Synthesis of a Phosphorus-Containing Hybrid Porphyrin

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ABSTRACT

A phosphorus-containing hybrid porphyrin was successfully prepared via the BF₃-promoted dehydrative condensation between α₄-phosphatripyrrane and 2,5-bis[hydroxy(phenyl)methyl]thiophene. The NMR and UV−vis absorption spectra, electrochemical measurements, and DFT calculations revealed that the α₃-P,N₂,S-hybrid porphyrin exhibits high aromaticity as an 18π-electron system in terms of both geometric and magnetic criteria.

Porphyrins are one of the most widely studied aromatic macrocycles because of their important roles in biological, materials, and coordination chemistry. Chemical modification of the core of porphyrins is a highly promising approach to developing new classes of dyes and catalysts, as the electronic structures and coordination environments of the porphyrin ring can be changed dramatically. In this respect, much attention has been paid to the chemistry of core-modified porphyrins, such as carbaporphyrins, N-confused porphyrins, chalcogen-containing porphyrins, and pyriporphyrins. Incorporating a phosphorus atom at the core of the porphyrin ring, namely, replacing a pyrrole ring with phosphole, seems a quite promising strategy for altering significantly the optical, electrochemical, and coordinating properties of the porphyrin macrocycle. In 2003, Delaere and Nguyen predicted the ground state electronic structures of unsubstituted monophospha- and diphosphaporphyrins based on density functional theory (DFT) calculations and concluded that these porphyrins would exhibit reasonable aromaticity. Experimentally, however, phosphorus-containing porphyrins have long been untouched. Recently, we...
established a convenient method for the preparation of 2,5-difunctionalized phospholes, which have proven to be reliable starting materials for phosphorus-containing hybrid calixpyrroles and calixphyrins. Here, we report the first example of a phosphorus-containing hybrid porphyrin as a new family of core-modified porphyrins. Both experimental and theoretical results clearly demonstrate that the \(\sigma^3\)-P,N,S-hybrid porphyrin possesses high aromaticity with a relatively narrow HOMO-LUMO gap.

Scheme 1 illustrates the synthesis of \(\sigma^3\)-P,N,S-hybrid porphyrin 6. Treatment of 2,5-bis(hydroxymethyl)-1-phenyl-1-thiophosphate (1) with excess pyrrole in the presence of BF\(_3\)-promoted dehydrative condensation of 2 with 2,5-bis(hydroxy(phenyl)methyl)thiophene (3) gave \(\sigma^3\)-P,N,S-porphyrinogen (4) in 36% yield as a mixture of diastereomers. Desulfurization of 4 with excess P(NMe\(_2\))\(_3\) in refluxing toluene yielded \(\sigma^3\)-P,N,S-porphyrinogen (5), which was subsequently oxidized by 2,3-dichloro-6,6-dicyanobenzoquinone (DDQ) to afford the target compound 6 in 14% yield (from 4) as an air- and heat-stable reddish purple solid.

The structure of \(\sigma^3\)-P,N,S-hybrid porphyrin 6 was fully characterized by mass spectrometry and NMR spectroscopy. In the HR-FAB-MS spectrum, the parent ion peak (M\(^+\)) was observed at m/z 612.1788 (calcd for C\(_{41}\)H\(_{29}\)N\(_2\)PS, 612.1789). In the \(\text{\textsuperscript{1}}\)H NMR spectrum, the \(\text{\textsuperscript{1}}\)H and \(\text{\textsuperscript{31}}\)P NMR spectra of 6 were characterized by mass spectrometry and NMR spectroscopy. The downfield and upfield appearances of these peaks are indicative of a ring current effect derived from the porphyrin \(\pi\)-circuit. The \(\text{\textsuperscript{1}}\)H NMR spectrum of 6 (\(\delta\) 18.6) was also very shielded as compared to that (\(\delta\) 26.7) of \(\sigma^3\)-P,N,S-calixphyrin 7\(\text{\textsuperscript{10}}\) (Figure 1) and those (\(\delta\) 32.0–36.0) of 2,5-disubstituted 1-phenylphospholes bearing 1-thiophosphate (1) with excess pyrrole in the presence of BF\(_3\)-promoted dehydrative condensation of 2 with 2,5-bis(hydroxy(phenyl)methyl)thiophene (3) gave \(\sigma^3\)-P,N,S-porphyrinogen (4) in 36% yield as a mixture of diastereomers. Desulfurization of 4 with excess P(NMe\(_2\))\(_3\) in refluxing toluene yielded \(\sigma^3\)-P,N,S-porphyrinogen (5), which was subsequently oxidized by 2,3-dichloro-6,6-dicyanobenzoquinone (DDQ) to afford the target compound 6 in 14% yield (from 4) as an air- and heat-stable reddish purple solid.

