5150 J. Phys. Chem. 1984, 88, 5150–5154

ARTICLES

Excimer Emission in Protonated Pyridine Systems. 2. Excimer Emission of Protonated Dipyridylalkanes in Solution at Room Temperature and 77 K

Takashi Handa,* Yoshio Utena, and Hirofumi Yajima

Department of Applied Chemistry, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan *(Received: October 31, 1983; In Final Form: March 6, 1984)*

Emission properties of (2-pyridyl)-$(CH_2)_n$-(2-pyridyl) (n = 2, 3, 5, and 7) and (4-pyridyl)-$(CH_2)_n$-(4-pyridyl) (n = 2, 3, and 5) were studied in solution in the presence of trifluoroacetic acid at room temperature and 77 K. At room temperature, only 1,3-di(2-pyridyl)propane exhibits a very weak fluoroescence at approximately 6900 cm^{-1} to the red of the normal fluorescence. This band is ascribed to an intramolecular excimer fluorescence between the protonated pyridine moieties. However, 4,4′-dipyridylalkanes do not fluoresce. At 77 K, being specific to a mixed solvent of tetrahyrofuran, methanol, and methyltetrahydrofuran (4:3:1 by volume), the protonated 2,2′-dipyridylalkanes exhibit a structureless band around around 325 nm besides the normal fluorescence band, but they exhibit no excimer fluorescence. On the other hand, the protonated 4,4′-dipyridylalkanes apparently exhibit only a structureless band around 325 nm. The 325-nm fluorescence band comes from a dimerlike excimer in which the protonated pyridine moieties interact intermolecularly in the excited state. The efficiency of the dimerlike excimer formation is independent of the length of methylene chain. From studies on the effects of solvent and temperature on the dimerlike excimer emission, it is found that the formation of the dimerlike excimer is strongly related to a solvent cage effect.

Introduction

Many studies have been made on the intramolecular excimer formation of α,ω-diphenylalkanes,[1] α,ω-dinaphthylalkanes,[2] and related molecules[3,4] The n = 3 rule of Hirayama shows that the propane chain is the only chain which satisfies the distance and overlap requirements for intramolecular excimer formation. In addition to these geometrical requirements, excimer formation is controlled by the motions of both the chromophore and the intrachain.[2,3] A perfect overlapping sandwich configuration is preferred for excimer formation.[1,2,5-7]

Recently, we reported that protonated mono- and dialkylpyridines exhibit only a single band around 295 nm, but they exhibit no excimer fluorescence at room temperature and, further, that being specific to the mixed solvent of tetrahydrofuran, methanol, and methyltetrahydrofuran (4:3:1 by volume), they exhibit a characteristic fluorescence around 325 nm at 77 K.[8] This band is assigned to an emission from the intramolecular dimerlike excimer formed between the two protonated monoalkylpyridines (and dialkylpyridines) and the most important factor for dimerlike excimer formation is a mixed solvent cage effect. This dimerlike excimer fluorescence appears to be unique to mono- and dialkylpyridines in aza-aromatic compounds. Up to now, no studies on intramolecular excimer formation have been reported on compounds where the two pyridine groups are separated by a number of ethylene chains.

This paper deals with emission properties in a series of (2-pyridyl)-$(CH_2)_n$-(2-pyridyl) (n = 2, 3, 5, and 7) and (4-pyridyl)-$(CH_2)_n$-(4-pyridyl) (n = 2, 3, and 5) in solution in the presence of trifluoroacetic acid at room temperature and 77 K. In addition, we studied the effects of the solvent and temperature on dimerlike excimer formation.

Experimental Section

Materials. 1,2-Di(2-pyridyl)ethane (2-DPEt) and 1,3-di(2-pyridyl)propane (2-DPPr) were prepared by treating 2-picolyllithium in tetrahydrofuran solution at −70 °C with α-chloromethylpyridine or β-bromoethylpyridine. The reaction mixture was treated with water and completely extracted with ether. After the ether was removed, the residue was either recrystallized from n-hexane or distilled under reduced pressure.[9] 1,5-Di(2-pyridyl)pentane (2-DPPe) and 1,7-di(2-pyridyl)heptane (2-DPHp) were made from 2-picolyllithium and the appropriate polymethylene bromides by the same method as those used for 2-DPEt and 2-DPPr and purified by distillation under reduced pressure.[9] The structures of these compounds were confirmed by H NMR spectroscopy and elemental analysis.

