Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Electrocatalytic Water Oxidation by a Macrocyclic Cu(II) Complex in Neutral Phosphate Buffer

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Materials and equipments

All buffers were prepared with reagent-grade water (18 MΩ-cm resistivity). All organic solvents were used without further purification. The 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (TMC) ligand and $Cu(NO_3)_2 \cdot 3H_2O$ were purchased from Aladdin chemical company. Carbon cloth was purchased from Shanghai Hesen Electric Co., Ltd. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses were carried out by FEI Nova NanoSEM 450 instrument equipped with a EDS detector. High-resolution mass spectra were recorded on a Q-Tof Micromass spectrometer (Manchester, England). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer.

Synthesis of Catalysts

$Cu_2(BPMAN)(\mu\text{-}OH)(CF_3SO_3)_3$ was prepared by previous report.[1] Complex **1** was prepared by a modification of a previously published method.[2] $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol) was added to a acetonitrile solution (40 mL) containing TMC ligand (0.256 g, 1.0 mmol). The mixture was stirred at room temperature for 4 hours. The solution was then concentrated to ~ 5 mL under vacuum followed by the addition of 50 mL diethyl ether. The precipitation was generated immediately. The product was obtained in a yield of 88% (0.405 g). The crystal was obtained by slow diffusion of diethyl ether into an acetonitrile solution of **1** at room temperature. TOF-MS: Calcd for $[Cu(TMC)NO_3]^+$ ($C_{14}H_{32}CuN_5O_3$): 381.1796; found: 381.1800. Calcd for $[Cu(TMC)]^{2+}/2$ ($C_{14}H_{32}CuN_4$): 159.5956; found: 159.5955. UV-Vis: absorption band at 303 nm ($\varepsilon \sim 5.2\times10^3$ M^{-1} cm^{-1}).

Anode fabrication

Prior to anode preparation, CC was stabilized at anodic potential for 30 min in 0.1 M pH 7 phosphate buffer. To prepare the working electrodes, 2 μmol of catalysts and 20 μL of 5 wt. % Nafion solution were dissolved in ethanol (180 μL) with sonication. Then, 40 μL of this solution was drop-casted onto 1 cm^2 CC and left to dry at 353 K in oven, yielding a catalyst loading of 0.4 μmol on the CC. The CuO_x/CC was obtained based on our previous report,[3] the CuO_x was electrodeposited on CC from a pH 9 0.2 M borate buffer containing 0.5 M $Cu(NO_3)_2$ for 3 h. The electrode was rinsed with deionized water and dried in ambient air. CuO_x/CC (with Nafion) was prepared by drop-casting 40 μL 0.5 wt. % Nafion solution onto CuO_x/CC.

Electrochemical measurements

Electrochemical measurements were performed with a CHI760E electrochemical workstation. All the electrochemical measurements were conducted in pH 7 phosphate buffer in a three electrode system, platinum wire counter electrode, Ag/AgCl reference electrode, and either a glassy carbon or FTO working electrode. The electrochemical measurements for homogenous WOCs were conducted with 1 mM catalyst (based on copper atom) under nitrogen. The bulk electrolysis was conducted at 1.64 V with FTO or CC as working electrode under generally stirring. The Faradic efficiency data was collected in a gas-tight cell. Prior to measurement, the solution was degassed by bubbling Ar. The amount of evolved oxygen in the headspace was measured by a gas chromatograph.