The structure of \(\sigma^3\)-P,N,S-hybrid porphyrin 6 was fully characterized by mass spectrometry and NMR spectroscopy. In the HR-FAB-MS spectrum, the parent ion peak (M\(^+\)) was observed at m/z 612.1788 (calcd for C\(_{41}\)H\(_{29}\)N\(_2\)PS, 612.1789). In the \(\text{\textsuperscript{1}}\)H NMR spectrum, the meso, pyrrole-\(\beta\), and thiophene-\(\beta\) protons of 6 appeared at \(\delta\) 10.44 (d, \(\text{\textsuperscript{3}J}_{\text{H-H}} = 18.8\) Hz), 8.67 and 8.93, and 9.22, respectively, whereas the P-phenyl ortho-, meta-, and para-protons appeared at \(\delta\) 2.29, 5.27, and 5.66, respectively (Figure 2). The significant downfield and upfield
the same 3,4-C3 bridge.\(^{(6,13)}\) Thus, the hybrid porphyrin 6 is likely to possess high aromatic character. It should be noted here that the upfield shift (\(\Delta\delta/\text{ppm}\)) of the P-phenyl protons of 6 relative to the corresponding protons of 7 increases in the order para (1.61) < meta (2.01) < ortho (5.27). This implies that the P-phenyl group in 6 stands above the porphyrin \(\pi\)-plane like the \(N\)-methyl group in \(N\)-methylporphyrins.\(^{(14)}\) As a consequence, the ortho protons of the meso-phenyl groups, which would be oriented at a slant against the porphyrin plane, were differentiated at 25 °C.\(^{(15)}\) In the UV–vis absorption spectrum of 6 in CH2Cl2, the Soret band appeared at \(\lambda_{\text{max}}\) 440 nm (Figure 3a), which was red-shifted as compared to those of 5,10,15,20-tetraphenylporphyrin (TPP) 8a (\(\lambda_{\text{max}}\) 411 nm) and 21-thia-5,10,15,20-tetraphenylporphyrin 9a (\(\lambda_{\text{max}}\) 425 nm). The Q-type transitions between the phosphorus and sulfur atoms in 10 is \(\lambda_{\text{max}}\) 492, 518, 547, 647, and 718 nm. In contrast to \(8a\), \(J\). Am. Chem. Soc see: (a) Lavallee, D. K.; Gebala, A. E. Inorg. Chem. 1974, 13, 2004, (b) Lavallee, D. K.; Anderson, O. P. J. Am. Chem. Soc. 1982, 104, 4707.


(14) It is known that the \(N\)-methyl protons in \(N\)-methylporphyrins are significantly shielded as a result of the ring current effect. For example, see: (a) Lavallee, D. K.; Gebala, A. E. Inorg. Chem. 1974, 13, 2004, (b) Lavallee, D. K.; Anderson, O. P. J. Am. Chem. Soc. 1982, 104, 4707.

(15) These ortho protons (indicated as \(j\) in Figure 2) coalesced at 60 °C in \(\text{CDCl}_3\).

