

O-Alkylation of Dihydroxo(tetraarylporphyrinato)phosphorus(V) and Antimony(V) Complexes with Alkyl Halides

Yoshito Andou, Kazuki Ishikawa, Kensuke Shima, Tsutomu Shiragami,* Masahide Yasuda, and Haruo Inoue

Department of Applied Chemistry, Faculty of Engineering, Miyazaki University, and CREST, JST(Japan Science and Technology), Gakuen-Kibanadai, Miyazaki 889-2192

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The *O*-alkylation of dihydroxo(tetraarylporphyrinato)phosphorus(V) complexes with several kinds of alkyl bromide in MeCN in the presence of K_2CO_3 and 18-crown-6 ether produced dialkoxo(tetraarylporphyrinato)phosphorus(V) complexes in-moderate-good yields. Similar *O*-alkylation was applied to dihydroxo(tetraarylporphyrinato)antimony(V) complexes. The *O*-alkylation proceeded by the occurrence of an S_N2 attack of the alkoxide anion of the complexes at the carbon substituted with halides.

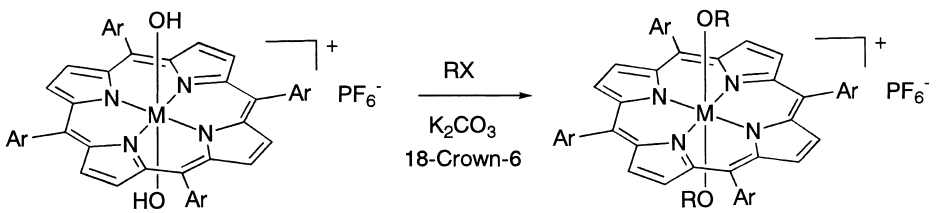
Porphyrinatometal complexes are chemically and biologically important molecules that have versatile catalytic capabilities in an electron-transfer reaction or energy transfer.[1] Therefore, a number of porphyrinatometal complexes have been synthesized.[2] Our interests have been paid to high-valent porphyrinatophosphorus(V) and antimony(V) complexes having a variety of axial ligands from the standpoints of the photoelectronic properties, redox electrochemistry, and catalytic activities.[3,4] However, convenient methods to introduce axial ligands to the porphyrinatoantimony or phosphorus complexes have rarely been reported.

The synthesis of dialkoxo-coordinated tetraarylporphyrinatophosphorus(V) and antimony(V) complexes ([M(TAP)-$(OR)_2$]; M = P and Sb, TAP = tetraarylporphyrinato group) can be achieved by a substitution reaction of $[M(TAP)Br_2]$ with ROH or an alkylation reaction of $[M(TAP)(OH)_2]$ with RX (X = halide, tosylate etc.). However, the yields of the reaction of $[M(TAP)Br_2]$ with ROH have usually been low. Segawa and Shimidzu have preliminarily reported the *O*-alkylation of dihydroxo(tetraphenylporphyrinato)phosphorus ([P-$(TPP)(OH)_2$]; TPP = tetraphenylporphyrinato group) with alkyl halides (RX).[5] In order to develop a convenient and efficient method to prepare $[M(TAP)(OR)_2]$ (M = P and Sb), we investigated the scope and limitation of the *O*-alkylation of $[M(TAP)(OH)_2]$ complexes with RX.

Result and Discussion

As the starting materials, we used dihydroxo(tetraarylporphrinato)phosphorus(V) and antimony(V) hexafluorophosphate complex ($[P(TMP)(OH)_2]$ and $[M(TPP)(OH)_2]$; M = P and Sb, TMP = tetra(*p*-methoxyphenyl)porphyrinato group, see Scheme 1), which could be easily prepared by the hydrolysis of $[P(TMP)Cl_2]$, $[P(TPP)Cl_2]$ and $[Sb(TPP)Br_2]$, respectively.[5,6] Shimidzu and co-workers' method involved the *O*-alkylation of $[P(TPP)(OH)_2]$ with RX (R = Me, Et), having good leaving groups (X = I, $OSO_2C_6H_4Me$, OSO_2CF_3), which occurred in DMF in the presence of K_2CO_3 at room temperature.[5] We investigated the *O*-alkylations of $[M(TAP)(OH)_2]$ (M = P and Sb) using RX (X = Br and Cl), which are the more available alkyl reagents.

