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Journal of Photochemistry and Photobiology A: Chemistry 147 (2002) 191–197

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Synthesis and fluorescence study of a (2-naphthoxy)polyoxalkoxyantimony(V) tetraphenylporphyrin complex

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Received 14 August 2001; received in revised form 1 October 2001; accepted 31 October 2001

Abstract

The fluorescence spectra of (2-naphthoxy)polyoxalkoxyantimony(V) tetraphenylporphyrin complex (**1a–d**) were analyzed under the excitation of naphthoxy and porphyrin chromophores. The excitation energy of naphthoxy chromophore was transferred to the porphyrin moiety at the rate constants of 6.7–8.3 × 10^8 s^{-1}. The rate constants of energy transfer were nearly constant irrespective of the length of the methylene bridge. The emission of porphyrin chromophore was quenched by naphthoxy chromophore at rate constants of 10^7–10^{10} s^{-1} depending on both the solvent used and the length of the methylene bridge. Under the excitation of the naphthoxy chromophore of the triad system (**1d**) involving porphyrin, 2-naphthoxy, and 4-methoxyphenoxy chromophores, the excited singlet state of the porphyrin chromophore generated by the energy transfer from the naphthoxy chromophore was quenched by the naphthoxy and the methoxyphenoxy chromophores via non-radiative processes involving electron transfer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Antimony(V) tetraphenylporphyrin complex; Naphthoxy polyoxalkoxy; Axial ligands; Solvent effect; Intramolecular electron transfer; Intramolecular energy transfer

1. Introduction

Intramolecular electron and energy transfer systems between two chromophores involving the porphyrin chromophore have received much attention in elucidation of the natural photosynthetic systems [1,2]. Recently, a number of porphyrin complexes linked with some π-electron chromophore or porphyrin arrays have been synthesized and their photophysical properties involving the electron and the energy transfer process have been investigated [3–12]. Almost all previous reports have dealt with porphyrin chromophore with the second chromophores in parallel arrangement, thus focusing on the electron and energy transfer process in a horizontal direction to a porphyrin plane [3–12]. However, little is known about the electron and energy transfer in a vertical direction to a porphyrin plane [13]. It is one reason that there were no convenient methods to prepare diaxial ligand-coordinated metalloporphyrin complexes. It is well known that high-valent metalloporphyrin complexes having Ge(IV), Sn(IV), P(V), As(IV), and Sb(V) can covalently connect to axial ligands, differing from the transition-metal porphyrin complexes [1]. Segawa and coworkers [14–17] have extensively studied the energy and electron transfer of phosphorous porphyrin complexes having the chromophore on axial ligands. It is, however, not so easy to introduce unsymmetric axial ligands to the phosphorous porphyrins [18].

Therefore, our focus has been on antimony porphyrin complex having a chromophore on unsymmetric axial ligands from the standpoint of the energy and electron transfer between two chromophores. Here, we report on a convenient synthetic method and the fluorescence study of antimony(V) porphyrin complexes (**1a–d**) having 2-naphthoxy group as the second chromophore on the axial ligands (Scheme 1).

2. Experimental

2.1. Instruments

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were taken in $CDCl_3$ using tetramethylsilane as an internal standard on a Bruker AC 250P spectrometer at 250 and 62.9 MHz, respectively. SIMS and FAB-MS were obtained on a Hitachi M2000A spectrometer and on a JEOL JMS-HX 110 A spectrometer, respectively. UV spectra were measured on a Hitachi U2001 spectrometer. Oxidation and reduction potentials were measured for an acetonitrile solution of **1a–c** (1×10^{-2} M) in the presence of a supporting electrolyte (Et_4NBF_4; 0.1 M) at a scan rate of 0.3 V/s at 23 °C on a BAS

