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# Synthesis and spectroscopic analysis of tetraphenylporphyrinatoantimony(V) complexes linked to boron-dipyrrin chromophore on axial ligands

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**Abstract**

Tetraphenylporphyrinatoantimony(V) complexes, linked to boron-dipyrrin chromophores on axial ligands, were synthesized. The fluorescence spectra of **1a**, **1b** and **1c** (3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenyl]propoxo(methoxo)antimony(V) tetraphenylporphyrin bromide (**1a**); 6-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenyl]hexyloxo(methoxo)antimony(V) tetraphenylporphyrin bromide (**1b**); bis{3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenyl]propoxo}antimony(V) tetraphenylporphyrin bromide (**1c**)) were analyzed under the excitations of *N*,*N*′-difluorobornyl-5-dipyrrinylphenyl (Bdpy) and tetraphenylporphyrinatoantimony(V) (Sb(TPP)) chromophores. Under the irradiation of Bdpy chromophore, the excitation energy was transferred from Bdpy chromophore to the Sb(TPP) moiety at 0.13–0.40 of the quantum yields, even in a polar solvent. On the other hand, the emission of Sb(TPP) chromophores was quenched by Bdpy chromophores at rate constants of $10^8$–$10^9$ $s^{-1}$, independent of on the solvent polarity. Under the excitation of the Bdpy chromophore of **1d** (3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenyl]propoxo(phenyloxo)antimony(V) tetraphenylporphyrin bromide) involving both the Bdpy and the phenoxy chromophores on the axial ligands, the excited singlet state of the Sb(TPP) chromophore generated by the energy transfer from the Bdpy chromophore was quenched by the phenoxy ligand via non-radiative processes involving electron transfer. However, rapid back electron-transfer may occur because no absorption of the anion radical of Sb(TPP) was observed by nanosecond laser photolysis.


*Keywords:* Tetraphenylporphyrinatoantimony(V) complex; Boron-dipyrrin chromophore; Axial ligands; Intramolecular energy transfer

## 1. Introduction

Metalloporphyrin chromophores play important roles as energy-harvest pigments in natural photosynthesis [1,2] and the photosensitizer operating under visible light irradiation [3,4]. The photophysical properties of a number of metalloporphyrin complexes linked with some second chromophores have received much attention in relation to the intramolecular electron and energy-transfer processes [5–16]. Previous studies on the interaction between the porphyrin chromophore and the second chromophores have focused on the electron and energy-transfer processes in a horizontal direction to a porphyrin plane [5–16]. However, little is known about electron and energy transfers between the porphyrin chromophore and the second chromophores linked on axial ligands [17–20]. Many studies on electron and energy transfer in a vertical direction to a porphyrin plane are restricted in the capped-type porphyrin compounds linked to the second chromophore at the rim of the porphyrin ring with a spacer [21–25].

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On the other hand, it is well known that the porphyrin complexes of 14 and 15 groups high-valent metals, such as $Ge^{IV}$, $Sn^{IV}$, $P^{V}$, $As^{IV}$, and $Sb^{V}$ connect covalently with axial ligands [26–29]. Recently, the energy and electron transfers of phosphorous porphyrin complexes having a second chromophore on axial ligands have been reported [30–34]. Our attention has been devoted to $Sb^{V}$ porphyrin complexes, which are able to connect covalently with axial ligands through oxygen [35–39], nitrogen [40], and sulfur atoms [41], resulting in a highly stabilized complex compared with other six-coordinated metalloporphyrin complexes prepared so far. Moreover, two axial ligands can be unsymmetrically introduced into the $Sb^{V}$ porphyrin complexes. Therefore, we have focused on the vertical direction energy-transfer between the antimony porphyrin chromophore and the second chromophores on unsymmetric axial ligands. Recently, we have elucidated that energy transfer from the axial ligand to the porphyrin chromophore in (2-naphthoxy)polyoxalkyloxoantimony(V) tetraphenylporphyrinato complexes occurred with 17–24% efficiency in such non-polar solvents as toluene [41]. A boron-dipyrrin chromophore (Bdpy) group is a good energy-donating group that can absorb visible light [42,43]. In order to achieve efficient energy transfer between the axial second chromophore and metalloporphyrin chromophore, we have investigated the synthesis of tetraphenylporphyrinatoantimony(V) complexes linked to Bdpy chromophore on axial ligands and their spectroscopic analysis.

## 2. Experimental

### 2.1. Instruments and spectral measurement

$^{1}H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were taken in $CDCl_3$ using $Me_4Si$ as an internal standard on a Bruker AC 250P spectrometer at 250 MHz and 62.9 MHz, respectively. MS (SIMS) spectra were obtained on a Hitachi M2000A spectrometer. UV spectra were measured on a Hitachi U2001 spectrometer. Oxidation and reduction potentials were measured for an MeCN solution of **1a**, **1b** and **1c** ($1 \times 10^{-2}$ 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 cyclic voltammetry using a platinum-disk working electrode, a carbon counter electrode, and an $Ag/AgNO_3$ reference electrode. The half-peak of oxidation ($E^{ox}_{1/2}$) and the half-peak of reduction potentials ($E^{red}_{1/2}$) versus $Ag/AgNO_3$ were modified to those versus SCE by the addition of +0.23 V. The MM2 calculation was performed using SPARTAN on a Silicon Graphics O2 workstation.

The time-resolved fluorescence spectra were measured by a single-photon counting method using the second harmonic generation (SHG, 410 nm) of a Ti:saphire laser (Spectra-Physics, Tsunami 3950-L2S, 1.5 ps fwhm) and a streakscope (Hamamatsu Photonics, C43334-01) equipped with a polychromator (Action Research, SpectraPro 150) as an excitation source, and a detector, respectively [44,45]. Lifetimes were evaluated with software attached to the equipment.

Nanosecond transient absorption measurements were carried out using SHG (532 nm) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns fwhm) as an excitation source. For transient absorption spectra in the near-IR region (400–1200 nm) and the time-profiles, monitoring light from a pulsed Xe-lamp was detected with a Ge-APD (Hamamatsu Photonics, B2834) [45,46]. For spectra in the visible region, a Si-PIN photodiode (Hamamatsu Photonics, S1722-02) was used as the detector [45,46].

### 2.2. Materials

Spectral-grade 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. Preparation of alkyloxo(bromo)tetraphenylporphyrinatoantimony(V) bromide ([Sb(TPP)(OR)Br]$^{+}$Br$^{-}$)

Dibromo(tetraphenylporphyrinato)antimony(V) bromide ($[Sb(TPP)Br_2]^{+}Br^{-}$) was prepared according to the reported method [47]. An MeCN–MeOH solution (1:1, v/v, 80 ml) of $[Sb(TPP)Br_2]^{+}Br^{-}$ (300 mg; 0.31 mmol) was refluxed until the Soret band shifted from 427.8 nm to 423.7 nm. After evaporation, the crude $[Sb(TPP)(OMe)Br]^{+}Br^{-}$ was purified with a column chromatography on silica gel (Fuji Silysia BW 300) using $CHCl_3$–MeOH (10:1, v/v). The preparation of $[Sb(TPP)(OPh)Br]^{+}Br^{-}$ was performed by heating MeCN solution (40 ml) containing $[Sb(TPP)Br_2]^{+}Br^{-}$ (200 mg; 0.21 mmol), phenol (968 mg; 10.3 mmol), and pyridine (3 ml) at 65 °C until the Soret band shifted from 427.8 nm to 423.5 nm. After the evaporation, the $CH_2Cl_2$ solution of the residue was poured into hexane (300 ml) to give the precipitate. The crude $[Sb(TPP)(OPh)Br]^{+}Br^{-}$ was purified by a column chromatography on silica gel using $CHCl_3$–MeOH (10:1, v/v).

