

Electronic Supplementary Information

Enhancement of 4-electron O₂ reduction by a Cu(II)-pyridylamine complex *via* protonation of a pendant pyridine in the second coordination sphere in water

Hiroaki Kotani, Tomomi Yagi, Tomoya Ishizuka, and Takahiko Kojima*

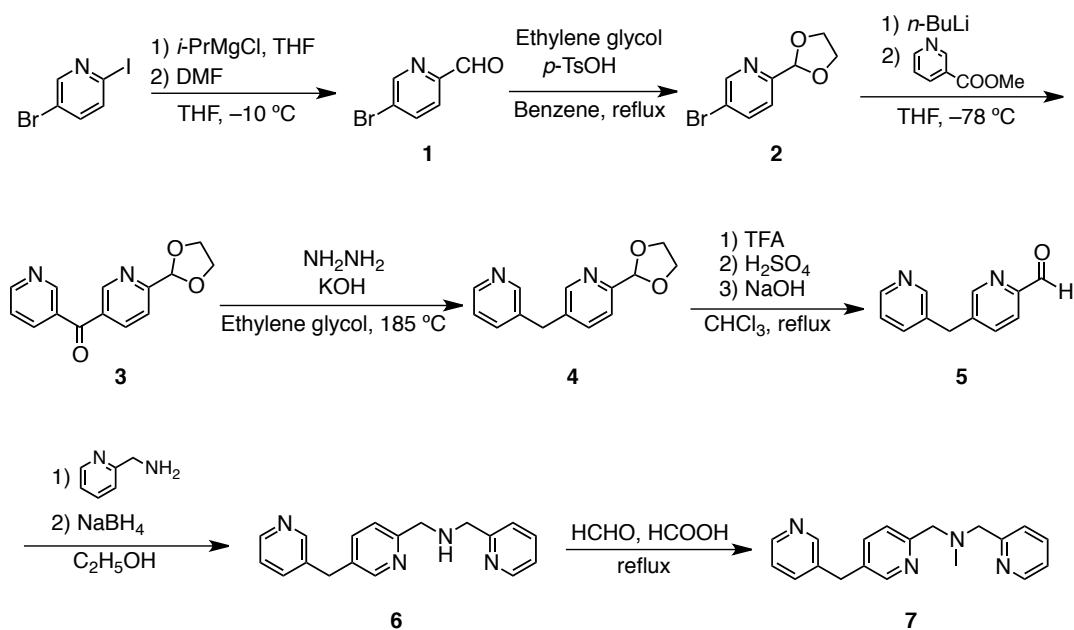
*Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1
Tennoudai, Tsukuba, Ibaraki 305-8571, Japan*

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Experimental Section

General. NMR measurements were performed on JEOL EX270 and EX400, and Bruker AVANCE400 spectrometers. UV-vis absorption spectra were measured on a Shimadzu UV-3600 and UV-2450 spectrometers at room temperature. ESI-TOF-MS spectra were obtained on a JEOL JMS-T100CS mass spectrometer. A BAS ALS-710D electrochemical analyzer was used for electrochemical measurements. THF was distilled over Na/benzophenone under Ar before use. Chemicals were used as received unless otherwise noted. *N,N*-Bis(2-pyridylmethyl)amine and *N*-methyl-*N,N*-bis(2-pyridylmethyl)amine are abbreviated as bpa and Mebpa, respectively.

Synthesis.



5-Bromo-2-pyridinecarboxaldehyde (1). This compound was synthesized according to the literature procedure.¹ ¹H NMR (CDCl₃): δ 7.84 (d, J = 8.3 Hz, 1H), 8.02 (dd, J = 7.0, 2.4 Hz, 1H), 8.84 (d, J = 8.3 Hz, 1H), 10.03 (s, 1H).

5-Bromo-2-[1,3]dioxolan-2-yl-pyridine (2). A solution of 1 (922.6 mg, 4.96 mmol), ethylene glycol (560 μ L, 9.90 mmol), and *p*-toluenesulfonic acid (1.70 g, 9.87 mmol) in benzene (18 mL) were heated to reflux to accumulate water in a Dean-Stark apparatus. The solution was neutralized with saturated NaOH aq. The aqueous layer was extracted with dichloromethane for several times, and the organic layers were combined and dried over anhydrous Na₂SO₄.

The solvent was removed under reduced pressure to give orange oil, which was dried *in vacuo*. Purification was made by column chromatography on alumina using ethyl acetate/hexane (7:3, v/v) as an eluent to afford orange oil (0.804 g, 3.50 mmol, 71% yield). ¹H NMR (CDCl₃): δ 4.10 (m, 4H), 5.80 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.84 (dd, *J* = 8.3, 2.3 Hz, 1H), 8.66 (d, *J* = 2.2 Hz, 1H).

Pyrid-3-yl-2'-([1,3]dioxolan-2-yl)-pyrid-3-yl-methanone (3). Under Ar, the solution of **2** (359.3 mg, 1.56 mmol) in anhydrous THF (6 mL) was added at -78 °C into *n*-butyl lithium (1.6 M, 1.38 mL, 1.58 mmol), which was diluted with anhydrous THF (5 mL). The solution was kept at -78 °C with stirring for 30 min, and then the solution of methyl nicotinate in anhydrous THF (10 mL) was added slowly at -78 °C with stirring for 10 min. After stirring for 30 min at -78 °C, the solution was allowed to warm slowly to -20 °C over 3 h. After further warming to room temperature and then stirring for 2 days, the solution was quenched with addition of the mixture of water : methanol : conc. HCl = 5 : 5 : 1 v/v/v, and was further added NaOH aq to adjust pH to be 11. The mixture was extracted with dichloromethane several times, and the organic layer was combined and dried over anhydrous Na₂SO₄. The brown oil obtained was chromatographed on silica-gel using ethyl acetate/methanol (7:3, v/v) as the eluent. The solvent was removed under reduced pressure to give orange oil, which was dried *in vacuo*. (218.3 mg, 0.853 mmol, 55% yield). ¹H NMR (CDCl₃): δ 4.14 (m, 4H), 5.92 (s, 1H), 7.46 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 8.10 (dt, *J* = 7.9, 2.1 Hz, 1H), 8.16 (dd, *J* = 8.1, 2.1 Hz, 1H), 8.83 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.98 (dd, *J* = 5.1, 2.1 Hz, 1H).

