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The synthesis and spectral properties of amber phthalocyanines

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ABSTRACT

Novel antimony(V)-phthalocyanine complexes, $[Sb(tObpc)(OH)_2]^+$, $[Sb(tppc)(OH)_2]^+$, and $[Sb(tppc)Cl_2]^+$ (where tObpc and tppc denote tetra(*n*-butoxy)phthalocyaninate, $C_{48}H_{48}N_8O_4^{2-}$, and tetrakis(2′,6′-dimethylphenoxy)phthalocyaninate, $C_{64}H_{48}N_8O_4^{2-}$, respectively) were synthesized by oxidizing the corresponding antimony(III) derivatives either with *tert*-butyl perbenzoate or sulfuryl chloride. The compounds are dissimilar to conventional phthalocyanines in that they are of amber color in solution. Optical properties were studied by absorption and magnetic circular dichroism spectroscopy. The amber color was attributed to a combination of an intense absorption band (Q-band; $\log(\varepsilon/M^{-1}\,cm^{-1}) = ca.\ 5$) at ~735–760 nm, which was red-shifted by ~1000–1200 cm^{-1} compared to conventional phthalocyanines and a less intense ($\log(\varepsilon) = ca.\ 4$) but broad band at ~400–500 nm, which is not observed for conventional phthalocyanines. The additional band at ~400–500 nm was considered to be a red-shifted Soret band.

1. Introduction

Phthalocyanines and their metal complexes (hereafter referred as Pc's) are versatile compounds and have attracted much attention in many industrial and medical fields, such as dyes and pigments, photovoltaic and solar cells, charge generating material (CGM), optical data storage, infrared cut-filter, photodynamic cancer therapy, nonlinear optics, sensors, one-dimensional metal and semiconductor, and electrochromism [1–3].

Conventional Pc's are generally blue in color because they intensely absorb red light (650–700 nm; $\log(\varepsilon/M^{-1}\,cm^{-1}) = ca.\ 5$, this being termed a Q-band and assigned to a π–π* (HOMO–LUMO) transition in character) but are transparent in other parts of the visible spectrum [4–6]. Some Pc's also absorb violet light (380–420 nm; $\log(\varepsilon) = ca.\ 4$) and hence they may display a green color. In any case, the appearance of the main band in 650–700 nm and the essential transparency in other parts of the spectrum determine the color of the Pc. Hence, if a Pc has a considerably red-shifted Q-band and an extra band in other parts of the spectrum, the Pc should show a non-blue/green color. This possibility was exemplified by Kobayashi and coworkers, who reported octaphenyl-substituted Pc's that exhibit ocher and red colours [7]. In this case, the Pc's were unusual in that the macrocycle was significantly distorted from planarity owing to steric hindrance between the neighboring peripheral phenyl groups [8].

The present authors have reported that the presence of an antimony ion in the cavity of a phthalocyanine macrocycle, irrespective of its oxidation state, gives rise to a significant red-shift of the Q-band (by ca. 1100–1600 cm^{-1}) [9–19]. In addition, it is known that alkoxyl- and phenoxyl-substituted Pc's show an extra band at the red-flank of the Soret band, which has been assigned as a n–π* transition involving lone pair orbitals of oxygen atoms in the alkoxyl/phenoxyl groups [20]. Therefore, antimony derivatives of Pc's bearing alkoxyl or phenoxyl groups as peripheral substituents, of which the corresponding phthalonitriles (as the starting material) are easily prepared or even commercially available, may show a different color. Nyokong's group has studied antimony derivatives of octaphenoxyl-substituted phthalocyanines [21]. Although an extra band ~400 nm was observed for antimony(III) derivatives, little attention has been paid to this band and the color of the complexes. With respect to the corresponding antimony(V) derivatives, their spectral data are available only for the Q-region; nothing has been mentioned about the presence/absence of such an extra band in their "window" region probably because they had not isolated the compounds in analytically pure form at that stage. In this work, we will report syntheses of a few novel antimony(V)-phthalocyanines bearing alkoxyl or phenoxyl groups as peripheral substituents (Fig. 1). As is described below, we have successfully accomplished a new approach to non-blue/green Pcs with the aforementioned strategy.

In addition to that, as is described below, the new Pcs absorb a wide range of visible light. Therefore, these should be of interest

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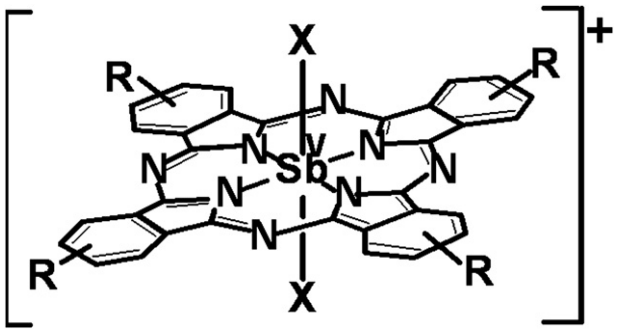

Fig. 1. Antimony(V)-phthalocyanine complexes studied in this work, $[Sb(tppc)(OH)_2]^+$ (R = 2′,6′-dimethylphenoxyl, X = OH^-), $[Sb(tppc)Cl_2]^+$ (R = 2′,6′-dimethylphenoxyl, X = Cl^-), andv$[Sb(tObpc)(OH)_2]^+$ (R = n-butoxyl, X = OH^-). The tetra substituted Pcs are mixtures of four regioisomers based on the position of peripheral substituents. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

to those who work not only with dyes and pigments but also with solar cells and CGM. It should be noted that antimony(V) derivatives may be attractive from the viewpoint of their potential application to chemotherapy of protozoan parasite endemic in tropical and subtropical regions, such as *Leishmaniasis* because problems of clinical resistance to the existing pentavalent antimonals in use as the first line drugs have become aggravated [22–24].

2. Experimental

2.1. Materials

2.1.1. Starting materials

Commercially available 4-(2′,6′-dimethylphenoxy)phthalonitrile and 4-*n*-butoxyphthalonitrile (Tokyo Kasei) were purified by firstly passing a silica gel column (CH_2Cl_2) and then recrystallization from ethyl acetate/hexane and benzene/hexane, respectively. Antimony(III) iodide was purchased from Wako and used as received.

