Gram-scale synthesis of porphycenes through acid-catalyzed oxidative macrocyclizations of E/Z-mixed 5,6-diaryldipyrroethenes

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Materials and measurements.

All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. ¹H NMR, and ¹³C NMR spectra were recorded using a Bruker Avance 500 NMR spectrometer. ¹⁹F NMR spectra were recorded using a JEOL JNM-ECZ400 NMR spectrometer. Chemical shifts were referenced against tetramethysilane or residual solvent peak as an internal standard. ESI-MS was performed using a Bruker microTOF II instrument. MALDI-TOF mass spectra were performed using a Bruker MALDI-TOF-MS Autoflex III. UV–vis absorption spectra were recorded using a Hitachi U-3310 spectrophotometer. Fluorescence excitation and emission spectra were collected at room temperature on a Hitachi F-7000 fluorescence spectrometer. Emission spectra were collected in the range between 420-820 nm, with a scan speed of 240 nm/min, and the slits were set at 5.0 nm (excitation slit) and 5.0 nm (emission slit). The absolute photoluminescence quantum yields (Φₚₐ) were determined as a solution state using absolute PL quantum yields measurement system C9920-02 (Hamamatsu photonics) after excitation at 380 nm. Time-resolved photoluminescence lifetimes were carried out by using time-correlated single photon counting lifetime spectroscopy system, Quantaurus-Tau C11367-02 (Hamamatsu photonics). The decay constants and fitting parameters (τ₁, A₁) for transient decays were determined using the embedded software of Quantaurus-Tau.

Electrochemical studies were performed on Bioanalytical Systems CV-50W electrochemical workstations with a platinum wire as a counter electrode. A saturated calomel electrode or Ag/AgCl (saturated NaCl) electrode obtained from BAS was used as the reference electrode. Working electrode was a polished disk involving platinum material. All solvents were dried and distilled prior to use under N₂. Elemental analysis was performed at the Service Center of Elementary Analysis of Organic Compounds at Kyushu University.

X-ray crystal structural analysis.

PhPc: A single crystal of PhPc was mounted on a loop. X-ray diffraction patterns were recorded at −173 °C using a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromator and a Mo Kα radiation source (λ = 0.71073 Å).

CF₃Pc, FPc, CH₃Pc: A single crystal of 2 was mounted on a loop. X-ray diffraction patterns were recorded at −170 °C using a Bruker D8 Venture diffractometer equipped with a multilayered confocal mirror monochromator and a Mo Kα radiation source (λ = 0.71073 Å).

The data frames were integrated using SAINT¹ and merged to give a unique data set for structure determination. Absorption corrections were performed using SADABS.² The structures were refined using SHELXT (Sheldrick, 2015) and SHELXL (Sheldrick, 2015).³ All non-hydrogen atoms were anisotropically refined. Inner N–H hydrogen atoms were placed according to the Q-peaks. Other hydrogen atoms were placed using geometrically idealized positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-1868296 for PhPc, CCDC-1868292 for CF₃Pc, CCDC-1868294 for FPc, CCDC-1868293 for CH₃Pc. The data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].
Organic Synthesis.

Synthesis of \( E/Z \)-Ph.

\[
\begin{align*}
\text{TiCl}_4 & \quad \text{(18.2 g, 96.0 mmol)} \quad \text{was added dropwise to a dry THF (320 mL) solution of activated Zn powder (12.6 g, 192 mmol), at 0 \text{ } ^\circ \text{C} \text{ under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then } 1 \text{ (TCI, 98\%)} \quad \text{(4.11 g, 24.0 mmol)} \text{ in THF (25 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous NaHCO}_3 \text{ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na}_2\text{SO}_4. \text{ The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield } E/Z-\text{Ph as a yellow solid (1.65 g, 44.3\%). The } E:Z \text{ ratio of the isomers in the } E/Z \text{ mixture was determined as 2:1 by integration of the pyrroles } \alpha-\text{H proton signals in the } ^1\text{H NMR spectrum.} \quad ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta = 8.13 \text{ (brs, 2H } Z, \text{ NH), 7.47 (m, 10H } E, \text{ Ph), 7.29 (brs, 2H } E, \text{ NH), 7.10 (m, 10H } Z, \text{ Ph), 6.70 (m, 2H } Z, \text{ Py), 6.41 (m, 2H } E, \text{ Py), 6.14 (m, 2H } Z, \text{ Py), 5.89 (m, 4H } Z/E, \text{ Py), 5.32 (m, 2H } E, \text{ Py). Elemental analysis calcd (\%) for C}_{22}\text{H}_{18}\text{N}_2: C 85.13, H 5.85, N 9.03; found: C 85.16, H 5.90, N 9.05.}
\end{align*}
\]

Synthesis of PhPc using \( Z \)-Ph as a precursor.

\[
\begin{align*}
\text{To a 500 mL flask containing } Z-\text{Ph (100 mg, 0.322 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. } p-\text{TSA·H}_2\text{O 30.6 mg, 0.161 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (237 mg, 0.966 mmol) was added and stirred further 3 hours under air at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield Ph-Pc as a purple solid (45.0 mg, 45.8\%).} \quad ^1\text{H NMR (500 MHz, CDCl}_3\text{): } \delta = 9.43 \text{ (d, 4H, Py), 8.43 (d, 4H, Py), 7.71 (m, 8H, Ph), 7.38 (m, 12H, Ph), 5.98 (brs, 2H, NH). HRMS (FAB): } m/z \text{ calcd for C}_{48}\text{H}_{38}\text{N}_4\text{ [M]+ 614.2470; found: 614.2469.}
\end{align*}
\]

Synthesis of PhPc using \( E/Z \)-Ph as a precursor.
To a 500 mL flask containing \( E/Z\)-Ph (200 mg, 0.644 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. \( p\)-TSA·H\(_2\)O (61.2 mg, 0.322 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (475 mg, 1.93 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield \( \text{PhPc} \) as a purple solid (70.0 mg, 35.5%).

**Synthesis of \( \text{PhPc} \) using \( E\)-Ph as a precursor.**

To a 500 mL flask containing \( E\)-Ph (100 mg, 0.322 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. \( p\)-TSA·H\(_2\)O (30.6 mg, 0.161 mmol) was added and the mixture was allowed to stir for overnight. To the reaction mixture, chloranil (237 mg, 0.966 mmol) was added and stirred further 3 hours under air at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield \( \text{PhPc} \) as a purple solid (29.0 mg, 29.5%).

**Synthesis of \( \text{PhPc} \) using \( E/Z\)-Ph as a precursor by hypervalent iodine.**
[bis(trifluoroacetoxido)]benzene (PIFA) (138 mg, 0.322 mmol) in dry dichloromethane (5 mL) was quickly added to a stirred solution of \(E/Z\)-Ph (100 mg, 0.322 mmol) in dry dichloromethane (25 mL) in an ice bath. The solution was stirred for 1.5 h and the reaction was quenched with silica gel 60N (15 mL) and methanol (15 mL). The mixture was stirred overnight under air and evaporated to dryness. The resultant silica-gel mixture was charged on fresh silica gel 60N and eluted with dichloromethane to yield PhPc as a purple solid (1 mg, 1%).

**Synthesis of PhPc using \(E/Z\)-Ph as a precursor. (Large Scale)**

To a 3 L flask containing \(E/Z\)-Ph (1.50 g, 4.83 mmol), 3 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. \(p\)-TSA·H\(_2\)O (1.84 g, 9.66 mmol) was added and the mixture was allowed to stir overnight. To the reaction mixture, chloranil (3.56 g, 14.5 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield PhPc as a purple solid (0.903 g, 60.8%).