3-Pyridylmethyl-[1,3]dioxolan-2-yl-pyridine (4). To the solution of **3** (390.0 mg, 1.52 mmol) in ethylene glycol (10 mL) was added potassium hydroxide (199.8 mg, 3.56 mmol) and the mixture was stirred for 1 h. Then, hydrazine hydrate (176.8 mg, 3.51 mmol) was added and the mixture was heated to 185 °C. After heating at the temperature for 105 min, the reaction mixture was cooled to room temperature, diluted with water, and extracted with dichloromethane for several times. The organic layer was combined and dried over anhydrous Na₂SO₄. The filtrate was evaporated to dryness and dried *in vacuo* to give yellow oil (321.1 mg, 1.33 mmol, 88% yield). ¹H NMR (CDCl₃): δ 3.97 (s, 2H), 4.01 (m, 4H), 5.92 (s, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.47 (m, 3H), 8.45 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.48 (d, *J* = 2.7 Hz, 2H).

3-Pyridylmethyl-2-pyridinecarboxaldehyde (5). Compound **4** (321.1 mg, 1.33 mmol) dried under vacuum was dissolved in chloroform (60 mL) and trifluoroacetic acid (36 mL) was added to the solution. After refluxing the solution for 2 h, conc. H₂SO₄ (360 μL, 6.7 μmol) was added to the solution and the mixture was refluxed for 5 h. The solution was cooled to

room temperature and NaOH aq was added to adjust the solution pH to be 11. The mixture was extracted with dichloromethane several times, and the organic layers were combined and dried over anhydrous Na₂SO₄. The volatiles of the filtrate were evaporated to dryness and dried *in vacuo* to give yellow oil (188.0 mg, 0.949 mmol, 71% yield). ¹H NMR (CDCl₃): δ 4.06 (s, 1H), 7.16–7.25 (m, 1H), 7.43 (t, *J* = 5.6 Hz, 1H), 7.62 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.42–8.50 (m, 2H), 8.64 (s, 1H), 10.0 (s, 1H).

3-Pyridylmethyl-bpa (6). Compound **5** (155 mg, 0.58 mmol) in absolute ethanol (10 mL) was added to a solution of 2-picolyamine (61.51 mg, 0.57 mmol) in absolute ethanol (10 mL). After stirring at room temperature for 4 h, the solution was cooled to 0 °C and sodium borohydride (7.08 mg, 0.19 mmol) was added to the solution in small portions. After stirring the reaction mixture for 12 h at room temperature, the reaction was quenched by adding HCl aq and then NaOH aq was added to adjust the solution pH to be 11. The mixture was extracted with dichloromethane for several times, and the organic layers were combined and dried over anhydrous Na₂SO₄. The volatiles of the filtrate were evaporated to dryness and dried *in vacuo* to give brown oil (142.7 mg, 0.492 mmol, 85% yield). ¹H NMR (CDCl₃): δ 3.94 (d, *J* = 4.2 Hz, 4H), 3.96 (s, 1H), 7.11–7.30 (m, 4H), 7.32–7.43 (m, 2H), 7.61 (td, *J* = 6.1, 1.8 Hz, 1H), 8.42 (d, *J* = 1.8 Hz, 1H), 8.45–8.48 (m, 2H), 8.53 (d, *J* = 4.6 Hz, 1H).

3-Pyridylmethyl-Mebpa (7). Formic acid (98%, 260 μL) and formaldehyde (37%, 380 μL) were mixed, and then compound **6** (142.7 mg, 0.492 mmol) was added to the mixture. The mixture was refluxed for 12 h, cooled to room temperature, and NaOH aq was added. The solution was extracted with dichloromethane, and the organic layer was dried over anhydrous Na₂SO₄, and the volatiles of the filtrate were evaporated. The brown oil obtained was dried *in vacuo* (70.9 mg, 0.23 mmol, 47% yield). ¹H NMR (CDCl₃): δ 2.28 (s, 3H), 3.72 (d, *J* = 3.4 Hz, 4H), 3.93 (s, 1H), 7.11 (dd, *J* = 7.2, 6.4 Hz, 1H), 7.19 (t, *J* = 4.8 Hz, 1H), 7.38–7.47 (m, 4H), 7.61 (td, *J* = 7.7, 1.8 Hz, 1H), 8.40 (s, 1H), 8.42–8.48 (m, 2H), 8.51 (d, *J* = 4.2 Hz, 1H).

[Cu(NNN)](BF₄)₂. The solution of bpa (84.6 mg, 0.40 mmol) in methanol (5 mL) was added to the solution of Cu(BF₄)₂·6H₂O (137.8 mg, 0.40 mmol) in methanol (20 mL) under Ar. The mixture was stirred for 18 h at 50 °C under Ar and the solvent was removed under vacuum to obtain blue solid. Recrystallization was performed from methanol/ethyl acetate to give blue crystals (93.5 mg, 0.21 mmol, 53% yield). Anal. Calcd. for C₁₃H₁₅B₂CuF₈N₃: C 35.96, H 3.85, N 8.68, found: C 35.98, H 3.74, N 8.97. UV-Vis (H₂O at pH 4.5): λ_{max} [nm] (ε [M⁻¹ cm⁻¹]) = 660 (44).

[Cu(NNN-Py)](BF₄)₂. The solution of **7** (84.2 mg, 0.28 mmol) in methanol (5 mL) was added

to a solution of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (96.0 mg, 0.28 mmol) in methanol (20 mL) under Ar. The mixture was stirred for 18 h at 50 °C under Ar and the solvent was removed under vacuum. After addition of a small amount of methanol, the mixture was separated into a blue solution and pale blue solid. Recrystallization of the blue solution was performed from methanol/ethyl acetate to give blue crystals (46.0 mg, 0.09 mmol, 32% yield). Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{B}_2\text{CuF}_8\text{N}_4$: C 48.02, H 4.63, N 11.59, found: C 47.77, H 4.52, N 11.43. UV-Vis (H_2O at pH 4.8): λ_{max} [nm] (ϵ [$\text{M}^{-1} \text{cm}^{-1}$]) = 662 (115).