DFT calculations to reveal the optimized structures of \(\sigma^1\)-P,N2,S-hybrid 10, parent porphyrin 8b, and 21-thiaporphyrin 9b as models for 6, 8a, and 9a, respectively.\(^{(16)}\) As shown in Figure S5 in Supporting Information, the porphyrin planes of 8b and 9b are completely planar, whereas that of 10 is nonplanar. Thus, replacement of the NH unit of thiaporphyrin with the PPh unit (from 9b to 10) induces a distortion of the porphyrin plane, where all the heterole subunits are slightly tilted to make a dish-like macroyclic platform. Such a deviation is presumably caused by electrostatic repulsion between the phosphorus and sulfur atoms in 10.\(^{(17)}\)

The phosphorus center in 10 adopts a trigonal pyramidal geometry (\(\Sigma_{C-P-C} = 299.5^\circ\)), which prevents effective interaction between the phosphorus lone pair and the porphyrin 18\(\pi\)-circuit. Similar geometries at the phosphorus center (\(\Sigma_{C-P-X} = 292.4-296.1^\circ\); \(X = C, H\)) were reported for the 21-phospha- and 21,23-diphosphaporphyrins bearing \(P-\text{H}\) bonds,\(^{(6)}\) suggesting that the phosphorus lone pair in \(\sigma^1\)-\(\lambda^1\)-P-containing porphyrins essentially has an s character irrespective of the P substituents. The geometry of the \(P\)-phenyl group in 10 explains the \(1\)H NMR observation for 6 as well.

With the optimized structures in hand, we evaluated the aromaticity of 10 by comparing it with those of 8b and 9b. Despite the nonplanarity, the P,N2,S-hybrid 10 keeps high aromaticity in terms of a geometric criterion. The mean HOMA\(^{(18)}\) values for all 28 bonds of the porphyrin ring of 8b, 9b, and 10 were calculated to be 0.680, 0.645, and 0.550, respectively (Table 1). The rather low value of 10 as

<table>
<thead>
<tr>
<th>porphyrin</th>
<th>8b</th>
<th>9b</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>((X, Y))</td>
<td>((\text{NH}, \text{NH}))</td>
<td>((\text{NH}, \text{S}))</td>
<td>((\text{PPh}, \text{S}))</td>
</tr>
<tr>
<td>HOMA</td>
<td>0.680</td>
<td>0.645</td>
<td>0.550</td>
</tr>
<tr>
<td>18(\pi)</td>
<td>0.853</td>
<td>0.887</td>
<td>0.879</td>
</tr>
<tr>
<td>NICS (ppm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\alpha)</td>
<td>-16.5</td>
<td>-16.2</td>
<td>-15.6</td>
</tr>
<tr>
<td>(\beta)</td>
<td>-15.3</td>
<td>-15.9</td>
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</tr>
<tr>
<td>(\gamma)</td>
<td>-4.49</td>
<td>-2.54</td>
<td>-1.96</td>
</tr>
<tr>
<td>(\delta)</td>
<td>-19.0</td>
<td>-19.8</td>
<td></td>
</tr>
</tbody>
</table>

\(\ast\) Calculated using all 28 bonds of the porphyrin ring. \(\ast\) Calculated using 18 bonds of the \([18]\)annulene circuit.

Compared to those of 8b and 9b may be ascribed to distortion of the phosphole subunit.\(^{(19)}\) On the other hand, the HOMA values for the 18\(\pi\)-circuit (18 bonds consisting of C and N atoms) of 8b, 9b, and 10 are 0.853, 0.877, and 0.879, respectively, implying high aromaticity of 10 as a bridged annulene derivative. To evaluate the degree of aromaticity

![Figure 3](image-url). (a) UV–vis absorption spectra of 6 in CH2Cl2. (b) Cyclic voltamogram of 6; 0.1 M nBu4NPF6, Ag+/Ag (0.01 M AgNO3). Scan rate 20 mV s\(^{-1}\).
of 10 on the basis of a magnetic criterion, we also calculated NICS\textsuperscript{20} values at the porphyrin ring and heterole ring centers (Table 1). The NICS values at the center of the core atoms of 8b, 9b, and 10 are −16.5, −16.2, and −15.6 ppm, respectively,\textsuperscript{21} indicating that the aromaticity of the P,N\textsubscript{2},S-hybrid 10 is slightly weaker than those of 8b and 9b. Interestingly, the NICS value at the phosphole ring center (β) in 10 (−16.7 ppm) is much higher than that of the parent 1-phenylphosphole (−4.31 ppm).\textsuperscript{22} This reflects that the cyclic 1,3-diene unit of the phosphole ring is included in an 18π-electron system. Namely, the considerable ring current effect derived from the 18π-circuit was detected at the β position. By contrast, the NICS value at the γ position in 10 (−1.96 ppm) is much lower than the respective value of pyrrole, reflecting the strong 2-azafulvene character of the N-heterole rings.