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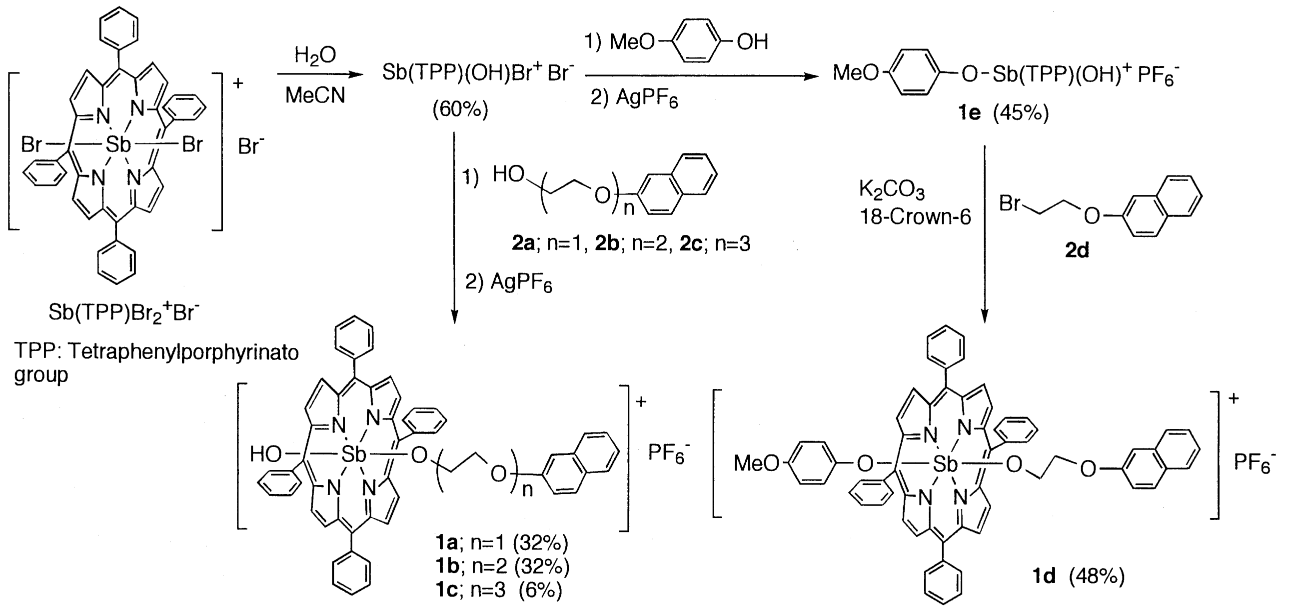
PII: S1010-6030(01)00635-9



Scheme 1.

cyclic voltammetry using a platinum disk working electrode, a carbon counter electrode, and a Ag/AgNO$_3$ reference electrode. Half-peak of oxidation ($E^{\mathrm{ox}}_{1/2}$) and half-peak of reduction potentials ($E^{\mathrm{red}}_{1/2}$) vs. Ag/AgNO$_3$ were modified to those vs. SCE by the addition of +0.23 V. The MM2 calculation was performed using SPARTAN on a Silicon Graphics O2 work station.

2.2. Materials

Spectral grade of benzene, toluene, and dichloromethane were used without further purification. 1,4-Dioxane and tetrahydrofuran were distilled from Na before use. MeCN was distilled from P_2O_5 and then CaH_2. *meso*-Tetraphenylporphyrin (H_2TPP, TPP = tetraphenylporphyrinato group), antimony bromide, and 18-crown-6 ether were purchased from Wako Chemicals.

2.3. The preparation of bromohydroxyantimony(V) tetraphenylporphyrin bromide (Sb(TPP)(OH)Br$^+$Br$^-$)

A pyridine solution (100 ml) containing H_2TPP (3.6 mmol) and antimony(III) bromide (11 mmol) was refluxed for 1 h, and Br_2 (2 ml) was added to the solution to form dibromoantimony(V) tetraphenylporphyrin bromide (Sb(TPP)Br$_2^+$Br$^-$) [19]. Then the mixture was poured into hexane (200 ml) to give the precipitate. The CH_2Cl_2 solution of the resulting precipitate was washed with hydrobromic acid and 150 ml of water. After the evaporation, the crude Sb(TPP)Br$_2^+$Br$^-$ was obtained in 98% yield. Sb(TPP)Br$_2^+$Br$^-$ was hydrolyzed in H_2O–MeCN (1:3) at 60 °C to give Sb(TPP)(OH)Br$^+$Br$^-$ in 60% yield.

Sb(TPP)(OH)Br$^+$Br$^-$. UV–Vis (MeCN) $\lambda_{\max}$/nm (log ε): 423 (4.78), 555 (3.35) and 596 (3.17); MS (SIMS) *m/z*: 831 [M$^+$]; ^{1}H NMR: δ = 7.84–7.89 (12H, m, Ph), 8.29 (4H, d, J = 6.8 Hz, Ph), 8.59 (4H, d, J = 5.7 Hz, Ph), and 9.42 (8H, s, pyrrole).