X-ray crystallography on CuNNN-Py.

A purple single crystal of **CuNNN-py** was grown by vapor diffusion of ethyl acetate into an acetone solution of **CuNNN-py**. All measurements were performed at 120 K on a Bruker APEXII Ultra diffractometer. The structure was solved by a direct method (SIR-97) and expanded with differential Fourier technique. All non-hydrogen atoms were refined anisotropically and the refinement was carried out with full matrix least squares on F . All calculations were performed using the Yadokari-XG crystallographic software package.² Crystallographic details are available in the cif format as ESI†.

ESR measurements.

ESR spectra were taken on a Bruker X-band spectrometer (EMXPlus9.5/2.7) under non-saturating microwave power conditions (2.0 – 4.0 mW) at 298 K. The magnitude of the modulation was chosen to optimize the resolution and the signal to noise ratio (S/N) of the observed spectrum (modulation amplitude, 10 – 20 G; modulation frequency, 100 kHz).

Electrochemical measurements.

Cyclic voltammetry (CV) of **CuNNN-Py** and **CuNNN** was carried out in H_2O containing 0.1 M KNO_3 as an electrolyte at 298 K under Ar or O_2 with use of a grassy carbon as a working electrode, a platinum wire as a counter electrode, and Ag/AgNO_3 as a reference electrode. The pH should be adjusted with HClO_4 aq and NaOH aq to pH 4.2 or pH 6.7. A BAS ALS-710D electrochemical analyzer was used for the electrochemical measurements. Then, apparent number of electrons used for O_2 reduction catalyzed by the Cu complexes was investigated with use of rotating ring-disk electrode (RRDE), which was consist of a glassy carbon as a working electrode and a platinum as a ring electrode.

Dimerization constant of CuNNN-py in D₂O.

The UV-Vis spectra of **CuNNN-py** were measured under various concentrations in D₂O, pH of which was set to be 4.2 and 6.6 (Fig S3). The *d-d* absorption band of **CuNNN-py** was sensitive to the concentrations at pH 6.6, whereas that was independent of the concentrations at pH 4.2. The absorption maxima was plotted against the concentrations and analysed with eqns (S1)-(S4) to obtain the equilibrium constant of the dimerization (*K*).

$$M_1 + 2M_2 = M_0 \quad (S1)$$

$$\lambda = \frac{M_1}{M_0}\lambda_1 + \frac{2M_2}{M_0}\lambda_2 \quad (S2)$$

$$K = \frac{M_2}{M_1^2} \quad (S3)$$

$$\lambda = \frac{\lambda_1 - \lambda_2}{4KM_0} (1 + \sqrt{1 + 8KM_0}) + \lambda_2 \quad (S4)$$

Here, *M*₀, *M*₁ and *M*₂ are the total concentrations of Cu(II) complexes with **NNN-py** as defined in eqn (S1), a monomer and a dimer formed in the solution, respectively. λ , λ_1 and λ_2 are the absorption maximum of the *d-d* transition at the concentration, that of the monomer, and the dimer, respectively. λ_1 (685 nm) and λ_2 (535 nm) were also obtained from the fitting analysis.

Detection of hydrogen peroxide (H₂O₂).

The amount of H₂O₂ generated by bulk electrolysis for 70 s with use of static potential at −0.8 V vs SCE in aqueous solution including **CuNNN-py** (0.4 mM) or **CuNNN** (0.4 mM), whose pH was set at pH 4 or pH 6, was estimated by iodometry. The procedure of the iodometry was indicated below: the reaction mixture after electrolysis was treated with an excess amount of NaI (1.0 M) and the amount of I₃[−] formed with oxidation of I[−] ion with H₂O₂ was determined by the absorbance at $\lambda_{\max} = 350$ nm obtained from the UV-vis spectra. For the calculation, $\epsilon = 31000 \text{ M}^{-1} \text{ cm}^{-1}$ was used as the absorption coefficient of I₃[−] ion.^{3,4}

Determination of stoichiometry in O₂ reduction.

Methyl viologen radical cation (MV^{•+}) was produced as a one-electron reductant through the reaction between methyl viologen (MV²⁺) and sodium dithionite under Ar atmosphere in aqueous solution at pH 4.2, which was adjusted by using HClO₄. UV-vis spectral change of MV^{•+} (0.20 mM) was observed at 298 K upon addition of 100 μL of air-saturated aqueous

solution at pH 4.2 containing **CuNNN-pyH⁺** (0.20 mM) and O₂ (0.26 mM) into 1.9 mL of MV⁺ solution (final concentration: **CuNNN-pyH⁺** (0.01 mM) and O₂ (0.013 mM)). The stoichiometry of the O₂ reduction was determined from the consumed amount of MV⁺ using O₂ reduction under O₂-limiting conditions ($4[\text{O}_2] < [\text{MV}^{+}]$; $[\text{O}_2] = 0.013 \text{ mM}$, $[\text{MV}^{+}] = 0.2 \text{ mM}$).

Computational method.

The structures of **CuNNN-py** complexes were optimized by using the B3LYP functional without solvent effects.⁵ The LanL2DZ basis set was used for all atoms. The program used was Gaussian 09.⁶

References.

