Supplementary Information

Biomimic O₂ Activation Hydroxylates a *meso*-Carbon of the Porphyrin Ring Regioselectively under Mild Condition

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1. Instrumentation and Materials

All solvents were distilled prior to use according to the standard protocols. All reagents were of the commercial reagent grade and were used without further purification except where noted. ¹H (600.17 MHz), ¹³C NMR (150.92 MHz) spectra were recorded on a Jeol ECA-600 spectrometer. Chemical shifts in CDCl₃ were reported in the scale relative to tetramethylsilane (0 ppm) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to CDCl₃ (77.0 ppm) as an internal reference, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, br = broadened). IR spectra were recorded on Shimadzu IRAffinity-1 using KBr pellets. UV/vis absorption spectra were recorded on a Shimazu UV-2600 and a Jasco V-570. Preparative gel permeation chromatography (GPC) was carried out with a Japan Analytical Industry LC-9201 chromatograph using a JAIGEL-H column (ϕ 20 × 600 mm, LC-9201 system) eluted by CHCl₃ at room temperature with the detection at 254 nm. Mass spectra were recorded on a Jeol JMS-T100LP using positive mode ESI-TOF method for methanol solutions. Cyclic voltammetry (CV) was carried out with Bas CV-50W using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). DFT calculations were carried out using the Spartan '04 package and performed at B3LYP/6-31G* level. Elemental analyses were taken on using Euro Vector EA3000. Crystallographic data were collected by Rigaku CCD mercury system using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). pK_a calculations of nitrogen bases were carried out using ACD/Lab software.

2. Experimental Section

Complexes $[Co^{II}(amtpp)]$ (1) and $[Co^{III}(lpp)(base)]$ were prepared according to the previously reported methods; See the reference 6 in the manuscript.

Synthesis of [Co(ampord)(OH)(1,2-Me₂Im)] (2) and [Co(amtpp)(1,2-Me₂Im)₂]Cl.



Scheme S1.

[Co^{III}(ampord)(OH)(1,2-Me₂Im)] (2)

Two equivalents of 1,2-dimethylimidazole (1,2-Me₂Im) was added to the CHCl₃ solution (10 mL) of **1** (50.0 mg, 70.0 μ mol), and then stirred for 6 h under air. The reaction mixture was purified by gel permeation chromatography (GPC). The brown crystals were obtained by recrystallization from CHCl₃/*n*-hexane (19.1 mg 31.8% yield).

¹H NMR (600 MHz, CDCl₃) δ 10.44 (s, 1H), 10.26 (s, 1H), 7.98-7.99 (m, 1H), 7.61-7.80 (m, 4H), 7.28-7.50 (m, 13H), 7.23-7.25 (m, 1H), 6.44-6.49 (m, 3H), 6.40 (d, *J* = 4.8 Hz, 1H), 6.36 (d, *J* = 4.8 Hz, 1H), 5.93-5.95 (m, 3H), 5.91 (d, *J* = 4.8 Hz, 1H), 5.88 (d, *J* = 4.1 Hz, 1H), 5.79 (d, *J* = 2.1 Hz, 1H), 3.46 (s, 3H), 1.40 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) d 168.0, 139.6, 138.7, 138.4, 137.5, 137.0, 136.7, 134.0, 133.2, 132.8, 132.6, 131.0, 128.7, 128.7, 128.6, 127.8, 127.6, 127.6, 120.6, 120.2, 118.9, 118.9, 117.1, 116.8, 99.9, 70.5, 33.8, 22.7; IR (KBr, cm⁻¹) 3420, 2926, 1694, 1580, 1557, 1323, 1277, 1065, 1020, 847, 791, 754, 721, 702; UV-vis (CHCl₃) : λ_{max} [nm] (ε [M⁻¹cm⁻¹]): 335.0 (27600), 439.5 (28000), 470.0 (34000), 502.0 (42700); ESI-TOF-MS (positive mode) *m*/*z* = 844.2 (calcd for C₅₀H₃₉CoN₇O₃ = 844.2 [*M* + H]⁺); Anal. Calcd. for C₅₂H₄₀Cl₆CoN₇O₃ (1082.57): C, 57.69; H, 3.72; N, 9.06. Found: C, 57.31; H, 3.76; N, 9.30.