In a similar way, the hydrolysis of $[Sb(TPP)Br_2]^{+}Br^{-}$ (300 mg; 0.31 mmol) was refluxed in MeCN–$H_2O$ solution (1:1, v/v, 80 ml) until the Soret band shifted to 417.6 nm. The resulting crude $[Sb(TPP)(OH)_2]^{+}Br^{-}$ was used for the following procedure without further purification.

$[Sb(TPP)(OMe)Br]^{+}Br^{-}$: yield 95%. UV–vis (MeCN) $\lambda_{max}$ (nm) ($\log \varepsilon$) 424 (5.55), 556 (4.16) and 596 (4.02); MS (SIMS) *m/z*: 844 [$M^{+}$]; $^{1}H$ NMR: $\delta = -2.04$ (3H, s), 7.8–8.0 (12H, m), 8.31 (4H, d, $J = 7.0$ Hz), 8.39 (4H, d, $J = 7.0$ Hz), 9.58 (8H, s).

$[Sb(TPP)(OPh)Br]^{+}Br^{-}$: yield 91%. UV–vis (MeCN) $\lambda_{max}$ (nm) ($\log \varepsilon$) 423 (5.54), 555 (4.16) and 596 (4.07); MS

(SIMS) *m/z*: 907 [$M^+$]; $^1$H NMR: $\delta$ = 1.62 (2H, d, *J* = 7.5 Hz), 5.76 (2H, t, *J* = 8.3 Hz), 6.06 (1H, t, *J* = 7.4 Hz), 7.804–8.00 (12H, m, Ph), 8.18 (4H, d, *J* = 6.3 Hz, Ph), 8.35 (4H, d, *J* = 6.0 Hz, Ph), and 9.552 (8H, s, pyrrole).

[Sb(TPP)$(OH)_2]^+Br^-$: yield 95%. UV–vis (MeCN) $\lambda_{max}$ (nm) (log $\varepsilon$) 417 (5.72), 550 (4.34), 590 (4.07); MS (SIMS) *m/z*: 767 [$M^+$]; $^1$H NMR $\delta$ = −4.19 (2H, br s), 7.89–7.84 (12H, m), 8.41 (8H, dd, *J* = 8.1, 1.9 Hz), 9.40 (8H, 12H).

### 2.4. Preparation of (*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenylalkanol (Bdpy-O-$(CH_2)_n$-OH)

A mixture of 4-hydroxybenzaldehyde (0.5 g; 4.09 mmol), pyrrole (10 ml), and $CF_3CO_2H$ (0.3 ml) was stirred for 1 h at room temperature. The crude product was subjected to column chromatography on silica gel using $CHCl_3$–MeOH (10:1, v/v) as an eluent. The resulting dipyromethane (1.92 g; 8.06 mmol) was reacted with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ; 1.82 g; 8.06 mmol) in toluene (100 ml) for 5 min. $Et_3N$ (8.4 ml; 0.06 mmol) and $BF_3.Et_2O$ (7.6 ml; 0.06 mmol) were added to the solution, which was allowed to stand for 1 h. After the treatment of aqueous KOH solution (100 ml), the toluene layer was separated. 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 eluent to give *N*,*N*′-difluoroboryl-5-(4-hydroxyphenyl)dipyridin (Bdpy-OH) in 11% yield.

$K_2CO_3$ (0.49 g; 3.52 mmol) and 3-bromopropanol (1 ml) were added to a DMF solution of Bdpy-OH (0.5 g; 1.76 mmol) and then the solution was heated at 100 °C for 24 h. After extraction with $CH_2Cl_2/H_2O$, the $CH_2Cl_2$ solution was evaporated, resulting in the crude **2a**, which was purified by column chromatograph on silica gel using $CHCl_3$–MeOH (10:1, v/v) as an eluent. The preparation of **2b** was performed by heating a DMF solution including Bdpy-OH (0.5 g; 1.76 mmol), $K_2CO_3$ (0.49 g; 3.52 mmol), and 6-bromohexanol (2 ml) at 100 °C for 28 h. The follow-up process was performed in a manner similar to the case of **2a**. In a similar way, the reaction of Bdpy-OH with $Br(CH_2)_3Br$ gave **2c**.

### 2.5. Preparation of 4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenylalkyloxoantimony(V) tetraphenylporphyrin bromide (**1a**, **1b** and **1d**)

An MeCN solution (30 ml) containing [Sb(TPP)$(OMe)Br^+]Br^-$ (50 mg; 0.05 mmol), Bdpy-O-$(CH_2)_3$OH (**2a** and **2b**; 2.56 mmol), and pyridine (2 ml) was refluxed under nitrogen atmosphere at 65 °C until the absorption spectra shifted to nearly 423 nm. Then the crude product was subjected to column chromatography on silica gel using 10:1 (v/v) $CHCl_3$–MeOH as an eluent to give **1a, 1b** and **1d**. The preparation of **1c** was performed by refluxing a MeCN (25 ml) solution containing [Sb(TPP)$(OH)_2^+]Br^-$ (20 mg; 0.02 mmol), Bdpy-O-$(CH_2)_3$Br (**2c**; 0.31 mmol), $K_2CO_3$ (0.58 mmol), and 18-crown-6 ether (0.004 mmol). The follow-up process was performed in a similar way to **1a, 1b** and **1d**.

3-[4-(*N*,*N*′-Difluorobornyl-5-dipyrrinyl)phenyl]propoxo-(methoxo)antimony(V) tetraphenylporphyrin bromide (**1a**): yield 32%; UV–vis (MeCN) $\lambda_{max}$ (nm) (log $\varepsilon$) 418 (5.57), 551 (4.23) and 591 (3.98); MS (SIMS) *m/z*: 1106 [$M^+$]; $^1$H NMR: $\delta$ = −2.40 (2H, t, *J* = 5.6 Hz, $CH_2$), −2.19 (3H, s, $OCH_3$), −1.19 (2H, t, *J* = 5.6 Hz, $CH_2$), 0.88 (2H, m, $CH_2$), 6.14 (2H, d, *J* = 8.5 Hz, $C_6H_4$), 6.55 (2H, d, *J* = 3.8 Hz, pyrrole), 6.78 (2H, d, *J* = 3.8 Hz, pyrrole), 7.30 (2H, d, *J* = 8.5 Hz, C6H4), 7.92 (3H, s, pyrrole), 7.92–7.98 (12H, m, Ph), 8.32 (8H, m, Ph), 9.52 (8H, s, pyrrole).

