared to the ICT emission (Figure 2B). In contrast to the CTAC effects on the emission spectra of the acids, addition of the anionic SDS or the neutral Brij 35 surfactants to the aqueous solution in the low pH range (1-3) did not affect the emission spectra. Particularly in the high pH (>6.0) solution, the weak emission was rather enhanced upon addition of the anionic surfactant SDS (data

**Table 1.** The ground- and excited-state acidities of 4BPCA in water and micellar solutions

Medium	$pK_a$	$pK_a^*$
Water	4.25	9.80
CTAC (20 mM)	2.30	7.85
SDS (15 mM)	5.59	11.14

not shown). These observations imply that SDS enhances  $pK_a$  of the acids to change the acid-base equilibrium while CTAC lowers the  $pK_a$ . Thus, the number of neutral species of the acids increases as compared to that of the anionic species in the SDS micellar solution and *vice versa* in the CTAC micellar solution. This implication is supported by the early reports<sup>18</sup> that solubilization or adsorption of dye molecules in the aqueous micellar solutions influences the acid-base equilibria of the dye significantly. Actually, both the ground  $pK_a$  and the excited  $pK_a^*$  of BPCA's, which are obtained by Foerster cycle calculation,<sup>22</sup> were found to be lower in the CTAC micellar solution than in water whereas they are higher in the SDS micelles (Table 1). Nevertheless, the difference between  $pK_a$  and  $pK_a^*$  in water is not significantly affected by the addition of the surfactants, indicating that both the ground-state and the excited-state charge transfer interactions of the benzene with the benzoic acid are equally affected by the surfactants. The ICT emission quantum yields of the neutral species are little affected or rather enhanced in the SDS or Brij 35 micellar solution as mentioned above, but their emission maxima are shifted to shorter wavelengths without change of the spectra shape, indicating that the neutral acids are entrapped even in the SDS or Brij 35 micellar phase which is less polar than the aqueous phase. When considering this, we can conclude that in the quenching of the ICT emission of BPCA's in the CTAC micellar solution the deprotonation seems to play a more important role than the decrease in the polarity of the microenvironment surrounding the acids.

In order to ascertain how the anionic and normal emissions are related to the ICT emission, we attempted to measure the excitation spectra of the CTAC micellar solutions containing  $2 \times 10^{-5}$  M acids by monitoring the anionic, the normal and the ICT emissions at 330, 350 and 360 nm, respectively. Unfortunately, it was very difficult to get the clearly resolved spectra because of the Raman scattering due to the low fluorescence quantum yield in the micellar solution. Therefore, we tried to carry out a ps-time-resolved study of the anionic, the normal and the ICT emission of BPCA's in the CTAC micellar solution. The fluorescence decay of 2BPCA in the micellar solution is still too weak to be detected in our apparatus with 290 nm laser pulse at which the optical density of 2BPCA is extremely low. However, the fluorescence decays of 4BPCA in the CTAC micellar solution (pH=3.0) could be clearly detected and they are shown in Figure 3 with the decay at 360 nm in the micelle-free aqueous solution (pH=3.0). The decay in the micelle-free aqueous solution at 360 nm is fitted to a single exponential with a lifetime of 1690 ps which is in good agreement with the previously obtained lifetime of the ICT emission.<sup>19</sup> This decay was found to be significantly faster and fitted to double exponential upon addition of CTAC, indicating that



**Figure 3.** Fluorescence decay curves ( $I(t)$ ) of  $2 \times 10^{-5}$  M 4BPCA in 20 mM CTAC micellar solutions (pH, 3.0) monitored at 360 nm, 350 nm and 330 nm. The curve (a) represents the decay curve measured in neat aqueous solution. The  $L(t)$  is the laser pulse function at 290 nm.

**Table 2.** Fluorescence lifetimes ( $\tau$ ) of 4BPCA in 20 mM CTAC micellar solution (pH, 3.0) analyzed from emission decays monitored at different wavelengths, 330, 350 and 360 nm corresponding to the anionic, the nonpolar and the ICT emission maximum, respectively.

Wavelength	$\tau_1$	$\tau_2$
330 nm	400 ps (98%) <1710 ps (100%)*	1430 ps (2%)
350 nm	480 ps (97%)	2240 ps (3%)
360 nm	540 ps (83%) <1700 ps (100%)*	1690 ps (17%)

\*The lifetime measured in water (pH, 3.0). Error limit:  $\pm 5\%$

the microenvironment of 4BPCA is changed from the polar aqueous bulk phase to the less polar micellar phase. The results of lifetime analysis from these decay curves are listed in Table 2 with the results obtained from other decay curves monitored at 330 and 350 nm. It is evident that the fluorescence decays in the micellar solutions at other emission wavelengths are also double exponential with two components of lifetimes with the short-lived decay component dominant. Thus, the long-lived decay may be assigned to 4BPCA molecules dissolved in the bulk aqueous phase while the short-lived decay may be assigned to the 4BPCA molecules associated with micelles. It is noteworthy that all the decay times of each emission are completely different from one another, supporting that there are three distinct sets of the 4BPCA molecules in the excited state in the micellar phase as well as in the aqueous phase.

