

Effects of an Axial Ligand on the Reduction Potential, Proton Dissociation, and Fluorescence Quantum Yield of Hydroxo(porphyrinato)antimony(V) Complexes

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The substituent effects on the reduction potentials ($E_{1/2}^{\text{red}}$), the proton dissociation constants of a hydroxo ligand (K_a), and the fluorescence quantum yields (Φ) in aryloxo(hydroxo)tetraarylporphyrinatoantimony(V) complexes were investigated. The $E_{1/2}^{\text{red}}$ and K_a values were affected by substituents in the axial aryloxo ligand but, little affected by substituents in the porphyrin ring. Since $E_{1/2}^{\text{red}}$ of tetraarylporphyrinatoantimony(V) complexes were higher than those of other metal-porphyrin complexes, it was suggested that the metal orbital greatly contributed to the LUMO level of the complex which can be related to the $E_{1/2}^{\text{red}}$ and K_a values. Therefore, the substituent effects of the axial aryloxo ligand on the $E_{1/2}^{\text{red}}$ and K_a values were attributed to the electron density of the antimony ion, which affected the LUMO level of the complexes. Moreover, the Φ of the porphyrin moiety depended on both the oxidation potential of the axial aryloxo ligands and the polarity of the solvent used. The fluorescences of the porphyrin moiety were quenched by the axial aryloxo ligands at rate constants of $10^8 - 10^{11} \text{ s}^{-1}$.

The synthesis and characterization of porphyrinatometal complexes have been extensively studied from the view points of biological interests involving the photosynthesis and redox processes for many years. Therefore, the most intense attention has been focused on transition-metal and typical low-valent element complexes of porphyrin. On the other hand, a typical high-valent element is expected to lower the LUMO and HOMO levels of porphyrinatometal complexes and to covalently bond with axial ligands, differing from the transition-metal complexes.^{1–3} Our attention has especially been paid to porphyrinatophosphorus(V) and antimony(V) complexes having the functionalized moieties on axial ligands. We have already reported the photoinduced intramolecular electron and energy transfer between a porphyrin ring and axial π -electron chromophores linked by a methylene chain in porphyrinatoantimony(V) complexes.^{4–5} However, there is no information about the properties of porphyrinatoantimony(V) complexes affected by π -electron chromophores directly coordinated to an antimony atom as an axial ligand without a methylene bridge.

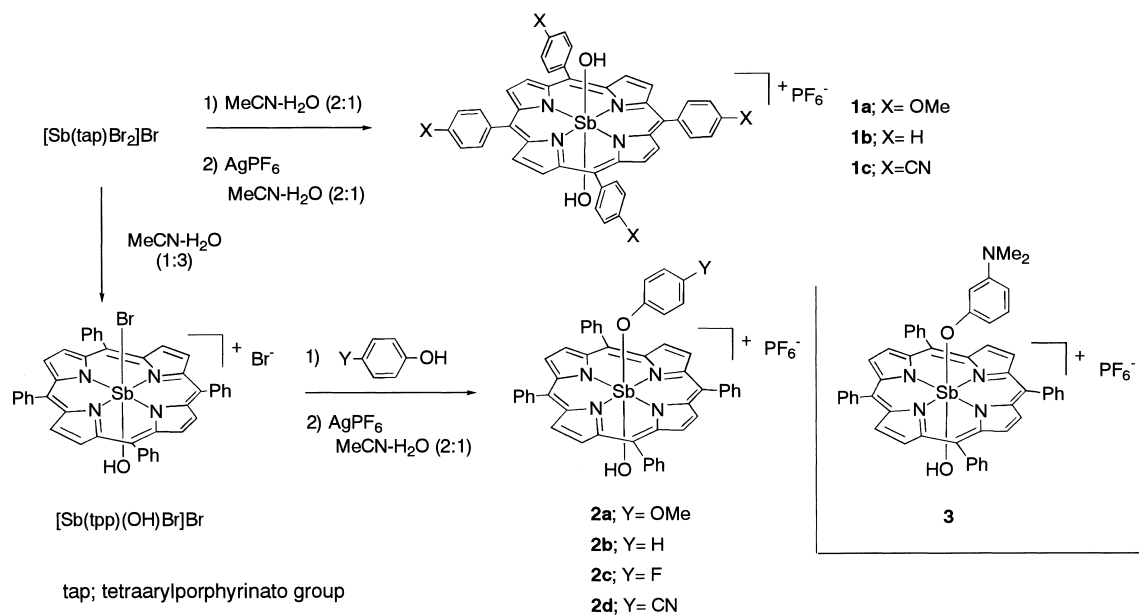
Here, we elucidate the effects of an axial aryloxo ligand in aryloxo(hydroxo)(tetraphenylporphyrinato)antimony(V) complexes, $[\text{Sb}(\text{tpp})(\text{OH})(\text{OAr})]^+$; tpp = tetraphenylporphyrinato group) on their electrochemical properties, proton dissociation of hydroxo ligand, and excited singlet-state properties.

