Amino(porphyrinato)antimony(V) Complexes as a Fluorosensor for Selective and Sensitive Detection of Trivalent Metal Cations

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The additive effects of metal cations on the fluorescence quantum yield (Φ_f) were investigated for weakemissive amino(tetraphenylporphyrinato)antimony(V) bromide (1). When the µmol dm⁻³ of trivalent metal cations such as Al³⁺, Ga³⁺, In³⁺, and Lu³⁺ were added to MeCN solution of 1, the Φ_f was remarkably enhanced. The dependences of Soret band shift and Φ_f upon the addition of trivalent metal cations revealed that a transition from S₂ state to the partially charge-shifted state was prevented by coordinating trivalent metal cations to the axial nitrogen atom of 1. 1 worked as a selective fluorosensor for detecting µmol dm⁻³ trivalent metal cations.

Fluorosensors have received much attention from the viewpoints of chemical, biological, and environmental sciences.¹⁻⁸ Most sensing mechanism of fluorescence are based on photoinduced electron transfer (PET).9-13 PET-fluorosensors are normally constructed from an electron-accepting fluorophore (A) which is linked by a spacer to an electron-donating site (D). Usually fluorescence of A disappears through ET-quenching by D. In the presence of analytes such as metal ions or cationic molecules, however, they disturb the PET, resulting in fluorescence from A (Scheme 1). Recently, we have successfully synthesized amino(methoxo)(tetraphenylporphyrinato)antimony(V) (1a) which has an amino group as an axial ligand.¹⁴ Weak fluorescence appears from **1a** under S₂-excitation because of the contribution of non-emissive charge-shifted (CS) state.¹⁴ Therefore, **1a** is the simplest directly connected D-A system (Scheme 1). However, the question of whether the CS state of 1a is controlled by a guest molecule has arisen. Here, we will investigate the ability of 1a and its analogous 1b and 1c as PET-fluorosensors for metal cations.

Under Soret band excitation of **1a** (0.5 μ M, μ M = 10⁻⁶ mol dm⁻³) at 420 nm, a weak S₁ fluorescence was observed at



Scheme 1. PET-fluorosensor and the structure of 1.



Figure 1. Maximum Φ_f of 1a in the presence of M^{n+} .

594 and 645 nm in MeCN in 0.0037 of quantum yield for fluorescence (Φ_f^0). This value was much smaller than that of dihydroxo(tetraphenylporphyrinato)antimony(V) bromide (**2**) ($\Phi_f^0 = 0.0518$) without D.¹⁴ Low Φ_f^0 can be attributed to the transition from S₂ to CS states which has the character of paramagnetic Sb^{IV}(tpp).^{14,15} The Φ_f^0 of **1b** was relatively large compared with **1a**. Probably, a proton transfer from axial hydroxo to amino ligand occurred partially to form the emissive zwitterion ([*i*-PrNH₂⁺-Sb(tpp)-O⁻]⁺Br⁻), because a hydroxo proton was acidic (pK_a = 10.7).¹⁶

By the addition of $M(ClO_4)_3$ ($M^{3+} = Al^{3+}$, Ga^{3+} , In^{3+} , and Lu³⁺) and HClO₄¹⁴ to an MeCN solution of **1a**, the fluorescence quantum yield (Φ_f) increased up to >0.029 at maximum points. The fluorescence enhancement factor (FE),¹¹ which is defined as $\Phi_{\rm f}/\Phi_{\rm f}^{0}$, were relatively high values (FE = 7.8–8.6) for 1a compared to a reported naphthalimide fluorosensor toward trivalent metal cations. However, $\Phi_{\rm f}$ remained unchanged upon addition of mono- and divalent ions such as Li⁺, Na⁺, K⁺, Zn²⁺, and Mg^{2+} (Figure 1). Moreover, a dependence of $\Phi_{\rm f}$ on the concentration of M³⁺ was observed. A typical example is the dependence of the $\Phi_{\rm f}$ of **1a** on μM concentration of Al³⁺ (Figure 2). The sensitivity toward M^{3+} was evaluated by the concentrations $(C_{1/2}^{F})$ required to enhance up to the half of the maximum fluorescence intensity. The $C_{1/2}^{F}$ of **1a** were 3.6 μ M for Al³⁺, 3.9 μ M for Ga³⁺, 3.6 μ M for In³⁺, 3.6 μ M for Lu³⁺, and 6.1 μ M for H⁺, respectively (Table 1). Also the $\Phi_{\rm f}$ of 1b gave smaller $C_{1/2}^{\text{F}}$ values than that of **1a**, as shown in Table 1. In the case of 1c, double changes were observed at 0.80 and 13 μ M of $C_{1/2}^{F}$ (Figure 3). The $C_{1/2}^{F}$ values of **1a–1c** are summarized in Table 1.

