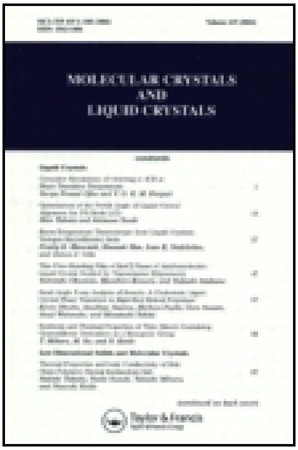

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Environmental Effects on Photochemical Properties of Betaine Dyes in Rigid Media

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We report luminescence of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (B30)- or other betaine dye-dispersed rigid media at 77 K and at room temperature (r.t.). Their luminescence in acetone at 77 K were remarkably influenced by water addition. UV-excited blue ~ bluish green luminescence of B30-dispersed polymers at r.t. we reported in our previous reports appeared to resemble that of B30-dispersed acetone at 77 K in the presence of water. It suggests the participation of protonation and/or deprotonation processes in the UV-excited states of B30. A weak emission shoulder in visible emission wavelength range was also observed for B30-dispersed polymeric solids at r.t., similar to those emission bands for betaine dye-dispersed polymeric solids or organic solvents at 77 K.

Keywords: betaine-30; luminescence; polymeric solid; steric hindrance

INTRODUCTION

2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (B30) [1–3] is a famous solvatochromic dye, with the color changing according to the solvent polarity. Its color is established as a solvent parameter, $E_T(30)$. We had reported the UV-excited blue ~ bluish green luminescence of B30- and other betaine dye-doped polymeric thin

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films [4,5], though B30 is known to be non-fluorescent in solutions at room temperature (r.t.) [6–8]. B30, 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium hydroxide inner salt hydrate (B1), and 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (B33) showed similar behaviors in poly(methyl methacrylate) (PMMA) solids. The emission wavelength (λ_{em}) was red shifted with the elongation of π-electrons conjugation, but the reason of the shorter λ_{em} than the $S_0 \rightarrow S_1$ absorption wavelength is still unknown [5].

In this study, we introduce another yellow ~ red luminescence of B30- and other betaine dye-dispersed rigid media at 77 K, and in some cases, this new luminescence was observed even at r.t. It has longer excitation wavelength (λ_{ex}) and λ_{em} than the previously reported UV-excited blue ~ bluish green luminescence. At first, we describe the 2D emission spectrum (it is called as "excitation emission matrix"; EEM [9]) of the above three betaine dyes in acetone (AcCO) and the effect of water addition. And then, we mention the EEMs of betaine dyes in other organic solvents and polymeric solids.

EXPERIMENTAL

B30 (90%, Sigma-Aldrich), B1 (97%, Sigma-Aldrich), B33 ($\geq$99%, Fluka) and a related compound, 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,4,6-triphenyl-pyridinium, perchlorate [1] (B26H) were purchased from Sigma-Aldrich Japan K.K. Concentrations of betaine dyes in polymeric solids were $1.01 \times 10^{-3}\,\mathrm{mol \cdot kg^{-1}}$, and those in solutions were up to $1 \times 10^{-4}\,\mathrm{mol \cdot L^{-1}}$. Acetone (AcCO), acetonitrle (ACN), benzene (Bz), and dimethylsulfoxide (DMSO) were "infinity pure" grade of Wako Pure Chemical Industries, Ltd. and 2-methyltetrahydrofuran (MTHF, $\geq$99%, Anhydrous) was a product of Sigma-Aldrich Co., these "freshly opened" solvents were used as dry solvents. Water, which was added into AcCO to change water content, was of fluorescence grade. PMMA (M_w: ~350,000), poly(benzyl methacrrylate) (PBzMA, Mw: ~70,000), and poly(cyclohexyl methacrylate) (PcHMA, Mw: ~65000) were purchased from Sigma-Aldrich Japan K.K. and used after reprecipitation. Each polymer was employed on solvent cast and spin-coating to obtain betaine dye-dispersed films. Details were described elsewhere [4,5]. Each polymer films were dried at a few tens degrees centigrade over the polymer's glass transition temperature (T_g) at least for 2 hours. We determined fluorescence spectra and EEMs with a Hitachi F-4500 Fluorescence Spectrophotometer equipped with a cryogenic option [4,5,10]. Sometimes, a vertical line at $\lambda_{em} \sim 815\,\mathrm{nm}$ was seen in EEMs, and it is conjectured to be negligible as it could be some problem of optical path. We used 5 mm ϕ

