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Monophosphaporphyrins: Oxidative π-Extension at the Peripherally Fused Carbocycle of the Phosphaporphyrin Ring

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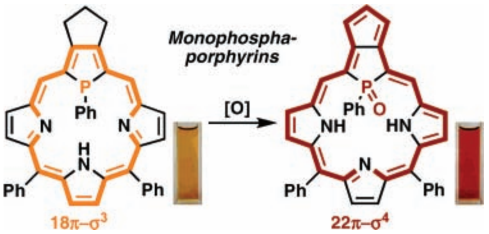
ABSTRACT



The 18π–σ^3- and 22π–σ^4-phosphaporphyrins were successfully prepared by an acid-promoted condensation between a phosphatripyrrane and a 2,5-bis[hydroxy(phenyl)methyl]pyrrole, and their structures, aromaticity, and optical and electrochemical properties were disclosed. Notably, a σ^4-phosphaporphyrinogen and the 18π–σ^3-phosphaporphyrin undergo oxidative π-extension at the peripherally fused carbocycle to afford the 22π–σ^4-phosphaporphyrin.

Chemical modification of the core nitrogen atoms of porphyrins is known to cause dramatic changes in the electronic structures of their π systems and their coordinating properties,[1] and hence, extensive studies have been devoted to explore the chemistry of core-modified porphyrins.[2,3] Replacing a pyrrole ring with a phosphole is a highly promising approach to provide new classes of porphyrin-based dyes and ligands, as the structure, aromaticity, and optical and electrochemical properties of the phosphole differ significantly from those of pyrrole.[4] Additionally, the electronic structures of the phosphole-conjugated π systems can be tuned by chemical functionalization at the phosphorus atom.[4d,f] Despite an early suggestive study,[5] however, the synthesis of phosphorus-containing porphyrins had not been

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(1) For reviews, see: (a) Latos-Grażyński, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego 2000; Vol. 2, Chapter 14, pp 361−416. (b) Chandrashekar, T. K.; Venkatraman, S. *Acc. Chem. Res.* **2003**, *36*, 676. (c) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134. (d) Furuta, H.; Maeda, H.; Osuka, A. *Chem. Commun.* **2002**, 1795. (e) Srinivasan, A.; Furuta, H. *Acc. Chem. Res.* **2005**, *38*, 10. (f) Chmielewski, P. J.; Latos-Grażyński, L. *Coord. Chem. Rev.* **2005**, *249*, 2510. (g) Stepień, M.; Latos-Grażyński, L. *Acc. Chem. Res.* **2005**, *38*, 88. (h) Gupta, I.; Ravikanth, M. *Coord. Chem. Rev.* **2006**, *250*, 468.

(2) N-Confused porphyrins and carbaporphyrins: (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (b) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. (c) Lash, T. D. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2533. (d) Berlin, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1820. (e) Furuta, H.; Maeda, H.; Osuka, A. *J. Am. Chem. Soc.* **2000**, *122*, 803. (f) Rachlewicz, K.; Wang, S.-L.; Ko, J.-L.; Hung, C.-H.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2004**, *126*, 4420. (g) Liu, D.; Ferrence, G. M.; Lash, T. D. *J. Org. Chem.* **2004**, *69*, 6079. (h) Stepień, M.; Latos-Grażyński, L.; Szterenberg, L.; Panek, J.; Latajka, Z. *J. Am. Chem. Soc.* **2004**, *126*, 4566.

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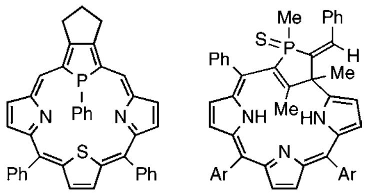
achieved until recently. In 2006, we successfully prepared P,S-containing hybrid porphyrin **1** (Figure 1),[6] which was found to possess high 18π-aromaticity with a narrow HOMO−LUMO energy gap. This result led us to reveal the structural, optical, and electrochemical properties of monophosphaporphyrins of a P,N_3-type, as these results should exhibit the intrinsic effects of the phosphole subunit more directly in comparison with P,N_2,S-hybrid **1**. Quite recently, Mathey and co-workers reported on the acid-promoted [3 + 1] condensation of a tripyrrane with a 2,5-bis[phenyl(hydroxy)methyl]phosphole, which resulted in the formation of a small amount of “P-confused” carbaporphyrinoid **2** (Figure 1).[7] We envisaged that our [3 + 1] approach using a phosphatripyrrane would be applicable to the synthesis of a normal P,N_3-type monophosphaporphyrin.[8]