In attempts to find the optimum conditions, control experiments were performed for the *O*-alkylation of $[P(TMP)(OH)_2]$



$[P(TMP)(OH)_2]$; M= P^V Ar= *p*-$MeOC_6H_4$- **1a-f**; M= P^V Ar= *p*-$MeOC_6H_4$-

$[P(TPP)(OH)_2]$; M= P^V Ar= Ph **1g-m**; M= P^V Ar= Ph

$[Sb(TPP)(OH)_2]$; M= Sb^V Ar= Ph **2a-d**; M= Sb^V Ar= Ph

Scheme 1.

(0.02 mmol) with *n*-PrX (X = Cl, Br, and I; 10–100 mmol) in the presence of K_2CO_3 (0.06 mmol) and 18-crown-6 ether (0.03 mmol) in the solvent (50 mL) under refluxing conditions. As alkylating agents, although *n*-PrBr and *n*-PrI were effective, *n*-PrCl was ineffective. Therefore, we used RBr as alkyl reagents because of easy handling and more available reagents. *O*-alkylation at room temperature required a longer reaction time. K_2CO_3/18-crown-6 was used as a base, because of the occurrence of a relatively clean reaction compared with the cases of other bases (e.g. pyridine, Et_3N, and NaH). It was found that MeCN and THF were better solvents, since *O*-alkylation with *n*-PrBr proceeded effectively. DMF was a poor solvent because of the occurrence of demetallation from the porphyrin complex, although Segawa et al. succeeded to carry out *O*-alkylation in DMF at room temperature.[5] Probably K_2CO_3 served as a stronger base under refluxing conditions to lead the demetallation. Therefore, *O*-alkylations were performed in MeCN in the presence of K_2CO_3/18-crown-6 under refluxing conditions throughout the present investigation.

The reaction progress from [M(TAP)$(OH)_2$] to [M(TAP)$(OR)_2$] (**1** (M = P) and **2** (M = Sb)) was followed by spectral changes of a Soret band of [M(TAP)$(OH)_2$]: λ_{max} = 440 nm for [P(TMP)$(OH)_2$], 424 nm for [P(TPP)$(OH)_2$], and 417 nm for [Sb(TPP)$(OH)_2$]. The structures of **1** and **2** were certainly confirmed by observing common up-field shifts of all protons on the alkyl group in the ^{1}H NMR spectra.

Although the *O*-alkylation of [P(TMP)$(OH)_2$] with *i*-PrBr gave **1b**, that with *i*-PrI did not at all, probably because an elimination of HI from *i*-PrI occurred predominantly. RCl were unreactive, except for the case of $PhCH_2Cl$. In the cases of RBr (R = CH_2=CH–CH_2–, Br$(CH_2)_3$–, and $CH_3(CH_2)_3$–) and $PhCH_2Cl$, the *O*-alkylation products (**1c–e** and **1f**) were obtained. A small amount of free base porphyrin (H_2TMP) was formed as a by-product, except for the case of entry 9. The *O*-alkylation of [P(TPP)$(OH)_2$] with RBr (R = Et, *n*-Pr, and CH_2=CH–CH_2–) and $PhCH_2Cl$ gave [P(TPP)$(OR)_2$] (**1g-i** and **1m**) in moderate-to-good yields. The *O*-alkylation of [P(TPP)$(OH)_2$] with $CH_3(CH_2)_n$Br (n = 5, 7, 9) smoothly gave **1j–l** irrespective of the long alkyl chain. No *O*-alkylation with *t*-BuBr, $HOCH_2CH_2Br$, $NCCH_2CH_2Br$, and $CF_3CH_2CH_2Br$ occurred at all. The present method was applied to the *O*-alkylation of [Sb(TPP)$(OH)_2$] with RBr (R = *n*-Bu, *i*-Pr, CH_2=CH–CH_2–, Br$(CH_2)_3$–) and $PhCH_2Cl$, which gave [Sb(TPP)$(OR)_2$] (**2a–d**) in moderate-to-good yields, except for entry 24. In the case of *i*-PrBr (entry 24), a mono-alkylated complex, [Sb(TPP)(OH)(O-*i*-Pr)] (**3**), was formed without the formation of [Sb(TPP)(O-*i*-Pr)$_2$]. The *O*-alkylation of [Sb(TPP)$(OH)_2$] with *i*-PrI, *t*-BuBr, $BrCH_2CH_2Br$, $NCCH_2CH_2Br$, and $CF_3CH_2CH_2Br$ gave little or no products. The results are summarized in Table 1.

