

Fluorescence Responses on Ion Recognition with 2-(4-Dialkylaminophenyl)ethoxyantimony(V) Tetraphenylporphyrin

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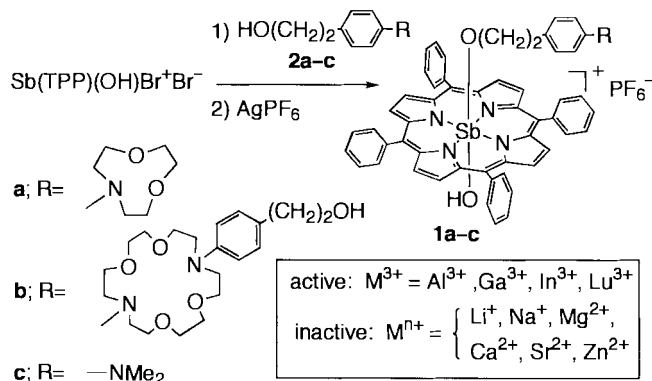
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The effects of metal ions on the fluorescence spectra of 2-phenylethoxyhydroxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1a–c**) involving azacrown ether on axial ligands were investigated. Trivalent metal ions such as Al³⁺, In³⁺, Ga³⁺, and Lu³⁺ which undergo the complexation with the azacrown ether remarkably enhanced the fluorescence quantum yields.

Photochemistry of the metalloporphyrin complex involving the second chromophores has been extensively studied.¹ We have interested on the photophysical properties of antimony(V) tetraphenylporphyrin complexes having second chromophore as the axial ligand (Sb(TPP)XY⁺ where TPP is tetraphenylporphyrinato group and X and Y denote axial ligands).² We² and other groups³ have elucidated that the fluorescences of Sb(TPP)XY⁺ were sensitively affected by the solvents polarity, the redox properties of the second chromophores, and the orientations to the second chromophores. On the other hand, azacrown ethers have received much attention in order to achieve stronger binding with metal ions than crown ethers.⁴ Here, we investigated fluorescence response on the ion recognition with the azacrown ether moiety on 2-phenylethoxyhydroxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1a–c**), as shown in Scheme 1.

We prepared **1** by the reaction of Sb(TPP)(OH)Br⁺Br⁻ with the substituted 2-phenethyl alcohols (**2**)⁵ (Scheme 1). Complexes **1a** and **1b** had the axial 2-(phenyl)ethoxy ligand containing aza-4,7-dioxa-1-cyclononyl and *N*-aryl-4,13-diaza-1,7,10,16-tetra-oxa-4-cyclooctadecyl ligands, respectively.⁶ It is expected that these second chromophores have both abilities of electron-donating and complexation with metal ions. [2-(4-Dimethylamino)phenyl]ethoxyhydroxyantimony(V) tetraphenylporphyrin (**1c**) was used as a complex without the azacrown ether.



Scheme 1.

Usual Sb(TPP)XY⁺ without second chromophore on axial ligands had a strong fluorescence under the excitation of porphyrin Soret band. For example, the fluorescence of dihydroxyantimony(V) tetraphenylporphyrin hexafluorophosphate (Sb(TPP)(OH)₂⁺PF₆⁻) was observed at 596 nm in MeCN with 0.0518 of the fluorescence quantum yield (Φ).⁷ On the contrary, **1a–c** showed only weak emission at 595 nm in MeCN: Φ = 0.0014 for **1a**, 0.0007 for **1b**, and 0.0033 for **1c**. The decreases of fluorescence intensity are due to the intramolecular quenching by the dialkylaniline chromophore.