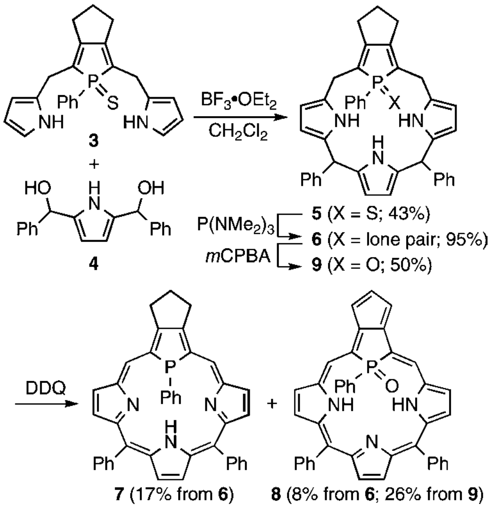
1 **2** (Ar = *p*-Tol)

Figure 1. P,N_2,S-porphyrin **1** and P-confused carbaporphyrinoid **2**.

Here, we report the first examples of two novel classes of monophosphaporphyrins, whose structures, aromaticity, and optical and electrochemical properties have been elucidated by spectroscopy, X-ray crystallography, and theoretical calculations. Notably, both σ^4-phosphaporphyrinogen and 18π−σ^3-phosphaporphyrin have been found to undergo oxidative π-extension at the peripherally fused five-membered carbocycle to afford an unprecedented type of 22π−σ^4-phosphaporphyrin.

The synthesis of monophosphaporphyrins is summarized in Scheme 1. The BF_3-promoted dehydrative condensation of σ^4-phosphatripyrrane **3**[6] with 2,5-bis[hydroxy(phenyl)methyl]pyrrole **4**[9] afforded σ^4-phosphaporphyrinogen **5** in 43% yield as a mixture of three diastereomers. Desulfurization of **5** with excess $P(NMe_2)_3$ in refluxing toluene produced σ^3-phosphaporphyrinogen **6**, which was subsequently treated with 3.3 equiv of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at room temperature to give two major products. Flash column chromatography of the crude reaction mixture on alumina yielded a reddish purple solid (hexane/EtOAc = 15/1, $R_f = 0.6$) and a dark-purple solid ($R_f = 0.3$), which were characterized as 18π−σ^3-phosphaporphyrin **7** and 22π−σ^4-phosphaporphyrin **8**, respectively, based on the spectroscopic and crystallographic analyses (vide infra). The DDQ oxidation of σ^4-phosphaporphyrinogen **9**, independently prepared by the oxygenation of **6** with *m*-chloroperbenzoic acid (*m*CPBA), afforded **8** in 26% yield as a sole isolable product. This result implies that **9** is a possible precursor for **8**.

Scheme 1. Synthesis of Monophosphaporphyrins **7** and **8**



The diagnostic spectral features of **7** and **8** are as follows. In the HR-FAB-MS spectra, the parent ion peaks (M^+) were observed at *m/z* 595.2182 for **7** (calcd for $C_{41}H_{30}N_3P$: 595.2177) and 609.1975 for **8** (calcd for $C_{41}H_{28}N_3OP$: 609.1970). In the ^1H NMR spectrum of **7**, meso and pyrrole-β protons appeared at δ 10.18 (d, $^3J_{P-H} = 16.1$ Hz) and 8.35−8.67, respectively, whereas NH and *P*-phenyl protons appeared at δ −0.59 and 2.43−5.68, respectively (Figure S1a, Supporting Information). It is apparent that the significant downfield and upfield shifts of these peaks stem from a ring current effect of the porphyrin 18π-electron circuit. On the other hand, the ^1H NMR spectrum of **8** displayed the meso, pyrrole-β, NH, and *P*-phenyl protons at δ 9.21 (d, $^3J_{P-H} =$ 35.6 Hz), 7.94−8.19, 5.40, and 5.60−6.92, respectively (Figure S1b, Supporting Information). Additionally, the

