

# An Extremely Air-Stable $19\pi$ Porphyrinoid

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**S** Supporting Information

**ABSTRACT:** A one-electron reduced species of a cationic phosphorus(V) tetraazaporphyrin complex has been isolated as an air-stable solid. Cyclic voltammetry and magnetic measurements showed the species to be a neutral  $\pi$  radical, and the solid state structure was elucidated by single crystal X-ray diffraction analysis. Magnetic circular dichroism spectroscopy and theoretical calculations also support a  $19\pi$  electron conjugated electronic circuit.

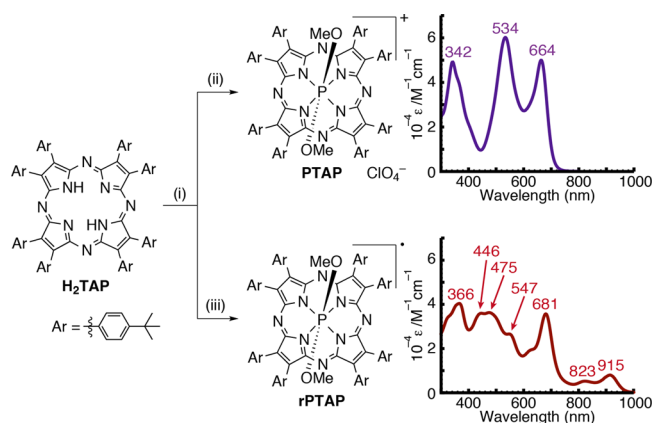
In recent years, stable organic radicals have attracted interest in various fields of both basic and applied chemistry. The radicals can be easily oxidized or reduced by external stimuli, which makes them good candidates for redox materials, such as used in electrochemical energy storage systems.<sup>1</sup> Strategies for achieving novel stable radicals are roughly divided into two types. One strategy introduces bulky substituents (a steric effect) to inhibit intermolecular coupling,<sup>2</sup> while the other adopts highly  $\pi$  conjugated systems, to stabilize the radical form by delocalizing electrons (an electronic effect).<sup>3</sup> (Aza)-porphyrinoids are a good source for designing stable radicals in this regard. Recently, for example, air-stable organic radicals in the form of oxidized species of expanded porphyrinoids have been reported.<sup>4</sup> Here, large (over  $22\pi$ -electrons in an aromatic form)  $\pi$  conjugated systems favor facile oxidation and stabilize the radical state. However, the synthetic cost of expanded porphyrinoids is often higher than for original  $18\pi$  porphyrinoids.

Instead of oxidizing porphyrinoids, one-electron reduction would also yield  $\pi$ -radicals. However, the isolation of reduced porphyrinoid radicals ( $(4n + 3)\pi$  electrons) is challenging, due to their ease of air-oxidation. On a similar note, we have targeted the isolation of reduced metallophthalocyanines (MPcs); these have been well-studied by *in situ* spectroscopic and electrochemical techniques.<sup>5</sup> To date, ring-reduced  $Pc^{3-}Mg$ <sup>6</sup> and  $Pc^{3-}M$  ( $M = Fe, Co$ )<sup>7</sup> and reduced  $PcH_2$  radical anions<sup>8</sup> have been reported, and their structural information is invaluable for interpreting the spectroscopic data; several  $Pc^{4-}$  species have also been isolated.<sup>9</sup> However, structurally characterized  $Pc^{3-}$  species are very rare and very air-sensitive. To overcome this practical limitation, highly electron deficient macrocycles may stabilize the reduced state, and it has been possible to reduce some types of azaporphyrin group 15 complexes under basic conditions, as Isago et al.<sup>10</sup> and we<sup>11</sup> have previously reported. However, every attempt at isolating the reduced species as an air-stable compound ended in failure, due to reoxidation during the separation processes in both solid and solution states. Herein, we report the first example of an

extremely air-stable reduced azaporphyrin (formally  $19\pi$  electrons).

Azaporphyrin phosphorus(V) complexes show unique optical properties in spite of their simple  $18\pi$  structures.<sup>11,12</sup> The electron deficient phosphorus(V) ion is crucial for producing these properties, and in principle, the complexes could be isolated as cationic complexes. We observed during our experiments, that the color of the crude solution of the octa-(*p*-*tert*-butylphenyl) TAP phosphorus(V) complex (PTAP<sup>12a</sup>) changed from purple to brown on adding triethylamine (Figure S1). The polarity of this brown species was much lower than that of the original cationic species, and we were able to isolate the brown species (rPTAP) as a stable solid by conventional  $Al_2O_3$  open column chromatography with a basic eluent ( $CH_2Cl_2$ -triethylamine) (Scheme 1). Peripheral *p*-*tert*-butylphenyl groups were suitable for isolation of the reduced species. The absorption properties of rPTAP are quite different from those of PTAP. The sharp absorption band at around 660 nm is retained (at 681 nm), while bands around 500 nm are broad and weak, and near-IR bands (915 and 823