[Co^{III}(amtpp)(1,2-Me₂Im)₂]Cl

Two equivalents of 1,2-dimethylimidazole (1,2-Me₂Im) was added to the CHCl₃ solution (10 mL) of **1** (50.0 mg, 70.0 μ mol), and then stirred for 6 h under air. The reaction mixture was purified by gel permeation chromatography (GPC). The crude product was obtained after removal of the solvent and purified by using silica gel column chromatography technique (dichloromethane/acetone = 80:20). The purple powder was obtained by recrystallization from CHCl₃/*n*-hexane (18.2 mg 27.6% yield).

¹H NMR (600 MHz, CDCl₃) δ 8.81-8.95 (m, 8H), 7.90 (d, J = 7.3 Hz, 2H), 7.52-7.63 (m, 11H), 7.24 (t, J = 7.8 Hz, 6H), 5.68 (d, J = 3.7 Hz, 2H), 4.43 (d, J = 1.8 Hz, 1H), 4.31 (d, J = 1.8 Hz, 1H), 3.56 (s, 3H), 3.36 (s, 3H), -0.24 (d, J = 1.8 Hz, 1H), -0.31 (d, J = 1.8 Hz, 1H), -2.17 (s, 3H), -2.26 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) d 160.8, 155.9, 148.1, 146.5, 144.5, 139.9, 136.6, 136.2, 136.0, 132.5, 131.7, 131.0, 129.2, 129.0, 128.1, 128.0, 127.9, 127.6, 126.8, 124.9, 124.6, 119.4, 116.8, 116.5, 33.9, 8.1; IR (KBr, cm⁻¹) 3446, 3123, 3022, 1668, 1639, 1612, 1566, 1537, 1526, 1510, 1371, 1350, 1312, 1287, 1236, 1207, 1182, 1101, 1074, 1041, 1005, 957, 847, 797, 748, 743, 708, 660, 642, 617; UV-vis (CHCl₃) : λ_{max}[nm] (ε [M⁻¹cm⁻¹]): 441.5 (19300), 560.5 (11800), 600.0 (6490); ESI-TOF-MS (positive mode) m/z = 906.3 (calcd for C₅₅H₄₅CoN₉O = 906.3 [M]⁺); Anal. Calcd. for C₅₅H₄₅ClCoN₉O (942.39): C, 70.10; H, 4.81; N, 13.38. Found: C, 70.38; H, 4.84; N, 13.11.

Isotope Labeling Experiments for Reaction of $[Co^{II}(amtpp)]$ (1) with $^{18}O_2$ and $H_2{}^{18}O$



Scheme S2.

(Top) Reaction of **1** with ${}^{16}O_2$. 1,2-Me₂Im (2 equiv.) was added to the CHCl₃ solution (10 mL) of **1** (10.0 mg, 14.0 µmol) under argon. Oxygen (${}^{16}O_2$) bubbled to reaction mixture for 3 min and then stirred for 6 h. The reaction mixture was investigated by ESI-TOF-MS. The obtained sample [Co^{III}(ampord- ${}^{16}O$)(${}^{16}OH$)(1-MeIm)] in this experiment is designated as **2a** in the chapter 5 (ESI-MS Spectra) of this Supporting Information (Figure S13).

(Middle) Reaction of **1** with ${}^{16}O_2$ in the presence of $H_2{}^{18}O.$ 1,2-Me₂Im (2 equiv.) and $H_2{}^{18}O$ (0.560 mL, 2000 equiv.) were added to a dry THF solution (10 mL) of **1** (10.0 mg, 14.0 µmol) under argon. Oxygen (${}^{16}O_2$) was bubbled to the reaction mixture for 3 min and then stirred for 2 days. The reaction mixture was investigated by ESI-TOF-MS. The obtained sample [Co^{III}(ampord- ${}^{16}O$)(${}^{16}OH$)(1-MeIm)] in this experiment is designated as **2b** in the chapter 5 (ESI-MS Spectra) of this Supporting Information (Figure S14).

(Bottom) Reaction of **1** with ¹⁸O₂. Complex **1** (10.0 mg, 14.0 µmol) was added to a Schlenk flask. The flask was degassed with argon, and then vacuated, followed by replaced with oxygen-18 (¹⁸O₂). The CHCl₃ solution (10 mL) of 1,2-Me₂Im (2 equiv.) was added to the solution, and stirred for 2 days. The reaction mixture was investigated by ESI-TOF-MS. The obtained sample [Co^{III}(ampord-¹⁸O)(¹⁸OH)(1-MeIm)] in this experiment is designated as **2c** in the chapter 5 (ESI-MS Spectra) of this Supporting Information (Figure S15).