6-[4-(*N*,*N*′-Difluorobornyl-5-dipyrrinyl)phenyl]hexyloxo(methoxo)antimony(V) tetraphenylporphyrin bromide (**1b**): yield 32%; UV–vis (MeCN) $\lambda_{max}$ (nm) (log $\varepsilon$) 418 (5.57), 551 (4.23) and 591 (3.98); MS (SIMS) *m/z*: 1148 [$M^+$]; $^1$H NMR: $\delta$ = −2.54 (2H, t, *J* = 5.6 Hz, $CH_2$), −2.19 (3H, s, $OCH_3$), −1.95 (2H, m, $CH_2$), −1.51 (2H, m, $CH_2$), −0.08 (2H, m, $CH_2$), 0.89 (2H, m, $CH_2$), 3.49 (2H, t, *J* = 5.6 Hz, $CH_2$), 6.53 (2H, d, *J* = 4.0 Hz, pyrrole), 6.78 (2H, d, *J* = 8.6 Hz, $C_6H_4$), 6.92 (2H, d, *J* = 4.0 Hz, pyrrole), 7.44 (2H, d, *J* = 8.7 Hz, $C_6H_4$), 7.91 (2H, s, pyrrole), 7.92–7.98 (12H, m, Ph), 8.33 (8H, m, Ph), 9.57 (8H, s, pyrrole).

Bis{3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenyl]propoxo}antimony(V) tetraphenylporphyrin bromide (**1c**): yield 58%; UV–vis (MeCN) $\lambda_{max}$ (nm) (log $\varepsilon$) 423 (5.49), 552 (4.10) and 592 (3.98), 497 (4.80); MS (SIMS) *m/z*: 1424 [$M^+$]; $^1$H NMR: $\delta$ = −2.42 (4H, t, *J* = 5.6 Hz, CH2), −1.21 (4H, t, *J* = 5.6 Hz, CH2), 0.88 (4H, m, CH2), 6.14 (4H, d, *J* = 4.0 Hz Ph), 6.55 (4H, d, *J* = 4.0 Hz, pyrrole), 6.77 (4H, m, pyrrole), 7.31 (4H, m, Ph), 7.95 (4H, s, pyrrole), 9.90–8.01 (12H, m, Ph), 8.32 (m, 8H, Ph), 9.49 (8H, s, pyrrole).

3-[4-(*N*,*N*′-Difluorobornyl-5-dipyrrinyl)phenyl]propoxo-(phenyloxo)antimony(V) tetraphenylporphyrin bromide (**1d**): yield 32%; UV–vis (MeCN) $\lambda_{max}$ (nm) (log $\varepsilon$) 418 (5.57), 551 (4.23) and 591 (3.98); MS (SIMS) *m/z*: 937 [$M^+$]; $^1$H NMR: $\delta$ = −2.20 (2H, t, *J* = 5.6 Hz, $CH_2$), −1.19 (2H, t, *J* = 5.6 Hz, $CH_2$), 0.88 (2H, m, $CH_2$), 1.67 (2H, d, *J* = 7.8 Hz, PhO), 5.73 (2H, d, *J* = 7.8 Hz, PhO), 6.04 (1H, t, *J* = 7.8 Hz, PhO), 6.18 (2H, d, *J* = 8.5 Hz, $C_6H_4$), 6.55 (2H, d, *J* = 3.8 Hz, pyrrole), 6.78 (2H, d, *J* = 3.8 Hz, pyrrole), 7.30 (2H, d, *J* = 8.5 Hz, C6H4), 7.92 (2H, s, pyrrole), 7.88–7.96 (12H, m, Ph), 8.13 (8H, d, *J* = 4.0 Hz, Ph), 8.38 (8H, d, *J* = 4.0 Hz, Ph), 9.49 (8H, s, pyrrole).

### 2.6. Measurement of fluorescence spectra of **1**

The fluorescence spectra of argon-purged solutions under the excitations of Bdpy chromophore at 490 nm and porphyrin chromophore at 420 nm were measured at room temperature on a Hitachi F4500 spectrometer. The concentrations of solutions of **1** were adjusted so that absorbance would be less than 0.08 at the excitation wavelength. According to the reported method [48], quantum yields for the fluorescence were determined. As an actinometer, an MeCN solution of

zinc(II) tetraphenylporphyrin with a fluorescence quantum yield of 0.029 [49] was used for the excitation of porphyrin chromophore at 420 nm. The quantum yield of **2a** in MeCN under excitation at 470 nm was determined to be 0.052 using an MeOH solution of Rhodamin B with the quantum yield of 0.4 under excitation at 470 nm.

## 3. Results

### 3.1. Preparation of fuctionalized Sb(TPP) complexes (*1*)

Alkyloxo(bromo)antimony(V) tetraphenylporphyrin bromide ($[Sb(TPP)(OR)Br]^+Br^-$; TPP denotes tetrapenylporphyrinato group) is a key precursor in our synthetic route to unsymmetric axial-ligand coordinated porphyrinatoantimony(V) complexes (Scheme 1). The $[Sb(TPP)(OR)Br]^+Br^-$ (R = Me, Ph) were prepared very smoothly by heating dibromoantimony(V) tetraphenylporphyrin bromide ($[Sb(TPP)Br_2{}^+]Br^-$) with ROH (R = Me, Ph) in MeCN. 4-(*N*,*N*′-Difluorobornyl-5-dipyrrinyl)phenoxyalkyloxo(alkyloxo)antimony(V) tetraphenylporphyrin bromide (**1a**, **1b** and **1d**) were prepared by the alcoholysis of $[Sb(TPP)(OR)Br]^+Br^-$ with 3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenoxy]propanol (**2a**) and 6-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenoxy]-hexanol (**2b**) under refluxing in MeCN (Scheme 1). The preparation of **1c** was performed by the alkylation of $[Sb(TPP)(OH)_2]^+Br^-$ with 3-[4-(*N*,*N*′-difluorobornyl-5-dipyrrinyl)phenoxy]propyl bromide (**2c**). The structures of **1a** and **1d** were confirmed by MS and NMR spectra. The redox potentials ($E_{1/2}$) in MeCN are summarized in Table 1.