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(3) Chalcogen-containing porphyrins: (a) Broadhurst, M. J.; Grigg, R.; Johnson, A. W. *J. Chem. Soc. C* **1971**, 3681. (b) Ulman, A.; Manassen, J. *J. Am. Chem. Soc.* **1975**, *97*, 6540. (c) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 4428. (d) Sessler, J. L.; Cyr, M.; Burrell, A. K. *Tetrahedron* **1992**, *48*, 9661. (e) Lee, C.-H.; Kim, H.-J. *Tetrahedron Lett.* **1997**, *38*, 3935. (f) Narayanan, S. J.; Sridevi, B.; Chandrashekar, T. K.; Ashwani, V.; Roy, R. *J. Am. Chem. Soc.* **1999**, *121*, 9053. (g) Abe, M.; Hilmey, D. G.; Stilts, C. E.; Sukumaran, D. K.; Detty, M. R. *Organometallics* **2002**, *21*, 2986.

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(6) Matano, Y.; Nakabuchi, T.; Miyajima, T.; Imahori, H.; Nakano, H. *Org. Lett.* **2006**, *8*, 5713.

(7) Duan, Z.; Clochard, M.; Donnadieu, B.; Mathey, F.; Tham, F. S. *Organometallics* **2007**, *26*, 3617.

(8) The [3 + 1] approach using phosphatripyrranes was successfully applied to the syntheses of P-containing calixphyrins and calixpyrroles. See: (a) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Imahori, H.; Ochi, N.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11760. (b) Matano, Y.; Nakabuchi, T.; Miyajima, T.; Imahori, H. *Organometallics* **2006**, *25*, 3105.

(9) Heo, P.-Y.; Lee, C.-H. *Bull. Korean Chem. Soc.* **1996**, *17*, 515.

peripheral protons that originate from a C_3-bridge of the phosphole backbone appeared at δ 8.16 (d, 2H) and 9.06 (dt, 1H), indicating that the π-circuit goes through the five-membered fused ring in **8**.[10] The degree of shielding and deshielding effects observed for **8** is considerably smaller than that of **7**, reflecting the difference in the planarity of their π-planes (vide infra). The ring current effect also emerged as upfield shifts of the ^{31}P peaks of **7** (δ −5.2) and **8** (δ 28.6), which are more shielded as compared to those of the respective precursors **6** (δ 30.4−32.7) and **9** (δ 59.2−59.6). The upfield shift ($\Delta\delta$/ppm) of the *P*-phenyl protons of **7** relative to the corresponding protons of **6** increases in the order ortho (−4.8) > meta (−2.0) > para (−1.6), implying that the *P*-phenyl group in **7** stands above the porphyrin π-plane. A similar trend was observed for the *P*-phenyl protons of **8**, though the degree of shielding effects ($\Delta\delta_{o,m,p} = -2.3, -0.9, -0.6$ vs **9**) is considerably smaller than that observed for **7**.

The structures of **7** and **8** were unambiguously determined by X-ray crystallography (Figure 2a,b).[11] The porphyrin ring in **7** is ruffled to make a slightly distorted 18π-plane, wherein the phosphole and three pyrrole rings are tilted from the 24-atom mean plane with dihedral angles of 9.6° and 3.8−15.4°, respectively. The phosphorus center adopts a trigonal pyramidal geometry with C−P−C bond angles of 91.12(13)−101.99(12)° ($\Sigma_{C-P-C} = 293.7°$), implying that the porphyrin π-circuit does not involve the P-lone pair. Consequently, the *P*-phenyl group is located above the porphyrin π-plane, as suggested by the NMR observations. The core of **7** provides a trapezoid cavity with $N_{22}-N_{24}$ and $P-N_{23}$ distances of 4.56 and 3.45 Å, respectively. On the other hand, **8** has a highly distorted structure, in which the phosphorus atom is deviated significantly from the porphyrin 22π-plane to avoid the steric congestion at the core. The phosphorus center adopts a tetrahedral geometry with C−P−C/C−P−O bond angles of 94.3(3)−107.5(2)°/108.1(3)−119.09(18)°. Owing to the hydrogen-bonding interaction between the NH protons and the *P*-oxo group, the fused phosphole ring is angled considerably to put the *P*-phenyl group on the outside. It seems likely that the *P*-oxo function plays a crucial role to stabilize the unprecedented type of 22π system. Except for the phosphorus atom, the fused bicyclic rings of the phosphole subunit are almost planar, reflecting the efficient π-extension at the C_3-backbone.

