A novel fluorescent 2,2′-bipyridine derivative prepared by coupling to a fluorescent aminophenazine – fluorescence properties and response toward various cations

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2,2′-Bipyridine (bpy), a non-fluorescent but good metal-chelating unit, and 2-aminophenazine (2-aphz), a good fluorescent unit, are integrated to give 7-aminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (7-amino-dppz) **1**. Compound **1** exhibits an efficient fluorescence at 517 nm ($\Phi = 0.24$, dichloromethane), which is similar to the parent 2-aphz. It is suggested that the orbitals involved in the photoexcitation process are mostly localized on the phenazine unit. However, addition of divalent metal ions such as Mg^{2+}, Ca^{2+} and Cu^{2+} causes a noticeable fluorescence response, which is attributed to coordination of these cations to the bpy chelation site of **1**. This behaviour indicates that sufficient electronic communication exists between the bpy chelation site and the phenazine fluorophore. 7-(4-*tert*-Butylbenzoylamino)dppz **2** also showed a fluorescence response towards divalent metal ions.

Introduction

Fluorescent artificial receptors are attracting considerable interest in sensory, biochemical, medical, photoelectronic and other applications.[1] These receptors are composed of a host unit (binding site) and a signaling unit (fluorescent site), and communication between the two units is essential for guest specific response. Though various molecular designs have been proposed in order to develop efficient fluorescent receptors,[2] most receptors are designed by introducing molecular recognition site(s) into known fluorophores. However, this approach alone is not sufficient to develop novel fluorescent receptors with high sensitivity or other useful properties, since connection of the host unit often attenuates the emission property of the parent fluorophore. In addressing this point, new design strategy, rendering fluorescence properties to a non-fluorescent functional unit, should be developed.

Polypyridyl compounds are useful molecular units as binding sites. They have multiple interaction sites, and the number of pyridine units is adjustable. 2,2′-Bipyridine (bpy) is the most studied among such compounds owing to its excellent property as a bidentate ligand and as a hydrogen bond acceptor.[3] Moreover, rational receptor design using more than one bpy unit can lead to selective and strong interaction with guests.[4] However, bpy itself is non-fluorescent,[5] and only a limited number of fluorescent bpy based species have been known until now.[6] We previously reported[6c] that 6-amino substitution is an effective method to convert non-fluorescent bpy to a strongly fluorescent species, and have demonstrated that the resultant fluorescent bpy derivative served as a highly sensitive fluorescent receptor for phosphodiester guests.[3b]

In this report, a new strategy for synthesizing fluorescent bpy species was studied. The essence of the molecular design is that a known fluorescent dye, 2-aminophenazine (2-aphz),[7] is 'integrated' with a non-fluorescent bpy. Fluorescence properties of the resultant 7-aminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (7-amino-dppz) and other dppz derivatives were examined. Direct integration of fluorophores with other aromatic systems usually results in loss of fluorescent properties because of alteration of the electronic state of the parent fluorophores. However, integration of 2-aphz might not impair the fluorescence properties of the aminophenazine fluorophore, since it was pointed out[8] that bpy-localized and phenazine-localized π^* orbitals have relatively small overlap. Semi-empirical molecular orbital calculations were performed,[9,10] and the response toward some metal ions is also described.

Experimental

Methods

^{1}H NMR spectra were recorded on a JEOL JNM-LA500 or EX-270 FT-NMR spectrometer in deuterated dimethyl sulfoxide (DMSO-d_6) or chloroform ($CDCl_3$) with tetramethylsilane as an internal standard with *J* values given in Hz. Absorption spectra were measured with a Shimadzu UV-2500PC spectrophotometer, and emission spectra with a Shimadzu RF-5300PC spectrofluorometer at 20 °C. Fluorescence quantum yields (Φ) were obtained using an ethanol solution of 2-aminopyridine ($\Phi = 0.37$, excitation at 285 nm) as a standard. Dppz derivatives were titrated with metal perchlorate salts in acetonitrile. The energy level calculations of molecular orbitals and related simulations were performed using MOPAC/AM1[9] and/or ZINDO[10] (CI = 9) methods on a CAChe system.