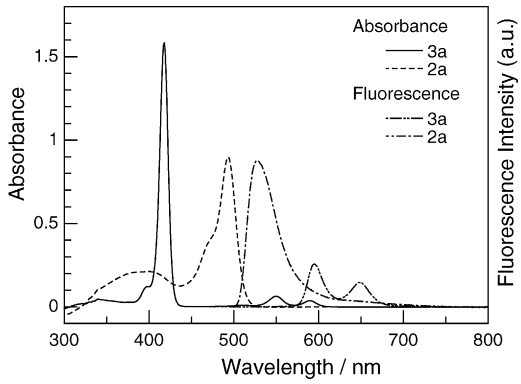
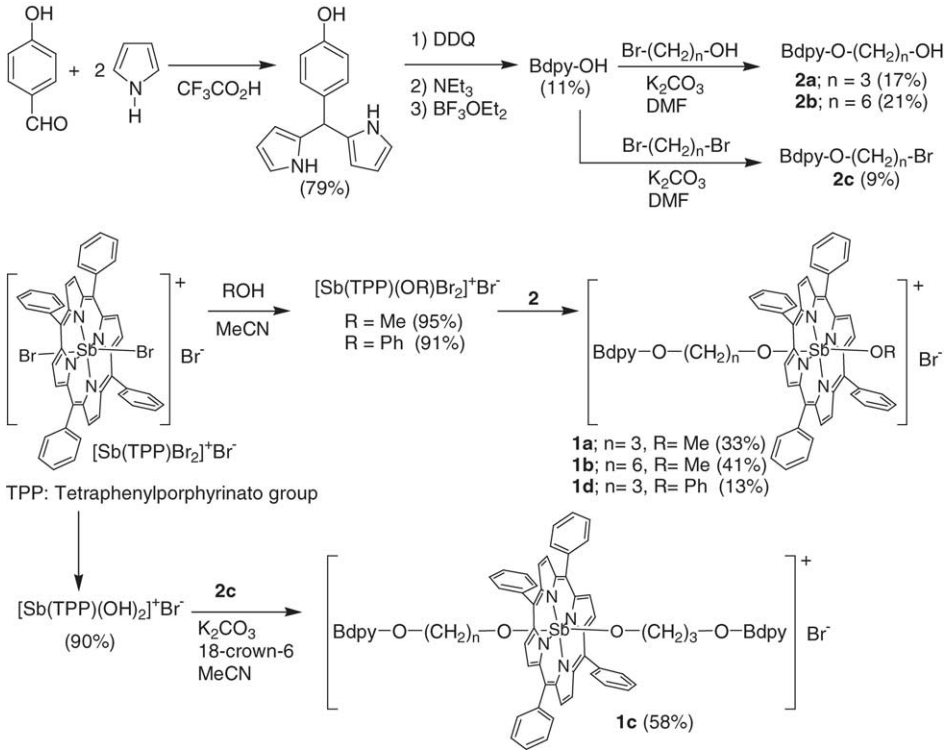



Fig. 1. Absorption and fluorescence spectra of **2a** (0.01 mM) and **3a** (0.01 mM) in MeCN. Excitation wavelength was 420 nm for **3a** and 470 nm for **2a**, respectively.

### 3.2. Steady-state absorption spectra

Fig. 1 shows the absorption and fluorescence spectra of **2a** and $[Sb(TPP)(OMe)_2]^+Br^-$ (**3a**) in MeCN. The absorption spectra of **1** are a superposition of the spectra of **3a** with a peak at 495 nm and **2a** with a Q-band at 550 and 590 nm with a strong Soret band at 415 nm, indicating no interaction in the




Scheme 1. Preparation of **1a**, **1b**, **1c** and **1d**.

Table 1
Characterization of **1a**, **1b**, **1c** and **1d** in MeCN

| **1** | $E^{ox}_{1/2}$ [a] (V) | $E^{red}_{1/2}$ [b] (V) | $\lambda_{max}$ (nm) (log $\varepsilon$)[c] | | $\lambda_{max}$ (nm)[d] ($\tau$/ns)[e] | | $r$ (Å)[f] |
|---|---|---|---|---|---|---|---|
| | | | Sb(TPP)[g] | Bdpy[h] | Sb(TPP)[g] | Bdpy[h] | |
| **1a** | 1.56 | −0.52 | 419 (5.3)<br>550 (3.9)<br>589 (3.6) | 495 (4.2) | 594 (1.31)<br>648 | 520 (0.29) | 6.53 |
| **1b** | 1.56 | −0.52 | 419 (5.3)<br>550 (3.9)<br>590 (3.6) | 495 (4.2) | 595 (1.16)<br>647 | 520 (0.023) | 8.08 |
| **1c** | 1.56 | −0.51 | 420 (5.3)<br>552 (3.9)<br>592 (3.7) | 495 (4.2) | 597<br>649 | 520 | 6.53 |
| **1d** | 1.56<br>0.93[i] | −0.46 | 421 (5.3)<br>552 (3.9)<br>592 (3.7) | 495 (4.2) | 594<br>649 | 520 | 6.53 |

[a] Half peak of oxidation potentials of Bdpy chromophore in **1**.
[b] Half peak of reduction potentials of Sb(TPP) chromophore in **1**.
[c] Absorption maxima.
[d] Emission maxima.
[e] The fluorescence lifetimes.
[f] Distance between C-5 of Bdpy and Sb atom calculated by MM2.
[g] For the porpyrin chromophore.
[h] For the Bdpy chromophore.
[i] Half peak of oxidation peak for axial phenyloxo ligand.

ground state. In polar solvents, these absorption bands of **3a** and the Sb(TPP) moiety in **1a**, **1b**, **1c** and **1d** were very sharp. On the other hand, when the absorption spectra of **3a**, **1a**, **1b** and **1c** were measured in toluene and benzene, these spectral shapes were remarkably destroyed. Also, when using $PF_6^-$ instead of $Br^-$ as a counter anion, the spectral shapes were destroyed even in polar solvents. These results were probably due to the aggregations of **3a** and the Sb(TPP) moiety in **1a**, **1b**, **1c** and **1d**.

### 3.3. Steady-state fluorescence spectra

As shown in Fig. 1, the fluorescence spectrum of **2a** at 520 nm is a mirror image of the absorption at 495 nm. Also, the fluorescence bands of **3a** at 595–640 nm are nearly mirror images of the absorptions at 550–590 nm. Although fluorescence peaks of the **3a** and the Sb(TPP) moiety in **1a**, **1b**, **1c** and **1d** were very sharp in polar solvents, these spectral shapes were remarkably destroyed, as well as the absorption spectra in a non-polar solvent, due to the aggregation of **3a** and the Sb(TPP) moiety in **1a**, **1b**, **1c** and **1d**. Therefore, the fluorescence spectra for quantitative analysis were measured in chloroform (CF), dichloromethane (DM), acetonitrile (AN), and methanol (ME). **3a** and **2a** were used as a model compounds for the analysis of the excited states of the Sb(TPP) and the Bdpy chromophores without the interaction of another chromophore, respectively (Scheme 2). Table 2 summarizes the quantum yields for the fluorescence emission of **2a** ($\Phi^{bdpy}_{2a}$) and **3a** ($\Phi_{3a}$). The $\Phi^{bdpy}_{2a}$ values, which are in the range of 0.052–0.183, decrease with the increase of solvent polarity measured by $E_T$ (30), as shown in Table 2. On the other hand, the quantum yields of **3a** ($\Phi_{3a}$) were almost the same when the solvent polarity was changed.

