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Control of absorption properties of tetraazaporphyrin group 15 complexes by modification of their axial ligands†

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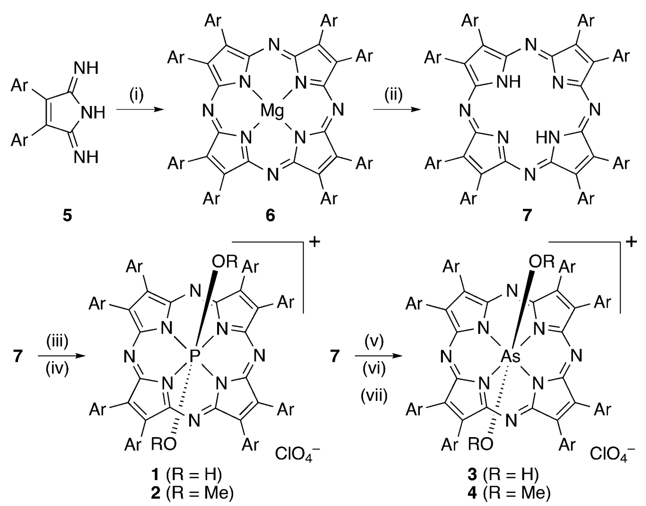
Tetraazaporphyrin (TAP) complexes with group 15 elements (phosphorus(V) or arsenic(V)) containing two axial OH ligands showed reversible spectroscopic changes with acid or base doping. Spectroscopic and theoretical analysis revealed that the modification of axial ligands can tune the interaction between peripheral substituents and the TAP macrocycle.

Controlling the spectral arrangement of optical properties in a reversible manner by external stimuli ("stimuli-responsive") is one of the most interesting and essential topics in chemistry, as well as in material and biological sciences.[1] In this regard, azaporphyrinoids, such as tetraazaporphyrins (TAP) and phthalocyanines (Pc), are good candidates as core structures of functional molecules, since they have intense absorption bands in the UV and visible regions (termed the Soret and Q bands), which can be fine-tuned using appropriate peripheral modifications.[2] Recently, we proposed a novel strategy for tuning the optical properties of azaporphyrinoids, where the combination of a simple macrocyclic ligand and main-group elements was used, accompanied by simple synthetic procedures.[3] In particular, TAP phosphorus(V) complexes (PTAPs) having eight aryl (Ar) groups at peripheral positions showed unique absorption properties.[4] An intense charge-transfer (CT) band[5] appeared between the Soret and Q bands in the absorption spectrum of PTAP, so that it can absorb light across the entire UV-vis region. Moreover, substitution at the peripheral groups of PTAP can tune both the position and intensity of the CT band in a rational manner. Hence, an appropriate combination between the core PTAP and substitution groups can establish a finely-tuned light harvesting over the complete UV-visible region. Herein, we report the synthesis and optical properties of TAP complexes with group 15 elements (phosphorus(V) or arsenic(V)) having hydroxyl groups as axial ligands. In the case of reported porphyrin phosphorus(V) complexes with hydroxyl groups, the proton of the hydroxyl group could be easily removed using a base, resulting in switching of the crystallographic structure of the porphyrin macrocycle.[6] We anticipated that the modification of the axial ligands of TAP by external stimuli would tune the optical properties of TAPs.

The synthetic procedure of TAPs is shown in Scheme 1. Bulky 3,5-di-*tert*-butylphenyl groups were used as peripheral aryl groups to improve the stability of the macrocycle against reduction by a base, *i.e.* bulky groups prevent the approach of a base to the macrocycle.[3b] Mg complex **6** was finally characterized by X-ray diffraction analysis of crystals as a species[7] having one H_2O molecule coordinated at the axial position (**6·H$_2$O**, Fig. S1, ESI†). Bulky peripheral groups surround the macrocycle, while the



Scheme 1 Synthesis of tetraazaporphyrin group 15 complexes. *Reagents and conditions*: (i) (^{n}BuO)$_2$Mg (1 eq.), ^{n}BuOH, reflux, 15 h, 83%; (ii) CF_3COOH, rt, 3 h, 68%; (iii) $POBr_3$ (25 eq.), pyridine, reflux, 20 h, then ROH, reflux, 3 h; (iv) $NaClO_4$, CH_3CN/CH_2Cl_2, rt, 12 h, 18% (for **1**), 19% (for **2**); (v) $AsCl_3$ (460 eq.), pyridine, reflux, 5 h; (vi) $HPyBr_3$ (7 eq.), rt, 30 min, and (vii) ROH, rt, 15 min, then $NaClO_4$, rt, 15 h, 6% (for **3**), 46% (for **4**). Ar = 3,5-di-*tert*-butylphenyl.