pyrex NMR tubes for the measurement at 77 K using liquid nitrogen as a refrigerant. A weak phosphorescence band ($\lambda_{em} \sim 700$ nm excited at $250 \sim 300$ nm) from tubes and/or a glass Dewar vessel was observed (as described before [10]). With F-4500 "phosphorescence" mode, an emission decay curve which has a lifetime (τ) longer than $\sim$10 ms is observed. It is not enough to judge if it has "phosphorescence" or not, as phosphorescence is possible to have much shorter τ (for example, a case of $\tau \sim 1\,\mu$s). Now we call the luminescence which has a decay observed with the "phosphorescence" mode as "slow luminescence", and it means that the luminescence has $\tau \sim 10$ ms or longer. Hereafter, all EEMs with no proviso mean that those were determined with F-4500 fluorescence mode. The systems of betaine dyes are expressed as "betaine dye/solvent", for example, B30/Bz stands for B30-dispersed Bz.

RESULTS AND DISCUSSION

Betaine Dye/AcCO at 77 K and the Effect of Water Addition

Each of B1, B30 and B33 was dissolved into AcCO and EEMs were determined with or without the addition of water. EEMs were shown in Figure 1. As shown in Figures 1(a)–1(h), all betaine systems showed luminescence. Most of the emission bands were approximately classified into three groups. In the absence of water for betaine dye/AcCO and other organic solvent systems, similar three emission bands were observed for each betaine dye (though the emission bands of B30/AcCO in Figure 1(d) was too weak to confirm the existence of the three emission bands, three bands could be observed for B30/organic solvents at 77 K as other betaine dye/organic solvents at 77 K). We call these emission bands as Band I ($\lambda_{ex1} \geq 440$ nm, $\lambda_{em1} \geq 550$ nm), Band II ($300\text{ nm} < \lambda_{ex2} < 440$ nm, $\lambda_{em2} \geq 440$ nm), and Band III ($\lambda_{ex3} \sim 300$ nm, $\lambda_{em3} \leq 450$ nm), and they were summarized in Table 1. We define Band II as the intermediate emission band appeared in the range between Band I and Band II in EEMs. As features of Band II are various, more detailed classification for Band II should be necessary in future. No "slow luminescence" was seen for betaine dyes in the absence of water, but for AcCO ("slow luminescence" EEM of AcCO was almost same to Fig. 1(i)). Though the dryness of the system couldn't be enough, as the solutions were handled under air, "slow luminescence" was observed for all betaine dyes with the excitation with λ_{ex} in the range of $350\text{ nm} \sim 400$ nm only in the presence of water. In the absence of water, each λ_{em1} was at 585, 725, 620 nm, for B1, B30, B33, respectively. The value of λ_{em1} was $\lambda_{B1em1} < \lambda_{B33em1} < \lambda_{B30em1}$. Band 1 seemed to be blue shifted in λ_{ex1} and λ_{em1}. For all betaine dyes,