Chemicals other than dppz derivatives and 2-aminophenazine were obtained commercially and were used as received. The fluorometric grade solvents used for spectroscopic measurements were purchased from Kanto Chemical Co. (acetonitrile and ethanol) and Dojin Chem. Co. (cyclohexane, dimethylformamide and dichloromethane). The following compounds were synthesized according to the reported procedure. 1,10-Phenanthroline-5,6-dione (phendione):[11] mp 264 °C (lit.,[11] 257 °C); 2-aminophenazine:[12] mp 265–266 °C (lit.,[12] 265–267 °C); **4**:[8] mp 253.6–254.4 °C (lit.,[8] 254–255 °C).

7-Methoxydipyrido[3,2-*a*:2′,3′-*c*]phenazine (3)

Phendione (33.0 mg, 0.16 mmol) and 4-methoxy-1,2-diaminobenzene hydrochloride (43.3 mg, 0.20 mmol) were dissolved in ethanol (150 ml) containing 1 ml of triethylamine and refluxed for 22 h. Precipitates were collected at room temperature and recrystallized from ethanol (25.7 mg, 52%): mp 230.8 °C (sublimes) (Found: C, 72.85; H, 3.9; N, 17.75. Calc. for $C_{19}H_{12}N_4O$: C, 73.1; H, 3.85; N, 17.95%); δ_H (270 MHz; $CDCl_3$)

7.59 (2H, m, 6 and 8 or 9-H), 7.79 (2H, m, 3 and 12-H), 8.23 (1H, d, *J* 9.6, 8 or 9-H), 9.26 (2H, td, *J* 4.6 and 1.9, 2 and 13-H), 9.62 (2H, m, 4 and 11-H).

7-Nitrodipyrido[3,2-*a*:2,3-*c*]phenazine (5)

Phendione (405 mg, 1.93 mmol) and 4-nitro-1,2-diaminobenzene (310 mg, 2.02 mmol) were dissolved in ethanol and refluxed for 4 h under N_2 atmosphere. Precipitates were collected by filtration, recrystallized from methanol, and dried *in vacuo* at 80 °C: pale greenish needles (558 mg, 88%); mp 306 °C (decomp.) (Found: C, 65.55; H, 2.65; N, 21.35. Calc. for $C_{18}H_9N_5O_2$: C, 66.05; H, 2.75; N, 21.4%); δ_H (500 MHz; $CDCl_3$) 7.82–7.84 (2H, 3 and 12-H), 8.47 (1H, d, *J* 9.5, 8 or 9-H), 8.66 (1H, d, *J* 9.5, 8 or 9-H), 9.25 (1H, s, 6-H), 9.30–9.33 (2H, 2 and 13-H), 9.58–9.61 (2H, 4 and 11-H); HRMS: found *m*/*z* 327.0727; calc. for $C_{18}H_9N_5O_2$: 327.0756.

7-Aminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (1)

To a solution of 7-nitro-dppz **5** (500 mg, 1.53 mmol) in methanol (1100 ml) was added 10% palladium on activated carbon (Pd/C; 150 mg), and then sodium tetrahydroborate (1.4 g) in portions at 0 °C. The reaction mixture was stirred for 17 h at room temperature, and the solution changed from greenish to brown. Then Pd/C was filtered off and the filtrate was evaporated. The resultant dark brown solid was dissolved in H_2O and extracted with chloroform. Removal of chloroform gave the crude product, which was purified by precipitation from the concentrated methanol solution: brown powder (388 mg, 86%); mp >330 °C (Found: C, 72.5; H, 3.7; N, 23.6. Calc. for $C_{18}H_{11}N_5$: C, 72.75; H, 3.75; N, 23.55%); δ_H (500 MHz; $CDCl_3$) 4.40 (2H, s, N*H*$_2$), 7.31 (1H, s, 6-H), 7.34 (1H, d, *J* 8.8, 8 or 9-H), 7.74–7.77 (2H, 3 and 12-H), 8.10 (1H, d, *J* 8.8, 8 or 9-H), 9.20–9.25 (2H, 2 and 13-H), 9.53–9.59 (2H, 4 and 11-H); HRMS: found *m*/*z* 297.0999; calc. for $C_{18}H_{11}N_5$: 297.1014.