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central magnesium ion deviates by 0.53 Å from the 4*N* mean plane as a result of the axial coordination. The macrocycle has a saddled structure (Δr^8 = 0.22), although the reported crystal structure[4] of PTAP exhibited a ruffled structure. The free-base TAP **7** was reacted with excess phosphorus oxybromide in pyridine, as previously reported.[4] After the reaction, the axial ligands may be Br at this stage. The reaction was quenched with water or methanol, such that hydroxy or methoxy groups could be introduced at the axial position of the phosphorus. Finally, the counter anion was replaced by excess $NaClO_4$, producing the desired complexes **1** (HO–P–OH) and **2** (MeO–P–OMe) as the perchlorate salts. Arsenic complexes containing different axial ligands (**3** and **4**) were also synthesized from **7** using $AsCl_3$ and $HPyBr_3$,[3b] and obtained as the perchlorate salts. All TAPs were characterized by ^{1}H and ^{31}P (**1** and **2**) NMR and MALDI-TOF-MS spectroscopy. These compounds exhibit good stability in air-saturated solution under ambient light.

The absorption spectra of **1–4** in CH_2Cl_2 are very similar in shape (Fig. S2, ESI†). All compounds show three intense bands at *ca.* 635–650, 510–535, and 335–340 nm, corresponding to the Q, CT, and Soret bands, respectively. The CT band is characteristic of PTAPs, as we have already reported, and can be assigned to CT transitions from the peripheral aryl groups to the TAP macrocycle.[4,9] The CT bands of AsTAPs appear in a longer wavelength region than those of PTAPs while the intensities are also larger than those of PTAPs. However, the differences in absorption properties between PTAPs and AsTAPs appear to be small. Interestingly, the color of the PTAP with hydroxyl groups **1** in CH_2Cl_2 solution gradually changed from purple to green upon addition of triethylamine (Fig. S3, ESI†). The spectroscopic changes across the entire UV-vis region are shown in Fig. 1a. The Q band of **1** at 636 nm shifted to shorter wavelength (at 617 nm), while the intense CT band at 515 nm diminished and shifted to 479 nm. After adding excess (~2 eq.) triethylamine, the spectral envelope resembled those of metalated TAP (Fig. S4, ESI†) and electron withdrawing group-substituted PTAP.[4] The original spectrum of **1** was restored upon addition of trifluoroacetic acid (Fig. 1b) and the clear isosbestic points during this transformation indicate an equilibrium between two species in solution. Reversible switching of the optical properties of Pcs by addition of an acid or a base has been reported previously, but spectral changes occurred only in the Q band region.[10] The switching of **1** observed here is the first example of a change across the entire UV-visible region. AsTAP **3** also showed a similar reversible spectrum change (Fig. S5, ESI†). However, a larger excess (~200 eq.) of triethylamine was required to complete the spectral transformation. A similar spectroscopic change was observed upon addition of DBU, but in this case, the spectral change occurred more efficiently, such that only 1 eq. of DBU was required to change the spectrum. This difference in the amount of base depends on their basicity, *i.e.* pK_as in acetonitrile of DBU and Et_3N are 24.16 and 18.63, respectively,[11] so that DBU is a stronger base. For species containing two OMe axial ligands (**2** and **4**), this kind of spectral change was not observed upon addition of excess amounts of an acid or a base, so that we can conclude that the axial hydroxyl groups of the group 15 elements are crucial for the reversible switching of the absorption properties to occur. Magnetic circular dichroism (MCD) spectra of both the acidic (**1·acidic**) and basic (**1·basic**) forms of **1** show typical features of phosphorus(V) and metalated TAPs, respectively (Fig. S6, ESI†). Here, typical Faraday *A* terms were detected for both the Soret and Q band regions, in agreement with the approximate D_{4h} symmetry of both **1·acidic** and **1·basic** in solution. Since the MCD intensity is associated with changes in orbital angular momenta between ground and excited states, the intense MCD signals for the Q band regions indicate that both species have 18π aromatic structures. Thus, oxidation or reduction of the TAP macrocycle does not occur by adding an acid or a base.