1,5-Di(4-pyridyl)pentane (4-DPPe) was synthesized by the same method as that for 2-DPPe, 4-picolyllithium being used instead of 2-picolyllithium. The obtained crude product is recrystallized from n-hexane to give colorless crystal: mp 57–58 °C; NMR ($CDCl_3$) δ = 1.6 (m, CH_2), 2.57 (t, CH_2), 7.04 (d, d, β-H of pyridyl), and 8.43 (d, d, α-H of pyridyl). Calcd for $C_{15}H_{18}N_2$: C, 79.65; H, 7.96; N, 12.39. Found: C, 79.62; H, 7.92; N, 12.28. 1,2-Di(4-pyridyl)ethane (4-DPEt) and 1,3-di(4-pyridyl)propane (4-DPPr) from Aldrich Chemical Co. were recrystallized from n-hexane.

1,3-Di(2-pyridyl)propane hydrochloride (2-DPPr·2-Cl) was prepared by the same method as that of the pyridinium hydrochloride.[10] The composition was checked by titrating a solution of the product in 50:50 water–methanol with a sodium hydroxide solution.

1,2-Dichloroethane (DCE), tetrahydrofuran (THF), methanol (MeOH), methyltetrahydrofuran (MTHF), isopentane, ethanol, ethyl ether, and methylcyclohexane (Dotite spectrosol) were purified by the usual methods. Ethylene glycol (Chromatographic grade) was used without further purification. Trifluoroacetic acid (TFA) was refluxed with P_2O_5 for 7 h and distilled over P_2O_5. The mixtures of THF, MeOH, and MTHF (4:3:1 by volume),

---

(1) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163.

(2) Chandross, E. A.; Dempster, C. J. *J. Am. Chem. Soc.* **1970**, *92*, 3586.

(3) Klöpffer, W. *Ber. Bunsenges. Phys. Chem.* **1970**, *74*, 693.

(4) Zachariasse, K. A.; Kühnle, W.; Weller, A. *Chem. Phys. Lett.* **1978**, *59*, 375.

(5) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3554.

(6) Chandross, E. A.; MacRae, E. G.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3546.

(7) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 355.

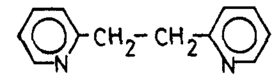
(8) Handa, T.; Utena, Y.; Yajima, H., to be published.

(9) Ishii, T.; Handa, T.; Utena, Y.; Yamauchi, T. *Rep. Prog. Polym. Phys. Jpn.* **1981**, *24*, 449.

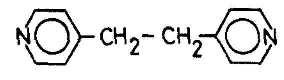
(10) Taylor, M. D.; Grant, L. R. *J. Chem. Educ.* **1955**, *32*, 35.

0022-3654/84/2088-5150$01.50/0

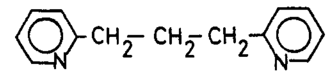
TABLE I: Structures of Dipyridylalkanes



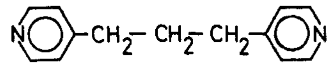
2-DPEt



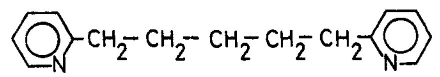
4-DPEt



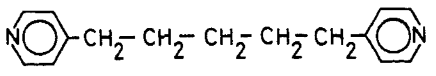
2-DPPr



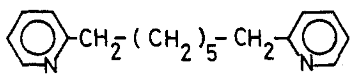
4-DPPr



2-DPPe



4-DPPe



2-DPHp

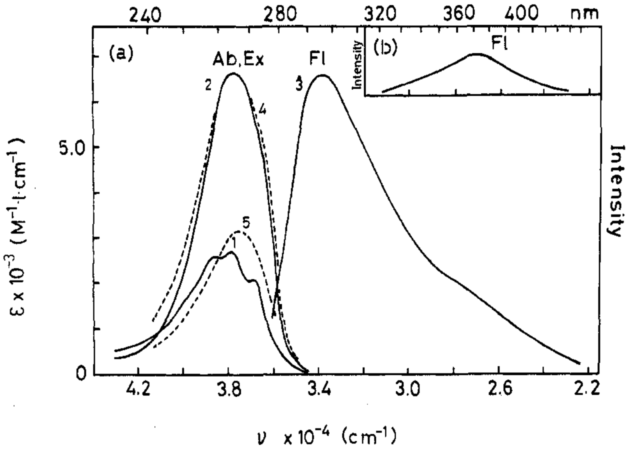


Figure 1. (a) Absorption (Ab), fluorescence (Fl), and fluorescence excitation (Ex) spectra of 2-DPPr in DCE in the presence of TFA at room temperature. 2-DPPr, 1.0 × 10^{-4} M (chromophore unit). Ab: TFA (M) (1) 0, (2) 8.62 × 10^{-3}. Fl: TFA (M) (3) 8.62 × 10^{-3}. Ex: TFA (M) (4) and (5) 8.62 × 10^{-3}, (4) Emi 300 nm, (5) Emi 370 nm. (b) Difference spectrum between the normalizing spectra of 2-DPPr and 2-DPHp–TFA systems.