7-(4-*tert*-Butylbenzoylamino)dipyrido[3,2-*a*:2′,3′-*c*]phenazine (2)

7-Amino-dppz **1** (60 mg, 0.201 mmol) and 4-*tert*-butylbenzoyl chloride (0.15 ml, 0.762 mmol) were dissolved in 20 ml dry acetonitrile containing 0.3 ml of triethylamine and refluxed for 2 h under N_2 atmosphere. The precipitate was collected by filtration, washed with acetonitrile, and dried *in vacuo* at 80 °C: yellow powder (83 mg, 90%); mp 345–347 °C (Found: C, 76.4; H, 4.95; N, 15.45. Calc. for $C_{29}H_{23}N_5O$: C, 76.15; H, 5.05; N, 15.3%); δ_H (500 MHz; $CDCl_3$) 7.58 (2H, d, *J* 7.7, *m*-H of Bu^{t}C$_6$H$_4$), 7.77–7.82 (2H, 3 and 12-H), 7.94 (2H, d, *J* 7.7, *o*-H of Bu^{t}C$_6$H$_4$), 8.13 (1H, d, *J* 8.3, 8 or 9-H), 8.26 (1H, s, amide-H), 8.31 (1H, d, *J* 8.9, 8 or 9-H), 8.76 (1H, s, 6-H), 9.25–9.28 (2H, 2 and 13-H), 9.58–9.64 (2H, 4 and 11-H); HRMS: found *m*/*z* 457.1885; calc. for $C_{29}H_{23}N_5O$: 457.1902.

Results

Syntheses of dppz derivatives

Coupling of 1,10-phenanthroline-5,6-dione, obtained by oxidation of 1,10-phenanthroline, and the corresponding 4-substituted 1,2-diaminobenzene gave 7-methoxy- (**3**), 7-nitro- (**5**), and unsubstituted (**4**) dppz in satisfactory yields. 7-Amino-dppz **1** was synthesized from **5** by reduction of its nitro group (Scheme 1). Subsequent reaction of **1** with 4-*tert*-butylbenzoyl chloride gave 7-(4-*tert*-butylbenzoylamino)-dppz **2**.

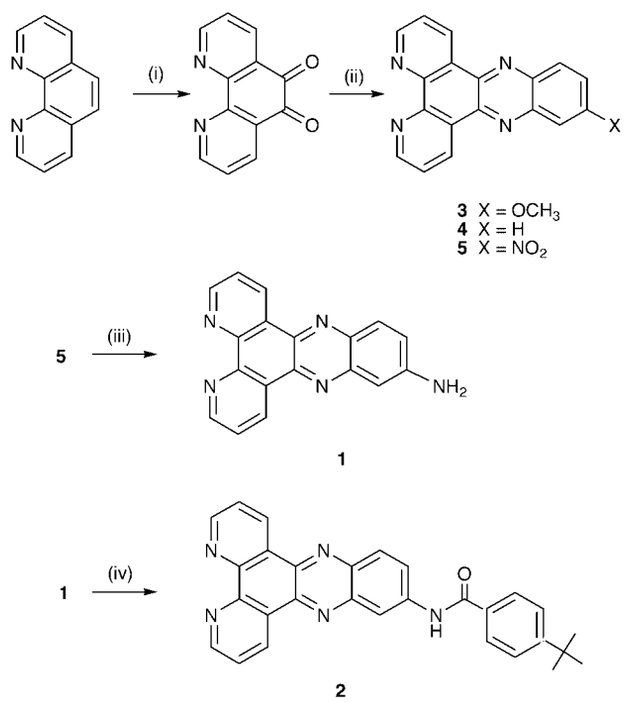
Electronic properties of the dppz derivatives

Table 1 lists the absorption maxima of the dppz derivatives measured in dichloromethane at 20 °C. While the dppz derivatives **2**, **3**, and **4** showed the lowest energy absorption band at *ca.* 400 nm, that of **1** appeared at much lower energy. There has been a report[13] that the lowest energy absorption of phenazine also experiences a considerable bathochromic shift upon 2-amino substitution.