2.4. Preparation of (2-naphthoxy)polyoxalkoxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1a–c**)

A MeCN solution (40 ml) containing Sb(TPP)(OH)Br$^+$ Br$^-$ (0.22 mmol) and (2-naphthoxy)polyoxalkanol (**2a–c**, 2.2 mmol) [20] was refluxed for 4 days until the spectral changes of absorption spectra became little. Then the solvent was evaporated and the residue dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed three times with 50 ml of H_2O. After the evaporation, the crude product was treated by $AgPF_6$ (2.2 mmol) to exchange counter anion, and then subjected to the column chromatography on silica gel (Fuji Silysia BW 300) using $CHCl_3$–MeOH (10/1, v/v) as an eluent to give **1a–c**.

*2-(2-Naphthoxy)ethoxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1a**).* Yield 32%; UV–Vis (MeCN) $\lambda_{\max}$/nm (log ε): 418 (5.57), 551 (4.23), and 591 (3.98); SIMS *m/z*: 937 [M$^+$]; ^{1}H NMR: δ = −3.30 (1H, brs, OH), −2.20 (2H, t, J = 4.8 Hz, CH$_2$), 0.76 (2H, t, J = 4.8 Hz, CH$_2$), 5.47–5.90 (2H, m, naphthoxy), 7.24–7.80 (5H, m, naphthoxy), 7.88–7.91 (12H, m, Ph), 8.15 (4H, d, J = 7.4 Hz, Ph), 8.43 (4H, t, J = 2.1 Hz, Ph), 9.43 (8H, s, pyrrole).

*5-(2-Naphthoxy)-3-oxa-1-pentoxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1b**).* Yield 32%; UV–Vis (MeCN) $\lambda_{\max}$/nm (log ε): 419 (5.55), 551 (4.21), and 590 (3.95); SIMS *m/z*: 981 [M$^+$]; ^{1}H NMR: $\delta = -3.56$ (1H, brs, OH), −2.45 (2H, t, $J = 5.0$ Hz, CH_2), 0.16 (2H, t, $J = 5.0$ Hz, CH_2), 1.90 (2H, t, $J = 4.8$ Hz, CH_2), 3.09 (2H, t, $J = 4.8$ Hz, CH_2), 6.62–7.40 (7H, m, naphthoxy), 7.71–7.90 (12H, m, Ph), 8.26 (4H, d, $J = 7.3$ Hz, Ph), 8.29–8.37 (4H, m, Ph), and 9.39 (8H, s, pyrrole).

*8-(2-Naphthoxy)-3,6-dioxa-1-octanoxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1c**).* Yield 6%; UV–Vis (MeCN) λ_{max}/nm ($\log\varepsilon$): 420 (5.34), 551 (3.96), and 591 (3.72); FAB-MS *m/z*: 1025.3 [M$^+$]; ^{1}H NMR: $\delta = -4.20$ (1H, brs, OH), −2.45 (2H, t, $J = 5.0$ Hz, CH_2), 0.04 (2H, t, $J = 5.0$ Hz, CH_2), 1.70 (2H, t, $J = 5.0$ Hz, CH_2), 2.67 (2H, t, $J = 5.0$ Hz, CH_2), 3.33 (2H, t, $J = 4.8$ Hz, CH_2), 3.66 (2H, t, $J = 4.8$ Hz, CH_2), 6.91–7.62 (7H, m, naphthoxy), 7.63–7.92 (12H, m, Ph), 8.26 (4H, d, $J = 7.2$ Hz, Ph), 8.43 (4H, m, Ph), and 9.44 (8H, s, pyrrole).

2.5. Preparation of 2-(2-naphthoxy)ethoxy-(4-methoxyphenoxy) antimony(V) tetraphenylporphyrin hexafluorophosphate (**1d**)

A MeCN solution containing Sb(TPP)(OH)Br$^+$Br$^-$ (0.55 mmol) and 4-methoxyphenol (33 mmol) was refluxed for 24 h. Then the solvent was evaporated and the residue dissolved in CH_2Cl_2. The CH_2Cl_2 solution was washed three times with water (50 ml). After the evaporation, the crude product was treated by $AgPF_6$ (2.2 mmol) to exchange counter anion and then was chromatographed on SiO_2 using $CHCl_3$–MeOH (10/1, v/v) as an eluent to give $(4\text{-MeOC}_6H_4O)Sb(TPP)OH^+PF_6^-$ (**1e**) in 45% yield.