2.1.2. Synthesis of dihydroxo(tetra-tert-butylphthalocyaninato) antimony(V) hexafluorophosphate, $[Sb(tbpc)(OH)_2]PF_6\cdot 3H_2O$

The triiodide salt, $[Sb(tbpc)(OH)_2]I_3\cdot 2H_2O$ (where tbpc denotes tetra-*tert*-butyl-phthalocyaninate, $C_{48}H_{48}N_8^{2-}$), was prepared in a way described previously [16]. To a dry flask containing 200 ml of dehydrated acetonitrile in which $[Sb(tbpc)(OH)_2]I_3\cdot 2H_2O$ (200 mg; 0.095 mmol) was dissolved, was added a dehydrated acetonitrile solution (4.0 ml) containing $AgPF_6$ (Aldrich; 1.0 mmol). The ensuing solution was stirred in the dark at room temperature and the reaction was monitored using absorption spectra. Absorption bands in the 300–400 nm region, which are characteristic of I_3^-, disappeared after 30 min, after which time, an additional acetonitrile solution (1.0 ml) containing $AgPF_6$ (0.30 mmol) was added. After stirring for 15 min in the dark, the reaction mixture was filtered to remove precipitated solid (AgI_3) and the filtrate evaporated to reduce its volume (5 ml). To this solution was added 200 ml of water to precipitate the desired compound. The solid was collected by filtration, washed with a small amount of water, and then dried at 80 °C under vacuum (142 mg). A portion (52 mg) of the crude hexafluorophosphate was twice recrystallized from benzene/hexane. The solid was collected by filtration and dried at 80 °C under vacuum (29 mg; yield 49%). Anal. Found: C, 52.38, H, 4.84, N, 10.14%. Calcd for $[Sb(tbpc)(OH)_2]PF_6\cdot 3H_2O$ ($C_{48}H_{56}O_5N_8SbPF_6$): C, 52.81; H, 5.17; N, 10.26%. IR/cm^{-1}; 844 (ν(P—F)) and 558 (δ(F-P-F)).

2.1.3. Synthesis of (tetra-n-butoxyphthalocyaninato)antimony(III) triiodide, $[Sb(tObpc)]I_3$

The antimony(III) complex was synthesized in essentially the same manner to that described for its tbpc analogue [11]. A mixture of 4-*n*-butoxyphthalonitrile (0.82 g; 4.0 mmol) and antimony iodide (1.0 g; 2.0 mmol) was fused in a sealed glass tube at 170 °C for 72 h. The reaction mixture solidified when it was allowed to cool down to room temperature. The solid was heated at 130 °C under vacuum for 72 h to remove unreacted starting materials and volatile byproducts. The desired product was extracted by *o*-dichlorobenzene (50 ml) and the solvent was evaporated. The residue was washed with 200 ml of CH_2Cl_2/hexane (4:46(v/v)) until the washings turned essentially colorless and the product was then dried 80 °C under vacuum to obtain a 668 mg of crude product (yield 51% assuming the product is analytically pure). This product was the desired compound as proven by ESI-MS (m/z = 921 (^{121}Sb(tObpc))$^+$ and 923 (^{123}Sb(tObpc))$^+$ in acetonitrile) and absorption spectra (λ_{max} = 771 nm in CH_2Cl_2). This compound was used in the next procedure although it is not sufficiently pure at this stage because much of antimony(III) derivatives are known to be lost during purification procedures [11,14].

2.1.4. Synthesis of dihydroxo(tetra-n-butoxyphthalocyaninato) antimony(V) triiodide, $[Sb(tObpc)(OH)_2]I_3$

The antimony(V) derivatives bearing axial hydroxyl groups were prepared in essentially the same manner as that for the tbpc analogue [16]. 556 mg of the crude $[Sb(tObpc)]I_3$ was dissolved in *tert*-butyl perbenzoate (Alfar Aesar; 11 ml) and the ensuing solution was heated at 50 °C with vigorous stirring for 45 min. The reaction was monitored using the absorption spectra of the solution (in CH_2Cl_2 solution). After the most prominent band at 771 nm ($[Sb(tObpc)]^+$) disappeared and a new band appeared at 741 nm, the mixture was ice-cooled to quench the reaction. 25 ml of hexane was added to precipitate the product and the solid was collected by centrifugation. The solids were further washed with 150 ml of CH_2Cl_2/hexane (1:4 (v/v)) until the washings turned essentially colorless and then dried at 80 °C under vacuum (514 mg). This was dissolved into acetone (14 ml) and the solution was filtered to remove insoluble impurities and then precipitated by the addition of a 36 ml of water. The solid was collected by centrifugation and again was dissolved into acetone and precipitated by the addition of water; these procedures were repeated (5 times in this case) until a considerable amount of solid became dispersed in the aqueous phase after centrifugation. The colloidal solution, after being added a small amount (ca. 4.5 ml) of aqueous Na_2SO_4 solution (ca. 1 M), was again centrifuged to remove the aqueous phase. The solid was dried at 80 °C under vacuum and then was dissolved into CH_2Cl_2 (25 ml) and filtered to remove Na_2SO_4. The solvent was evaporated out and the desired compound was recrystallized from CH_2Cl_2/hexane (6:45 (v/v)), washed with a 50 ml of CH_2Cl_2/hexane (1:9 (v/v)), and dried at 80 °C under vacuum (381 mg; yield 42% assuming that the starting antimony(III) derivative was analytically pure). This product has been found to be the desired compound by ESI-MS (m/z = 955 (^{121}Sb(tObpc)$(OH)_2$)$^+$ and 957 (^{123}Sb(tObpc)$(OH)_2$)$^+$ in acetonitrile). Anal. Found: C, 47.78, H, 4.06, N, 9.53%. Calcd for $[Sb(tObpc)(OH)_2]I_3$ ($C_{48}H_{50}O_6N_8SbI_3$): C, 43.11; H, 3.77; N, 8.38%. As triiodide salt was difficult to obtain in analytically pure form [14], we did not make further efforts to purify this product and have tried to replace the counter anion with hexafluorophosphate.