**Scheme 1. Synthesis of Cationic (PTAP) and Neutral (rPTAP) States of the Tetraazaporphyrin (TAP) Phosphorus(V) Complex and Their Absorption Spectra in  $CH_2Cl_2$ <sup>a</sup>**



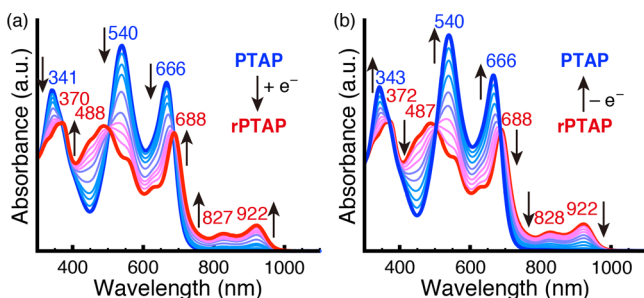
<sup>a</sup>Reagents and conditions: (i) POBr<sub>3</sub> (200 equiv), pyridine, 90°C, 15 h, then  $CH_2Cl_2/MeOH$ , rt, 1 day; (ii) separated by  $SiO_2$  column chromatography ( $CH_2Cl_2/MeOH/trifluoroacetic\ acid\ 90:9.5:0.5$ ), then  $NaClO_4$ ,  $CH_2Cl_2/CH_3CN$ , rt, 12 h, 56%; (iii) separated by  $Al_2O_3$  column chromatography ( $CH_2Cl_2/triethylamine\ 99.5:0.5$ ), 44%.

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nm) appear only for **rPTAP**. The observed HR-MALDI-FT-ICR-MS spectrum and CHN elemental analysis data provided a reasonable match with a compound whose molecular formula is  $C_{98}H_{110}N_8O_2P$ , constituting a TAP phosphorus complex without any ion, suggesting that **rPTAP** is a one-electron reduced neutral radical. **rPTAP** is extremely air- and photo-stable, such that a glovebox system is unnecessary for the entire synthetic process. Moreover, the absorption spectrum remained unchanged when **rPTAP** was stored as a solid in air under ambient light for more than 1 year.

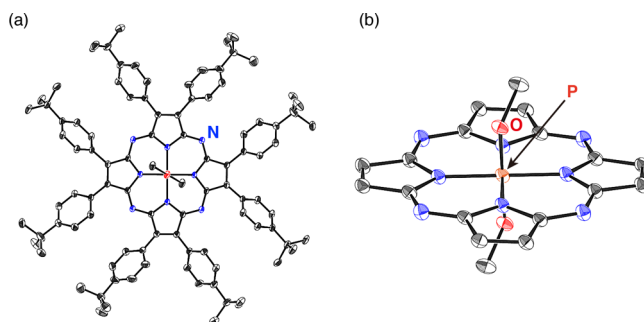
To confirm the redox properties of **rPTAP**, cyclic voltammograms of **PTAP** and **rPTAP** were measured in *o*-dichlorobenzene (*o*-DCB) (Figure S2). Since the redox potentials can be shifted anodically by insertion of a phosphorus(V) atom into the azaporphyrin core,<sup>12a</sup> the redox waves of **PTAP** appeared at only slightly less than 0 V vs  $Fc^+/Fc$ . Interestingly, the voltammogram of **rPTAP** is compatible with that of **PTAP**, showing five redox waves at similar positions to the redox waves of **PTAP**, indicating that **rPTAP** has very close redox behavior to **PTAP** and is a good multiple electron acceptor. For assignment of the redox relationship between **rPTAP** and **PTAP**, spectroelectrochemical measurements in *o*-DCB were performed. When a potential negative enough for the first reduction reaction to occur was applied to the solution of **PTAP** (Figure 1a), new weak bands appeared in the near-IR



**Figure 1.** (a) Spectral changes of **PTAP** solution by applying  $-0.2$  V potential vs Ag/AgCl reference electrode in *o*-DCB. (b) Spectral changes of **rPTAP** solution by  $0.3$  V potential vs Ag/AgCl reference electrode in *o*-DCB.

region, while the bands in the UV–vis region broadened, accompanying a set of clear isosbestic points. The final absorption spectrum fully matched the absorption spectrum of an as-prepared **rPTAP** solution. When the applied potential was returned to 0 V, the original spectrum was regenerated. More importantly, when a potential positive enough for the first oxidation reaction to occur was applied to the solution of as-prepared **rPTAP** (Figure 1b), the final absorption spectrum fully matched the absorption spectrum of **PTAP** and the changes were reversible. In summary, the spectroelectrochemical switching between **PTAP** and **rPTAP** was completely reversible, supporting the premise that **rPTAP** is an air-stable one-electron reduced species of **PTAP**.