**Synthesis of 2.**

Aluminum(III) chloride (9.60 g, 72.0 mmol) was mixed with dry dichloromethane (600 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Bis(trifluoromethyl)benzoyl chloride (10.8 mL, 60.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (4.58 mL, 66.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na\(_2\)SO\(_4\). The solvents were removed under reduced pressure and the crude product
was purified using silica-gel column chromatography (dichloromethane 100%) to yield 2 as a white solid (9.96 g, 54.0%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 9.62$ (brs, 1H, NH), 8.34 (s, 2H, Ar), 8.07 (s, 1H, Ar), 7.24 (m, 1H, Py), 6.86 (m, 1H, Py), 6.42 (m, 1H, Py). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 181.14$, 140.02, 132.21, 130.22, 128.95, 126.53, 125.12, 124.10, 121.93, 119.93, 111.95 ppm. Elemental analysis calcd (%) for C$_{13}$H$_7$F$_6$NO: C 50.83, H 2.30, N 4.56; found: C 50.61, H 2.22, N 4.55. HRMS (EI, m/z): Calcd for C$_{13}$H$_7$F$_6$NO [M]$^+$ 307.0432; found: 307.0429.

**Synthesis of 3.**

Aluminium(III) chloride (9.60 g, 72.0 mmol) was mixed with dry dichloromethane (600 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Difluorobenzoyl chloride (7.51 mL, 60.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (4.58 mL, 66.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na$_2$SO$_4$. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane 100%) to yield 3 as white solid (6.94 g, 55.8%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 9.63$ (brs, 1H, NH), 7.42 (m, 2H, Ar), 7.20 (m, 1H, Ar), 7.01 (m, 1H, Py), 6.91 (m, 1H, Py), 6.38 (m, 1H, Py). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 181.68$, 163.81, 161.72, 141.19, 130.35, 126.04, 119.67, 111.54, 107.07 ppm. Elemental analysis calcd (%) for C$_{11}$H$_7$F$_2$NO: C 63.77, H 3.41, N 6.76; found: C 63.79, H 3.34, N 6.78. HRMS (EI, m/z): Calcd for C$_{11}$H$_7$F$_2$NO [M]$^+$ 207.0496; found for 207.0495.

**Synthesis of 4.**

Aluminum(III) chloride (8.00 g, 60.0 mmol) was mixed with dry dichloromethane (500 mL) in a two-necked flask under nitrogen atmosphere. 3,5-Dimethylbenzoyl chloride (7.40 mL, 50.0 mmol) was added dropwise to the solution under stirring. After stirring for several minutes, pyrrole (3.82 mL, 55.0 mmol) was added and the solution was stirred overnight at room temperature. The reaction was quenched with 1 M aqueous HCl under cooling. The mixture was extracted with dichloromethane; the organic layer was washed with distilled water and brine, and dried over anhydrous Na$_2$SO$_4$. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane 100%) to yield 4 as a white solid (6.82 g, 68.4%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 9.62$ (brs, 1H, NH), 9.49 (s, 2H, Ar), 8.08 (s, 1H, Ar), 7.33 (m, 1H, Py), 6.90 (m, 1H, Py), 6.47 (m, 1H, Py). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 181.56$, 140.72, 132.21, 130.22, 128.95, 126.53, 125.12, 124.10, 121.93, 119.78, 111.95 ppm. Elemental analysis calcd (%) for C$_{13}$H$_7$F$_6$NO: C 50.83, H 2.30, N 4.56; found: C 50.61, H 2.22, N 4.55. HRMS (EI, m/z): Calcd for C$_{13}$H$_7$F$_6$NO [M]$^+$ 307.0432; found: 307.0429.
MHz, CDCl$_3$): $\delta = 9.68$ (brs, 1H, NH), 7.51 (s, 2H, Ar), 7.20 (s, 1H, Ar), 7.13 (m, 1H, Py), 6.89 (m, 1H, Py), 6.35 (m, 1H, Py), 2.39 (s, 6H, CH$_3$)$_3$. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 185.17, 138.41, 137.96, 133.49, 131.36, 126.71, 124.83, 119.14, 110.90, 21.26$ ppm. Elemental analysis calcd (%) for C$_{13}$H$_{13}$NO: C 78.36, H 6.58, N 7.03; found: C 78.31, H 6.51, N 6.80. HRMS (EI, m/z): Calcd for C$_{13}$H$_{13}$NO [M]$^+$ 199.0997; found: 199.0995.

Synthesis of E/Z-CF$_3$.

![Synthesis of E/Z-CF$_3$](image)

TiCl$_4$ (21.6 g, 114 mmol) was added dropwise to a dry THF (400 mL) solution of activated Zn powder (15.0 g, 229 mmol), at 0 °C under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then 2 (8.80 g, 28.6 mmol) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous NaHCO$_3$ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield E/Z-CF$_3$ as a yellow solid (3.50 g, 42.0%). The $E$ : $Z$ ratio of the isomers in the E/Z mixture was determined as 3:2 by integration of the pyrroles $\alpha$-H proton signals in the $^1$H NMR spectrum.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 8.16$ (brs, 2H$_Z$, NH), 7.81 (s, 2H$_E$, Ar), 7.76 (s, 4H$_E$, Ar), 7.62 (s, 2H$_Z$, Ar), 7.49 (s, 4H$_Z$, Ar), 7.39 (brs, 2H$_E$, NH), 6.82 (m, 2H$_Z$, Py), 6.62 (m, 2H$_E$, Py), 6.25 (m, 2H$_Z$, Py), 6.08 (m, 2H$_E$, Py), 6.03 (m, 2H$_Z$, Py), 5.64 (m, 2H$_E$, Py). Elemental analysis calcd (%) for C$_{26}$H$_{14}$F$_{12}$N$_2$: C 53.62, H 2.42, N 4.81; found: C 53.87, H 2.37, N 4.83. HRMS (EI, m/z): Calcd for C$_{26}$H$_{14}$F$_{12}$N$_2$ [M]$^+$ 582.0965; found: 582.0966.

Synthesis of E/Z-F.

![Synthesis of E/Z-F](image)

TiCl$_4$ (21.2 g, 112 mmol) was added dropwise to a dry THF (450 mL) solution of activated Zn powder (14.6
g, 224 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then 3 (5.80 g, 28.0 mmol) in THF (50 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous NaHCO₃ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield E/Z- F as a yellow solid (3.58 g, 66.9%). The E : Z ratio of the isomers in the E/Z mixture was determined as 2:1 by integration of the pyrroles α-H proton signals in the ¹H NMR spectrum. ¹H NMR (500 MHz, CDCl₃): δ = 8.03 (brs, 2H Z, NH), 7.40 (brs, 2H E, NH), 6.94 (m, 4H E, Ar), 6.86 (m, 2H E, Ar), 6.74 (m, 4H Z, Ar), 6.65-6.61 ( m, 2H Z, Ar /2Hz, Py), 6.58 (m, 2H E, Py), 6.19 (m, 2H Z, Py), 6.04 (m, 2H E, Py), 5.99 (m, 2H Z, Py), 5.57 (m, 2H E, Py). Elemental analysis calcd (%) for C₂₂H₁₄F₄N₂: C 69.11, H 3.69, N 7.33; found: C 69.06, H 3.72, N 7.25. HRMS (EI, m/z): Calcd for C₂₂H₁₄F₄N₂ [M]+ 382.1093; found: 382.1090.

**Synthesis of E/Z-CH₃.**

![Synthesis of E/Z-CH₃ diagram]

TiCl₄ (4.55 g, 24.0 mmol) was added dropwise to a dry THF (80 mL) solution of activated Zn powder (3.14 g, 48.0 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was refluxed for 3 h and then 4 (1.20 g, 6.00 mmol) in THF (25 mL) was added dropwise. The solution was heated for 5 h until the starting material was completely consumed (monitored using TLC). The reaction was quenched with 1 M aqueous NaHCO₃ solution. The mixture was filtered and the organic layer was extracted with diethyl ether from filtrate; the organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvents were removed under reduced pressure and the crude product was purified using silica-gel column chromatography (dichloromethane/hexane) to yield (E/Z)-CH₃ as a yellow solid (460 mg, 41.8%). The E : Z ratio of the isomers in the E/Z mixture was determined as 9:5 by integration of the pyrroles α-H proton signals in the ¹H NMR spectrum. ¹H NMR (500 MHz, CDCl₃): δ = 8.02 (brs, 2H Z, NH), 7.30 (brs, 2H E, NH), 7.10 (s, 6H E, Ar), 6.70 (m,6Hz, Ar /2Hz, Py), 6.45 (m, 2H E, Py), 6.17 (m, 2H Z, Py), 5.96 (m, 4H Z/E, Py), 5.38 (m, 2H E, Py), 2.37 (s, 12H E, CH₃), 2.12 (s, 12H Z, CH₃). Elemental analysis calcd (%) for C₂₆H₂₆N₂: C 85.21, H 7.15, N 7.64; found: C 85.29, H 7.20, N 7.59. HRMS (EI, m/z): Calcd for C₂₆H₂₆N₂ [M]+ 366.2096; found: 366.2095.