The pK_a values of [M(TAP)$(OH)_2$] were determined based on the spectral change by the addition of KOH: pK_a = 10.0 for [P(TMP)$(OH)_2$], pK_a = 9.5 for [P(TPP)$(OH)_2$], and pK_a = 10.3 for [Sb(TPP)$(OH)_2$]. Therefore, the axial hydroxy group of [P(TMP)$(OH)_2$], [P(TPP)$(OH)_2$], and [Sb(TPP)$(OH)_2$] can be readily dissociated by K_2CO_3. *O*-Alkylation proceeded by the occurrence of an S_N2 attack of [M(TAP)(OH)O^-] at the carbon substituted with halides. In the case of a secondary RX (e.g. *i*-PrBr), the S_N2 attack would be slow to give a mono-alkoxo complex, [Sb(TPP)(OH)(OR)]. The *O*-alkylation of [Sb(TPP)$(OH)_2$] with tertiary RX (e.g. *t*-BuBr) did not occur due to the steric hindrance.

An alternative synthetic method[7] of [Sb(TPP)$(OR)_2$] was attempted by the reaction of [Sb(TPP)Br_2] with ROH. However, the reaction of [Sb(TPP)Br_2] with ROH under refluxing conditions gave a mono-alkoxo complex, [Sb(TPP)(OR)Br]. For example, the reaction of [Sb(TPP)Br_2]$^+Br^-$ with EtOH gave [Sb(TPP)(OEt)Br]$^+Br^-$ (**4**; 95%).

In conclusion, the optimum route to [M(TAP)$(OR)_2$] (M = P and Sb) is the double *O*-alkylation of [M(TAP)$(OH)_2$] (M = P and Sb) with RBr under basic conditions. The present method will be applied to porphyrinatophosphorus and antimony complexes having various functionalized axial ligands.

Experimental

^{1}H NMR spectra were taken in $CDCl_3$ using tetramethylsilane as an internal standard on a Bruker AC 250P spectrometer at 250 MHz. UV spectra were measured on a Hitachi U2001 spectrometer. SIMS were obtained on a Hitachi M2000A spectrometer. High-resolution FAB-MS were obtained on a JEOL JMS-HX 110A spectrometer using *m*-nitrobenzyl alcohol as a matrix agent.

Materials. Reagents were obtained from the following sources: antimony(III) bromide, chloroform, acetonitrile, potassium carbonate, propyl bromide, isopropyl bromide, and butyl bromide from Nacalai Tesque; anhydrous pyridine, dichloromethane, hexane, methanol, hydrobromic acid, tetrahydrofurane, 18-crown-6 ether, butyl chloride, butyl iodide, propyl iodide, and 1,4-dibromobutane from Wako Pure Chemical Industries; tetraphenylporphyrin, *t*-butyl bromide, 3-bromo-1,1,1-trifluoropropane, benzyl bromide, and 1,3-dibromopropane from Tokyo Kasei; *N*,*N*-dimethylformamide from Katayama Kagaku; silver hexafluorophosphate, phosphoryl chloride, and tetra(4-methoxyphenyl)porphyrin from Aldrich.