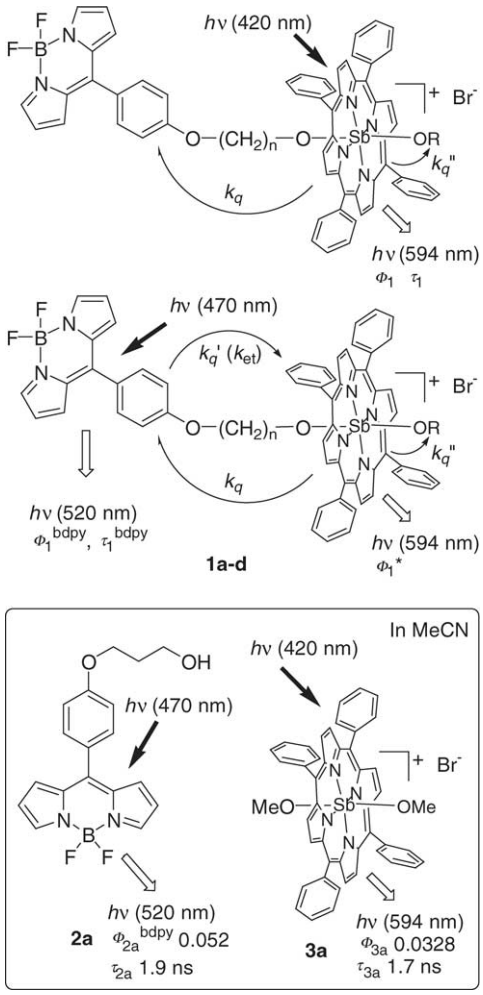
Under the selective excitation of the Sb(TPP) chromophores of **1a**, **1b**, **1c** and **1d** at 420 nm, the fluorescence coming from the Sb(TPP) chromophores was commonly observed near $\lambda_{max}$ 595 and 650 nm in the solvent used. The fluorescence quantum yields ($\Phi_1$) of Sb(TPP) chromophore under the excitation of the Sb(TPP) of **1a**, **1b**, **1c** and **1d** were about a half of $\Phi_{3a}$ of **3a**, as summarized in Table 3.

Fig. 2 shows the fluorescence spectra of **1a**, **1b**, and **1d** under selective excitation of the Bdpy moiety with 470 nm light. In the case of **1a**, the relative intensity of the Bdpy moiety at

Table 2
Fluorescence quantum yields of **2a** and **3a**

| Solvents[a] | $E_T$ (30)[b] | $\Phi^{bdpy}_{2a}$[c] | $\Phi_{3a}$[d] |
|---|---|---|---|
| | | $10^{-1}$ | $10^{-2}$ |
| TL | 33.9 | 1.80 | 2.88 |
| BZ | 34.5 | 1.73 | 2.83 |
| TF | 37.4 | 1.09 | 3.91 |
| CF | 39.1 | 1.83 | 2.65 |
| DM | 41.1 | 1.06 | 3.08 |
| AN | 46.0 | 0.47 | 3.28 |
| ME | 55.5 | 0.52 | 2.93 |

[a] TL: toluene, BZ: benzene, TF: tetrahydrofuran, CF: chloroform, DM: dichloromethane, AN: acetonitrile, ME: methanol.
[b] Empirical solvent parameter.
[c] Fluorescense quantum yield of **2a** under the excitation at 470 nm.
[d] Fluorescence quantum yield for $[Sb(TPP)(OMe)_2]^+Br^-$ (**3a**) under the excitation at 420 nm.




Scheme 2. Kinetic parameters for the analysis of fluorescence parameter.

520 nm is much smaller than that of the Sb(TPP) moiety at 610 and 655 nm, suggesting efficient quenching of the Bdpy moiety. For **1b**, the ratio of the fluorescence intensity of the Bdpy moiety is about a half of the Sb(TPP) moiety, indicating that the Bdpy moiety quenching is less efficient than

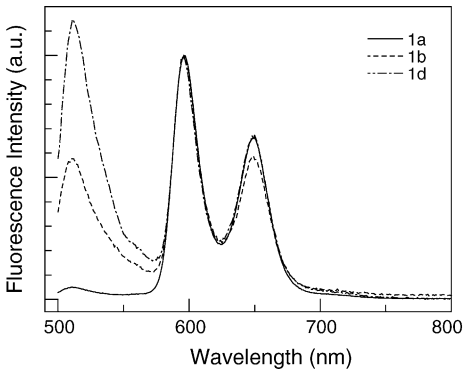



Fig. 2. Fluorescence spectra of **1a**, **1b** and **1c** under the excitation of Bdpy chromophore at 470 nm in MeCN. These spectra were normalized by the intensity of **1a** at 600 nm.

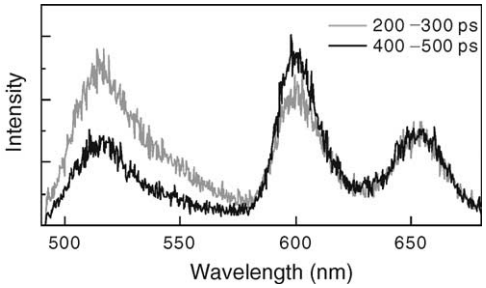



Fig. 3. Time resolved fluorescence of **1a** (0.01 mM) in MeCN after 410 nm laser irradiation.

that of **1a**. This may be more related to the long methylene chain of **1b** ($n = 6$) than that of **1a** ($n = 3$). Although **1d** has the same chain length as **1a**, the fluorescence intensities of both Bdpy and Sb(TPP) moieties were weak compared with **1a**. It is noteworthy that such a large difference was observed only by changing the axial ligand from the methoxy group to the phenoxy group. Under the excitation of Bdpy chromophores at 470 nm, the quantum yields of the fluorescences from the Sb(TPP) chromophores ($\Phi_1^*$) and the Bdpy chromophores ($\Phi_1^{bdpy}$) were estimated, as shown in Table 3. The $\Phi_1^{bdpy}$ values of **1a**, **1b**, **1c** and **1d** are about 1/100 of **2a**.

### 3.4. Time-resolved fluorescence spectra and lifetime

Fig. 3 shows the time-resolved fluorescence spectra of **1a** in MeCN. Although complete selective excitation of Bdpy moiety was impossible with our laser equipments, the rapid decay of the fluorescence of Bdpy chromophores was observed ($\tau_1^{bdpy} = 0.29$ ns), which is faster than $\tau_{2a}^{bdpy} = 0.53$ ns. From the decay rate of the fluorescence of Bdpy chromophore, the rate constant for phenomenon occurring from the excited singlet state of the Bdpy chromophores was evaluated. With the decay of the fluorescence of Bdpy chromophores, the rise of the fluorescence intensity of Sb(TPP) chromophores was observed, suggesting that energy transfer takes place from the excited singlet state of Bdpy moiety to Sb(TPP) chromophore. After reaching a maximum, the fluorescence of the Sb(TPP) chromophore in **1a**, **1b**, **1c** and **1d** begins to decay with lifetime ($\tau_1^{bdpy} = 1.3$) slightly shorter than that of **3a** ($\tau_{3a} = 1.7$ ns), suggesting some extra processes may occur between the excited singlet state of the Sb(TPP) and the Bdpy chromophores. In the case of **1d**, some extra processes may occur between the excited singlet state of Sb(TPP) chromophores and the axial phenoxy group.