Table 1 Absorption and fluorescence maxima of dppz derivatives in dichloromethane at 20 °C

Compound	λ_{abs}/nm (log ε/ dm^3 mol^{-1} cm^{-1})	λ_{fl}/nm (Φ)
1	428 (4.02)	517 (0.24)
2	406 (4.26)	439 (0.05)
3	400 (4.25)	422 (0.03)
4	378 (4.11)[a]	—(0)
5	390 (4.21), 500 (2.80)	—(0)

[a] Ref. 8.



Scheme 1 Syntheses of 7-substituted dppz derivatives. (i) Conc. H_2SO_4, conc. HNO_3, KBr, 80–85 °C, 2 h; (ii) 4-X-1,2-diaminobenzene, EtOH, reflux, 4 h; (iii) Pd/C, $NaBH_4$, MeOH, 17 h; (iv) 4-Bu^{t}C$_6$H$_4$COCl, NEt_3, CH_3CN, reflux, 2 h.

Absorption spectra of **1** and 2-aphz were simulated using the ZINDO (CI = 9) method after successive geometrical optimizations by MM2 and MOPAC/AM1 calculations. The simulated spectra were well consistent with the observed spectra. The lowest energy absorption of both compounds were shown to arise from the transitions from HOMO (π) and HOMO-3 (n) to the LUMO (π^*), and all were mostly localized on the phenazine moiety. The results thus suggest the phenazine unit to be mainly involved in the lowest-energy absorption of the dppz derivatives.

Fluorescence maxima measured in dichloromethane are also included in Table 1. Compound **1** containing a strong electron-donating amino group[14] exhibited a highly efficient yellow fluorescence (*ca.* 550 nm). On the other hand, **2** and **3** showed only a weak fluorescence at *ca.* 430 nm, and no detectable emission was observed from the parent compound **4** or the nitro derivative **5**.

The shape of the excitation spectrum of **1** was similar to the absorption spectrum in dichloromethane, though the maximum at *ca.* 300 nm (Fig. 1) was weaker. Therefore, the fluorescence emitting state of **1** is the lowest excited state.

Table 2 lists absorption and fluorescence maxima of **1** in various solvents. An increase of the solvent polarity shifts the maxima to longer wavelengths, and decreases the fluorescence intensity.

Table 2 Absorption and fluorescence maxima of **1** at 20 °C

Solvent	λ_{abs}/nm	λ_{fl}/nm (Φ)
Dichloromethane	428	517 (0.24)
Acetonitrile	438	534 (0.24)
DMF	454	555 (0.17)
Ethanol	452	565 (0.09)

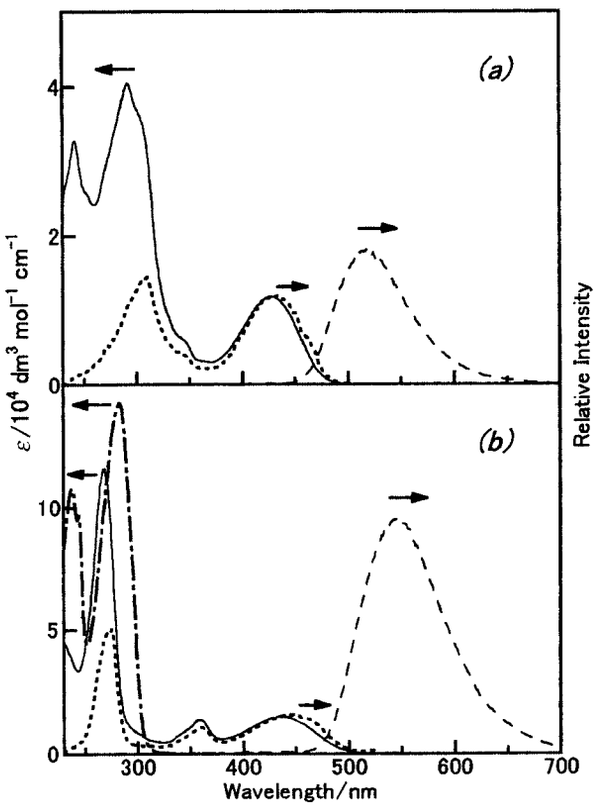


Fig. 1 Absorption (——), excitation (-----) and fluorescence (excitation at 366 nm; – – – – –) spectra of (*a*) **1** and (*b*) 2-aphz, and absorption spectrum of bpy (–·–·–·) in dichloromethane at 20 °C.