2.1.5. Synthesis of dihydroxo(tetra-n-butoxyphthalocyaninato) antimony(V) hexafluorophosphate, $[Sb(tObpc)(OH)_2]PF_6$

The conversion of the triiodide to hexafluorophosphate was carried out in essentially the same manner as that for the tbpc analogue. To 150 ml of dehydrated acetonitrile solution containing $[Sb(tObpc)(OH)_2]I_3$ (104 mg; 0.095 mmol assuming that the triodide

was analytically pure) was added dehydrated acetonitrile (4.5 ml) containing $AgPF_6$ (3.1 mmol) and the resulting mixture was stirred in the dark at room temperature. Additional acetonitrile (0.5 ml) containing $AgPF_6$ (0.34 mmol) was added after 30 min. After stirring for 30 min in the dark, the reaction mixture was filtered to remove precipitated solid (AgI_3) and the filtrate was evaporated to reduce its volume (30 ml). Crude hexefluorophosphate (103 mg) was obtained by pouring the solution into 150 ml of water and then treating in the same way as that for the tppc analogue. A portion (73 mg) of the crude hexafluorophosphate was dissolved in nitrobenzene (30 ml) to which was added 250 ml of benzene. A small amount of dark brown solid precipitated, which was removed by filtration. To the filtrate was added 300 ml of hexane to precipitate the desired product. This procedure was repeated twice. The solid was collected by filtration and dried at 80 °C under vacuum (31 mg; yield 42% assuming that the starting triiodide was analytically pure). Anal. Found: C, 52.58, H, 4.49, N, 10.33%. Calcd for $[Sb(tObpc)(OH)_2]PF_6$ ($C_{48}H_{50}O_6N_8SbPF_6$): C, 52.33; H, 4.57; N, 10.17%. IR/cm^{-1}; 845 (ν(P-F)) and 558 (δ(F-P-F)).

2.1.6. Synthesis of tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyaninatoantimony(III) triiodide, $[Sb(tppc)]I_3$

This complex was synthesized according to previously reported work [11]. A mixture of 4-(2′,6′-dimethylphenoxy)phthalonitrile (1.0 g; 4.0 mmol) and antimony iodide (0.5 g; 1.0 mmol) was fused in a sealed glass tube at 173 °C for 72 h. The reaction mixture was heated at 130 °C under vacuum for 72 h as was the case for the tObpc analogue. The desired product was extracted by CH_2Cl_2–MeOH mixed solvent (4:1 (v/v); 250 ml) and the solvent evaporated. The ensuing residue was washed with a 100 ml of CH_2Cl_2/hexane (8:42 (v/v)) until the washing turned essentially colorless and dried at 80 °C under vacuum to obtain a 1090 mg of crude product. A portion (890 mg) of the solid was dissolved in acetone (24 ml), to which was added 76 ml of water to precipitate the desired compound. The solid was collected by centrifugation, washed with acetone/water (1:4 v/v) until the washing turned essentially colorless, and then dried at 80 °C under vacuum. This solid was dissolved in CH_2Cl_2 (20 ml), and, after being filtered, the solvent was evaporated. The resulting solid was recrystallized from CH_2Cl_2/hexane (10:40 (v/v)), washed with the same solvent system, and dried at 80 °C under vacuum to obtain 732 mg of crude product, which was found to be the desired compound using ESI-MS (m/z = 921 (^{121}Sb(tObpc))$^+$ and 923 (^{123}Sb(tObpc))$^+$ in acetonitrile) and absorption spectra (λ_{max} = 771 nm in CH_2Cl_2). Yield; 49% (assuming that this is analytically pure). Although it is not sufficiently pure at this stage, this compound was used in the next procedure as is the case for tObpc analogue.

2.1.7. Synthesis of dihydroxo[tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyaninato]antimony(V) triiodide, $[Sb(tppc)(OH)_2]I_3$

The hydroxoantimony(V) derivatives was also synthesized according to previous work [16]. 730 mg of the crude $[Sb(tppc)]I_3$ (0.49 mmol assuming this material is analytically pure) was dissolved in *tert*-butyl perbenzoate (7.0 ml) and the solution was heated at 50 °C with vigorous stirring for 30 min. The reaction was monitored by measuring optical absorption spectra of the solution (in CH_2Cl_2 solution). After the most prominent band at 771 nm ([Sb(tppc)]$^+$) disappeared and a new band grew at 737 nm, the mixture was ice-cooled to quench the reaction. 93 ml of hexane was added to the mixture to precipitate the product. The solid was collected by centrifugation, washed with 50 ml of CH_2Cl_2/hexane (1:9 (v/v)) until the washing turned essentially colorless, and then dried at 80 °C under vacuum (691 mg). This was dissolved in benzene (40 ml), filtered and, to the filtrate, was added 150 ml of hexane to precipitate the desired compound (this procedure was repeated twice). The solid was collected by centrifugation, washed with a 400 ml of benzene/hexane (1:4 (v/v))and dried at 80 °C under vacuum (515 mg). The solid was again dissolved in acetone (10 ml) and precipitated by the addition of water (40 ml); this procedure was repeated 4 times until a considerable amount of solid became dispersed in the aqueous phase after centrifugation. The ensuing colloidal solution, to which 3 ml of aq Na_2SO_4 solution (~1 M) had been added, was centrifuged to remove the aqueous phase. The solid was dried at 80 °C under vacuum and then was dissolved in CH_2Cl_2 (25 ml) and filtered to remove Na_2SO_4. The solvent was evaporated and the desired compound was recrystallized from CH_2Cl_2/hexane (6:45 (v/v)), washed with a 50 ml of CH_2Cl_2/hexane (1:9 (v/v)), and dried at 80 °C under vacuum (371 mg; yield 50% assuming that both the starting antimony(III) derivative and the product were analytically pure). This product has been found to be the desired compound by ESI-MS (m/z = 1147 (^{121}Sb(tppc)(OH)$_2$)$^+$ and 1149 (^{123}Sb(tppc)(OH)$_2$)$^+$ in acetonitrile). Anal. Found: C, 53.92, H, 3.65, N, 7.85%. Calcd for $[Sb(tppc)(OH)_2]I_3$ ($C_{64}H_{50}O_6N_8SbI_3$): C, 50.25; H, 3.29; N, 7.33%. As is the case for tObpc analogue, we did not make further efforts to purify this product.

2.1.8. Synthesis of dihydroxo[tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyaninato]antimony(V) hexafuluorophosphate, $[Sb(tppc)(OH)_2]PF_6$

The conversion of the triiodide to hexafluorophosphate was carried out using the same method as that recounted for the tObpc analogue. To 10 ml of a dehydrated acetonitrile solution containing $[Sb(tppc)(OH)_2]I_3$ (460 mg; 0.30 mmol assuming that the triodide was analytically pure), was added a dehydrated acetonitrile solution (40 ml) containing $AgPF_6$ (2.0 mmol). The ensuing mixture was stirred for 42 h in the dark at room temperature and the reaction mixture was then filtered to remove precipitated solid (AgI_3) and the crude hexefluorophosphate (291 mg) was obtained by pouring the filtrate into 50 ml of water and then treating in the same way as that for the tppc and tObpc analogues. The solid was dissolved in 100 ml of benzene and the solution filtered to remove insoluble solids; this procedure was repeated (three times in this case) until nothing remained on the filter. The filtrate was evaporated to reduce its volume to 20 ml and then 120 ml of hexane was added to precipitate the desired product, which was collected by filtration and dried at 80 °C under vacuum (167 mg (0.13 mmol); yield 45% assuming that the starting triiodide was analytically pure). Anal. Found: C, 59.53, H, 4.16, N, 8.71%. Calcd for $[Sb(tppc)(OH)_2]PF_6$ ($C_{64}H_{50}O_6N_8SbPF_6$): C, 59.41; H, 3.90; N, 8.66%. IR/cm^{-1}; 847 (ν(P-F)) and 558 (δ(F-P-F)).