General Procedure of *O*-Alkylation. A dry MeCN solution (50 mL) containing RX (1 mL; 10–100 mmol), [M(TAP)$(OH)_2$] (M = P or Sb; 0.02 mmol),[5,6] K_2CO_3 (0.06 mmol), and 18-crown-6 (0.03 mmol) was refluxed at 85 °C under a nitrogen atmosphere. The mixture was cooled, filtered, and concentrated in vacuo. A dichloromethane solution of the crude product was added into hexane to form the precipitate. The dichloromethane solution of the precipitate was washed three times with 50 mL portions of H_2O. After removing the solvent, the crude product was subjected to the column chromatography on silica gel (Fuji-Silysia FL60D) to give [M(TAP)$(OR)_2$].

Dipropoxo[tetra(4-methoxyphenyl)porphyrinato]phosphorus(V) Hexafluorophosphate (1a). UV–vis λ_{max}/nm (log ε) 441 (5.46), 566 (4.08), 612 (3.87); ^{1}H NMR δ −2.48 (4H, dt, $J_{P\text{-}H}$ = 11.4, J = 5.7 Hz, CH_2), −1.50 (4H, m, CH_2), −1.15 (6H, t, J = 7.4 Hz, CH_3), 4.04 (12H, s, OMe), 7.32 (8H, d, J = 8.6 Hz, Ph), 7.88 (8H, d, J = 8.6 Hz, Ph), 9.05 (8H, d, $J_{P\text{-}H}$ = 2.7 Hz, pyrrole). HRMS (FAB) Found: *m*/*z* 881.3468. Calcd for $C_{54}H_{50}N_4O_6P$: M^+, 881.3468. Anal. Calcd for $C_{54}H_{50}N_4O_6P_2F_6{\cdot}C_6H_{14}$: C 64.74; H, 5.80; N, 5.03%. Found: C, 63.84; H, 6.15; N, 4.25%.

Diisopropoxo[tetra(4-methoxyphenyl)porphyrinato]phosphorus(V) Hexafluorophosphate (1b). UV–vis λ_{max}/nm (log ε) 441 (5.46), 566 (4.08), 612 (3.87); SIMS *m*/*z* 881 (M^+); ^{1}H NMR δ −2.8 – −2.5 (2H, m, CH), −2.25– −2.23 (12H, m, CH_3), 4.03 (12H, s, OCH_3), 7.30 (8H, d, J = 8.7 Hz, Ph), 7.89 (8H, d, J = 8.7 Hz, Ph), 9.06 (8H, d, $J_{P\text{-}H}$ = 2.8 Hz, pyrrole).

Bis(allyloxo)[tetra(4-methoxyphenyl)porphyrinato]phos-

Table 1. *O*-Alkylation of [M(TAP)$(OH)_2$](M = P and Sb) with RX[a)]

