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Azaporphyrin phosphorus(V) complexes: synthesis, structure, and modification of optical properties

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Azaporphyrinoids, such as phthalocyanines (Pcs), tetraazaporphyrins (TAPs), and tetrabenzotriazacorroles (TBCs), are some of the most well-known and successful artificial dyes and pigments in modern material chemistry. Modifications of the macrocyclic core, periphery, and central element have attracted a great deal of interest in materials sciences due to generation of unique optical and electronic properties. However, the synthesis of most azaporphyrinoids with novel physical properties generally needs long, tedious procedures. On the other hand, the introduction of a phosphorus(V) atom into simple (known) azaporphyrin macrocycles is not necessarily difficult and can generate changes in the structural and optical properties. This paper provides an overview of the recent development of azaporphyrin phosphorus(V) complexes with unique structural and optical properties. Optical properties are discussed based on a combination of experimental absorption spectra, electrochemical properties, and theoretical molecular orbital calculations. These complexes are relatively easy to synthesize, are robust and free from transition metals, and have predictable properties.

Introduction

The bright colors of organic dyes have attracted a great deal of interest in a variety of fields. In nature, various types of organic dyes can be found. The isolation of natural organic dyes is one of the most attractive research areas in the field of natural product chemistry. From the first synthesis of Mauve by Sir Perkin in 1856,[1,2] development of artificial organic dyes has also been a central research topic in the field of industrial chemistry. The interest in dyes is not only due to their good appearance, but also due to their unique electronic properties. Recently, various types of materials for dye-sensitized solar cells (DSSCs),[3] organic field-effect transistors (OFETs),[4,5] organic photovoltaics (OPVs),[6,7] photosynthesis,[8] and chemical sensors[9–11] have been synthesized with reference to synthetic or natural dyes and pigments.

Porphyrin derivatives (porphyrinoids) are omnipresent in nature, and can be key components in biological functions. Typical porphyrin derivatives consist of four pyrrole units, which are linked by four carbon bridges (Scheme 1). The 18π-electron conjugated system of porphyrins which satisfies the Hückel definition of aromaticity ($(4n + 2)\pi$ electrons) is also a key subject of both practical and theoretical studies. On the other hand, after the discovery of an insoluble blue pigment in the early 20th century[12] and the subsequent structural determination,[13,14] phthalocyanines (Pcs) have become well known as successful artificial dyes and pigments. Pcs consist of four isoindole units linked by four nitrogen bridges instead of the carbon in normal porphyrins. Taking the aromatic skeleton of benzoporphyrins as a reference, the replacement of four *meso*-carbons with nitrogen atoms generates Pcs. Tetraazaporphyrins (TAPs) are the congeners of Pcs, whose structure is obtained by removing the four peripheral benzene rings from the Pc macrocycle. Pcs, TAPs, and porphyrinoids having *meso*-nitrogens are collectively called "azaporphyrinoids."

Some of the functional properties of azaporphyrinoids are often correlated with their color, so that tuning of the absorption properties is one of the most important topics in this area. Fig. 1a shows a typical electronic absorption spectrum of metallated Pcs. The sharp, intense band observed in the lowest energy region (*ca.* 650–700 nm) is a π–π* transition, referred to as the Q band. The broad band in the 300–400 nm region consists of several transitions, and is referred to as the Soret band. In particular, the intense Q band of azaporphyrins is a more attractive feature compared to the weak Q band of normal porphyrins. The peripheral positions are denoted as α and β in Fig. 1b. Peripheral modification of Pcs is a classical but the most common approach to modify their Q bands. Based on the knowledge accumulated to date, a number of azaporphyrin derivatives have been synthesized to achieve the target of adjusting the position and intensity of the Q band. In 2010,

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we edited one book on hitherto-reported absorption spectra of azaporphyrins.[15] Three common approaches exist for tailoring the absorption properties: (1) extending the π conjugation by benzoannulation and/or expansion of the macrocycle;[16–19] (2) oligomerization of macrocycles;[20–22] and (3) lowering of molecular symmetry.[23–25] However, these "π electron-modified" approaches have several disadvantages: the synthesis and separation of these types of compounds are often difficult, while the total yield is not necessarily high. Moreover, benzoannulated compounds are prone to oxidation due to a high HOMO level, and hence are sensitive to oxygen in air.

In this paper, we demonstrate an alternative strategy to overcome these problems. Since azaporphyrins contain a rigid, square planar central environment, various metals in the periodic table can be introduced into the central core. However, azaporphyrins containing "non-metal", main-group elements are still rare. These elements have notable features, such as effective orbital interactions, diversity of coordination, and large electronegativity,[26] so that their introduction into azaporphyrins can be expected to change the spectroscopic properties significantly without special π electron-modification of the parent macrocycle. In particular, pentavalent phosphorus (P(v)) has a high electronegativity (2.1) with a high valency, but few P(v) phthalocyanines (PPcs)[27–33] and no characterized P(v) tetraazaporphyrins (PTAPs) had been reported prior to our first PPc paper in 2011.[34] Although most P(v) complexes are provided by a one-step synthesis from known azaporphyrin derivatives, novel and unique optical properties are observed after the introduction of P(v). In a later section, we introduce the synthesis and characterization of P(v) complexes and their unique optical properties with a focus on our recent work. Basic optical properties and theoretical investigations of typical azaporphyrins are excluded, because some comprehensive reviews and textbooks have been published elsewhere.[15,23,35–37]

Synthesis and characterization

Synthesis of parent macrocycles

Porphyrins without a central element are usually called "metal-free" porphyrins. However, phosphorus is a nonmetallic element, so that we propose to call this kind of azaporphyrin a "free-base" azaporphyrin. Free-base azaporphyrins are important precursors for obtaining complexes containing various central elements, including the P(v) ion. The lithium method,[38] which is a cyclotetramerization reaction of 1,2-dicyanobenzene derivatives (phthalonitriles) in the presence of lithium alkoxide, provides easy access to free-base Pcs. On the other hand, free-base TAPs could be obtained by direct tetramerization of pyrroline-2,5-diimine or dicyanoethylene in low yield (Scheme 2). The template method is another way of producing a cyclotetramerized compound. The TAP Mg complex can be obtained in moderate yields by the template method, and subsequent demetallation using an acid, such as acetic acid or trifluoroacetic acid, leads to the corresponding free-base TAP.[39] The progress of demetallation can be easily followed by measuring the UV-vis spectra of the

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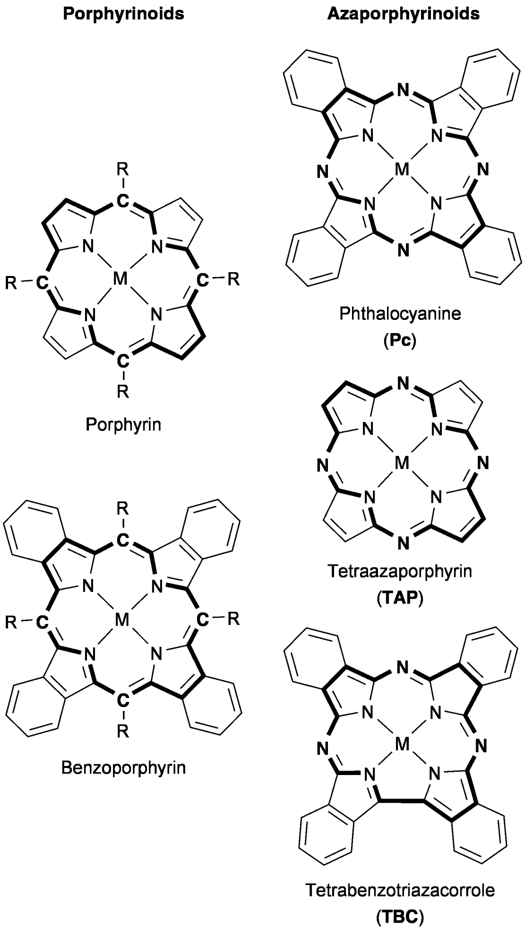
Taniyuki Furuyama

Taniyuki Furuyama was born in Tochigi, Japan, in 1982. He received his PhD of Pharmaceutical Sciences degree from The University of Tokyo in 2010 under the supervision of Profs. Masanobu Uchiyama and Yuichi Hashimoto. After he worked at RIKEN as a postdoctoral researcher for three months, he was appointed as an Assistant Professor at the Department of Chemistry, Graduate School of Science, Tohoku University (Prof. Kobayashi's group) in 2010. He then moved to the Graduate School of Natural Science and Technology, Kanazawa University, as an Associate Professor in 2015. His research interests cover the synthesis and theoretical chemistry of porphyrinoids and conjugated molecules with novel structures and unique properties. He was awarded a PCCP prize for Outstanding Achievement of Young Scientists from RSC and Chemical Society of Japan in 2015 and a Pharmaceutical Society of Japan Award for Young Scientists in 2017.

Nagao Kobayashi

Nagao Kobayashi received a Dr Sc. degree from Tohoku University in 1978 for his study on the MCD and CD spectroscopy of peroxidase and catalase. In 1986, he obtained a Dr of Pharmacy degree based on a study of the electrocatalytic reduction of oxygen in the presence of water-soluble porphyrins and phthalocyanines. From April 1995 to March 2015, he was a full professor at the Department of Chemistry, Graduate School of Science, Tohoku University. His research interests cover many different areas of porphyrin and phthalocyanine chemistry, with a strong focus on synthesis, electrochemistry, and optical spectroscopy and has published ca. 500 papers, including reviews. The CD and MCD spectroscopy is a key area of expertise, and he published a textbook on CD and MCD from RSC in 2012. Since April 2015, he has been a research professor at Shinshu University in Ueda. He received a Chemical Society of Japan Award for Creative Work in the chemistry of giant aromatic molecules in 2007, a Society of Porphyrin & Phthalocyanine Award in Phthalocyanine Chemistry in 2014, and a Japanese Association for Organic π-Electron Systems Award in 2016.