Results

Hydroxo(tetraarylporphyrinato)antimony(V) Complexes. The substituent effects on the reduction potential, the proton dissociation, and the fluorescence quantum yield were in-

vestigated for dihydroxo(tetraarylporphyrinato)antimony(V) complexes (**1a–c**) having substituents ($X = \text{OMe}, \text{H}, \text{CN}$) on the tetraphenylporphyrinato ring and aryloxo(hydroxo)(tetraphenylporphyrinato)antimony(V) complexes (**2a–d**) having substituents ($Y = \text{OMe}, \text{H}, \text{F}, \text{CN}$) on the aryloxo axial ligand (Scheme 1). Moreover, (*m*-dimethylaminophenoxy)-(hydroxo)(tetraphenylporphyrinato)antimony(V) complex (**3**) was used for the substituent effect on the fluorescence spectra.

Substituent Effect on Reduction Potentials. The half peak of the reduction potentials ($E_{1/2}^{\text{red}}$) of **1a–c** and **2a–d** are summarized in Table 1. Figure 1 shows a voltammogram of **1a** as a typical example. The first reduction peaks of **1a–c** were reversible, since the ratio ($i_{\text{pc}}/i_{\text{pa}}$) of the peak current intensity at a cathodic sweep (i_{pc}) to that at an anodic sweep (i_{pa}) were measured to be 0.8–1.0, and the peak potential differences (ΔE_p) between the cathodic and anodic sweeps at the first reduction potential were 40–80 mV, which were theoretically predicted. Moreover, ΔE values, which are the differences between the first reduction peaks and the second reduction peaks of **1a–c**, were 0.43–0.48 V. Similar $i_{\text{pc}}/i_{\text{pa}}$, ΔE_p values, and ΔE values were reported for the reversible process of various octaethylporphyrinatometal complexes.^{6–7} On the other hand, the oxidation potentials of **1a–c** did not show reversible peaks. Therefore, the reductants of **1a–c** were stable compared with their cation radicals. A similar behavior was observed for **2a–d**. If the reductant generated by the first reduction is the π -radical anion, this process does not become reversible by the following process (protonation e.t.c.). Therefore, the reductants can be assigned to a valence change of antimony from five to four in the reduction process.

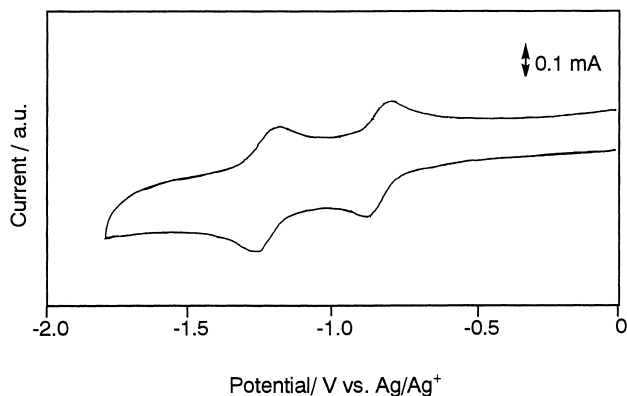


Scheme 1.

Table 1. Redox Potential and K_a of **1a–c** and **2a–d**

	$K_a/10^4$	$E_{1/2}^{\text{red}}/\text{V}$			$E_{1/2}^{\text{ox}}/\text{V}$	
		First ^{a)}	Second ^{b)}	$\Delta E^{\text{c)}$	Por ^{d)}	Ligand ^{e)}
1a	0.83	−0.51	−0.99	0.48	1.40	
1b	0.43	−0.51	−0.95	0.44	1.40	
1c	1.33	−0.52	−0.95	0.43	1.41	
2a	0.56	−0.54	−0.90	0.36	1.64	0.70
2b	0.56	−0.46	−0.87	0.41	1.50	0.93
2c	3.63	−0.46	−0.87	0.41	1.55	1.39
2d	5.33	−0.46	−0.85	0.39	1.76	1.59

a) The half-peak of first reduction potential of porphyrinato moiety. b) The half-peak of second reduction potential of porphyrinato moiety. c) ΔE values were differences between first and second half-peaks of reduction potentials of porphyrinato moiety. d) The half-peak of oxidation potential of porphyrinato moiety. e) The half-peak of oxidation potential of the axial aryloxo ligand.

