Zn^{II} Complexes Coordinated by Fluorescent Ligand 2-(4-*tert*-Butylphenyl)imidazo[4,5-*f*]-1,10-phenanthroline

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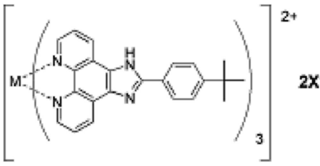
New Zn^{II} complexes with fluorescent ligand $[Zn(bpimp)_3]X_2$ (bpimp: 2-(4-*tert*-butylphenyl)imidazo[4,5-*f*]-1,10-phenanthroline) were prepared. While the ligand does not exhibit fluorescence in the solid state, the new Zn^{II} complexes exhibit fluorescence in solution and solid states. On the other hand, Ni^{II}– and Co^{II}–bpimp complexes do not exhibit strong fluorescence in solution and in the solid states.

Organic compounds exhibiting fluorescence have attracted our attention because of their relevance the fields of photochemistry and optoelectronic devices.[1] Although there are many reports on the organic fluorophores, those in the solid state are relatively limited. This limitation is because many organic fluorophores in the solid states quench fluorescence;[2–5] the quenching mechanisms and preparation of new solid-state fluorophores are being studied actively. In the previous work, we report that the fluorescence of clathrate hosts were enhanced to various degrees depending on the enclathrated guest in the solid state and suggest that destruction of π–π interaction between the hosts in the solid state brought about fluorescence.[6–8]

In the present letter, preparation and characterization of Zn^{II}–bpimp [bpimp: 2-(4-*tert*-butylphenyl)imidazo[4,5-*f*]-1,10-phenanthroline; Chart 1] is reported. The Zn^{II}–bpimp complexes have the following features. 1) Zn is an essential element in living organisms. Bioinorganic-chemical and medical studies of fluorescent Zn^{II} complexes are applicable to biology and medicine. 2) It is expected that bpimp coordinates to Zn^{II} to form the octahedrally coordinated $[Zn(bpimp)_3]^{2+}$ ion as with $[Zn(phen)_3]^{2+}$. 3) There are few reports concerning octahedrally coordinated Zn^{II} mononuclear complexes containing fluorescent ligands except for Schiff bases or azaaromatic derivatives.[9–15] 4) Bpimp exhibits fluorescence in solution but not in the solid state. Fluorescence of Zn^{II}–bpimp complexes have not been reported. 5) The Zn^{II} in diamagnetic $[Zn(bpimp)_3]X_2$ has the closed d^{10} shell as Cu^I.[15] Many fluorescent complexes of Cu^I has been reported. The present study of Zn^{II}–bpimp complexes provides a starting point for octahedral Zn^{II} complexes with ligand-centered fluorescence.

The ligand bpimp was prepared according to a method described in the literature.[16] $[Zn(bpimp)_3]Cl_2$ (**1a**) was synthesized by the following procedure: to a solution of bpimp (110 mg, 3.1×10^{-4} mol) in MeOH (10 cm^3) was added a solution of $ZnCl_2$ (14 mg, 1.03×10^{-4} mol) in H_2O (10 cm^3). After stirring the mixed solution for 1 h at room temperature, the precipitated complex **1a** was filtered off, and then washed with H_2O and MeOH. Yield: 102 mg (72%). Anal. Found (calcd for $C_{69}H_{74}N_{12}O_7Cl_2Zn$ (**1a**$\cdot 7H_2O$)): C, 62.75 (62.79); H, 5.36 (5.65); N, 12.54 (12.74)%. ^{1}H NMR (δ, DMSO-d_6): 1.33(s), 7.42(br), 7.56(d), 8.14(br), 8.22(d), 8.86(br), 9.19(br). Complexes **1b** and **1c** were prepared in the same manner as for **1a**, except for the use of $ZnBr_2$ and $ZnSO_4\cdot 7H_2O$ instead of $ZnCl_2$, respectively.[17]



1a: M = Zn, $2X^- = 2Cl^-$
1b: M = Zn, $2X^- = 2Br^-$
1c: M = Zn, $2X^- = SO_4^{2-}$
2: M = Ni, $2X^- = SO_4^{2-}$
3: M = Co, $2X^- = SO_4^{2-}$

Chart 1.

UV–vis absorption spectral data of bpimp and M^{II}–bpimp complexes in MeOH are listed in Table 1. The spectral patterns of **1a**–**1c** resemble each other at 220–400 nm, as the absorbance arising from the $[Zn(bpimp)_3]^{2+}$ cation is much larger than that arising from the anions. The ε_{max} of each of the coordinating bpimp (three bpimp coordinate to one M^{II}) is 39300–54300 (118000/3–163000/3) $M^{-1}\,cm^{-1}$ at ca. 280 nm, and is larger than that of a free ligand (31400 $M^{-1}\,cm^{-1}$).

Figure 1 shows emission spectral data of bpimp and Zn^{II}–bpimp complexes in various solvents (excitation spectra of bpimp and $[Zn(bpimp)_3]Cl_2$: Figures A and B in the Supporting Information).[19] From the figure, the following are clarified. The emission λ_{max} shows a large red shift in polar solvents. The

Table 1. UV–vis absorption spectral data of bpimp and M^{II}–bpimp complexes in MeOH

Compound	Absorbance[a]			
	λ_{max}/nm (ε_{max}/$M^{-1}\,cm^{-1}$)			
Bpimp	225 (24100),	275 (31400),	288 (27600),	ca. 355 (ca. 2100)[sh]
1a	223 (80600),	280 (126000),	299 (100000),	ca. 370 (ca. 6800)[sh]
1b	223 (81600),	280 (129000),	300 (103000),	ca. 370 (ca. 6800)[sh]
1c[a]	224 (—),	279 (—),	293 (—),	ca. 375 (—)[sh]
2	220 (70300),	283 (118000),	ca. 295 (ca. 101000)[sh],	ca. 375 (ca. 4420)[sh]
3	222 (64000),	283 (137000),	ca. 300 (ca. 107000)[sh],	ca. 380 (ca. 5190)[sh]

[sh]Shoulder band. [a]In a MeOH solution: saturated at room temperature.