**Synthesis of CF₃Pc.**
To a 500 mL flask containing E/Z-CF₃ (200 mg, 0.343 mmol), 200 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. p-TSA·H₂O (32.5 mg, 0.171 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (253 mg, 1.03 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield CF₃Pc as a purple solid (160 mg, 80.5%).

1H NMR (500 MHz, CDCl₃): δ = 9.61 (d, 4H, Py), 8.47 (d, 4H, Py), 8.14 (s, 8H, Ar), 7.97 (s, 4H, Ar), 5.68 (brs, 2H, NH). 13C NMR (125 MHz, CDCl₃): δ = 145.72, 145.12, 137.16, 132.46, 131.68, 130.74, 127.35, 124.16, 121.99, 121.07 ppm. 19F NMR (376 MHz, CDCl₃): δ = -64.24. HRMS (FAB): m/z calcld for C₅₂H₂₃F₂₄N₄ [M]+ 1158.1461; found for 1158.1460.

Synthesis of CF₃Pc. (Large Scale)

To a 3 L flask containing E/Z-CF₃ (1.50 g, 2.58 mmol), 1.5 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. p-TSA·H₂O (245 mg, 1.29 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (1.97 g, 7.74 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield CF₃Pc as a purple solid (1.06 g, 70.9%).

Synthesis of FPc. (Large Scale)
To a 3 L flask containing E/Z-F (2 g, 5.23 mmol), 3 L of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. p-TSA·H$_2$O (497 mg, 2.61 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (3.86 g, 15.7 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield FPc as a purple solid (1.42 g, 71.6%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 9.51 (d, 4H, Py), 8.49 (d, 4H, Py), 7.28 (m, 8H, Ar), 6.99 (m, 4H, Ar), 5.66 (brs, 2H, NH). $^{13}$C NMR (125 MHz, THF-$d_8$): $\delta$ = 148.41, 146.26, 140.98, 137.74, 132.33, 128.41, 127.50, 117.61, 103.36 ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -112.58. HRMS (FAB): m/z calcd for C$_{44}$H$_{22}$F$_8$N$_4$ [M]$^+$ 758.1716; found for 758.1715.

Synthesis of CH$_3$Pc.

To a 500 mL flask containing E/Z-CH$_3$ (100 mg, 0.273 mmol), 160 mL of dry dichloromethane was added and stirred for 15 min under nitrogen atmosphere with light protection. p-TSA·H$_2$O (259 mg, 1.36 mmol) was added and the mixture was allowed to stirred for overnight. To the reaction mixture, chloranil (201 mg, 0.819 mmol) was added and stirred further 3 hours at room temperature. The reaction mixture was passed through short alumina and dry silica gel and further purified by silica gel column chromatography (dichloromethane/hexane) to yield CH$_3$Pc as a purple solid (46.0 mg, 46.4%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 9.41 (d, 4H, Py), 8.52 (d, 4H, Py), 7.30 (s, 8H, Ar), 6.99 (s, 4H, Ar), 5.94 (brs, 2H, NH), 2.36 (s, 24H, CH$_3$). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ = 145.80, 144.27, 136.06, 134.91, 131.85, 131.73, 130.86, 127.58, 124.83, 21.21 ppm. HRMS (FAB): m/z calcd for C$_{52}$H$_{46}$N$_4$ [M]$^+$ 726.3722; found for 726.3723.
Fig. S1. $^1$H NMR spectrum of $E$-Ph in CD$_2$Cl$_2$ at different times.
**Fig. S2** $^1$H NMR spectrum of Z-Ph in CD$_2$Cl$_2$ at different times.

E:Z = 2:1
1 day later

0 h

**Fig. S3** $^1$H NMR spectrum of E/Z-Ph in CD$_2$Cl$_2$ at different times.
Fig. S4 $^1$H NMR spectrum of compound 1 in CDCl$_3$ at room temperature.
Fig. S5 $^{13}$C NMR spectrum of compound 1 in CDCl$_3$ at room temperature.

Fig. S6 $^1$H NMR spectrum of $E/Z$-Ph in CDCl$_3$ at room temperature.
**Fig. S7** $^1$H NMR spectrum of $Z$-Ph in CDCl$_3$ at room temperature.

**Fig. S8** $^1$H NMR spectrum of $E$-Ph in CDCl$_3$ at room temperature.
Fig. S9 $^1$H NMR spectrum of 2 in CDCl$_3$ at room temperature.
Fig. S10 $^{13}$C NMR spectrum of compound 2 in CDCl$_3$ at room temperature.

Fig. S11 $^1$H NMR spectrum of 3 in CDCl$_3$ at room temperature.
Fig. S12 $^{13}$C NMR spectrum of 3 in CDCl$_3$ at room temperature.

Fig. S13 $^1$H NMR spectrum of 4 in CDCl$_3$ at room temperature.
Fig. S14 $^{13}$C NMR spectrum of 4 in CDCl$_3$ at room temperature.

Fig. S15 $^1$H NMR spectrum of $E/Z$-CF$_3$ in CDCl$_3$ at room temperature.
**Fig. S16** $^1$H NMR spectrum of $E/Z$-CF$_3$ in CDCl$_3$ at room temperature

**Fig. S17** $^1$H NMR spectrum of $E/Z$-F in CDCl$_3$ at room temperature
Fig. S18 $^1$H NMR spectrum of $E/Z$-F in CDCl$_3$ at room temperature

Fig. S19 $^1$H NMR spectrum of $E/Z$-CH$_3$ in CDCl$_3$ at room temperature
**Fig. S20** $^1$H NMR spectrum of $E/Z$-CH$_3$ in CDCl$_3$ at room temperature.

**Fig. S21** $^1$H NMR spectrum of PhPc in CDCl$_3$ at room temperature.
**Fig. S22** $^{13}$C NMR spectrum of PhPc in CDCl$_3$ at room temperature.

**Fig. S23** $^1$H NMR spectrum of CF$_3$Pc in CDCl$_3$ at room temperature
Fig. S24 $^{13}\text{C}$ NMR spectrum of CF$_3$Pc in CDCl$_3$ at room temperature
Fig. S25 $^{19}$F NMR spectrum of CF$_3$Pc in CDCl$_3$ at room temperature.
Fig. S26 $^1$H NMR spectrum of FPc in CDCl$_3$ at room temperature

Fig. S27 $^{13}$C NMR spectrum of FPc in THF-$d_8$ at room temperature
Fig. S28 $^{19}$F NMR spectrum of FPe in CDCl$_3$ at room temperature.
Fig. S29 $^1$H NMR spectrum of CH$_3$Pc in CDCl$_3$ at room temperature