Fig. 1. Cyclic voltammogram of **1a** at 0.3 V/s rate in MeCN.

Substituent Effect on the Proton Dissociation Constants of Hydroxo Ligand in **1a–c** and **2a–d**. By the addition of

an aqueous KOH solution into a MeCN–H₂O (7:3, v/v) solution of **2a**, the absorption maximum (λ_{max}) of the Soret band was shifted from 419 nm to 422 nm with an isobestic point at 420 nm, as shown in Fig. 2. Upon the addition of HClO₄ to an alkaline solution, the shifted Soret band returned to the original position, thus revealing that the spectral change was due to a reversible proton-dissociation process (Scheme 2). Moreover, no occurrence of the substitution of the phenoxy group with a hydroxy group was confirmed by FAB-MS measurements of complexes treated by an acid and a base. The proton-dissociation constant (K_a) of **2a** was estimated from the concentration of KOH required for a half shift of the maximum shift in plots of the λ_{max} vs the concentration of KOH (Fig. 2).

Substituent Effect on Fluorescence Quantum Yield.

The fluorescence of **1a–c** appeared at λ_{max} of 594–597 nm in MeCN with Φ of 0.00468–0.0518. Also, the fluorescence spectra **2a–d** appeared at 594–597 nm in MeCN under the excitation of a porphyrinato chromophore at 420 nm. However, the Φ of **2a** (X = OMe) was extremely smaller than those for **2b** (X = H), **2c** (X = F), and **2d** (X = CN) (Table 2). The absorption spectra of **2a–d** were essentially similar to those of **1a–c**, except for the appearance of an extra band due to the axial aryloxo ligand at a shorter wavelength than 300 nm. Thus, no strong interaction between the porphyrin ring and the axial aryloxo ligand in the ground state was confirmed by the similarity of the Soret bands between **1a–c** and **2a–d**. In the case of **2a**, therefore, the occurrence of intramolecular fluorescence quenching by the axial aryloxo ligand was supposed.

In the case of **3**, having a dimethylaminophenyl group as the axial ligand, the fluorescence quantum yield was very small, probably due to intramolecular quenching of the porphyrin moiety by the axial aryloxo ligand, similar to the case of **2a** mentioned above. However, the addition of HClO₄ (3.2×10^{-2} mol dm^{−3}) to a MeCN solution of **3** restored the fluorescence intensity from 0.002 to 0.015, as shown in Fig. 3. The restoration of the fluorescences by the addition of the acid can be at-

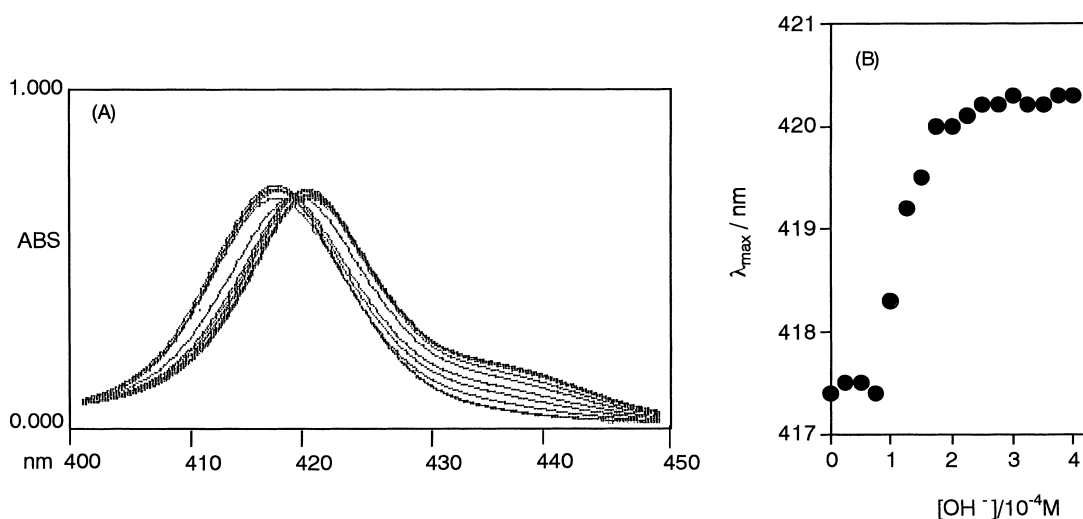
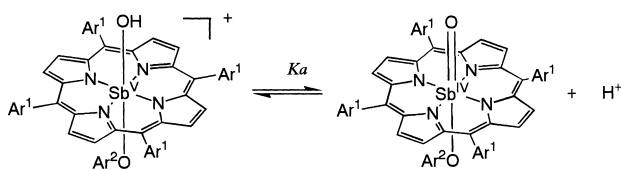


