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Synthesis, Spectral, and Electrochemical Characterization of the First Arsenic(V)-Phthalocyanines

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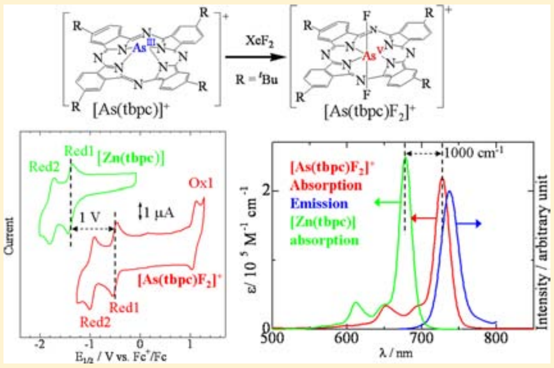
Supporting Information

ABSTRACT: The first arsenic(V)-phthalocyanines, $[As(tbpc)X_2]^+$, where tbpc denotes tetra(*tert*-butyl)phthalocyaninate, $C_{48}H_{48}N_8{}^{2-}$ and X = F, Cl, and Br) have been prepared through an appropriate oxidative addition process to a highly soluble arsenic(III) derivative, $[As(tbpc)]^+$. Among them, $[As(tbpc)F_2]^+$ has been isolated as $PF_6{}^-$ salt. Unlike conventional metal derivatives of phthalocyanines, they show a significantly red-shifted (by >1000 cm^{-1}) Q-band and facile reduction of the macrocyclic ligand (redox potentials for $[As(tbpc)F_2]^+$ have been determined by cyclic voltammetry; 1.13 V vs ferricinium$^+$/ferrocene (tbpc$^{-/2-}$), −0.45 V (tbpc$^{2-/3-}$), and −0.90 V (tbpc$^{3-/4-}$), of which the values are anodically shifted by about 1 V) as compared to those of conventional phthalocyanines. Although the anomaly in their spectral and electrochemical properties is similar to that of the known antimony analogues, the arsenic-phthalocyanines have been found less stable.



INTRODUCTION

Phthalocyanines (Pcs) are known as versatile dye staffs and enjoy a variety of industrial and medical applications,[1] such as nonlinear optics,[2] optical data storage,[3] solar cells,[4] charge-generating materials for photocopiers and laser-printers,[5] elecrochromic displays,[6] photosensitizers for solar cells[7] and photocatalysts,[8] photodynamic therapy (PDT)[9] of tumors and photodynamic antimicrobial therapy (PACT),[10] semiconductors[11] and synthetic metals,[12] and so on. As Pcs are so useful and are known to make compounds with almost all metal and metalloid elements, derivatives of essentially all metal/metalloid elements have been investigated[1] since Linstead and his coworkers developed their works in the early 20th century.[13] Nevertheless, those of group-15 elements have been essentially ignored until the first bismuth(III)[14] and antimony(V)[15] derivatives were reported by our groups in 1994. What is interesting with the group-15 elements is the anomaly in their spectral and electrochemical characteristics. We have reported that bismuth- and antimony-Pcs show their most prominent optical absorption band (Q-band) at a significantly red-shifted position (by more than 1000 cm^{-1} as compared to those of the other metal/metalloid derivatives).[14,15] Moreover, it has been found that antimony(V) complexes undergo facile Pc-ligand-reduction: the first reduction potentials are −0.2 to ∼ −0.3 V vs ferricinium$^+$/ferrocene (Fc$^+$/Fc; hereafter, all the redox potentials are referred to Fc$^+$/Fc), of which the values are anodically shifted by about 1 V).[15−17] Later, Fox and Goldberg have reported similar characteristics for a phosphorus(V) derivative.[18] These findings are quite interesting because the Q-band position[19−21] and Pc-centered redox potentials[22,23] do not very much depend on the nature of central metal/metalloid elements.

Nowadays, derivatives of phosphorus(V),[24] arsenic(III),[25] and antimony(III),[26] as well as bismuth(III)[27] and antimony-(V)[16,17,26g,28−33] are known, but they are still uncommon. This is rather surprising because porphyrin analogues, which have a similar tetra-pyrrole molecular skeleton, have been relatively well studied.[34] In particular, no arsenic(V)-Pc is known despite that arsenic(III)-Pcs are known and antimony(III)-Pcs can readily be converted to the corresponding antimony(V)-Pcs.[16,26f,30−32] This is not only because of poor solubility of the known arsenic(III)-complexes ligating the pc ligand (pc denotes unsubstituted phthalocyaninate, $C_{32}H_{16}N_8{}^{2-}$) in common organic solvents but also provably because of their instability exemplified in this work and of the toxicity of arsenic.[35] We herein introduced bulky groups on the periphery of the macrocyclic ligand to improve the solubility of arsenic(III)-Pcs as the starting material in the succeeding reactions. In this paper, we report the syntheses of arsenic(V)-Pcs through appropriate oxidative addition process to the highly soluble arsenic(III)-Pc and also their chemical, spectral, and electrochemical properties for the first time.