Entry	M	Y[b)]	R	X	Solvent	Product (Yield/%)
1	P	OMe	*n*-Pr	I	MeCN	**1a** (73)
2	P	OMe	*n*-Pr	Cl	MeCN	**1a** (0)
3	P	OMe	*n*-Pr	Br	MeCN	**1a** (93)
4	P	OMe	*n*-Pr	Br	THF[c)]	**1a** (96)
5	P	OMe	*n*-Pr	Br	DMF[d)]	**1a** (0)
6	P	OMe	*i*-Pr	Br	MeCN	**1b** (91)
7	P	OMe	*i*-Pr	I	MeCN	**1b** (0)
8	P	OMe	CH_2=$CHCH_2$–	Br	MeCN	**1c** (65)
9	P	OMe	$Br(CH_2)_3$–	Br	MeCN	**1d** (100)
10	P	OMe	$CH_3(CH_2)_5$–	Br	MeCN	**1e** (33)
11	P	OMe	$PhCH_2$–	Cl	MeCN	**1f** (77)
12[e)]	P	H	Et	Br	MeCN	**1g** (74)[f)]
13	P	H	*n*-Pr	Br	MeCN	**1h** (91)
14	P	H	CH_2=$CHCH_2$–	Br	MeCN	**1i** (82)
15	P	H	$CH_3(CH_2)_5$–	Br	MeCN	**1j** (24)
16	P	H	$CH_3(CH_2)_7$–	Br	MeCN	**1k** (75)
17	P	H	$CH_3(CH_2)_9$–	Br	MeCN	**1l** (52)
18	P	H	$PhCH_2$–	Cl	MeCN	**1m** (96)
19	Sb	H	*n*-Bu	Br	MeCN	**2a** (73)
20	Sb	H	*n*-Bu	Cl	MeCN	**2a** (0)
21	Sb	H	CH_2=$CHCH_2$–	Br	MeCN	**2b** (86)
22	Sb	H	$Br(CH_2)_3$–	Br	MeCN	**2c** (43)
23	Sb	H	$PhCH_2$–	Cl	MeCN	**2d** (47)
24	Sb	H	*i*-Pr	Br	MeCN	**3** (11)[g)]

a) All reaction was carried out for the solution (50 mL) containing [M(TAP)$(OH)_2$] (0.02 mmol), RX (10–100 mmol), K_2CO_3 (0.06 mmol), and 18-crown-6 (0.03 mmol) at refluxing temperature for 24 h. b) *p*-Substituents on the aryl group of the porphyrin ring (*p*-Y–C_6H_4–; Y = OMe and H). c) Tetrahydrofuran. d) *N*,*N*-Dimethylformamide. e) Reaction for 27 h. f) *O*-Alkylation of $[P(TPP)(OH)_2]^+Cl^-$ with EtI in the presence of K_2CO_3 in DMF at room temperature gave **1g** in 76% yield. See Ref. 5. g) Isolated as [Sb(TPP)(OH)(O-*i* -Pr)] (**3**).

phorus(V) Hexafluorophosphate (1c). UV–vis λ_{max}/nm (log ε) 441 (5.46), 566 (4.08), 612 (3.87); SIMS *m*/*z* 877 (M^+); ^{1}H NMR δ −1.77 (4H, m, CH_2), 2.61–3.65 (6H, m, CH=CH_2), 4.03 (12H, s, OCH_3), 7.30 (8H, d, J = 8.7 Hz, Ph), 7.87 (8H, d, J = 8.7 Hz, Ph), 9.06 (8H, d, $J_{P\text{-}H}$ = 2.8 Hz, pyrrole). Anal. Calcd for $C_{54}H_{46}N_4O_6P_2F_6$·C_6H_{14}: C, 64.98; H, 5.45; N, 5.05%. Found: C, 64.83; H, 5.58; N, 4.62%.

Bis(3-bromopropoxo)[tetra(4-methoxyphenyl)porphyrinato]phosphorus(V) Hexafluorophosphate (1d). UV–vis λ_{max}/nm (log ε) 441 (5.46), 566 (4.08), 612 (3.87); SIMS *m*/*z* 1039 (M^+); ^{1}H NMR δ −2.24 (4H, dt, $J_{P\text{-}H}$ = 12.6, J = 6.3 Hz, CH_2), −0.99 (4H, quint, J = 6.3 Hz, CH_2), 1.20 (4H, t, J = 6.3 Hz, CH_2Br), 4.03 (12H, s, OCH_3), 7.30 (8H, d, J = 8.7 Hz, Ph), 7.91 (8H, d, J = 8.7 Hz, Ph), 9.06 (8H, d, $J_{P\text{-}H}$ = 2.7 Hz, pyrrole).