Since the S_2 excited state is too short-lived to interact with μM of M^{3+} , it should be taken into account that M^{3+} interact



Figure 2. (A) Spectral change of fluorescence spectra of 1a when $0-20 \,\mu$ mol of Al(ClO₄)₃ was added to MeCN solution of 1a. (B) Plots of Φ_f vs. [Al(ClO₄)₃] in 1a (\oplus) and 1b (\bigcirc).

Figure 3. Dependence of Φ_f of **1c** on [Al³⁺].

Table 1. $C_{1/2}$ Values of 1 toward M^{3+} and H^+ Ions

1	${{ { { { \! \! \! \! \! \! \! \! \! \! \! \! \! \! \! $	$E^{\rm ox}/{ m V}^{ m b)}$	$E^{\rm red}/{\rm V^{c)}}$	$C_{1/2}^{\rm F}/10^{-6}{\rm M}(C_{1/2}^{\rm A}/10^{-6}{\rm M})^{\rm d})$				
				Al ³⁺	Ga ³⁺	In ³⁺	Lu ³⁺	H^+
1a	0.0037	1.59	-0.79	3.6 (3.2)	3.9 (3.9)	3.6 (3.5)	3.6 (3.2)	6.1 (10.2)
1b	0.0100		-0.81	2.6 (3.2)	3.0 (9.8)	2.3 (5.9)	2.3 (2.3)	4.4 (10.0)
1c	0.0042	—	-0.83	0.8	0.6	1.5	2.2	3.0

a) The fluorescence quantum yields in the absence of additive. b) The oxidation potentials vs. Ag/Ag^+ (See Ref. 14). c) The reduction potentials vs. Ag/Ag^+ . d) $C_{1/2}^{F}$ is the concentration required to enhance up to half maximum determined by dependence on fluorescence quantum yields. The values in parenthesis were $C_{1/2}^{A}$ determined from on absorption spectra.



Figure 4. Spectral change of absorption spectra of the Soret band of **1a** when $0-20 \,\mu\text{M}$ of Al(ClO₄)₃ was added to MeCN solution of **1a** and a plot of ΔA versus [Al³⁺].

with 1 in the ground state.¹⁵ Figure 4 shows the dependence of absorption spectra of 1a on $[Al^{3+}]$. With an increase of $[Al^{3+}]$, absorbance (A) increases along the red shift of λ_{max} from 421.8 to 422.8 nm. An isosbestic point appears at 419.1 nm. Furthermore, the reduction potential of 1a shifts positively direction ($\Delta E^{\text{red}} = 0.26 \text{ V}$) in the presence of Al³⁺. These results suggest that the complex between 1 and Al^{3+} (1/ Al^{3+}) should be formed in the ground state through the coordination of M^{3+} with the nitrogen lone pair of the axial amino ligand. From Hill plot analysis based on Figure 4, the stoichiometric ratio of the complex $(1a/Al^{3+})$ was determined to be 1:1 (see Supporting Information). On the other hand, M^+ and M^{2+} cations affected neither the Soret band nor reduction potential of 1 at all (see Supporting Information). Furthermore, neither spectral change of the Soret band nor the shift of reduction potential was observed in the case of 2. The basicity of the axial amino ligand of 1a was very poor since the acid dissociation constant (pK_a) for the conjugated acid of the axial amino ligand was reported to be 4.41, a value smaller than that of aniline $(pK_a = 4.63)$.¹⁴ Accordingly, trivalent metal cations, which are more strongly Lewis acidic than mono- or divalent

metal cations, might only lead to the selective interaction with an axial amino ligand on **1**. The concentrations $(C_{1/2}^{A})$ required to show half the maximum difference absorbance (ΔA) were determined, as shown in Table 1. These $C_{1/2}^{A}$ values are in good agreement with $C_{1/2}^{F}$ values. Therefore, it suggested that the dependence of Φ_{f} on $[M^{3+}]$ could be attributed to the complexation of **1** with M^{3+} in the ground state.