Fig. 2. (A) Spectral change of Soret band of **2a** in MeCN-H₂O (4:1 v/v) solution by the addition of aqueous KOH solution. (B) Plots of $\lambda_{\max}$ vs the concentration of OH⁻.



Scheme 2.

Table 2. Fluorescence Properties of **2a-d**

2	$\Phi/10^{-3}$ ^{a)}	$\Delta G/\text{eV}$ ^{b)}	$\log k_q$ ^{c)}	$\lambda_{\max}/\text{nm}$
2a	0.3	-0.84	11.2	597, 645
2b	2.4	-0.69	10.3	596, 647
2c	6.9	-0.23	9.6	594, 647
2d	29.8	-0.03	8.9	594, 646

a) Fluorescence quantum yields at the excitation at 420 nm in MeCN.

b) $\Delta G = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - E^{0-0}$ where $E^{0-0} = 2.08$ eV.

c) k_q values were calculated by the following equation: $k_q = (\Phi_0/\Phi - 1)/\tau_f$ where τ_f was 1.7 ns and Φ_0 was 0.0518 (Data from Ref. 5).

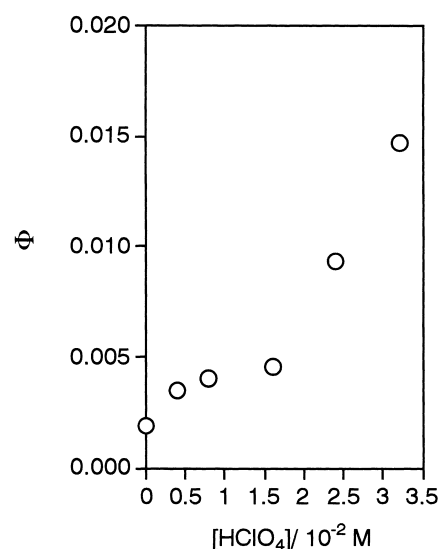


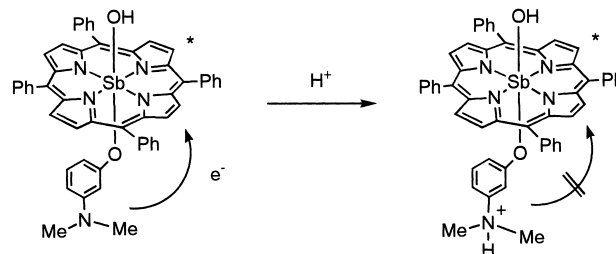
Fig. 3. The change of fluorescence quantum yields of **3** with HClO₄ in MeCN.

tributed to a decrease in the electron-donating ability of the axial aryloxo group by protonation on the nitrogen atom of the dimethylaminophenoxy axial ligand (Scheme 3).

The fluorescence spectra of **2b** were measured in toluene, benzene, 1,4-dioxane, tetrahydrofuran, ethyl acetate, dichloromethane, and acetonitrile upon the excitation of porphyrin Soret band ($\lambda = 420$ nm). The emission maxima ($\lambda_{\max}$) of **2b** were observed at 596 nm independently on the solvent used, while the fluorescence quantum yield (Φ) depended on the solvent used, as shown in Table 3.