2.1.9. Synthesis of dichloro[tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyaninato]antimony(V) tetrachloroantimonate(III), $[Sb(tppc)Cl_2]SbCl_4$

The dichloroantimony(V) derivatives was synthesized according to previous work [15]. A mixture of 250 mg of crude $[Sb(tppc)]I_3$ (0.17 mmol assuming this material is analytically pure) and a 4.0 ml of sulfuryl chloride (Wako; 50 mmol) was allowed to react at room temperature with vigorous stirring for 30 min. The reaction was monitored by measuring absorption spectra of the reaction mixture in CH_2Cl_2. After a sharp band at 757 nm (attributable to the desired product) appeared and a less sharp band ~771 nm (the starting material) completely disappeared, the reaction was quenched by precipitating the product by addition of hexane (45 ml) to the mixture. The precipitate was separated from the solution by centrifugation and was twice washed with CH_2Cl_2/hexane (2:48 v/v) until the washing turned essentially colorless, and then dried under vacuum at 80 °C. This solid was dissolved in CH_2Cl_2 (45 ml) and the solution was filtered three times until nothing remained on the filter. The solvent was evaporated to obtain the crude, dark brown product (238 mg) which was again dissolved in benzene (45 ml) and the solution was filtered three times until nothing remained on the filter.

To the filtrate was added 200 ml of hexane to precipitate the solid which was collected by filtration, washed with hexane (20 ml), and dried at 80 °C under vacuum (134 mg; 0.093 mmol. Yield 54% assuming the starting material was analytically pure). This has been identified as the desired product by ESI-MS in acetonitrile (the isotopic pattern was so complicated that readers should see the Supporting material). Anal. Found: C, 52.92, H, 3.26, N, 7.70%. Calcd for $[Sb(tppc)Cl_2]SbCl_4$ ($C_{64}H_{54}O_4N_8Cl_6Sb_2$): C, 53.04; H, 3.34; N, 7.73%.

Our attempts to prepare the corresponding hexafluorophosphate in a similar way to that for $[Sb(tppc)(OH)_2]PF_6$ were unsuccessful. Treatments with $AgPF_6$ in acetonitrile just resulted in recovery of the starting $SbCl_4^-$ salt.

2.1.10. Synthesis of [tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyaninato]copper(II), [Cu(tppc)]

To a hexanol (3 ml) solution containing a mixture of 4-(2′,6′-dimethylphenoxy)phthalonitrile (2.0 mmol) and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU; 4.0 mmol), was added 1.3 mmol of CuCl. The mixture was refluxed at 80 °C with stirring for 64 h. After the mixture was allowed to cool to room temperature, 50 ml of ethanol was added to precipitate the product, which was collected by centrifugation, washed twice with ethanol (50 ml) until the washing turned essentially colorless, and dried at 80 °C under vacuum (452 mg). This was dissolved in chloroform and passed through a silica gel (Merck Silicagel 60) column to remove dark brown impurities which were strongly adsorbed on silica. This was further chromatographed over a silica gel column (Merck Silicagel 60; chloroform) and then recrystallized from chloroform/hexane, and dried at 80 °C under vacuum to obtain a 300 mg (0.28 mmol; yield 57% vs. phthalonitrile) of the desired compound. MS (MALDI; 2,3-dihydroxybenzoic acid as a matrix); m/z = 1055 (M^+) Anal. Found: C, 72.24, H, 4.64, N, 10.40%. Calcd for [Cu(tppc)] ($C_{64}H_{48}O_4N_8$): C, 72.75; H, 4.58; N, 10.60%.

2.1.11. Synthesis of tetrakis{4-(2′,6′-dimethylphenoxy)} phthalocyanine, H_2tppc

A hexanol (5 ml) solution containing a mixture of 4-(2′,6′-dimethylphenoxy)phthalonitrile (4.0 mmol) and 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU; 7.6 mmol) was refluxed at 80 °C with stirring for 94 h. After the mixture was allowed to cool to room temperature, 50 ml of ethanol was added to precipitate the product, which was collected by centrifugation, washed twice with ethanol (50 ml) until the washing turned essentially colorless, and dried at 80 °C under vacuum (653 mg). This was dissolved into chloroform and passed through a silica gel (Merck Silicagel 60) column to remove dark brown impurities which strongly adsorb on silica. This was further chromatographed over a silica gel column (Merck Silicagel 60; benzene/chloroform (1:1)) and then recrystallized from chloroform/hexane, and dried at 80 °C under vacuum to obtain a 260 mg (0.26 mmol; yield 52% vs. phthalonitrile) of the desired compound. MS (MALDI; no matrix); m/z = 994 (M^+). Anal. Found: C, 76.98, H, 5.34, N, 10.97%. Calcd for H_2tppc ($C_{64}H_{50}O_4N_8$): C, 77.24; H, 5.06; N, 11.26%.

All the other chemicals were of reagent grade and used without further purification.

2.2. Measurements

All the measurements of optical absorption spectra were performed with a Shimadzu UV-160A, a Shimadzu UV-1800, or a Hitachi U-3500 spectrophotometer at room temperature (24 ± 1 °C). Magnetic circular dichroism (MCD) spectra were recorded on a JASCO J-720 spectropolarimeter equipped with a JASCO MCD-104 electromagnet, which is capable to generate magnetic fields of up to 0.8 T. A constant field of a magnitude of 0.65 T was applied to sample solutions during the measurements. ESI-MS spectra were measured with a JEOL-JMS-T100LC mass spectrometer both in the positive and negative modes. MALDI-TOF mass spectra were recorded on a Bruker-Daltonics-Autoflex mass spectrometer operating in the positive ion mode.