ethylene glycol and H_2O (1:1 by volume) (EGW), ethyl ether, isopentane, and ethanol (5:5:2 by volume) (EPA), and methylcyclohexane and isopentane (1:6 by volume) (MP) were used as solvents at 77 K. The fluorescence spectra of the following systems were unable to be measured because of an insoluble character (IS) and an opaque glass state (OG) produced by cooling to 77 K: 2-DPHp (2.0 × 10^{-4} M) in the EGW (IS); 2,2′- and 4,4′-dipyridylalkanes (~5 × 10^{-4} M chromophore unit) –TFA (~8 × 10^{-4} M) systems in MP (OG). Therefore, the measurements in MP were made at given concentration of 2.0 × 10^{-4} and 4.31 × 10^{-4} M for 2,2′- and 4,4′-dipyridylalkanes, and TFA, respectively.

Measurements. Absorption, fluorescence, fluorescence excitation, and fluorescence polarization spectra, and quantum yields and lifetimes were obtained at room temperature or 77 K by the same procedures as described in a previous paper.[8] All sample solutions were not degassed because no differences in spectra or lifetimes were observed.

Results and Discussion

Absorption and Fluorescence Spectra at Room Temperature. The structural formulas of dipyridylalkanes are summarized in Table I. The absorption and fluorescence spectra of 2-DPPr, 2-DPHp, and 4-DPPr in DCE in the presence of TFA are shown in Figures 1–3, together with the fluorescence excitation spectra. The absorption spectrum of 2-DPPr exhibits a vibrational structure with a main peak at 263.0 nm. On addition of a saturated TFA concentration of 8.62 × 10^{-3} M, the maximum molar extinction coefficient increases from 2.6 × 10^3 to 6.3 × 10^3 and the main peak wavelength is shifted to the red by about 2 nm. Furthermore, the spectral shape is broadened. The identical concentration of TFA causes similar changes in the spectrum of 2-DPHp (Figure 2). As for 4-DPPr–TFA system, the maximum molar extinction coefficient increases from 1.7 × 10^3 to 4.5 × 10^3 and the main peak wavelength is shifted to the blue by about 2.5 nm. In the wavelength region from about 270 to 280 nm, the intensity decreases compared with that of 4-DPPr in DCE. These spectral

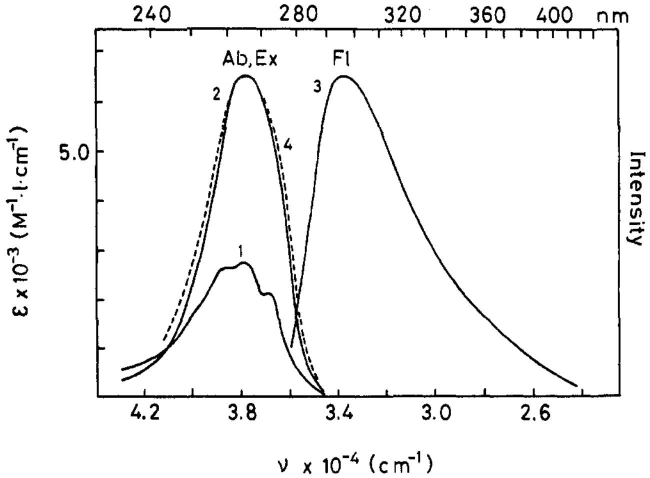


Figure 2. Absorption (Ab), fluorescence (Fl), and fluorescence excitation (Ex) spectra of 2-DPHp in DCE in the presence of TFA at room temperature. 2-DPHp, 1.0 × 10^{-4} M (chromophore unit). Ab: TFA (M) (1) 0, (2) 8.62 × 10^{-3}. Fl: TFA (M) (3) 8.62 × 10^{-3}. Ex: TFA (M) (4) 8.62 × 10^{-3}, Emi 300 nm.