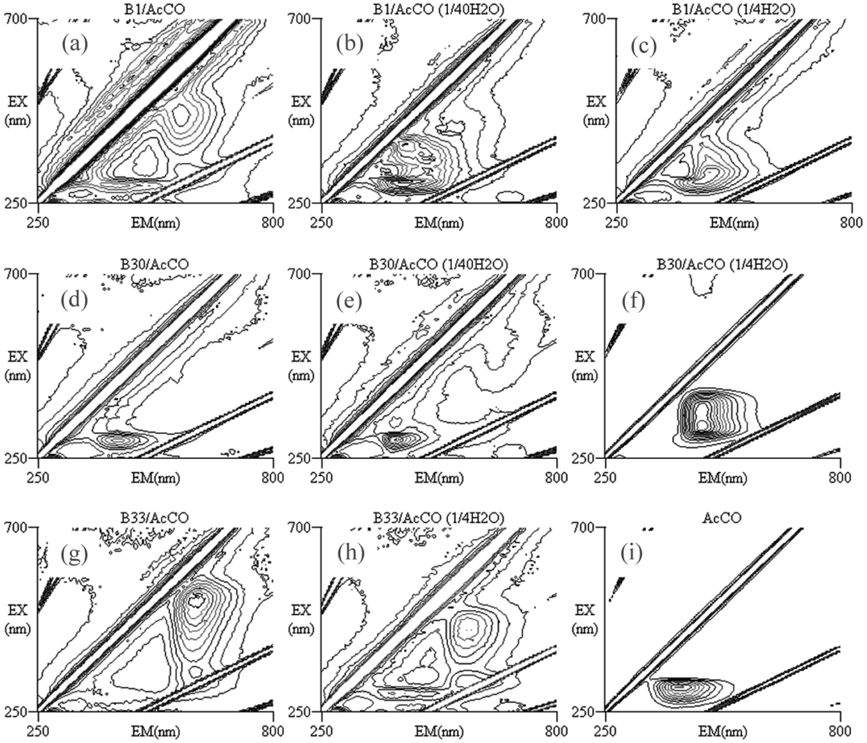

FIGURE 1 EEMs of betaine dye/AcCO and AcCO at 77 K. (a) B1/AcCO, (b) B1/AcCO with 1/40 H_2O (v/v), (c) B1/AcCO with 1/4 H_2O (v/v) (d) B30/AcCO, (e) B30/AcCO with 1/40 H_2O (v/v), (f) B30/AcCO with 1/4 H_2O (v/v), (g) B33/AcCO, (h) B30/AcCO with 1/4 H_2O (v/v), and (i) pure AcCO.

the blue shift of λ_{ex1} was in harmony with that of their solvatochromic properties. As Vitha reported [11], the absorption bands in visible region of all betaine dyes/AcCO were significantly blue shifted according with the water addition. Band I of B1/AcCO and B30/AcCO were much influenced with water addition, contrary to that of B33/AcCO. Both B1/AcCO and B30/AcCO, with a large amount of water, Band I disappeared. It seems to be natural that the *pKa* value of each betaine dye in protonated form was reported to be 8.55, 8.64, and 4.78 for B1, B30, and B33, respectively [12,13]. Other two emission bands (Band II and Band III) showed no significant blue shift in λ_{ex2} and λ_{ex3}. Band III which has the shortest λ_{ex} and λ_{em} could be assigned to the luminescence of AcCO, judging from the similarity to the emission band of AcCO (Fig. 1(i)). The other emission band, Band II was significantly varied with water addition. The large blue shift of λ_{em}

TABLE 1 Emission Bands (λ_{ex} λ_{em}) Appeared in Betaine Dye/AcCO at 77 K

Dye \ Band	I		II[†]		II′[†]		III	
B1	465	585	335	590	–	–	295	410
B1 1/40 H_2O	445	565	325	495	390	440	305	450
B1 1/4 H_2O	(470)[‡]	(565)	325	465	(360)	(465)	305	450
B30	605	725	–	–	(450)	(570)	295	435
B30 1/40 H_2O	515	655	(345)	(645)	(365)	(440)	(295)	(420)
B30 1/4 H_2O	–	–	325	475	365	475	(295)	(475)
B33	525	620	350	625	–	–	295	410
B33 1/4 H_2O	450	600	325	585	(295)	(505)	295	420
AcCO	–	–	–	–	–	–	310	415

[†] As various Band II-type emission bands appear in some cases, the emission bands which have $\lambda_{ex} \sim 325$ nm are listed as Band II and the others are listed as Band II′.

