Supplementary Information for

Title: Synthesis of a Hetero-Dinuclear Metal Complex in a Porphyrin/Phthalocyanine Four-Fold Rotaxane

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General Methods.

Synthetic procedures were carried out under dry nitrogen atmosphere, unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Phthalocyanine 5, \([2\cdot5H]^\cdot5\text{BARF}^-\) were prepared according to the literature procedures.\(^1\) \(^1\)H, \(^13\)C NMR spectra were recorded on a JEOL JNM-A600 (600 MHz for \(^1\)H) spectrometer or a JEOL JNM-ECS400 (400 MHz for \(^1\)H; 100 MHz for \(^13\)C) spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for \(^1\)H and \(^13\)C NMR measurements in CDCl\(_3\). Elemental analysis were performed on a Yanaco MT-6 analyzer. Silica gel column chromatographies and thin-layer (TLC) chromatography were performed using Merck silica gel 60 and Merck silica gel 60 (F254) TLC plates, respectively. ESI mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software. MALDI-TOF mass spectrometry was performed with a Bruker Ultraflex III.

The absorption spectra were recorded with a JASCO V-570 spectrophotometer under nitrogen atmosphere in CH\(_2\)Cl\(_2\) solutions at 20 ± 0.1 °C in 1.0 cm quartz cells.
Synthesis of Zinc Phthalocyanine 1

To a solution of phthalocyanine 5 (100 mg, 50 μmol) in a 5:1 mixture of CHCl₃ and MeOH (v/v 12 mL) was added a solution of Zn(OAc)₂ (10.2 mg, 56 μmol) in MeOH (2 mL) dropwise. After the resulting mixture was refluxed at 70 °C for 24 hrs, additional amounts of Zn(OAc)₂ (31.5 mg, 172 μmol) and MeOH (8 mL) were added. The solution was stirred for further 72 hrs, and then diluted with CHCl₃ (100 mL). The solution was washed with water (40 mL × 3) and brine (40 mL) successively, dried over Na₂SO₄, filtered, and evaporated to obtain title compound 1 as a green solid (100 mg, 49 μmol, 97%). ¹H NMR (400 MHz, CDCl₃:CD₃CN = 4:1 / TMS): δ = 8.81 (brs, 4H), 6.83 (m, 16H), 4.45 (brs, 9H), 4.01 (brs, 11H), 3.87 (brs, 6H), 3.70 (m, 28H). ¹³C NMR (100 MHz, CDCl₃): δ = 152.3, 150.1, 148.6, 131.7, 121.4, 114.0, 10.9, 10.8, 69.5, 69.1. MS (ESI-TOF, positive) m/z: calcd for 2081.7: C₁₀₄H₁₂₀N₈O₃ZnNa ([1+Na]⁺), found: 2081.6. Anal. Calcd for C₁₀₄H₁₂₂N₈O₃₃Zn (1+H₂O): C, 60.13; H, 5.92; N, 5.39. Found: C, 60.03; H, 6.04; N, 5.33 (0.12% error).
Figure S1  $^1$H-NMR of 1.
Synthesis of [3·4H]^{4+}·4Cl^{−} \textsuperscript{1)}

A solution of a zinc phthalocyanine 1 (34 mg, 17 µmol) in CHCl\textsubscript{3} (13.8 mL) was added dropwise to a solution of porphyrin [2·5H]^{5+}·5BARF\textsuperscript{−} (99 mg, 17 µmol) in acetone (2.8 mL). The resulting mixture was stirred at room temperature for 14 hrs and then P(OEt)\textsubscript{3} (0.69 mL, 4.1 mmol) was added. After stirring for 82 hrs, it was poured into a 1:1 mixture of hexane and Et\textsubscript{2}O (100 mL). The black-green precipitate was collected by centrifugation and dried under vacuum (167 mg). After the precipitate was dissolved in MeOH (20 mL), ion exchange resin (IRA 400J–CL (Cl\textsuperscript{−} form), 20 mL) was added to remove BARF\textsuperscript{−}. The mixture was kept standing at room temperature for 30 minutes, and then the resin was filtered off. This ion exchange procedure was repeated by 4 times. The filtrate was concentrated under reduced pressure to obtain blackish green solid (52 mg), which was purified by silica gel column chromatography (3 cm\texttimes{} 26 cm, CHCl\textsubscript{3}:MeOH = 4:1 – 1:1 – CHCl\textsubscript{3}:MeOH:H\textsubscript{2}O:brine = 20:20:2:1) to obtain three fractions 1-3 (numbered from the top).

The crude product obtained from fraction 1 (28 mg) was dissolved in MeOH (10 mL) and BARF\textsuperscript{−} was removed by using ion exchange resin (IRA 400J CL (Cl\textsuperscript{−} form), 10 mL). Then the resulting solid (23 mg) was purified by PTLC to obtain black green solid (6.7 mg, 1.6 µmol, 9%).