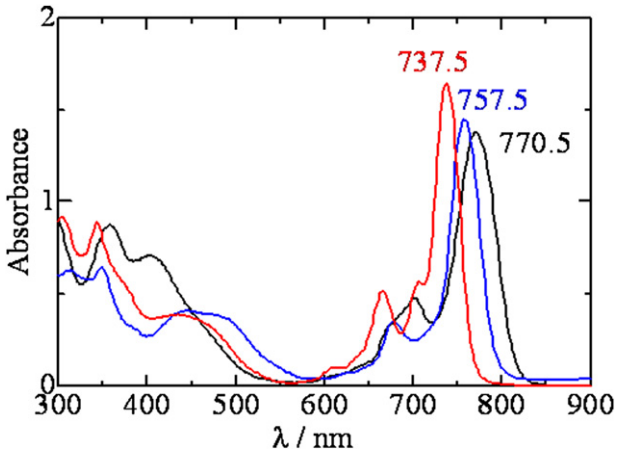

Fig. 2. Spectral changes of $[Sb(tppc)]I_3$ in CH_2Cl_2 before and after oxidation; before oxidation (black solid line), after oxidation with perbenzoate (red), and after SO_2Cl_2-oxidation (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3. Results and discussion

3.1. Oxidation of antimony

Although both pentavalent and trivalent antimony gives rise to a significant red-shift of Q-band [9–19], we decided to employ the former derivatives because antimony ion in the latter is known to be labile and hence antimony(III) complexes are readily demetallated to form H_2Pc[1] [11,14]. The desired $[Sb(Pc)X_2]^+$ (X = OH^- or Cl^-) complexes have been successfully synthesized through oxidative addition process using organic peroxide (for X = OH^-) and sulfuryl chloride (X = Cl^-) as the oxidant. Fig. 2 shows typical spectral changes between before and after the oxidation of $[Sb(tppc)]^+$ with *tert*-butyl perbenzoate and SO_2Cl_2. The broad absorption band at around 770 nm attributable to the starting $[Sb(tppc)]^+$ disappeared and a new sharp band around 737 nm (for X = OH^-) and 755 nm (X = Cl^-) grew in intensity. The spectra of the products are characteristic of antimony(V) derivatives [9,10,12–19,21]. The oxidation with SO_2Cl_2 is very rapid and completed within a few minutes even at room temperature. On the other hand, the reaction with peroxide is rather slow and it takes 30–40 min at 50 °C to complete. Although heat accelerates the oxidation, the desired product is considered unstable in the presence of peroxide [14,16]. Actually when the mixture was allowed to react at 80 °C, the oxidation more rapidly proceeded, but the reaction mixture turned colorless within 1 h. Therefore, we made efforts to keep the reaction temperature around 50 °C or below.

A trace amount of byproducts ($[Sb(Pc)(OH)(benzoate)]^+$; where Pc = pc and tbpc, benzoate = $C_6H_5COO^-$) have been detected in ESI-MS spectra of crude oxidation products although we obtained analytically pure dihydroxo species at the final stage [14,16]. This is the case also for the tppc and tObpc analogues. In particular, in the case of tObpc derivative, we have obtained different products under some experimental conditions. Under conditions described in the

[1] When we do not want to specify peripheral substituents on phthalocyanine, we hereafter refer to the macrocyclic ligand as Pc.

experimental section, the oxidation almost exclusively gave [Sb(tObpc)(OH)$_2$]$^+$. However, when the starting [Sb(tObpc)]I$_3$ was not sufficiently purified (in particular, when the sublimation procedure was skipped), the crude products included not only [Sb(tObpc)(OH)$_2$]$^+$ but also [Sb(tObpc)(OH)(benzoate)]$^+$ and [Sb(tObpc)(benzoate)$_2$]$^+$ in comparable ratio (all the species have been detected by ESI-MS). Under some conditions, the product was exclusively composed of [Sb(tObpc)(benzoate)$_2$]$^+$. We could isolate neither [Sb(tObpc)(OH)(benzoate)]$^+$ nor [Sb(tObpc)(benzoate)$_2$]$^+$ because of lack of reproducibility of the experiments, but the benzoato species can be easily distinguished from the desired dihyroxo species by absorption spectroscopy because the Q-band maximum wavelengths of the formers are longer than that of the latter (e.g., λ_{max} = 752 nm for [Sb(tObpc)(benzoate)$_2$]$^+$ in CH_2Cl_2 whereas 741 nm for [Sb(tObpc)(OH)$_2$]$^+$). We did not make efforts to synthesize the di(benzoato) species for the aforementioned reason. It seems that SbI_3 can facilitate acylation of the axial hydroxyl groups.

3.2. Colors of the complexes

Fig. 3 shows the optical absorption spectra of [Sb(tppc)(OH)$_2$]$^+$, [Sb(tppc)Cl$_2$]$^+$, and [Sb(tObpc)(OH)$_2$]$^+$ in CH_2Cl_2 and those of [Cu(tppc)] and H$_2$tppc for comparison. The spectra of [Cu(tppc)] and H$_2$tppc are characteristic of normal metal- and metal-free Pcs, respectively [4–6]. The two species intensely absorb red light (Q-band) while they are essentially transparent in the window region as mentioned in the introduction and hence they show a blue color (Fig. 4). It should be noted that the position of the Q-band does not change very much depending on the nature of the central metal apart from some exceptions [4–6]. On the other hand, although the spectra of antimony(V) derivatives are similar to that of copper derivative and hence are characteristic of monomeric metal–Pc complexes, their Q-band significantly red-shifts by ca. 1000–1200 cm^{-1} as is the case for antimony(V) derivatives [9,10,12–19,21]. In addition to that, an extra broad band appeared in 400–550 nm region, where normal Pcs (e.g., [Cu(tppc)] and H$_2$tppc) are essentially transparent. Hence coloration due to the extra band is outstanding, making the antimony (V) derivatives to show a non-blue color. The [Sb(tppc)(OH)$_2$]$^+$ and [Sb(tObpc)(OH)$_2$]$^+$ look more bluish than [Sb(tppc)Cl$_2$]$^+$ because the Q-band of dihydroxo species is located at a slightly shorter wavelength than that of the corresponding dichloro species [14–16] and hence the presence of a weak satellite band at a blue flank of the Q-band (660–670 nm; assigned as vibronic structures of Q-band [4–6]) makes the Pcs blueish. Careful comparison between the tppc and tObpc analogues finds that the Q-band of [Sb(tObpc)(OH)$_2$]$^+$ is much broader (its full width of half maxima is 1027 cm^{-1}) than those of [Sb(tppc)(OH)$_2$]$^+$ (752 cm^{-1}) and the corresponding pc (497 cm^{-1}) [14] and tbpc (695 cm^{-1}) [15] analogues. This is probably due to aggregation of [Sb(tObpc)(OH)$_2$]$^+$. It is well known that aggregation of Pc macrocycles gives rise to a significant spectral change due to exciton coupling [4–6]. As the presence of the axial OH ligands in [Sb(tObpc)(OH)$_2$]$^+$ molecule prevents aggregation in a face-to-face manner (i.e., H-aggregation), this species is likely to J-aggregate. This has been evidenced by the red-shift of the Q-band [32] as shown in Fig. 5, in which absorption spectra of [Sb(tObpc)(OH)$_2$]PF$_6$ in CH_2Cl_2 at various concentrations are compared. The spectra are similar but the apparent molecular extinction coefficient at around the Q-band decrease whereas those at the red-flank of the Q-band increase with an increase in concentration. We have reported that, unlike majority of Pcs [11,25–31], absorbance at Q-band maxima of antimony(V) derivatives obey Lambert–Beer's law in the concentration range where absorption spectra can be monitored by using optical cells with a path length of 1–10 mm [10,12,14,16]. This is probably because of steric hindrance due to the presence of axial ligands as well as electric repulsion due to their positive charge [12]. It is well known that Pcs bearing long alkyl chains as peripheral substituents behave as liquid crystals [33]. Likewise, the presence of the four *n*-butoxyl groups (though not so long) may allow this species to aggregate more easily than the tppc and tbpc analogues.

