Supporting Information

Monophosphaporphyrins: Oxidative $\pi$-Extension at the Peripherally-Fused Carbocycle of the Phosphaporphyrin Ring

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Contents:
General: SI-2
Density Functional Theory (DFT) Calculations on Model Compounds: SI-6
Figures S1~S10: SI-8
General

$^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra were measured in CDCl$_3$ or CD$_2$Cl$_2$. Chemical shifts are reported as the relative value vs. tetramethylsilane ($^1$H, $^{13}$C) and H$_3$PO$_4$ ($^{31}$P), respectively. MALDI-TOF and HR-FAB-MS mass spectra were measured using CHCA and 3-nitrobenzyl alcohol as matrices, respectively. Electrochemical measurements were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ [0.01 M AgNO$_3$, 0.1 M nBu$_4$NPF$_6$ (MeCN)] reference electrode. The potentials were calibrated with ferrocenium/ferrocene [$E_{\text{mid}} = +0.20$ V vs Ag/AgNO$_3$]. Dichloromethane (CH$_2$Cl$_2$) and toluene and THF were distilled from CaH$_2$ (CH$_2$Cl$_2$, toluene) or sodium benzophenone ketyl (THF) before use. The phosphatripyrrane $^3$ and 2,5-dibenzoylpyrrole$^2$ were prepared according to the reported procedure. Other chemicals and solvents were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted. Thin-layer chromatography was performed with Alt. 5554 DC-Alufolien Kieselgel 60 F$_{254}$ (Merck). Gravity column chromatography was carried out using Silica gel or Alumina in open air.

Synthesis and Characterization of 5–9

$\sigma^4$-Porphyrinogen 5: NaBH$_4$ (720 mg, 18.9 mmol) was added to a solution of 2,5-dibenzoylpyrrole (110 mg, 0.39 mmol) in THF/MeOH (total 24 mL; v/v = 3/1), which was then stirred for 30 min at room temperature. After adding a mixture of water (10 mL) and CH$_2$Cl$_2$ (30 mL), the organic phase was separated, dried over K$_2$CO$_3$, and evaporated. The crude product 4 was dissolved in CH$_2$Cl$_2$ solution (120 mL) containing 3 (120 mg, 0.30mmol), followed by addition of BF$_3$·OEt$_2$ (39 µL, 0.30mmol). After 5 min of stirring at room temperature, Et$_3$N (75 µL, 0.54 mmol) was added and the

resulting mixture was washed with distilled water (50 mL), dried over Na₂SO₄, and evaporated. The crude product was subjected to silica gel column chromatography (CH₂Cl₂/hexane = 2/1) to give 5 as a mixture of three diastereomers (Rₜ = 0.5–0.6; 82 mg, 43%). The ¹H and ³¹P NMR spectra indicated that three major diastereomers (A, B, C) were included in a ratio of 10:5:4. ¹H NMR (400 MHz, CDCl₃, 25°C): Diastereomer A: δ 1.92–2.00 (m, 1H), 2.06–2.14 (m, 1H), 2.31–2.43 (m, 4H), 3.42–3.50 (m, 4H), 5.25 (s, 1H), 5.40 (s, 1H), 5.47–5.48 (m, 1H), 5.53–5.54 (m, 1H), 5.72–5.73 (m, 1H), 5.81–5.82 (m, 1H), 6.09 (dd, J = 2.9 Hz, J = 2.9 Hz, 1H), 7.11–7.37 (m, 10H), 7.47–7.54 (m, 3H), 7.67 (br-s, 1H), 7.83–7.89 (m, 2H), 9.64 (br-s, 1H), 10.10 (br-s, 1H); Diastereomer B: δ 1.86–1.93 (m, 1H), 2.06–2.14 (m, 1H), 2.31–2.39 (m, 4H), 3.42–3.50 (m, 4H), 5.41–5.42 (m, 4H), 5.82–5.83 (m, 2H), 6.16 (d, J = 2.4 Hz, 2H), 7.12–7.40 (m, 10H), 7.45–7.54 (m, 3H), 7.67 (br-s, 1H), 7.82–7.87 (m, 2H), 9.64 (br-s, 2H); Diastereomer C: δ 2.02–2.09 (m, 2H), 2.30–2.46 (m, 4H), 3.34–3.42 (m, 2H), 3.62–3.75 (m, 2H), 5.33 (s, 1H), 5.41 (s, 1H), 5.65–5.66 (m, 1H), 5.68–5.69 (m, 1H), 5.79–5.80 (m, 1H), 5.84–5.85 (m, 2H), 5.99–6.00 (m, 1H), 7.14–7.33 (m, 15H), 7.79 (br-s, 1H), 8.05 (br-s, 2H), 9.99 (br-s, 2H); ³¹P{¹H} NMR (162MHz, CDCl₃, 25 °C): δ 70.4, 71.2, 72.0; MS (MALDI-TOF): m/z 633 (M⁺).

