Supporting Information

First entry into nonmetal-centred porphycenes: synthesis of a phosphorus(V) complex of octaethylporphycene

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Experimental section

Materials.

All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. Free-base 2,3,7,8,12,13,17,18-octaethylporphyrin (H₂OEP) was purchased from Tokyo Kasei Co. Ltd. Free-base H₂OEPc was prepared according to literature methods.¹

Physical measurements.

UV–vis–NIR absorption spectra were obtained on a Hitachi U-3310 spectrophotometer. FT-IR spectra were recorded with KBr method on a JASCO FT/IR-460 Plus spectrometer. ¹H NMR spectra were obtained on a Bruker AVANCE 500 FT-NMR spectrometer in CDCl₃ or CD₃CN using tetramethylsilane as an internal reference. ³¹P{¹H} NMR spectra were obtained with the same spectrometer using H₃PO₄ as an external reference. Electrospray ionization time-of-flight mass spectrometry (ESI-TOF-MS) was carried out with a JEOL JMS-T100CS.

Electrochemical and spectroelectrochemical study.

Cyclic voltammograms (CVs) were recorded with an ALS 630c instrument (Bioanalytical Systems) using a three-electrode cell consisting of glassy carbon ($\phi = 3.0 \text{ mm}$), Pt coil and Ag/AgCl as working, counter and reference electrodes, respectively. Prior to the measurements, electrolyte solutions were deaerated by passing nitrogen for 15 min. Under the present conditions, the half-wave potential ($E_{1/2}$) of ferrocene/ferricinium (Fc/Fc⁺) couple was obtained at +0.48 V vs. Ag/AgCl.

Controlled-potential UV–vis–NIR absorption spectroscopy was carried out under the N₂ atmosphere with a Jasco V-670KS spectrophotometer equipped with a potentiostat/galvanostat (HA-301; Hokuto Denko) and a function generator (HB-104, Hokuto Denko). An optically-transparent thin-layer electrode cell (optical path length, 1 mm) with Pt mesh, Pt wire, and Ag/AgCl as working, counter and reference electrodes, respectively. Elemental analyses were conducted at the Service Center of Elemental Analysis of Organic Compounds at Kyushu University.

Luminescence study.

Emission and excitation spectra were recorded at room temperature on a Hitachi FL4500 spectrometer using CH_2Cl_2 as a solvent. Solutions were prepared at a concentration where absorbance at excitation wavelength of 398 and 407 nm for **1** and **2**, respectively (absorption maxima of the Soret bands), becomes 0.10. The absolute photoluminescence quantum yields (Φ_f) were obtained on an absolute PL quantum yields measurement system C9920-02 (Hamamatsu photonics).

Single-crystal X-ray diffraction study.

Single crystals of **1** and **2** suitable for X-ray diffraction study were obtained by recrystallization from CH_2Cl_2/n -hexane and MeOH, respectively, at room temperature. Reflection data were collected at 100 K on a Bruker SMART APEX CCD detector with graphite-monochromated Mo *K* α radiation ($\lambda = 0.71073$ Å) and a 2-kW rotating anode generator. The data frames were integrated using SAINT (Version 6.45) and merged

to give a unique data set for the structure determination. Empirical absorption corrections by SADABS² were carried out. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELX suite of programs.³ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined.

Density functional theory (DFT) calculations.

DFT calculations were performed at the B3LYP/6-31G+(d,p) level with the *Gaussian 09* suite of program.^{4,5} For calulations, the peripheral ethyl groups in **1** and H₂OEPc were replaced by methyl groups and the counter anion PF_6^- was omitted. To calculate the frontier orbital energy, the polarized continuum model (PCM) in CH_2Cl_2 was used.⁶ Optimized molecular structures and orbitals were visualized by *GaussView 5*.

Synthesis of $[P(OEPc)(OMe)_2]PF_6(1)$.