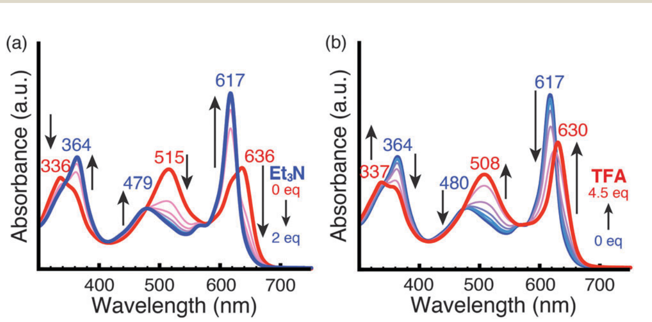

Fig. 1 Spectral changes of **1** solution by (a) adding Et_3N (0–2 eq.) and then (b) adding TFA (~4.5 eq.) in CH_2Cl_2.

To enhance the interpretation of the spectral changes, a ^{1}H NMR titration experiment of **1** in $CDCl_3$ was carried out (Fig. 2a). Under an excess amount of an acid or a base, a single set of peaks assignable to the peripheral aryl groups appeared in the normal aromatic region. During the addition of triethylamine or trifluoroacetic acid, the peaks gradually shifted. Under around neutral conditions, the peaks broadened. From the absorption and MCD spectra, the reason for the broad peaks can be attributed to an equilibrium between two similar species of approximate D_{4h} symmetry. The sharp peaks under both acidic and basic conditions indicate that intermediates of **1** are diamagnetic, hence a one electron oxidation and/or reduction of the TAP ligand through the addition of an acid or a base can be ruled out. Although the difference in peaks under the two states can be distinguished, the small difference in a chemical shift (<0.1 ppm) reveals that the electronic structure of the peripheral aryls and the TAP macrocycle was only marginally changed by the addition of an acid or a base. To confirm the effect at the central phosphorus atom, ^{31}P NMR spectra of **1** under acidic and basic conditions were also measured (Fig. 2b). Only one kind of peak at −193 or −173 ppm was observed under acidic or basic conditions, respectively. Both kinds of peaks were consistent with those of hexacoordinated phosphorus representations,[12] lying within the central cavity of the TAP macrocycle. The large (20 ppm) downfield shift under basic conditions, which was also observed in porphyrin phosphorus complexes with axial hydroxyl groups,[6] supports the conclusion that the nature of the phosphorus atom changed as a result of the addition of an acid or a base. Based on the results of the spectroscopic changes, proposed structures of **1** under acidic and basic conditions are