σ³-Phosphaporphyrinogen 6: To a toluene solution (10 mL) of 5 (135 mg, 0.21 mmol) was added P(NMe₂)₃ (0.25 mL, 1.4 mmol), and the mixture was then stirred under reflux for 40 h. The resulting mixture was concentrated under reduced pressure and subjected to silica gel column chromatography (hexane/CH₂Cl₂ = 1/1) to give 6 as a mixture of diastereomers (Rₜ = 0.4–0.5; 120 mg, 95%): The ratio of the three diastereomers (A, B, C) was found to be 10:4:4. ¹H NMR (400 MHz, CDCl₃, 25°C): Diastereomer A: δ 2.12–2.16 (m, 2H), 2.22–2.34 (m, 2H), 2.51–2.59 (m, 2H), 3.34–3.42 (m, 2H), 3.62–3.75 (m, 2H), 5.33 (s, 1H), 5.41 (s, 1H), 5.65–5.66 (m, 1H), 5.68–5.69 (m, 1H), 5.79–5.80 (m, 1H), 5.84–5.85 (m, 2H), 5.99–6.00 (m, 1H), 7.14–7.33 (m, 15H), 7.79 (br-s, 1H), 8.23 (br-s, 1H), 8.35 (br-s, 1H); Diastereomer B: δ 2.19–2.28 (m, 2H), 2.35–2.39 (m, 2H), 2.57–2.62 (m, 2H), 3.39–3.43 (m, 2H), 3.68–3.77 (m, 2H), 5.40 (s, 2H), 5.73–5.74 (m, 2H), 5.78–5.80 (m, 4H), 7.14–7.32 (m, 15H), 7.81 (br-s, 1H), 7.98 (br-s, 2H); Diastereomer C: δ 2.22 (m, 4H), 2.54 (m, 2H), 3.35–3.42 (m, 2H).
7 and 8: To a solution of 6 (25 mg, 0.042 mmol) in degassed toluene (4 mL), was added a toluene (2 mL) solution of DDQ (31 mg, 0.14 mmol) over 15 min at room temperature. After stirred for 30 min, the reaction mixture was filtered through a pad of alumina (2 cm dia × 1.5 cm, CH₂Cl₂, then EtOAc). Further purification of the crude products by alumina column chromatography, followed by recrystallization from CH₂Cl₂/hexane, afforded 7 (hexane/EtOAc = 15/1, Rᶠ = 0.6) as a reddish purple solid (4.2 mg, 17%) and 8 (hexane/EtOAc = 15/1, Rᶠ = 0.3) as a dark-purple solid (2.0 mg, 8%).

18π-σ³-Phosphaporphyrin 7: ¹H NMR (400 MHz, CDCl₃, 25°C): δ –0.59 (br-s, 1H), 2.43 (dd, J = 7.3 Hz, 3Jₚ,H = 4.4 Hz, 2H), 3.06 (m, 1H), 3.33 (m, 1H), 3.83 (m, 2H), 4.53 (m, 2H), 5.23 (dd, J = 7.3 Hz, 7.3 Hz, 2H), 5.68 (t, J = 7.3 Hz, 1H), 7.69 (m, 6H), 7.97 (d, J = 7.3 Hz, 2H), 8.24 (m, 2H), 8.35 (d, J = 4.4 Hz, 2H), 8.62 (d, J = 2.0 Hz, 2H), 8.67 (d, J = 4.4 Hz, 2H), 10.18 (d, 3Jₚ,H = 16.1 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25°C): δ 28.78 (s), 30.30 (s), 120.61 (d, J = 4.8 Hz), 124.77 (d, J = 4.8 Hz), 125.03 (s), 125.73 (s), 126.49 (s), 127.70 (d, J = 16.3 Hz), 127.99 (d, J = 9.6 Hz), 131.45 (s), 132.53, (s), 134.15 (s), 134.56 (s), 135.97 (s), 137.55 (s), 140.06 (d, J = 16.3 Hz), 153.29 (s), 159.36 (d, J = 3.8 Hz); ³¹P{¹H} NMR (162MHz, CDCl₃, 25 °C): δ –5.2; UV/Vis (CH₂Cl₂): λmax (ε) 431 (137000), 486 (8600), 522 (9000), 555 (6100), 636 (2000), 701 nm (3100); MS (FAB): m/z = 596 [M+H]+; HR-FAB-MS: Calcd for C₄₁H₃₀N₃P [M+], 595.2177; Found, 595.2182. In the ¹³C{¹H} NMR spectrum, one carbon peak could not be detected.