Free-base porphycene H₂OEPc (20 mg, 3.74×10^{-2} mmol) was dissolved in a distilled 2,6-dimethylpyridine (5 mL) and an excess amount of POBr₃ (562 mg, 1.96 mmol) was added. The mixture was stirred for 1 h at room temperature to give green solution with a Soret band centred at 470 nm and a Q-band centered at 600 nm which differ from the spectra of the H₂OEPc ($\lambda_{max} = 384, 577, 627$ and 668 nm). The solvent was removed in vacuo, and the residue was dissolved in MeOH and refluxed for 5 h. After cooling to room temperature, CH₂Cl₂ (50 mL) and distilled water (50 mL) were added. The products were extracted three times to the organic phase. After evaporation, the products remained were purified by column chromatography of neutral alumina (activity III) with use of 3% MeOH-CH₂Cl₂ as an eluent. The major band was collected and evaporated. The residue obtained was dissolved in CH₂Cl₂ (25 mL). To this was added an aqueous solution (25 mL) of KPF₆ (344 mg, 1.87 mmol), and the mixture was stirred for 12 h at room temperature. The organic phase was washed with H_2O and the solvent was completely removed by rotary evaporation. Recrystallization of the residue from CH_2Cl_2/n -hexane (1:3, v/v) gave needle-like purple crystals of 1. Yield: 12.2 mg (42%). Anal. Calcd for C₃₈H₅₀N₄P₂F₆: C, 59.21; H, 6.54; N: 7.27. Obsd: C, 58.49; H, 6.43; N: 7.13. ¹H NMR (500 MHz, CDCl₃, 298 K) δ 9.90 (s, 4H, meso-H), 4,11 (q, J = 7.5 Hz, 16H, CH_2 in Et), 1.91 (t, J = 7.6 Hz, 12H, CH_3 in Et), 1.74 (t, J = 7.6 Hz, 12H, CH_3 in Et), -2.57 (d, ${}^{3}J_{PH} =$ 26.20 Hz, 6H, OMe). ³¹P NMR (CDCl₃, 298 K): δ-144.97 (central P), -144.16 (PF₆⁻). UV-vis (CH₂Cl₂) λ_{max} $/ \text{ nm} (\varepsilon / \text{M}^{-1} \text{ cm}^{-1})$: 398 (202,000), 599 (61,000).

Synthesis of $[P(OEP)(OMe)_2]PF_6(2)$.

This compound was synthesized in a similar procedure to that for **1** except that H₂OEP was used instead of H₂OEPc. Compound **2** was finally recrystallized from MeOH and obtained as plate-like purple crystals. Yield: 24.2 mg (56%). Anal. Calcd for C₃₈H₅₀N₄P₂F₆: C, 59.21; H, 6.54; N: 7.27. Obsd: C, 59.40; H, 6.54; N: 7.27. ¹H NMR (500 MHz, CDCl₃, 298 K) δ 9.51 (s, 4H, meso-*H*), 3.97 (q, *J* = 7.6 Hz, 16H, *CH*₂ in Et), 1.84 (t, *J* = 7.7 Hz, 24H, *CH*₃ in Et), -2.45 (d, ³*J*_{PH} = 26.13 Hz, 6H, *OMe*). ³¹P NMR (CDCl₃, 298 K): δ -176.33 (central *P*), -144.33 (*P*F₆⁻). UV–vis (CH₂Cl₂) λ_{max} / nm (ε / M⁻¹ cm⁻¹): 407 (263,000), 546 (10,000), 590 (19,500).

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Fig. S1 ORTEP drawings for one of two crystallographically independent molecules (molecule **A**) in **1** at 100 K with selected atomic labelling scheme. (a) Front views from different angles. (b) Side views from different angles. Thermal ellipsoids at a 50% probability level are drawn. Hydrogen atoms are omitted for clarity. Color codes: P, orange; C(ring), dark gray; C(Et), pale gray; N, pale blue; O, red.



Fig. S2 ORTEP drawings for one of two crystallographically independent molecules (molecule **B**) in **1** at 100 K with selected atomic labelling scheme. (a) Front views from different angles. (b) Side views from different angles. Thermal ellipsoids at a 50% probability level are drawn. Hydrogen atoms are omitted for clarity. Color codes: P, orange; C(ring), dark gray; C(Et), pale gray; N, pale blue; O, red.



Fig. S3 ORTEP drawings for **2** at 100 K with selected atomic labelling scheme. (a) Front views from different angles. (b) Side view. Thermal ellipsoids at a 50% probability level are drawn. Hydrogen atoms are omitted for clarity. Color codes P: orange; C(ring), dark gray; C(Et), pale gray; N, pale blue; O, red.



Fig. S4 Bond distances (Å) in the octahedral geometry around phosphorus centres in (a) molecules A and B of 1 and (b) 2.



Fig. S5 Displacement (values in Å) of skeletal carbon atoms and P(V) centres in (a) 1 and (b) 2 with respect to the respective mean planes calculated with four pyrrole nitrogen atoms (N1 to N4). Positive and negative vaues are indicated in red and blue, respectively.



Fig. S6 Graphical representation of displacement of skeletal carbon and nitrogen atoms along with P(V) centres in (a) 1 and (b) 2 with respect to the respective mean planes calculated with four pyrrole nitrogen atoms (N1 to N4).



Fig. S7 Definition of mean planes to represent the conformational distorsion of the porphycene ring in **1** (left) and the porphyrin ring in **2** (right).