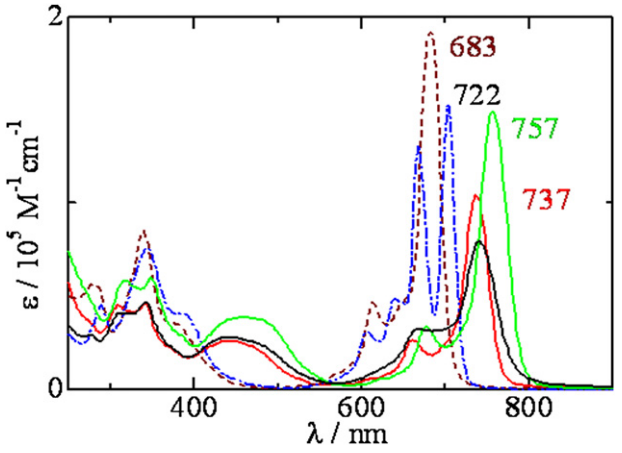

Fig. 3. Optical absorption spectra of [Sb(tppc)(OH)$_2$]PF$_6$ (red solid line), [Sb(tppc)Cl$_2$]SbCl$_4$ (green solid), [Sb(tObpc)(OH)$_2$]PF$_6$ (black solid), [Cu(tppc)] (brown broken), and H$_2$tppc (blue dot-dash) in CH_2Cl_2. All the spectra were measured in the concentration range (below 5 × 10^{-6} M) where absorbance obeyed Lambert–Beer's law and hence effects of aggregation are negligible. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.3. Absorption spectra in the Soret and extra band region

Since optical absorption by PF_6^- and $SbCl_4^-$ is negligible in this region [19,34], we may assume that all the absorption bands observed are ascribable to the antimony-Pcs. The spectra of [Sb(tObpc)(OH)$_2$]$^+$, [Sb(tppc)(OH)$_2$]$^+$, and [Sb(tppc)Cl$_2$]$^+$ in 250–550 nm region are similar to each other. All the three species show a broad band at around 400–550 nm and three bands at around 350, 310, and 270 nm although the latter one is observed as a shoulder for the tppc derivatives. Each absorption band of [Sb(tppc)Cl$_2$]$^+$ slightly red-shifts as compared to the corresponding band of [Sb(tppc)(OH)$_2$]$^+$ as is the case for tbpc analogues [10,15,16]. Absorbance of the two tppc derivatives in 250–300 nm is higher than that of the tObpc analogue probably because of the presence of peripheral phenoxyl groups. Gouterman and his coworkers have expected on their calculation study that some degenerate π–π* transitions should appear for phthalocyanines in UV region (B, N, L, and C bands going from lower to higher energy) [4,35]. A few decades later, Stillman and his coworkers have shown that the lowest energy absorption band in the UV region should be a mixture of two π–π* transitions and hence they have argued that this band should be called as B1 and B2 bands [4,36,37]. We have reported absorption spectra of [Sb(pc)(OH)$_2$]PF$_6$ and assigned that the absorption bands observed in near-UV region as such [14]. It should be noteworthy that these bands, except the B1/B2 bands, are hardly observed for majority of phthalocyanines in solution because common organic solvents normally absorb UV light and hence the other bands are hidden in the solvent absorption. Actually, available spectral data were limited to those observed in vapor phase, thin film, or Ar matrix [35–39]. The significant red-shifts of the π–π* transitions for antimony(V) derivatives (e.g., red-shifted by ca. 1000–1200 cm^{-1} for Q-band as compared to copper analogue) may have allowed us to observe these transitions in solution phase [16].

It is known that some Pcs show one or more extra bands in the "window" region. For example, one-electron-oxidized Pcs (e.g. radical cation, pc$^{-\bullet}$) show a characteristic band around 500 nm, which makes the Pcs red or orange [40]. However, as

Fig. 4. The colors of CH_2Cl_2 solutions containing H_2tppc, [Cu(tppc)], [Sb(tppc)Cl_2]$SbCl_4$, [Sb(tppc)$(OH)_2$]PF_6, and [Sb(tObpc)$(OH)_2$]PF_6,(on going from the leftmost to the rightmost). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

electrochemical studies on antimony(V)-Pcs have found that they are easy to reduce ($E_{1/2}(pc^{2-}/pc^{3-})$ = ca. −0.2 V vs. ferricinium/ferrocene) while hard to oxidize ($E_{1/2}(pc^{-}/pc^{2-})$ = ca. 1.3 V) [9,13,15,18,19], it is unlikely that antimony(V) derivatives are oxidized under such conditions. Some Pcs containing a transition metal (e.g. manganese(II) [41,42], iron(II) [43], cobalt(I) [25,43–45], etc) in their cavity are also known to show an extra band around 500 nm [4–6], which has been assigned as a charge transfer (MLCT or LMCT) band. But this possibility may also be excluded because antimony(V) belongs to the main group and has a closed shell. Kobayashi and his coworkers have attributed the appearance of extra bands for main–group complexes of octaphenyl-substituted derivatives to an enhanced metal-ligand (Pc) interaction due to a significant deformation of the Pc ligand from planarity [7]. However, such an interaction cannot be expected in this case because tObpc and tppc ligands are both planar. The possibility that the origin of the extra bands can be a n–π* transition (involving lone pairs in the peripheral substituents) in character will be found unlikely in the following discussion.