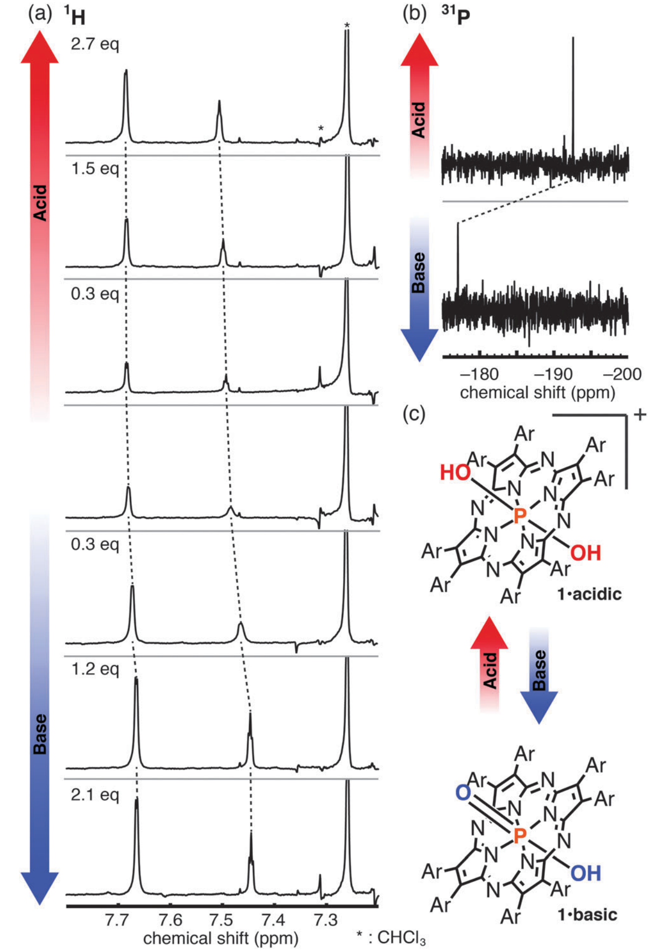

Fig. 2 (a) ^{1}H NMR titration of **1** solution in $CDCl_3$ with Et_3N (base) or CF_3COOD (acid). (b) ^{31}P NMR spectra of the basic and acidic states of **1**. (c) Proposed structures of the basic and acidic states of **1**.

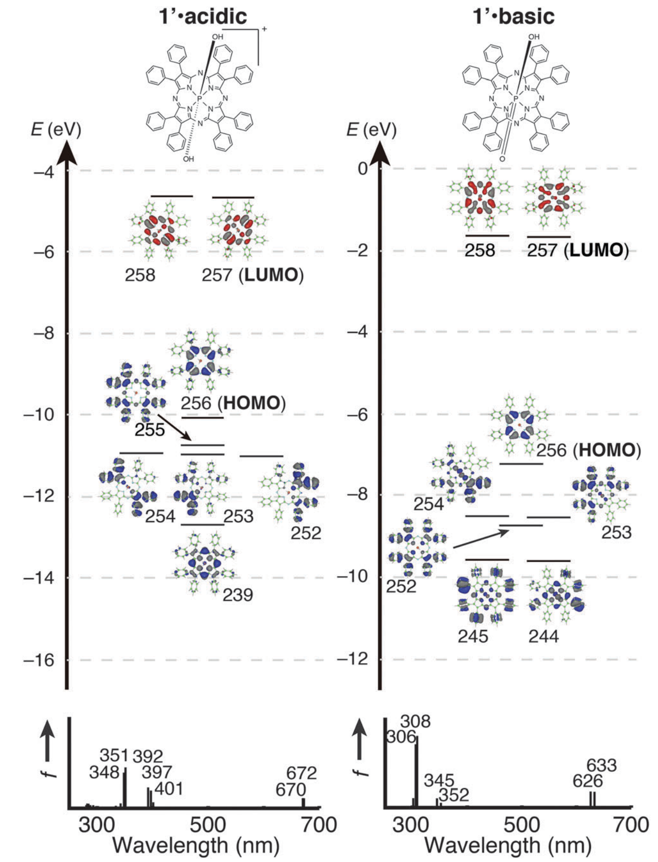

Fig. 3 Partial molecular energy diagrams and orbitals of the basic and acidic states of **1′** (top) and their calculated absorption spectra (bottom). Blue and red plots indicate occupied and unoccupied MOs, respectively. For **1′·basic**, an axial-oxygen-centered orbital, HOMO − 1 (255), was omitted for clarity since transitions from this MO have no intensity. Calculations were performed at the LC-BLYP/6-31G*//B3LYP/6-31G* level (for details, see the ESI†).

shown in Fig. 2c. The proton at the hydroxyl group can be easily removed by a base, so that the cationic form of PTAP is neutralized. Thus, the bonding characteristic of the central phosphorus atom in the basic state of **1** may be hexacoordinated bearing a P═O double bond, as previously found by X-ray diffraction in some porphyrin phosphorus complexes.[6] The difference in the bonding characteristics of the phosphorus atom correlates the quite different absorption properties between acidic and basic conditions. The difference in the amount of base required to change the absorption spectra of AsTAP **3** can also be explained. The different acidity (pK_a = 2.12 for H_3PO_4 and 2.22 for H_3AsO_4[13]) of the proton at P–OH or As–OH appears to be the origin of the different reactivity between **1** and **3** to a base.