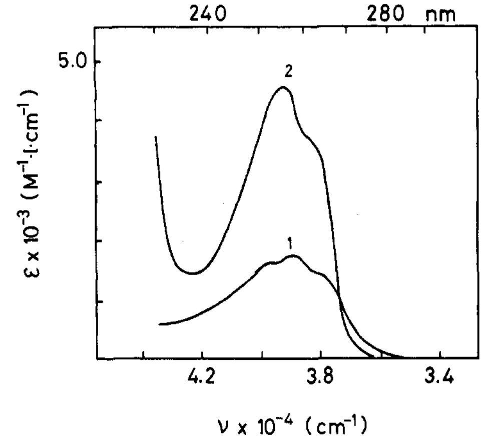


Figure 3. Absorption spectra of 4-DPPr in DCE in the presence of TFA at room temperature. 4-DPPr: 1.0 × 10^{-4} M (chromophore unit). TFA (M) (1) 0, (2) 8.62 × 10^{-3}.

TABLE II: Absorption and Fluorescence Data for the 2,2′- and 4,4′-Dipyridylalkanes in DCE in the Presence of TFA at Room Temperature

		protonated molecule[a]					
sample	λ_{max},[b] nm (ϵ_{max})	λ_{max}, nm (ϵ_{max})	λ_{max}, nm	$\phi_M \times 10^3$	$\phi_E \times 10^3$	τ_M, ns	τ_E, ns
2-Etpy[e]	263.0 (2.7×10^3)	265.0 (6.8×10^3)	295.0	7.8		<0.5	
2-DPEt	263.0 (2.7×10^3)	265.5 (6.9×10^3)	295.5	8.9		<0.5	
2-DPPr	263.0 (2.6×10^3)	265.0 (6.8×10^3)	295.0 370[c]	8.1	0.3	<0.5	*d*
2-DPPe	263.0 (2.6×10^3)	265.0 (6.7×10^3)	296.0	8.0		<0.5	
2-DPHp	263.0 (2.7×10^3)	265.0 (6.6×10^3)	295.0	8.7		<0.5	
4-Mepy[f]	257.5 (1.7×10^3)	254.5 (4.6×10^3)					
4-DPEt	257.5 (1.6×10^3)	254.3 (4.5×10^3)					
4-DPPr	257.5 (1.7×10^3)	254.5 (4.5×10^3)					
4-DPPe	257.5 (1.6×10^3)	254.5 (4.4×10^3)					

[a] TFA, 8.62×10^{-3} M. ϕ_M and ϕ_E are the quantum yields of the monomer and the excimer fluorescence bands. τ_M and τ_E are the lifetimes of the excimer fluorescence. [b] ϵ_{max} is the maximum molar extinction coefficient. [c] Peak wavelength of the excimer fluorescence band. [d] The lifetime was not obtained because the fluorescence intensity is too weak to be measured. [e] 2-Ethylpyridine. [f] 4-Methylpyridine.

changes are very similar to those of 2-ethyl- and 4-methylpyridine–TFA systems.[8] This result indicates that there is no appreciable intramolecular interaction between the two protonated moieties in the ground state.

Although 2-DPPr and 2-DPHp are not fluorescent in DCE (within the detectable limit), the addition of TFA remarkably changes their fluorescence characteristics. The fluorescence spectrum of a 2-DPHp solution containing a saturated TFA concentration of 8.62×10^{-3} M exhibits a weak and broad band with a peak at 295.0 nm. This spectrum is approximately a mirror image of the absorption spectrum. The fluorescence excitation spectrum monitored at 300 nm is similar to the absorption spectrum, but its peak wavelength is shifted to the red by about 1 nm as compared with that of the absorption spectrum. These results suggest that the 295-nm band is the fluorescence of the protonated pyridine moiety. The fluorescence lifetime is shorter than 0.5 ns (instrumental limit) and the quantum yield is 8.7×10^{-3}.

On the other hand, the fluoresence spectrum of the 2-DPPr–TFA system differs from that of the 2-DPHp–TFA system. The spectrum consists of two bands appearing around 295 and 370 nm (a very weak shouder). The former band corresponds to the fluorescence of the protonated pyridine moiety. Simply normalizing the two spectra at the peak wavelength and substracting the monomerlike fluorescence for the 2-DPHp–TFA system gives a structureless band for the 2-DPPr–TFA system whose peak appears at about 370 nm and its position is located at about 6900 cm^{-1} to the red of the monomer fluorescence (Figure 1b). The 370-nm fluorescence spectrum has no mirror image in the absorption spectrum. The fluorescence excitation spectra monitored at 300 and 370 nm are identical with each other, and their spectra are similar to the absorption spectrum. The lifetime of the 370-nm fluorescence is not obtained because the intensity is too weak to be measured. Furthermore, we measured the fluorescence spectrum of a concentrated system of 2-DPPr (1.0×10^{-3} M chromophore) and TFA ($\sim 10^{-2}$ M). It was found that the ratio of the 370-nm to the 295-nm intensities is the same as that obtained for the 2-DPPr–TFA system in Figure 1a. Also, the 370-nm fluorescence is not observed at 77 K (Figure 4a).