Discussion

Effects of an Axial Aryloxo Ligand. Scheme 4 shows a typical energy diagram between the metal orbital and the porphyrin orbital. Because the LUMO levels of the high-valent metal ion are lower, i.e. the reduction potentials of the metal ion shifts to the positive side, the LUMO level in the porphyrin-



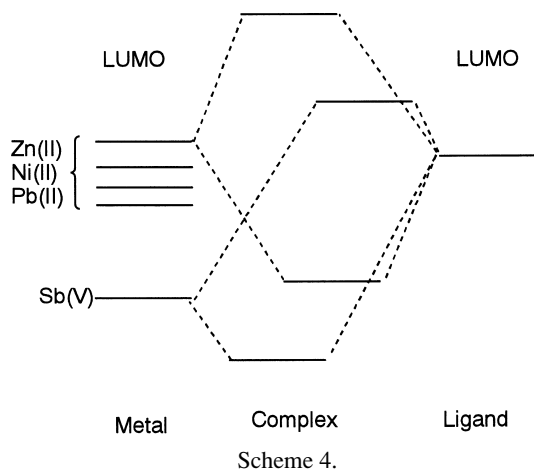
Scheme 3.

natometal complex is simultaneously lower and the contributions of the metal orbital to the LUMO of the complexes are greater. On the other hand, porphyrinatometal complexes (i.e. Zn(II), Ni(II)) having largely negative reduction potentials have a higher LUMO level, which can be predominantly affected by the porphyrin orbitals. Previous reports have eluci-

Table 3. Fluorescence Quantum Yields of **2b**

Solvent ^{a)}	$E_T(30)^b)$	$\Phi_0/10^{-3}$ c)	$\Phi/10^{-3}$	$\log k_q^d)$
TL	33.9	29	21	8.35
BZ	34.5	28	20	8.37
DO	36.0	36	18	8.77
TF	37.4	39	2	10.0
EA	38.1	40	3	9.8
DM	41.1	35	3	9.8
AN	46.0	52	2	10.2

a) TL; toluene, BZ; benzene, DO; 1,4-dioxane, TF; tetrahydrofuran, EA; ethyl acetate, DM; dichloromethane, and AN; acetonitrile. b) Empirical solvent parameter. c) Fluorescence quantum yield for **1b**. Data from Ref. 5. d) $\log k_q$ values of **2b** were calculated by the following equation: $k_q = (\Phi_0/\Phi - 1)/\tau_f$ where τ_f for **1b** was 1.7 ns.



dated that the reduction of porphyrinatometal complexes (metal = Zn(II), Ni(II), Pb(II) etc.) occurred mainly in the porphyrin ring, while the reduction of tetraphenylporphyrinatocobalt(III) occurred on the metal-orbitals.⁸

Based on the above discussion, the LUMO level of high-valent porphyrinatoantimony complexes were suggested to be predominantly affected by the metal orbitals. Therefore, the first reduction potentials from Sb(V) to Sb(IV), and the proton-dissociation constants (K_a) should be affected by the substituents (X) on the axial aryloxo ligand, rather than the substituents (Y) on the porphyrin ring. In fact, $E_{1/2}^{\text{red}}$ of **2a–d** varied from -0.54 V (**2a**; Y = OMe) to -0.46 V (**2d**; Y = CN), while a small substituent effect of X on $E_{1/2}^{\text{red}}$ was observed; e.g. -0.52 V for **1a** (X = OMe) and -0.51 V for **1c** (X = CN). Furthermore, the measured K_a values of **1a–c** and **2a–d** are listed in Table 1. Along with an increase in the electron-withdrawing character of X and Y, the K_a values increased. The K_a values were strongly affected by the substituents (Y) on the aryloxo ligand, but were only slightly affected by the substituents (X) on the porphyrin ring. Thus, both the first reduction potential and the proton dissociation constants (K_a) were affected by the substituents (Y) on the axial aryloxo ligand.

Kinetic Treatment for Fluorescence Quenching. Using **1b** as a model compound for the hydroxo(porphyrinato)anti-

mony(V) complex without an interaction with the axial ligand, the rate constants (k_q) for the quenching of porphyrin moiety in the excited singlet state of **2a–d** by the axial aryloxo ligands were estimated by the following equation, where τ_f and Φ_0 are the fluorescence lifetime (1.7 ns) and the fluorescence quantum yield (0.0518) of **1b** in MeCN, respectively:⁵

$$k_q = (\Phi_0 / \Phi - 1) / \tau_f \quad (1)$$

The free-energy changes (ΔG) of the intramolecular electron transfer from the axial aryloxo ligand to the excited singlet state of the porphyrin moiety of **2a–d** were calculated by the Rehm–Weller equation (Eq. 2)⁹ using the oxidation potentials ($E_{1/2}^{\text{ox}}$) of the axial aryloxo ligand, $E_{1/2}^{\text{red}}$ of the porphyrin ring, and the excitation energy (E^{0-0}). The Coulombic term was estimated to be very small, since a positive charge transfer from the porphyrinato chromophore to the axial ligands caused no change in the total charge. Thus, the ΔG values for **2a–d** were calculated to be exoergic, as shown in Table 2.

