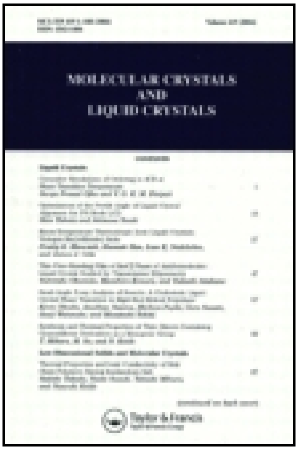

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Effects of Molecular Structure on Luminescent Properties of Betaine Dyes

Satoko Nishiyama [a] , Masahiro Tajima [b] & Yasuhiko Yoshida [a] [b]

[a] Bio-Nano Electronics Research Center, Toyo University, Kawagoe, Saitama, Japan

[b] Department of Applied Chemistry, Graduate School of Engineering, Toyo University, Kawagoe, Saitama, Japan

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Satoko Nishiyama
Bio-Nano Electronics Research Center, Toyo University, Kawagoe, Saitama, Japan

Masahiro Tajima
Department of Applied Chemistry, Graduate School of Engineering, Toyo University, Kawagoe, Saitama, Japan

Yasuhiko Yoshida
Bio-Nano Electronics Research Center and Department of Applied Chemistry, Graduate School of Engineering, Toyo University, Kawagoe, Saitama, Japan

We compared spectral properties of Betaine-30 (B30) with other similar betaines or triphenylpyridine. They showed similar UV-absorption and shorter emission spectra in polymeric solids. The emission wavelength appeared to be red shifted with increasing polarity of the solvent or CT characteristics of dye molecule. Other dyes would be able to be used as B30 for a kind of polarity indicators, furthermore, B30 appeared to be most stable among them. We also compared their semiempirical M.O. calculation results. INDO/S calculations showed CT characteristics of their absorption bands in visible region.

Keywords: betaine-30; $E_T(30)$; INDO/S; luminescence; steric hindrance

INTRODUCTION

We previously reported the emission spectra of a solvatochromic dye, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (B30, see the

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Address correspondence to Yasuhiko Yoshida, Department of Applied Chemistry, Faculty of Engineering, Toyo University, Kujirai 2100, Kawagoe, Saitama 350-8585, Japan. E-mail: yoshida@eng.toyo.ac.jp

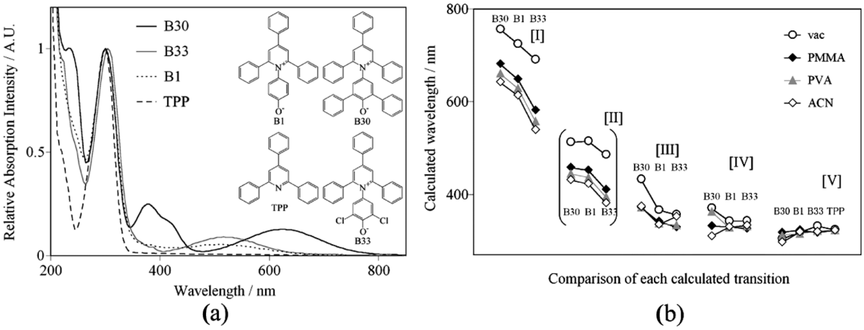


FIGURE 1 Absorption spectra and chemical structures dye molecules (a) and several calculated transition wavelengths of dyes (b). (a) The structures of dyes (B1, B30, B33 and TPP) are shown inside of the absorption spectra. (b) Transition states of all dyes are calculated in vacuum, PMMA, PVA, and ACN which have oscillator strengths ≥ 0.1 (except [II], which have oscillator strengths ~0.05, plotted points of [II] are packed in a round bracket).

inset of Fig. 1) [1–3] dispersed polymeric solids [4]. $E_T(30)$, a solvent parameter which indicates the polarity of the system, is estimated with the spectral shift of the charge transfer (CT) absorption band of B30 [1–3]. Though B30 is said to be non-fluorescent in solutions because of the very fast energy transfer from dye molecules to solvent molecules [5], we observed luminescence for B30-dispersed polymer thin films [4,6]. The emission wavelength (λ_{em}) was different in different polymers. In our previous study, as rigid polymeric systems, poly(methyl methacrylate) (PMMA) and poly(vinyl alcohol) (PVA), were used. Each λ_{em} was determined for B30/PMMA and B30/PVA as an attempt for determination of the polarity of those polymers using luminescence (We use the abbreviation, “B30/polymer” for B30-dispersed polymer samples, hereafter). Though we also prepared B30-dispersed polystyrene (PSt), we could not determine the luminescence of B30/PSt was weak because of the huge PSt absorption band is located near by. In this study, we re-examined the case of B30/PSt.