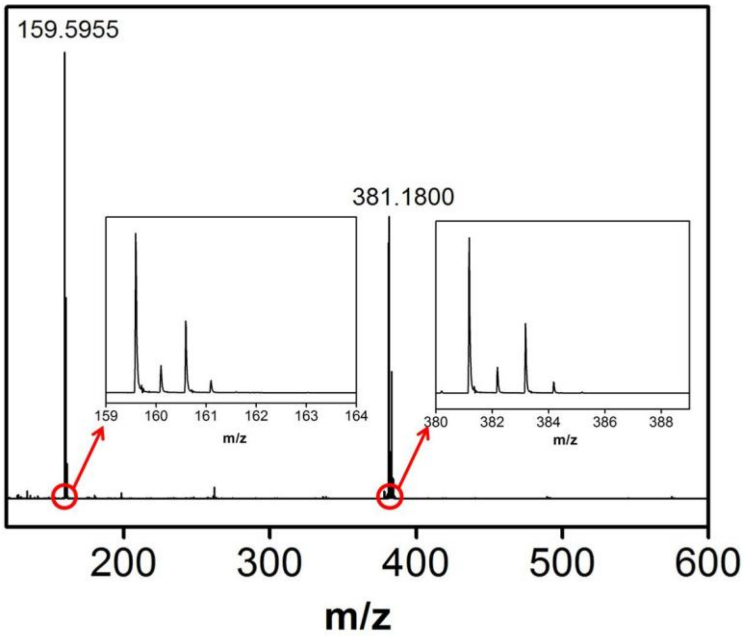

Figure S1. The high-resolution mass spectra of complex **1** in acetonitrile.

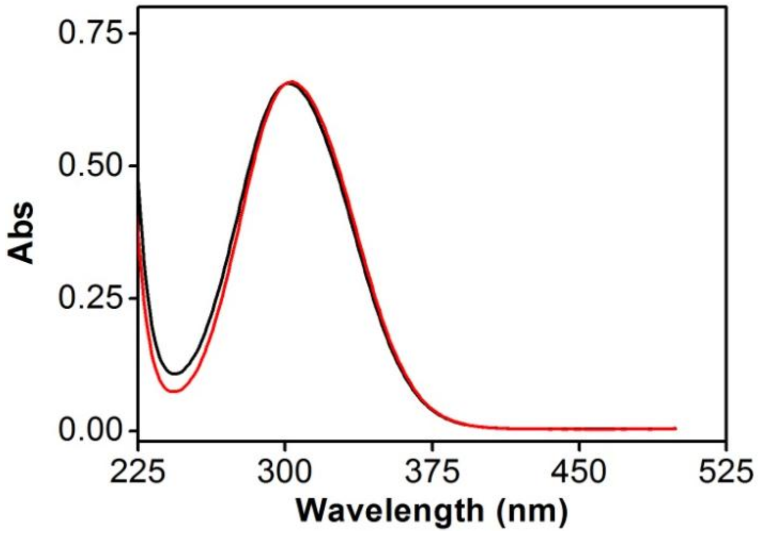

Figure S2. UV-visible spectra of **1** in 0.1 M phosphate buffer at pH 7.0 before (black) and after (red) aging for one week.

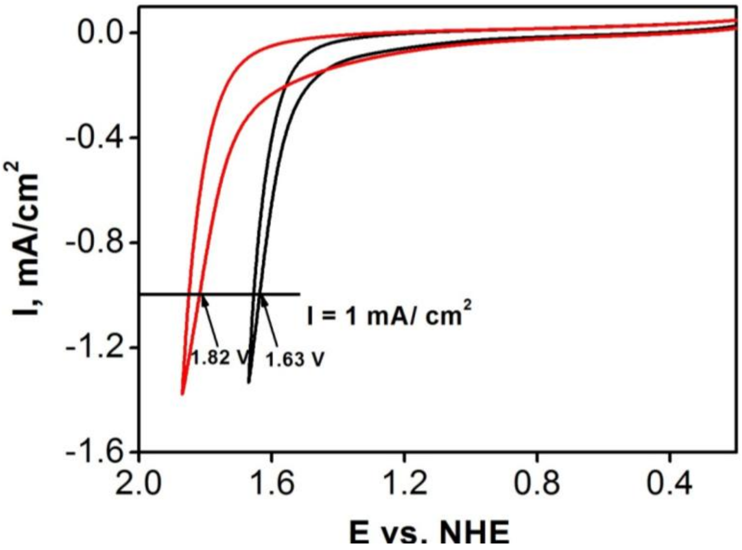

Figure S3. Cyclic voltammograms (CV) of **1** (black) and $[Cu_2(BPMAN)(\mu\text{-}OH)]^{3+}$ (red) in 0.1 M pH 7 phosphate buffer. The current density of 1 mA/cm^2 was obtained at 1.63 V for complex **1** and 1.82 V for $[Cu_2(BPMAN)(\mu\text{-}OH)]^{3+}$.

