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

Shin-ichiro Tsunami,[1] Hirotaka Fujiwara,[2] Jin Matsumoto,[2] Tsutomu Shiragami,*[2] and Masahide Yasuda[2]

[1]Miyazaki Prefecture Environmental Science Association, 6258-20 Tayoshi, Miyazaki 880-0911

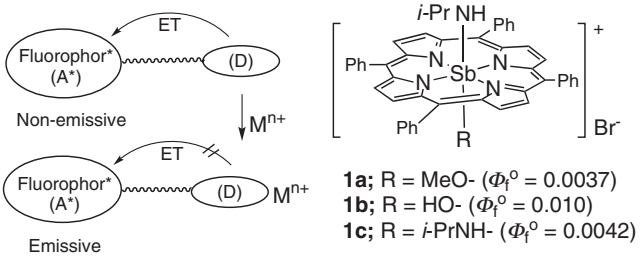
[2]Department of Applied Chemistry, Faculty of Engineering, University of Miyazaki, Gakuen-Kibanadai, Miyazaki 889-2192

Received August 7, 2009
E-mail: t0g109u@cc.miyazaki-u.ac.jp

The additive effects of metal cations on the fluorescence quantum yield (Φ_f) were investigated for weak-emissive amino(tetraphenylporphyrinato)antimony(V) bromide (**1**). When the μmol dm^{-3} of trivalent metal cations such as Al^{3+}, Ga^{3+}, In^{3+}, and Lu^{3+} 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 S_2 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 photo-induced 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 S_2-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 μM, μM = 10^{-6} mol dm^{-3}) at 420 nm, a weak S_1 fluorescence was observed at



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

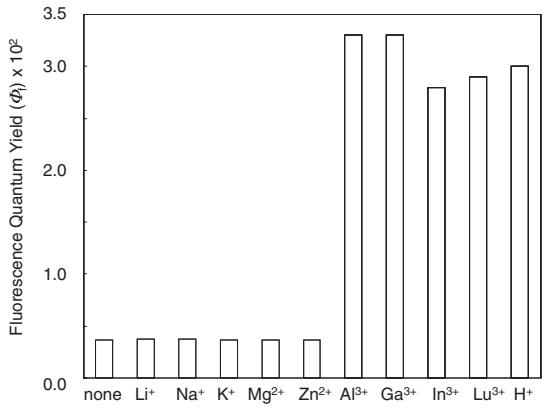


Figure 1. Maximum Φ_f of **1a** in the presence of M^{n+}.

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 S_2 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*-PrNH$_2^+$–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 Lu^{3+}) and HClO$_4$[14] 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 Φ_f/Φ_f^0, were relatively high values (FE = 7.8–8.6) for **1a** compared to a reported naphthalimide fluorosensor toward trivalent metal cations. However, Φ_f remained unchanged upon addition of mono- and divalent ions such as Li^+, Na^+, K^+, Zn^{2+}, and Mg^{2+} (Figure 1). Moreover, a dependence of Φ_f on the concentration of M^{3+} was observed. A typical example is the dependence of the Φ_f of **1a** on μM concentration of Al^{3+} (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 μM for Al^{3+}, 3.9 μM for Ga^{3+}, 3.6 μM for In^{3+}, 3.6 μM for Lu^{3+}, and 6.1 μM for H^+, respectively (Table 1). Also the Φ_f of **1b** gave smaller $C_{1/2}^F$ values than that of **1a**, as shown in Table 1. In the case of **1c**, double changes were observed at 0.80 and 13 μM 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

Published on the web December 18, 2009; doi:10.1246/bcsj.20090206

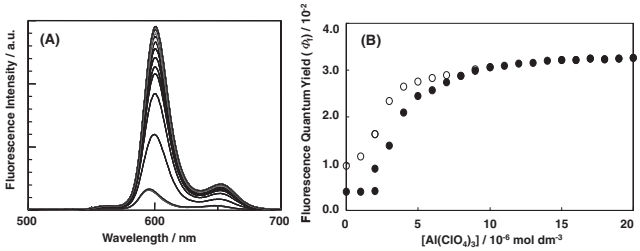


Figure 2. (A) Spectral change of fluorescence spectra of **1a** when 0–20 μmol of $Al(ClO_4)_3$ was added to MeCN solution of **1a**. (B) Plots of Φ_f vs. $[Al(ClO_4)_3]$ in **1a** (●) and **1b** (○).