Synthesis of [Co^{III}(lpp)(1,5-Cy₂Im)] (3).



Scheme S3.

Two equivalents of 1,5-dicyclohexylimidazole (1,5-Cy₂Im) was added to a CHCl₃ solution (10 mL) of **1** (50.0 mg, 70.0 μ mol), and then stirred for 2 days under air. The reaction mixture was purified by gel permeation chromatography (GPC). The green crystals were obtained by recrystallization from CHCl₃/*n*-hexane (30.2 mg, 44.1% yield).

¹H-NMR (600 MHz, CDCl₃) δ 8.79 (s, 1H), 7.77-7.80 (m, 4H), 7.33-7.53 (m, 15H), 6.88 (s, 1H), 6.86 (d, J = 4.6 Hz, 1H), 6.83 (d, J = 4.6 Hz, 1H), 6.67-71 (m, 3H), 6.49 (d, J = 4.6 Hz, 1H), 6.17 (d, J = 4.6 Hz, 1H), 5.76 (s, 1H), 5.61 (d, J = 4.6 Hz, 1H), 3.40-3.44 (m, 1H), 2.10-2.14 (m, 1H), 1.78-1.82 (m, 2H), 1.60-1.73 (m, 7H), 1.47-1.53 (m, 2H), 1.03-1.27 (m, 8H), 0.90-0.96 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) d 183.4, 177.0, 166.9, 164.1, 163.6, 163.2, 149.0, 146.5, 141.5, 141.0, 139.8, 139.6, 137.7, 136.9, 136.6, 136.4, 136.3, 136.0, 135.1, 134.1, 132.0, 131.8, 131.4, 131.0, 130.6, 129.7, 128.1, 127.8, 127.7, 127.5, 127.4, 127.3, 126.7, 126.2, 124.3, 123.5, 122.6, 122.2, 122.1, 121.8, 121.6, 74.0, 54.8, 34.7, 34.3, 33.5, 33.3, 33.0, 26.2, 26.1, 25.7, 25.6, 25.5, 24.7; IR (KBr, cm⁻¹) 3502, 3055, 3026, 2926, 2853, 1694, 1628, 1541, 1489, 1369, 1348, 1277, 1254, 1173, 1061, 1018, 1007, 951, 750, 712, 700, 550, 420; UV-vis (CHCl₃): λ_{max}[nm] (ε [M⁻¹cm⁻¹]): 343.0 (27700), 635.0 (11800); ESI-TOF-MS (positive mode) m/z = 978.4(calcd for C₆₀H₅₃CoN₇O₃ = 978.4 [M + H]⁺); Anal. Calcd. for C₆₀H₅₂CoN₇O₃ (978.03): C, 73.68; H, 5.36; N, 10.02. Found: C, 73.29; H, 5.06; N, 10.03.

3. Crystallographic Data

X-ray Diffraction Studies.

Single crystal of **2** was sealed in a glass capillary with its mother liquid. Each single crystal of **3** was mounted on MicroMount loop (MiTeGen) with Paraton-N (Hampton Research). Each of them was flash frozen to 173 K in a liquid nitrogen cooled stream of nitrogen. Data collections were carried out on a Rigaku CCD mercury system fitted with a monochromatic Mo K*a* radiation source ($\lambda = 0.71069$ Å). The summarized data of the X-ray measurements are given in Table S1. Eighteen preliminary data frames were measured at 0.5° increments of ω , to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at 0.5° intervals of ω . The intensity images were integrated using the CrystalClear program package, and the empirical absorption correction was applied for the data. The structures were solved by direct methods, SIR-92 ([Co^{III}(ampord)(OH)(1,2-Me_2Im)] (2)), SHELXS-97 ([Co^{III}(lpp)(1,5-Cy_2Im) (3)] program and refined using the SHELXL-97 program.