(a) Twist angles $\underline{\theta}_{A/C}$ and $\underline{\theta}_{B/D}$ defined by two mean planes of pyrrole rings A to D



(b) Dihedral angles $\phi_{A/B}$, $\phi_{B/C}$, $\phi_{C/D}$, and $\phi_{D/A}$ defined by two mean planes of the pyrrole rings A to D



(c) Dihedral angles $\phi_{N4/A}$ to $\phi_{N4/D}$ defined by mean plane N4 and mean plane of pyrrole rings A to D:



(d) Dihedral angles $\phi_{\rm A/B}$ to $\phi_{\rm D/A}$ defined by mean plane N4 and mean planes E to H:



Fig. S8 Definition of (a) twist angles and (b to d) three types of dihedral angles constructed with mean planes as defined in Fig. S7.

| Angles of Defined Mean Planes ^a | $[P(OEPc)(OMe)_2]PF_6(1)$ | | $[P(OEP)(OMe)_2]PF_6(2)$ |
|--|---------------------------|-------------------|--------------------------|
| | Molecule A | Molecule B | |
| (i) Twist angles ^b | | | |
| $	heta_{ m A/C}$ | 34.89 | 22.18 | 62.38 |
| $	heta_{ m B/D}$ | 32.27 | 24.08 | 59.64 |
| Averaged | 33.58 | 23.13 | 61.01 |
| (ii) Dihedral angles ^c | | | |
| $\phi_{ m A/B}$ | 155.33 | 163.69 | 137.52 |
| $\phi_{ m B/C}$ | 156.03 | 170.11 | 137.50 |
| $\phi_{ m C/D}$ | 158.99 | 162.57 | 138.96 |
| $\phi_{\mathrm{D/A}}$ | 155.20 | 154.90 | 137.68 |
| Averaged | 156.39 | 162.82 | 137.92 |
| (iii) Dihedral angles ^d | | | |
| $\phi_{ m N4/A}$ | 19.04 | 13.34 | 30.69 |
| $\phi_{ m N4/B}$ | 15.40 | 11.87 | 30.47 |
| $\phi_{ m N4/C}$ | 16.04 | 10.91 | 31.70 |
| $\phi_{ m N4/D}$ | 16.87 | 13.63 | 29.20 |
| Averaged | 16.84 | 12.44 | 30.52 |
| (iv) Dihedral angles ^e | | | |
| $\phi_{ m N4/E}$ | 14.84 | 11.91 | 25.57 |
| $\phi_{ m N4/F}$ | 11.01 | 9.67 | 26.37 |
| $\phi_{ m N4/G}$ | 15.45 | 9.77 | 26.28 |
| $\phi_{ m N4/H}$ | 16.92 | 9.55 | 24.84 |
| Averaged | 14.56 | 10.23 | 25.77 |

Table S1. Summary of Twist Angles and Dihedral Angles (deg) Observed for 1 (Molecules A and B) and 2.

^{*a*} Mean planes A to H are defined in Fig. S7. ^{*b*}Defined by (a) in Fig. S8. ^{*c*}Defined by (b) in Fig. S8. ^{*d*}Defined by (c) in Fig. S8. ^{*e*}Defined by (d) in Fig. S8.



Fig. S9 ¹H NMR spectra of (a) **1** and (b) **2** (CDCl₃, 298 K) with their chemical diagrams and proton labelling scheme.



Fig. S10 ³¹P NMR spectra of (a) **1** and (b) **2** (CDCl₃, 298 K) with their chemical diagrams and phosphorus labelling scheme.



Fig. S11 Frontier molecular orbitals for (a) 2,3,6,7,12,13,16,17-octamethylporphycene (H₂OMePc) and (b) *trans*-dimethoxido-2,3,6,7,12,13,16,17-octamethylporphycenatophosphrus(V) cation ([P(OMePc)(OMe)₂]⁺) with their corresponding energy levels obtained from DFT calculations. The arrows indicate the HOMO–LUMO gaps (ΔE).



Fig. S12 Full representation of frontier molecular orbitals for H₂OMePc with DFT calculations.



Fig. S13 Full representation of frontier molecular orbitals for $[P(OMePc)(OMe)_2]^+$ with DFT calculations.



Fig. S14 Controlled-potential UV-vis-NIR absorption spectra of **1** in 0.1 M n-Bu₄NPF₆-CH₂Cl₂ using Pt mesh as a working electrode. Spectral change under the control of electrode potential at (a) –0.65 V and (b) –1.20 V vs. Ag/AgCl are shown. Upward and downward arrows above the absorption peaks indicate the gradual increase and decrease in absorbance, respectively, with time at the given electrode potential applied.



Fig. S15 (a) Absorption (solid lines) and emission (broken lines) spectra of 1 (blue, $\lambda_{ex} = 398$ nm) and 2 (red, $\lambda_{ex} = 407$ nm) in CH₂Cl₂ at 298 K. Solution concentration was adjusted to absorbance = 0.10 at the excitation wavelength, λ_{ex} . (b) Excitation spectra of 1 (blue, $\lambda_{f1} = 642$ nm) and 2 (red, $\lambda_{f1} = 600$ nm). Luminescence spectra of 1 (blue line) and 2 (red line) in CH₂Cl₂ at 298 K.