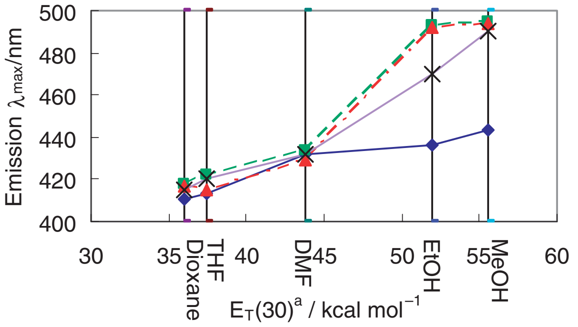


Figure 1. Emission λ_{max} of bpimp, **1a**, **1b**, and **1c** in various solvents: bpimp (◆); **1a** (■); **1b** (▲); and **1c** (×).
$E_T(30)$ (kcal mol^{-1}): empirical scale of solvent polarity derived from negatively solvatochromic pyridinium *N*-phenolate betaine.[18]

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Table 2. Emission spectral data of bpimp and its complexes in MeOH solution (Concentration: $1.0 \times 10^{-6}\,\mathrm{mol\,cm^{-3}}$)

Compound	Emission	Excitation	Quantum	Relative Quantum
	λ_{max}/nm	λ_{max}/nm	Yield Φ	Yield
Bpimp	443	308	0.038	1.00
1a	495	313	0.056	1.47
1b	494	318	0.049	1.29
1c	491	317	0.029	0.76
2	425	324	0.002	0.05
3	444	313	0.005	0.13

Table 3. Emission spectral data of bpimp and **1a**–**1c** in the solid state

Compound	Excitation	Emission	Φ[a]
	λ_{max}/nm	λ_{max}/nm	
Bpimp	510	545	0.001
1a	453	510	0.050
1b	453	508	0.038
1c	455	530	0.031

[a] Φ: Fluorescence quantum yields.

emission λ_{max} of the Zn^{II} complexes is located in a wider range (414–501 nm) than that of bpimp (415–440 nm). A greater dependence of the Stokes shift value on the solvent polarity is observed in the Zn^{II}–bpimp complexes than in bpimp ligand itself, which suggests that the increase in polarity that accompanies photoexcitation of the Zn^{II} complexes is larger than that of bpimp ligand itself.

The fluorescence quantum yields (Φ) in MeOH of **1a**–**1c** are nearly equal to that of bpimp (Table 2). These results are in contrast to the results observed in the solid state (vide post). It is notable that the Φ of **1a**–**1c** with $3d^{10}$ electron configuration are much larger than those of **2** and **3** which have partially filled 3d orbitals.

The emission spectral data of bpimp and **1a**–**1c** in the solid states are listed in Table 3. The Φ of free bpimp is considerably low (0.001) in the solid state, and its quantum yield is 1/30–1/50 of those of **1a**–**1c**. The π–π interaction between the free ligands in the solid state quenches the fluorescence,[6–8] but it is believed that the π–π interaction is disrupted in **1a**–**1c**. For more detail discussion, X-ray analysis of the Zn–bpimp complexes is necessary.

The emission λ_{max} of **1a**–**1c** vary considerably with solvent as mentioned above. On the other hand, in **1a**–**1c** (which contain different counter anions) in the solid state, the emission λ_{max} appears in a narrow range (508–530 nm; Figure C)[19] and these λ_{max} are longer than those observed in MeOH. The Φ of **1a**–**1c** in the solid state are nearly equal to those in MeOH solution (Tables 2 and 3).

The excitation λ_{max} of bpimp and **1a**–**1c** in solid state shifted to longer side by ca. 140 nm than those in MeOH. Similar large shifts have also been observed in metal complexes such as Bpic–Zn and Cu.[20] It may be the π–π inter-ligand interaction between the complex cations happen in the solid states, which decreases the energy gap between the π and π^* orbitals of the ligand.[20] Though the interaction occasionally causes quenching of emission, the present Zn–bpimp complexes exhibited emission in the solid states. Further research toward a better explanation for the phenomenon is currently in progress.

In summary, $[Zn(bpimp)_3]X_2$ complexes were newly prepared. When the bpimp coordinates to the Zn^{II}, the fluorescence of the ligand improved. In the present **1a**–**1c**, we can obtain larger ε_{max}, longer fluorescent λ_{max}, larger Φ and larger solvent effect in solution, compared to the corresponding values for the bpimp. Moreover, **1a**–**1c** exhibited fluorescence in the solid states.

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17 **1b**: Yield: 116 mg (82%). Anal. Found (calcd for $C_{69}H_{74}N_{12}O_7Br_2Zn$ ($[Zn(bpimp)_3]Br_2 \cdot 7H_2O$)): C, 59.12 (58.83); H, 5.27 (5.30); N, 11.78 (11.94)%. **1c**: Yield: 120 mg (84%). Anal. Found (calcd for $C_{69}H_{82}N_{12}O_{15}SZn$ ($[Zn(bpimp)_3]SO_4 \cdot 11H_2O$)): C, 58.50 (58.49); H, 5.53 (5.83); N, 11.67 (11.87)%.

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19 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/jounals/chem-lett/index.html.

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