Fluorescence response of 1 and 2 toward metal cations

The effect of metal ions on the fluorescence properties of **1** was examined in acetonitrile at 20 °C. The presence of alkali metal cations caused little effect on the absorption and fluorescence spectra. On the other hand, addition of Mg^{2+} led to a small but noticeable red shift (*ca.* 20 nm) of the lowest-energy absorption band with a clear isosbestic point at 440 nm, while the band below 300 nm showed a much clearer change [Fig. 2(*a*)]. The fluorescence of **1** was also affected by addition of Mg^{2+}, shifting to lower energy. As shown in the inset, the fluorescence intensity at 550 nm decreased sharply up to addition of 0.5 equivalents of Mg^{2+}, and then gradually increased to become almost saturated. The results indicated formation of both 1:2 (Mg^{2+}: **1**) and 1:1 complexes [eqns. (1) and (2)].

$$M^{2+} + 2\,(\mathbf{1}) \overset{K_{s2}}{\rightleftharpoons} [M(\mathbf{1})_2]^{2+} \quad (1)$$

$$M^{2+} + \mathbf{1} \overset{K_{s1}}{\rightleftharpoons} [M(\mathbf{1})]^{2+} \quad (2)$$

The 1:2 complex is the dominant species at low concentrations of Mg^{2+}, while the 1:1 complex becomes the major species when the concentration of Mg^{2+} is sufficiently high. Association constants of the 1:2 (K_{s2}) and 1:1 (K_{s1}) complexes were estimated to be 9×10^{13} dm^6 mol^{-2} and 2×10^7 dm^3 mol^{-1}, respectively, by computational simulation.

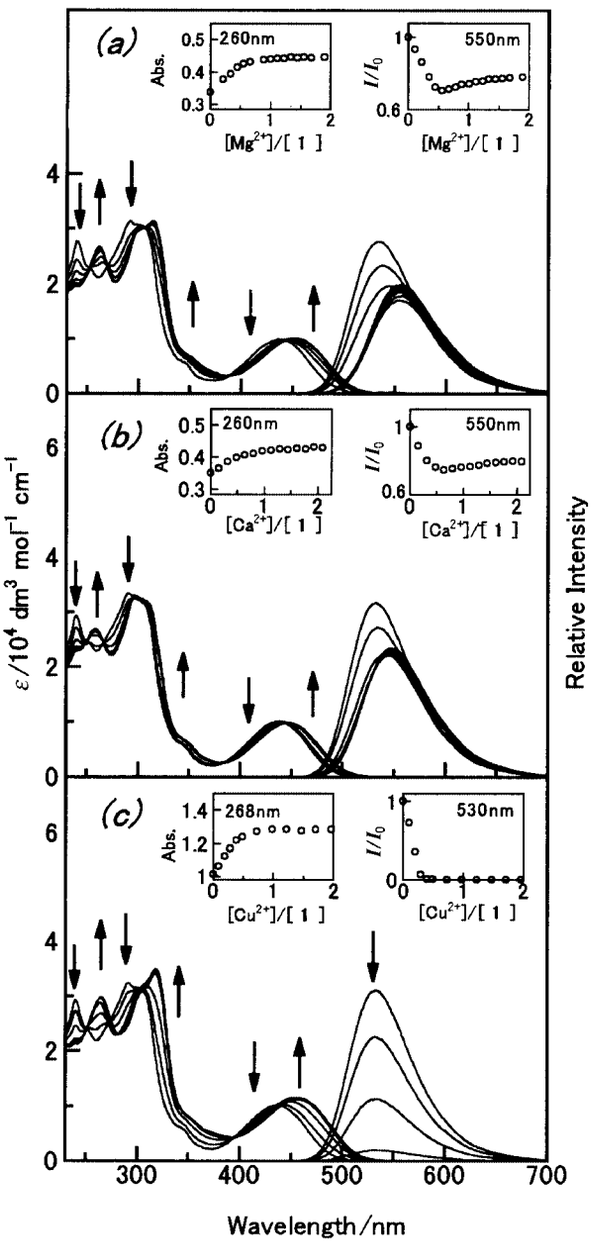


Fig. 2 Absorption and fluorescence spectral titration of **1** (1.60×10^{-5} dm^3 mol^{-1}) upon addition of (*a*) Mg^{2+}, (*b*) Ca^{2+} and (*c*) Cu^{2+} (0–2 equiv.) in acetonitrile at 20 °C.