A MeCN solution (50 ml) containing **1e** (0.15 mmol), 2-(2-naphthoxy)ethyl bromide (**2d**) (1.5 mmol), K_2CO_3 (0.06 mmol), and 18-crown-6 ether (0.2 mmol) was heated at 85 °C for 24 h. The reaction was followed by the spectral changes of a Soret band. After the evaporation, the CH_2Cl_2 solution of the residue was poured into hexane (300 ml) to give a precipitate. The CH_2Cl_2 solution of the precipitate was washed with water (50 ml) for three times. After the removal of the solvent, the crude product was purified by the column chromatography on silica gel using $CHCl_3$–MeOH (10/1, v/v) as eluents to give **1d** in 48% yield.

1d: UV–Vis (MeCN) λ_{max}/nm ($\log\varepsilon$): 423 (5.49), 554 (4.08), and 594 (3.87); FAB-MS *m/z*: 1057 and 1059 [M$^+$]; ^{1}H NMR: $\delta = -1.97$ (2H, t, $J = 5.6$ Hz, CH_2), −1.04 (2H, t, $J = 5.6$ Hz, CH_2), 3.29 (3H, s, MeO), 5.25 (2H, d, $J = 5.0$ Hz, phenoxy), 5.54 (1H, d, $J = 7.9$ Hz, naphthoxy), 5.84 (1H, d, $J = 9.2$ Hz, naphthoxy), 7.28 (2H, d, $J = 5.0$ Hz, phenoxy), 7.58–7.90 (5H, m, naphthoxy), 7.62–7.90 (12H, m, Ph), 8.21 (4H, d, $J = 6.8$ Hz, Ph), 8.27 (4H, d, $J = 6.8$ Hz, Ph), and 9.46 (8H, s, pyrrole).

1e: UV–Vis (MeCN) λ_{max}/nm ($\log\varepsilon$): 418 (5.53), 552 (4.27), and 592 (4.04); SIMS *m/z*: 873 [M$^+$]; ^{1}H NMR: $\delta = -2.90$ (1H, brs, OH), 1.52 (2H, d, $J = 9.1$ Hz, phenoxy), 3.28 (3H, s, MeO), 5.23 (2H, d, $J = 9.1$ Hz, phenoxy), 7.86–7.92 (12H, m, Ph), 8.11 (4H, d, $J = 7.1$ Hz, Ph), 8.44–8.47 (4H, m, Ph), and 9.42 (8H, s, pyrrole).

2.6. Measurement of fluorescence spectra of **1a–d**

The fluorescence lifetimes were measured by single-photon-counting method on a Horiba NAES 550 spectrometer. Fluorescence spectra were measured at room temperature for argon-purged solutions under the excitations of naphthoxy chromophore at 320 nm and porphyrin chromophore at 420 nm on a Hitachi F4500 spectrometer. The concentrations of the solution of **1a–d** were adjusted for absorbance to be less than 0.08 at the excitation wavelength. According to the reported method [21], quantum yields for the fluorescence were determined. As an actinometer, a benzene solution of naphthalene (the quantum yield is 0.19 [22]) was used for the excitation of naphthoxy chromophore at 320 nm and a benzene or MeCN solution of zinc(II) tetraphenylporphyrin (the quantum yield is 0.033 in benzene and 0.029 in MeCN [23]) was used for the excitation of porphyrin chromophore at 420 nm.

3. Results

3.1. Preparation of **1a–e**

For our synthetic route to unsymmetric axial ligand-coordinated antimony(V) porphyrin complexes, Sb(TPP)(OH)Br$^+$Br$^-$ is a key precursor. Therefore, we need to find the optimum reaction conditions to prepare effectively Sb(TPP)(OH)Br$^+$Br$^-$ by the mono-hydrolysis of $Sb(TPP)Br_2{}^+Br^-$. The optimum hydrolysis of $Sb(TPP)Br_2{}^+Br^-$ was performed in H_2O–MeCN (1:3) at 60 °C to give Sb(TPP)(OH)Br$^+$Br$^-$ in 60% yield along with the formation of $Sb(TPP)(OH)_2{}^+Br^-$ (40%). The reaction in higher aqueous content of H_2O–MeCN and other reaction solvents (e.g. DMF, THF), in the presence of bases (e.g. pyridine, Et_3N), and at higher temperature reduced the yield.