22π-σ⁴-Phosphaporphyrin 8: ¹H NMR (400 MHz, CDCl₃, 25°C): δ 5.40 (br-s, 2H), 5.60 (dd, J = 7.3 Hz, 3Jₚ,H = 12.2 Hz, 2H), 6.60 (m, 2H), 6.92 (t, J = 7.6 Hz, 1H), 7.68 (m, 8H), 7.94 (s, 2H), 8.02 (d, J = 4.4 Hz, 2H), 8.16 (d, J = 3.9 Hz, 2H), 8.19 (d, J = 4.4 Hz, 2H), 8.25 (d, J = 7.3 Hz, 2H), 9.06 (dt, J = 3.9 Hz, 5Jₚ,H = 5.4 Hz, 1H), 9.21 (d, 3Jₚ,H = 35.6 Hz, 2H); ¹³C{¹H} NMR (100 MHz, CDCl₃, 25°C): δ 106.29 (d, J = 12.5 Hz), 112.09 (d, J = 7.7 Hz), 125. 13 (d, J = 24.9 Hz), 125.93 (s), 126.91 (s), 127.55
(d, J = 12.5 Hz), 128.03 (s), 128.29 (s), 129.26 (d, J = 9.9 Hz), 130.98 (s), 131.39 (s), 133.47 (d, J = 9.6 Hz), 135.00 (s), 137.82 (s), 141.82 (s), 142.25 (s), 143.17 (s), 143.70 (s), 146.07 (d, J = 7.7 Hz), 156.34 (s); $^{31}$P{$^1$H} NMR (162MHz, CDCl$_3$, 25 °C): δ 28.6; UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (ε) 422 (42100), 494 (77200), 649 (9100), 708 nm (11400); MS (FAB): m/z 610 [M+H]$^+$; HR-FAB-MS: Calcd for C$_{41}$H$_{28}$N$_3$OP [M$^+$], 609.1970; Found, 609.1975.

$\sigma^4$-Phosphaporphyrinogen 9: A CH$_2$Cl$_2$ solution (6 mL) of m-chloroperbenzoic acid (29 mg, 0.13 mmol) was added dropwise at −30 °C to a solution of 6 (61 mg, 0.10 mmol) in 9 mL of CH$_2$Cl$_2$. The mixture was stirred at 0 °C for 1 h and then concentrated under reduced pressure. The solid residue was subjected to silica-gel column chromatography (CH$_2$Cl$_2$/hexane = 1/1) to give 9 as a mixture of three diastereomers ($R_f$ = 0.3–0.4; 31 mg, 50%). The ratio of the three diastereomers (A, B, C) was found to be 10:4:3. $^1$H NMR (400 MHz, CDCl$_3$, 25°C): Diastereomer A: δ 1.92–2.00 (m, 1H), 2.02–2.11 (m, 1H), 2.43–2.54 (m, 4H), 3.35–3.63 (m, 4H), 5.32 (s, 1H), 5.42 (s, 1H), 5.49–5.51 (m, 1H), 5.57 (dd, J = 2.9 Hz, J = 2.9 Hz, 1H), 5.76 (dd, J = 2.9 Hz, J = 2.9 Hz, 1H), 5.79 (dd, J = 2.4 Hz, J = 2.4 Hz, 1H), 5.90 (dd, J = 2.4 Hz, J = 2.4 Hz, 1H), 6.13 (dd, J = 2.9 Hz, J = 2.9 Hz, 1H), 7.10–7.34 (m, 8H), 7.43–7.56 (m, 5H), 7.76–7.81 (m, 2H), 7.89 (br-s, 1H), 10.05 (br-s, 1H), 10.40 (br-s, 1H); Diastereomer B: δ 1.92–2.00 (m, 1H), 2.02–2.11 (m, 1H), 2.38–2.58 (m, 4H), 3.38–3.62 (m, 4H), 5.42 (s, 2H), 5.69 (d, J = 2.4 Hz, 2H), 5.81–5.83 (m, 4H), 7.13–7.26 (m, 10H), 7.46–7.56 (m, 3H), 7.71–7.79 (m, 2H), 8.24 (br-s, 1H), 10.23 (br-s, 2H); Diastereomer C: δ 1.90–2.16 (m, 2H), 2.35–2.46 (m, 2H), 2.53–2.62 (m, 2H), 3.41–3.66 (m, 4H), 5.44 (s, 2H), 5.46–5.47 (m, 2H), 5.81–5.82 (m, 2H), 6.19 (d, J = 2.4 Hz, 2H), 7.16–7.30 (m, 10H), 7.46–7.54 (m, 3H), 7.71–7.80 (m, 2H), 8.22 (br-s, 1H), 10.21 (br-s, 2H); $^{31}$P{$^1$H} NMR (162MHz, CDCl$_3$, 25 °C): δ 59.2, 59.5, 59.6; MS (MALDI-TOF): m/z 617 (M$^+$).