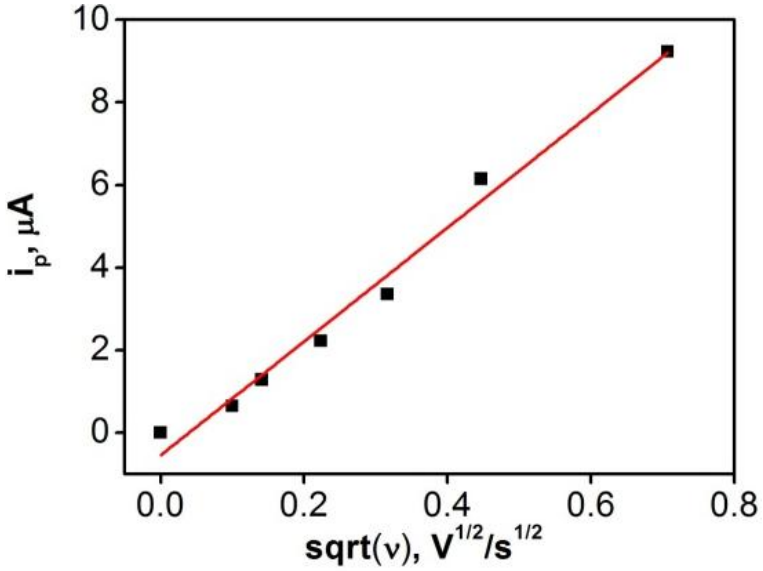

Figure S4. Dependence of the peak current (background subtracted) for the Cu(II/I) couple of complex **1** on the square root of scan rate with standard three electrode system in 0.1 M pH 7 phosphate buffer.

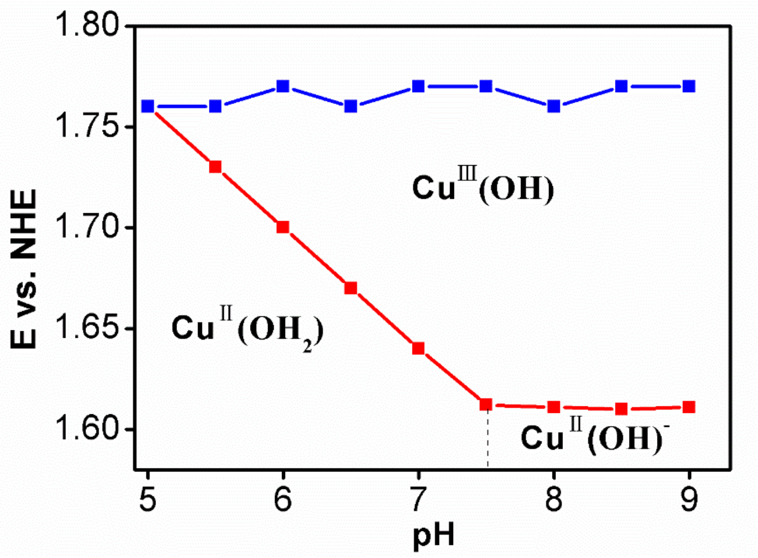

Figure S5. Pourbaix diagram for complex **1** between pH 5-9 phosphate buffer.