Bis(hexyloxo)[tetra(4-methoxyphenyl)porphyrinato]phosphorus(V) Hexafluorophosphate (1e). UV–vis λ_{max}/nm (log ε) 441 (5.46), 566 (4.10), 612 (3.88); SIMS *m*/*z* 965 (M^+); ^{1}H NMR δ −2.46 (4H, dt, $J_{P\text{-}H}$ = 15.0, J = 7.5 Hz, CH_2), −1.57 (4H, quint, J = 7.5 Hz, CH_2), −0.91 (4H, quint, J = 7.5 Hz, CH_2), −0.09 (4H, quint, J = 7.5 Hz, CH_2), 0.35 (10H, m, CH_2 and CH_3), 4.05 (12H, s, OCH_3), 7.33 (8H, d, J = 8.7 Hz, Ph), 7.89 (8H, d, J = 8.7 Hz, Ph), 9.08 (8H, d, $J_{P\text{-}H}$ = 2.9 Hz, pyrrole).

Bis(benzyloxo)[tetra(4-methoxyphenyl)porphyrinato]phosphorus(V) Hexafluorophosphate (1f). UV–vis λ_{max}/nm (log ε) 440 (5.45), 566 (4.09), 612 (3.90); SIMS *m*/*z* 977 (M^+); ^{1}H NMR δ −1.26 (4H, d, $J_{P\text{-}H}$ = 9.90 Hz, CH_2), 4.02 (12H, s, OCH_3), 4.60 (4H, d, J = 7.3 Hz, Ph), 6.39–6.62 (6H, m, Ph), 7.23 (8H, d, J = 8.7 Hz, Ph), 7.61 (8H, d, J = 8.7 Hz, Ph), 9.05 (8H, d, $J_{P\text{-}H}$ = 3.0 Hz, pyrrole).

Diethoxo(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1g). UV–vis λ_{max}/nm (log ε) 423 (5.39), 554 (4.12), 597 (3.79); SIMS *m*/*z* 733 (M^+); ^{1}H NMR δ −2.29–−2.37 (4H, dt, $J_{P\text{-}H}$ = 12.6, J = 6.3 Hz, CH_2), −1.74 (6H, t, J = 6.3 Hz, CH_3), 7.74–7.79 (12H, m, Ph), 7.96 (8H, d, J = 6.5 Hz, Ph), 9.06 (8H, d, $J_{P\text{-}H}$ = 2.9 Hz, pyrrole). Anal. Calcd for $C_{48}H_{38}N_4O_2P_2F_6$: C 65.60; H, 4.36; N, 6.38%. Found: C, 66.22; H, 4.50; N, 6.36%.

Dipropoxo(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1h). UV–vis λ_{max}/nm (log ε) 423 (5.40), 555 (4.10), 598 (3.80); SIMS *m*/*z* 761 (M^+); ^{1}H NMR δ −2.48 (4H, dt, $J_{P\text{-}H}$ = 12.6, J = 6.3 Hz, CH_2), −1.48 (4H, m, CH_2), −1.13 (6H, t, J = 6.3 Hz, CH_3), 7.79–7.97 (20H, m, Ph), 9.07 (8H, d, $J_{P\text{-}H}$ = 2.8 Hz, pyrrole).

Bis(allyloxo)(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1i). UV–vis λ_{max}/nm (log ε) 423 (5.43), 554 (4.09), 602 (3.83); ^{1}H NMR δ −1.78 (4H, m, CH_2), 2.65–3.65 (6H, m, CH=CH_2), 7.77–7.97 (20H, m, Ph), 9.06 (8H, d, $J_{P\text{-}H}$ = 2.9 Hz, pyrrole). HRMS (FAB) Found: *m*/*z* 757.2732. Calcd for $C_{50}H_{38}N_4O_2P$: M^+, 757.2732. Anal. Calcd for $C_{50}H_{38}N_4O_2P_2F_6$: C, 66.52; H, 4.24; N, 6.21%. Found: C, 66.44; H, 4.84; N, 5.65%.