### 3.5. Nano-second transient absorption spectra

In order to elucidate the participation of the electron transfer quenching, a nanosecond laser flash photolysis technique was employed. It is well known that the excitation of $[Sb(V)TPP(OMe)_2]^+Br^-$ (**3a**) resulted in the characteristic transient absorption due to the excited triplet state where intense sharp absorption appeared in the 400–500 nm region

Table 3
Quantum yield and quenching rate constant for the fluorescence of **1a**, **1b**, **1c** and **1d**

| 1 | Solvents | $\Phi_1/10^{-2}$[a] ($k_q/10^9$ s$^{-1}$)[b] | $\Phi_1^{bdpy}/10^{-2}$[c] ($k_q'/10^{10}$ s$^{-1}$)[d] | $\Phi_1^*/10^{-3}$[e] | $\Phi_{ent}$[f] ($k_{ent}/10^9$ s$^{-1}$)[g] | $k_q''/10^9$ s$^{-1}$[h] |
|---|---|---|---|---|---|---|
| **1a** | CF | 1.85 (0.25) | 0.26 (3.65) | 6.13 | 0.33 (12.0) | |
| | DM | 1.60 (0.54) | 0.19 (2.88) | 6.16 | 0.38 (11.0) | |
| | AN | 1.25 (0.96) | 0.16 (1.49) | 5.00 | 0.40 (5.96) | |
| | ME | 1.27 (0.77) | 0.21 (1.25) | 4.85 | 0.38 (4.75) | |
| **1b** | CF | 2.27 (0.10) | 0.91 (1.01) | 8.07 | 0.36 (3.62) | |
| | DM | 2.27 (0.21) | 0.60 (0.88) | 7.36 | 0.32 (2.81) | |
| | AN | 1.91 (0.42) | 0.33 (0.52) | 7.41 | 0.39 (2.03) | |
| | ME | 1.70 (0.43) | 0.43 (0.76) | 4.86 | 0.29 (2.25) | |
| **1c** | CF | 2.19 (0.12) | 0.30 (3.16) | 2.83 | 0.13 (4.08) | |
| | DM | 1.51 (0.61) | 0.18 (3.06) | 4.07 | 0.27 (8.22) | |
| | AN | 0.87 (1.63) | 0.12 (2.02) | 3.04 | 0.35 (7.02) | |
| | ME | 0.74 (1.74) | 0.15 (1.78) | 2.64 | 0.36 (6.36) | |
| **1d** | CF | 0.44 (2.95) | 0.33 (3.20) | 0.72 | 0.16 (5.12) | 2.45 |
| | DM | 0.60 (2.43) | 0.20 (3.06) | 0.54 | 0.09 (2.75) | 1.27 |
| | AN | 0.62 (2.52) | 0.05 (5.45) | 0.14 | 0.02 (1.09) | 0.78 |
| | ME | 0.42 (3.52) | 0.10 (3.00) | 0.27 | 0.06 (1.80) | 1.54 |

[a] Fluorescence quantum yield from Sb(TPP) chromophore under excitation at 420 nm.
[b] $k_q = (\Phi_{3a}/\Phi_1 - 1)/\tau_{3a}$.
[c] Fluorescence quantum yield from Bdpy chromophore under excitation at 470 nm.
[d] $k_q' = (\Phi_2^{bdpy}/\Phi_1^{bdpy} - 1)/\tau_2^{bdpy}$.
[e] Fluorescence quantum yield from Sb(TPP) chromophore under excitation of the Bdpy chromophore at 470 nm.
[f] Quantum yield for energy transfer $\Phi_{ent} = \Phi_1^*/\Phi_1$.
[g] Rate constant for the energy transfer from Bdpy group to the porphyrin chromophore: $k_{ent} = \Phi_{ent}k_q'$.
[h] The quenching rate constants for the fluorescence of Sb(TPP) chromophore by axial phenoxy ligand determined by the following equation; $k_q'' = (\Phi_{1a}/\Phi_{1d} - 1)/\tau_1$; where $\tau_1 = 1.31$ ns.

and broad absorption appeared from 600 to 900 nm, as shown in Fig. 4A. Fig. 4B shows the transient spectra excitation of **3a** in MeCN in the presence of electron-donating substrates such as *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB; $Me_2NC_6H_4$-$C_6H_4NMe_2$) under excitation at 524 nm. The excitation of **3a** induce electron transfer from TMB to **3a** via the triplet state of **3a**, giving the intense absorption of the cation radical of TMB at 1040 and 900 nm (lifetime = 5 μs) and relatively weak absorptions at 700 and 800 nm. The latter can be attributed to the one-electron reduced complex of $[Sb^V(TPP)(OMe)_2]^+$, which can be expressed in the forms of $Sb^{IV}(TPP)(OMe)_2$ and/or $[Sb^V(TPP)(OMe)_2]^\bullet$ [44]. In order to avoid the overlapping of absorption of donor cation radical, therefore, laser-flash photolysis of **3a** was performed in the presence of diethylaniline (DEA) acting as electron donor (Fig. 4C). With the disappearance of the absorption bands of the triplet state of **3a**, new peaks at 700 and 800 nm were observed. Since the radical cation of DEA may appear shorter than 420 nm, the observed transient peaks at 700 and 800 nm in Fig. 4C can be unambiguously attributed to $[Sb^V(TPP)(OMe)_2]^\bullet$ or $Sb^{IV}(TPP)(OMe)_2$ formed by the electron transfer from DEA to the triplet state of **3a**.

On the other hand, the transient spectra of **1a**, **1b**, and **1d** under excitation of the Sb(TPP) moiety at 524 nm showed broad absorption in the 600–900 nm region and sharper three absorption peaks in the 400–600 nm region; the appearance of broad absorption in the 600–900 nm region suggests that the triplet excited state of the Sb(TPP) moiety in **1** was formed via the intersystem crossing from the singlet excited state of the Sb(TPP). However, a comparison of the region of 600–850 nm in Fig. 5 with pure triplet–triplet absorption band in Fig. 4A shows that the peaks at 700 and 800 nm seem to be overlapped, suggesting the formation of $[Sb^V(TPP)(OMe)_2]^\bullet$ moiety or $Sb^{IV}(TPP)(OMe)_2$ moiety. Three peaks in the 400–600 nm range of **1** were different from the absorption spectra of the excited triplet state of **3a** (Fig. 4A). However, the electron transfers from Bdpy to excited singlet state of the Sb(TPP) in **1a**, **1b**, **1c** and **1d** were as slow as competition with the formation of the triplet state of **1**.