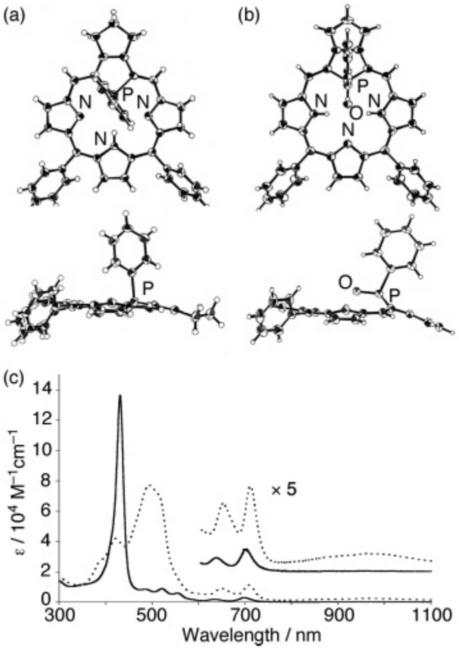

Figure 2. ORTEP diagrams of **7** (a) and **8** (b). Top views (upper) and side views (lower). (c) UV−vis absorption spectra of **7** (solid line) and **8** (dotted line) in CH_2Cl_2.

In the UV−vis absorption spectrum of **7** in CH_2Cl_2 (Figure 2c and Table 1), a Soret band appeared at λ_{max} 431 nm, which is red-shifted relative to that of 5,10,15,20-tetraphenylporphyrin (TPP) **10** (λ_{max} 411 nm) and blue-shifted compared to that of P,N$_2$,S-hybrid **1** (λ_{max} 440 nm). The Q-type transitions of **7** were observed at λ_{max} 486−701 nm. In marked contrast, the UV−vis absorption spectrum of **8** showed split Soret bands (λ_{max} 422 and 494 nm) and a remarkably broad, low energy band reaching into a near-infrared region. Such spectral features have been characteristically observed for π-extended porphyrins with peripherally fused carbocycles.[12]

Table 1. UV−vis Absorption Maxima (in CH_2Cl_2) and Redox Potentials (in CH_2Cl_2; vs Fc/Fc$^+$)^a of **1**, **7**, **8**, and **10** (TPP)

compd	λ_{max}(Soret; Q), nm	$E_{ox,1}$, V	$E_{red,1}$; $E_{red,2}$, V	ΔE, V^b
1^c	440; 492, 518, 547, 647, 738	+0.45	−1.36; −1.56	1.81
7	431; 486, 522, 555, 636, 701	+0.38	−1.51; −1.74	1.89
8	422, 494; 649, 708, 730−1100	+0.44	−1.21; −1.49	1.65
10^d	411; 511, 545, 588, 646	+0.58	−1.73; −2.06	2.31

^{a} Reference electrode: Ag/Ag$^+$ [0.01 M $AgNO_3$, 0.1 M *n*-Bu_4NPF_6 (MeCN)]. ^{b} $E_{ox,1} - E_{red,1}$. ^{c} Data from ref 6. ^{d} Data from ref 3g.