The aim of this study is to obtain information about the relationships between the emission wavelength and charge distribution with comparing B30 and other similar betaine dyes, 1-(4-hydroxyphenyl)-2,4,6-triphenylpyridinium hydroxide inner salt hydrate (B1), 2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (B33), and a similar molecule, 2,4,6-triphenylpyridine (TPP) (molecular structures of these dyes are shown in the inset of Fig. 1), for the elucidation of the photoemission processes of these dyes in solid phase. Using molecular orbital (M.O.) calculations, we considered the polarities of each excited state of above dyes.

EXPERIMENTAL

Dyes, B30 (90%, Sigma-Aldrich), B33 ($\geq$99%, Fluka) and TPP (as a product of Sigma-Aldrich's Rare Chemical Library), were purchased from Sigma-Aldrich Japan K.K. B1 was synthesized by the previously reported method [1,7]. UV or Fluorescence grade solvents were used in this study. PMMA (Sigma-Aldrich, Average M_w: $\sim$ 350,000), PVA (Kanto Chemicals Co., $M_w \sim 22{,}000$, hydrolyzed at $86.5 \sim 89$ mol %), and PSt (Sigma-Aldrich, 182427, typical M_w is 280,000) were used as received. For the preparation of polymer thin films, acetone, water, and benzene were used as solvent for PMMA, PVA, and PSt, respectively. Each betaine or TPP was added as a small amount of acetone solution to polymer solutions, and mixed together. Each dye was added in the ratio, 1×10^{-3} mol/kg polymer (in previous study, we used $10^{-2} \sim 10^{-5}$ mol dye/kg polymer [4]). Mikasa Spincoater 1H-D7 spin-coating machine was used for preparing polymer thin films on quartz substrates (rotated at 1500 rpm for 60 s). Polymer films were dried *in vacuo* above *Tg* (130°C for PMMA, 110°C for PSt, and 70°C for PVA) or dried at room temperature (r.t.). UV-vis absorption spectra were recorded with a Hitachi U-3200 Spectrophotometer. We determined fluorescence spectra and excitation emission matrixes (EEMs) [8] with Hitachi F-4500 Fluorescence Spectrophotometer [4,9,10]. M.O. calculations were done using semiempirical methods, as preliminary calculations. Molecular geometry optimization for each state (S_n, $n = 0 \sim 3$) were calculated by MOPAC2002 [11] using the AM1 Hamiltonian [12] for all betaines and TPP. Absorption spectra were also calculated using INDO/S method in MOS-F ver.6.0A [13] for each molecule. For polymer models, we used typical values of dielectric constants and refractive indexes, 3.9 and 1.49 for PMMA, 6.9 and 1.53 for PVA, respectively.

RESULTS AND DISCUSSION

Betaines and TPP Absorption Bands in Acetonitrile

Each dye was dissolved in acetonitrile (ACN). As ε values (ε:absorption coefficient) of the betaine dyes are different each other, the absorption spectra were normalized with the absorbance at 300 nm. The relative intensities were depicted in Figure 1(a). In $200 \sim 300$ nm region, two absorption bands are seen for all dyes, and the positions of those bands are very similar. It could correspond to the similarity of the absorption bands of those dyes at 300 nm. For the comparisons among the observed absorption bands, INDO/S calculation wavelengths of transition states for each molecule in vacuum, PMMA, PVA and ACN are grouped into five groups and displayed in Figure 1(b) for five calculated excited states which have relatively large oscillator strengths (except [II]).