The energy level of the charge-separated state of **1a** was estimated to be 0.53 eV lower than the S₂ state ($E_{S2} = 2.92 \text{ eV}$) by Rehm–Weller calculation assuming that E^{ox} of *i*-PrNH ligands equaled that of *n*-PrNH₂ ($E^{\text{ox}} = 1.60 \text{ V}$).¹⁷ Under excitation of the Q-band at 550 nm, however, the fluorescence quenching occurred, although the energy level of the charge separated state of **1a** was higher than that of the S₁ state ($E_{\text{S1}} = 2.08 \text{ eV}$). It is suggested that the charge transfer in the Sb–N bond to make the partially CS state in the ground state, judging from the λ_{max} (421.8 nm) of **1a** appearing at longer wavelength compared with that of **2** (417 nm). On the other hand, in the presence of the proton and trivalent metal cations, the selective formation of $1/M^{3+}$ prevents the formation of partial CS state in the ground state (Scheme 2).

In conclusion, we elucidated that 1 operated as a selective fluorosensor to detect M^{3+} ions such as Al^{3+} , Ga^{3+} , In^{3+} , and Lu^{3+} on a μ M-order.

Experimental

Instruments. UV–vis absorption spectra and fluorescence spectra of solutions were measured on a Hitachi U2001 spectrometer and on a Hitachi F4500 spectrometer, respectively. ¹H NMR spectra were taken in CDCl₃ using Me₄Si as an internal standard on a Bruker AC 250P spectrometer at 250 MHz. SIMS spectra were obtained on a Hitachi M-2000AM spectrophotometer. All chemicals were of the best commercial grades available.



Scheme 2. Plausible mechanism on enhancement of $\Phi_{\rm f}$.



Scheme 3. Synthesis of 1.

Preparation of 1. An MeCN solution (50 cm^3) containing **4b** (1.1 mmol) and *i*-PrNH₂ (2 cm³) was stirred for 4 h at room temperature. The solvent was evaporated and the residue was dissolved in CH₂Cl₂. The CH₂Cl₂ solution was washed three times with 50 cm³ portions of H₂O. After evaporation, the crude product was chromatographed on silica gel (Fuji Silysia BW-300) using CHCl₃-MeOH (10:1 v/v) as an eluent to give **1b** (Scheme 3). The synthesis of **1c** was performed by stirring an MeCN solution (50 cm³) containing **3** (1.1 mmol) and *i*-PrNH₂ (2 cm³) and purifying by the same procedures as with **1b**. The spectral data of **1** are shown below. On ¹H NMR measurements, peaks of NH proton in **1** were not all observed due to extremely broad lines. The preparation of **1a** from **4a** was already reported in a previous paper.¹⁴

Hydroxo(isopropylamino)(tetraphenylporphyrinato)antimony(V) bromide (**1b**). Yield 68% from **4b**; SIMS: m/z 808 (M⁺); ¹H NMR (CDCl₃): δ –3.92 (1H, m, Sb–N–CH–), –2.29 (6H, d, J = 6.2 Hz, –C(CH₃)₂), 7.82–7.88 (12H, m, Ph), 8.27 (4H, d, J = 6.4 Hz, Ph), 8.58 (4H, d, J = 6.4 Hz, Ph), 9.33 (8H, s, pyrrole).

Di(isopropylamino)(tetraphenylporphyrinato)antimony(V) bromide (1c). Yield 1.2% from 3; SIMS: m/z 847 (M⁺ – 2); ¹H NMR (CDCl₃): δ –4.01 (2H, m, Sb–N–CH–), –2.36 (12H, d, J = 6.2 Hz, –C(CH₃)₂), 7.87–7.96 (12H, m, Ph), 8.31 (8H, m, Ph), 9.40 (8H, s, pyrrole). Measurements of Fluorescence Quantum Yields. The concentration of 1 in MeCN solutions was adjusted for the absorbance to be less than 0.1 at the excitation wavelength (420 nm). The fluorescence quantum yields ($\Phi_{\rm f}$) were determined by using an MeCN solution of 2 ($\Phi_{\rm f} = 0.0518$) as an actinometer.¹⁴

Measurements of Redox Potentials. The oxidation and reduction potentials of a dried MeCN solution of 1 (1×10^{-2} M) in the presence of a supporting electrolyte (Et₄NBF₄; 0.1 M) were measured by cyclic voltammetry at a scan rate of 300–500 mV s⁻¹ at 25 °C on a BAS CV-50W cyclic voltammeter using a carbon-disk working electrode, a Pt counter electrode, and an Ag/AgNO₃ reference electrode.

Supporting Information

The Hill plot in the case of 1a and Al^{3+} and the absorption spectra of 1a in the presence of M^+ and M^{2+} . This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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