[‡] Numbers in parentheses are weak and the wavelengths are not sure.

of Band II for B1/AcCO and B30/AcCO according with water addition could suggest the excited state protonation and deprotonation of dye molecules. The emission intensity of B30 seemed to be the weakest, and it might be reasonable, because B30 had been reported to be

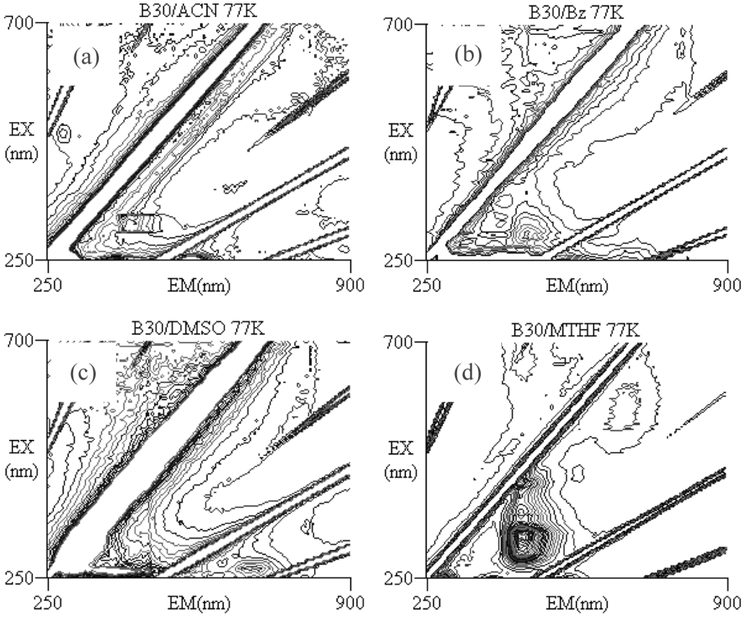

FIGURE 2 EEMs of B30 in various organic solvents at 77 K. Solvent is (a) ACN, (b) Bz, (c) DMSO, or (d) MTHF, respectively.

non-fluorescent [6–8]. The effect of water addition in AcCO should correspond to the interaction between B30 and hydrogen bond donors (HBDs), as Coleman and Murray reported in B30/ACN [14]. Those results mean a possibility to determine the concentration of water or other HBDs in those rigid systems using betaine dyes. It would be convenient as many solvents are frozen to become clouded at cryogenic temperature.

Betaine Dyes/Other Organic Solvents at 77 K

In ACN, Bz, DMSO, and MTHF, B30 (and other betaine dyes) showed similar luminescence to those in AcCO. Figure 2 depict the luminescence of B30/organic solvents. In MTHF (Fig. 2(d)), an emission band, which corresponds to Band I, located at (580 nm, 675 nm) was seen. But in other solvents (Figs. 2(a)–2(c)), only a weak shoulder was seen. No evidence is obtained but it could be caused by the high content of water residue in MTHF, which is dissolved during the preparation of solutions. From these results, we can suppose that Band I should be originated from some betaine dye-HBD complexes. As Aldoshin *et al.* reported [15], protonated betaine dyes show luminescence with UV-excitation at low temperature, the "slow luminescence" which was also observed in B30 and other betaine dye/organic solvent systems with UV-excitation might have some relationships between protonation and/or deprotonation processes in their UV-excited states.

B30 Luminescence in Polymeric Solids at r.t. and at 77 K

To compare the microenvironment in polymeric solids, we measured B30/PMMA, PBzMA, and PcHMA. The results are in Figures 3(a)–3(d). Figs. 3(a)–3(c) were recorded at r.t. and Figure 3(d) was recorded at 77 K. Almost all the EEMs of B30/polymer showed a very weak long wavelength emission shoulder, which is similar to Band I in B30/AcCO. In polymeric solids, the positions of the absorption bands were difficult to determine, as the EEMs were determined with small flakes of B30-dispersed and dried polymers put into a tube. PBzMA and PcHMA were used to check the effect of steric hindrance around the methacrylate ester group in the polymer chain. However, the effect of the substitution at ester group could not be confirmed. Judging from the appearance of a weak Band I-like emission shoulder for B30/PMMA, the hardness around the ester group could be more effective than the steric hindrance. The reason of the appearance of the Band I-like emission shoulder for those B30/polymer systems (it had never appeared for the polymeric samples used in our previous reports