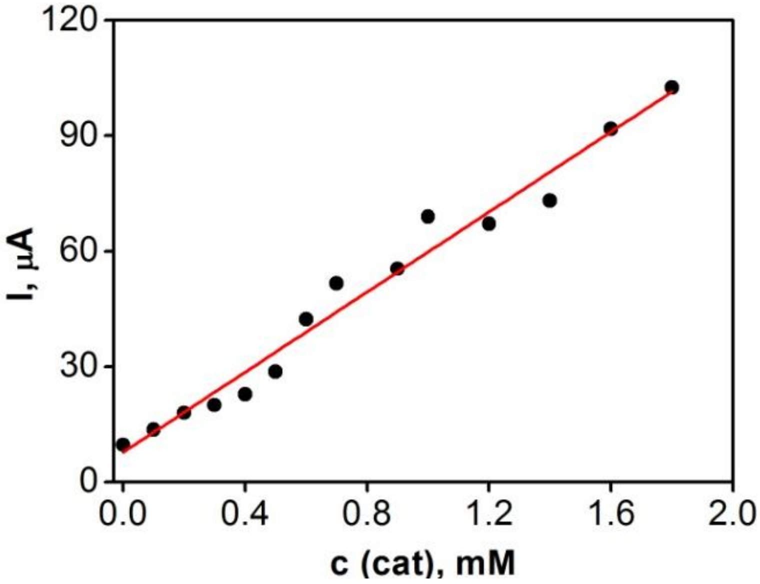

Figure S6. Catalytic current at 1.64 V as a function of the catalyst concentration measured in 0.1 M pH 7 phosphate buffer.

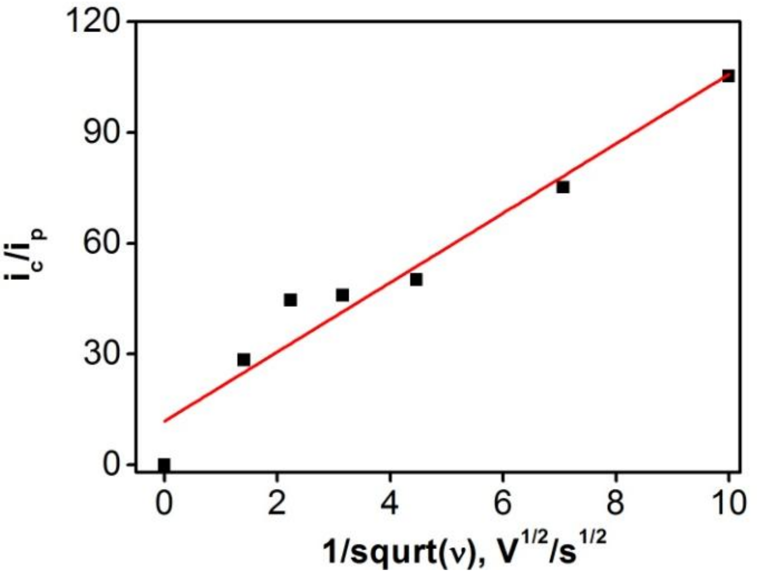

Figure S7. Plot of i_{cat}/i_p vs $1/\upsilon^{1/2}$ at 1.77 V in 0.1 M pH 7 phosphate buffer containing 1.0 mM catalyst.