RESULTS AND DISCUSSION

Little is known on chemistry of arsenic(III)-Pcs because they have been investigated only in their solid state. A Polish group has reported a few works on arsenic(III) derivatives ligating pc but their investigations were limited to crystal structures and

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physical properties in solid state.[15] This is probably because those arsenic derivatives are little soluble in common organic solvents. Actually, we have prepared [Sb(pc)]I_3,[30] of which the molecular structure[26a−c] is very close to that of arsenic(III)-Pc,[25a] as a precursor to make antimony(V) derivatives. But its poor solubility in nondonor solvents (e.g., CH_2Cl_2 or dichlorobenzene) and its instability in donor solvents (e.g., acetone and DMF, in which the central arsenic is readily removed from the cavity of the macrocyclic ligand although more soluble) made it quite difficult to isolate in an analytical pure form. This is the reason why we decided to introduce *tert*-butyl groups into the periphery of the macrocycle to improve solubility of arsenic(III)-Pc. By fusing a mixture of *tert*-butyl-substituted phthalonitrile and AsI_3, we successfully synthesized $[As(tbpc)]^+$ (tbpc denotes tetra-*tert*-butylphthalocyaninate, $C_{48}H_{48}N_8^{2-}$), which is highly soluble in common organic solvents, such as CH_2Cl_2, acetone, acetonitrile, *o*-dichlorobenzene, etc., (e.g., > 10^{-2} M in CH_2Cl_2) although labile in them as stated later. The product has been identified by ESI-MS and optical absorption spectrum (that is very close to that of [Sb(tbpc)]I_3 (Figure 1).[26e−g,31] Its counteranion is considered to be I_3^- on the basis of the similarity in the spectra in 300−450 nm.[26e,30−32]

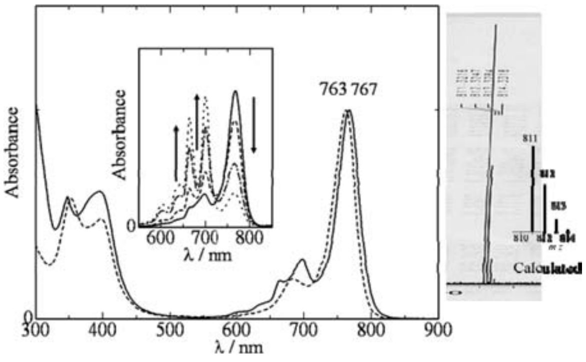
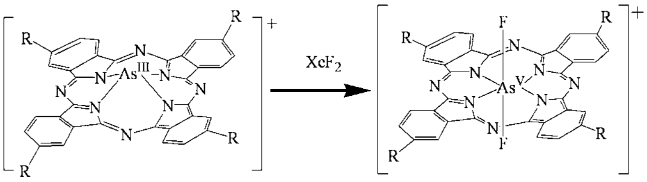


Figure 1. Normalized optical absorption (left), experimental and calculated mass spectra (right) of [As(tbpc)]I_3 in CH_2Cl_2 (for the full mass spectrum, see Figure S1, Supporting Information). Absorption spectrum of [Sb(tbpc)]I_3 is also shown for comparison. Inset shows spectral changes observed with an elapse of time (each spectrum was measured every 20 min).

We also modified the procedure to synthesize the arsenic(III) derivative by using AsI_3 as the arsenic source instead of elemental arsenic and I_2 to make the desired compound under milder conditions (in the earlier works, the temperature was 200 °C).[25] We have found that use of phthalonitrile derivatives with lower melting points can initiate the reaction at lower temperature.[26e,30,31] Nevertheless, the reaction of *tert*-butylphthalonitrile (whose melting point is much lower than that of unsubstituted phthalonitrile) and AsI_3 did not proceed below 200 °C and worked only above 200 °C. Hence, the mechanism of tetracyclization of phthalonitrile derivatives to form Pc with arsenic can be different from that with antimony. We did not attempt to prepare the Pc macrocycle first and then to insert an arsenic ion into its cavity because it should be quite hard to do on the basis of our educated experience on antimony derivatives.[30] Our decision has been found correct on the basis of the instability of $[As(tbpc)]^+$ in solution. The arsenic(III) derivative is quite labile even in nondonor solvents such as CH_2Cl_2 and is readily demetalated to generate H_2tbpc, as shown in the inset in Figure 1. The intense band around 766 nm ($[As(tbpc)]^+$) almost vanished within an hour, and coincidently, twin peaks around 663 and 700 nm (attributable to H_2tbpc) grew with an elapse of time, indicating occurrence of demetalation at a moderate rate even in nondonor solvent at room temperature (it should be noted that the corresponding antimony(III) derivative is quite stable in CH_2Cl_2[26e,f]). Therefore, we had to give up isolation of [As(tbpc)]I_3 in analytically pure form and used it as the starting material in the succeeding steps without further purification.

By oxidizing $[As(tbpc)]^+$ with XeF_2, we have successfully synthesized stable arsenic(V)-Pc, $[As(tbpc)F_2]^+$, for the first time (Scheme 1). Although crystal structure of arsenic(V)-Pc is unknown, it is reasonable to assume the *trans* (not *cis*) configuration on the basis of the crystal structures of known porphyrin analogues.[34a] Figure 2 shows the absorption spectra of a CH_2Cl_2 solution containing $[As(tbpc)]^+$ before and after the addition of XeF_2. The reaction was very rapid and completed within a few minutes. The Q-band sharpened and somewhat blue-shifted after oxidation, as is the case for oxidation of antimony(III) analogues.[16,26f,30−32] The product has been identified as $[As(tbpc)F_2]^+$ by ESI-MS (Figure 2, inset). The reaction needed to be quenched quickly once the reaction completed; otherwise, the reaction mixture (dark green) gradually turned reddish brown and the Q-band disappeared.