Synthesis of 8 from 9: To a solution of 9 (12 mg, 0.019 mmol) in degassed toluene (3 mL), was added a toluene (2 mL) solution of DDQ (15 mg, 0.064 mmol) over 15 min at room temperature. After stirred
for 1 h, the reaction mixture was filtered through a pad of alumina (2 cm dia × 1.5 cm, CH$_2$Cl$_2$ then EtOAc). Further purification of the crude product by alumina column chromatography, followed by recrystallization from CH$_2$Cl$_2$/hexane, afforded 8 as a dark-purple solid (3.1 mg, 26%).

**X-ray Crystallographic Analyses of 7 and 8:** Single crystals suitable for X-ray analysis were grown from CH$_2$Cl$_2$–MeOH at room temperature. X-ray crystallographic measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K$_\alpha$ radiation (0.71070 Å) at –150 °C. The data were corrected for Lorentz and polarization effects. The structures were solved by using direct methods$^3$ and refined by full-matrix least squares techniques against $F^2$ using SHELXL-97.$^4$ The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the rigid model.

**Photosensitized Oxidation of 7 to 8:** A CH$_2$Cl$_2$ solution of 7 (1.0 × 10$^{-5}$ M) in a quartz cuvette capped with a Teflon-coated silicone septum was bubbled with oxygen for 10 min and then monitored by UV/vis absorption spectroscopy. The results are shown in Figure S2.

**Density Functional Theory (DFT) Calculations on Model Compounds:** The structures of 11 and 12, as models for 7 and 8, respectively, were optimized using density functional theory (DFT). The basis set used was 6-311G(d,p).$^5$ The functionals of DFT was the Becke 1988 exchange and Lee-Yang-Parr correlation functionals (B3LYP).$^6$ The nucleus independent chemical shift (NICS) values$^7$ were

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$^4$ Sheldrick, G. M. SHELXL-97, University of Göttingen, Germany, 1997.


calculated at the Hartree-Fock level with gauge-including atomic orbitals (GIAOs) at the DFT optimized structures. The basis set used in the NICS value computations was 6-31+G(d). The optimized structures are depicted in Figures S3(a) and S4(a), and the bond lengths of the optimized structures are shown in Figures S3(b) and S4(b). The molecular orbitals near in energy to HOMO and LUMO are also depicted in Figures S3(c) and S4(c). All the calculations were carried out using the Gaussian 03 suite of programs. In the optimized structure of 11, the P-phenyl ring is found to be parallel to the P–HN axis. However, the difference in energy between the optimized structure and the structure in which the P-phenyl ring is rotated by 90 degrees (i.e., the P-phenyl ring is vertical to the P–NH axis) is negligible (0.16 kcal mol⁻¹). Thus, the binding for the P-phenyl ring rotation is considered to be very weak.

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Figure S1. $^1$H NMR spectra of (a) 7 and (b) 8 in CDCl$_3$ (400 MHz). Asterisks (*) indicate the peaks of residual solvents and hydrocarbons.

Figure S2. Time-dependence of the oxidative $\pi$-extension from 7 to 8, as monitored by UV-Vis absorption spectroscopy in CH$_2$Cl$_2$ at 25 °C. [7]$_0$ = 1.0 $\times$ 10$^{-5}$ M. (a) In the dark (solid line, 0 h; dotted line, 24 h); (b) under normal light (0~12 h).
Figure S3. The results of DFT calculations for model compound 11. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, and P atoms are indicated as gray, light blue, blue, and orange balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg). (c) Molecular orbitals near HOMO and LUMO (orbital energies in eV).

Figure S4. The results of DFT calculations for model compound 12. (a) Optimized structure: top (upper) and side (lower) views. The C, H, N, and P atoms are indicated as gray, light blue, blue, and orange balls, respectively. (b) Selected bond lengths (Å) and bond angles (deg). (c) Molecular orbitals near HOMO and LUMO (orbital energies in eV).
Figure S5. Cyclic voltammograms of (a) 7 and (b) 8. 0.1 M $n$Bu$_4$NPF$_6$, Ag/Ag$^+$ (0.01 M AgNO$_3$). Scan rate 20 mV s$^{-1}$. Asterisk (*) indicates Fc/Fc$^+$ couple.
Figure S6. $^1$H NMR spectrum of 5 in CDCl$_3$. 
Figure S7. $^1$H NMR spectrum of 6 in CDCl$_3$. 
Figure S8. $^1$H NMR spectrum of 9 in CDCl$_3$. 

SI– 13
Figure S9. $^{13}$C NMR spectrum of 7 in CDCl$_3$. 
Figure S10. $^{13}$C NMR spectrum of 8 in CDCl$_3$. 