| Table S1. Crystallographic | lata for [Co ^{III} (ampord)(| 1,2-Me ₂ Im)(OH)] (2) | and [Co ^{III} (lpp) |
|-------------------------------|---------------------------------------|----------------------------------|------------------------------|
| $(1,5-Cy_2Im)]$ (3). | | | |

| compound | [Co ^{III} (ampord)(OH) | [Co ^{III} (lpp)(1,5- |
|---|-------------------------------------|--|
| | $(1,2-Me_2Im)](2)$ | $Cy_2Im)](3)$ |
| formula | $C_{52}H_{40}Cl_6CoN_7O_3$ | C _{63.25} H _{55.25} Cl _{9.75} CoN ₇ O ₃ |
| fw | 1082.58 | 1366.03 |
| lattice | monoclinic | triclinic |
| <i>a</i> , Å | 10.7642(5) | 12.8053(7) |
| b, Å | 20.7043(12) | 12.8800(6) |
| <i>c</i> , Å | 22.5542(12) | 21.7874(17) |
| α, ° | | 87.958(6) |
| <i>β</i> , ° | 96.087(3) | 80.671(6) |
| γ, ^ο | | 62.793(4) |
| $V, Å^3$ | 4998.2(5) | 3150.6(4) |
| space group | <i>P</i> 2 ₁ /n (No. 14) | <i>P</i> -1 |
| Ζ | 4 | 2 |
| r (calcd), g cm ⁻³ | 1.439 | 1.440 |
| m (MoK α), mm ⁻¹ | 0.715 | 0.737 |
| rediation (l, Å) | 0.7107 | 0.7107 |
| temp, K | 293 | 173 |
| reflns collected | 31876 | 20445 |
| unique reflns | 8708 | 10799 |
| param refined | 757 | 1018 |
| $R_1 \left[I > 2\sigma \left(I \right) \right]$ | 0.0777 | 0.0538 |
| wR_2 [all data] | 0.1395 | 0.1138 |
| GOF | 1.002 | 1.015 |



Figure S1. X-ray crystal structure of $[Co^{III}(ampord)(OH)(1,2-Me_2Im)]$ (2) (hydrogen atoms and solvents are omitted for clarity. thermal ellipsoids represent 30% probability).



Figure S2. Disordered structure of $[Co^{III}(ampord)(OH)(1,2-Me_2Im)]$ (2) (hydrogen atoms and solvents are omitted for clarity; selected bond distances (Å) and angles (deg)).



Figure S3. X-ray crystal structure of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) (hydrogen atoms and solvents are omitted for clarity. thermal ellipsoids represent 30% probability; selected bond distances (Å) and angles (deg))



Figure S4. Disordered structure of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) (hydrogen atoms and solvents are omitted for clarity).



Figure S5. Crystal packing diagrams of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) (hydrogen atoms and solvents except selected one are omitted for clarity).

4. NMR Spectra



Figure S6. ¹H NMR spectrum of [Co^{III}(ampord)(OH)(1,2-Me₂Im)] (2) in CDCl₃.



Figure S7. ¹³C NMR spectrum of [Co^{III}(ampord)(OH)(1,2-Me₂Im)] (2) in CDCl₃.



Figure S8. ¹H NMR spectrum of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl in CDCl₃.



Figure S9. ¹³C NMR spectrum of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl in CDCl₃.



Figure S10. ¹H NMR spectrum of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) in CDCl₃.



Figure S11. ¹³C NMR spectrum of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) in CDCl₃.

5. ESI-MS Spectra



Figure S12. Full ESI-TOF-MS spectrum of $[Co^{III}(ampord-{}^{16}O)({}^{16}OH)(1-MeIm)]$ (2a) (Isolated from the reaction of $[Co^{II}(amtpp)]$ (1) with ${}^{16}O_2$).



Figure S13. ESI-TOF-MS spectrum of $[Co^{III}(ampord-{}^{16}O)({}^{16}OH)(1-MeIm)]$ (2a) (Isolated from the reaction of $[Co^{II}(amtpp)]$ (1) with ${}^{16}O_2$).



Figure S14. ESI-TOF-MS spectrum of $[Co^{III}(ampord-{}^{16}O)({}^{16}OH)(1-MeIm)]$ (2b) (Isolated from the reaction of $[Co^{II}(amtpp)]$ (1) with ${}^{16}O_2$ in the presence of $H_2{}^{18}O$).