The relationships among calculated wavelengths (λ_{calc}s) of betaines are $\lambda_{\mathrm{calc,B30}} > \lambda_{\mathrm{calc,B1}} > \lambda_{\mathrm{calc,B33}}$ for [I] ~ [III]. It could correspond to the solvatochromic characteristics of these betaines in visible region. It is in harmony with the absorption bands of these betaines have CT characteristics [1 ~ 3]. For [IV] and [V], $\lambda_{\mathrm{calc.}}$s doesn't depend on the molecular difference or solvent polarity. All betaines and TPP have absorption bands around 300 nm (shown in Fig. 1a). These observed and calculated results would suggest that the absorption bands in UV-region have characteristics of π-π^* transition. Though the numbers of transition bands and the wavelengths are different from those in observed spectra, it is somwhat inevitable for the calculation results, as the methods of calculation don't consider the effect of temperature and the effects of polymeric solvent molecules (the bulkiness and the low mobility). As B30 is known to have a thermochromic feature (a large blue-shift of the CT band by freezing) [14], the calculated absorption bands (calculated at 0 K) would be red-shifted at higher temperature (r.t.) in solvents of low molecular weight. Contrary to low molecular weight solvents, in polymeric solids, we observed no significant change in fluorescence spectra of B30/PMMA at 77 K from those at r.t. and phosphorescence [15]. Though the lifetimes of their luminescence at 77 K were different from those at r.t., fluorescence spectra and EEMs of B30/PMMA were almost same [15]. From the fast observations of $S_0 \rightarrow S_3$ excitation (the relaxation process is $S_3 \rightarrow S_1 \rightarrow {}^{\tau}S \rightarrow S_0$; ${}^{\tau}S$: thermally excited state) [16], it is natural if B30/PMMA shows thermochromic features in emission spectrum. Nevertheless, we couldn't observe a notable change. The reason why B30/PMMA doesn't show large thermal effect would be the stiffness or some kind of polymer effect of PMMA. Within the degree of freedom in polymeric solids, the excited state-B30 molecules wouldn't exist in S_1 state. Judging from $\lambda_{\mathrm{em}} < \lambda_{\mathrm{abs}}$ $_{\mathrm{abs}}$ ($S_0 \rightarrow S_1$), the observed emission band around 450 nm of B30/PMMA originated from some higher excited states of B30 or B30-containing complex. As we described in our previous report [4], it wouldn't be an exception of Kasha's rule [17] and the absence of S_1 state in the photo-excited process should occur in polymeric solvents. With AM1 calculation, S_1 state was optimized in a different distorted form from other higher excited states (data not shown). Though the method is a semiempirical one, it can be possible.

Comparing Emission Bands of Betaines and TPP in Polymeric Solids

Each observed λ_{em} is summarized in Table 1. In Figures 2(a)–(d), 3(a), 3(c), and 3(d), EEMs and emission spectra of B1, B33 and TPP dispersed

TABLE 1 Typical Values of λ_{em} for Each Dyes in Polymeric Solids

Dye Polymer	λ_{em} in PMMA	λ_{em} in PVA	λ_{em} in PSt
B30	460[*]	467[*]	451[§]
B1	453[‡][§]	460[‡][§]	n.d.[¶]
B33	430[§]	–[†]	n.d.[¶]
TPP	349	355[§]	n.d.[¶]

[*] Data from Ref. 4. [†] Not observed. [¶] Not determined.

[‡] Decomposition of the dye was observed in the emission spectrum.

[§] Emission wavelength is not stable because of the weakness of the emission intensity or the effect of matrix absorption (at short λ_{ex}.).

in PMMA are lined up. In Figures 2(e)–(h), 3(b), and 3(e), EEMs and emission spectra of B1, B33 and TPP dispersed in PVA are lined up. TPP, B1 and B33 (in PMMA) showed emission bands similar to those of B30, and the observed λ_{em} of TPP, B1 and B33 showed shorter λ_{em}s than correspondent λ_{em} of B30. B33/PVA did not show any emission band except scattering. In emission spectra of B33/PMMA (Fig. 3(c)), λ_{em} is not stable. From these results, B33 is not so suitable to determine the polarity in polymeric solids, comparing with B30. B1/ PVA showed similar emission bands to B30/PVA, on the contrary to B33/PVA. Though the features of the emission band and EEMs of B1/polymer is similar to B30/polymer, the emission intensities of B1 was much lower from those of B30 and other emission bands at shorter wavelength appeared. The shorter emission bands would be due to the decomposition of B1 in the preparing process. At this point, B30 can be considered to be better than B1. Also λ_{em} of TPP/PVA is longer than those of TPP/PMMA.