The unexpected formation of the π-extended phosphaporphyrin **8** is of utmost interest from a mechanistic point of

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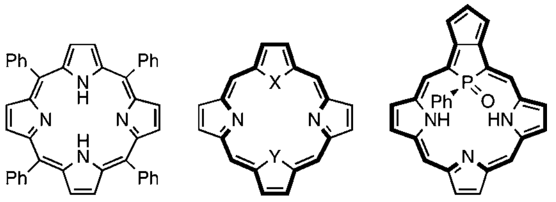
(10) In **8**, the NH resonance may also be influenced by the hydrogen-bonding interaction with the *P*-oxo group.

(11) **7**: formula $C_{41}H_{30}N_3P$, monoclinic, $P2_1/a$, $a = 17.924(4)$ Å, $b = 8.0399(16)$ Å, $c = 21.092(4)$ Å, $\beta = 103.350(4)°$, $V = 2957.2(10)$ Å^3, $Z = 4$, $r_{calcd} = 1.338$ g cm^{-3}, $m = 1.297$ cm^{-1}, collected 22168, independent 6706, parameters 407, $R_w = 0.1399$, $R = 0.0781$ ($I > 2.00s(I)$), GOF = 1.058. **8**: formula $C_{42}H_{30}Cl_2N_3OP$, monoclinic, $P2_1/m$, $a = 8.6044(16)$ Å, $b = 15.398(3)$ Å, $c = 13.408(3)$ Å, $\beta = 106.679(6)°$, $V = 1701.7(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.356$ g cm^{-3}, $\mu = 2.77$ cm^{-1}, collected 11692, independent 3283, parameters 247, $R_w = 0.1314$, $R = 0.0728$ ($I > 2.00\sigma(I)$), GOF = 1.026.

(12) (a) Lash, T. D.; Chandrasekar, P. *J. Am. Chem. Soc.* **1996**, *118*, 8767. (b) Gill, H. S.; Harmjanz, M.; Sntamaria, J.; Finger, I.; Scott, M. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 485. (c) Cammldge, A. N.; Scalfe, P. J.; Berber, G.; Hughes, D. L. *Org. Lett.* **2005**, *7*, 3413. (d) Shen, D. M.; Liu, C.; Chen, Q. Y. *Chem. Commun.* **2005**, 4982. (e) Sahoo, A. K.; Mori, S.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7972.

view.[13] As described above, **9** was found to be a precursor of **8**. To verify another possible pathway to **8**, we monitored the aerobic oxidation of **7** by UV−vis absorption spectroscopy. When an O_2-saturated CH_2Cl_2 solution[14] of **7** (1.0×10^{-5} M) was placed under normal lighting conditions, **7** was gradually converted to **8** as depicted in Figure S2 (Supporting Information). When the same solution was placed in the dark, no spectral change was observed. These results suggest that the photosensitized aerobic oxidation of **7** is also a possible route to **8** under the flask-scale experimental conditions. To our knowledge, this is the first example for the oxidative π-extension at the peripherally fused five-membered carbocycle of the porphyrin ring without the making or breaking of C−C bonds.[15,16]

To gain a deep insight into the aromaticity of **7** and **8** in terms of a magnetic criterion, we calculated NICS[17] values for their model compounds **11** and **12** by the DFT method (for details, see Figures S3 and S4 in the Supporting Information). The C−X/C═X bond alternation (X = C,N) in the optimized structures clearly shows the significant contribution of the π-circuits indicated as bold lines in Figure 3. The NICS value at the center of the four heteroatoms of **11** was determined as −13.8 ppm, which is somewhat smaller than those of the parent porphyrin **13** (−16.5)[6,18] and the P,N_2,S-hybrid model **14** (−15.6),[6] but much larger than the NICS value at the center of the two facing nitrogen atoms of **12** (−9.9). The theoretical results for the magnetic shielding effect are in good accordance with the experimental results. The relatively low aromaticity of **8** is attributable to the highly distorted structure of its 22π-annulene circuit.



10

11 (X = PPh; Y = NH)
13 (X = Y = NH)
14 (X = PPh; Y = S)

12

Figure 3. TPP **10** and porphyrin models **11**−**14**.