Scheme 1 Structures of representative porphyrinoids and azaporphyrinoids. The bold lines indicate each conjugation circuit.

generated characteristic Q band in the visible-to-near-IR regions. However, there are several problems for characterizing azaporphyrins. The parent azaporphyrin macrocycle has low solubility in general organic solvents, and even if the solubility is high enough (~1 mM), ^{1}H NMR spectra often show broad, unclear signals due to severe aggregation. In our work, bulky aryl groups[40] were introduced at peripheral positions of the macrocycle to improve the solubility and avoid irregular aggregation in solution. This kind of azaporphyrin provides high solubility in general organic solvents and nonaggregated features even at high concentrations. Consequently, all azaporphyrins could be characterized by ^{1}H NMR and HR-MALDI-FT-ICR mass spectroscopy.

Introduction of phosphorus(v) ion

The valence of the phosphorus reagent is essential for the introduction of the phosphorus ion into the Pc or TAP macrocyclic core. Pentavalent phosphorus is originally required (Scheme 3a). Phosphorus oxychloride ($POCl_3$) was reported to be a good source,[31] while phosphorus oxybromide ($POBr_3$) reacts with Pc or TAP free-base complexes more effectively.[29,32] After the reaction is completed, the axial ligand of phosphorus might be a halogen. Since a P–halogen bond is water-sensitive, the mixture was quenched by alcohol, to introduce axial alkoxide ligands.

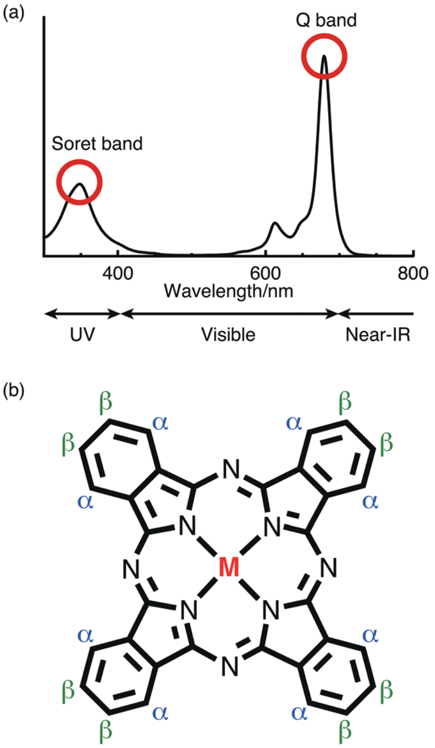
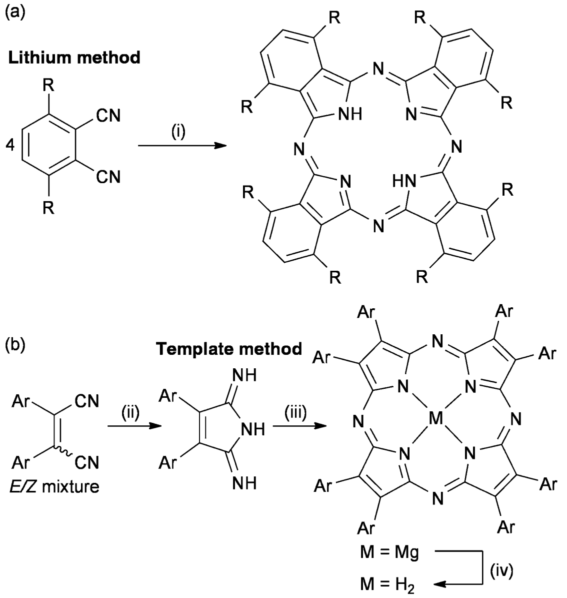
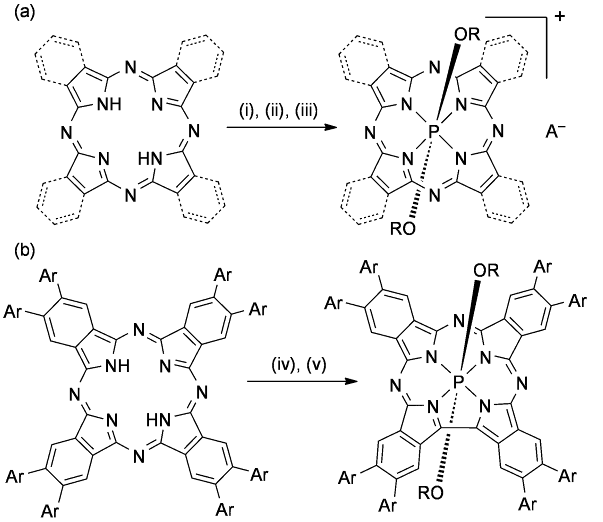


Fig. 1 (a) Typical absorption spectrum of a metallated Pc with D_{4h} symmetry. (b) Molecular structure of Pc. Peripheral positions are denoted as α and β.



Scheme 2 Representative synthesis of (a) Pc and (b) TAP free-base complexes. *Reagents and conditions*: (i) ROLi, ROH, reflux, 2–3 h; (ii) sodium, NH_3 (gas), ethylene glycol, 100 °C, 3–5 h; (iii) $(RO)_2Mg$, ROH, reflux, 1 day; (iv) CF_3COOH, rt, 30 min. R = ^{n}Bu or ^{n}Pent.

The resulting P(v) complexes were cationic salts containing a mixture of several counter anions. With the aim of isolating a discrete counter anion for further characterization, counter anion exchange with an excess amount of salt was required.



Scheme 3 Representative synthesis of (a) Pc or TAP and (b) TBC phosphorus complexes. *Reagents and conditions*: (i) $POBr_3$, pyridine, rt–reflux, 12–24 h; (ii) ROH, rt–reflux, 12–24 h; (iii) salt; (iv) PX_3 (X = Cl or Br), pyridine, 1–6 h; (v) ROH. R = methyl or triphenylsilyl.

Although trivalent phosphorus reagents (PCl_3 or PBr_3) were effective for obtaining P(V) complexes, a ring-contraction reaction due to such reagents often occurs, and tetrabenzotriazacorrole (TBC) P(V) complexes may be obtained directly from free-base Pc complexes by the reaction (Scheme 3b). Goldberg *et al.* prepared a corrolazine (triazacorrole) P(V) complex as a precursor of free-base corrolazine from free-base TAP and PBr_3.[41] In their paper, they mentioned that a PTAP was obtained in a very small yield, but they were unable to characterize it. We succeeded in the first practical synthesis of PTAP from free-base TAP and $POBr_3$, and the structure was determined by several spectroscopic methods.[42] Although the absorption spectrum of TBC phosphorus(V) complexes was assigned as a Pc P(III) complex in the early investigation of Pc phosphorus complexes,[27,43] the ring-contracted TBC structure was later unambiguously elucidated by X-ray diffraction analysis of single crystals.[41,44,45]

Since the nuclear spin quantum number and natural abundance of ^{31}P are 1/2 and 100%, ^{31}P NMR spectroscopy is a useful method for characterizing and investigating P(V) complexes. The chemical shifts in ^{31}P NMR spectra are sensitive to the coordination number of the phosphorus center.[31] Normal P(V) complexes which have 6-coordinate phosphorus with two axial ligands appear at −180 to −200 ppm, while the signals of 5-coordinate phosphorus compounds are mostly found at −90 to −110 ppm.[46] The shielding effect of the diatropic ring current also affects the chemical shift. The clear dependence of the parent macrocycle appears as Pc (−160 to −180 ppm)[29,34] < TAP (−180 to −190 ppm)[42] < TBC (to −200 ppm),[32,44] indicating that the trend of the shielding effect of the macrocycle is Pc < TAP < TBC.

Structural features

No X-ray crystallographic structures of an azaporphyrin P(V) complex had been reported prior to our report on PPc in 2011.[34] Single crystals suitable for X-ray analysis were obtained by slow diffusion of an insoluble solvent into a solution of azaporphyrin. A representative X-ray crystallographic structure of the α-$(PhS)_8$Pc P(V) complex hexafluorophosphate salt **1** is shown in Fig. 2. The Pc macrocycle is severely ruffled, due to the small atomic radius (106 pm) of the phosphorus(V) ion,[47,48] while normal Pc complexes have near-planar structures. The degree of ruffling of the core (Δ*r*) can be calculated, as described by eqn (1).

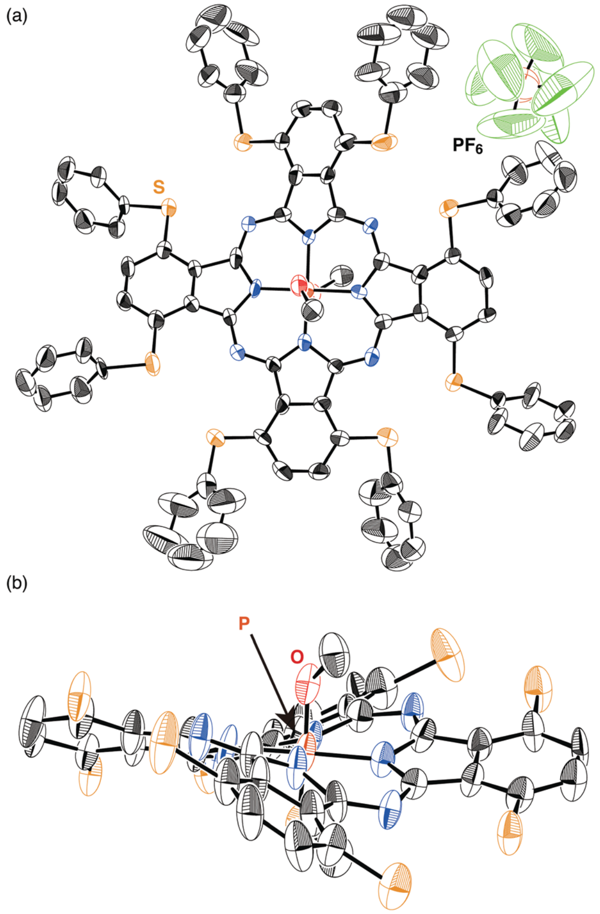


Fig. 2 X-ray crystal structure of α-$(PhS)_8$Pc phosphorus(V) complex hexafluorophosphate salt (**1**). The thermal ellipsoids were scaled to the 50% probability level. (a) Top view; (b) side view (peripheral substituents and counteranion omitted). H atoms and the solvent molecule have been omitted for clarity.

$$\Delta r = \sqrt{\left(\frac{\sum_{i=1}^{24} r_i^2}{24}\right)} \qquad (1)$$

where r_i is the deviation of each atom from the 4*N* mean plane of the macrocycle. 24 atoms are defined by four pyrrolic moieties and four nitrogen atoms at the *meso*-positions. Δ*r* depends on the structure of the macrocycle. The Δ*r* value of PPc **1** having eight PhS groups at the α positions (0.43) is larger than that of PTAP[42] substituted by eight *p*-*tert*-butylphenyl groups at the pyrrole β positions (0.26). The distance between the two pyrrole nitrogens at opposite sides of the core in typical metalloTAPs is *ca.* 3.8–3.9 Å[49,50] and that of the α-$(PhS)_8$Pc zinc complex is 3.96 Å.[51] In the case of PPc and PTAP, the distances are 3.67 Å and 3.68 Å, respectively. This strongly suggests that the small central phosphorus(v) ion (106 pm) shrinks the macrocycle.