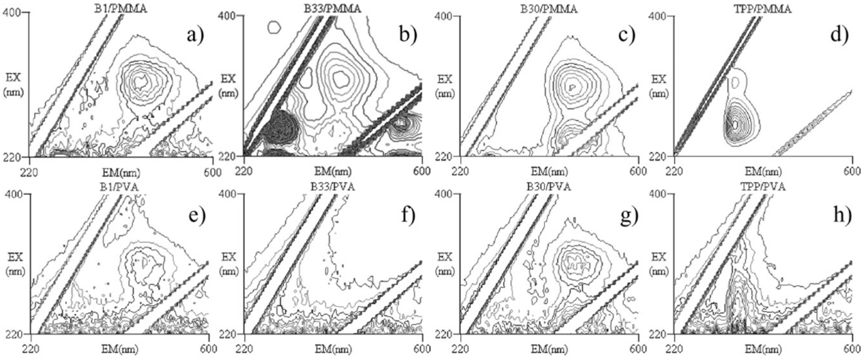
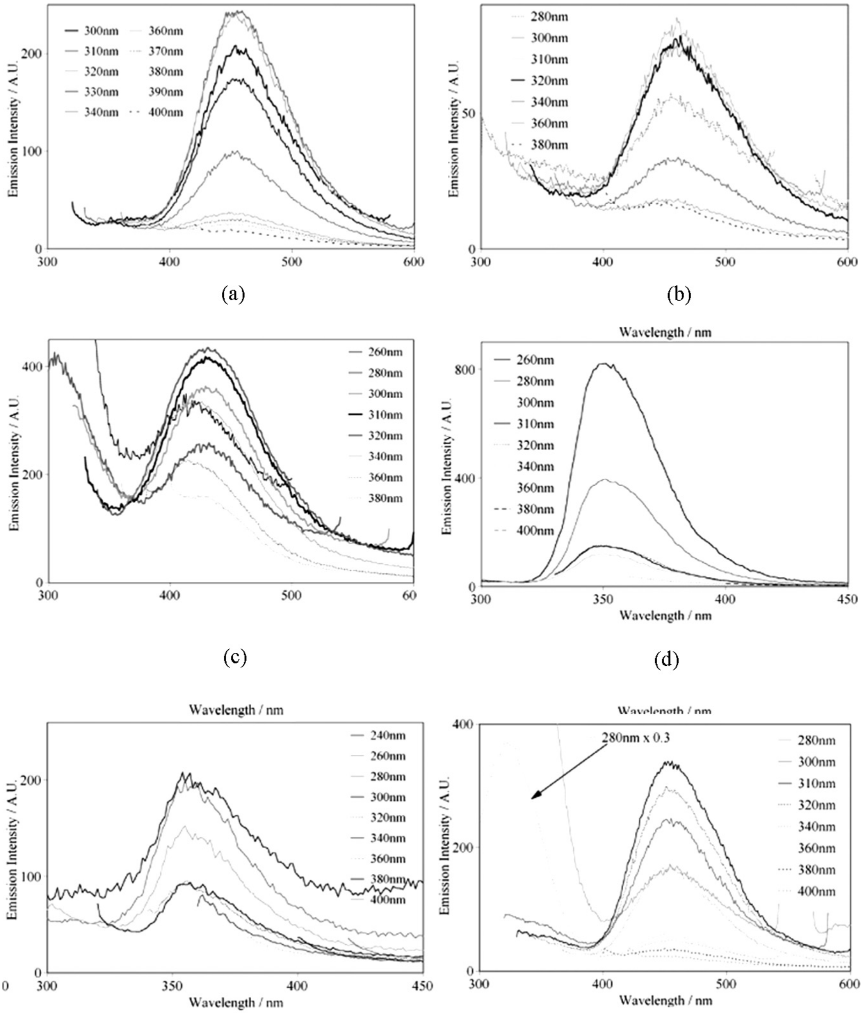


FIGURE 2 EEMs of B1,B30, B33 and TPP in polymeric solids (upper: PMMA, lower: PVA). Dispersed dyes are B1 (a, e), B33 (b, f), B30 (c, g), and TPP (d, h).



(a) (b)

(c) (d)

(e) (f)

FIGURE 3 Emission spectra of B1, B33 or TPP in PMMA or PVA and B30/PSt. The wavelengths indicated in the legends are the excitation wavelengths. Dispersed dyes are B1 (a) B1/PMMA, (b) B1/PVA), B33 (c) B33/PMMA), TPP (d) TPP/PMMA, (e) TPP/PVA), and B30 (e) B30/PSt).

It can be considered as solvatochromic characteristics of all betaines and TPP, though TPP is different from betaines at the point of charge. All betaines are zwitterions and TPP is not. We need to confirm the extent of the participation of some protonated-TPP or other cationic species originated from TPP.