Scheme 1. Oxidative Addition of XeF_2 to $[As(tbpc)]^+$



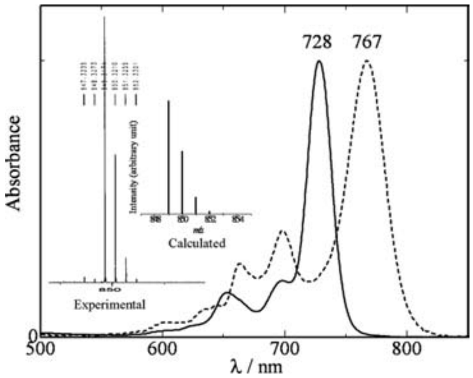


Figure 2. Absorption spectra of a CH_2Cl_2 solution containing $[As(tbpc)]^+$ before (dashed line) and after the addition of XeF_2 (solid line). Spectra are normalized. Insets show experimental and calculated mass spectra of the product ($[As(tbpc)F_2]^+$).

Although the initial product obtained in this way has been assigned as AsF_4^- salt only on the basis of the elemental analytical data, the presence of this anion could not be experimentally confirmed (e.g., ESI-MS (negative scan)). Therefore, the existing counteranion has been replaced by PF_6^- through $AgPF_6$ treatment according to our previous works.[16,30,31] Although no detectable change was seen in optical absorption spectra in the range of 250−900 nm before and after the treatment (because both the two anions are transparent in this spectral region), a considerable change was observed in IR spectra (Figure 3). These spectra of the two salts are essentially the same except for the appearances of intense absorption bands around 840 and 560 cm^{-1} and reduction of intensity of a medium band around 685 cm^{-1} after the AgPF$_6$ treatment. The former two bands are attributable to ν(P−F) and δ(F−P−F), respectively.[17,30,31,37] The latter one may be assigned as ν(As−F)[37,38] because such a band is not observed for [Sb(tbpc)Cl$_2$]SbCl$_4$, [Sb(tbpc)(OH)$_2$]I$_3$, or [Sb(tbpc)]I$_3$.[32] The decrease in intensity of this band suggests the presence of one or more anionic species that have As−F bond(s) in the initial product, which may be AsF$_4^-$, as is supported by the elemental analytical data.

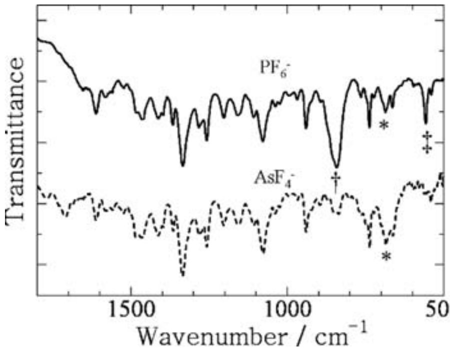


Figure 3. Infrared spectra of [As(tbpc)F$_2$]AsF$_4$ (broken line) and [As(tbpc)F$_2$]PF$_6$ (solid line). The daggered, double-daggered, and asterisked peaks are assignable to ν(P−F), δ(F−P−F), and ν(As−F) vibrations of the counteranions, respectively.

We have also attempted to synthesize [As(tbpc)Br$_2$]$^+$ and [As(tbpc)Cl$_2$]$^+$ in a similar way by using Br$_2$ and SO$_2$Cl$_2$ as the oxidants[16] (in these cases, use of solvents is not mandatory), respectively, in place of XeF$_2$. The reactions worked as expected, and generation of the desired products have been confirmed on the basis of their ESI-MS and optical absorption spectra (Figures S2 and S3, Supporting Information). Here again, the Q-bands sharpened and somewhat blue-shifted upon oxidation. However, the products have been found unstable even in CH$_2$Cl$_2$ at room temperature (under the same conditions, the corresponding antimony derivatives are stable enough to be isolated[16]). Spectral changes observed for [As(tbpc)Br$_2$]$^+$ after being dissolved in CH$_2$Cl$_2$ are shown in Figure 4. The most intense absorption band at 734 nm, which is assigned as Q-band of [As(tbpc)Br$_2$]$^+$, lowered with an elapse of time, and at the same time, absorption bands at 766, 700, and 663 nm grew. The 766 nm band is attributed to [As(tbpc)]$^+$ because it disappeared upon the addition of Br$_2$ to the solution, and the 734 nm band retained the initial intensity. This indicates that [As(tbpc)Br$_2$]$^+$ is unstable and gradually reduced to arsenic(III) species.[16] The twin peaks at 700 and 663 nm are attributable to H$_2$tbpc, which may have been generated from [As(tbpc)]$^+$ (Figure 1). This compound is much less stable in benzene because its spectrum in the solvent is essentially the same as that of a mixture of [As(tbpc)]$^+$ and H$_2$tbpc. We have reported that the corresponding antimony analogues, [Sb(tbpc)Br$_2$]$^+$ and [Sb(pc)Br$_2$]$^+$, are readily reduced to [Sb(tbpc)]$^+$ and [Sb(pc)]$^+$, respectively, under mild conditions although they are stable enough to be isolated in analytically pure forms.[16] Therefore, [As(tbpc)Br$_2$]$^+$ is considered to likewise change to [As(tbpc)]$^+$ through reductive elimination of Br$_2$. [As(tbpc)Cl$_2$]$^+$ is a little more stable than [As(tbpc)Br$_2$]$^+$ but not sufficiently stable enough to be isolated. Its Q-band gradually lowered (decreased by 2−3% in 1 h in CH$_2$Cl$_2$ and by 9% in benzene). In addition, our attempts to isolate [As(tbpc)Cl$_2$]$^+$ as PF$_6^-$ salt in a similar way to that for [As(tbpc)F$_2$]$^+$ were unsuccessful because its Q-band blue-shifted by about 270 cm^{-1} after being treated with AgPF$_6$. On the basis of the spectral change, the axial chloride ions may have been replaced by hydroxide (the Q-band of known [Sb(Pc)(OH)$_2$]$^+$ appears at a shorter wavelength than that of the corresponding dichloro analogues[16,28,31,32]). It is also noteworthy that the same AgPF$_6$ treatment on antimony analogues did not give rise to cleavage of Sb−Cl bond.[32] It seems that the order in the stability of the arsenic(V)-Pcs is parallel to that in As-X bond dissociation energies in a series of AsX$_2$ species (i.e., As−F (4.196 eV) > As−Cl (2.56 eV) > As−Br (1.99 eV)).[39] We have shown a similar tendency for antimony(V)-Pcs in that the resistivity to the reduction of the central element to antimony(III) is parallel to the order of Sb-X bond strength (Sb−OH ≫ Sb−Cl > Sb−Br).[16]