Non-planar type Pcs are known not only for phosphorus(v) complexes, but also for Pcs with bulky peripheral substituents at the α positions. For example, the crystallographic structure of an α-Ph_8Pc free-base complex shows a highly-saddled structure (Δr = 0.58).[52] Phosphorus(v) insertion into the macrocycle proceeded smoothly, and single crystals of the phosphorus(v) complexes suitable for X-ray analysis were obtained.[53] During this process, the type of distortion was changed from a saddle to a ruffled structure, while the value of Δr = (0.57) was almost identical. However, the distance between the two pyrrole-nitrogen atoms at opposite sides (*ca.* 3.68 Å) for the phosphorus(v) complex is shorter than that in the free-base complex (*ca.* 3.9 Å), indicating that the structural influence of only one phosphorus(v) ion is greater than the influence of the eight bulky phenyl substituents at the α positions.

Phthalocyanines absorbing near-IR light beyond 1000 nm

Early investigations. Table 1 shows a list of the absorption properties of Pc P(v) complexes. In 1981, Gouterman *et al.* reported the first synthesis of P(v)Pc as a byproduct of the synthesis of a P(III) complex.[27] As mentioned above, the "P(III) complex" was not a Pc complex, and people now believe it was a TBC P(v) complex from the shape of the absorption spectra. The P(III) ion may not be introduced into a typical azaporphyrin macrocycle due to its large ionic radius. The P(v)Pc has marginal solubility in pyridine, while the original unsubstituted free-base Pc is scarcely soluble in the same solvent. The sharp Q band of P(v)Pc appears at around 670 nm, and the entire absorption spectrum can be interpreted as that of typical Pcs with D_{4h} chromophore symmetry. For more than two decades after the first synthesis, the substitution effects of P(v)Pc have not been discussed. In 2003, Goldberg *et al.* reported the synthesis of a α-$(BuO)_8$Pc P(v) complex.[31] The Q band of the corresponding free-base complex appeared at 760 nm (13.158k cm^{-1}) in toluene, due to an electron-donating effect of butyloxy oxygen.[54] After insertion of a P(v) ion into α-$(BuO)_8PcH_2$, the Q band was further red-shifted by *ca.* 130 nm to 889 nm (11.249k cm^{-1}) in methanol, although the Q bands of unsubstituted or alkyl-substituted Pcs shifted to the red by at most 18 nm (Table 1). The Q band of the α-$(BuO)_8$ naphthalocyanine free-base complex appears at 864 nm (11.574k cm^{-1}) in toluene.[55] Therefore, the effect of the P(v) ion for red-shifting the Q band (1.909k cm^{-1}) was larger than that (1.584k cm^{-1}) of increasing the size of the entire π-conjugation system by four benzo rings. The redox potentials of the α-$(BuO)_8$Pc P(v) complex shifted anodically compared to those of the corresponding free-base complex, indicating that the P(v) complex is more difficult to oxidize than the free-base complex. These effects are to be expected from the positive charge (large electronegativity) of the P(v) ion. On the other hand, a β-tetraaryloxy-substituted Pc P(v) complex has also been synthesized,[56] and its Q band appeared at a shorter wavelength (683 nm in ethanol) compared to the corresponding α-substituted Pc (889 nm).[31] In the next section, we will undertake a systematic comparison among peripheral substituents and central elements in Pcs.

Peripheral substitution effects of phosphorus(v) complexes

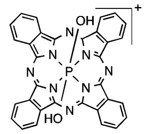
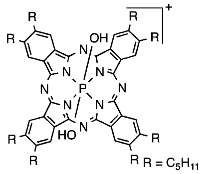
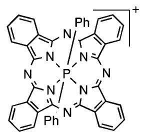
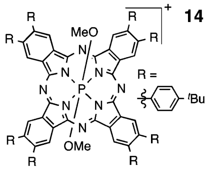
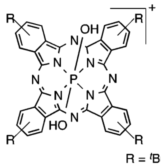
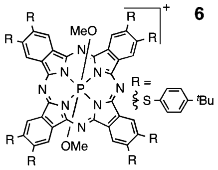
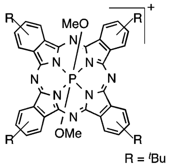
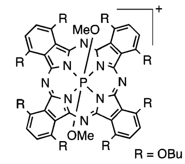
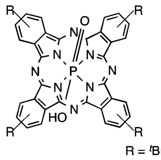
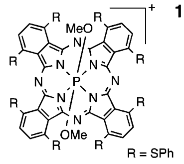
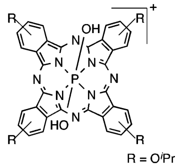
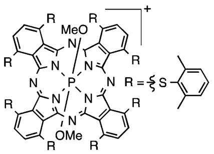
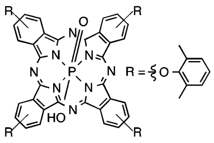
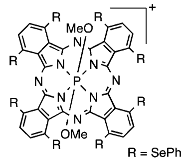
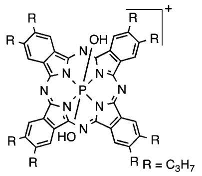
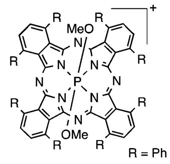
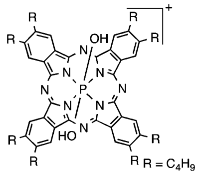
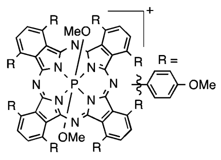
Fig. 3 shows the absorption spectra of several metallo- and phosphorus(v) complexes of tetra *tert*-butylated Pc substituted at the β-position (β-^{t}Bu_4Pc) and α-$(PhS)_8$Pc. Peripheral substitutions affect the orbital energies of Pcs. Gouterman's four-orbital model[57] is an efficient model for assigning the typically intense absorption bands (Q and Soret bands) in porphyrinoids with D_{4h} symmetry. Since the Q band is assigned to a transition from the HOMO to the LUMO and LUMO+1, changing the energy levels of the HOMO, LUMO and LUMO+1 shifts the position of the Q band. In the HOMO of unsubstituted Pc, the MO coefficient at the α-carbon is large, so that the introduction of electron-donating groups at the α positions destabilizes the HOMO energy significantly (Scheme 4).[34,54] The effect of the central element (positive charge) is large for the LUMO since the MO coefficient of the central pyrrole nitrogen is large. The introduction of metal ions having positive charge into the Pc core, therefore, stabilizes particularly the LUMO energy. In this way, the introduction of electron-donating groups at the α positions and highly positive (or high valent) metal ions into the core makes the HOMO–LUMO gap smaller, thereby shifting the Q band to longer wavelengths. Hence, for example, the trivalent MnPc is empirically known to have its Q band in the longer wavelength region (*ca.* 730 nm) compared to other divalent metalloPcs (*ca.* 650–680 nm) including Mn(II)Pcs.[58,59] When the central transition metal is the same, except for the phosphorus(v) complexes, the difference of the Q band position between β-^{t}Bu_4Pc and α-$(PhS)_8$Pc is in a narrow range (155–111 nm, *ca.* 2.4–2.2k cm^{-1}), as previously measured experimental data substantiate.[15] Hence for the transition metal Pcs, the position of the Q band is approximately predictable from the data of β-^{t}Bu_4Pcs.

Interestingly, the Q band of the α-$(PhS)_8$Pc P(v) complex **1** was detected further to the red, at 1018 nm in chloroform. The energy difference between the corresponding free-base complex **2** and **1** (210 nm, *ca.* 2.5k cm^{-1}) is more than four times that between β-^{t}Bu_4Pc free-base (**3**) and its P(v) complex (**4**) (30 nm, *ca.* 0.67k cm^{-1}). Since P is not a heavy atom and **1** has a rigid structure, it showed a distinct fluorescence beyond 1000 nm, with a relatively high quantum yield (λ_{em} = 1067 nm, $\Phi_{FL} = 9 \times 10^{-3}$ in chloroform).[51] Although the photostability of compounds absorbing light in the near-IR region is generally low, the photostability of **1** in solution is higher than that of the commercially available near-IR fluorescence dye IR-1048.[60] The phtostability of **1** is close to that of the β-^{t}Bu_4Pc copper complex, since they are bleached after the irradiation of sunlight for *ca.* 130 and 160 hours, respectively.