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- 6 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, 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, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

Table S1. X-ray Crystallographic Data for $[\text{Cu}(\text{BF}_4)_2(\text{NNN-py})]_2$ ($(\text{CuNNN-py})_2$)

	$[\text{Cu}(\text{BF}_4)_2(\text{NNN-py})]_2$
formula	$\text{C}_{19}\text{H}_{20}\text{B}_2\text{CuF}_8\text{N}_4$
formula wt	541.55
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	14.516(7)
b (Å)	9.366(4)
c (Å)	15.706(7)
α (deg)	90
β (deg)	97.731(7)
γ (deg)	90
V (Å ³)	2115.9(17)
Z	4
$R1(\%)$	5.08
GOF	0.886

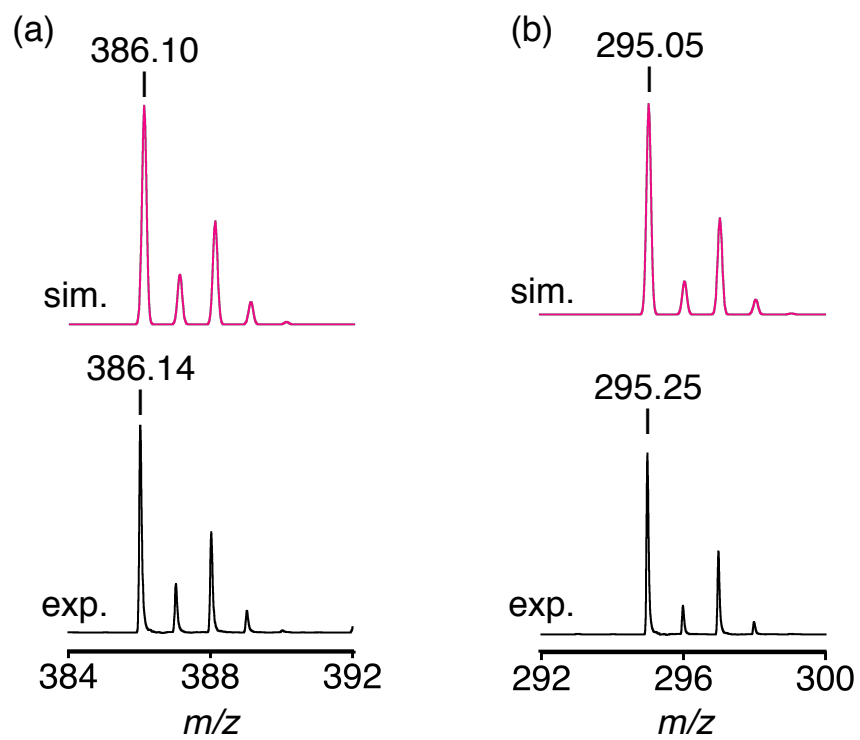


Fig. S1 ESI-TOF-MS of (a) $[Cu(F)NNN-py]^+$ and (b) $[Cu(F)NNN]^+$ in acetonitrile: Black trace, experimentally observed; pink trace, simulated.

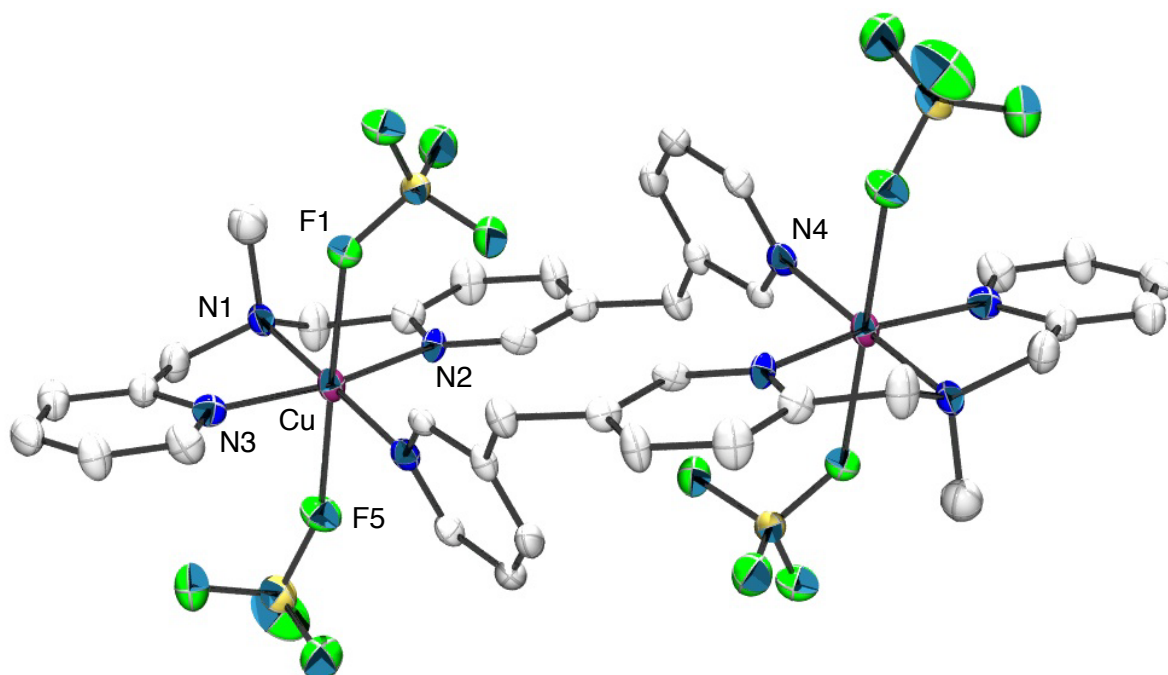


Fig. S2 An ORTEP presentation of the crystal structure of $[\text{Cu}(\text{BF}_4)(\text{NNN-py})]_2$ ($(\text{CuNNN-py})_2$) with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Cu-N1 2.034(5), Cu-N2 2.003(5), Cu-N3 1.992(5), Cu-N4 2.001(5), Cu-F1 2.407(4), Cu-F5 2.522(5); N1-Cu-N2 83.0(2), N1-Cu-N3 82.6(2), N2-Cu-N3 165.6(2), N1-Cu-N4 177.0(2).