Table 1. Characterization of **1a–c**

1	CHF ^a / 10 ⁻⁶ mol dm ⁻³ (K / 10 ³ mol ⁻¹ dm ³) ^b				ΔG / eV ^c
	(d/pm) ^d	Al ³⁺ (136)	Ga ³⁺ (152)	In ³⁺ (188)	
1a	1.5 (91)	1.0 (111)	5.0 (67)	1.6 (63)	-0.34
1b	1.5 (91)	1.1 (119)	4.0 (67)	1.6 (63)	-0.29
1c	2.3 (91)	2.2 (145)	2.2 (67)	1.7 (100)	-0.40

^aThe concentration for half of maximum fluorescence intensity. ^bStability constants for **2a–c** with Mⁿ⁺ obtained from the UV-spectra. ^cFree energy changes for the electron transfer from the excited singlet state of the Sb(TPP) chromophore to the second chromophore calculated by Rehm–Weller equation: ΔG = E_{1/2}^{ox} - E_{1/2}^{red} - E⁰⁻⁰ where E_{1/2}^{ox} were 0.74, 0.72, and 0.68 V for **1a–c**, respectively, E_{1/2}^{red} were -1.00, -1.07, -1.00 V for **1a–1c**, respectively, and E⁰⁻⁰ = 2.08 eV. ^dIon diameters from Reference 10.

The fluorescences of **1a–c** were restored by the addition of M(ClO₄)₃: M³⁺ = Al³⁺, Ga³⁺, In³⁺, and Lu³⁺, but were not affected by the addition of M(ClO₄)_n: Mⁿ⁺ = Li⁺, Na⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Zn²⁺. Figure 1 shows the dependence of Φ on the concentration of M(ClO₄)_n in a MeCN solution of **1a–c** (0.5 μM, 1 μM = 1 × 10⁻⁶ mol dm⁻³). Prominent observation is that the fluorescence of **1a** showed sharp hysteric response to the concentration of M³⁺ ions. The concentration for the half of the maximum fluorescence intensity (CHF) at **1a** were 1.5 μM for Al³⁺, 1.0 μM for Ga³⁺, and 1.6 μM for Lu³⁺ and relatively large value (5.0 μM) for In³⁺ (Table 1). Also the fluorescence of **1b** showed similar hysteric changes by the additions of 1.0–1.6 μM of Al³⁺, Ga³⁺, and Lu³⁺ and of 4.0 μM of In³⁺. In the case of **1c** without the azacrown ether, the recognition of these metal ions was not specific with small hysteric behavior. The stability constants (K) of **2a–c** with M³⁺ were obtained from the UV-spectral changes (Table 1).

By the addition of HClO₄ (1.0 mM), the fluorescences were restored to 0.026 for **1a**, 0.019 for **1b**, and 0.023 for **1c**. Free energy changes (ΔG) for an intramolecular electron transfer from axial ligands to porphyrin moiety was calculated to be negative by Rehm–Weller equation⁸ using half-peak of oxidation potentials (E_{1/2}^{ox} vs SCE) of the axial ligands and half-peak of reduction potentials (E_{1/2}^{red}) of the porphyrin chromophore, and the excitation energy (E⁰⁻⁰). Therefore, the quenching