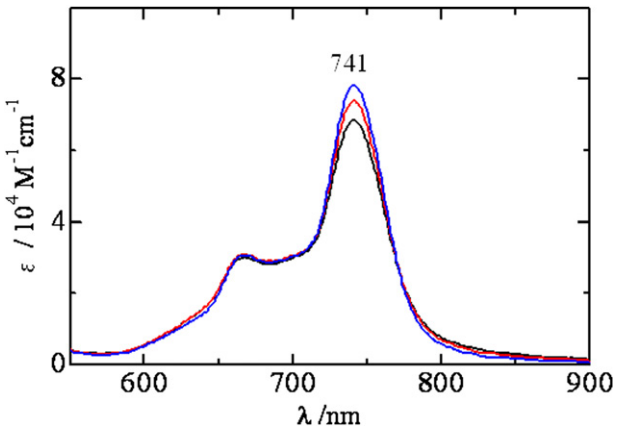

Fig. 5. Optical absorption spectra (around the Q-band) of [Sb(tObpc)$(OH)_2$]PF_6 in CH_2Cl_2 at various concentrations; 2.28×10^{-4} M (black), 1.14×10^{-4} M (red), and 1.43×10^{-5} M (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

3.4. MCD (magnetic circular dichroism) study

In order to investigate the origin of the extra band, MCD spectra of [Sb(tObpc)$(OH)_2$]PF_6 and [Sb(tppc)$(OH)_2$]PF_6 in CH_2Cl_2 solution have been studied as well as the corresponding tetra-*tert*-butyl and unsubstituted analogues for comparison (Fig. 6). Both the optical absorption and MCD spectra for tObpc and tppc complexes are essentially the same, apart from the broadening of the Q-band for [Sb(tObpc)$(OH)_2]^+$ and slightly higher absorbance for [Sb(tppc)$(OH)_2]^+$ in the 250–300 nm regions as described above. The MCD spectra of the two species around the Q-band show a distinct *s*-shaped curve centered at the absorption maximum wavelength and hence this signal is dominated a Faraday's A-term indicating that this transition is orbitally degenerate [4]. This is also the case for tbpc and pc analogues. This band is assigned as an electronic transition from non-degenerate HOMO to doubly degenerate LUMO [4,36,37]. At the blue flank of the Q-band, are observed two less intense Gaussian signals of a positive and negative sign with their peak and valley wavelengths centered at the absorption maximum wavelengths. These signals are dominated by a Faraday's B-term indicating that these transitions are orbitally non-degenerate. These bands are assigned as vibronic progressions of the Q-band [4]. If the extra absorption around 500 nm is composed of a single band, the corresponding MCD spectra should be dominated by either a Faraday's A-term or a B-term. Nevertheless, the spectra around the 400–550 nm are quite complicated, suggesting that this absorption should be an overlapping of more than one band. It is easily found that both the absorption and MCD spectra in 250–370 nm region are close to each other for the four [Sb(Pc)$(OH)_2]^+$ complexes; three weak absorption bands around 350, 310, and 270 nm and three s-shaped curves centered at the absorption maximum wavelengths. We have studied optical absorption and MCD spectra of [Sb(pc)$(OH)_2]^+$ and assigned the three bands as degenerate N, L, and C bands after Gouterman's nomenclature, going from lower to higher energy [14]. Therefore, we may likewise assign those bands for the other three complexes. The absorption band around 400 nm for tbpc derivative may be assigned as B1/B2 bands based on the analogy with the unsubstituted derivative. Careful comparison among the four complexes has found that a broad band around 370–450 nm region (tentatively assigned as B1/B2 bands above) observed for

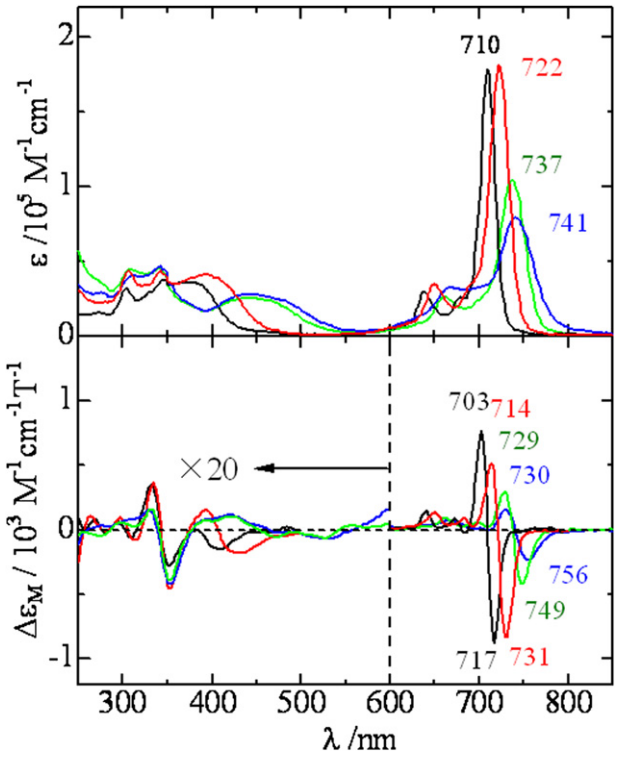

Fig. 6. Optical absorption (top) and MCD (bottom) spectra of $[Sb(tppc)(OH)_2]PF_6$ (green) $[Sb(tObpc)(OH)_2]PF_6$ (blue), $[Sb(tbpc)(OH)_2]PF_6$ (red), and $[Sb(pc)(OH)_2]PF_6$ (black), in CH_2Cl_2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