(16) The structures were optimized by the DFT method at the level of B3LYP/6−311G(d,p). In the optimized structure of 10, the P-phenyl ring is vertical to the P−S axis. However, the difference in energy between the optimized structure and the structure in which the P-phenyl ring is rotated by 90° (i.e., the P-phenyl ring is parallel to the P−S axis) is very small (1.87 kcal mol\textsuperscript{−1}). Thus, the binding for the P-phenyl ring rotation is considered to be very weak.

(17) It has been reported that substitution of an NH unit of 8b by a PH unit does not distort the carbon skeleton of the porphyrin ring. See ref. 6.


(19) In the phosphole ring of 10, the phosphorus atom is slightly deviated from the 1,3-diene unit with a dihedral angle of 2.4°.

(20) NICS: Nuclear Independent Chemical Shift. The NICS values were calculated at the level of GIAO-RHF/6-31+G(d) at the optimized geometries. For details, see Supporting Information.


(22) At the same level of calculations, the NICS values of pyrrole, thiophene, and 1-phenylphosphole were determined as −15.0, −13.2, and −4.31, respectively. For the reported NICS values of these heteroles, see: (a) Dransfeld, A.; Nyulasi, L.; Schleyer, P. R. Inorg. Chem. 1998, 37, 4413. (b) Delaere, D.; Dransfeld, A.; Nguyen, M. T.; Vanquickenborne, L. G. J. Org. Chem. 2000, 65, 2631. (c) Cyrański, M. K.; Krygowski, T. M.; Katritzky, A. R.; Schleyer, P. R. J. Org. Chem. 2002, 67, 1333.

To gain insight into the HOMO and LUMO energies of the P,N\textsubscript{2},S-hybrid porphyrin 6, redox potentials were measured by cyclic voltammetry (CV) and/or differential pulse voltammetry (DPV). As shown in Figure 3b, the electrochemical oxidation process of 6 is irreversible, and the first oxidation potential of 6 was determined by the DPV measurement to be +0.45 V (vs Fe/Fe\textsuperscript{3+}),\textsuperscript{23} which is more cathodic than the reported values for 8a (E\textsubscript{1/2} +0.58 V) and 9a (E\textsubscript{1/2} +0.62 V). On the other hand, electrochemical reduction of 6 occurred quasi-reversibly, and the first and second reduction potentials (E\textsubscript{1/2}) were determined as −1.36 and −1.56 V (vs Fe/Fe\textsuperscript{3+}), respectively, which are more anodic than those of 8a (−1.73 and −2.06 V) and 9a (−1.55 and −1.82 V). These data suggest that modification of the core of the porphyrin from an NH to a PH unit basically narrows the HOMO–LUMO energy gap.\textsuperscript{24}

In summary, we successfully prepared a phosphorus-containing core-modified porphyrin for the first time. We found that the σ\textsuperscript{2},P,N\textsubscript{2},S-hybrid porphyrin is composed of a bridged [18]annulene π-system and displays high aromaticity in terms of both geometric and magnetic criteria. This class of compounds is expected to behave as macrocyclic, multidentate phosphorus ligands with characteristic optical properties. In this context, the coordination chemistry of phosphorus-containing porphyrins is worthy of further study.

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Supporting Information Available: Experimental details, 1H NMR spectra, and DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The second oxidation potential of 6 was determined to be 0.97 V (vs Fe/Fe\textsuperscript{3+}) by the DPV measurement.

(24) The HOMO–LUMO energy gaps (eV) of 8b, 9b, and 10 were computed by the DFT method to be 2.94, 2.83, and 2.59, respectively.