$$\Delta G = E_{1/2}^{\text{ox}} - E_{1/2}^{\text{red}} - E^{0-0} - \text{Coulombic term} \quad (2)$$

Figure 4 shows the dependence of $\log k_q$ on the ΔG in MeCN. The $\log k_q$ values decreased remarkably along with an increase in the ΔG value. Since the fluorescence quenching proceeded via an intramolecular process, the k_q value exceeded the 10^{10} order, which was the diffusional-controlled limit when ΔG was -0.84 . Moreover, the plots of $\log k_q$ of **2b** in given solvents vs the empirical parameter $E_T(30)$, which show the scale of the solvent polarity, are shown in Fig. 5.¹⁰ The $\log k_q$ values increased along with an increase in $E_T(30)$, thus suggesting that k_q should strongly depend on the used solvent polarity.^{11–13} These results showed that the fluorescence quenching occurred mainly by the electron-transfer process.

Thus, in the case of high-valent porphyrinatometal complexes, it is suggested that substituents on the axial aryloxo ligand remarkably influence the chemical properties of the porphyrinatometal complex.

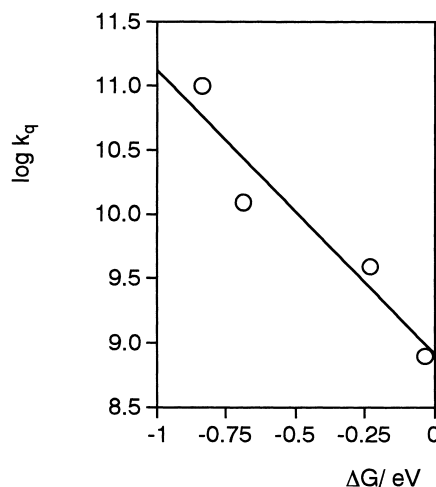


Fig. 4. Plots of $\log k_q$ vs ΔG for the fluorescence quenching of **2** in MeCN.

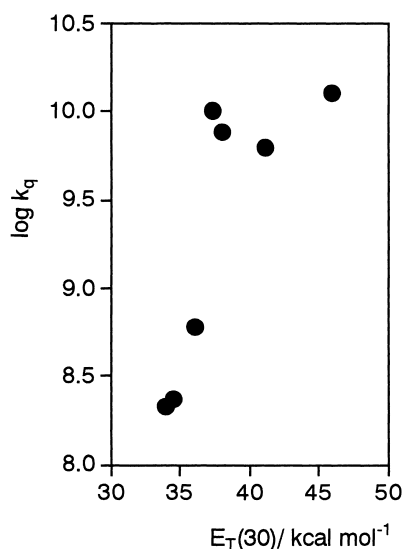


Fig. 5. Plots of $\log k_q$ vs $E_T(30)$ for the fluorescence quenching of **2b**.

Experimental

Instruments and Materials. ^1H NMR spectra were taken in CDCl_3 on a Bruker AC250P spectrometer at 250 MHz. SIMS was obtained on a Hitachi M2000A spectrometer, respectively.

Spectral grades of benzene, toluene, and dichloromethane were used without any further purification. 1,4-Dioxane and tetrahydrofuran were distilled from Na before use. MeCN was distilled from P_2O_5 and then CaH_2 . Phenol, 4-cyanophenol, 4-fluorophenol, 4-methoxyphenol and 3-(dimethylamino)phenol were purchased from Wako Pure Chemical Industries and Nacalai Tesque, Inc., respectively. Tetra(4-methoxyphenyl)porphyrin ($[\text{H}_2(\text{tmp})]$) was obtained from Tokyo Kasei Co. Ltd. According to a reported method,¹⁴ tetra(4-cyanophenyl)porphyrin ($[\text{H}_2(\text{tcp})]$) were prepared by the reaction of 4-cyanobenzaldehyde with pyrrole.