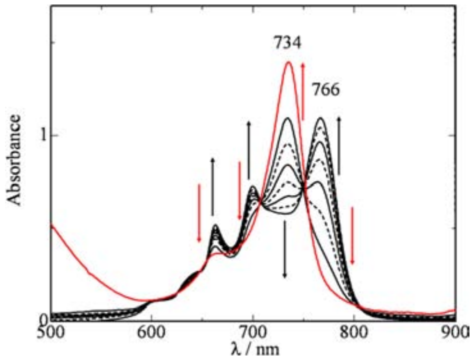


Figure 4. Spectral changes observed for [As(tbpc)Br$_2$]$^+$ in CH$_2$Cl$_2$ with an elapse of time (black lines; monitored every 20 min) and that observed upon the addition of Br$_2$ to the final solution (red line). The black and red arrows denote directions of spectral changes before and after the addition of Br$_2$, respectively.

Figure 5 (top) shows optical absorption spectra of [As(tbpc)F$_2$]PF$_6$ in CH$_2$Cl$_2$. As PF$_6^-$ is transparent in this spectral region, the spectra observed may be assumed to be

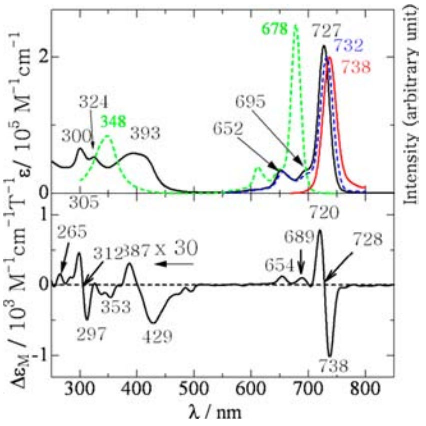


Figure 5. (Top) optical absorption (black, solid line), emission (red, solid line), and the associated excitation spectra (blue, broken line) of [As(tbpc)F$_2$]PF$_6$ in CH$_2$Cl$_2$, as well as absorption spectrum of [Zn(tbpc)] (green, broken line) and (bottom) MCD spectra of [As(tbpc)F$_2$]$^+$ in the same solvent.

from the $[As(tbpc)F_2]^+$ chromophere alone. A very intense absorption band appears around 727 nm with satellites at 695 and 652 nm. It is characteristic of monomeric metal-Pc complexes.[19−21] This intense band is generally called as the Q-band of phthalocyanines and is assigned as an electronic transition from the nondegenerate HOMO to the doubly degenerate LUMO in character.[19] As a distinctive s-shaped curve (i.e., a couple of positive/negative signals going from higher to lower energy) centered at the absorption maximum wavelength (Faraday A-term[19]) is observed in the associated MCD (magnetic circular dichroism) spectrum (Figure 5, bottom), we assigned this band likewise. The satellites at slightly shorter wavelengths may be assigned as vibronic progression on the basis of the appearance of Gaussian curves centered at the absorption maxima (Faraday B-terms) in the MCD spectrum.[19] It should be mentioned that the Q-band appears at a considerably longer wavelength as compared to majority of metal-Pc complexes (as an example of conventional metal-Pcs, that of [Zn(tbpc)] is shown for comparison), as is the case for known antimony(V) derivatives.[15−17,26f,g,28,30−33] Dichloromethane solutions containing $[As(tbpc)F_2]PF_6$ show the same spectra irrespective of their concentrations, and the optical intensity at the Q-band maximum obeyed Lambert−Beer's law up to the upper limit of concentration range where absorbance can be monitored with commercially available optical cells. Therefore, no detectable aggregation was observed up to about 10^{-4} M. Furthermore, essentially the same spectra were observed in methanol, acetonitrile, acetone, ethanol, ethyl acetate, THF, DMF, DMA, $CHCl_3$, benzene, pyridine, chlorobenzene, *o*-1,2-dichlorobenzene, nitrobenzene, and 1-chloronaphthalene solutions although the Q-band positions varied depending on the nature of the solvent. Figure 6 shows plots of the Q-band position in energy (cm^{-1}) in various solvents against refractive indices of the solvents in the form of Onsager's solvent polarity function.[40] The 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 metal-Pc 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 metal-*Pc*.[30,31,41] 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 macrocyclic ligand and induced dipole moment temporarily generated in the surrounding solvent molecules.[40] That is, the Q-band position of $[As(tbpc)F_2]^+$ in a specific solvent is determined by the refractive index of the solvent alone,[40] unlike that of $[Sb(tbpc)(OH)_2]^+$ (shown as open circles in Figure 6) or other antimony(V) derivatives bearing axial OH groups that are capable to chemically interact with the surrounding solvent molecules (maybe through hydrogen bonding[30−32]). In DMF, DMSO, methanol, and THF, a few more additional weak absorption bands were observed around 580 and 770 nm. As similar absorption bands have been reported for $[Sb(pc)Cl_2]^+$ in CH_2Cl_2 when it is reduced by BH_4^-,[29] the additional bands are considered to be due to generation of one-electron or a more reduced form of $[As(tbpc)F_2]^+$. It is well known that Pcs show remarkable spectral changes upon reduction.[19−21] As is discussed in more detail later, this arsenic(V) derivative has quite small Pc-centered reduction potentials. Therefore, it is likely that $[As(tbpc)F_2]^+$ is readily reduced by a trace amount of reducing impurities in these solvents.