Synergistic effect of main-group elements

The position of the substituents in P(v) complexes is also a critical factor in shifting the Q band to the red beyond 1000 nm (Fig. 4).[51] As previously investigated,[54] the Q band of the β-(4-^{t}$BuC_6H_4S)_8$Pc free-base complex **5** in chloroform

Table 1 Position of Q bands of phthalocyanine phosphorus(v) complexes

Structure[a]	Solvent	Position (nm), (Intensity)	Ref.	Structure[a]	Solvent	Position (nm), (intensity)	Ref.
	Pyridine Pyridine DMSO	653 669 (lg ε = 1.00) 671 (48 900)	27 29 33		Pyridine	685 (lg ε = 1.00)	29
	DMSO	671 (47 800)	33	**14** 	CH_2Cl_2	747 (192 000)	42
	Pyridine Pyridine	677 (lg ε = 1.00) 677	29 32	**6** 	$CHCl_3$	790 (120 000)	51
4 	$CHCl_3$	716	51		Methanol	889 (91 000)	31
	$CHCl_3$	660	30	**1** 	$CHCl_3$	1018 (39 000)	34
	Pyridine	685	28		CH_2Cl_2	1032 (120 000)	51
	Ethanol	683	56		$CHCl_3$	1033 (39 000)	34
	Pyridine	684 (lg ε = 1.00)	29		CH_2Cl_2	852 (110 000)	53
	Pyridine	688	32		CH_2Cl_2	916 (101 000)	53

[a] A counter anion of the cationic complex was omitted for clarity.

(721 nm, center of Q_x and Q_y bands) lies at a shorter wavelength (by *ca.* 90 nm, *ca.* 1.5k cm^{-1}) than that of the α-substituted free-base Pc **2** (809 nm). With the introduction of P(v) ion into **5**, the Q band shifted to 790 nm (**6**), but the difference (*ca.* 70 nm, *ca.* 1.2k cm^{-1})

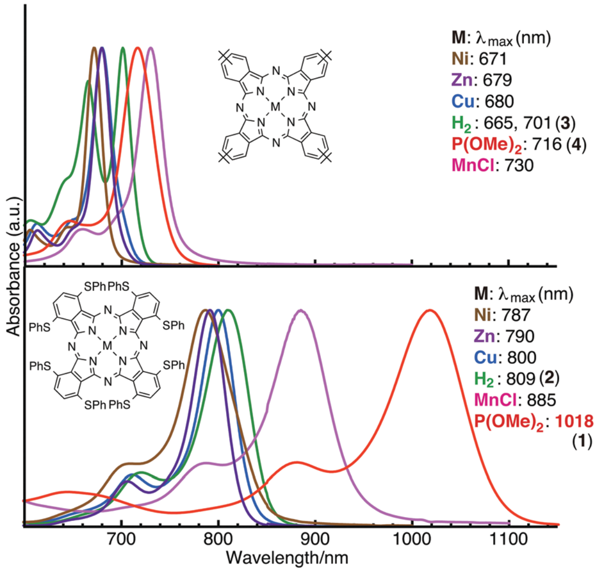


Fig. 3 Absorption spectra of metallated and phosphorus(V) complexes of β-^{t}Bu$_4$Pc (top) and those of α-(PhS)$_8$Pc (bottom) in chloroform.

was smaller than that between α-substituted free-base **2** and its P(V) complex **1** (210 nm, *ca.* 2.5k cm^{-1}). Estimation of the values of redox potentials is also important in order to determine the origins of the red-shift of the Q-band wavelength accompanying the introduction of phosphorus(V). Fig. 5 displays cyclic voltammograms of free-base **2** and its P(V) complex **1** in *o*-dichlorobenzene (*o*-DCB) in the presence of 0.1 M ^{n}Bu$_4$NClO$_4$ as a supporting electrolyte. The first oxidation ($E_{1\text{ox}}$) and reduction ($E_{1\text{red}}$) of free-base **2** appeared at 0.16 and −1.23 V ($E_{1\text{ox}} - E_{1\text{red}}$ = 1.39 V), while those of *tert*-butylated H$_2$Pc under the same conditions[19] appeared at 0.26 and −1.44 V ($E_{1\text{ox}} - E_{1\text{red}}$ = 1.70 V). After the introduction of a phosphorus(V) ion into **2**, the redox potentials shifted anodically (0.37 and − 0.55 V, $E_{1\text{ox}} - E_{1\text{red}}$ = 0.92 V). Since it is well established that the HOMO and LUMO energies of Pc derivatives correlate well with their first oxidation and reduction potentials,[61] the introduction of phosphorus(V) greatly stabilizes both the HOMO and LUMO levels. In particular, the change in reduction potential (0.68 V) is larger than that of oxidation potential (0.21 V), indicating that the stabilization of the LUMO is larger than that of the HOMO.

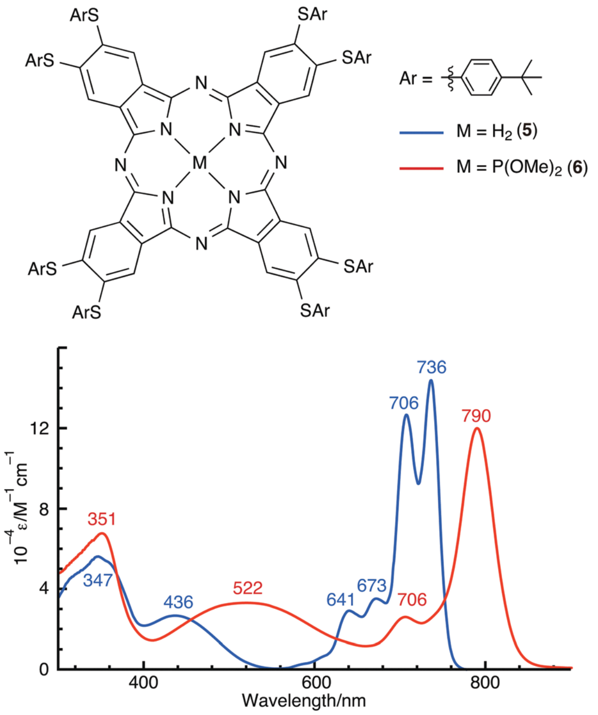
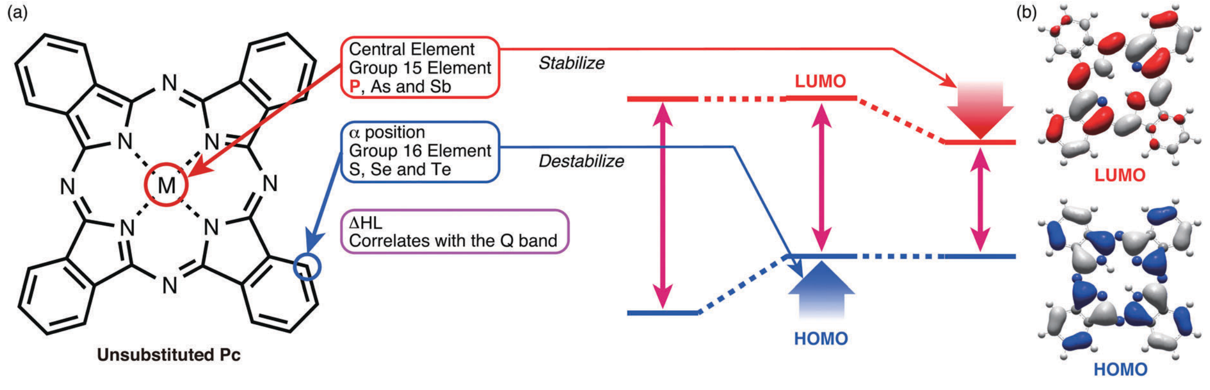


Fig. 4 Absorption spectra of β-(thioaryl)$_8$ substituted free-base (blue) and phosphorus (red) complexes in chloroform.

Therefore, the origin of the red-shift of the Q band after the introduction of phosphorus(V) is mainly due to a significant stabilization of the LUMO level. The low HOMO energy is also important for high photostability of compounds with a narrow HOMO–LUMO gap.

Molecular orbital calculations are often useful in explaining the effects related to the Pc ligand, peripheral substituents, and the central phosphorus(V) ion. Although the B3LYP/6-31G* level of calculation is generally not suitable for obtaining exact experimental optical properties in the whole spectral region, the correlation between the experimental and theoretical values of MO energy levels in the Q band region is quite good and can be discussed.[62,63] Since the synthesized Pcs have bulky peripheral groups to improve their solubility in organic solvents, model structures where a part of the substituents was replaced by



Scheme 4 (a) Molecular design principle of near-IR absorbing Pcs. (b) Frontier orbitals of an unsubstituted free-base Pc.

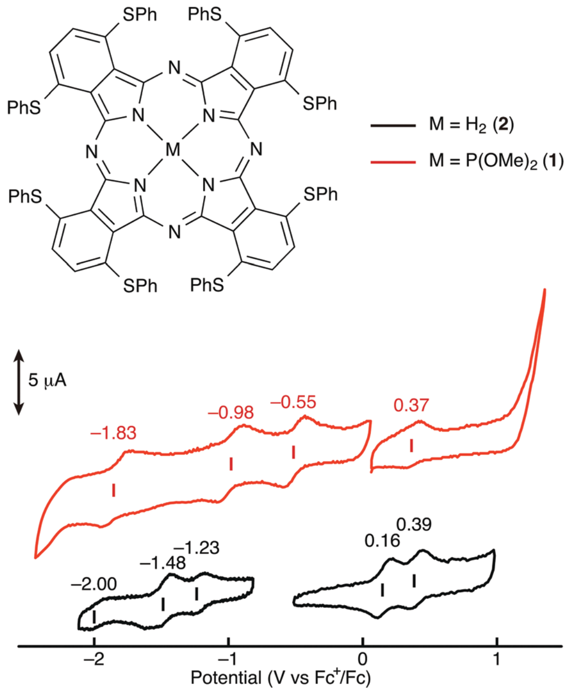


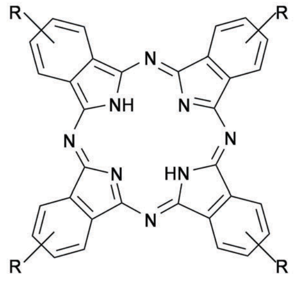
Fig. 5 Cyclic voltammetry data for α-$(PhS)_8$ substituted free-base (**2**, black) and phosphorus (**1**, red) complexes. Cyclic voltammograms were acquired from 1.0 mM solutions of analyte in 0.1 M $^nBu_4NClO_4$/*o*-DCB. Ferrocene was used as an internal standard and set to 0 V.