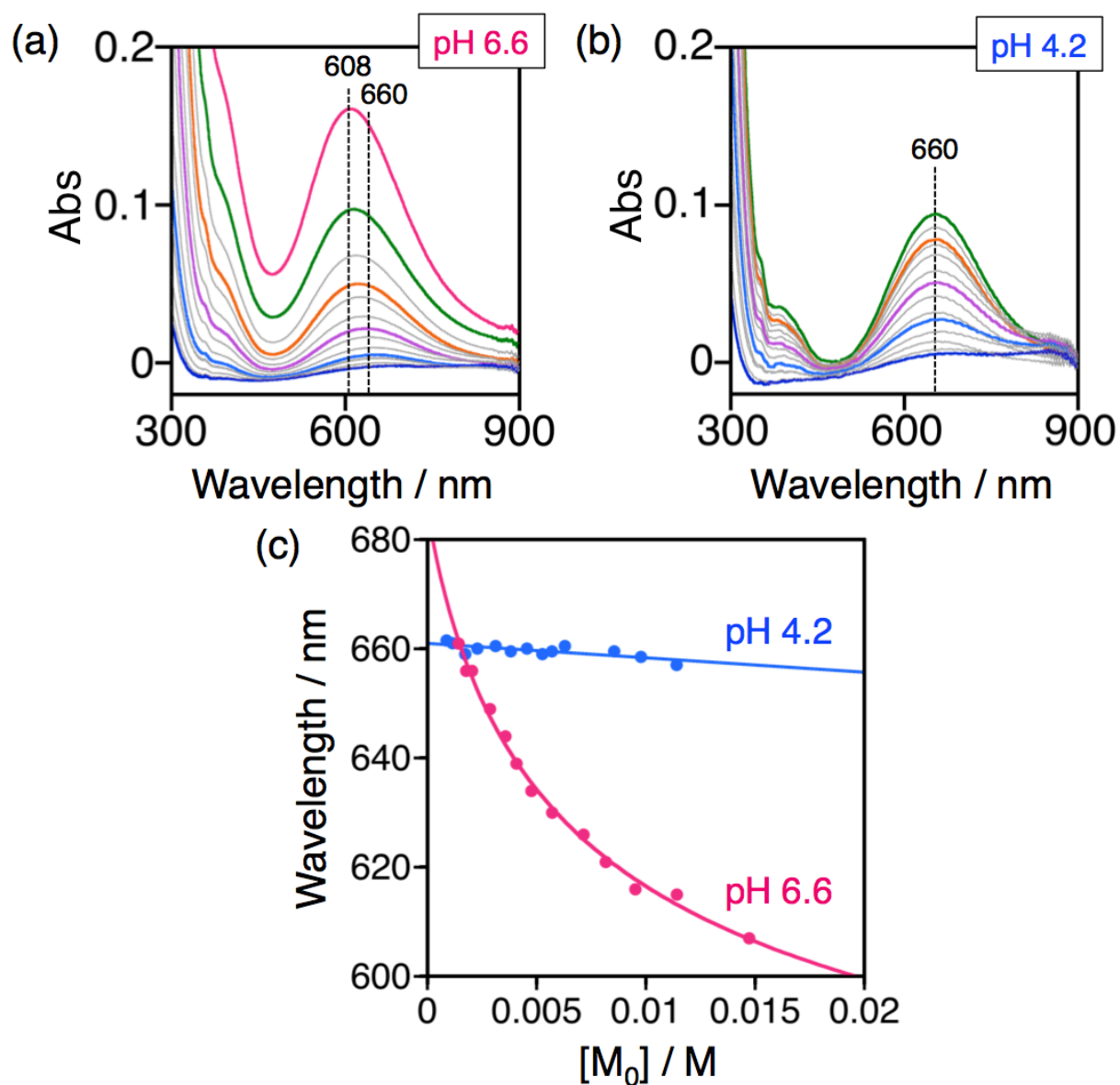


Fig. S3 UV-vis spectra observed in (a) aqueous solution (pH 6.6) containing $(\text{CuNNN-py})_2$ (1.02 – 14.7 mM) and (b) aqueous solution (pH 4.2) containing $(\text{CuNNN-py})_2$ (0.86 – 11.4 mM) at 298 K. (c) Plots of the wavelength at absorption maximum vs. $[M_0]$, which is defined as in eqn S1 in the experimental section in the ESI.