For Ca^{2+}, the fluorescence intensity decreased more moderately and then slightly increased as the Ca^{2+} concentration was increased [Fig. 2(*b*)]. The results also showed that the 1:2 complex was initially formed, and the 1:1 complex subsequently increased as the Ca^{2+} concentration was increased. The association constants, K_{s2} and K_{s1}, were estimated to be 5×10^{11} dm^6 mol^{-2} and 2×10^6 dm^3 mol^{-1}, respectively.

A paramagnetic divalent cation such as Cu^{2+} caused similar absorption spectral changes as those observed for Mg^{2+} and Ca^{2+}, but fluorescence was totally quenched even at low concentrations [Fig. 2(*c*)].

Compound **2** showed no change in absorption or fluorescence spectra on addition of Na^+. However, addition of Mg^{2+} and Ca^{2+} led to a noticeable increase in the fluorescence (Fig. 3). For Mg^{2+}, as is evident from the plot of fluorescence intensity at 475 nm shown in the inset, the fluorescence intensity drastically increased up to addition of 0.5 equivalent of Mg^{2+}, suggesting formation of the 1:2 (Mg^{2+}: **2**) complex. The association constant of the 1:2 complex (K_{s2}) was too large (>10^{15} dm^6 mol^{-2}) to be estimated. On the other hand, for Ca^{2+}, the fluorescence intensity increased more gradually. The plot of

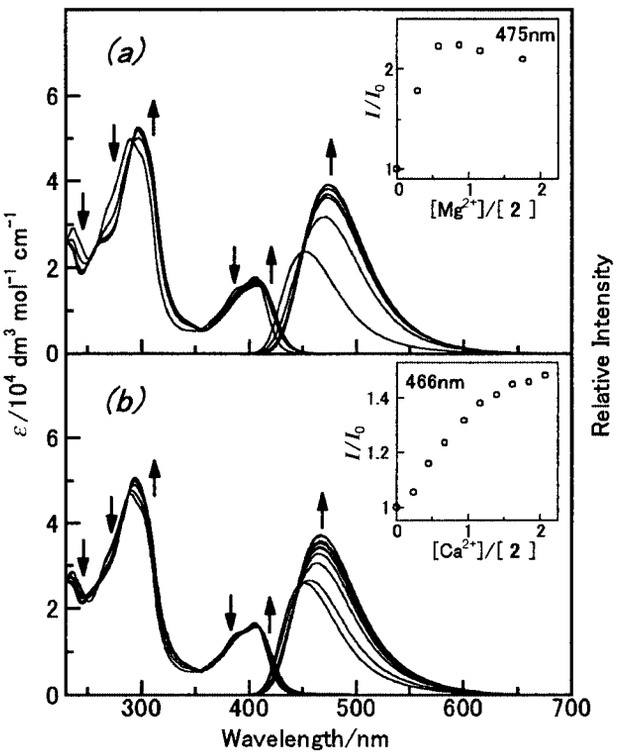


Fig. 3 Absorption and fluorescence spectral titration of **2** (2.22×10^{-5} dm^3 mol^{-1}) upon addition of (*a*) Mg^{2+}, (*b*) Ca^{2+} (0–2 equiv.) in acetonitrile at 20 °C.

fluorescence intensity *vs.* the concentration of Ca^{2+} was well simulated by the assumption of formation of a 1:1 complex [eqn. (2)]. Formation of the 1:2 complex was negligibly small under the experimental conditions, and the association constant of the 1:1 complex (K_{s1}) was determined as 1.4×10^5 dm^3 mol^{-1}.