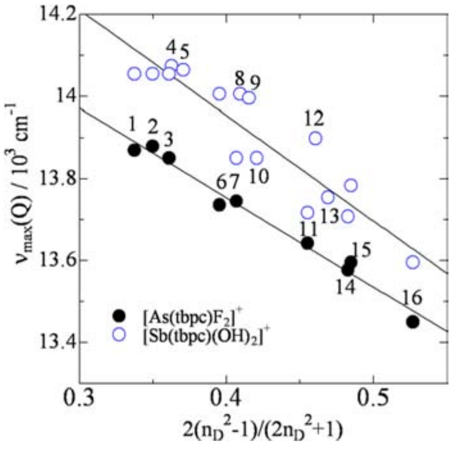


Figure 6. Solvatochromic shifts in the Q-band position as a function of refractive indices of solvents. The closed and open circles denote those for $[As(tbpc)F_2]^+$ and $[Sb(tbpc)(OH)_2]^+$, respectively. The integers near the plots represent the solvent studied: (1) MeOH, (2) CH_3CN, (3) acetone, (4) EtOH, (5) EtOAc, (6) THF, (7) CH_2Cl_2, (8) DMF, (9) dimethylacetoamide, (10) $CHCl_3$, (11) benzene, (12) pyridine, (13) chlorobenzene, (14) *o*-dichlorobenzebe, (15) nitrobenzene, and (16) 1-chloronaphthalene.

In the Soret region, at least four absorption bands are observed: a broad band around 360−440 nm, one middle band at 300 nm, and two weak bands at 324 and 250 nm (Figure 5). The first broad one is considered to be two overlapped bands on the basis of the corresponding MCD spectrum, i.e., no simple A-term or B-term. We have observed a similar band in this region for antimony(V) derivatives and have assigned this band as an overlap of B1/B2 bands[30,31,33] by an analogy to the known zinc- and magnesium-Pcs.[30,42] The corresponding absorption band appears at 348 nm for [Zn(tbpc)] in the same solvent. Here again, a large red-shift (about 3300 cm^{-1}) is observed. The weak 324 nm may be considered to be an overlap of more than one band for the same reason. On the other hand, a s-shaped curve was observed in the MCD spectrum around 305 nm with its center close to the absorption maximum wavelength, suggesting that the electronic transition is orbitally doubly degenerate. The weak 250 nm band is so close to the edge of the spectral window in CH_2Cl_2 that it is hard to be assigned. However, the transition can be degenerate on the basis of the associated MCD spectrum that appears s-shaped. Absorption bands observed in this region have been theoretically studied and assigned as mixtures of more than one one-electron transition from nondegenerate to degenerate molecular orbitals.[19] Gouterman and co-workers have expected the appearance of many electronic absorption bands for Pcs, which are assigned as degenerate $\pi-\pi^*$ transitions in character, in higher energy regions than B bands on the basis of their theoretical works.[19,43] Therefore, these bands may be assigned likewise. It should be noteworthy that these bands are hardly observed for majority of Pcs in solutions because common organic solvents normally absorb ultraviolet light, and hence, these bands are hidden in their absorption. Actually, available spectral data are limited to those observed in vapor phase, thin film, or argon matrix.[43,44] The significant red-shifts of the $\pi-\pi^*$ transitions for arsenic(V) derivatives (e.g., red-shifted by about 1100 cm^{-1} for Q-band as compared to zinc analogue) may have allowed us to observe these transitions in solution phase.

A typical optical emission spectrum of $[\mathrm{As(tbpc)F_2}]^+$ is shown in Figure 5 (top). The emission peak appears at 738 nm in $\mathrm{CH_2Cl_2}$, of which the value is reasonable with the small Stoke's shift (196 $\mathrm{cm^{-1}}$) from the absorption peak taken into consideration.[45] The associated excitation spectrum (the monitoring wavelength = 760 nm) shows its peak at 732 nm and is similar to the absorption spectrum measured in the same solvent. Hence, we assigned the emission from the singlet excited state of $[\mathrm{As(tbpc)F_2}]^+$. The quantum yield of the emission has been evaluated as about 0.03 using that for $\mathrm{H_2}$tbpc (0.85) as the standard.[46] This value, however, is rather tentative because the emission range of this species was beyond the available range of the spectrophotometer used, and hence, the intensity of only the most intense emission band was evaluated. We have reported lower fluorescence quantum yields for $[\mathrm{Sb(tbpc)Cl_2}]^+$ (~0.01), $[\mathrm{Sb(pc)Cl_2}]^+$ (~0.01),[28] $[\mathrm{Sb(tbpc)Br_2}]^+$ (~0.001),[16] and $[\mathrm{Sb(tbpc)(OSO_3H)_2}]^+$ (~0.005).[33] The quantum yield for the arsenic(V) derivative in this work is more than three times as large as those for the antimony(V) analogues probably because of the effect of the presence of a heavy atom (antimony) for the latter, which facilitates singlet−triplet intersystem crossing in the π-system due to a metal-induced strong spin−orbit coupling.[47]