The reactions of Sb(TPP)(OH)Br$^+$Br$^-$ with alcohols and alkyl halide underwent the substitution of the Br-ligand and the *O*-alkylation of the hydroxyl-ligand of the complexes, respectively. The reaction of Sb(TPP)(OH)Br$^+$Br$^-$ with **2a–c** under refluxing in MeCN and subsequent anion exchange with $AgPF_6$ gave (2-naphthoxy)polyoxalkoxyantimony(V) tetraphenylporphyrin hexafluorophosphate (**1a–c**) (Scheme 1). Also, the reaction of Sb(TPP)(OH)Br$^+$Br$^-$ with 4-methoxyphenol gave $(4\text{-MeOC}_6H_4O)Sb(TPP)OH^+PF_6^-$ (**1e**) after the anion exchange with $AgPF_6$.

The *O*-alkylation of Sb(TPP)(OH)Br$^+$Br$^-$ with a variety of alkyl halides under basic conditions have been achieved.[1] Therefore, we applied the *O*-alkylation to the synthesis of 2-(2-naphthoxy)ethoxy-(4-methoxyphenoxy) antimony(V) tetraphenylporphyrin hexafluorophosphate (**1d**) which have unsymmetrically two chromophores on axial ligands. The

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[1] Details for the *O*-alkylation with alkyl halde will be published elsewhere.

Table 1
Fluorescence quantum yields under the excitation of porphyrin chromophore

Solvents[a]	$E_T(30)$[b]	$\Phi_0^{por} \times 10^2$[c]	$\Phi_1^{por} \times 10^2$ $(\log k_q)$[d]		
			1a	**1b**	**1c**
TL	33.9	2.88	2.54 (7.90)	2.77 (7.37)	2.32 (8.15)
BZ	34.5	2.83	2.66 (7.58)	2.77 (7.37)	2.11 (8.30)
DO	36.0	3.63	0.96 (9.21)	2.20 (8.58)	2.14 (8.61)
TF	37.4	3.91	1.04 (9.95)	1.04 (9.21)	2.26 (8.63)
DM	41.1	3.54	0.18 (10.04)	0.99 (9.18)	1.59 (8.86)
AN	46.0	5.18	0.18 (10.21)	0.82 (9.50)	1.20 (9.29)

[a] TL: toluene; BZ: benzene; DO: 1,4-dioxane; TF: tetrahydrofuran; DM: dichloromethane; AN: acetonitrile.

[b] Empirical solvent parameter in kcal/mol.

[c] Fluorescence quantum yield for $Sb(TPP)(OH)_2{}^+PF_6{}^-$.

[d] $k_q = (\Phi_0^{por}/\Phi_1^{por} - 1)/\tau_0^{por}$.

Table 2
Fluorescence of **1a–d** under the excitation of 2-naphthoxy chromophore in toluene

	Quantum yield[a]			$k'_q \times 10^{-9}\,s^{-1}$[b]	$k_{et} \times 10^{-8}\,s^{-1}$[c]	$E_{1/2}^{red}(V)$[d]	$E_{1/2}^{ox}(V)$[e]	ΔG (eV)		r (Å)[f]
	Φ_1^{nap}	Φ_2^{por}	Φ_{et}[g]					Por[h]	Nap[i]	
1a	0.0065	0.0043	0.17	4.89	8.3	−0.50	1.33	−0.25	−1.71	5.8
1b	0.0084	0.0049	0.18	3.77	6.7	−0.50	1.38	−0.20	−1.66	7.1
1c	0.0107	0.0056	0.24	2.94	7.2	−0.51	1.35	−0.22	−1.68	10.5
1d	0.0190	NO[j]	–	1.62	–	−0.91	1.43[k]	+0.26	−1.20	5.8

[a] Measured using naphthalene ($\Phi_0 = 0.19$) as an actinometer.

[b] $k'_q = (\Phi_0^{nap}/\Phi_1^{nap} - 1)/\tau_0^{nap}$, where $\tau_0^{nap} = 13$ ns and $\Phi_0^{nap} = 0.42$ for 2-methoxynaphthalene in toluene.

[c] Rate constant for the energy transfer from 2-naphthoxy group to the porphyrin chromophore: $k_{et} = k'_q \Phi_{et}$.

[d] Half-peak of reduction potential (vs. SCE) for porphyrin chromophore.

[e] Half-peak of oxidation potential (vs. SCE) for 2-naphthoxy chromophore.

[f] Distance between antimony atom and C2 carbon of 2-methoxynaphthoxy group calculated by MM2 method.

[g] Quantum yield for energy transfer: $\Phi_{et} = \Phi_2^{por}/\Phi_1^{por}$, where $\Phi_1^{por} = 0.0254$, 0.0277, and 0.0232 for **1a–c** in toluene.

[h] Under excitation of the porphyrin chromophore at 420 nm: $E^{0\text{–}0} = 2.08$ eV.