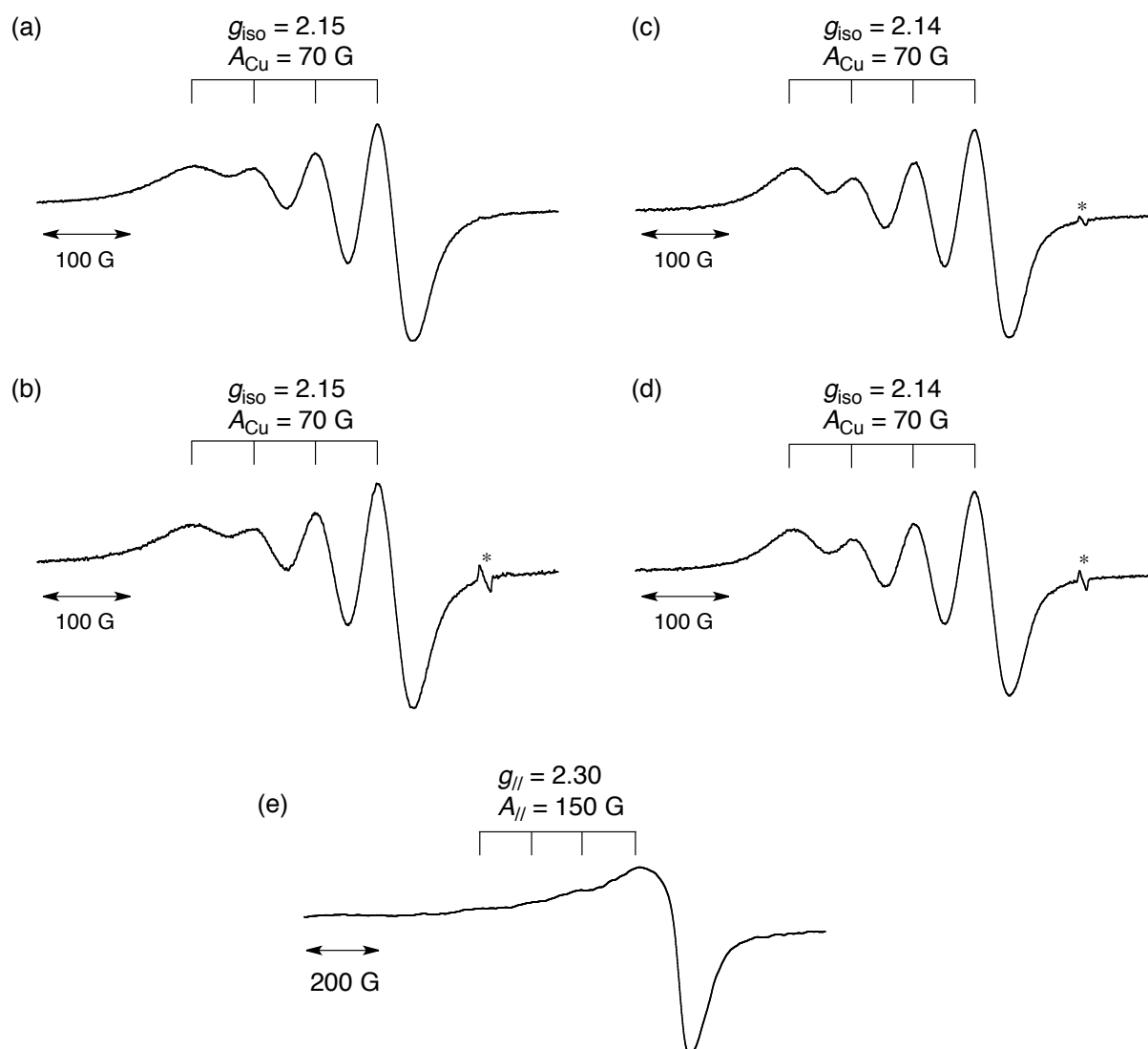


Fig. S4 ESR spectra of $(CuNNN-py)_2$ (1.2 mM) in aqueous solution at (a) pH 4.2 and (b) pH 6.7 at 298 K. In light of the association constant ($79 M^{-1}$), at the concentration, $(CuNNN-py)_2$ should dissociate to afford monomeric species at pH 6.7. ESR spectra of $CuNNN$ (3.7 mM) in aqueous solution at (c) pH 4.2 and (d) pH 6.7 at 298 K. (e) ESR spectrum of $(CuNNN-py)_2$ mixed with Al_2O_3 in a solid state at 298 K. The asterisks denote impurities in the ESR tubes.

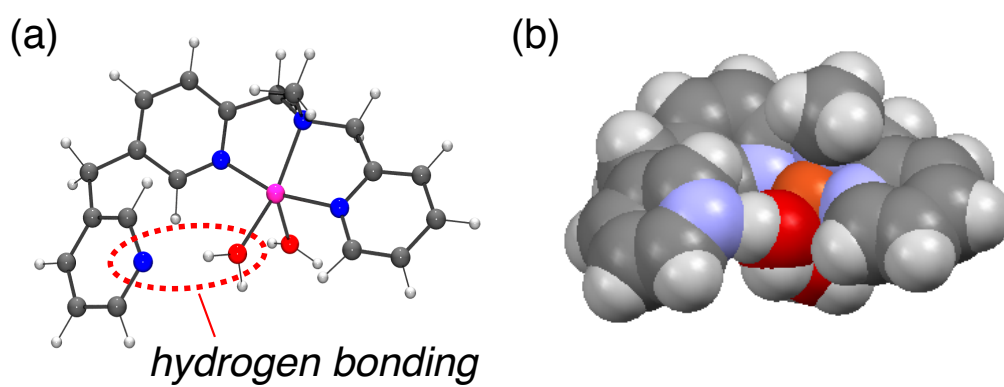


Fig. S5 A DFT-optimized structure of **CuNNN-py**. (a) Ball and stick and (b) space-filling representation.

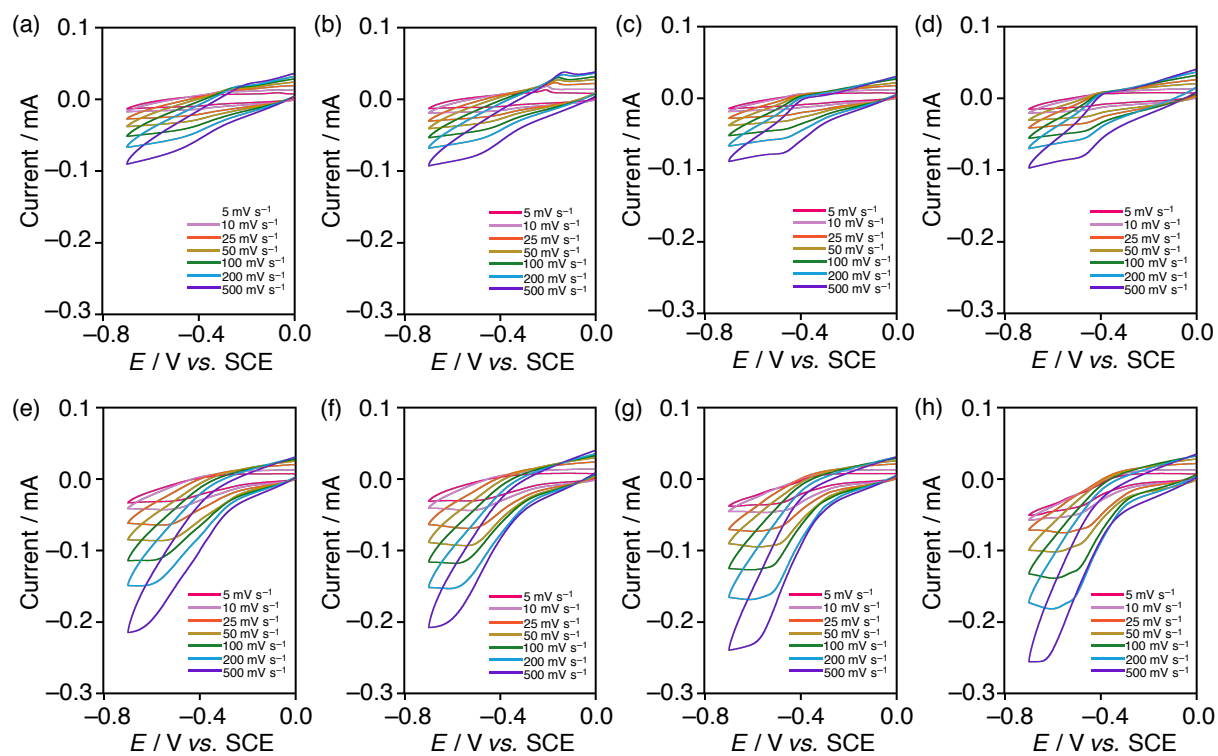


Fig. S6 Cyclic voltammograms of **CuNNN-py** (a) pH 4.2 and (b) pH 6.7 under Ar, and (e) pH 4.2, (f) pH 6.7 under O₂. **CuNNN** (c) pH 4.2, (d) pH 6.7 under Ar, and (g) pH 4.2, (h) pH 6.7 under O₂.