Redox potentials for $[\mathrm{As(tbpc)F_2}]^+$ have been determined by cyclic voltammetry. A typical voltammogram in $\mathrm{CH_2Cl_2}$ containing tetrabutylaamonium hexafluorophosphate (TBAH, 0.1 M) as supporting electrolyte is shown in Figure 7. One oxidation and two reduction waves have been observed. Their half-wave potentials, $E_{1/2}$, and peak separation, ΔE, values have been obtained by $(E_{\mathrm{pa}} + E_{\mathrm{pc}})/2$ and $(E_{\mathrm{pa}} - E_{\mathrm{pc}})$, respectively, where E_{pa} and E_{pc} denote anodic and cathodic current peak potentials, respectively. The $E_{1/2}$ (ΔE/mV) values have been determined in this way as 1.13 V (70), −0.45 V (80), and −0.90 V (90) for the first oxidation, the first and second reduction waves, respectively. On the basis of the ΔE values, these redox couples are all one-electron process (the ΔE value for $\mathrm{Fc^+/Fc}$ couple was 70 mV under the same conditions). For each wave, the ratio of anodic/cathodic peak current was unity, and their peak currents were proportional to square root of scanning rates. Therefore, all the redox processes have been found quasi-reversible. Figure 8 shows an absorption spectral change observed during controlled-potential electrolysis around the first reduction potential. The intense Q-band around 727 nm lowered as the electrolysis proceeded, and at the same time, new absorption bands appeared around 1050 and 600 nm. The working solution gradually reproduced the initial spectrum when the applied potentials were removed. The drastic changes upon electrolysis clearly indicate that the first reduction is an electron transfer involving the macrocyclic ligand.[22,48,49] We have also reported that one-electron-reduced species of $[\mathrm{Sb(pc)Cl_2}]^+$ (i.e., $\mathrm{pc^{3-}}$ species) shows distinctive sharp absorption bands around 1050 and 600 nm.[15,29] Thus, the first reduction undoubtedly involves $\mathrm{tbpc^{2-}/tbpc^{3-}}$ couple. The potential differences between the first oxidation and first reduction and between the first and second reduction are 1.58 and 0.45 V, respectively. As these values are typical of those for Pcs in which their central metals are redox-inactive,[22,29a,49] the first oxidation and the second reduction may be likewise assigned as Pc-centered, i.e., $\mathrm{tbpc^{-}/tbpc^{2-}}$ and $\mathrm{tbpc^{3-}/tbpc^{4-}}$ couples, respectively. It should be noted that our attempts to monitor spectral changes during electrolysis around the first oxidation potential were unsuccessful because of instability of the oxidized species. Intensity of all the absorption bands lowered as the electrolysis proceeded, but removal of the applied potential did not reproduce the initial spectrum. We have also reported that the oxidized species of $[\mathrm{Sb(pc)Cl_2}]^+$ is unstable.[17]

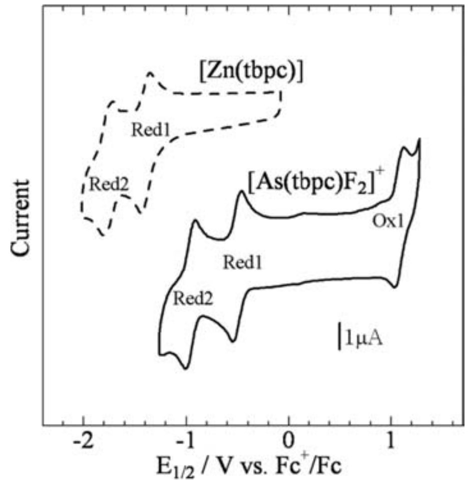


Figure 7. Typical cyclic voltammogram of $[\mathrm{As(tbpc)F_2}]\mathrm{PF_6}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M TBAH as supporting electrolyte (solid line) at a scanning rate of 100 mV $\mathrm{s^{-1}}$ and that of [Zn(tbpc)] for comparison (broken line). The Ox1, Red1, and Red2 represent the first oxidation, the first and second reduction waves, respectively.

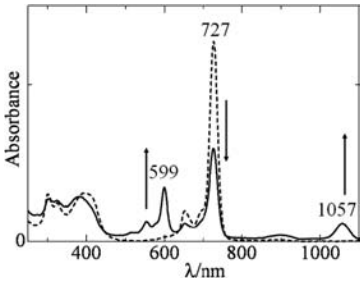


Figure 8. An optical absorption spectral change observed during controlled-potential electrolysis of $[\mathrm{As(tbpc)F_2}]\mathrm{PF_6}$ in $\mathrm{CH_2Cl_2}$ containing 0.03 M TBAH as supporting electrolyte around the first reduction potential (at −0.48 V).

It is quite interesting that the reductions of the macrocyclic ligand occur at such small potentials. The first reduction wave is anodically shifted by about 1 V as compared to those of conventional Pcs (a typical voltammogram for [Zn(tbpc)] measured under the same conditions is shown in Figure 7 as an example of conventional Pcs for comparison). It is well-known that redox potentials of metal-Pcs do not very much depend on the nature of the central metal element:[22,23] For example, reported half-wave potentials for a $\mathrm{tbpc^{2-/3-}}$ redox couple determined in the same solvent are −1.31 V for [Cu(tbpc)], −1.17 V for $\mathrm{H_2}$tbpc, −1.60 V for [Mg(tbpc)], and −1.39 V for [Zn(tbpc)].[50] Although the macrocyclic ligands are easier to reduce (and hence more difficult to oxidize) with an elevated polarizing power (ze/r; where ze and r denote the positive charge and ionic radius of the central metal, respectively),[49] such a large anodic shift for the arsenic(V) derivative can not be rationalized. Contributions from the peripheral substituents to the facile reduction are much less likely because *tert*-butyl is an electron-donating group and hence will make the macrocycle less easy to be reduced.[51] It should be noted that the effects of substituents and central metals have been studied only for neutral Pcs but not for cationic species. Therefore, the facile Pc-centered reduction may be attributed, as is the case for the antimony(V) derivatives,[15,30,31] to the presence of positive charge on the reaction center (note that both the arsenic and antimony derivatives are monocation), which significantly reduces electron density in the macrocyclic ligand.