[i] Under excitation of the 2-naphthoxy chromophore at 320 nm: $E^{0\text{–}0} = 3.54$ eV.

[j] Not observed.

[k] Half-peak of oxidation potential (vs. SCE) of the 4-methoxyphenoxy group was 1.09 V.

reaction of **1e** with **2d** in the presence of K_2CO_3/18-crown-6 gave **1d** in 48% yield.

As an alternative method to prepare **1e**, we attempted the reaction of $Sb(TPP)Br_2{}^+PF_6{}^-$ with 4-methoxyphenol. However, **1e** was produced in low yield along with the formation of a large amount of H_2TPP. Probably H_2TPP was formed by the reduction from Sb(V) of $Sb(TPP)Br_2{}^+PF_6{}^-$ to Sb(III) by 4-methoxyphenol.

3.2. Fluorescence spectra

Under the excitation of porphyrin chromophore of **1a–c** at 420 nm, the emission from the porphyrin chromophore was observed at λ_{max} (596 nm) independently on solvent polarity. The fluorescence quantum yields (Φ_1^{por}) in several kinds of solvents are summarized in Table 1.

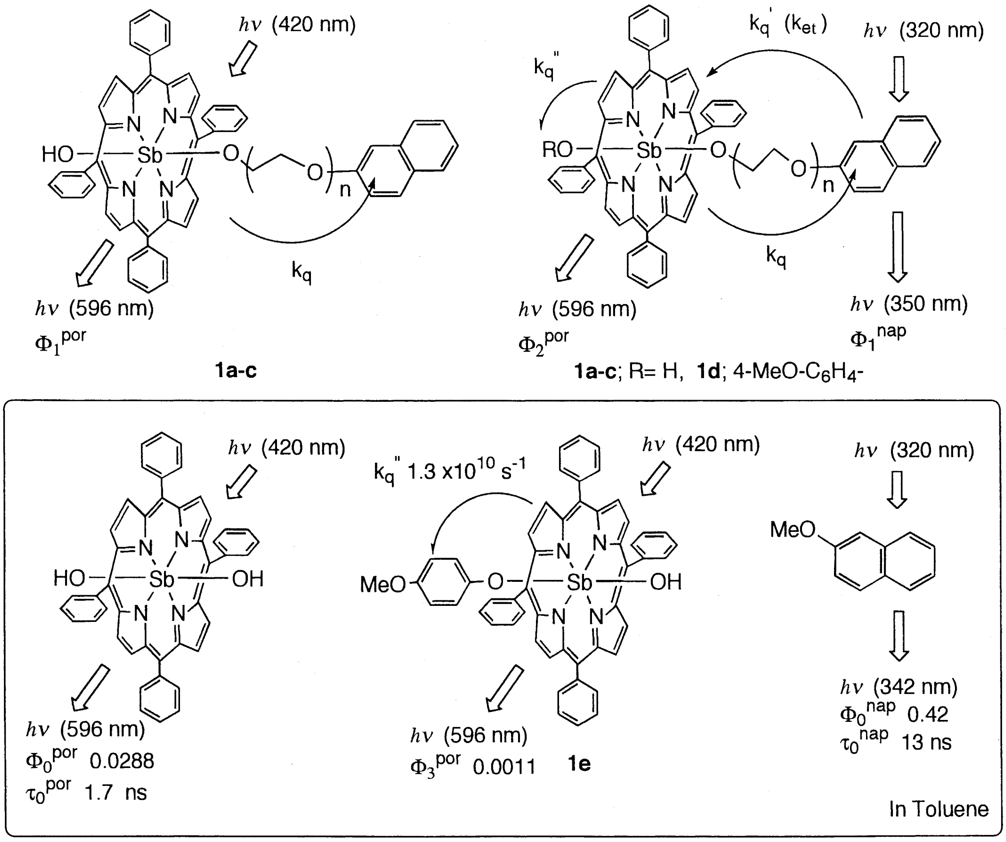
Under the excitation of naphthoxy chromophore of **1a–c** at 320 nm, two emissions at 350 and 596 nm were observed in toluene, whereas one emission at 350 nm was observed in the other solvents. The emission at 350 and 596 nm can be assigned to the emissions from the naphthoxy and porphyrin chromophores, respectively. The quantum yields of the fluorescence from the porphyrin moiety (Φ_2^{por}) and the naphthoxy chromophore (Φ_1^{nap}) in toluene are listed in Table 2.