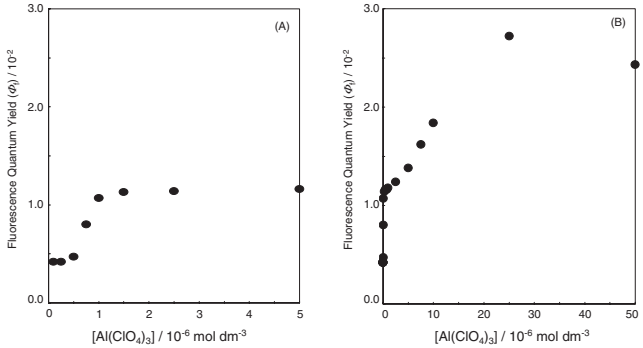


Figure 3. Dependence of Φ_f of **1c** on $[Al^{3+}]$.

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

1	Φ_f^{0} a)	E^{ox}/V b)	E^{red}/V c)	$C_{1/2}{}^F/10^{-6}$ M ($C_{1/2}{}^A/10^{-6}$ M) 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.

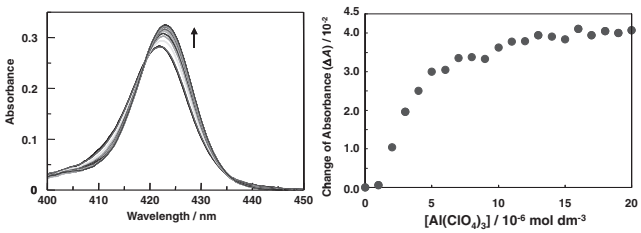


Figure 4. Spectral change of absorption spectra of the Soret band of **1a** when 0–20 μM of $Al(ClO_4)_3$ was added to MeCN solution of **1a** and a plot of ΔA versus $[Al^{3+}]$.

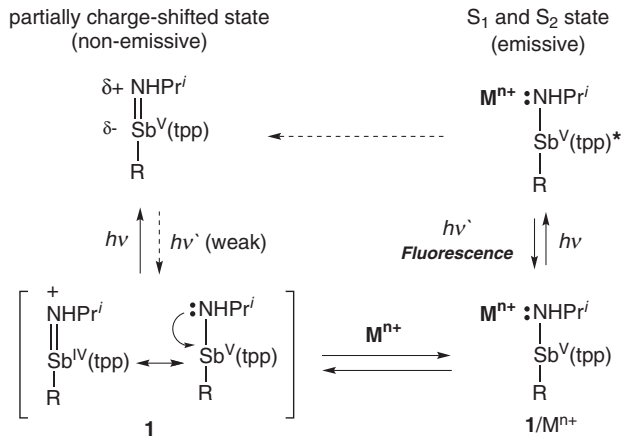
with **1** in the ground state.[15] Figure 4 shows the dependence of absorption spectra of **1a** on $[Al^{3+}]$. With an increase of $[Al^{3+}]$, absorbance (A) increases along the red shift of λ_{max} from 421.8 to 422.8 nm. An isosbestic point appears at 419.1 nm. Furthermore, the reduction potential of **1a** shifts positively direction ($\Delta E^{red} = 0.26$ V) in the presence of Al^{3+}. 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 S_2 state ($E_{S2} = 2.92$ eV) by Rehm–Weller calculation assuming that E^{ox} of *i*-PrNH ligands equaled that of *n*-$PrNH_2$ ($E^{ox} = 1.60$ 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 S_1 state ($E_{S1} = 2.08$ 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).