Bis(hexyloxo)(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1j). UV–vis λ_{max}/nm (log ε) 423 (5.43), 553 (4.09), 590 (3.88); SIMS *m/z* 845 (M^+); ^{1}H NMR δ −2.48 (4H, dt, $J_{P\text{-}H}$ = 15.0, J = 7.5 Hz, CH_2), −1.56 (4H, quint, J = 7.5 Hz, CH_2), −0.90 (4H, quint, J = 7.5 Hz, CH_2), −0.09 (4H, quint, J = 7.5 Hz, CH_2), 0.30 (10H, m, CH_2 and CH_3), 7.81–7.97 (20H, m, Ph), 9.08 (8H, d, $J_{P\text{-}H}$ = 2.6 Hz, pyrrole).

Bis(octyloxo)(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1k). UV–vis λ_{max}/nm (log ε) 423 (5.43), 555 (4.09), 602 (3.83); SIMS *m/z* 901 (M^+); ^{1}H NMR δ −2.48 (4H, dt, $J_{P\text{-}H}$ = 15.2, J = 7.6 Hz, CH_2), −1.56 (4H, quint, J = 7.6 Hz, CH_2), −0.90 (4H, quint, J = 7.6 Hz, CH_2), −0.08 (4H, quint, J = 7.6 Hz, CH_2), 0.36 (4H, quint, J = 7.6 Hz, CH_2), 0.60–0.83 (14H, m, CH_2 and CH_3), 7.81–7.97 (20H, m, Ph), 9.08 (8H, d, $J_{P\text{-}H}$ = 2.5 Hz, pyrrole).

Bis(decyloxo)(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1l). UV–vis λ_{max}/nm (log ε) 423 (5.43), 553 (4.10), 598 (3.87); SIMS *m/z* 957 (M^+); ^{1}H NMR δ −2.48 (4H, dt, $J_{P\text{-}H}$ = 15.0, J = 7.5 Hz, CH_2), −1.56 (4H, quint, J = 7.5 Hz, CH_2), −0.91 (4H, quint, J = 7.5 Hz, –CH_2–), −0.07 (4H, quint, J = 7.5 Hz, CH_2), 0.36 (4H, quint, J = 7.5 Hz, CH_2), 0.64 (4H, quint, J = 7.5 Hz, CH_2), 0.73–1.12 (18H, m, CH_2 and CH_3), 7.81–7.88 (20H, m, Ph), 9.08 (8H, d, $J_{P\text{-}H}$ = 2.3 Hz, pyrrole).

Bis(benzyloxo)(tetraphenylporphyrinato)phosphorus(V) Hexafluorophosphate (1m). UV–vis λ_{max}/nm (log ε) 423 (5.40), 555 (4.05), 600 (3.84); SIMS *m/z* 857 (M^+); ^{1}H NMR δ −1.30 (4H, d, $J_{P\text{-}H}$ = 9.90 Hz, CH_2), 4.63 (4H, d, J = 7.3 Hz, Ph), 6.41–6.64 (6H, m, Ph), 7.69–7.77 (20H, m, Ph), 9.07 (8H, d, $J_{P\text{-}H}$ = 2.9 Hz, pyrrole).

Dibutoxo(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2a). UV–vis λ_{max}/nm (log ε) 419 (5.42), 550 (4.11), 590 (3.85); ^{1}H NMR δ −2.58 (4H, t, J = 6.0 Hz, CH_2), −1.95 (4H, quint, CH_2), −1.62 – −1.52 (4H, m, CH_2), −0.60 (6H, t, J = 6.0 Hz, CH_3), 7.95–8.35 (20H, m, Ph), 9.54 (8H, s, pyrrole). HRMS (FAB) Found: *m/z* 879.2659. Calcd for $C_{52}H_{46}N_4O_2Sb$: M^+, 879.2659. Anal. Calcd for $C_{52}H_{46}N_4O_2PF_6Sb\cdot 2C_6H_{14}$: C, 64.16; H, 6.23; N, 4.68%. Found: C, 63.57; H, 6.28; N, 4.14%.