As a model compound for analysis of the excited states of the porphyrin and the naphthoxy chromophores without the interaction of another chromophore, $Sb(TPP)(OH)_2{}^+PF_6{}^-$ and 2-methoxynaphthalene were used, respectively (Scheme 2).

4. Discussion

4.1. Estimation of free energy changes for the electron transfer between two chromophores

The free energy changes (ΔG) required for the electron transfer between two chromophores are calculated by Rehm–Weller equation (Eq. (1)) [24] using half-peak of oxidation potential of the naphthoxy chromophore ($E_{1/2}^{ox}$), half-peak of reduction potential of the porphyrin



Scheme 2.

chromophore ($E^{\mathrm{red}}_{1/2}$), and the excitation energy ($E^{0\text{–}0}$) of the chromophores: $E^{0\text{–}0}$ for the porphyrin and the naphthoxy chromophores are 2.08 and 3.54 eV, respectively (Table 2).

$$\Delta G = E^{\mathrm{ox}}_{1/2} - E^{\mathrm{red}}_{1/2} - E^{0\text{–}0} \tag{1}$$

The ΔG's for the electron transfer from the excited singlet state of the porphyrin chromophore to the naphthoxy chromophore in ground state in **1a–c** were slightly negative, while those from the excited singlet state of the naphthoxy moiety to the porphyrin moiety in ground state were largely exoenergic.

4.2. Fluorescence under the excitation of porphyrin chromophore

The quenching rate constants (k_{q}) of the porphyrin chromophore in the excited singlet state by the naphthoxy chromophore were estimated by Eq. (2) where τ_0^{por} and Φ_0^{por} are the fluorescence lifetime and the fluorescence quantum yields of $\mathrm{Sb(TPP)(OH)_2{}^+PF_6{}^-}$ in the given solvents, respectively. Since τ_0^{por} values were 1.5–1.8 ns in solvent used, we employed 1.7 ns for MeCN solution. Moreover, λ_{max} and shapes in the UV and the emission spectra of **1a–c** were same as those of $\mathrm{Sb(TPP)(OH)_2{}^+PF_6{}^-}$, revealing absence of the interaction between two chromophores in the ground and excited states.

$$k_{\mathrm{q}} = \frac{\Phi_0^{\mathrm{por}}/\Phi_1^{\mathrm{por}} - 1}{\tau_0^{\mathrm{por}}} \tag{2}$$

The k_{q} values depended on both the length of methylene bridge and the solvent used. Fig. 1 shows the plots of $\log k_{\mathrm{q}}$ vs. the empirical solvent parameter $E_{\mathrm{T}}(30)$ [25]. The $\log k_{\mathrm{q}}$ values increased as $E_{\mathrm{T}}(30)$ parameter increases, revealing that the fluorescence quenching occurred mainly by the electron transfer process [26–28].

4.3. Fluorescence under the excitation of naphthoxy chromophore

The quenching rate constants (k'_{q}) of the naphthoxy chromophore in the excited singlet state by the porphyrin chromophore were calculated by Eq. (3) where the fluorescence quantum yield (Φ_0^{nap}) and fluorescence lifetime (τ_0^{nap}) of 2-methoxynaphthalene in toluene were 0.42 ns [22] and 13 ns [20], respectively.

The quantum yields (Φ_{et}) for the energy transfer from the naphthoxy chromophore in the excited singlet state to the porphyrin chromophore were determined by Eq. (4) where Φ_1^{por} were 0.0254, 0.0277 and 0.0232 for **1a–c** in toluene,

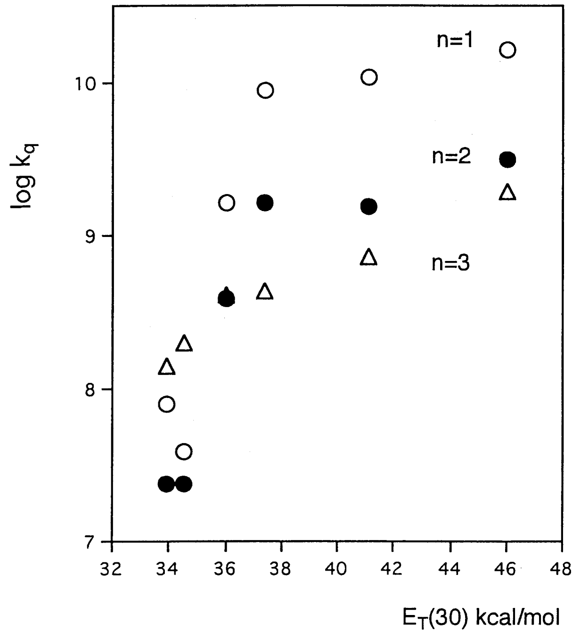


Fig. 1. Plots of $\log k_q$ vs. $E_T(30)$ in the fluorescence study of **1a** (○), **1b** (●), and **1c** (△).