From these results, the 370-nm band can be attributed to an emission from the excimer in which the two protonated pyridine moieties in 2-DPPr interact intramolecularly in the excited state.

4-DPPr exhibits no observable fluorescence even in the presence of TFA. This fluorescence characteristic is identical with that of the 4-methylpyridine–TFA system.[8]

The spectral data for other molecules are shown in Table II. The quantum yield of the normal fluorescence in the series of 2,2′-dipyridylalkanes is parallel to that of the 2-ethylpyridine–TFA system and is not strongly affected by the length of methylene chain. The quantum yield of the excimer fluorescence is on the order of 10^{-4}. The quantum yield ratio of the excimer to the normal fluorescence is ca. 4×10^{-2} and this value is found to be one order of magnitude smaller than that of 1,3-diphenylpropane.[1] This result suggests that excimer formation of the 2-DPPr–TFA system is less favorable than that of 1,3-diphenylpropane due to the repulsion between the positively charged pyridine moieties.

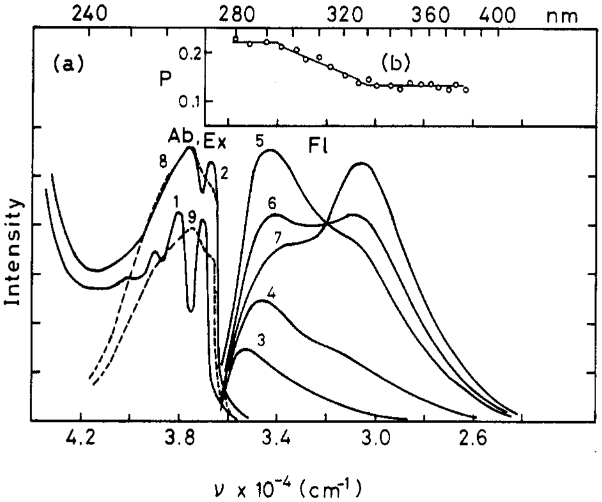


Figure 4. (a) Absorption (Ab), fluorescence (Fl), and fluorescence excitation (Ex) spectra of 2-DPPr in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA at 77 K. 2-DPPr, 2.0×10^{-4} M (chromophore unit). Ab: TFA (M) (1) 0, (2) 4.31×10^{-4}. Fl: TFA (M) (3) 1.72×10^{-5}, (4) 6.46×10^{-5}, (5) 1.03×10^{-4}, (6) 2.16×10^{-4}, (7) 4.31×10^{-4}. Ex: TFA (M) (8) and (9) 4.31×10^{-4}, (8) Emi 330 nm, (9) Emi 300 nm. (b) Fluorescence polarization spectrum; TFA (M), 4.31×10^{-4}.

Absorption and Fluorescence Spectra at 77 K. The absorption and fluorescence spectra of 2-DPPr in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA are shown in Figure 4a, together with the fluorescence excitation spectra. The absorption spectrum of 2-DPPr exhibits a fine vibrational structure with a main peak at 263.0 nm. The addition of a saturated TFA concentration of 4.31×10^{-4} M has the effect of increasing the intensity and the shift of the main peak to the red by about 2 nm. Futhermore, the spectral shape is slightly broadened. These spectral changes are very similar to those of the 2-DPPr–TFA system in DCE at room temperature except for