^{1}H NMR spectral changes of 1 and 2 upon addition of Mg^{2+}

To investigate the binding sites of **1** and **2** toward divalent metal cations, changes in proton chemical shifts were examined in acetonitrile-d_3. Upon addition of an equimolar amount of Mg^{2+} (5×10^{-4} mol dm^{-3}), 4,11-H and 3,12-H signals of **1** (5×10^{-4} mol dm^{-3}) were shifted downfield by *ca.* 0.3 and 0.2 ppm, respectively, while the chemical shifts of the other protons remained unchanged. Similar results were obtained for **2**. These results confirmed that the binding site of both **1** and **2** with Mg^{2+} was *via* bipy nitrogens rather than phenazine nitrogens or the amino/amide group.

Discussion

Molecular design and fluorescence properties of 1

Though the concept of molecular design adopted in this study is simple, there have been few examples successfully integrating a fluorescent unit to bpy. Since condensation of the aromatic ring system is likely to change the electronic state of the parent fluorescent molecule, structural integration often diminishes its fluorescence properties. In this study, however, the novel fluorescent bpy derivative **1** was successfully developed by integration of 2-aphz with bpy, despite the fully π-conjugated electronic system of **1**. Moreover, the fluorescence properties of **1** were essentially the same as for the parent fluorophore.

It was pointed out by Amouyal *et al.*[8] that the bpy-localized π* and phenazine-localized π* orbitals are rather separated within dppz. This may be the reason for the successful integration and for the undiminished fluorescence relative to 2-aphz. In addition, the absorption spectrum of **1** was roughly reproducible by superimposing those of bpy and 2-aphz (Fig. 1). These results show that the optically responsible orbitals of **1** were spatially separated in the bpy and 2-aphz units and did not have strong electronic interaction, although the conjugation system was extended by integration of the two units.

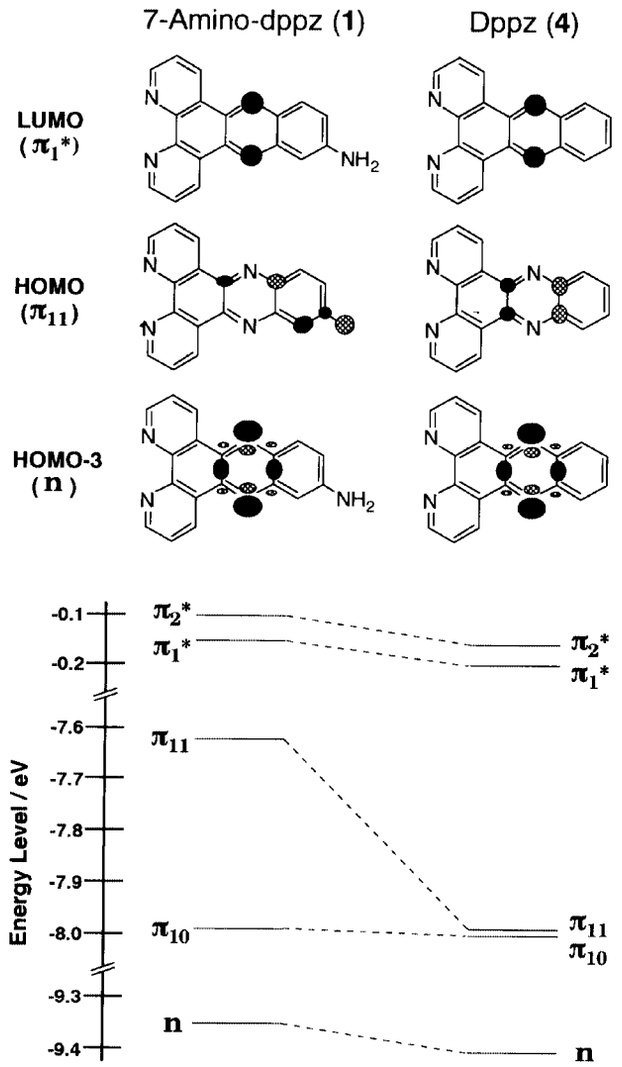


Fig. 4 Calculated molecular orbital (upper) and energy diagram (lower) of **1** and **4** by MOPAC/AM1.