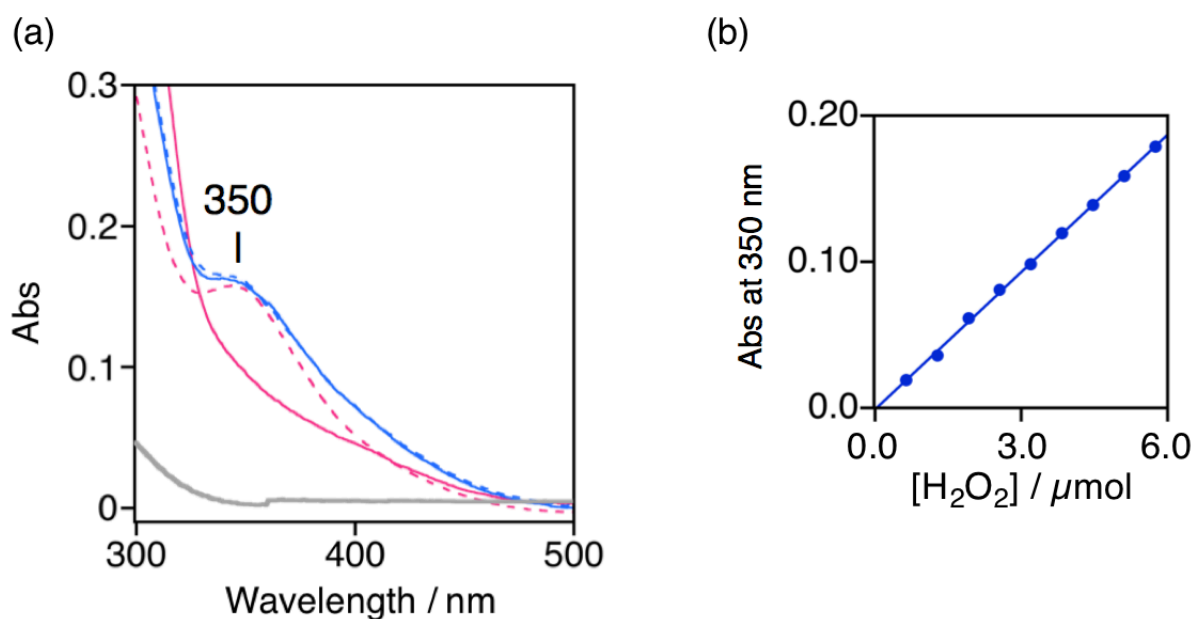


Fig. S7 (a) Absorption spectra observed in H₂O₂ quantification by iodometry in the aqueous solution at pH 4.2 (solid line) and pH 6.7 (dotted line) after bulk electrolysis of **CuNNN-py** (pink) and **CuNNN** (blue) at -0.8 V vs. SCE for 70 sec under O₂. The gray line denotes UV-vis spectrum of **CuNNN** at pH 6.7 before bulk electrolysis. (b) A calibration curve based on absorbance at 350 nm for iodometry.

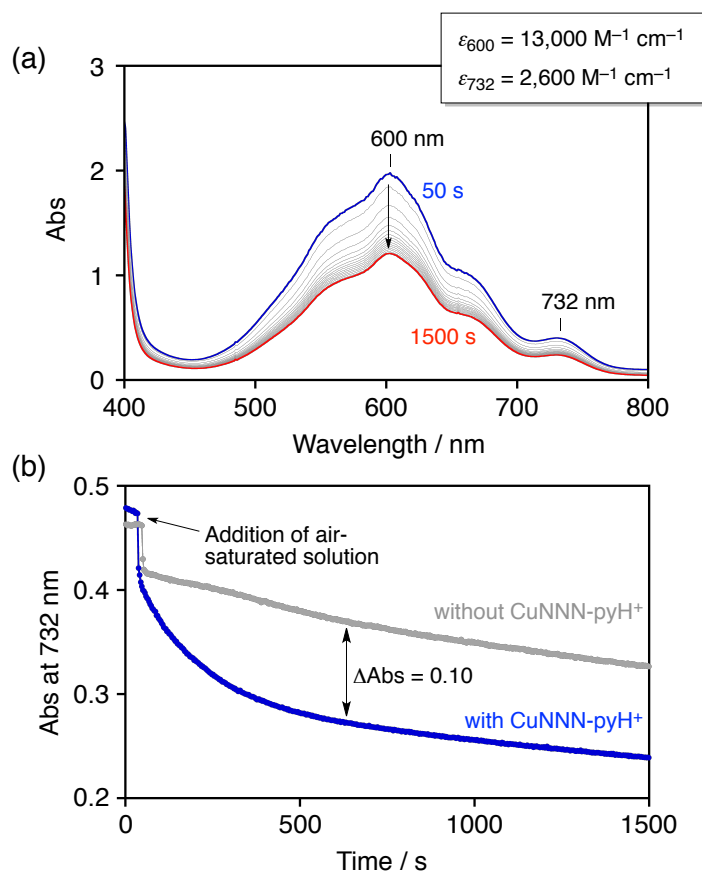


Fig. S8 (a) UV-vis spectral change of methyl viologen radical cation ($\text{MV}^{\bullet+}$, 0.2 mM) as a one-electron reductant upon addition of pH 4.2 aqueous solution containing **CuNNN-pyH⁺** (0.01 mM) and O_2 (0.013 mM) at 298 K. (b) Time profiles at 732 nm upon addition of pH 4.2 aqueous solution containing O_2 (0.013 mM) with and without **CuNNN-pyH⁺**.