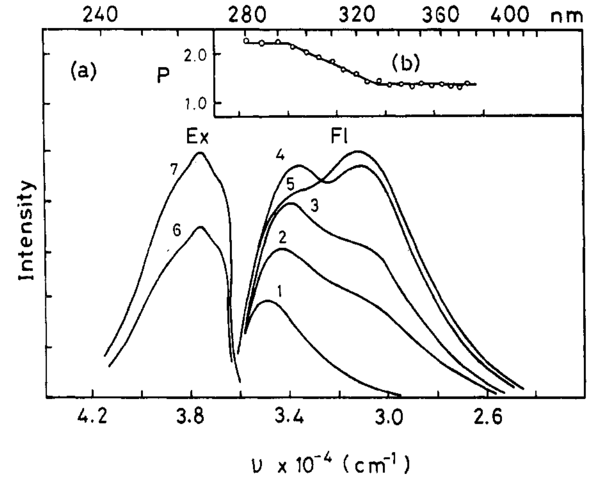


Figure 5. (a) Fluorescence (Fl) and fluorescence excitation (Ex) spectra of 2-DPHp in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA at 77 K. 2-DPHp, 2.0 × 10^{-4} M (chromophore unit). Fl: TFA (M) (1) 1.72 × 10^{-5}, (2) 8.62 × 10^{-5}, (3) 1.21 × 10^{-4}, (4) 2.16 × 10^{-4}, (5) 4.31 × 10^{-4}. Ex: TFA (M) (6) and (7) 4.31 × 10^{-4}, (6) Emi 300 nm, (7) Emi 330 nm. (b) Fluorescence polarization spectrum; TFA (M), 4.31 × 10^{-4}.

a narrowing of the vibrational structures. This result suggests that there is no appreciable ground-state interaction between the two protonated pyridine moieties.

2-DPPr is not fluorescent at 77 K nor at room temperature. However, the addition of TFA produces more complex changes than expected. At a low concentration of TFA (1.72 × 10^{-5} M), the spectrum exhibits a single band with a peak at 285.0 nm. This band corresponds to the fluorescence of the protonated pyridine moiety.[8] As the TFA concentration is increased the 285-nm (monomer) fluorescence intensity increases and a new fluorescence appears around 325 nm. Above a TFA concentration of a 1.72 × 10^{-4} M, the monomer fluorescence intensity decreases and the 325-nm fluorescence intensity increases accompanied by an isoemissive point at 305 nm. The intensities of the two bands are constant above a TFA concentration of a 4.31 × 10^{-4} M. This 325-nm fluorescence spectrum has no mirror image relation to the absorptive spectrum. The fluorescence excitation spectra (TFA, 4.31 × 10^{-4} M) monitored at 300 and 370 nm are coincident with each other, and these spectra are similar to the absorption spectrum. The lifetimes of the monomer and 325-nm fluorescences (TFA, 4.31 × 10^{-4} M) are 0.3 and 4.2 ns, respectively. In the rigid glass solution at 77 K, no excimer fluorescence is observed. The fluorescence and fluorescence excitation spectra of 2-DPHp–TFA system also exhibit similar features. (An isoemissive point is observed above a TFA concentration of a 2.16 × 10^{-4} M) (Figure 5a).

The fluorescence polarization spectrum of the 2-DPPr–TFA system is shown in Figure 4b. The degree of polarization, p, is observed to decrease from 0.21 (in the monomer band region) to 0.14 (in the 325-nm band region) with increasing wavelength. The fluorescence polarization spectrum of the 2-DPHp–TFA system also exhibits a similar feature (Figure 2b). This result suggests that the geometrical configuration of the 325-nm fluorescence species is independent of the length of the methylene chain.

4-DPPr, which is not fluorescent at room temperature, exhibits a very weak fluorescence in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA as shown in Figure 6. Each of the spectra apparently exhibits a broad band with a peak at 326.0 nm and the spectral shape is similar to that of the 325-nm fluorescence band in the 2-DPPr–TFA system. The fluorescence intensity leveled off above a TFA concentration of a 4.31 × 10^{-4} M. The fluorescence excitation spectrum (TFA, 4.31 × 10^{-4} M) monitored at 330 nm exhibits a vibrational structure with the main peak at 256.0 nm, and this spectrum is similar to the absorption spectrum of the 4-methylpyridine–TFA system.[8] Although each of the spectra exhibits only a broad band, the best-fit simulation of the deconvolution in the decay curve (TFA, 4.31 × 10^{-4} M) suggests the presence of two species, one of which is presumably a monomer species and the other is the 325-nm species. The lifetime of the latter is 6.2 ns, while that of the former is 0.9 ns.

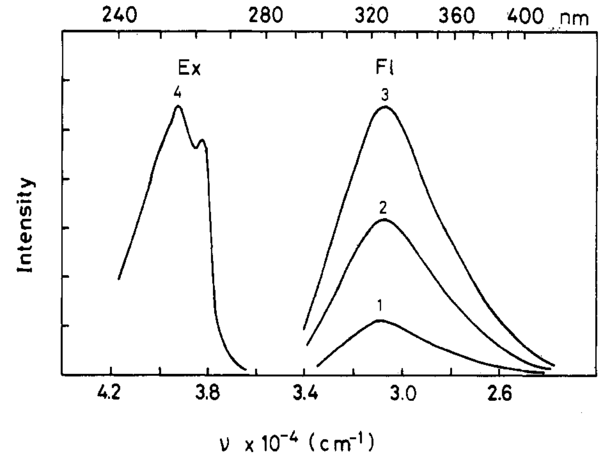


Figure 6. Fluorescence (Fl) and fluorescence excitation (Ex) spectra of 4-DPPr in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA at 77 K. 4-DPPr, 2.0 × 10^{-4} M (chromophore unit). Fl: TFA (M) (1) 4.31 × 10^{-5}, (2) 1.21 × 10^{-4}, (3) 4.31 × 10^{-4}. Ex: TFA (M) (4) 4.31 × 10^{-4}, Emi 330 nm.