Preparation of 1a–c, 2a–d and 3. According to the literature,¹⁵ a pyridine solution (100 mL) of SbBr_3 (14 mmol) in the presence of $[\text{H}_2(\text{tmp})]$, $[\text{H}_2(\text{tpp})]$, or $[\text{H}_2(\text{tcp})]$ (0.7 mmol) was refluxed for 4 h. To the solution, Br_2 (1.8 mL) was added to form $[\text{Sb}(\text{tmp})\text{Br}_2]^+\text{Br}^-$, $[\text{Sb}(\text{tpp})\text{Br}_2]^+\text{Br}^-$ or $[\text{Sb}(\text{tcp})\text{Br}_2]^+\text{Br}^-$, respectively. The mixtures were then poured into hexane (200 mL) to give a precipitate. A CH_2Cl_2 solution of the precipitate was washed with hydrobromic acid (47%) and 150 mL of water. After evaporation, the hydrolysis of crude $[\text{Sb}(\text{tmp})\text{Br}_2]^+\text{Br}^-$, $[\text{Sb}(\text{tpp})\text{Br}_2]^+\text{Br}^-$, or $[\text{Sb}(\text{tcp})\text{Br}_2]^+\text{Br}^-$ in H_2O –MeCN (1:3, v/v) at 60 °C followed by a treatment with AgPF_6 (6.3 mmol) gave $[\text{Sb}(\text{tmp})(\text{OH})_2]^+\text{PF}_6^-$ (**1a**), $[\text{Sb}(\text{tpp})(\text{OH})_2]^+\text{PF}_6^-$ (**1b**),⁵ and $[\text{Sb}(\text{tcp})(\text{OH})_2]^+\text{PF}_6^-$ (**1c**), respectively. The crude products were purified by the column chromatography on silica gel (Fuji Silysia BW 300) using CH_2Cl_2 –MeOH (10:1, v/v) as an eluent.

Mono-hydrolysis of $[\text{Sb}(\text{tpp})\text{Br}_2]^+\text{Br}^-$ was performed in H_2O –MeCN (6:4) to give $[\text{Sb}(\text{tpp})(\text{OH})\text{Br}]^+\text{Br}^-$.⁵ A MeCN solution (40 mL) containing $[\text{Sb}(\text{tpp})(\text{OH})\text{Br}]^+\text{Br}^-$ (0.22 mmol) and the corresponding phenol derivative (2.2 mmol) was refluxed for 6 h. After the absorption spectra was shifted to a shorter wavelength, the solvent was evaporated and then solved in CH_2Cl_2 . The CH_2Cl_2 solution was washed three times with 50 mL portions of H_2O . After evaporation, the crude product was treated by AgPF_6 (2.2 mmol) to exchange the counter anion, and was then chro-

matographed on SiO_2 using CHCl_3 –MeOH (10:1, v/v) as an eluent to give **2a–d** and **3**.

Dihydroxo[tetra(4-methoxyphenyl)porphyrinato]antimony(V) Hexafluorophosphate (1a). Yield 79%; UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 431 (5.55), 558 (4.31), 604 (4.45); SIMS m/z 887 (M^+); ^1H NMR δ –4.20(2H, brs, OH), 4.14 (12H, s, OMe), 7.41 (8H, d, J = 8.6 Hz, $-\text{C}_6\text{H}_4-$), 8.28 (8H, d, J = 8.6 Hz, $-\text{C}_6\text{H}_4-$), 9.48 (8H, s, pyrrole).

Dihydroxo[tetra(4-cyanophenyl)porphyrinato]antimony(V) Hexafluorophosphate (1c). Yield 60%; UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 416 (5.62), 548 (4.49), 586 (4.30); SIMS m/z 867 (M^+); ^1H NMR (in CD_3CN) δ 8.28 (8H, d, J = 8.2 Hz, $-\text{C}_6\text{H}_4-$), 8.49 (8H, d, J = 8.2 Hz, $-\text{C}_6\text{H}_4-$), 9.50 (8H, s, pyrrole).

Hydroxo(4-methoxyphenoxy)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2a). Yield 45%. UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 418 (5.53), 552 (4.27), and 592 (4.04); SIMS m/z 873 (M^+). ^1H NMR δ –2.90 (1H, br, OH), 1.52 (2H, d, J = 9.2 Hz, $-\text{OC}_6\text{H}_4-$), 3.28 (3H, s, OMe), 5.23 (2H, d, J = 9.2 Hz, $-\text{OC}_6\text{H}_4-$), 7.86–7.92 (12H, m, Ph), 8.11 (4H, d, J = 6.8 Hz, Ph), 8.44–8.47 (4H, m, Ph), 9.42 (8H, s, pyrrole).

Hydroxo(phenoxy)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2b). Yield 34%. UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 418 (5.51), 550 (4.20), and 590 (3.96); SIMS m/z 843 (M^+). ^1H NMR δ –2.90 (1H, br, OH), 1.62 (2H, d, J = 7.9 Hz, OPh), 5.71–6.07 (3H, m, OPh), 7.68–7.97 (12H, m, Ph), 8.15 (4H, d, J = 6.7 Hz, Ph), 8.44 (4H, d, J = 6.7 Hz, Ph), 9.48 (8H, s, pyrrole).