respectively. Since k'_q was larger in two orders than the other decay pathways (e.g. $1/\tau_0^{nap}$), the rate constant (k_{et}) for the energy transfer can be calculated by Eq. (5):

$$k'_q = \frac{\Phi_0^{nap}/\Phi_1^{nap} - 1}{\tau_0^{nap}} \tag{3}$$

$$\Phi_{et} = \frac{\Phi_2^{por}}{\Phi_1^{por}} \tag{4}$$

$$k_{et} = \Phi_{et} k'_q \tag{5}$$

The quenching process should involve the electron transfer process, since the ΔG for electron transfer from the excited singlet state of naphthoxy chromophore to porphyrin chromophore is substantially negative. The k_q^1 values decreased at the longer methylene bridge, while the k_{et} values of **1a–c** were nearly constant ($6.7–8.3 \times 10^8\,s^{-1}$) irrespective of the length of the methylene bridge (Table 2). Therefore, the decrease of k_q^1 is suggested to be due to slow electron transfer process at longer distance between two chromophores [26]. Also, Hirakawa and Segawa [17] have concluded that the efficiency of the energy transfer increased with increasing the distance between two chromophores in the phosphorous porphyrin complexes having pyrene chromophore on the axial ligands.

The preferred conformation of **1a–c** calculated by MM2 took the structure where the 2-naphthoxy group was bending over the porphyrin chromophore rather than locating in perpendicular to porphyrin chromophore. Nevertheless, the distances between two chromophores increased as the methylene bridge increased (Table 2).

As a result, the excitation energy of the naphthoxy chromophore is transferred to the porphyrin chromophore at $k_{et} = 6.7–8.3 \times 10^8\,s^{-1}$ and the resulting excited state of the porphyrin chromophore is quenched by the naphthoxy chromophore at $k_q = 2.3–14.1 \times 10^7\,s^{-1}$ (Table 1).

4.4. Fluorescence of the triad system (**1d**)

The fluorescence study was performed to **1d** which are the triad system involving porphyrin, 2-naphthoxy, and 4-methoxyphenoxy chromophores. Since three chromophores of **1d** are isolated together, the analysis for **1d** is subjected to the analysis for **1a** and **1e**. Therefore, the rate constant (k_{et}) for the energy transfer of **1d** is estimated to be $8.3 \times 10^8\,s^{-1}$ of **1a**. The resulting excited singlet state of the porphyrin was quenched by both the naphthoxy and 4-methoxyphenoxy chromophores. The quenching rate constant (k_q) by the naphthoxy is estimated to be $k_q = 7.9 \times 10^7\,s^{-1}$, that is k_q for **1a**. The estimation of the quenching rate constant (k''_q) by the 4-methoxyphenoxy was performed as follows. The k''_q for the fluorescence of the porphyrin chromophore by the 4-methoxyphenoxy chromophore in **1e** is calculated to be $1.3 \times 10^{10}\,s^{-1}$ by Eq. (6) where Φ_3^{por} is the fluorescence quantum yield of **1e**. Therefore, k''_q of **1d** is equal to $1.3 \times 10^{10}\,s^{-1}$. The quenching process of the excited singlet state of the porphyrin by 4-methoxyphenoxy chromophores is mainly electron transfer process since the oxidation potential of 4-methoxyphenoxy chromophores ($E_{1/2}^{ox} = 1.09\,V$) is substantially low.

$$k''_q = \frac{\Phi_0^{por}/\Phi_3^{por} - 1}{\tau_0^{por}} \tag{6}$$

In conclusion, we constructed the antimonyporphyrin complex having chromophores on the axial ligands and analyzed the quenching process between chromophores. The excitation energy of naphthoxy chromophore of **1a–c** could be transferred to the porphyrin chromophore and the resulting excited singlet state of the porphyrin chromophore was quenched by the naphthoxy chromophore via the electron transfer process in polar solvents and via non-radiative processes other than electron transfer in non-polar solvents. In the case of **1d**, the excitation energy of porphyrin chromophore transferred from the naphthoxy chromophore was quenched by the naphthoxy and the methoxyphenoxy chromophores via non-radiative processes involving electron transfer, respectively.

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