hydrogen were used (Table 2). Partial MOs related to the Q band absorption for the six representative compounds are shown in Fig. 6. The energies of the HOMOs and LUMOs were in good agreement with the experimental cyclic voltammograms. Even for the P(V) complexes, the calculated transitions in the Q band region are composed of the HOMO, LUMO, and LUMO+1. These orbitals derived from Gouterman's model[57] indicate that the absorption bands can be explained in a manner similar to typical free-base or metallated Pcs. Moreover, the calculated potential gap between the LUMO and HOMO, $\Delta(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})_{\mathrm{calcd}}$, exhibits a clear correlation with the experimental potential differences derived from their absorption spectra $\Delta(E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})_{\mathrm{exp}}$ (Fig. 7). This simple relationship indicates that the extent of the Q band shift upon introducing peripheral substituents and central phosphorus(V) can be predicted independently by MO calculations, even for Pcs absorbing in the near-IR region beyond 1000 nm. A similar relationship has also been demonstrated in the context of a series of radially symmetric fused-ring-expanded zinc(II) porphyrinoids[62] and nonplanar core-modified tetrabenzoporphyrins.[63]

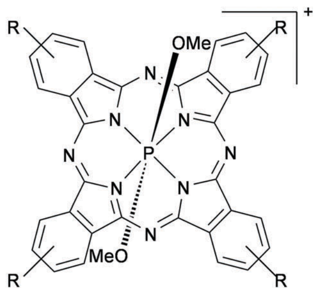
Tetrabenzotriazacorroles: a variant of low-symmetry Pcs

Optical properties. Tetrabenzotriazacorrole (TBC) is an 18π aromatic Pc-corrole analog, in which one *meso* nitrogen atom of Pc is replaced with a direct bond between the α-carbons on neighboring pyrrole moieties. The first practical synthesis of a

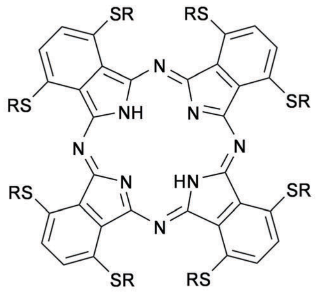
Table 2 Model structures for molecular orbital calculations



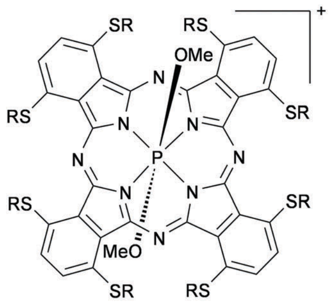
Group A (PcH_2)
Synthesized: R = ^tBu (**3**)
Calculated: R = H (**3'**)



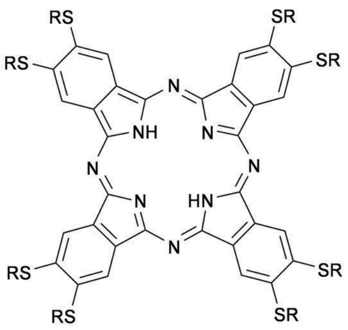
Group B ($PcP(OMe)_2$)
Synthesized: R = ^tBu (**4**)
Calculated: R = H (**4'**)



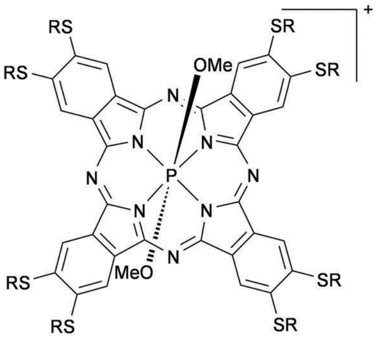
Group C (α–$(RS)_8PcH_2$)
Synthesized: R = Ph (**2**)
Calculated: R = H (**2'**)



Group D (α–$(RS)_8PcP(OMe)_2$)
Synthesized: R = Ph (**1**)
Calculated: R = H (**1'**)



Group E (β–$(RS)_8PcH_2$)
Synthesized: R = 4-$^tBuC_6H_4$ (**5**)
Calculated: R = H (**5'**)



Group F (β–$(RS)_8PcP(OMe)_2$)
Synthesized: R = 4-$^tBuC_6H_4$ (**6**)
Calculated: R = H (**6'**)

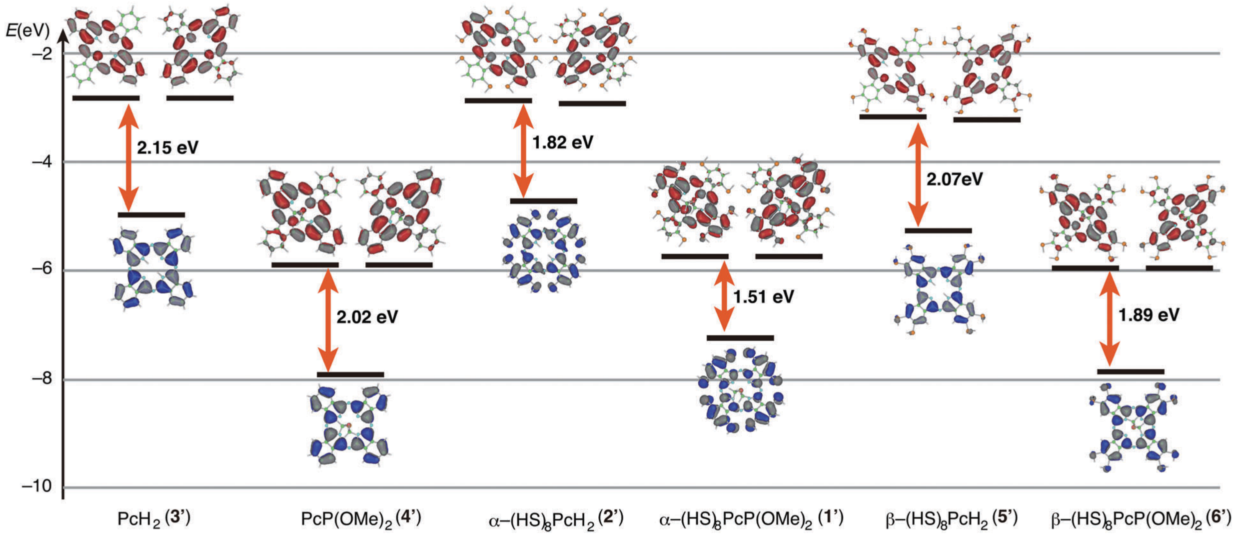


Fig. 6 Energy levels of frontier MOs and their contour plots obtained from calculations. Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were performed at the B3LYP/6-31G* level.

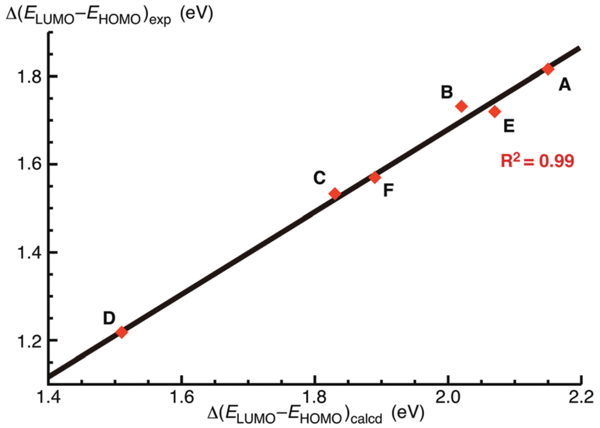
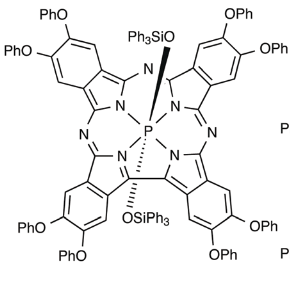
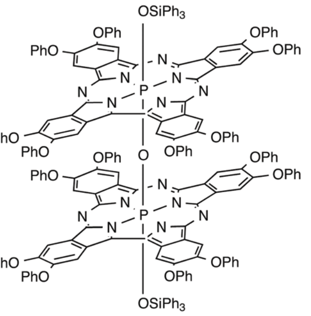


Fig. 7 The relationship between the calculated and experimental energies ($\Delta(E_{\text{LUMO}} - E_{\text{HOMO}})$) of the six representative Pcs.



7 (monomer)



8 (homodimer)

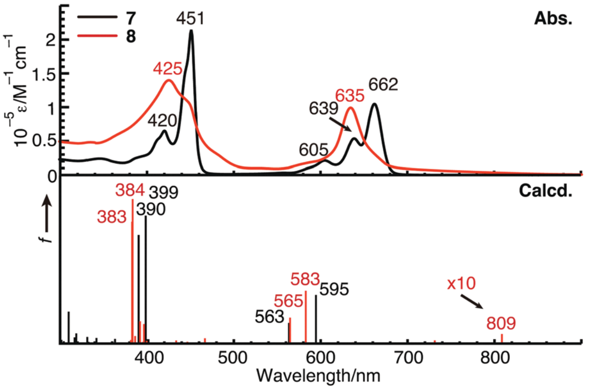


Fig. 8 UV-vis absorption (in chloroform) (top) and theoretical absorption spectra (bottom) of PTBC monomer (black) and homodimer (red). Calculations were carried out at the B3LYP/6-31G* level of theory.