We also showed emission spectra of B30/PSt in Figure 3(f). As we described in our previous study [4], luminescence of B30/PSt was easily quenched or very weak than the emission band of PSt, which is located at shorter λ. On the other hand, the values of λ_{em} for almost all B30/PSt spin coated thin films were $\sim 451\,\text{nm}$. So we report the value of λ_{em} for B30/PSt as 451 nm for the present (this value is entered in Table 1). The intensity ratio of both B30 and PSt emission bands are not constant.

Considerations on the Excited States of Betaines and TPP

The calculated charges at the nitrogen atom in pyridinium or pyridine ring, the oxygen atom in phenolate, and the substituents at 2,5-positions of phenolate are depicted in Figure 4. Contrary to the charges on the nitrogen atom (Fig. 4(a)) and the oxygen atom (Fig. 4(b)), which have similar tendencies for each dye, the charge on the substituent appeared to be different. The charge of the substituted chlorine of B33 is much negative than hydrogen of B1 or phenyl of B30. As the degrees of charge localization on the nitrogen and the oxygen are similar for these three dyes, the difference in the extent

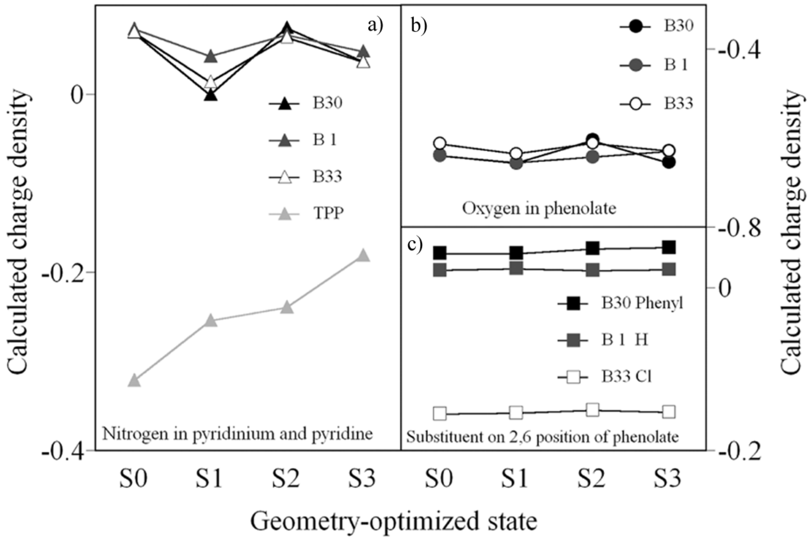


FIGURE 4 Changes in the calculated charges of each state for betaines and TPP.

of CT characteristics of these dyes would be caused from these differences and the size of the substituents. Comparing each state, the charges on the oxygen and the substituent is nearly constant, but the charge on the nitrogen is much different. The decrease of the positive charge from S_0 to S_1 matches to the CT characteristics of these betaines. The change in the degree of stabilization with increasing solvent polarity ΔE_s appeared to be different for S_0, S_1 and S_2 (data not shown). Though all of them shows blue shift in the longer transition bands, the degree of ΔE_s was calculated to be in the order, $\Delta E_s(S_1) > \Delta E_s(S_0) \geq \Delta E_s(S_2)$. It could be interpreted as the order of the polarity of each state as follows, (polarity of S_2) $\geq$ (polarity (polarity of S_0) $>$ (polarity of S_1). It could be in harmony with the red shift of the observed emission bands with increasing solvent polarity of all betaines and TPP. A red shift in luminescence often occurs in the cases which polar excited state and less-polar ground state are concerning, as the excited state is stabilized and the ground state is not stabilized in polar solvents. Of course, the nature of the observed emission bands are still in question and more detailed study is necessary.

CONCLUSIONS

From the emission spectra of these betaines and TPP, the features of the UV-excited emission bands are found to be similar. The emission wavelength with UV-excitation appeared to be red shifted increasing solvent polarity. The emission wavelengths was different for each molecule ($\lambda_{\mathrm{em,TPP}} < \lambda_{\mathrm{em,B33}} < \lambda_{\mathrm{em,B1}} < \lambda_{\mathrm{em,B30}}$). The reason of the difference in λ_{em} of each molecule could be considered in the difference of the stabilization of the excited states. The results of semiempirical M.O. calculations show the difference in the charges on nitrogen atom and the substituent on 2,5-positions of phenolate and suggest the effect of the charge distribution.

Unfortunately, the spectral shift of λ_{em} of these dyes-dispersed polymeric solids was found not to be as large as that of CT absorption bands of these dyes. However, we found the possibility to determine or indicate some rigidness or mobility in local- or micro-environment of the system using this kind of luminescence.

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