The solid state structure of **rPTAP** was unambiguously elucidated by X-ray diffraction analysis of crystals obtained from a toluene solution of **rPTAP** (Figure 2). For comparison with the structure of **PTAP**, the selected bond lengths and structural deviations from the 4N mean plane of the TAP macrocycles ( $\Delta r$ )<sup>11b</sup> for **rPTAP** and our previously reported X-ray structure of **PTAP**<sup>12a</sup> are shown in Figures S3 and S4, respectively. The phosphorus atom sits in the center of the 4N plane ( $\Delta 4N$



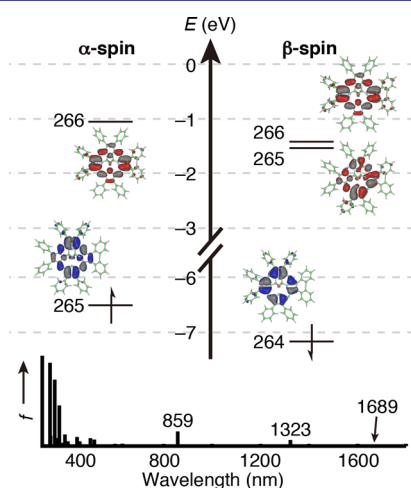
**Figure 2.** X-ray crystal structure of **rPTAP**. The thermal ellipsoids were scaled to the 50% probability level. (a) Top view; (b) side view (peripheral substituents are omitted). In both views, hydrogen atoms have been omitted for clarity.

$< 0.005$  Å), and the macrocycle is highly planar ( $\Delta r = 0.06$ ), although the reported structures of TAP or Pc phosphorus(V) complexes are ruffled, due to the small atomic radius (98 pm) of the phosphorus atom.<sup>13</sup> Indeed, the bond lengths between phosphorus and the pyrrole-nitrogen in **rPTAP** are longer than those of **PTAP**. More interestingly, two kinds of P–N bond lengths were found (1.8654(14) and 1.8745(14) Å) for **rPTAP**, while all P–N bond lengths in **PTAP** are the same (1.839(2) Å), indicating that the chromophore symmetry has been slightly altered. The HOMA indexes for the internal cross<sup>14</sup> in **rPTAP** and **PTAP** are 0.84 and 0.90, respectively. Hence no significant bond-length alternation was observed for the C–N bonds even in the core structure of **rPTAP**, similarly as for those of **PTAP** (a typical  $18\pi$  aromatic molecule). The molecules stack closely in the solid-state.

However, the EPR spectra of **rPTAP** in 1.0 and 0.1 mM solution in degassed  $CH_2Cl_2$  showed a singlet with  $g = 2.01$  and 2.001 (Figure S5), respectively, characteristic of a delocalized radical having an unpaired electron ( $S = 1/2$ ); no hyperfine coupling to nitrogen atoms was observed even in diluted and degassed solution (as per similar  $Pc^{3-}$  systems). The VT  $^1H$  NMR spectrum of **rPTAP** in toluene- $d_8$  was also measured (Figure S6). No peaks were found in the normal region for aromatic protons (ca. 6–9 ppm). However, broad signals were observed at low-field (10.7 and 18.0 ppm at 298 K), which could be assigned to paramagnetically shifted aryl protons of the peripheral substituents. A reversible temperature dependence was also observed between 298 and 353 K whereby the two peaks shift linearly toward the diamagnetic region with higher temperature, reaching 10.2 and 17.7 ppm at 353 K, consistent with **rPTAP** containing an unpaired electron. The  $^{31}P$  NMR signal for **rPTAP** is a simple very broad (approximately 25 ppm) peak centered at  $-233$  ppm; its extreme broadness is consistent with the paramagnetism (Figure S7). Finally, the spin density distribution of the model compound **rPTAP'**, where the peripheral substituents of **rPTAP** were replaced by phenyl groups, was calculated (Figure S8). The calculations implied the unpaired electron density to be encompassed over the TAP macrocycle, as well as no spin-density at the central phosphorus. Furthermore, the calculated positive charge on the central phosphorus was unchanged between **PTAP'** and **rPTAP'** (Table S2), confirming the valence of the phosphorus center in **rPTAP** to be +5.