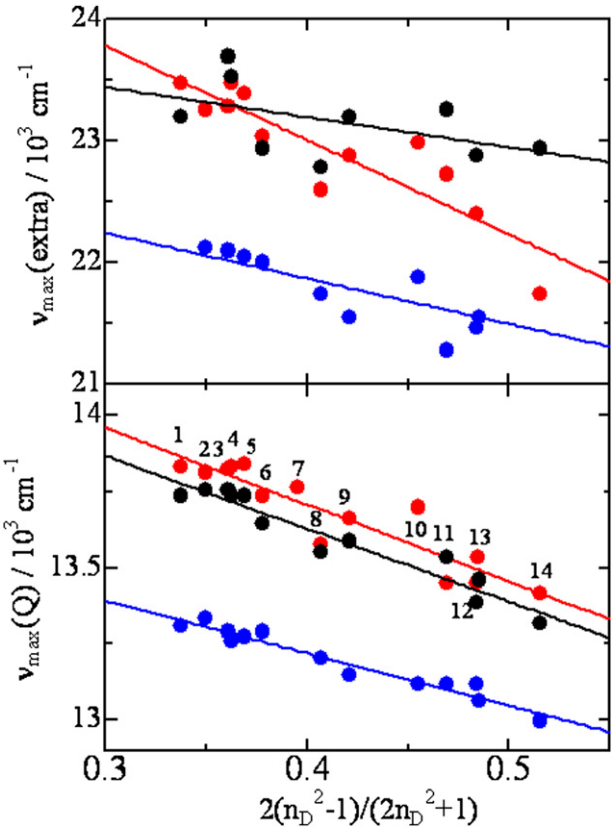

Fig. 7. Plots of the peak positions of the extra bands (top) and Q-bands (bottom) of $[Sb(tppc)(OH)_2]PF_6$ (red circles) $[Sb(tObpc)(OH)_2]PF_6$ (black), $[Sb(tppc)Cl_2]SbCl_4$ (blue) in various solvents against the refractive indices of the solvents in the form of Onsagar's solvent optical polarity function. The numbers (1–14) in the figure denote as follows: 1; methanol, 2; acetonitrile, 3; acetone, 4; ethanol, 5; ethyl acetate, 6; nitromethane, 7; THF, 8; CH_2Cl_2, 9; $CHCl_3$, 10; C_6H_6, 11; chlorobenzene, 12; *o*-dichlorobenzene, 13; nitorbenzene, 14; *o*-dibromobenzene. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

unsubstituted and *tert*-butyl-substituted derivatives is missing in the spectra of the tObpc and tppc analogues. Interestingly, MCD spectra around the extra bands of the tppc and tObpc derivatives are similar to those around the B1/B2 bands of the other two. Therefore, both the absorption and MCD spectra of the four species are essentially the same if we assume that the extra bands for tppc and tObpc derivatives and the broad bands around 400 nm for $[Sb(pc)(OH)_2]^+$ and $[Sb(tbpc)(OH)_2]^+$ have the same origin and that these bands red-shifted in the same order as that for the Q-band (i.e., pc < tbpc < tppc < tObpc). If this is true, it is quite unlikely that the extra bands are n–π* transitions in character, because pc and tbpc do not have a lone pair in their peripheral substituents. Thus, it seems reasonable to assign the extra bands as their B1/B2 bands for $[Sb(tppc)(OH)_2]^+$ and $[Sb(tObpc)(OH)_2]^+$, as is the case for the pc and tbpc analogues.

It seems that the intensity of Q-band tends to decrease (pc > tbpc > tppc > tObpc) as the band red-shifts and at the same time that of the corresponding Faraday's A-term lowers in this order. Similar tendency has been reported elsewhere [46,47] but a clear-cut explanation to these phenomena has not been given until today.

3.5. Solvent effects

As $[Sb(tObpc)(OH)_2]^+$, $[Sb(tppc)(OH)_2]^+$, and $[Sb(tppc)Cl_2]^+$ are all soluble in many of common organic solvents, solvent-dependence of their absorption spectra have been studied. Both $[Sb(tppc)(OH)_2]^+$ and $[Sb(tppc)Cl_2]^+$ show small but non-negligible shifts in peak positions of their Q-band and the extra band although the spectra in solutions are essentially the same as that in CH_2Cl_2 (Fig. 3). In Fig. 7, is shown the solvent-dependence of the extra (top) and Q-bands (bottom) of the two complexes as a function of refractive indices in the form of Onsagar's solvent polarity function. Both the complexes show the same tendency in that their Q-band appears at a longer wavelength in a solvent with a larger refractive index. We have reported fairly good linear correlations between Q-band positions of some metal–phthalocyanine complexes in solution and refractive indices of the solvents unless the solvent induces a chemical reaction involving the phthalocyanines or gives rise to a specific chemical interaction with the chromophore [12]. This phenomenon can be rationalized in terms of stabilization of the Franck-Condon excited state of the chromophore by an interaction between the transition dipole moment in the chromophore and induced dipole moment generated temporarily in the surrounding solvent molecules [48]. That is, the Q-band position in a specific solvent is determined by the optical polarizability of the solvent alone unless chemical interaction is involved [12]. The plots for $[Sb(tppc)(OH)_2]^+$ are considerably deviated from linearity unlike the case for $[Sb(tppc)Cl_2]^+$. This indicates the presence of some chemical interaction between the chromophore and the surrounding solvent molecules through the axial OH groups (e.g., hydrogen bonding) [14,16]. The extra bands (Fig. 7 top) similarly behave in that they appear at a longer wavelength in a solvent with a large refractive index. This suggests that the extra band should be of the same character as that of Q-band (i.e., mainly a π–π* transition) and hence support the assignment of this band as the Soret (B1/B2) band. The poor linear relationship of the extra band than

that of Q-band is understandable if the assignment is correct, because it is known that scattering of plots for Soret band is more significant than those for Q-band in solvatochromism of metal-free porphyrins [49]. This is because the Q-band of Pcs is an essentially pure monoelectonic transition while the Soret band is a mixture of a few transitions with comparable ratios [4]. In addition to that, we have reported that the solvent-dependence of B1/B2 bands is much more significant than that of Q-band for $[Sb(pc)(OH)_2]^+$ [14].

The solvatochromic behavior of the *n*-butoxyl-substituted derivative is more rigorous than those of the tppc analogues because of the presence of more or less aggregation effects (as mentioned above). It is well known that susceptibility to aggregation depends on the nature of the solvent system [50,51]. The much more scattered plots for tObpc derivative than the tppc analogues may be rationalized as follows. Aggregation of Pc macrocycles generally gives rise to a significant spectral change, like blue-/red-shift, broadening, or splitting of the absorption band, as mentioned above. In particular, as the extra band is considerably broadened unlike the well-isolated Q-band, presence of any small portion of aggregated species can shift the absorption maximum wavelength. Eventually, Fig. 7 shows considerably scattered plots for tObpc derivative with respect to the extra band.

4. Conclusions

Three novel antimony(V) phthalocyanines that show an amber color have been synthesized by cyclic tetramerization of alkoxyl- and phenoxyl-substituted phthalonitrile in the presence of SbI_3 and then by oxidizing the produced antimony(III)-Pcs with *tert*-butyl perbenzoate or sulfuryl chloride through an oxidative addition process. They show an amber color in solution unlike normal Pcs. Their non-blue coloration is attributable to a significant red-shift of the Q-band and appearance of a new broad band around 400–500 nm (where normal Pcs do not absorb light). MCD and solvent-dependence study on the extra band have suggested that this band should be significantly red-shifted Soret (B1/B2) band.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.dyepig.2010.06.007.

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