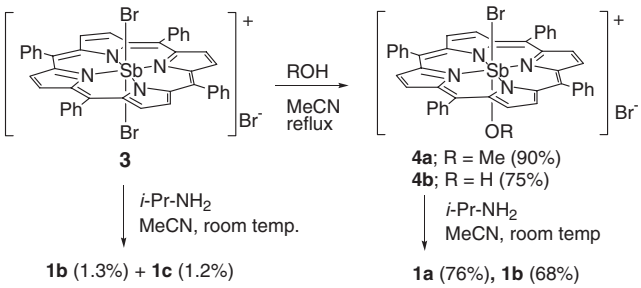
In conclusion, we elucidated that **1** operated as a selective fluorosensor to detect M^{3+} ions such as Al^{3+}, Ga^{3+}, In^{3+}, and Lu^{3+} on a μM-order.

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. ^{1}H NMR spectra were taken in $CDCl_3$ using Me_4Si 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 Φ_f.



Scheme 3. Synthesis of **1**.

Preparation of 1. An MeCN solution (50 cm^3) containing **4b** (1.1 mmol) and *i*-$PrNH_2$ (2 cm^3) was stirred for 4 h at room temperature. The solvent was evaporated and the residue was dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed three times with 50 cm^3 portions of H_2O. After evaporation, the crude product was chromatographed on silica gel (Fuji Silysia BW-300) using $CHCl_3$–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 cm^3) containing **3** (1.1 mmol) and *i*-$PrNH_2$ (2 cm^3) 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 ($CDCl_3$): δ −3.92 (1H, m, Sb–N–CH–), −2.29 (6H, d, $J = 6.2$ Hz, –$C(CH_3)_2$), 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 ($CDCl_3$): δ −4.01 (2H, m, Sb–N–CH–), −2.36 (12H, d, $J =$ 6.2 Hz, –$C(CH_3)_2$), 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 (Φ_f) were determined by using an MeCN solution of **2** ($\Phi_f = 0.0518$) 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 (Et_4NBF_4; 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 $Ag/AgNO_3$ 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/.

References

1 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515.

2 A. P. de Silva, B. McCaughan, B. O. F. McKinney, M. Querol, *Dalton Trans.* **2003**, 1902.

3 P. Jiang, Z. Guo, *Coord. Chem. Rev.* **2004**, *248*, 205.

4 K. Rurack, U. Resch-Genger, *Chem. Soc. Rev.* **2002**, *31*, 116.

5 V. Balzani, J. van de Loosdrecht, A. Mecati, N. Sabbatini, J.-M. Lehn, R. Ziessel, *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 190.

6 S. Aoki, H. Kawatani, T. Goto, E. Kimura, M. Shiro, *J. Am. Chem. Soc.* **2001**, *123*, 1123.

7 K. Okamoto, S. Fukuzumi, *J. Am. Chem. Soc.* **2004**, *126*, 13922.

8 A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42.

9 B. Ramachandram, G. Saroja, N. B. Sankaran, A. Samanta, *J. Phys. Chem. B* **2000**, *104*, 11824.

10 J. Yuasa, S. Fukuzumi, *J. Am. Chem. Soc.* **2008**, *130*, 566.

11 D. Staneva, I. Grabchev, J.-P. Soumillion, V. Bojinov, *J. Photochem. Photobiol., A* **2007**, *189*, 192.

12 H.-Y. Luo, J.-H. Jiang, X.-B. Zhang, C.-Y. Li, G.-L. Shen, R.-Q. Yu, *Talanta* **2007**, *72*, 575.

13 Y. Andou, K. Shima, T. Shiragami, M. Yasuda, *Chem. Lett.* **2001**, 1198.

14 S. Tsunami, K. Tanaka, J. Matsumoto, T. Shiragami, M. Yasuda, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 583.

15 M. Fujitsuka, D. W. Cho, T. Shiragami, M. Yasuda, T. Majima, *J. Phys. Chem. B* **2006**, *110*, 9368.

16 T. Shiragami, Y. Andou, Y. Hamasuna, F. Yamaguchi, K. Shima, M. Yasuda, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1577.

17 C. K. Mann, *Anal. Chem.* **1964**, *36*, 2424.