Figure S15. ESI-TOF-MS spectrum of $[Co^{III}(ampord-{}^{18}O)({}^{18}OH)(1-MeIm)]$ (2c) (Isolated from the reaction of $[Co^{II}(amtpp)]$ (1) with ${}^{18}O_2$).



Figure S16. Full ESI-TOF-MS spectrum of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl.



Figure S17. ESI-TOF-MS spectrum of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl.



Figure S18. Full ESI-TOF-MS spectrum of [Co^{III}(lpp)(1,5-Cy₂Im)] (3).



Figure S19. ESI-TOF-MS spectrum of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3).

6. IR Spectra



Figure S20. IR spectrum of [Co^{III}(ampord)(OH)(1,2-Me₂Im)] (2).



Figure S21. IR spectrum of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl.



Figure S22. IR spectrum of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3).

7. UV/Vis Absorption spectra



Figure S23. UV/vis absorption spectra of [Co^{II}(amtpp)] (1) in CHCl₃.



Figure S24. UV/vis absorption spectra of $[Co^{III}(ampord)(OH)(1,2-Me_2Im)]$ (2) in CHCl₃.



Figure S25. UV/vis absorption spectra of [Co^{III}(amtpp)(1,2-Me₂Im)]Cl in CHCl₃.



Figure S26. UV/vis absorption spectra of $[Co^{III}(lpp)(1,5-Cy_2Im)]$ (3) in CHCl₃.

8. Cyclic Voltammetry



Figure S27. Cyclic voltammograms (0.1 V·s⁻¹) in CH₂Cl₂ (0.5 M TBAP). a) $[Co^{II} (amtpp)]$ (1) b) $[Co^{II} (amtpp)]$ (1) and presence of 1,2-Me₂Im (2 equiv.) c) $[Co^{III} (ampord)(OH)(1,2-Me_2Im)]$ (2).

[S1] A. El-Kasmi, D. Lexa, P. Maillard, M. Momenteau, J. -M. Savéant, J. Am. Chem. Soc., **1991**, 113, 1586.

The treatment of $[Co^{II}(amtpp)]$ (1) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

Complex 1 (50.0 mg, 70.0 μ mol) and DDQ (31.8 mg, 1.40 mmol) were dissolved in methanol (30 mL). The reaction mixture was allowed to stir for a day, and then the solvent was removed by evaporation. The obtained crude product was dissolved in chloroform and filtered off. The solvent of the filtrate was removed in vacuo, and the obtained product was recrystallised from chloroform/*n*-hexane under argon. The obtained product was confirmed to be the starting material by UV/Vis absorption and ESI-TOF Mass spectrum. The recovery yield was virtually quantitative.

The treatment of $[Co^{II}(amtpp)]$ (1) wutg DDQ in the presence 1,2-Me₂Im.

Complex 1 (50.0 mg, 70.0 μ mol), 1,2-Me₂Im (13.5 mg, 1.40 mmol) and DDQ (31.8 mg, 1.40 mmol) were dissolved in a methanol (30 mL) under argon. The reaction mixture was allowed to stir for a day, and then the solvent was removed by evaporation. The crude product was dissolved in chloroform and filtered off under argon. The solvent of the filtrate was removed by evaporation, and the obtained product was recrystallised from chloroform/*n*-hexane under argon. The product was confirmed to be [$3 \cdot (1,2-Me_2Im)$] by UV/Vis absorption and ESI-TOF Mass spectrum. The yield was virtually quantitative.

9. pK_a of Nitrogen Bases

 pK_a calculations of axial ligands (1-MeIm, 3,5-Me₂Py, (*S*)-bifonazole, (*S*)-Nicotine, (*S*)-Cotinine, 1,2-Me₂Im and 1,5-Cy₂Im) were carried out using ACD/Lab Software (http://acdlabs.com/). The calculated values are listed in below (Figure S28).



Figure S28. pK_a of axial ligands.

10. DFT Calculations

DFT calculations of [Co^{II}(amtpp)(1-MeIm)] and [Co^{II}(amtpp)(1,2-Me₂Im)] were carried out using the Spartan '04 package of Wavefunction Icn. (http://www.wavefun.com). The calculations are performed at the B3LYP/6-31G* level.



Figure S29. DFT-optimized structure of [Co^{II}(amtpp)(1-MeIm)] and [Co^{II}(amtpp)(1,2-Me₂Im)].