4-Fluorophenoxy(hydroxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2c). Yield 13%. UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 419 (5.52), 551 (4.23), and 590 (3.95); SIMS m/z 861 (M^+). ^1H NMR δ –2.62 (1H, br, OH), 1.50–1.55 (2H, t, J = 8.2 Hz, $-\text{OC}_6\text{H}_4-$), 5.38 (2H, t, J = 8.2 Hz, $-\text{OC}_6\text{H}_4-$), 7.84–7.89 (12H, m, Ph), 8.11 (4H, d, J = 6.8 Hz, Ph), 8.44 (4H, d, J = 6.8 Hz, Ph), 9.40 (8H, s, pyrrole).

4-Cyanophenoxy(hydroxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2d). Yield 37%. UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 419 (5.54), 550 (4.19), and 591 (3.93); SIMS m/z 868 (M^+). ^1H NMR δ –2.45 (1H, br, OH), 1.65 (2H, d, J = 8.7 Hz, $-\text{OC}_6\text{H}_4-$), 6.02 (2H, d, J = 8.6 Hz, $-\text{OC}_6\text{H}_4-$), 7.87–7.94 (12H, m, Ph), 8.12 (4H, d, J = 6.6 Hz, Ph), 8.47–8.50 (4H, m, Ph), 9.49 (8H, s, pyrrole).

3-(Dimethylamino)phenoxy(hydroxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (3). Yield 44%. UV–vis $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) 419 (5.53), 551 (4.14) and 590 (3.88); SIMS m/z 886 (M^+). ^1H NMR δ –2.90 (1H, br, OH), 0.87–1.01 (1H, m, $-\text{OC}_6\text{H}_4-$), 2.14 (6H, s, Me), 2.86 (1H, s, $-\text{OC}_6\text{H}_4-$), 5.30–5.57 (2H, m, $-\text{OC}_6\text{H}_4-$), 7.84–7.90 (12H, m, Ph), 8.12 (4H, d, J = 6.8 Hz, Ph), 8.46 (4H, d, J = 6.8 Hz, Ph), 9.43 (8H, s, pyrrole).

Measurements of Redox Potentials. The oxidation and reduction potentials were measured by cyclic voltammetry for MeCN solution of **1a–c** and **2a–d** (1×10^{-2} M) in the presence of a supporting electrolyte (Et_4NBF_4 ; 0.1 M) at a scan rate of 0.3–0.5 V/s at 23 °C on a BAS CV-50W cyclic voltammeter using a carbon-disk working electrode, a carbon counter electrode, and an Ag/AgNO_3 reference electrode. The half-peaks of the oxidation ($E_{1/2}^{\text{ox}}$) and reduction potentials ($E_{1/2}^{\text{red}}$) vs Ag/Ag^+ were modified to those vs SCE by the addition of +0.23 V.

Proton Dissociation Constants. The absorption spectra of a MeCN– H_2O (4:1, v/v, 10 mL) solution containing **1a–c** and **2a–d** (2×10^{-6} mol dm^{-3}) were observed on a Hitachi U2001 spectrometer. The proton dissociation constants for **1a–c** or **2a–d** were estimated based on the spectral change of the Soret band by the addi-

tion of $2.5 \times 10^{-2} \text{ cm}^3$ portions of a $1 \times 10^{-2} \text{ mol dm}^{-3}$ aqueous KOH solution.¹⁶

Fluorescence Quantum Yields. The fluorescence spectra were measured on a Hitachi F4500 spectrometer at room temperature under excitations of the porphyrinato chromophore at 420 nm. The concentrations of solutions of **1b**, **2a–d**, and **3** were adjusted for the absorbance to be less than 0.08 at the excitation wavelength. According to the reported method,¹⁷ the quantum yields for the fluorescence were determined using a benzene or MeCN solution of tetraphenylporphyrinatozinc(II) (the quantum yield is 0.033 in benzene and 0.029 in MeCN)¹⁸ as an actinometer.

The fluorescence spectral change of **3** in MeCN was observed upon the addition of HClO_4 ($0.4 - 3.2 \times 10^{-3} \text{ mol dm}^{-3}$) at room temperature under excitations of the porphyrin chromophore at 420 nm.

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