stable TBC was reported by Fujiki *et al.* as a germanium complex.[64,65] TBC P(v) complexes (PTBCs) can be synthesized from the corresponding symmetric Pcs in moderate yield, although the separation of low-symmetry Pcs is generally not easy.[23] Here, PTBC is focused on, as a variant of low-symmetry Pcs. The two axial ligands of PTBC are changeable, so that the μ-oxo homodimer of PTBC could be synthesized.[44] UV-vis absorption spectra of monomer (**7**) and μ-oxo dimeric (**8**) PTBC in chloroform are shown in Fig. 8. The removal of an aza-nitrogen results in marked changes in the spectroscopic properties due to the loss of the main C_4 axis of symmetry and changes in the energies of the frontier orbitals. The a_{2u} MO from Gouterman's model[57] is destabilized due to the large MO coefficients on the aza-nitrogens. The spectrum of **7** exhibits similarities to the spectrum of tetrabenzoporphyrins.[66] For example, the Soret band shifts to the red (451 nm) compared to typical symmetric Pcs (*ca.* 320–380 nm). The intense absorption bands of **8** are blue-shifted to 635 and 425 nm with concomitant broadening. This feature may suggest that the gap between the HOMO and LUMO increases after the μ-oxo dimer formation; however, cyclic voltammograms of monomer **7** and homodimer **8** indicated that the gap decreased after the formation. This contradiction can be interpreted by the presence of a weak, broad band in the near-IR region (680–800 nm) of **8**. In the theoretical absorption spectrum of the homodimer (Fig. 8), the weak band was estimated at

809 nm, and is composed of a transition from the HOMO to LUMO. The lowest-energy transition is forbidden, and can be assigned to the experimental weak band in the near-IR region. Therefore, the transition component of the intense band in the Q band region of homodimer (635 nm in chloroform) is completely different from that of the monomer (662 nm). These spectroscopic features of the dimer can be interpreted conceptually by considering exciton coupling interactions between the cofacially-arranged monomer units (H-type aggregate).[67]

Generation of singlet oxygen for photodynamic therapy. Photodynamic therapy (PDT) involves the administration of a tumor-localizing photosensitizing agent, followed by activation of the agent by light of a specific wavelength. This novel clinical method against cancer has already been available for patients with early and advanced stage cancer of the lungs, digestive tract, and genitourinary tract.[68] Singlet oxygen ($O_2(^1\Delta_g)$) is believed to be the initial agent in PDT, so that a photosensitizing agent requires a high singlet oxygen quantum yield (Φ_Δ) for light in the near-IR region, that is the "near-IR window" in biological tissue (650–1350 nm).[69]

In order to determine singlet oxygen quantum yields, direct measurement of the generated photosensitized singlet oxygen luminescence at around 1270 nm is the most reliable photophysical method. However, special instruments are required for the detection of the near-IR luminescence. A steady-state method[70] is a convenient method for the determination of Φ_Δ, in which a solution containing a photosensitizer, oxygen and a quencher is irradiated under near-IR light, and the decay of the quencher is monitored. The most common chemical quencher in organic solvents is 1,3-diphenylisobenzofuran (DPBF), which has an intense absorption band at around 410 nm. After the reaction with singlet oxygen, the band is diminished. Therefore, the photobleaching rate can be determined by the decay of the band using a standard spectrophotometer. Eqn (2) is employed for the calculations:

$$\Phi_\Delta = \Phi_\Delta^{\mathrm{Std}} \frac{R \cdot I_{\mathrm{abs}}^{\mathrm{Std}}}{R^{\mathrm{Std}} \cdot I_{\mathrm{abs}}} \tag{2}$$

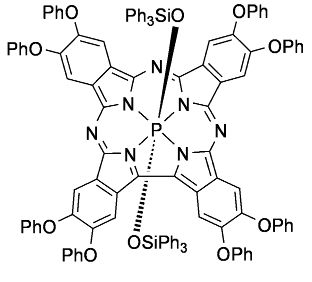
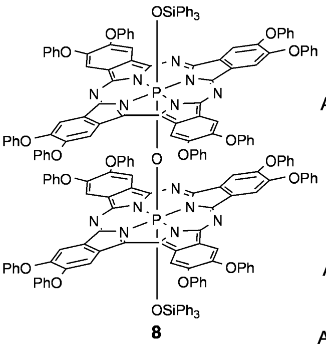
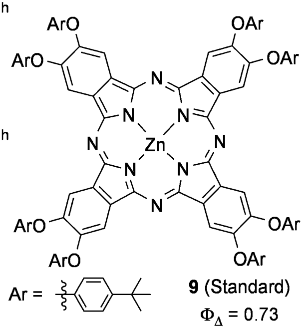
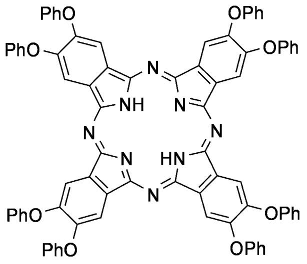
where $\Phi_\Delta^{\mathrm{Std}}$ is the singlet oxygen quantum yield for the standard. R and R_{Std} are the DPBF photobleaching rates in the presence of the samples and standard, respectively. I_{abs} and $I_{\mathrm{abs}}^{\mathrm{Std}}$ are the rates of light absorption by the samples and standard, respectively.

PTBCs are good candidates for efficient photosensitizers of PDT. For example, oxophosphorus TBCs have been shown to possess good photodynamic efficiency toward HeLa cells.[71] Zhang and Tung reported photophysical properties of sulfonated PTBC.[72] The PTBC shows very high triplet (Φ_T = 0.64 in DMSO) and singlet oxygen quantum yields (Φ_Δ = 0.88 in DMSO). Nyokong *et al.* have also reported high Φ_Δ values of PTBCs (Φ_Δ = 0.52–0.74 in DMSO) and biological applications.[73,74] Such high Φ_Δ values are considered to be not caused by a heavy-metal effect, but to be due to the low-symmetry chromophore of TBC. Table 3 shows the singlet oxygen quantum yields determined by a steady-state method using the β-(4-^{t}BuC$_6$H$_4$O)$_8$Pc zinc complex (**9**) as a standard (Φ_Δ = 0.73 in chloroform[75]). The quantum yield of the TBC monomer is higher (Φ_Δ = 0.75) than free-base Pc (Φ_Δ = 0.25). Therefore, the high value of **9** can be assigned to the heavy-metal effect of zinc. Taking all the above into account, it is concluded that the chromophore symmetry is a critical factor for improving the quantum yield. On the other hand, the cofacial type homodimer **8** had a low quantum yield (Φ_Δ = 0.20) due to H-type aggregation, which reduces the lifetime of the excited state by enhanced radiationless excited-state dissipation.[76]

Tetraazaporphyrins: absorbing light across the entire UV-vis region

Enhancement of charge-transfer transitions. Fig. 9 shows absorption spectra of TAP and Pc P(v) complexes. The UV-vis spectrum of the TAP magnesium complex (MgTAP, **12**) is characteristic of metallated TAPs with D_{4h} symmetry,[36] resembling that of typical metallated or P(v) Pc complexes (Table 1). Interestingly, the absorption envelope of the (4-^{t}BuC$_6$H$_4$)$_8$TAP P(v) complex **11** is quite different from those of free-base and typical metallated TAPs. Here, a Q band-like absorption was observed at 664 nm, while another broad, intense absorption band appeared between the Soret (342 nm) and Q bands at 534 nm. Therefore, the "third" intense absorption band is a characteristic of only the TAP P(v) complex. Furthermore, the absorption envelope of the Pc P(v) complex with eight aryl groups at peripheral positions **14** resembles those of regular metallated Pcs and alkyl-substituted P(v) Pcs.

Table 3 Singlet oxygen quantum yield of azaporphyrinoids in chloroform

 **7** Φ_Δ = 0.75	 **8** Φ_Δ = 0.20	 **9** (Standard) Φ_Δ = 0.73	 Φ_Δ = 0.25

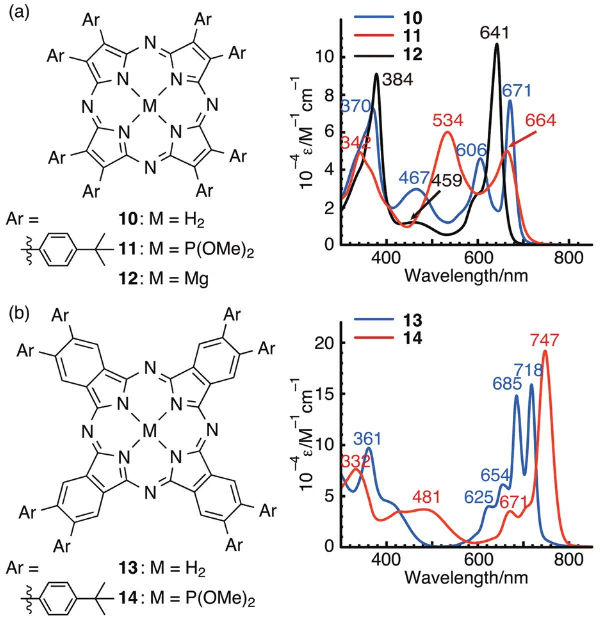


Fig. 9 (a) UV-vis absorption spectra of (a) tetraazaporphyrin and (b) phthalocyanine complexes in dichloromethane.

Although a broad band appeared at 481 nm, the relative intensity of the Q band of **14** is smaller than that of PTAP **11**.

In the case of MgTAP **12** having eight aryl groups, a broad, weak absorption band appeared (459 nm) between the Soret and Q band regions, while the absorption spectrum of the ^{t}Bu$_4$TAP Mg complex did not show this band.[77] The differences suggest the importance of peripheral aryl substituents for the generation of the band between the Soret and Q bands. Finally, the assignment of the bands was achieved by molecular orbital calculations of octaphenyl TAPs **11′** (PTAP) and **12′** (MgTAP) (Fig. 10). The calculated transitions at 359 nm for Mg complex **12′** are composed of transitions from the orbitals that are localized on the lone pairs of the *meso*-nitrogens and peripheral aryl moieties to the degenerate LUMOs that are localized on the TAP core (e_{gx} and e_{gy}-like orbitals in Gouterman's model),[57] supporting the suggestion that these transitions possess some character of n–π*[78] and charge-transfer (CT) transitions from the peripheral aryl moieties to the TAP macrocycle. The calculated spectrum of P(V) complex **11′** contains several stronger transitions with similar characteristics, but to longer wavelength than those of **12′**, in accord with the experimental absorption spectra of **11** and **12** (Fig. 9). Hence, it is inferred that the introduction of the phosphorus(V) ion into the TAP core enhanced the CT band between the Soret and Q bands. The broad band of P(V)Pc **14** at 481 nm could also be assigned to a CT transition from the peripheral octaphenyl groups to the Pc core.[42] However, the calculated CT transitions of the model P(V)Pc were weaker than those of PTAP, indicating that the effect of the P(V) ion is relatively weak in the peripherally aryl-substituted Pcs.