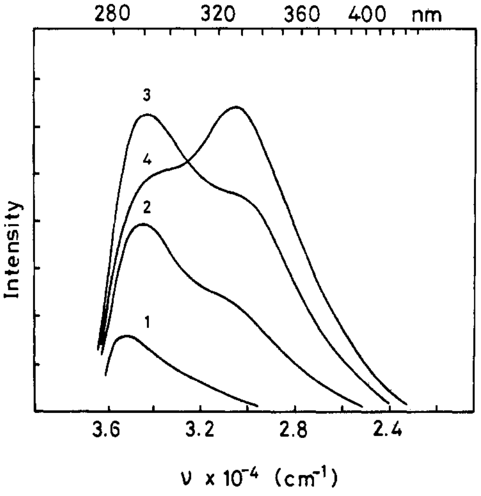


Figure 7. Fluorescence spectra of 2-DPPr·2HCl in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) at 77 K: (1) 2.5 × 10^{-5} M, (2) 5.0 × 10^{-5} M, (3) 2.0 × 10^{-4} M, (4) 4.0 × 10^{-4} M. The concentration is a chromophore unit.

In order to determine whether the 325-nm fluorescence comes from the intra- and intermolecular interaction between the protonated pyridine moieties, the fluorescence spectra of 2-DPPr·2HCl in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) were measured at 77 K. As seen from Figure 7, the 325-nm fluorescence intensity shows a strong concentration dependence.

From above-mentioned fluorescence properties, the 325-nm band can be attributed to an intermolecular dimerlike excimer fluorescence formed between the protonated pyridine moieties.

The spectral data of other molecules are shown in Table III. The intensity ratio of the dimerlike excimer to the monomer fluorescence bands in the series of 2,2′-dipyridylalkanes is ca. 7 and this value is parallel to that of the 2-ethylpyridine–TFA system. This result indicates that the efficiency of the dimerlike excimer formation is independent of the length of methylene chain. Also, the lifetime of the dimerlike excimer fluorescence in the series of 2,2′- and 4,4′-dipyridylalkanes stays in the range from 4 to 6 ns, irrespective of the length of the methylene chain.

Temperature Effect on Dimerlike Excimer Fluorescence. The fluorescence spectra of 2-DPPr in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA

TABLE III: Fluorescence Data for 2,2′- and 4,4′-Dipyridylalkanes in the Mixed Solvent of THF, MeOH, and MTHF (4:3:1 by Volume) in the Presence of TFA at 77 K[a]

sample	$\lambda_{\max}$,[b] nm	I_D/I_M[c]	τ_M	τ_D[d]
2-Etpy[e]	325.0	6.7	0.8	4.3
2-DPEt	328.0	5.6	1.1	3.9
2-DPPr	325.0	8.1	0.3	4.2
2-DPPe	326.0	7.9	0.6	3.2
2-DPHp	322.0	7.2	0.8	4.9
4-Mepy[f]	~325 s		0.5	5.1 (1.3)
4-DPEt	325.0		0.4	4.3 (1.0)
4-DPPr	326.0		0.9	6.2 (0.7)
4-DPPe	325.0		0.3	5.2 (0.8)

[a] TFA, 4.31 × 10^{-4} M. [b] Peak of the dimerlike excimer fluorescence. s denotes shoulder. [c] The ratio of the dimerlike excimer to the normal fluorescence band intensities. [d] τ_M and τ_D are the lifetimes of the normal and the dimerlike excimer fluorescence. The two-exponential fit (in parentheses) was in better agreement with the decay curve than the one-exponential fit. [e] 2-Ethylpyridine. [f] 4-Methylpyridine.

at several temperatures are shown in Figure 8. In the temperature region from 298 to 193 K, each of the spectra consists of normal and excimer bands. (The latter band is extremely weak around 370 nm.) Further cooling to temperatures below 123 K produces a remarkable enhancement of the normal fluorescence intensity and the obvious appearance of the dimerlike excimer fluorescence. However, the excimer band can be hardly recognized at 123 K because of the enhancement of the total fluorescence intensity. Thereby, the intensities of the monomer and dimerlike excimer fluorescence are seen to be remarkably increased by lowering temperature below 123 K. For the purpose of comparison, the fluorescence spectrum at 77 K is shown in the figure. In this measurement, an isoemissive point, which was recognized at 305 nm in Figure 4a, was not observed. Identical measurements were performed for the 2-DPHp–TFA system and the appearance temperature of the dimerlike excimer fluorescence was found to be the same as that of the 2-DPPr–TFA system.