■ CONCLUSION

We have successfully prepared a highly soluble arsenic(III)-Pc as a precursor by introducing bulky *tert*-butyl groups on the periphery of the macrocyclic ligand, which has allowed us to study its chemistry in solution for the first time. Consequently, we succeeded in syntheses of the first arsenic(V) derivatives through the oxidative addition process by using XeF_2, SO_2Cl_2, and Br_2 to yield $[As(tbpc)F_2]^+$, $[As(tbpc)Cl_2]^+$, and $[As(tbpc)Br_2]^+$, respectively. The latter two species are less stable than the corresponding known antimony analogues. In particular, $[As(tbpc)F_2]^+$ has been found sufficiently stable and has been isolated as PF_6^- salt in an analytically pure form, and their spectral and electrochemical properties have been studied for the first time. These characteristics have been found quite unusual as compared to conventional Pcs and close to those of known antimony(V) analogues. This work would also be helpful to predict stability of unknown phosphorus(III)-Pcs or phosphorus(V) derivatives bearing halide ions at their axial sites. The spectral data should be useful to scientists who are interested in spectroscopy and electronic structures of this class of chromophores because there is no need to consider a heavy atom effect (relativistic quantum chemistry) in computational calculations unlike the case of antimony analogues.

■ EXPERIMENTAL SECTION

(Tetra-*tert*-butyl-phthalocyaninato)arsenic(III) Triiodide, $[As(tbpc)]I_3$. In a typical experiment, a mixture of 4-*tert*-butylphthalonitrile (300 mg; 1.63 mmol) and arsenic(III) iodide (185 mg; 0.40 mmol) was fused at 200 °C in a sealed glass tube for 24 h. The reaction mixture turned green within a few hours and solidified when it was allowed to cool to room temperature. The crude product was extracted with CH_2Cl_2 and was precipitated by addition of the same volume of hexane. The solid was collected by centrifugation, washed with CH_2Cl_2/hexane (1/9 (v/v)) until the washing turned almost colorless, and dried at 60 °C under vacuum (80 mg; yield 16% vs 4-*tert*-butyl-phthalonitrile assuming the product is analytically pure). ESI-MS: m/z 811 (M+; see also Figure S1, Supporting Information). The crude product was found to be a mixture of arsenic(III)-Pc, $[As(tbpc)]I_3$, and a small amount (<5%) of metal-free phthalocyanine (H_2tbpc) on the basis of optical absorption spectra of the crude product in CH_2Cl_2 (Figure 1; the difference between the arsenic and antimony derivatives around 650−700 nm may be due to contamination of H_2tbpc in the former). The arsenic derivative has been found unstable and readily demetalated in common organic solvents as mentioned above. Hence, we used the crude product in the succeeding steps without further purification. The arsenic(III) derivative obtained in this way is a mixture of four regioisomers based on the positions of the peripheral *tert*-butyl groups because we did not make any efforts to prepare a specific isomer.

Difluoro(tetra-*tert*-butyl-phthalocyaninato)arsenic(V) Tetrafluoroarsenate(III), $[As(tbpc)F_2]AsF_4$. In a typical experiment, a 102 mg (0.084 mmol; assuming the starting material was analytically pure) of $[As(tbpc)]I_3$ was dissolved into dehydrated CH_2Cl_2 (3 mL) in a Teflon vial. To the solution was added 200 mg (0.68 mmol) of XeF_2. The solution was allowed to react at room temperature with vigorous stirring for 15 min. The color of the solution (dark green) turned dark brown within a few minutes. This solution was quickly poured into hexane (8 mL) to quench the reaction and precipitate the reaction product (it should be noted that prolonged reaction time (e.g., 1 h) significantly reduced its yield). The solid was collected by centrifugation, washed with CH_2Cl_2/hexane (1 mL:8 mL) 4 times until the washing turned almost colorless, and dried at 80 °C under vacuum overnight. This solid was dissolved into CH_2Cl_2 (3 mL) and filtered to remove insoluble impurity, and the solution was evaporated to dryness. This was twice recrystallized from CH_2Cl_2/hexane (1 mL/8 mL) and dried under vacuum at 80 °C for 1 h. A 45 mg (0.045 mmol) amount of the desired product was obtained as a dark green crystalline solid (as a mixture of four regioisomers as mentioned above). Yield: 54% (assuming that the starting material was analytically pure). ESI-MS (CH_2Cl_2): 849 ($C_{48}H_{48}N_8AsF_2$; M^+). Anal. Calcd (%) for $C_{48}H_{48}N_8As_2F_6$: C, 57.61; H, 4.83; N, 11.20. Found C, 57.55; H, 5.01; N, 10.95.

Difluoro(tetra-*tert*-butyl-phthalocyaninato)arsenic(V) Hexafluorophosphate, $[As(tbpc)F_2]PF_6$. In dehydrated acetonitrile (4 mL) was dissolved 11.9 mg of the AsF_4^- salt (0.017 mmol), and dehydrated acetonitrile solution (4.5 mL) containing $AgPF_6$ (0.39 mmol) was added to the solution. The solution was allowed to react with stirring at room temperature. After 15 min, an additional 0.5 mL of dehydrated acetonitrile solution containing $AgPF_6$ (0.043 mmol) was added to the mixture to complete the reaction. After 15 min, the solution was filtered to remove insoluble byproduct, and the volume of the filtrate was reduced to about 2 mL by evaporation. This was added to water (40 mL) to precipitate the desired product. The light green solid was collected by filtration and dried overnight under vacuum at 80 °C to give 11.6 mg of crude product. This was twice recrystallized from CH_2Cl_2/hexane (5 mL/50 mL) and dried for 3 h at 80 °C under vacuum to obtain 6 mg (0.006 mmol) of the desired compound. Yield: 36%. Anal. Calcd (%) for $C_{48}H_{49}N_8O_{0.5}AsPF_8$, ($[As(tbpc)F_2]PF_6\cdot0.5H_2O$): C, 57.43 H, 4.92 N, 11.16. Found C, 57.40; H, 5.21; N, 10.87.