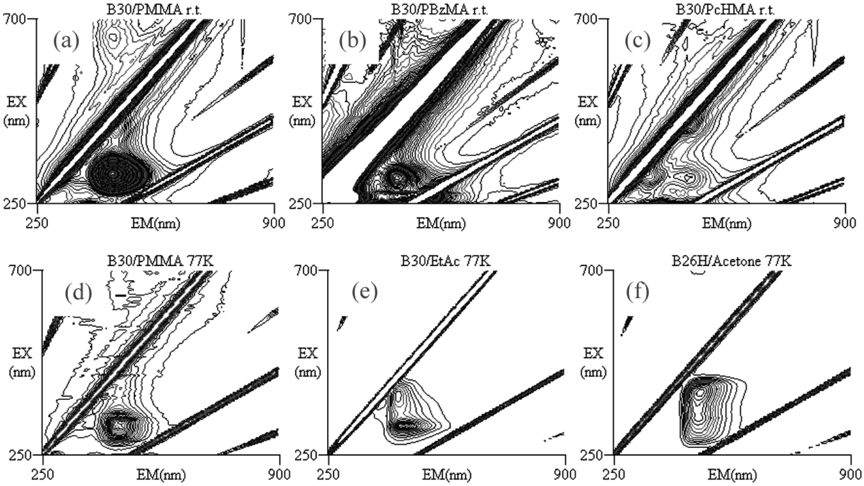

FIGURE 3 EEMs of B30 in various polymers at r.t. or 77 K, B30/EtAc at 77 K, and B26H/Ac at 77 K. (a) B30/PMMA at r.t., (b) B30/PBzMA at r.t., (c) B30/PcHMA at r.t., and (d) B30/PMMA at 77 K, (e) B30/EtAc at 77 K, and (f) B26H/AcCO at 77 K.

[4,5], as the preparation procedures were not same to those used in this study) is not clear, but the solvent or water residue mingled in the preparation procedures could play an important role. As all the long emission shoulder is very weak and it can be seen not all samples, we have to determine more numbers of samples and it is necessary to check the effect of the solvent or water residue in polymers and in organic solvents.

Comparison of UV-excited Emission Band of B30/Polymer with Related Compounds

In the solvents having an ester group or a carbonate, the color of B30 immediately disappeared when B30 dissolved in those solvents, it resembles to the behavior of B30 in acidic solvents such as acetic acid. We examined EtAc, phenyl acetate and diethyl carbonate. As a typical ester solvent, EtAc was used and the EEM of B30/EtAc is shown in Figure 3(e). The UV-excited emission bands of B30/PMMA are much similar to those of B30/EtAc. Judging from the resemblance among B30/PMMA, B30/EtAc, and B30/AcCO with 1/4 H_2O (v/v) (shown in Figure 1(f)), the features of blue ~ bluish green luminescence of B30/polymers couldn't be originated from "the polymer effects", for example, free volume of the polymer. We also determined B26H as these kinds of dyes are known to show luminescence [15]. The UV-excited emission band was seen for many B30/polymers or organic solvents [4,5]. B26H/AcCO at 77 K showed similar emission band (shown in Fig. 3(f)). The emission band appeared in the EEM of B26H/AcCO ($\lambda_{em} \sim 485$ nm) is similar to Band II of B30/AcCO with 1/4 H_2O (v/v), and is a little bit similar to B30/PMMA. At this moment in time, the UV-excited emission band of B30/polymer might be involved with protonation and/or deprotonation processes of betaine dye molecules in the ground and/or UV-excited states.

CONCLUSIONS

We measured EEMs of betaine dyes in frozen organic solvents at 77 K and found a weak emission shoulder (classified as Band I). A similar emission shoulder was observed for some B30/polymer samples at 77 K and at r.t. Band I could be originated from betaine dye-HBD complexes, because this type of luminescence was enhanced with the presence of HBD molecules in the system.

UV-excited emission bands of B30/polymer [4,5] might have a relationships with protonation and/or deprotonation processes in their ground and/or UV-excited states. No polymer effect was confirmed because of the similar phenomena (Band II type emission bands) could be seen for betaine dye/non-polymeric organic solvent systems.

The luminescence of betaine dyes are much complicated, detailed study is necessary to elucidate the mechanism of the luminescence. At least, the rigidity of the solvent is appeared to be important, and hydrogen bond could play an important role in the ground and/or excited states.

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