Fig. S30 $^{13}$C NMR spectrum of CH$_3$Pc in CDCl$_3$ at room temperature
Table S1 Crystallographic data for PhPc

| Compound                  | PhPc |
|---------------------------|------|
| CCDC No.                  | 1868296 |
| empirical formula         | C_{44}H_{30}N_{4}, 2(CHCl_{3}) |
| formula weight            | 853.46 |
| temperature [K]           | 100 |
| wavelength [Å]            | 0.71073 |
| crystal system            | triclinic |
| space group               | P -1 |
| a [Å]                     | 9.235(16) |
| b [Å]                     | 9.638(17) |
| c [Å]                     | 11.86(2) |
| α [°]                     | 78.93 |
| β [°]                     | 76.86(5) |
| γ [°]                     | 73.21(4) |
| Volume [Å³]               | 975(3) |
| Z                         | 1 |
| Density (calculated) [g/cm³] | 1.454 |
| Absorption coefficient [mm⁻¹] | 0.482 |
| F(000)                    | 438.0 |
| θ [°]                     | 1.78 to 28.70 |
| Reflections collected     | 6705 |
| Independent reflections   | 4940 [R(int) = 0.0.347] |
| Data / restraints / parameters | 4940 / 0 / 257 |
| Goodness-of-fit on F²     | 1.107 |
| R1a [I>2σ(I)]             | 0.0618 |
| wR2b (all data)           | 0.1604 |
| Largest diff. peak and hole [e.Å⁻³] | 0.545 and -0.550 |
| Compound       | CF₃Pc |
|---------------|-------|
| CCDC No.      | 1868292 |
| empirical formula | C₂₂H₂₂F₂₄N₄ |
| formula weight | 1158.74 |
| temperature [K] | 103 |
| wavelength [Å] | 0.71073 |
| crystal system | monoclinic |
| space group   | C 2/c |
| a [Å]         | 35.48(3) |
| b [Å]         | 14.931(11) |
| c [Å]         | 8.852(6) |
| α [°]         | 90 |
| β [°]         | 99.42(2) |
| γ [°]         | 90 |
| Volume [Å³]   | 4626(6) |
| Z             | 4 |
| Density (calculated) [g/cm³] | 1.664 |
| Absorption coefficient [mm⁻¹] | 0.167 |
| F(000)        | 2312 |
| θ [°]         | 2.21 to 23.25 |
| Reflections collected | 20383 |
| Independent reflections | 3322 [R(int) = 0.2320] |
| Data / restraints / parameters | 3322 / 0 / 365 |
| Goodness-of-fit on F² | 1.031 |
| R1 [I>2σ(I)]  | 0.0988 |
| wR2 (all data) | 0.2659 |
| Largest diff. peak and hole [e.Å⁻³] | 0.406 and −0.363 |
Table S3 Crystallographic data for FPc

| Compound       | FPc                  |
|----------------|----------------------|
| CCDC No.       | 1868294              |
| empirical formula | C_{24}H_{22}F_{8}N_{4}\cdot 0.793(C_2H_4Cl_2) |
| formula weight | 837.12               |
| temperature [K] | 103                  |
| wavelength [Å] | 0.71073              |
| crystal system | monoclinic           |
| space group    | P 21/n               |
| a [Å]          | 8.4081(6)            |
| b [Å]          | 13.0237(9)           |
| c [Å]          | 17.9996(12)          |
| α [°]          | 90                   |
| β [°]          | 103.022(2)           |
| γ [°]          | 90                   |
| Volume [Å^3]   | 1920.4(2)            |
| Z              | 2                    |
| Density (calculated) [g/cm^3] | 1.448 |
| Absorption coefficient [mm^{-1}] | 0.219 |
| F(000)         | 851.3                |
| θ [°]          | 2.94 to 25.20        |
| Reflections collected | 86147 |
| Independent reflections | 3444 \[R_{int} = 0.0751\] |
| Data / restraints / parameters | 3444 / 0 / 272 |
| Goodness-of-fit on F^2 | 1.073 |
| R1 [I>2σ(I)] | 0.0566               |
| wR2 (all data) | 0.1716               |
| Largest diff. peak and hole [e.Å^{-3}] | 0.992 and −0.507 |
| Compound       | CH$_3$Pc |
|---------------|----------|
| CCDC No.      | 1868293  |
| empirical formula | C$_{52}$H$_{46}$N$_4$ |
| formula weight | 726.93   |
| temperature [K] | 103      |
| wavelength [Å] | 0.71073  |
| crystal system | monoclinic |
| space group | P 21/n |
| a [Å]         | 8.7406(11) |
| b [Å]         | 15.369(2)  |
| c [Å]         | 16.406(2)  |
| $\alpha$ [°] | 90        |
| $\beta$ [°]  | 103.303(4) |
| $\gamma$ [°] | 90        |
| Volume [Å$^3$] | 2144.8(5) |
| Z             | 2         |
| Density (calculated) [g/cm$^3$] | 1.126 |
| Absorption coefficient [mm$^{-1}$] | 0.066 |
| $F(000)$      | 772.0     |
| $\theta$ [°] | 1.84 to 27.51 |
| Reflections collected | 32049 |
| Independent reflections | 4877 [$R_{int} = 0.0509$] |
| Data / restraints / parameters | 4877 / 168 / 262 |
| Goodness-of-fit on $F^2$ | 1.095 |
| $R1$ [$I>2\sigma(I)$] | 0.0611 |
| $wR2$ (all data) | 0.1848 |
| Largest diff. peak and hole [e.Å$^{-3}$] | 0.983 and −0.467 |
Optical properties:

**Fig. S31** (a) Absorption spectra of PhPc, CF<sub>3</sub>Pc, FPc, and CH<sub>3</sub>Pc in CH<sub>2</sub>Cl<sub>2</sub>. (b) Emission spectra of PhPc, CF<sub>3</sub>Pc, FPc, and CH<sub>3</sub>Pc in CH<sub>2</sub>Cl<sub>2</sub> (1×10⁻⁶ M). Excitation at their Soret band.

Lifetime measurements:
Fig. S32  Fluorescence-decay profile of porphycene derivatives in CH$_2$Cl$_2$.

Electrochemical Data:
Fig. S33 Cyclic voltammogram (black line) and differential pulse voltammogram (red line) of porphycene derivatives in CH$_2$Cl$_2$. 
Computational Studies

The potential energy curves (PECs) for the rotation around the C=C bond shown in Fig. S34 were calculated using the DFT(ωB97XD)/6-31G(d,p) method because intramolecular van der Waals interaction could be expected. The rotation was controlled by changing the pyrrole-C=C-pyrrole dihedral angle (φ). In the calculations, we firstly located the energy minima corresponding to the E- and Z-forms. Then, φ was modulated at the 5° increment. At the curve crossing regions, the increment was set to 1°. The other degree of freedom except for φ was fully optimized. Because of the relative orientations of the pyrrole and phenyl groups, we obtained some PECs in each system. Fig. 2 (b) and (c) show the PECs connecting the lowest-energy points at each configuration. The transition state was located through polynomial fitting (up to the 6-th order) at around the two local minima corresponding to the E- and Z-forms.

Results and Discussion

To understand the E/Z-isomerization, we conducted a computational investigation of the potential energy curve (PEC) along the reaction coordinate for the E/Z-isomerization of Ph and its protonated form (Ph+H) using DFT. For comparison, compounds with Me groups in place of the phenyl groups in Ph, hereafter denoted as Me and Me+H, were also calculated. The dihedral angle (φ), defined in Fig. 34(a), was manually modulated and other degrees of freedom were optimized at each point (each value of φ).
Fig. S34 (a) The pyrrole(Pyr)-C=C-pyrrole dihedral angle ($\phi$) taken as a reaction coordinate in the E/Z isomerization, and the potential energy curves (b) before and (c) after protonation of Ph and Me (denoted as Ph+H and Me+H, respectively) calculated by using the DFT(B97xd)/6-31G(d,p) method. Arrow indicates the important reaction intermediate.

Table S5 Summary of energy minima and transition state (TS) on the potential curves of Ph, Me, and their protonated forms. The reaction coordinate is $\phi$ (unit in degree) defined in Fig. S34(a). The relative energy ($\Delta E$) from the Z-type conformation is tabulated in kcal/mol unit.

| Molecule | Z-type | TS | E-type |
|----------|--------|----|--------|
|          | $\phi$ | $\Delta E$ | $\phi$ | $\Delta E$ | $\phi$ | $\Delta E$ |
| Ph       | 15.0   | 0.0  | 88.8   | 31.4  | 167.3 | -0.1  |
| Ph+H     | 30.0   | 0.0  | 70.6   | 3.0   | 95.0  | 0.9   |
| Me       | 10.0   | 0.0  | 91.5   | 35.6  | 169.5 | 3.0   |
| Me+H     | 33.6   | 0.0  | 82.3   | 7.1   | 95.0  | 6.2   |

The obtained PECs highlighted the essential differences between Ph and Me. Before protonation, the both systems had two energy minima corresponding to the E and Z forms. Starting from the E form, the dihedral distortion resulted in system destabilization of the system. When $\phi$ was nearly 90° (see Table S5), the PEC had a maximum corresponding to the transition state. In the unprotonated form, the activation energies of Ph and Me were 31.5 and 32.6 kcal/mol, respectively. These energies indicate that the isomerization is very difficult.