Molecular orbital (MO) calculations were performed for proposed structures of PTAPs with acidic and basic states. Model structures (**1′·acidic** and **1′·basic**) whose peripheral substituents were replaced by phenyl groups were used for simplicity. Partial MO energy diagrams of the model structures are shown in Fig. 3, with the results of TDDFT calculations at the LC-BLYP[4,14]/6-31G*//B3LYP/6-31G* level of theory summarized in Table S2 (ESI†). The optimized structure of **1′·acidic** is a distorted ruffled structure (Δr = 0.17), while that of **1′·basic** adopts a planar structure (Δr = 0.09). The bond lengths of the central phosphorus and axial oxygen of **1′·basic** (1.711 and 1.519 Å) are either shorter or longer than those of **1′·acidic** (1.676 and 1.675 Å), in good agreement with the crystal structures of reported porphyrin phosphorus complexes having a P–OH single bond and a P═O double bond.[6] The calculated MO energies of **1′·basic** are higher than those of **1′·acidic**, since the electronic structure of **1′·basic** is neutral. For both states, the HOMO, LUMO, and LUMO + 1 are dominated by the TAP orbitals, which corresponded to the a_{1u}-, e_{gy}- and e_{gx}-like orbitals in Gouterman's model.[15] Therefore, these calculated transitions at 672 and 670 nm (for **1′·acidic**) and 633 and 626 nm (for **1′·basic**) can be assigned to the experimental Q bands. The calculated HOMO–LUMO energy gap of **1′·basic** is slightly larger than that of **1′·acidic**, so that the position of the Q band of **1** shifts slightly to shorter wavelength when a base is added. The calculated bands (401, 397, and 392 nm) of **1′·acidic** are composed of transitions from the HOMO − 1, HOMO − 2, HOMO − 3 and HOMO − 4 to the degenerate LUMOs. The HOMO − 1 to HOMO − 4 are localized on the peripheral phenyl rings, so that these bands can be assigned to CT transitions, as previously calculated for $PTAP(OMe)_2$.[4] Similar CT transitions were also calculated at slightly higher energy (352 and 345 nm) for **1′·basic**. However, these bands were estimated to be weaker than those of **1′·acidic**, in agreement with the experimental observations. In the MCD spectrum of **1·basic**, a weak Faraday *A* term[9] was observed (495 and 443 nm) between the Soret and Q bands, indicating that the corresponding absorption band at 479 nm can be assigned to transitions to degenerate orbitals (Fig. S6, ESI†). Hence, the calculated CT transitions of **1′·basic** clearly explain the spectroscopic alternation between **1′·acidic** and **1′·basic**. The calculated MOs also suggest that the electronic configuration of the central group 15 atom can switch not only the structures of the TAP macrocyclic core, but also the effect of the peripheral aryl moieties.

In summary, "stimuli-responsive" TAP group 15 complexes have been developed, in which the optical properties across the entire UV-visible region can be altered by the addition of an acid or a base. Titration experiments suggest that the modification of the axial ligands is crucial for controlling the optical properties of TAPs. ^{31}P NMR spectra of acidic and basic conditions indicate that the bond configuration of phosphorus(V) can be changed after the proton at the hydroxyl group of axial ligands has been removed by a base, without structurally modifying the π-conjugated system of the TAPs. Finally, the bond configuration under basic conditions was assigned to a hexacoordinated phosphorus(V) atom having a P═O double bond. The results of MO calculation also support the model, revealing that the interaction between the peripheral aryl moieties and the TAP macrocyclic core (*i.e.* the CT band) can be switched by altering the electronic configuration of the central group 15 element. Further work is currently underway to synthesize TAP complexes with group 15 elements having various axial and peripheral ligands, with the aim of developing novel chemo- or biosensing probes through the ensemble of the TAP macrocycle, peripheral substituents and axial ligands.

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