## 4. Discussion

### *4.1. Estimation of free energy changes in the electron transfer between two chromophores*

The free energy changes ($\Delta G$) required for the electron transfer between two chromophores are calculated by the Rehm–Weller equation (Eq. (1)) [50] using the half-peak of oxidation potential of the Bdpy chromophore ($E_{1/2}^{ox}$), the half-peak of reduction potential of the Sb(TPP) chromophore ($E_{1/2}^{red}$), and the excitation energies ($E^{0-0}$) for the Sb(TPP) and the Bdpy chromophores, which were 2.08 and 2.44 eV, respectively (Table 1). The $\Delta G'$s for the electron transfer from the excited singlet state of the Sb(TPP) chromophore

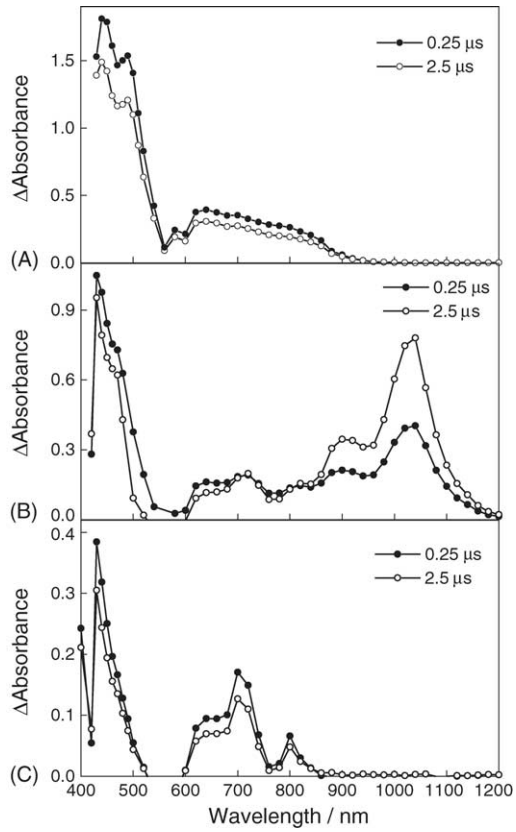



Fig. 4. Transient spectra of **3a** (0.1 mM): (A) in the absence and (B) in the presence of tetramethylbenzidiene (TMB; 0.2 mM); (C) in the presence of *N*,*N*-dimethylaniline (DEA; 5 mM) in MeCN after 532 nm laser irradiation.

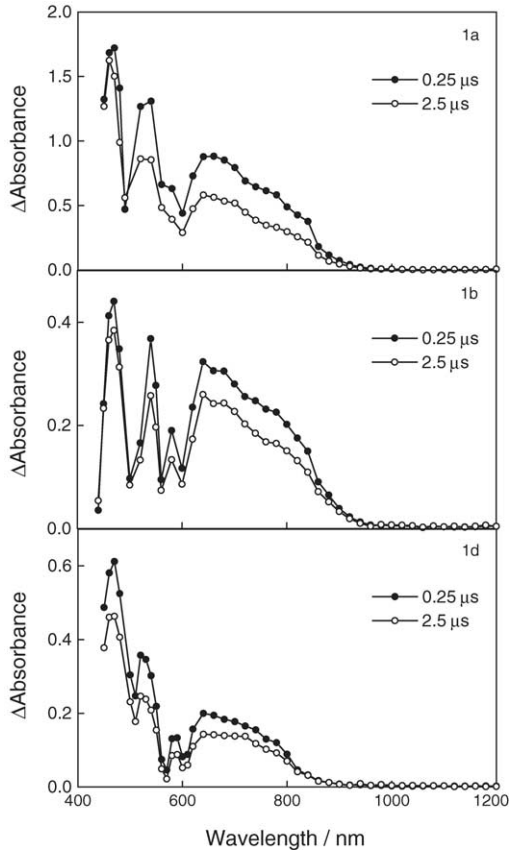
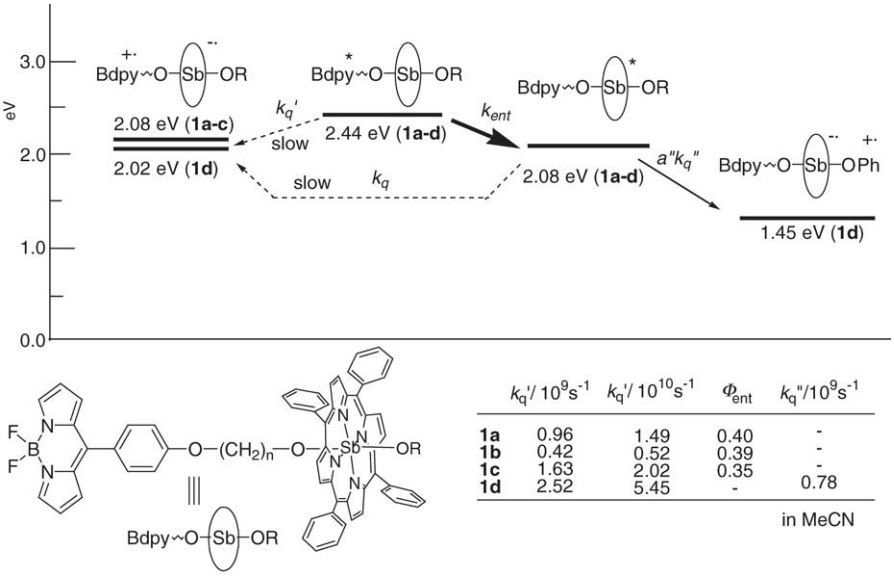



Fig. 5. Transient spectra of **1a**, **1b**, and **1d** under excitation of Sb(TPP) chromophore at 524 nm in MeCN.

to the Bdpy chromophore of **1a**, **1b** and **1c** were nearly zero, while $\Delta G$ was slightly exoergonic for the case of **1d**. The $\Delta G'$s for the electron transfer from the excited singlet state of the Bdpy moiety to the Sb(TPP) moiety were calculated to be exoergonic. The energy diagrams are shown in Scheme 3.

$$\Delta G = E^{\mathrm{ox}}_{1/2} - E^{\mathrm{red}}_{1/2} - E^{0-0} \quad (1)$$




| | $k_q'/10^9\,s^{-1}$ | $k_q'/10^{10}\,s^{-1}$ | $\Phi_{ent}$ | $k_q''/10^9\,s^{-1}$ |
|---|---|---|---|---|
| **1a** | 0.96 | 1.49 | 0.40 | - |
| **1b** | 0.42 | 0.52 | 0.39 | - |
| **1c** | 1.63 | 2.02 | 0.35 | - |
| **1d** | 2.52 | 5.45 | - | 0.78 |

in MeCN

Scheme 3. Energy diagram for the reactive species of **1a**, **1b**, **1c** and **1d**.

### 4.2. Fluorescence under the excitation of Sb(TPP) chromophore

The shapes and $\lambda_{max}$ in the UV–vis and the emission spectra of **1a**, **1b** and **1c** were the same as those of **3a**, revealing an absence of interaction between the two chromophores in both the ground and excited states. The fluorescence lifetimes ($\tau_1$) of Sb(TPP) chromophore were determined to be 1.31 and 1.16 ns in MeCN for **1a** and **1b**, respectively. These values were very close to the fluorescence lifetime of **3a** ($\tau_{3a}$), which were 1.5–1.8 ns in the solvent used. Under the excitation of Sb(TPP) chromophore at 420 nm, the fluorescence quantum yields ($\Phi_1$) were the constancy of the solvent; 0.0125–0.0185 for **1a** and 0.0170–0.0227 for **1b**. The quenching rate constants ($k_q$) of the excited singlet state of Sb(TPP) chromophore by the Bdpy chromophore were calculated by Eq. (2) using the observed $\Phi_1$, $\tau_{3a}$ (1.7 ns for MeCN), and $\Phi_{3a}$ for **3a**. The $k_q$ values predicted that the quenching of the excited singlet state of Sb(TPP) by the Bdpy chromophore would be very slow ($k_q < 10^9\ s^{-1}$).