In contrast, protonation at the ethylene moiety drastically changes the PECs. In this case, two energy minima appear at around 30° and 95°, with the transition states located at 71° and 82° in Ph+H and Me+H, respectively. The lower energy conformation is now the Z-type form rather than the E-type form. The barrier heights from the E-type forms of Ph+H and Me+H are 2.1 and 0.9 kcal/mol, respectively. These values are consistent with the decrease in the bond order of the C–C bonds (from double bond to single bond) after protonation. The lowering of the barrier heights clearly indicates that rotation along the C–C bond easily occur to predominantly yield the Z-type form. Another interesting feature is the shallow barrier height of Z-type Me and an energy difference between the two minima of 6.0 kcal/mol. These features suggest that the Z-type form is the major conformation in Me+H due to both thermodynamic and kinetic stabilities. In contrast, the PEC for Ph+H shows a bistable character around the TS, with an energy difference between the E- and Z-type forms of only 0.9 kcal/mol. This indicates that these two forms may exist thermodynamically. The relative conversion between these forms is less favorable than in Me+H, both thermodynamically and kinetically. Such features were unchanged, even when the solvent effect of CH2Cl2 was accounted for using the polarizable continuum model (PCM).

The computational results suggest that gram-scale synthesis from Ph should have become possible due to the enhanced (relative) stability of the Z-type form of the protonated species. Therefore, we can conclude that the reactive intermediate might be trapped owing to the phenyl group in Ph. As the optimized geometries show that buckling of the phenyl group occurred at the TS, steric repulsion would be a factor in the larger activation energy compared with that of Me.
Quantum mechanical calculations were performed with Gaussian 09 Program. All calculations were done by Density functional theory (DFT) with restricted Becke’s three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) was used. The 6-31G(d,p) basis set was used for all atoms. The initial geometry was taken from the X-ray crystallographic structures. The molecular orbitals were visualized using ChemCraft.

**Table S6** Selected orbital energies of optimized structures of PhPc, CF₃Pc.

| Optimized structure of porphycene |  |  |
|-----------------------------------|---|---|
| LUMO+1                           | -1.50 | -2.34 |
| LUMO                              | -2.78 | -3.53 |
| HOMO                              | -5.15 | -5.93 |
| HOMO-1                            | -5.21 | -6.00 |

**Table S7** Selected orbital energies of optimized structures of FPc and CH₃Pc.

| Optimized structure of porphycene |  |  |
|-----------------------------------|---|---|
| LUMO+1                           | -1.97 | -1.38 |
| LUMO                              | -3.19 | -2.66 |
| HOMO                              | -5.58 | -5.02 |
| HOMO-1                            | -5.65 | -5.08 |
Table S8 Comparison between crystal structures and optimized structures of porphycene derivatives.
|                          | N1–N2 (Å) | N1–N3 (Å) |
|--------------------------|-----------|-----------|
| DFT optimized PhPc       | 2.884     | 2.590     |
| Crystal structure PhPc   | 2.874     | 2.547     |
| DFT optimized CF₃Pc      | 2.881     | 2.595     |
| Crystal structure CF₃Pc  | 2.894     | 2.552     |
| DFT optimized FPc        | 2.881     | 2.593     |
| Crystal structure FPc    | 2.866     | 2.562     |
| DFT optimized CH₃Pc      | 2.885     | 2.590     |
| Crystal structure CH₃Pc  | 2.873     | 2.568     |
Fig. S35 Frontier molecular orbitals of meso-tetraarylporphycene derivatives based on DFT/B3LYP/6-31G(d,p) calculations. Energy levels of the HOMO-1, HOMO, LUMO, LUMO+1 molecular orbital of the meso-tetraarylporphycene derivatives were depicted.
Coordinates of the optimized structure of PhPc:

C  2.791727833  1.628598574  0.019968358  0.019968358
C  2.871820160  3.065849041  0.073257221  0.073257221
H  3.789275092  3.632678093  0.101306529  0.101306529
C  1.589917024  3.561512812  0.085849130  0.085849130
H  1.290929735  4.599452869  0.123916420  0.123916420
C  0.696281809  2.445574976  0.044149234  0.044149234
C -0.716123146  2.423828422  0.047988456  0.047988456
C -1.603194849  3.561512812  0.085849130  0.085849130
H -1.306970373  4.603620172  0.144767066  0.144767066
C -2.869704721  3.058852127  0.092498184  0.092498184
H -3.794902199  3.613285837  0.130027084  0.130027084
C -2.748421259  1.605563663  0.029610961  0.029610961
C -3.857303945  0.706346041  0.012172114  0.012172114
C -3.877141821 -0.710008953 -0.005472510 -0.005472510
C -5.196327065  1.404221086  0.023656862  0.023656862
C -5.923035650  1.548718490  1.213006713  1.213006713
H -5.525388793  1.132236739  2.133468923  2.133468923
C -7.143743422  2.223994794  1.224717432  1.224717432
H -7.692248817  2.327599957  2.156605690  2.156605690
C -7.657071759  2.767877254  0.046333738  0.046333738
H -8.607724346  3.293022003  0.055683181  0.055683181
C -6.939163921  2.635735472 -1.142966135 -1.142966135
H -7.327862602  3.059055157 -2.064818536 -2.064818536
C -5.716962917  1.962304552 -1.15224954 -1.15224954
H -5.155823637  1.868892814 -2.077545223 -2.077545223
C -5.221754540 -1.395754483 -0.021558384 -0.021558384
C -5.747695944 -1.956036199  1.151022589  1.151022589
H -5.189049423 -1.867753844  2.078375296  2.078375296
C -6.973602406 -2.622690845  1.136431696  1.136431696
H -7.366959646 -3.046988794  2.055824756  2.055824756
C -7.689497572 -2.745912784 -0.054974753 -0.054974753
H -8.643200125 -3.265384028 -0.068425114 -0.068425114
C -7.170672882 -2.200268528  1.230197152  1.230197152
H -7.717907246 -2.296933569 -2.163540627 -2.163540627
C -5.946089522 -1.532346921  1.213447581  1.213447581
H -5.544169770 -1.114063739 -2.131160747 -2.131160747
N -1.425061314  1.272695028  0.007364862  0.007364862
N  1.458628307   1.317505456   0.004407178
H  1.156489641   0.302493904   -0.005686874
C  -2.791728357  -1.628597680  -0.019972210
C  -2.871821139  -3.065848210  -0.073253259
H  -3.789276140  -3.626771114  -0.101298831
C  -1.589918363  -3.561512579  -0.085842594
H  -1.290931429  -4.599452943  -0.123904001
C  -0.696282815  -2.445574871  -0.044148325
C  0.716122141  -2.423828797  -0.047987486
C  1.603193827  -3.564245245  -0.101292766
H  1.306969288  -4.603620838  -0.144760051
C  2.869703927  -3.058852656  -0.092498188
C  3.794901469  -3.613286456  -0.130027715
H  2.748420613  -1.605563853  -0.029614074
C  3.857303495  -0.706345744  -0.012179176
C  3.877141456   0.710009545   0.005465956
C  5.196327113  -1.404220419  -0.023661674
C  5.923035068  -1.548723295  -1.213011550
H  5.525387206  -1.132246269  -2.13475591
C  7.143743104  -2.223999318  -1.224719792
H  7.692247759  -2.327608906  -2.156608013
C  7.657072500  -2.767875756  -0.046337779
H  8.607725352  -3.293020172  -0.055681395
C  6.939165720  -2.635728328   1.142966077
H  7.327865407  -3.059043208   2.064820304
C  5.716964346  -1.962297848   1.15222668
H  5.155825781  -1.868881511   2.077543037
C  5.221754741  -1.395754393   0.021557300
C  5.747698431   1.956042020  -1.151020097
H  5.189053010  -1.867765142  -2.078374121
C  6.973605475   2.622695587  -1.136423732
H  7.366964356   3.046998250  -2.055813945
C  7.689499159   2.745910291   0.054984403
H  8.643202136   3.265380593   0.068438899
C  7.170672511   2.200259950   1.230203122
H  7.717905764   2.296919234   2.163547855
C  5.946088464   1.532339534   1.213448359
H  5.544167124   1.114051351   2.131158694
### Coordinates of the optimized structure of CF$_3$Pc:

| Atom | X       | Y       | Z       | E       | σ       |
|------|---------|---------|---------|---------|---------|
| F    | 6.807340047 | 4.998335805 | 0.635144183 |
| F    | 5.777431790 | 6.712081422 | -0.215007575 |
| F    | 2.889865887 | 8.284996129 | 4.237247277 |
| F    | 3.867676962 | 2.171306568 | 7.605520370 |
| F    | 6.792963783 | 6.902781768 | 1.697178866 |
| F    | 3.439229581 | 4.097542647 | 6.697910108 |
| F    | 5.460118167 | 3.634937833 | 7.373720097 |
| F    | 2.519486824 | 6.521779758 | 5.458943552 |
| F    | 1.025791465 | 7.174222338 | 4.024422988 |
| F    | 7.897160377 | 1.374421274 | 2.165088031 |
| F    | 8.574541335 | 1.845098052 | 4.183659529 |
| F    | 7.800053335 | -0.134070334 | 3.724597382 |
| N    | 1.385442919 | -0.231321545 | 1.298191619 |
| N    | -0.492879914 | -1.897961446 | -0.114341340 |
| C    | 2.354565835 | 0.248036151 | 2.129449621 |
| C    | -0.844222638 | -4.116101560 | 0.032117461 |
| H    | -1.259618841 | -5.096393841 | -0.142974643 |
| C    | 2.295533345 | 2.767863776 | 1.593387104 |
| C    | 0.382350222 | -2.382057837 | 0.809885533 |
| C    | 4.168403005 | 4.449105569 | 1.33304286 |
| H    | 4.640728430 | 3.783506060 | 0.619386862 |
| C    | 2.772265599 | 1.606516235 | 2.250892873 |
| C    | 2.958962233 | 4.080111792 | 1.934505765 |
| C    | 1.298921693 | -1.564863852 | 1.506478880 |
| C    | 2.366554303 | 4.960777349 | 2.844839973 |
| H    | 1.419917679 | 4.700736590 | 3.307119348 |
| C    | -1.267768589 | -2.904483244 | -0.623033486 |
| C    | 2.902884658 | -0.858404874 | 2.909628271 |
| H    | 3.676072463 | -0.786271702 | 3.659226174 |
| C    | 2.245602111 | -1.985344289 | 2.516020322 |
| H    | 2.387848957 | -2.993176500 | 2.881212140 |
| C    | 0.165250095 | -3.793130815 | 0.905771641 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | 0.706248143 | -4.466156295 | 1.555358823 |
| C       | 6.045310997  | 6.068976597  | 0.944367025 |
| C       | 5.203909641  | 1.446660302  | 2.918591734 |
| H       | 5.419542813  | 1.022973395  | 1.943662410 |
| C       | 2.986792368  | 6.169006549  | 3.172838870 |
| C       | 3.891290671  | 1.808960739  | 3.243358602 |
| C       | 6.241263480  | 1.636987790  | 3.833822429 |
| C       | 4.680966539  | 2.548230050  | 5.418131286 |
| C       | 2.356842265  | 7.046290457  | 4.224215256 |
| C       | 4.777329255  | 5.663422615  | 1.651840404 |
| C       | 3.640642200  | 2.350219379  | 4.508842912 |
| H       | 2.630143158  | 2.631921533  | 4.783014249 |
| C       | 7.634235168  | 1.185593506  | 3.476106430 |
| C       | 4.365760338  | 3.117994781  | 6.777959385 |
| C       | 4.194676492  | 6.527868577  | 2.579685954 |
| H       | 4.675054782  | 7.463493218  | 2.836867669 |
| C       | 5.987928127  | 2.193823742  | 5.086879779 |
| H       | 6.796416559  | 2.360510691  | 5.787486739 |
| H       | -0.648789320 | -0.901833880 | -0.435598038 |
| F       | -6.807340047  | -4.998335805  | -0.635144183 |
| F       | -5.777431790  | -6.712081422  | 0.215007575 |
| F       | -2.889865887  | -8.28496129   | -4.237247277 |
| F       | -3.867676962  | -2.171306568  | -7.605520370 |
| F       | -6.792963783  | -6.902781768  | -1.697178866 |
| F       | -3.439229581  | -4.097542647  | -6.697910108 |
| F       | -5.460118167  | -3.634937833  | -7.373720097 |
| F       | -2.519486824  | -6.521779758  | -5.458943552 |
| F       | -1.025791465  | -7.174222338  | -4.02442988 |
| F       | -7.897160377  | -1.374421274  | -2.165088031 |
| F       | -8.574541335  | -1.845098052  | -4.183659529 |
| F       | -7.800053335  | 0.134070334   | -3.724597382 |
| N       | -1.385442919  | 0.231321545   | -1.298191619 |
| N       | 0.492879914   | 1.897961446   | 0.114341340 |
| C       | -2.354565835  | -0.248036151  | -2.129449621 |
| C       | 0.844222638   | 4.116101560   | -0.032117461 |
| H       | 1.259618841   | 5.096393841   | 0.142974643 |
| C       | -2.295533345  | -2.767863776  | -1.593387104 |
| C       | -0.382350222  | 2.382057837   | -0.809885533 |
|  | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       | C       |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|  | -4.168403005 | -4.449105569 | -1.333304286 | 47 | -4.640728430 | -3.783506060 | -0.619386862 | 47 | -2.772265599 | -1.606516235 | -2.250892873 | 47 | -2.958962233 | -4.080111792 | -1.934505765 | 47 | -1.298921693 | 1.564863852 | -1.506478880 | 47 | -2.366554303 | -4.960777349 | -2.844839973 | 47 | -1.419917679 | -4.700736590 | -3.307119348 | 47 | 1.267768589 | 2.904483244 | 0.623033486 | 47 | -2.902884658 | 0.858404874 | -2.909628271 | 47 | -3.676072463 | 0.786271702 | -3.659226174 | 47 | -2.245602111 | 1.985344289 | -2.516020322 | 47 | -2.387488957 | 2.993176500 | -2.881212140 | 47 | -0.165250095 | 3.793130815 | -0.905771641 | 47 | -0.706248143 | 4.466156295 | -1.555358823 | 47 | -6.045310997 | -6.068976597 | -0.944367025 | 47 | -5.203909641 | -1.446660302 | -2.918591734 | 47 | -5.419542813 | -1.022973395 | -1.943662410 | 47 | -2.986792368 | -6.169006549 | -3.172838870 | 47 | -3.891290671 | -1.808960739 | -3.243358602 | 47 | -6.241263480 | -1.636987790 | -3.833822429 | 47 | -4.680966539 | -2.548230050 | -5.418131286 | 47 | -2.356842265 | -7.046290457 | -4.224215256 | 47 | -4.777329255 | -5.663422615 | -1.651840404 | 47 | -3.640642200 | -2.350219379 | -4.50842912 | 47 | -2.630143158 | -2.631921533 | -4.783014249 | 47 | -7.634235168 | -1.185593506 | -3.476106430 | 47 | -4.365760338 | -3.117994781 | -6.777953858 | 47 | -4.194676492 | -6.527868577 | -2.579685954 | 47 | -4.675054782 | -7.463493218 | -2.836867669 | 47 | -5.987928127 | -2.193823742 | -5.086879779 | 47 | -6.796416559 | -2.360510691 | -5.787486739 | 47 | 0.648789320 | 0.901833880 | 0.435598038 | 47
### Coordinates of the optimized structure of FPc:

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| F    | -5.061082 | 5.480898  | 4.088678  |
| F    | -3.964613 | 2.049203  | 7.110595  |
| F    | 0.810874  | 4.713223  | 7.017551  |
| F    | -0.109223 | 7.622966  | 3.440303  |
| N    | -0.745068 | -1.496512 | -0.926066 |
| N    | -1.571882 | 0.349676  | 1.125940  |
| H    | -0.584580 | 0.607438  | 0.844627  |
| C    | -1.975723 | -1.536948 | -0.366673 |
| C    | -2.379826 | -0.633668 | 0.640506  |
| C    | -0.686249 | -2.494196 | -1.854530 |
| C    | -2.217798 | 1.080252  | 2.086129  |
| C    | -3.629549 | -0.537583 | 1.330163  |
| H    | -4.483147 | -1.180469 | 1.169100  |
| C    | -3.534778 | 0.510278  | 2.213626  |
| C    | -4.299226 | 0.861235  | 2.889149  |
| C    | -1.691742 | 2.192367  | 2.797604  |
| C    | -2.764174 | -2.600616 | -0.948494 |
| C    | -3.783047 | -2.856394 | -0.691480 |
| C    | -1.965339 | -3.198074 | -1.877327 |
| H    | -2.218389 | -4.030181 | -2.516439 |
| C    | -0.423712 | 2.813127  | 2.691844  |
| C    | -2.671826 | 2.764398  | 3.793316  |
| C    | -3.425932 | 3.900487  | 3.474122  |
| H    | -3.311640 | 4.404717  | 2.522198  |
| C    | -0.170813 | 3.995273  | 3.597263  |
| C    | -4.339055 | 4.387882  | 4.402085  |
| C    | -2.863590 | 2.132199  | 5.029273  |
| H    | -2.304921 | 1.244009  | 5.300338  |
| C    | -0.269297 | 5.298382  | 3.090975  |
| H    | -0.540921 | 5.482541  | 2.058107  |
| C    | -3.789133 | 2.659645  | 5.922669  |
| C    | -4.545593 | 3.790469  | 5.639840  |
| H    | -5.261859 | 4.186461  | 6.348696  |
| C    | 0.201764  | 3.800156  | 4.933022  |
| H    | 0.300895  | 2.806093  | 5.352170  |
| C    | 0.451715  | 4.908574  | 5.734004  |
| C    | -0.009255 | 6.373216  | 3.933400  |
Coordinates of the optimized structure of CH₃Pe:

N  -0.786761636  -1.401304383  -1.034772635
N  -1.626966131   0.462745258  1.001038088
C  -2.061857049  -1.338076851  -0.588324623
C  -0.734794874  -2.372653791  -1.992196500
C  -2.289361175   1.227630039  1.923567820
C  -0.411194170   2.773191046  2.744061119
C  -0.130882138   3.899390269  3.710325276
C   0.070131008   3.641619214  5.070603520
H  -0.001626442   2.619845692  5.432787008
C  -2.066847905  -2.947252159  -2.154711802
H  -2.334376717  -3.730373976  -2.847455759
C  -2.886625929  -3.02980869  -1.277515404
H  -3.946668525  -2.46553045   -1.122184032
C  -1.734832806   2.268434099  2.719032374
C  -2.472441602  -0.427025108   0.410229530
C  -0.015385590   5.215490134  3.246605147
H  -0.150974887   5.417233960   2.187174328
C  -3.766529467  -0.230273340   0.986321462
H  -4.656766967  -0.785077503   0.725686162
C  -3.659038401   0.782053392  1.909938124
H  -4.446265840   1.189607051  2.524685134
C  -2.746030071   2.896516597   3.647021844
C  0.370515560   4.673186522   5.967098229
C  0.475034553   5.97611539   5.474090086
H  0.717910971   6.787436368   6.160488701
C  0.282270474   6.268710158   4.118748007
C  -3.339913727   4.123512079   3.336923230
H  -3.047282122   4.639774133   2.426954981
C  -3.144136592   2.226805847   4.812061730
H  -2.697700794   1.264339224   5.048179375
C  0.559338431   4.383982699   7.438031273
H  1.211140263   5.123924827   7.912017187

50
|   |          |          |          |
|---|----------|----------|----------|
| H | 0.996672756 | 3.393944111 | 7.598880942 |
| H | -0.399765976 | 4.405141634 | 7.970639178 |
| C | 0.375431121 | 7.688590615 | 3.609606536 |
| H | 1.050578233 | 8.291260265 | 4.224512928 |
| H | -0.604929528 | 8.181340096 | 3.625404382 |
| H | 0.736833985 | 7.721140995 | 2.577358156 |
| C | -4.307218967 | 4.692990594 | 4.174047713 |
| C | -4.106119515 | 2.770850166 | 5.668927170 |
| C | -4.679257788 | 4.003293391 | 5.332154641 |
| H | -5.436676355 | 4.432732471 | 5.985155450 |
| C | -4.919233633 | 6.032855858 | 3.837676840 |
| H | -5.084315672 | 6.139517406 | 2.760906566 |
| H | -4.261851384 | 6.855112793 | 4.146570507 |
| H | -5.878965663 | 6.173771314 | 4.343088119 |
| C | -4.506011999 | 2.055705591 | 6.938683269 |
| H | -3.961744208 | 2.451411389 | 7.805336429 |
| H | -4.290512079 | 0.984975944 | 6.880183042 |
| H | -5.573873336 | 2.175809787 | 7.147112799 |
| H | -0.599386163 | 0.638394649 | 0.814309307 |
| N | 0.786761636 | 1.401304383 | 1.034772635 |
| N | 1.626966131 | -0.462745258 | -1.001038088 |
| C | 2.061857049 | 1.338076851 | 0.588324623 |
| C | 0.734794874 | 2.372653791 | 1.992196500 |
| C | 2.289361175 | -1.227630039 | -1.923567820 |
| C | 0.411194170 | -2.773191046 | -2.744061119 |
| C | 0.130882138 | -3.899390269 | -3.710325276 |
| C | -0.070131008 | -3.641619214 | -5.070603520 |
| H | 0.001626442 | -2.619845692 | -5.432787008 |
| C | 2.066847905 | 2.947252159 | 2.154711802 |
| H | 2.334376717 | 3.730373976 | 2.847455759 |
| C | 2.888625929 | 2.302980869 | 1.277515404 |
| H | 3.946668525 | 2.465533045 | 1.122184032 |
| C | 1.734832806 | -2.268434099 | -2.719032374 |
| C | 2.472441602 | 0.427025108 | -0.410229530 |
| C | 0.015385590 | -5.215490134 | -3.246605147 |
| H | 0.150974888 | -5.417233960 | -2.187174328 |
| C | 3.766529467 | 0.230273340 | -0.986321462 |
| H | 4.656766967 | 0.785077503 | -0.725686162 |