The crude product obtained from fraction 2 (12 mg) was further purified by PTLC (CHCl\textsubscript{3}:MeOH = 4:1) to obtain blackish green solid (10 mg). Recrystallization from a mixed solvent system composed of CHCl\textsubscript{3}:MeOH = 4:1 / toluene / Et\textsubscript{2}O gave the title compound as a black green solid (6.5 mg, 1.5 µmol, 9%).

Totally, 13.2 mg (3.1 µmol, 18%) of the title compound was obtained.
\(^1\)H NMR (600 MHz, CDCl\(_3\)/TMS): \(\delta = 8.27\text{-}8.03\) (m, 14H), 7.69 (br, 4H), 7.33 (br, 9H including CHCl\(_3\)), 7.20 (br, 8H), 7.07 (br, 4H), 6.89 (br, 13H), 6.80 (br, 14H), 4.66 (br, 8H), 4.55 (br, 12H), 4.37\text{-}3.81 (m, 100H), 3.69 (br, 15H), 3.30 (br, 20H), 1.96\text{-}1.87 (m, 62H including H\(_2\)O), 1.64 (br, 18H), 0.75 (br, 23H). MS (MALDI-TOF, positive) \(m/z\): calcd for 4156.9: C\(_{220}\)H\(_{275}\)N\(_{20}\)O\(_48\)P\(_4\)Zn\((3\text{+H}^+)\), found: 4156.8. Anal. Calcd for C\(_{232}\)H\(_{310}\)Cl\(_4\)N\(_{52}\)O\(_{52}\)P\(_4\)Zn\((3\text{·4H}^+)\cdot4\text{Cl}^+\cdot\text{H}_2\text{O}+3\text{Et}_2\text{O})\): C, 61.35; H, 6.88; N, 6.17. Found: C, 61.59; H, 6.56; N, 5.95 (0.32\% error).

**Figure S2**  COSY spectrum of the four-fold rotaxane \([3\text{·4H}^+]\cdot4\text{Cl}^+\cdot\text{H}_2\text{O}+3\text{Et}_2\text{O})\) in CDCl\(_3\) at 298 K.
Figure S3. Partial COSY spectrum of the four-fold rotaxane [3·4H]^+·4Cl^- in CDCl\textsubscript{3} at 298 K.
Figure S4. Partial COSY spectrum of the four-fold rotaxane [3-4H]4+·4Cl− in CDCl₃ at 298 K.
Synthesis of $[4\cdot4H]^{4+}\cdot4Cl^-$

A solution of Cu(OAc)$_2$ (2.56 mg, 14.1 μmol) in MeOH (5.0 mL) was added dropwise to a solution of $[3\cdot4H]^{4+}\cdot4Cl^-$ (59.6 mg, 13.9 μmol) in MeOH (8.0 mL). The resulting mixture was refluxed at 60 ºC for 21 hrs and then the volatile compounds were evaporated off. After the crude material was dissolved in CHCl$_3$ (200 mL), the resulting solution was washed with brine (100 mL × 10), dried over anhydrous Na$_2$SO$_4$, filtered, and evaporated to obtain title compound blackish green solid (50.5 mg, 11.5 μmol, 82%). MS (MALDI-TOF, positive) m/z: calcd for 4217.7: C$_{220}$H$_{273}$N$_{20}$O$_{48}$P$_4$ZnCu (4+H)$^+$, found: 4218.0. Anal. Calcd for C$_{232}$H$_{302}$Cl$_{16}$CuN$_{20}$O$_{51}$P$_4$Zn ($[4\cdot4H]^{4+}\cdot4Cl^-\cdot4CHCl_3\cdotH_2O\cdot2Et_2O$): C, 55.65; H, 6.08; N, 5.59. Found: C, 55.88; H, 6.18; N, 5.55 (0.23% error).
Figure S5. UV-Vis absorption spectra of $[4\cdot 4H]^{4+}\cdot 4\text{Cl}^-$ (black line), 1 (orange line), and Cu(II) porphyrin 6 (blue line) in CH$_2$Cl$_2$ (2.0 μM) at 20 °C.
Figure S6. Photometric titration of the $[4 \cdot 4H]^4+ \cdot 4Cl^-$ with phosphazene base (P1-tBu). $[4 \cdot 4H]^4+ \cdot 4Cl^-$ was dissolved in CH$_2$Cl$_2$ at a concentration of $2.0 \times 10^{-6}$ M at 20 °C. (a) The spectral change during the addition of 0 – 60 equivalents of P1-tBu. The spectral change of the Q-band of the Zn$^{2+}$-phthalocyanine unit during the addition of (b) 0 – 5 equivalents (an isosbestic point was observed at 685 nm) and (c) 5 – 60 equivalents (an isosbestic point was observed at 697 nm) of P1-tBu.
Reference.