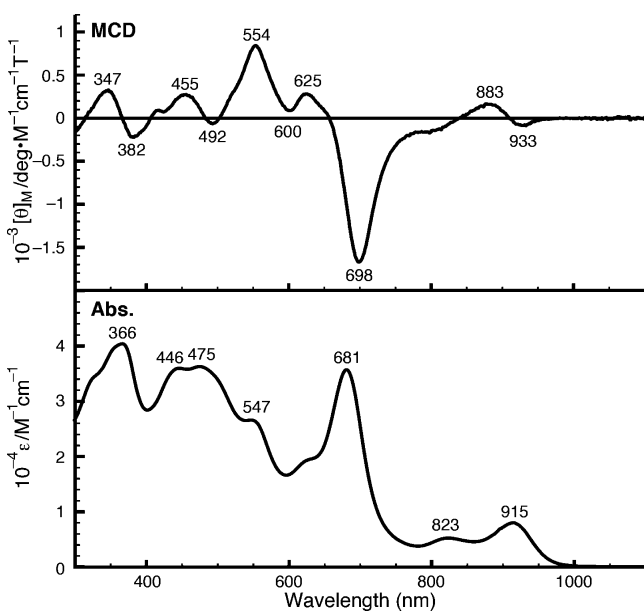
All electrochemical, spectroscopic, and theoretical results support the premise that the valence of the **rPTAP** macrocyclic core is  $-3$  and that the complete **rPTAP** molecule is an air-stable neutral radical. With this air-stable, reduced azaporphyr-

inoid in hand, the absorption properties of  $-3$  azaporphyrins could be investigated unambiguously. Here, partial MO energy diagrams of **rPTAP'** and the calculated stick absorption spectrum are shown in Figure 3, with the results of TDDFT



**Figure 3.** Partial molecular energy diagrams and orbitals of **rPTAP'** (top) and its calculated absorption spectrum (bottom). Calculations were performed at the ULC-BLYP/6-31G\*\*//UB3LYP/6-31G\* level.

calculations summarized in Table S3. A magnetic circular dichroism (MCD) spectrum also gives information on the electronic structure of azaporphyrin,<sup>15</sup> so that the detailed absorption and MCD spectra of **rPTAP** are shown in Figure 4.



**Figure 4.** UV-vis-NIR absorption (bottom) and MCD (top) spectra of **rPTAP** in  $\text{CH}_2\text{Cl}_2$ .

It was proposed in a previous report<sup>5b</sup> that the ground state of  $-3$  phthalocyanines was distorted from  $D_{4h}$  symmetry to  $C_{2v}$  symmetry due to Jahn–Teller effects.<sup>16</sup> Indeed, the bond lengths between phosphorus and the pyrrole nitrogens in the X-ray crystallographic structure are slightly altered, as depicted in Figure S3. In the MCD spectrum at longer wavelengths, relatively weak and strong Faraday  $B$  terms were observed at 933 and 883 nm, corresponding to the absorption band at 915

nm, reflecting the altered structure. An intense Faraday  $B$  term appeared at 698 nm, so that the change of orbital angular momentum between the ground and excited states for the absorption band at 681 nm appears to be larger than for other bands. Theoretical calculations for the  $-3$  TAP ligand also support the experimental results. Although many orbitals contribute to the calculated low-energy bands (Figure S10), in each band we could find mainly contributing one  $\pi \rightarrow \pi^*$  transition. The SOMO (265A)  $\rightarrow$  LUMO (266A) intrashell transition was estimated to lie beyond 1500 nm (1689 nm); however, this transition should be forbidden, which may not appear in the experimental spectra. The HOMO (264B)  $\rightarrow$  LUMO (265B or 266B) transitions were estimated at 1323 and 859 nm, which are allowed transitions from  $M_L = \pm 4$  to  $\pm 5$ . The properties of the calculated bands and MCD spectra support the assignment of the absorption bands at 915 and 681 nm to  $\pi \rightarrow \pi^*$  bands calculated at 1323 and 859 nm, respectively. The corresponding occupied and unoccupied orbitals are delocalized on the TAP core, without localization at peripheral phenyl rings.

In summary, an extremely air-stable  $19\pi$ -electron azaporphyrin has been prepared and characterized; it was easily obtained from the reduction of a cationic phosphorus-containing complex of TAP. The central phosphorus(V) atom<sup>17</sup> and peripheral bulky groups may be crucial to stabilize the reduced state. VT-NMR and EPR spectra support the premise that the unpaired electron is delocalized on the TAP macrocycle. Finally, analysis of absorption and MCD spectra, together with theoretical calculations concluded that **rPTAP** is the first example of an isolated  $-3$  TAP complex, namely, a  $19\pi$  azaporphyrinoid. Although various synthetic, spectroscopic and electrochemical methodologies on unstable compounds have been developed and established in modern chemistry, a new compound with easy handling in air and a simple synthetic method should open the door to practical and commercial applications. Further work is currently underway to prepare a series of stable  $19\pi$  porphyrinoids for developing novel materials with unpaired electrons.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional spectroscopic and calculation results, full details of experimental and calculation procedures, and X-ray crystallographic data (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b05781.

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### Notes

The authors declare no competing financial interest.

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