Bis(allyloxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2b). UV–vis λ_{max}/nm (log ε) 420 (5.34), 551 (3.96), 591 (3.72); SIMS *m/z* 847 and 849 (M^+); ^{1}H NMR δ −1.72 (4H, dt, J = 3.1, 1.6 Hz, CH_2), 2.50 (2H, quint, J = 1.6 Hz, CH=), 3.25–3.68 (4H, m, =CH_2), 7.91–8.33 (20H, m, Ph), 9.55 (8H, s, pyrrole). Anal. Calcd for $C_{50}H_{38}N_4O_2PF_6Sb\cdot C_6H_{14}$: C, 62.29; H, 4.85; N, 5.19%. Found: C, 63.27; H, 4.19; N, 5.78%.

Bis(3-bromopropoxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2c). UV–vis λ_{max}/nm (log ε) 419 (5.67), 551 (4.28), 590 (4.03); SIMS *m/z* 1009 (M^+); ^{1}H NMR δ −2.54 (4H, t, J = 5.5 Hz, CH_2), −1.08 (4H, quint, J = 5.5 Hz, CH_2), 0.63 (4H, t, J = 5.5 Hz, CH_2), 7.89–8.38 (20H, m, Ph), 9.53 (8H, s, pyrrole).

Bis(benzyloxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (2d). UV–vis λ_{max}/nm (log ε) 420 (5.33), 550 (3.98), 591 (3.75); SIMS *m/z* 947 and 949 (M^+); ^{1}H NMR δ −1.10 (4H, s, CH_2), 3.67 (4H, d, J = 7.5 Hz, Ph), 6.32–6.70 (6H, m, Ph), 7.94–8.21 (20H, m, Ph), 9.47 (8H, s, pyrrole). Anal. Calcd for $C_{58}H_{42}N_4O_2PF_6Sb\cdot C_6H_{14}$: C 65.15; H, 4.78; N, 4.75%. Found: C, 64.80; H, 4.21; N, 5.17%.

Hydroxo(isopropoxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (3). UV–vis λ_{max}/nm (log ε) 421 (5.45), 550 (4.08), 590 (3.90); SIMS *m/z* 809 and 811 (M^+); ^{1}H NMR δ −3.32– −3.43 (1H, m, CH), −2.52 (6H, d, J = 6.2 Hz, –CH_3), 7.85-7.94 (12H, m, Ph), 8.22 (4H, d, J = 7.3 Hz, Ph), 8.48 (4H, d, J = 7.3 Hz, Ph), 9.45 (8H, s, pyrrole). Axial hydroxy group was not observed in ^{1}H NMR spectra. Anal. Calcd for $C_{47}H_{36}N_4O_2PF_6Sb$: C 59.08; H, 3.80; N, 5.86%. Found: C, 60.29; H, 3.71; N, 5.82%.

Bromo(ethoxo)(tetraphenylporphyrinato)antimony(V) Hexafluorophosphate (4). UV–vis λ_{max}/nm (log ε) 424 (5.33), 557 (3.98), 596 (3.75); ^{1}H NMR δ −2.29 (3H, quint, J = 6.9 Hz, –CH_3), −2.18 (2H, t, J = 6.9 Hz, –CH_2), 7.90–8.00 (12H, m, Ph), 8.31 (4H, d, J = 6.6 Hz, Ph), 8.38 (4H, d, J = 6.6 Hz, Ph), 9.56 (8H, s, pyrrole). HRMS (FAB) Found: *m/z* 857.0876. Calcd for $C_{46}H_{33}BrN_4OSb$: M^+, 859.0872. Anal. Calcd for $C_{46}H_{33}BrN_4OSbPF_6\cdot C_6H_{14}$: C, 57.27; H, 4.34; N, 5.14%. Found: C, 56.38; H, 4.00; N, 5.33%.

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