Effects of peripheral and axial substituents. If the band between the Soret and Q bands is a CT band between the peripheral aryl moiety and the central TAP core, changing the peripheral substituents on the aryl group may alter its position and intensity in PTAP spectra. The absorption spectra of a series of PTAPs with substituted aryl moieties are shown in Fig. 11. Both the Q and CT bands were dependent on the substituents in the visible region, although the reported absorption spectra of typical metallated TAPs are only slightly perturbed by the substituents.[79,80] More interestingly, the absorption envelope of *meta*-methoxyphenyl substituted PTAP **17**[81] is quite different from that of *para*-methoxyphenyl substituted PTAP **15** by just altering the substituent positions. Both the position and intensity of the peaks of PTAPs exhibit a notable correlation with the Hammett σ_p or σ_m values[82] of substituents on the aryl moieties (Fig. 12). Plots of the position of both the Q and the CT bands and the ratio of the intensity of the Q bands to that of the CT bands *versus* the Hammett σ_p or σ_m values of substituents exhibit good linearity. In the case of a methoxy group, a *para*-substituted

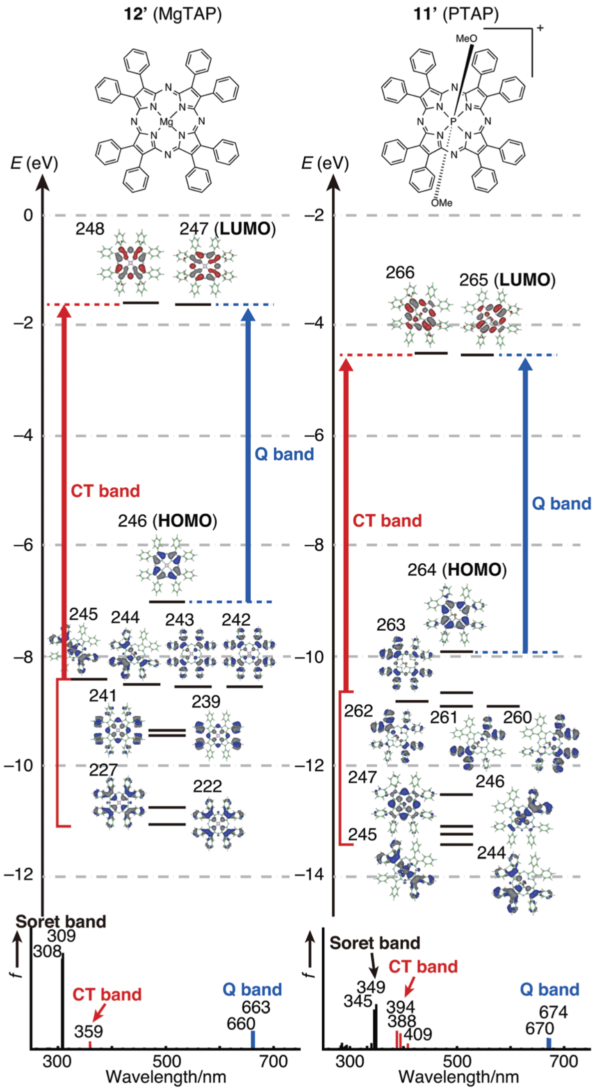


Fig. 10 Partial molecular energy diagram and orbitals of Ph$_8$TAPs (and) their calculated absorption spectra (bottom). Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were performed at the LC-BLYP/6-31G*//B3LYP/6-31G* level.

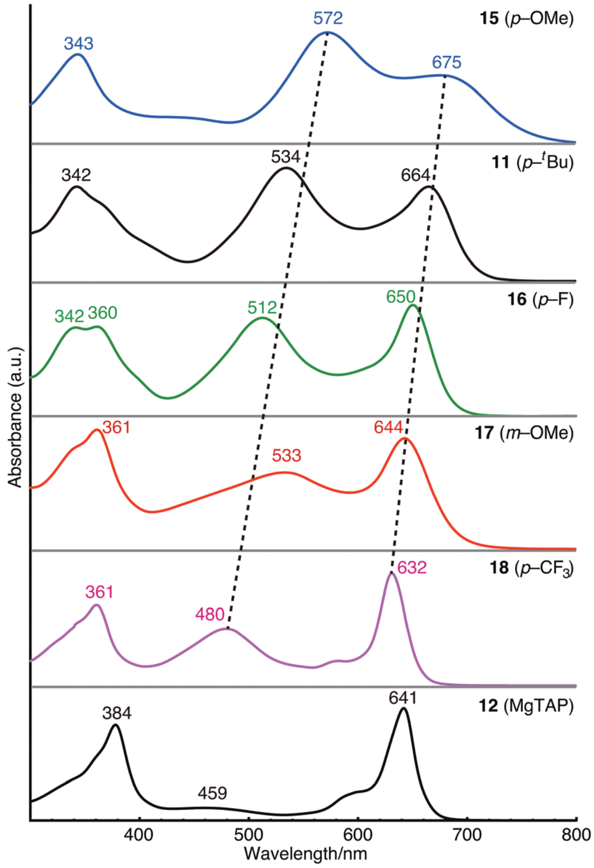


Fig. 11 UV-vis absorption spectra of a series of PTAPs in CH_2Cl_2.

methoxy group is a well-known electron-donating group, originating from the mesomeric effect of the oxygen lone pairs, while a *meta*-substituted methoxy group is an electron-withdrawing group, as a result of the larger electronegativity of oxygen compared to carbon. Thus, the Hammett σ_p and σ_m values of methoxy groups indicate that the role of the substituent depends on its position. This correlation can be useful in fashioning new PTAPs designed to access appropriate optical properties over a wide range of the visible region. Electron-donating nitrogen[83–85] or sulfur[86,87] directly attached to the TAP macrocyclic core have also been investigated. The introduction of electron-donating groups onto the *para*-position of the aryl substituents of PTAP can shift the CT and Q bands to longer wavelengths (Fig. 11), so that nitrogen or sulfur linked at the *para*-position of the peripheral phenyl groups of PTAPs shows broad, intense absorption bands in the visible to near-IR region. The absorption spectra of these PTAPs cover a wide range of the UV-visible to near-IR region (up to 950 nm) as a result of the effect of the highly positively charged central phosphorus(V) ion and the peripheral electron-rich heteroatoms.[88]

A central phosphorus ion has two axial ligands. In the case of reported porphyrin P(V) complexes with hydroxyl groups at the axial positions, the proton of the hydroxyl group could be easily removed using a base, resulting in switching of the crystallographic structure of the porphyrin macrocycle.[46,89] In the case of PTAPs, changing the axial ligands can switch not only the structures of the TAP macrocyclic core, but also the effect of the peripheral aryl moieties. The absorption spectrum of PTAP with hydroxyl groups **19**[90] in dichloromethane gradually changed upon addition of a weak base (triethylamine) (Fig. 13a).

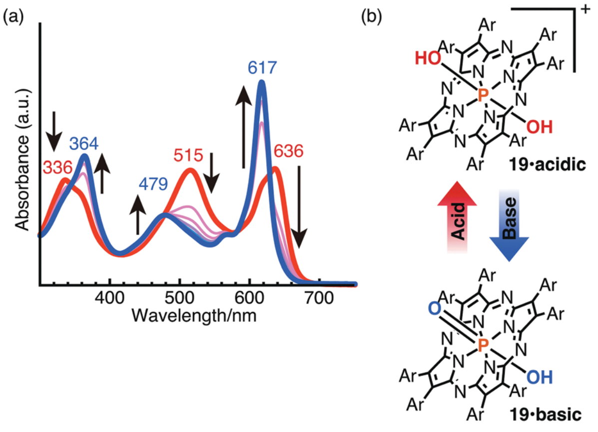


Fig. 13 (a) Spectral changes of a solution of **19** by adding triethylamine (0–2 eq.) in CH_2Cl_2 and (b) proposed structures of the basic and acidic states of **19**.

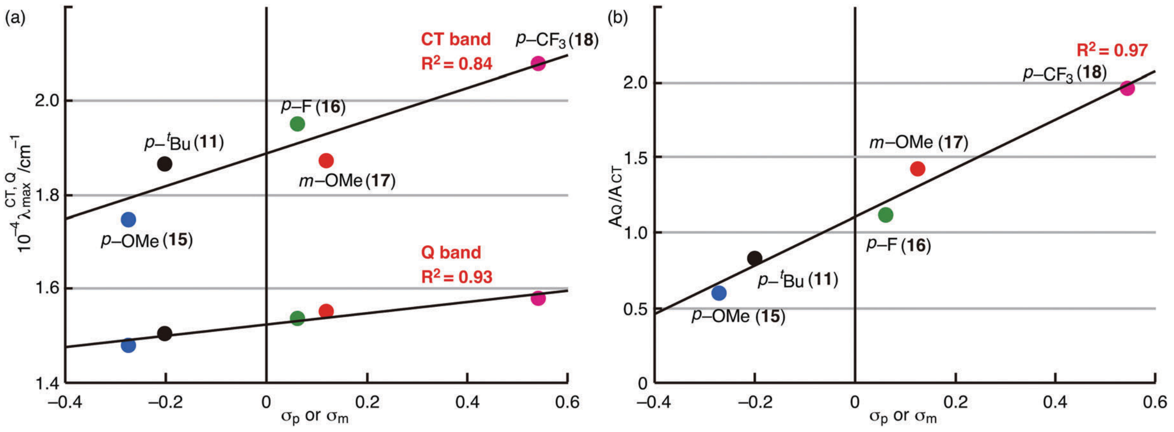
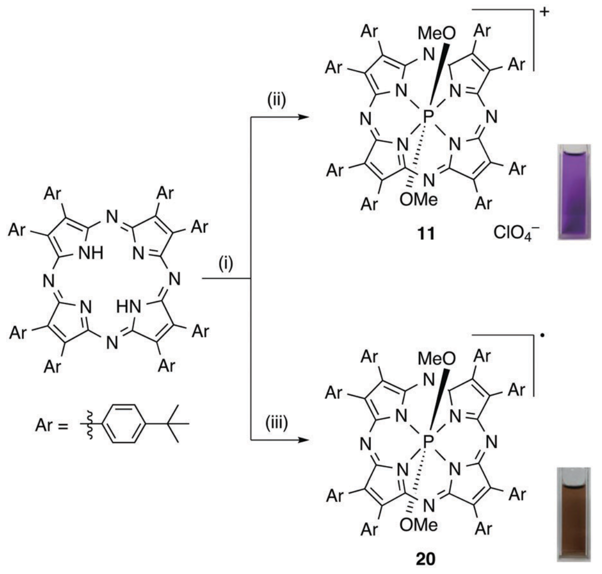


Fig. 12 Plots of (a) position of the CT and the Q bands, and (b) ratio of A_Q to A_{CT} *versus* Hammett σ-values derived from the PTAPs.