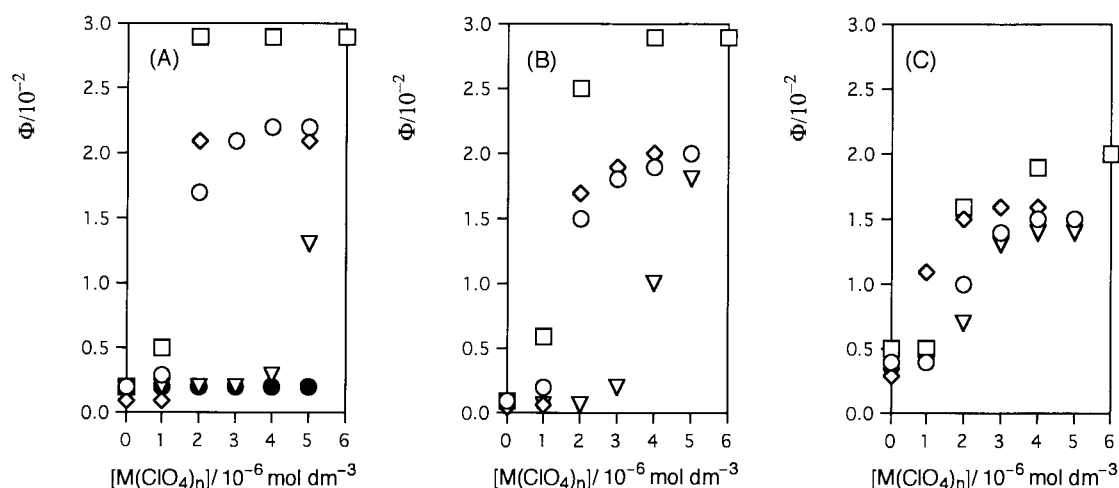


Figure 1. Plots of Fluorescence Quantum Yields (Φ) vs the Concentration of the Given Metal Perchlorate $[M(\text{ClO}_4)_n]$ for (A) **1a**, (B) **1b**, and (C) **1c**: $M^{n+} = \text{Al}^{3+}$ (\circ), Ga^{3+} (\diamond), In^{3+} (∇), Lu^{3+} (\square), and Li^+ , Na^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Zn^{2+} (\bullet).

process should mainly proceed by the electron transfer process from the dialkylaniline chromophore to the porphyrin ring. The restoration of the Φ by the addition of H^+ and Al^{3+} can be attributed to the decrease of electron-donating ability of the dialkylaniline chromophore by the addition of H^+ and Al^{3+} with nitrogen lone pair on the aniline moiety.

The azacrown ether rings prevent from free access of metal ions to lone pair of nitrogen atom, but the metal ions fitted to cavity size of the azacrown ethers were allowed to interact to nitrogen atom. The In^{3+} was too large size to interact with azacrown ether ring. The Lu^{3+} enhanced the fluorescence intensity at low concentration irrespective of large ion diameter. The complexation of the lanthanide ion with nitrogen atom is different from the group 13 metal ion, probably the occurrence of the complexation with oxygen atoms of the azacrown ether. Since the inverse of CHF values disagreed with K values, the fluorescence restoration of **1a-c** should be attributed to loose complexation of M^{3+} with the azacrown ether moiety.

Thus, fluorescence response on μM -order of M^{3+} were observed. The present recognition and the fluorescence were achieved on separate parts, although usual fluorescence responses have performed by the direct interaction of M^{n+} with the fluorophore.⁹ Therefore, it is possible to design more versatile recognition part independently on the fluorescence part.

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- 6 **1a**: Yield 15 %; UV-vis (MeCN) λ_{max} , nm (log ϵ): 261 (4.47), 419 (5.67), 551 (4.26); SIMS: m/z 1000 (M^+); ^1H NMR δ -2.43 (2H, t, $J = 7.5$ Hz, CH_2), -1.17 (2H, t, $J = 7.5$ Hz, CH_2), 3.34-3.64 (12H, m, CH_2), 4.93 (2H, d, $J = 8.6$ Hz, Ph), 5.89 (2H, d, $J = 8.6$ Hz, Ph), 7.79-7.89 (12H, m, Ph), 8.20 (4H, d, $J = 6.9$ Hz, 4H, Ph), 8.42 (4H, d, $J = 6.9$ Hz, Ph), 9.43 (8H, s, pyrrole). **1b**: Yield 20 %; UV-vis (MeOH) λ_{max} , nm: (log ϵ) 260 (4.60), 419 (5.61), 551 (4.22); SIMS: m/z 1251 (M^+); ^1H NMR δ -2.53 (2H, t, $J = 6.5$ Hz, CH_2), -1.26 (2H, t, $J = 6.5$ Hz, CH_2), 2.59 (2H, t, $J = 6.5$ Hz, CH_2), 3.27-3.62 (26H, m, CH_2), 4.82 (2H, d, $J = 8.6$ Hz, Ph), 5.88 (2H, d, $J = 8.6$ Hz, Ph), 6.56 (2H, d, $J = 8.4$ Hz, C_6H_4), 6.94 (2H, d, $J = 8.4$ Hz, C_6H_4), 7.74-7.86 (12H, m, Ph), 8.11 (4H, d, $J = 8.0$ Hz, Ph), 8.23 (4H, d, $J = 8.0$ Hz, Ph), 9.33 (8H, s, pyrrole).
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