$$k_q = \frac{\Phi_{3a}/\Phi_1 - 1}{\tau_{3a}} \tag{2}$$

The $k_q$ value did not depend on either the solvent polarity or the length of the methylene bridge (Table 3). Moreover, the transient absorptions of $Sb^{IV}$(TPP) species were not clearly observed under excitation of Sb(TPP) chromophores of **1a** and **1b**. Therefore, it can be concluded that the participation of the electron-transfer process in quenching the excited singlet state of Sb(TPP) chromophore with the Bdpy chromphore is very small in **1**. These results contrast those in the case of (2-naphthoxy)polyoxalkyloxoantimony tetraphenylporphyrin complexes [41], where the fluorescence quenching of Sb(TPP) chromophore by the naphthoxy group was rapid, as was the increase of the solvent polarity and increase of the distance between the two chromophores. In the latter case, the dependence of $k_q$ on solvent polarity and the distance between the two chromophores was attributable to the occurrence of the electron-transfer process.

### 4.3. Fluorescence under the excitation of Bdpy chromophore

The fluorescence quantum yields ($\Phi_1^{bdpy}$) from the Bdpy chromophore of **1** under the excitation of Bdpy chromophore at 470 nm were 0.0016–0.0026 for **1a** and 0.0033–0.0091 for **1b**, much smaller than the fluorescence quantum yield of **2a** ($\Phi_2^{bdpy} = 0.047 - 0.183$) [42,43]. Moreover, the lifetimes ($\tau_1^{bdpy}$) of the Bdpy chromophore of **1a** and **1b** were 290 ps and 23 ps, respectively, which were much shorter than the lifetime of **2a** ($\tau_2^{bdpy}$: 1.9 ns) [42,43]. The quenching rate constants ($k'_q$) of the excited singlet state of Bdpy chromophore by the Sb(TPP) chromophore was calculated by Eq. (3). The $k'_q$ values were $10^{10}\ s^{-1}$ order. The quantum yields ($\Phi_{ent}$) for the energy transfer from Bdpy chromophores in the excited singlet state to Sb(TPP) chromophores was determined by Eq. (4). The $\Phi_{ent}$ was 0.33–0.40 for **1a** and 0.29–0.36 for **1b**, regardless of the solvent polarity. Since $k'_q$ was larger in the two orders than the other decay pathways (e.g. $1/\tau_2^{bdpy}$), the rate constant ($k_{ent}$) for the energy transfer can be calculated by Eq. (5).

$$k'_q = \frac{\Phi_2^{bdpy}/\Phi_1^{bdpy} - 1}{\tau_2^{bdpy}} \tag{3}$$

$$\Phi_{ent} = \frac{\Phi_1^*}{\Phi_1} \tag{4}$$

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

The $k_{ent}$ value should be affected by the distance between the Bdpy and the Sb(TPP) chromophores. The $k_{ent}$ value decreased as the length of the methylene bridge increased (Table 3). Also, the $k_{ent}$ value of **1a** decreased, as the solvent polarity increased (Table 3). Solvent polarity might affect the conformation of axial Bdpy ligands. The favorable conformation of **1a** and **1b** calculated by the MM2 program took the structure where the Bdpy group was bent over the porphyrin chromophore rather than being located perpendicular to the porphyrin chromophore. Since the Sb(TPP) moiety was cationic, solvation with a polar solvent might disturb the approach of the Bpdy chromophore to the Sb(TPP) chromophores, resulting in a larger distance between the two chromophores. There were apparent differences in $k_{ent}$ and $\Phi_{ent}$ between **1a** and **1c** having two axial Bdpy ligands. As a result, the excitation energy of the Bdpy chromophores was transferred to the Sb(TPP) chromophores with high efficiency: $\Phi_{ent} = 0.35$–$0.40$ for **1a**, **1b** and **1c** in MeCN. The excited singlet states of the Sb(TPP) chromophore were very slowly quenched by the Bdpy chromophore ($k_q = 2.5 - 9.6 \times 10^8\ s^{-1}$) (Table 2).

### 4.4. Fluorescence of *1d* involving axial phenoxy ligand

The fluorescence study of **1d,** involving Sb(TPP), Bdpy, and phenoxy chromophores, was performed. Since the three chromophores of **1d** are isolated from each other, **1d** was subjected to the same analysis as **1a**. The excited singlet state of the Sb(TPP) was quenched by both the Bdpy and phenoxy chromophores. The Bdpy quenching rate constant ($k_q$) for **1d** was assumed to be the same as $k_q$ for **1a**, that is $2.5$–$9.6 \times 10^8\ s^{-1}$. However, the $k_q$ value determined by kinetic treatment was $2.43$–$3.52 \times 10^9\ s^{-1}$, which is larger than that of **1a**. Therefore, the occurrence of electron-transfer quenching by phenoxy group should be taken into account.

The quenching rate constant ($k''_q$) of the fluorescence of Sb(TPP) by phenoxy group was determined by comparison of $\Phi_1$ between **1a** and **1d** according to Eq. (6), where $\Phi_{1a}$ and $\Phi_{1d}$ are the fluorescence quantum yield of the porphyrin chromophore of **1a** and **1d** under excitation of the porphyrin chromophore, respectively. According to Eq. (6), $k''_q$ was estimated

to be 0.78–2.45 × $10^9$ $s^{-1}$. The quenching process of the excited singlet state of porphyrin by the phenoxy chromophores might be mainly an electron-transfer process, since the process is energetically favorable. However, the transient spectra of **1d** did not show peaks due to the $Sb^{IV}$ tetraphenylporphyrine species ($Sb^{IV}$(TPP)), which might appear at 700 and 800 nm. The charge recombination between $Sb^{IV}$(TTPP) and the anion radical of the phenoxy moiety probably occurred within a laser pulse (ca. 6 ns). Also, the $k'_q$ values of **1d** were larger than those of **1a**, while the $k_{ent}$ values were smaller than those of **1a**. Therefore, the quenching of Bdpy chromophore by the Sb(TPP) chromophore in **1d** should include the other process involving an electron-transfer process, since the free energy change from the excited singlet state of Bdpy chromophore to the Sb(TPP) chromophore is negative.

$$k''_q = \frac{\Phi_{1a}/\Phi_{1d} - 1}{\tau_1} \quad (6)$$

In conclusion, we can easily construct the porphyrinatoantimony complex having the second chromophores such as Bdpy on the axial ligands. From the analysis of the fluorescence quenching process between chromophores, it is seen that the excitation energy of the Bdpy chromophores of **1a**, **1b** and **1c** could be transferred to the porphyrin chromophores with high efficiency (0.13–0.40). The excited singlet state of the porphyrin chromophore was scarcely quenched by the Bdpy chromophore via the electron-transfer process even in polar solvents. In the case of **1d**, the excitation energy of porphyrin chromophore transferred from the Bdpy chromophore was quenched by the phenoxy chromophores via non-radiative processes involving electron transfer.

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