51
| Atoms | X          | Y          | Z          |
|-------|------------|------------|------------|
| C     | 3.65938401 | -0.782053392 | -1.909938124 |
| H     | 4.446265840 | -1.189607051 | -2.524685134 |
| C     | 2.746030071 | -2.896516597 | -3.647021844 |
| C     | -0.370515560 | -4.673186522 | -5.967098229 |
| C     | -0.475034553 | -5.978611539 | -5.474090086 |
| H     | -0.717910971 | -6.787436368 | -6.160488701 |
| C     | -0.282270474 | -6.268710158 | -4.118748007 |
| C     | 3.339913727 | -4.123512079 | -3.336923230 |
| H     | 3.047282122 | -4.639774133 | -2.426954981 |
| C     | 3.144136592 | -2.226805847 | -4.812061730 |
| H     | 2.697700794 | -1.264392224 | -5.048179375 |
| C     | -0.559338431 | -4.383982699 | -7.438031273 |
| H     | -1.211140263 | -5.123924827 | -7.912017187 |
| H     | -0.996672756 | -3.393944111 | -7.598889042 |
| H     | 0.399765976 | -4.405141634 | -7.970639178 |
| C     | -0.375431121 | -7.688590615 | -3.609606536 |
| H     | -1.050578233 | -8.291260265 | -4.224512928 |
| H     | 0.604929528 | -8.181340096 | -3.625404382 |
| H     | -0.736833985 | -7.721140995 | -2.577358156 |
| C     | 4.307218967 | -4.692990594 | -4.174047713 |
| C     | 4.106119515 | -2.770850166 | -5.668927170 |
| C     | 4.679257788 | -4.003293391 | -5.332154641 |
| H     | 5.436676355 | -4.432732471 | -5.985155450 |
| C     | 4.919233633 | -6.032855858 | -3.837676840 |
| H     | 5.084315672 | -6.139517406 | -2.760906566 |
| H     | 4.261851384 | -6.855112793 | -4.146570507 |
| H     | 5.878965663 | -6.173771314 | -4.343088119 |
| C     | 4.506011999 | -2.055705591 | -6.938683269 |
| H     | 3.961744208 | -2.451411389 | -7.805336429 |
| H     | 4.290512079 | -0.984975944 | -6.880183042 |
| H     | 5.573873336 | -2.175809787 | -7.147112799 |
| H     | 0.599386163 | -0.638394649 | -0.814309307 |
Coordinates of the optimized structure of PhCF₃Pe:

|   |   |   |   |
|---|---|---|---|
| N | 3.700135116 | 1.271297722 | 0.103274385 |
| N | 3.732791882 | -1.312448569 | -0.098199840 |
| H | 3.430253946 | -0.301530377 | -0.013345106 |
| N | 0.851615620 | -1.267948038 | -0.103359166 |
| N | 0.819590797 | 1.319293212 | 0.110222600 |
| H | 1.121366544 | 0.308929315 | 0.020743496 |
| C | -5.494779118 | 2.570683062 | 0.263611619 |
| H | -6.477823279 | 3.021690946 | 0.309627846 |
| C | -0.511790840 | 1.630030919 | 0.151660629 |
| C | 6.132100987 | 0.705847016 | 0.063122089 |
| C | -5.644811134 | 2.026504638 | 2.724025896 |
| C | 2.972056470 | -2.434737818 | -0.221354939 |
| C | -5.378971958 | -3.079675390 | 2.198590603 |
| C | -1.572767760 | -0.698378483 | -0.067014044 |
| C | -0.469659500 | -1.599621071 | -0.150672025 |
| C | 5.148222858 | 3.045854354 | 0.321235884 |
| H | 6.074522004 | 3.593819390 | 0.400335987 |
| C | 2.994671309 | 2.416957722 | 0.231388054 |
| C | -0.593772603 | -3.043388277 | -0.314798931 |
| H | -1.517489084 | -3.597128362 | -0.390827368 |
| C | 0.673073074 | -3.547607426 | -0.358428313 |
| H | 0.967906745 | -4.581768654 | -0.473183246 |
| C | 5.066537232 | -1.621047495 | -0.137414344 |
| C | -2.945218669 | 1.374850860 | 0.140316153 |
| C | 5.024838547 | 1.599941017 | 0.148396047 |
| C | 5.146944160 | -3.051877217 | -0.298049710 |
| H | 6.064878225 | -3.613947208 | -0.369595055 |
| C | 6.151322610 | -0.708181878 | -0.056731993 |
| C | -3.491677682 | -1.957421818 | 0.995529379 |
| H | -2.950581959 | -1.943230681 | 1.935546885 |
| C | 3.866610987 | -3.545400445 | -0.346196149 |
| H | 3.567786103 | -4.577560076 | -0.461608195 |
| C | 8.010534644 | -2.050275338 | 1.004104474 |
| H | 7.444247359 | -2.041281172 | 1.930988711 |
| C | 1.560140580 | -2.414328071 | -0.224764766 |
| C | -4.753961942 | -2.549700707 | 0.934111861 |
| C | 9.454527645 | -2.088945855 | -1.377461841 |

53
|   |       |       |       |
|---|-------|-------|-------|
| H | 10.009892712 | -2.105190220 | -2.310742825 |
| C | 0.689651694  | 3.551204244  | 0.357446068  |
| H | 0.987927637  | 4.583708359  | 0.470685646  |
| C | -4.920919518 | 2.009676563  | 1.402358118  |
| C | -0.593243347 | 3.057933640  | 0.310259820  |
| H | -1.508679484 | 3.624931657  | 0.381179014  |
| C | 3.883729273  | 3.550415960  | 0.369433172  |
| H | 3.588601893  | 4.583642249  | 0.492000122  |
| C | 1.582287955  | 2.441686873  | 0.232115610  |
| C | -2.920491872 | -1.375081438 | -0.142237475 |
| C | -1.592168366 | 0.710262339  | 0.066287296  |
| C | 8.230679894  | -1.422792683 | -1.313685002 |
| H | 7.837937346  | -0.924503637 | -2.194599363 |
| C | -4.783036765 | 2.542587914  | -0.936046533 |
| C | 7.471623656  | 1.400071389  | 0.120670739  |
| C | 7.496014811  | -1.390485634 | -0.120799770 |
| C | -3.628942239 | -1.427544700 | -1.346131564 |
| H | -3.198577660 | -0.991303962 | -2.241463236 |
| C | -3.655760116 | 1.420356828  | 1.343449603  |
| H | -3.225024785 | 0.982852843  | 2.237924453  |
| C | -5.463766738 | -2.584941049 | -0.266598933 |
| H | -6.444110190 | -3.041690872 | -0.313098543 |
| C | 9.236242717  | -2.714483143 | 0.942248051  |
| H | 9.621461688  | -3.217106309 | 1.824763845  |
| C | 8.209036280  | 1.444587520  | 1.311297312  |
| H | 7.821009125  | 0.950730572  | 2.196887462  |
| C | 9.201930600  | 2.726480369  | -0.955464412 |
| H | 9.581941249  | 3.225664592  | -1.842209871 |
| C | -3.517286956 | 1.957600653  | -0.996845909 |
| H | -2.975244598 | 1.947718591  | -1.936376201 |
| C | -5.408898201 | 3.072402335  | -2.200276201 |
| C | 7.980217921  | 2.054437841  | -1.009969690 |
| H | 7.411080328  | 2.037065296  | -1.934974325 |
| C | 9.428805820  | 2.119060893  | 1.368058362  |
| H | 9.985769955  | 2.145600629  | 2.300190581  |
| C | 9.930292600  | 2.760451966  | 0.234338341  |
| H | 10.880232385 | 3.284906694  | 0.278768827  |
| C | 9.962212095  | -2.735271384 | -0.249236852 |
H     10.915440611  -3.253192779  -0.299224127
C     -5.613758536  -2.043746487  -2.727721067
C     -4.890834611  -2.023953480  -1.405726400
F     -5.715953300   0.786698516   3.257005199
F     -5.002132133  2.803063006   3.62356536
F     -6.903631573  2.496849791   2.610657307
F     -4.490514716  3.657389146  -3.001109925
F     -6.369061955  3.986014827  -1.943853163
F     -5.981682248  2.079810022  -2.917061100
F     -4.459587888  -3.659228122   3.001998975
F     -5.956738844  -2.087694091   2.912838302
F     -6.335494655  -3.997433769   1.943179668
F     -4.95637466   -2.798657208  -3.637047250
F     -5.709738430  -0.80405863   -3.249500000
F     -6.863203120  -2.539648589  -2.619523576

References
1. Bruker AXS, *SAINT*, Bruker AXS Inc., Madison, WI, USA. 2017.
2. Bruker AXS, *SADABS*, Bruker AXS Inc., Madison, WI, USA. 2016.
3. a) G. M. Sheldrick, *Acta Cryst.* 2015, **A71**, 3–8; b) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.
4. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ransinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.