Reaction of (Tetra-*tert*-butyl-phthalocyaninato)arsenic(III) with Br_2. In a typical experiment, 53 mg (0.045 mmol; assuming the starting material was analytically pure) of $[As(tbpc)]I_3$ was dissolved into CH_2Cl_2 (1 mL). Into the solution was added 50 μL (0.97 mmol) of Br_2. The solution was allowed to react at room temperature with vigorous stirring for 1 h. Meanwhile, the color of the solution (dark green) turned dark brown (the spectral change is shown in Figure S2, Supporting Information). After the solvent and an excess amount of Br_2 was evaporated, the remaining black solid was again dissolved into CH_2Cl_2 (1 mL) and filtered to remove insoluble impurity. To the solution was added hexane (8 mL) to precipitate the desired product as a yellowish green solid. The solid was collected by centrifugation, washed with CH_2Cl_2/hexane (1 mL/8 mL) four times until the washing turned almost colorless, and dried at 60 °C under vacuum overnight (55 mg). The product obtained in this way was identified as the desired $[As(tbpc)Br_2]^+$ on the basis of ESI-MS (Figure S2, Supporting Information, inset). The yield at this stage is 100%, assuming the starting material is analytically pure and the counteranion of the product is IBr_2^-.[16] However, because this compound has been found quite unstable as described in the main text, we did not make efforts to further purify this material.

Reaction of (tetra-*tert*-butyl-phthalocyaninato)arsenic(III) with SO_2Cl_2. In a typical experiment, a mixture of 107 mg (0.090 mmol; assuming the starting material was analytically pure) of $[As(tbpc)]I_3$ and SO_2Cl_2 (1.5 mL; 19 mmol) was allowed to react for 40 min at room temperature. Meanwhile, the color of the solution (dark green) turned dark brown (the spectra in CH_2Cl_2 before and after the reaction are shown in Figure S3, Supporting Information). To the reaction mixture was added hexane (8 mL) to precipitate the product. The solid was collected by centrifugation and again dissolved into CH_2Cl_2 and filtered to remove insoluble impurity. Hexane (8 mL) was added to the filtrate to precipitate the product. The solid was recrystallized from benzene/hexane (0.5 mL/9 mL) three times to remove a small amount of H_2tbpc. This solid was dried at 80 °C under vacuum overnight (55 mg, yield; 98% assuming the starting material is analytically pure and the counteranion of the product is ICl_2^-). The product obtained in this way was identified as the desired

$[As(tbpc)Cl_2]^+$ on the basis of ESI-MS (Figure S3, Supporting Information, inset). However, because this compound has been found unstable as described in the main text, we did not make efforts to further purify this material.

Other Chemicals. Arsenic(III) iodide (Sterm Chemicals), *tert*-butyl-phthalonitrile (Tokyo Chemical, Inc.), xenon fluoride (Matrix Scientific), $AgPF_6$ (Aldrich), and dehydrated acetonitrile and CH_2Cl_2 (Nakarai) used for the syntheses were commercially available and used as received. The CH_2Cl_2 used for measurement of emission spectra was of fluorometry grade (Kanto Chemicals) and used as received. Tetrabutylammonium hexafuluorophosphate (TBAH) and CH_2Cl_2 used for electrochemical and spectroelectrochemical works were purified by recrystallization (from ethyl acetate/hexane (twice)) and by distillation (over P_2O_5 just prior to its use) of commercially available products (Tokyo Chemical, Inc.), respectively. The other chemicals and solvents were of reagent grade and used without further purification unless otherwise noted.

Measurements. The measurements of optical absorption spectra were performed with a Shimadzu UV-160A or a Shimadzu UV-1800 spectrophotometer. 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. Emission spectra were recorded on a Hitachi F-2500 fluorescence spectrophotometer. Fourier-transform IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer by a diffuse reflectance method in KBr media. Voltammetric measurements were performed with a Hokuto Denko HA-501 potentiostat/galvanostat. Conventional three-electrode-cells were used, where a glassy carbon disk, a platinum wire, and an AgCl-coated Ag-wire were used as working, auxiliary, and pseudo reference electrodes, respectively. The potentials were calibrated by ferrocenium$^+$/ferrocene (Fc^+/Fc) redox couple as an internal standard. An apparatus for electrochemical reduction (controlled-potential electrolysis) was the same as that used in voltammetry except that a platinum mesh was used as the working electrode instead of a glassy carbon disk. A portion of the working solution containing 0.03 M TBAH, which was electrolyzed at an appropriate potential, was pipetted and immediately submitted to spectroscopic measurements. All measurements were done at room temperature (25 ± 1 °C). All ESI-MS spectra were recorded on a Micromass LCT ESI-TOF MS spectrometer (in Tohoku University).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A full ESI-MS spectrum of $[As(tbpc)]^+$ and optical absorption and ESI-MS spectra of the oxidation products ($[As(tbpc)Br_2]^+$ and $[As(tbpc)Cl_2]^+$). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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