After adding excess base, the spectral envelope resembled those of metallated TAPs and electron-withdrawing group-substituted PTAPs. The original spectrum of **19** was restored upon addition of acid. The proposed mechanism, based on the case of porphyrin, is shown in Fig. 13b. The calculated MOs supported the premise that the spectral changes could be assigned to a change in the electronic configuration of the central phosphorus(v) ion by the deprotonation of the hydroxyl groups.

A 19π porphyrinoid: an extremely air-stable one-electron reduced species. Stable organic radicals can easily be oxidized or reduced by external stimuli, used, for example, in electrochemical energy storage systems.[91,92] Recently, air-stable organic radicals in the form of oxidized species of small[93–95] or expanded porphyrinoids[96–98] have been reported. Although one-electron reduced species of porphyrinoids are also π-radicals, the isolation of reduced porphyrinoid radicals ($(4n + 3)\pi$ electrons) is challenging, due to their ease of air-oxidation. Ring-reduced phthalocyanines (Pc^{3-}, Pc^{4-} or radical anions) have also been reported,[99–101] and their structural information was invaluable for interpreting the spectroscopic data.[102–104] However, structurally characterized Pc^{3-} species are very rare and air-sensitive.

Electron-deficient group 15 elements can stabilize the reduced state, and it has been possible to reduce some types of azaporphyrin group 15 complexes under basic conditions.[51,88,105,106] Stable reduced states of porphyrinoid P(v) complexes have also been reported.[107–109] Recently, we found that the one-electron reduced species of P(v)TAP with bulky peripheral substituents was exceptionally stable under air and moisture conditions.[110] The original P(v)TAP (**11**) was isolated under acidic conditions as a cationic complex in the form of a purple powder, while the one-electron reduced species (**20**) was isolated under basic conditions as a neutral complex in the form of a brown powder (Scheme 5). The brown species was stored as a solid in air under ambient light for more than two years. The spectroelectrochemical switching between **11** and **20** was completely reversible (Fig. 14). When a potential negative enough for the first reduction reaction to occur was applied to a solution of **11**, the final absorption spectrum fully matched the absorption spectrum of an as-prepared solution of **20**. When a potential positive enough for the first oxidation reaction to occur was applied to the solution of **20**, the final absorption spectrum fully matched the absorption spectrum of an as-prepared solution of **11**. The X-ray crystallographic structure, magnetic circular dichroism (MCD) spectrum, and theoretical calculations of **20** also matched the properties of reported one-electron reduced species of azaporphyrins as temporally generated species. Finally, **20** could be concluded to be the first example of a fully-characterized air-stable 19π porphyrinoid. The nitrogen atoms at the *meso*-position may also be crucial for stabilizing the reduced state. Recently, Matano *et al.* succeeded in isolating one- (19π) and two- (20π) electron reduced species of diazaporphyrin derivatives as air-stable compounds.[111]



Scheme 5 Synthesis of cationic (18π, **11**) and neutral (19π, **20**) states of PTAP and photographs of the solutions of complexes in CH_2Cl_2. *Reagents and conditions*: (i) $POBr_3$ (200 eq.), pyridine, 90 °C, 15 h, then CH_2Cl_2/MeOH, rt, 1 day; (ii) separated by SiO_2 column chromatography (CH_2Cl_2–MeOH–trifluoroacetic acid 90 : 9.5 : 0.5), then $NaClO_4$, CH_2Cl_2/CH_3CN, rt, 12 h, 56%; (iii) separated by Al_2O_3 column chromatography (CH_2Cl_2–triethylamine 99.5 : 0.5), 44%.

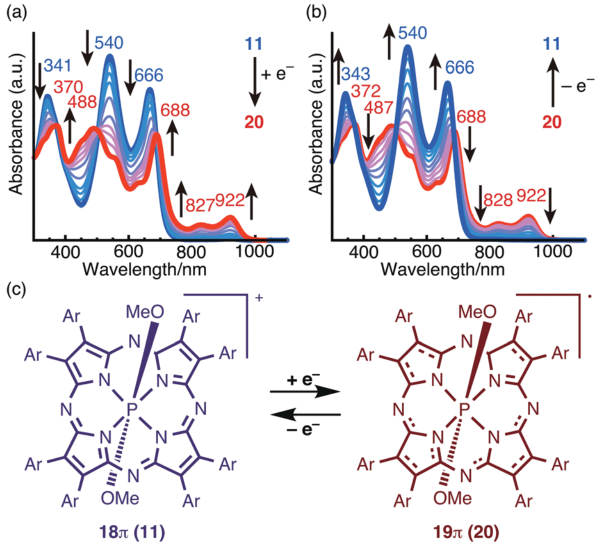


Fig. 14 (a) Spectral changes of a solution of **11** by applying the first reduction potential in *o*-DCB. (b) Spectral changes of a solution of **20** by applying the first oxidation potential in *o*-DCB. (c) Redox scheme of PTAP.

Conclusions and future perspectives

In the history of phthalocyanine chemistry, P(v) complexes have had marginal attention in the fields of synthetic, physical and material chemistry. One reason for this may be the mediocre optical properties of the initially-synthesized P(v) complexes. The diamagnetic properties appear to be another reason for a low level of attention in magnetic science. In this paper, we have shown that the introduction of phosphorus(v) "enhances" the substitution effects of the optical properties. The combination of peripheral substituents and central phosphorus(V) is critical for obtaining novel optical properties, such as absorption and emission in the near-IR region beyond 1000 nm. The choice of parent macrocycle is also important. We demonstrated that P(V) complexes of Pc, TBC and TAP show quite different optical properties. In particular, the optical properties of P(V) Pcs and TAPs should be considered from "different" viewpoints, while those of general metallated Pcs and TAPs can be considered from "similar" viewpoints.[36] A one-electron reduced species of P(V) TAP has outstanding stability under air and moisture conditions, suggesting that P(V) complexes may become new candidates for magnetic materials. The simple "π electron-unmodified" approach is a novel strategy for designing optical properties with simple, traditional compounds, although the "π electron-modified" approach known to date often needs long reaction sequences.

Basic synthetic methodologies, characterization, and the effects of phosphorus(V) on the optical properties have been established, as described in this paper. In the last part, we would like to discuss some future areas of interest in this field. (1) Introduction of a P(V) ion into recently-synthesized contracted or expanded (aza)porphyrinoids: the aim of this is to find new compounds showing unusual spectroscopic and electrochemical properties. As described above, the choice of parent macrocycle is a critical factor for optical properties of phosphorus(V) complexes. Recently, a number of novel contracted or expanded (aza)porphyrinoids have been synthesized,[35,112–114] so that the phosphorus(V) complexes of these macrocycles may show novel optical properties. In particular, low-symmetry azaporphyrinoids[115–117] may be good candidates due to an intense Q band in the visible-to-near-IR region. (2) Functionalization of P(V) complexes without changing their optical properties: if we find interesting optical properties in P(V) complexes, for practical applications we may want to attach these compounds to substrates without changing their optical properties. In this respect, the introduction of functional groups at axial positions may be effective, since changing the axial ligand generally affects these properties only marginally, as has been substantiated using silicone(IV) Pc complexes.[118,119] A novel procedure for introducing various anchoring groups at axial positions will be required in the future. (3) Finding neutral azaporphyrin complexes having optical properties similar to P(V) ionic complexes: except for a few examples, P(V) complexes are cationic species. Since ionic compounds consist of cationic and anionic parts, the intermolecular π–π interaction of Pc and azaporphyrins in the solid state is considered to be usually weak. If neutral P(V) complexes with similar optical properties are developed, these compounds may have better electronic properties in the solid state. The key role of the central phosphorus is its large electronegativity. Accordingly, main-group elements with large electronegativity may replace the role of phosphorus. (4) Estimation of the origin of the high stability of the one-electron reduced radical: our extremely stable 19π radical species[110] belongs to a new category of stable organic radicals. However, other one-electron reduced species with different peripheral substituents or macrocycles have not yet been isolated. For materials applications, the reason for the high stability should be clarified. The balance between the bulkiness of the peripheral substituents and the high electronegativity of central elements such as phosphorus(V) may be important. Further investigations into the elucidation of structure–stability relationships will be required.

Azaporphyrin P(V) complexes have simple chemical structures when drawn on paper, but produce unique structural and optical properties by a suitable combination of parent macrocycle and peripheral substituents. Investigation of their properties requires a combination of finely tuned synthetic routes, spectroscopic analysis and theoretical calculations. Hence, the P(V) complexes are milestones in a synergy of different scientific fields. We hope that this work will help inspire investigations of novel optical and electronic materials/devices based on azaporphyrin P(V) complexes in the near future.

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