For the strong temperature dependence of the normal fluorescence, it seems that the equilibrium between the pyridine moiety, TFA, and the protonated pyridine moiety moves toward the formation of the protonated pyridine moiety, and the collision quenching between the protonated pyridine moiety and the solvent molecule decreases with lower temperature. The anomalous appearance of the dimerlike excimer fluorescence below 123 K follows the same trend as that observed for the 2-ethylpyridine–TFA system.[8] The appearance temperature (123 K) of the dimerlike excimer fluorescence of the 2-DPPr–TFA system is found to be approximately the same as that of the endothermic peak (129.7 K) of the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume).[8] This result suggests that the formation of the dimerlike excimer is attained through a structural change of the mixed solvent due to volume expansion.

Solvent Effect on Dimerlike Excimer Formation at 77 K. The fluorescence spectrum of the 2-DPPr (2.0 × 10^{-4} M chromophore unit)–TFA (4.31 × 10^{-4} M) system in EPA exhibits only a single band around 290 nm and this fluorescence lifetime is shorter than 0.5 ns. Even in a concentrated system of 2-DPPr (~0.2 M chromophore unit) and TFA (~0.3 M), no dimerlike excimer fluorescence is observed. Likewise, in the EGW and MP solvents, the spectrum of the 2-DPPr–TFA system exhibits no dimerlike excimer fluorescence. As for the 2-DPHp–TFA system, a similar fluorescence characteristic is observed. On the other hand, 4-DPPr is not fluorescent in these solvents even in the presence of TFA. This fluorescence characteristic is the same as that of the 4-methylpyridine–TFA system.[8] The situation in the appearance of the dimerlike excimer fluorescence seems to be like that observed in the glassy state of pyrene[11] and naphthalene.[12] The evidence that the emission of dimerlike excimer fluorescence exhibits a remarkable solvent dependence indicates that the nature and shape of the solvent cage, which is determined by the microscopic structure of the frozen solvent, play an important role in dimerlike excimer formation.

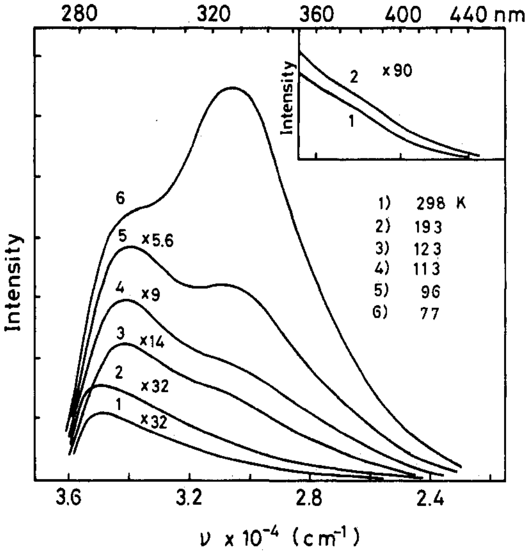


Figure 8. Temperature dependence in the fluorescence spectra of 2-DPPr in the mixed solvent of THF, MeOH, and MTHF (4:3:1 by volume) in the presence of TFA. 2-DPPr, 2.0 × 10^{-4} M (chromophore unit). TFA, 4.31 × 10^{-4} M. The fluorescence spectrum at 298 K was measured by using a 10-mm cell.

Registry No. 2-DPEt, 4916-40-9; 2-DPPr, 15937-81-2; 2-DPPe, 30561-90-1; 2-DPHp, 57476-56-9; 4-DPEt, 4916-57-8; 4-DPPr, 17252-51-6; 4-DPPe, 25382-33-6; TFA, 76-05-1; THF, 109-99-9; MTHF, 25265-68-3; MeOH, 67-56-1.

---

(11) Ferguson, J. *J. Chem. Phys.* *1965*, *43*, 306.

(12) Kawakubo, T.; Okada, M.; Shibata, T. *J. Phys. Soc. Jpn.* **1966**, *21*, 1469.