To evaluate HOMO and LUMO energies of the newly prepared monophosphaporphyrins, we measured redox potentials of **7** and **8** by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). As shown in Figure S5 (Supporting Information), the electrochemical oxidation processes of **7** and **8** are irreversible, whereas the reduction processes are reversible or quasi-reversible. The first oxidation and reduction potentials of **7** ($E_{\mathrm{ox},1} = +0.38$ V; $E_{\mathrm{red},1} = -1.51$ V vs Fc/Fc$^+$, determined by DPV) are more cathodic and more anodic as compared to the respective values reported for TPP **10** ($E_{\mathrm{ox},1} = +0.58$ V; $E_{\mathrm{red},1} = -1.73$ V vs Fc/Fc$^+$).[3g] The differences in the first oxidation and reduction potentials (ΔE) listed in Table 1 clearly indicate that the HOMO−LUMO energy gap of **7** ($\Delta E = 1.89$ V) is much narrower than that of **10** ($\Delta E = 2.31$ V) and slightly wider than that of **1** ($\Delta E = 1.81$ V). Thus, the energy levels of the frontier orbitals vary largely by the incorporation of one phosphole subunit into the porphyrin ring. On the other hand, **8** showed $E_{\mathrm{ox},1}$ and $E_{\mathrm{red},1}$ at +0.44 V and −1.21 V, respectively, both of which are shifted to the positive side as compared to the corresponding potentials of **7**. It should be noted that the oxidative π-extension perturbs the LUMO more significantly than the HOMO, yielding the narrower HOMO−LUMO energy gap ($\Delta E = 1.65$ V) for **8** in comparison with **7**.

In summary, we have successfully prepared two classes of P,N_3-type core-modified porphyrins and unveiled their structures, aromaticity, and optical and electrochemical properties for the first time. The formation of 22π−σ^4-phosphaporphyrin via oxidative π-extension at the peripherally fused carbocycle represents the characteristic role of the incorporated phosphole subunit, which also dramatically alternates the HOMO and LUMO energy levels of the porphyrin ring. Further research in our laboratory will focus on the coordinating properties of a series of phosphorus-containing core-modified porphyrins as novel macrocyclic, π-conjugated mixed-donor ligands.

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Supporting Information Available: Experimental details, ^{1}H and ^{13}C NMR spectra, DFT computational results, and CIF files for **7** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The oxidation of the C_3 fragment was not observed in the synthesis of the P,N_2,S-hybrid **1**.

(14) The solubilities of dioxygen (0.21 atm) in CH_2Cl_2 and in toluene are 2.2 mM (at 20 °C) and 2.1 mM (at 25 °C), respectively. See: Murov, S. L.; Camichael, I.; Hug, G. L. In *Handbook of Photochemistry*, 2nd ed.; Dekker: New York, 1993; Table 12-3, pp 289−293.

(15) The oxidative π-extension at the peripherally fused *six-membered* carbocycles of tetrahydrobenzoporphyrins with DDQ has been used for the synthesis of benzoporphyrins. (a) Lash, T. D. *Energy Fuels* **1993**, *7*, 166. (b) Nguyen, L. T.; Senge, M. O.; Smith, K. M. *J. Org. Chem.* **1996**, *61*, 998. (c) Finikova, O. S.; Cheprakov, A. V.; Vinogradov, S. A. *J. Org. Chem.* **2005**, *70*, 9562. (d) Lash, T. D. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, Chapter 10, pp 125−199 and references cited therein.

(16) Quite recently, Smith and co-workers reported the synthesis of metallocene-fused porphyrins via reductive π-extension of the β-fused five-membered ring under basic condition. Wang, H. J. H.; Jaquinod, L.; Olmstead, M. M.; Vicente, M. G. H.; Kadish, K. M.; Ou, Z.; Smith, K. M. *Inorg. Chem.* **2007**, *46*, 2898.

(17) The NICS (nuclear independent chemical shift) values were calculated with the GIAO-RHF method at the DFT-optimized geometries [GIAO-RHF/6-31+G(d)//B3LYP/6-311G(d,p)].

(18) For the NICS values of porphyrins, see: (a) Cyrañski, M. K.; Krygowski, T. M.; Wisiorowski, M.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 177. (b) Furuta, H.; Maeda, H.; Osuka, A. *J. Org. Chem.* **2001**, *66*, 8563.