The electronic states of **1** and **4** were further examined by semi-empirical MO calculation by MOPAC/AM1, with the molecular orbitals, HOMO-3 (n), HOMO (π_{11}), and LUMO (π_1*) shown in Fig. 4. The results clearly demonstrate that the HOMO and LUMO orbitals are localized on the phenazine unit, and that these orbitals are involved in the lowest energy absorption band. This result is in accord with the experimental observation that the fluorescence of **1** is similar to its parent compound, 2-aphz.

The simulation, as expected, also showed that the energy level of π_{11} (HOMO) of **4** became considerably higher upon amino substitution while the n and π_1* (LUMO) were only slightly affected. Therefore, the red shift of the lowest energy absorption band of **1** is due to the resultant decrease in the π–π* energy gap by elevation of the HOMO level. As described in the Results section, the emitting level of **1** is the lowest singlet excited state, and the lowest energy absorption consists of the π–π* (HOMO to LUMO) and n–π* (HOMO-3 to LUMO) transitions. Therefore, a decrease in the π–π* transition energy might reduce possible quenching of the excited state through n–π* transition and contribute to the efficient fluorescence of **1**.

Fluorescence response of 1 and 2 toward metal cations

As a fluorescent receptor, communication between the recognition site and the fluorescent site is essential. In this case, sufficient communication between the bpy and phenazine unit was evidenced by the absorption and fluorescence spectral changes of **1** in the presence of divalent metal ions, despite the fact that the phenazine-localized orbitals responsible for the fluorescence were rather separated from the bpy-localized orbitals.

^{1}H NMR spectral titration of **1** with Mg^{2+} showed downfield shifts of protons only on the bpy unit, which confirmed chelation of the metal ion to the bpy site. This was also supported by the electronic spectral titration of 2-aphz and 1,10-phenanthroline, *i.e.*, addition of Mg^{2+} or Ca^{2+} led to no absorption and fluorescence change of 2-aphz, but induced a remarkable change in the absorption of 1,10-phenanthroline. On the other hand, both the bpy-centered absorption at *ca.* 300 nm and the phenazine-centered absorption at 430 nm of **1** shifted to longer wavelengths on addition of Mg^{2+}. Therefore, the observed red-shift of the absorption spectrum of **1** is the result of the metal chelation to the bpy site, confirming that there exists sufficient communication between the bpy and the 2-aphz units.

It is to be noted that association constants of **1** with Mg^{2+} and Ca^{2+} were large and association took place almost quantitatively even at $[M^{2+}] = 10^{-6}$ mol dm^{-3}. The larger association constants for Mg^{2+} relative to Ca^{2+} may be due to the smaller ionic radius of Mg^{2+}.

Fluorescence of **2** increased 2 and 1.5 times upon association with Mg^{2+} and Ca^{2+}, respectively. For Mg^{2+}, the fluorescence quantum yield was raised to >0.1. ^{1}H NMR spectral titration indicated chelation of the metal ions to the bpy unit, rather than the 5-nitrogen or C=O of the amide bond and so there is no clear explanation of the fluorescence enhancement. Metal chelation, however, might suppress a non-radiative process involving the amide unit.

Conclusion

We have presented a novel approach for synthesizing fluorescent 2,2′-bipyridine (bpy) derivatives. Integration of the known fluorophore 2-aminophenazine (2-aphz) with bpy successfully yielded fluorescent 7-amino-dppz **1**, and its fluorescence properties were very similar to 2-aphz. It was suggested that the emitting state of **1** was localized on the phenazine unit, which appeared to be the reason that the fluorescence of 2-aphz was not attenuated through condensation. On the other hand, chelation of metal cations to the bpy site induced a fluorescence change, which evidenced sufficient communication between the two units. Thus, appropriate electronic separation but sufficient communication between the two units is realized by the integration strategy, offering a novel approach for designing functional fluorescent bpys.

Since **1** contains both a bpy chelating site and an amino group suitable for introducing additional functional units, the fluorescence properties of **1** can be controlled by metal chelation and/or further modification of the amino group.

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