Comments. The ϵ value at 732 nm of $\text{MV}^{\bullet+}$ was estimated to be $2600 \text{ M}^{-1} \text{ cm}^{-1}$ compared to that at 600 nm of $\text{MV}^{\bullet+}$ according to the literature (K. Tsukahara and R. G. Wilkins, *J. Am. Chem. Soc.* 1985, **107**, 2632). The O_2 concentration in air-saturated aqueous solution has been reported to be 0.26 mM (C. E. D. Chidsey, and co-authors, *J. Phys. Chem. A* 2007, **111**, 12641). Thus, the spectral change at 732 nm ($\Delta \text{Abs} = 0.10$) in the presence of **CuNNN-pyH⁺** indicated that 0.038 mM of $\text{MV}^{\bullet+}$ was consumed ($n_{\text{cat}} = 2.92 \text{ e}^-$): The consumed amount of $\text{MV}^{\bullet+}$ (0.038 mM) was more than that required amount of $\text{MV}^{\bullet+}$ (0.026 mM) for 2e^- -reduction of O_2 . In other words, the stoichiometry of the O_2 reduction could be determined from the consumed amount of $\text{MV}^{\bullet+}$ using O_2 reduction under O_2 -limiting conditions ($4[\text{O}_2] < [\text{MV}^{\bullet+}]$; $[\text{O}_2] = 0.013 \text{ mM}$, $[\text{MV}^{\bullet+}] = 0.2 \text{ mM}$).

Table S2. Cartesian coordinates of the optimized structure of **CuNNN-py**.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	-1.895036	0.938197	-0.633013
C	5.241582	-1.868704	0.476339
C	4.160533	-2.766257	0.384115
C	2.875274	-2.256465	0.149063
C	1.810271	1.591255	1.905392
C	-2.947313	1.734517	-0.134337
C	-2.610017	3.050711	0.24239
C	-1.267754	3.490415	0.182468
C	-0.265335	2.582874	-0.180245
C	1.227395	2.851257	-0.153598
C	3.330108	1.428057	-0.057909
C	3.699098	-0.037499	0.106553
C	5.004794	-0.485537	0.34452
H	6.24644	-2.235772	0.661801
H	4.304434	-3.834945	0.499856
H	2.00472	-2.899519	0.0966
H	0.762856	1.666551	2.209029
H	2.222805	0.65618	2.29012
H	-2.073502	-0.061074	-1.001411
H	-3.375236	3.724866	0.618855
H	-1.009451	4.503155	0.474948
H	1.594664	3.025629	-1.172424
H	1.466854	3.737335	0.446581
H	4.02	2.068927	0.50668
H	3.39768	1.71811	-1.114172
H	5.819349	0.226588	0.433493
N	-0.597287	1.314566	-0.576947
N	1.909833	1.62357	0.399259

N	2.658097	-0.921658	-0.000232
Cu	0.895672	-0.037841	-0.390897
O	-0.296989	-1.765975	-0.171359
H	2.366379	2.4333	2.339343
C	-4.330552	1.113457	0.104
H	-4.799263	1.625774	0.95548
H	-4.987445	1.296943	-0.75704
C	-4.236097	-0.39636	0.352729
C	-3.129586	-0.921852	1.05038
C	-5.130067	-1.329348	-0.211754
H	-2.448719	-0.266536	1.585751
C	-4.854814	-2.708128	-0.103827
H	-6.015238	-0.993442	-0.746408
C	-3.635704	-3.120081	0.465639
H	-5.540425	-3.446363	-0.506267
H	-3.338113	-4.163882	0.472543
N	-2.767026	-2.229931	1.023316
H	-0.31116	-2.333446	-0.966431
H	-1.036627	-2.044145	0.472465
O	1.026624	-0.497697	-2.564227
H	1.752312	-0.986556	-3.000715
H	0.459121	-0.059811	-3.229184

Table S3. Cartesian coordinates of the optimized structure of $\text{Cu}^{\text{II}}(\text{OOH})(\text{NNN-pyH}^+)$.

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	1.712588	1.10231	0.600107
C	-5.255209	-2.1049	-0.168991
C	-4.123123	-2.94064	-0.107495
C	-2.854994	-2.351727	0.004634
C	-2.15099	1.582474	-1.932211
C	2.732394	1.920802	0.084608
C	2.33862	3.196017	-0.379051
C	0.981423	3.583769	-0.346827
C	0.013502	2.657801	0.074666
C	-1.496658	2.875319	0.072638
C	-3.52188	1.323511	0.118794
C	-3.796554	-0.174803	0.004734
C	-5.088583	-0.706821	-0.116759
H	-6.24898	-2.532585	-0.2615
H	-4.217628	-4.02034	-0.148529
H	-1.943779	-2.940604	0.054032
H	-1.12622	1.69365	-2.297915
H	-2.539337	0.622757	-2.281711
H	1.910374	0.124682	1.015177
H	3.077636	3.884788	-0.781653
H	0.68468	4.568943	-0.692029
H	-1.834227	3.063285	1.099317
H	-1.766715	3.749646	-0.533603
H	-4.308319	1.892564	-0.396576
H	-3.538107	1.611499	1.177363
H	-5.947531	-0.045061	-0.17132
N	0.403903	1.42989	0.521303
N	-2.162277	1.62609	-0.430708

N	-2.706382	-1.001531	0.063439
C	-0.995936	-0.016098	0.312249
O	0.462591	-1.112969	-0.491055
H	-2.768714	2.390243	-2.350849
C	4.175875	1.419149	-0.016041
H	4.64578	1.884996	-0.893971
H	4.752602	1.772986	0.849839
C	4.334547	-0.102161	-0.107836
C	3.344405	-0.910645	-0.688053
C	5.468937	-0.762688	0.419696
H	2.425513	-0.53904	-1.119624
C	5.568734	-2.169634	0.387398
H	6.272578	-0.185451	0.870214
C	4.507388	-2.923609	-0.120735
H	6.440358	-2.676869	0.784401
H	4.486084	-4.006765	-0.116866
N	3.428546	-2.268638	-0.63398
O	-1.366444	-0.021891	2.546456
H	-1.876994	-0.711992	3.014023
H	-0.80577	0.476117	3.1728
O	0.458456	-2.586394	-0.782745
H	0.013064	-2.647248	-1.663583
H	2.569916	-2.775155	-0.903959