The portion of the long-lived decay component for the ICT (360 nm, 1690 ps) is greatly reduced in parallel with the increased portion of the short-lived decay component (540 ps) which is similar to the value obtained from ethanol solution.<sup>19</sup> The long lifetime of the ICT emission in aqueous solution has been interpreted to be due to formation of a

hydrogen-bonded exciplex which may stabilize the ICT state.<sup>19</sup> These imply that the ICT state of 4BPCA in the micellar phase is not sufficiently solvated by water so that the ICT state is destabilized probably due to the decrease in polarity and/or the lack of the specific hydrogen-bonding interaction in the micellar phase. This is consistent with the observation that the proportion of short-lived decay component of the nonpolar (350 nm) or the anionic emission (330 nm) increases at the expense of the corresponding value for the ICT emission, supporting that the enhanced anionic and nonpolar emission of BPCA's originates from the decrease of ICT emission in the same micellar phase as discussed above. The particular interesting observation in the steady-state study is that the anionic emission at 330 nm at the high micellar concentration is relatively enhanced, as compared to the quenching of the ICT emission. The fluorescence decay at 330 nm shows that the lifetime of the anionic emission aqueous bulk phase (1430 ps) is greatly shortened in the micellar phase (400 ps). Thus, the shortening of the lifetime of the anionic emission in the micellar phase may be also due to the lack of the hydrogen-bonding interaction of the anionic 4BPCA. Thus, this study again may confirm the contention that the ICT process for BPCA's is dependent on the specific hydrogen-bonding interaction with the media.<sup>19</sup> Nonetheless it should be noted that the BPCA's could be entrapped in the SDS or Brij 35 micellar phase but their ICT emission is not quenched (*vide supra*). This indicates that the decrease in the hydrogen-bonding ability or the polarity is not the primary factor for quenching of the ICT emission in the micellar phase. The deprotonation induced by the cationic surfactant is the primary step in quenching of the ICT emission of BPCA's in the CTAC micellar solution. A proton transfer (protonation) quenching of the ICT emission has been observed for a basic dye, 1-(*p*-aminophenyl) pyrene in alcohol-water solution.<sup>21</sup> However, our observation with BPCA's would represent the first example of the proton-transfer quenching of the ICT emission from an acidic ICT molecule in the presence of micellar solution.

## Conclusion

This work demonstrates that the strong ICT emission of BPCA's in water is effectively quenched upon addition of a cationic surfactant, CTAC. The pH effects on the fluorescence spectra of the acids suggest that quenching of the ICT emission is mostly due to the surfactant-induced deprotonation of the acids.

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## Polymerization of *p*-Chlorophenyl Propargyl Ether by Molybdenum- and Tungsten- Based Catalysts

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The Polymerization of *p*-chlorophenyl propargyl ether (CPE) was carried out using various transition metal catalysts. The catalytic activity of MoCl<sub>5</sub>-based catalysts was greater than that of WCl<sub>6</sub>-based catalysts. MoCl<sub>5</sub> alone and MoCl<sub>5</sub>-cocatalyst systems polymerized CPE very effectively to give a high yield of poly(CPE). In most cases, the polymer yield was quantitative and the average molecular weight ( $\bar{M}_n$ ) was in the range of 9,000 and 17,000. The NMR, IR, UV-visible spectra indicated that the present poly(CPE) has a linear conjugated polyene structure having *p*-chlorophenyl oxymethylene substituent. The poly(CPE) was mostly dark-brown colored powder and was completely soluble in various organic solvents such as chloroform, methylene chloride, THF, chlorobenzene, etc. The X-ray diffraction analysis indicated that the present poly(CPE) is amorphous.

### Introduction

The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of polymers with a conjugated system, which can be used as organic semiconductors.<sup>1,2</sup> Polyacetylene has been the simplest conjugated organic conducting polymer, of which a rapidly increasing interest is being aroused in recent years, since the discovery of the high electric conductivity of the doped polyacetylene was found in 1977.<sup>3</sup> A number of studies for the polymerization of acetylene have been discussed on the synthesis method, structure properties correlations, electric and optical properties, and various cells application for practical purpose.<sup>4-6</sup>

However, polyacetylene was insoluble in any organic solvent and unstable to air oxidation. To solve these drawback, various mono- and disubstituted acetylene derivatives were

synthesized and polymerized.<sup>7,8</sup>

A few study on the polymerization of propargyl derivatives, such as propargyl halide,<sup>9</sup> phenyl propargyl ether,<sup>9</sup> dipropargyl ether,<sup>10</sup> etc., those are monosubstituted acetylenes, has been published.

In recent years we have reported the polymerization of propargyl halides,<sup>11,12</sup> propargyl ethers,<sup>13</sup> and propargyl amines<sup>14</sup> and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether,<sup>15</sup> dipropargyl diphenylmethane,<sup>16</sup> dipropargylsilanes,<sup>17</sup> dipropargylgermaniums, etc. And also the polymerization of phenyl and para-substituted phenyl (substituent=OMe, CN) propargyl ethers was carried out and the physical properties of the resulting polymers were characterized.<sup>19,20</sup> However, in these polymerizations, the polymer yield and the molecular weight were relatively low. In some cases, a small amount of insoluble polymer was also produced.