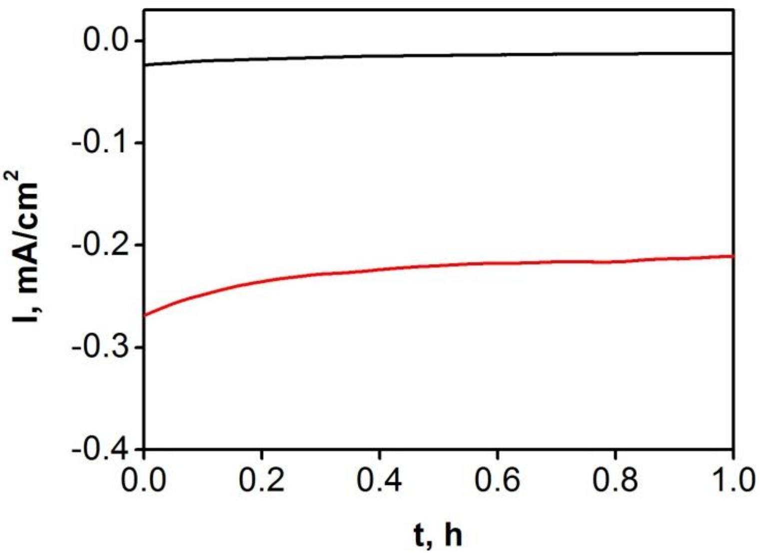

Figure S8. Bulk electrolysis with (red) and without (blank) **1** (1 mM) in 0.1 M pH 7 phosphate buffer at 1.64 V. Working electrode, FTO; reference electrode, Ag/AgCl; counter electrode, Pt.

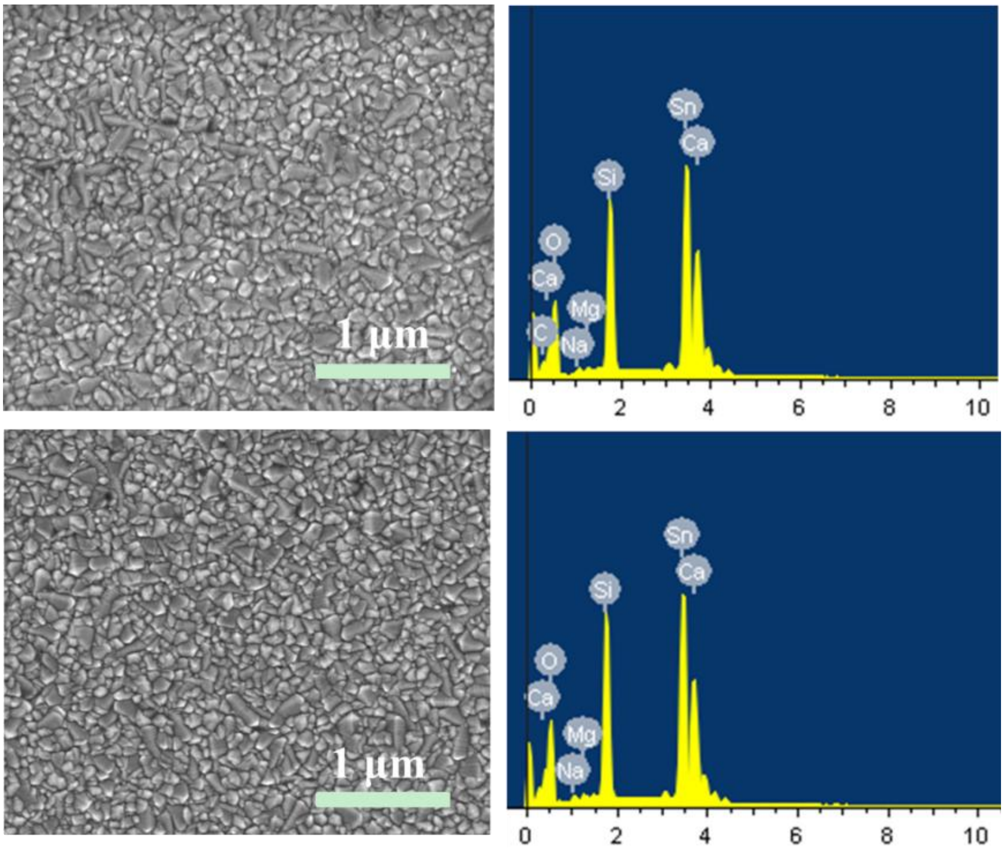

Figure S9. Scanning electron microscopes (SEM) images and the energy-dispersive X-ray spectra (EDS) of the FTO anode before (top) and after (bottom) continuous electrolysis at 1.64 V in 0.1 M pH 7 phosphate buffer containing 1.0 mM complex **1**.

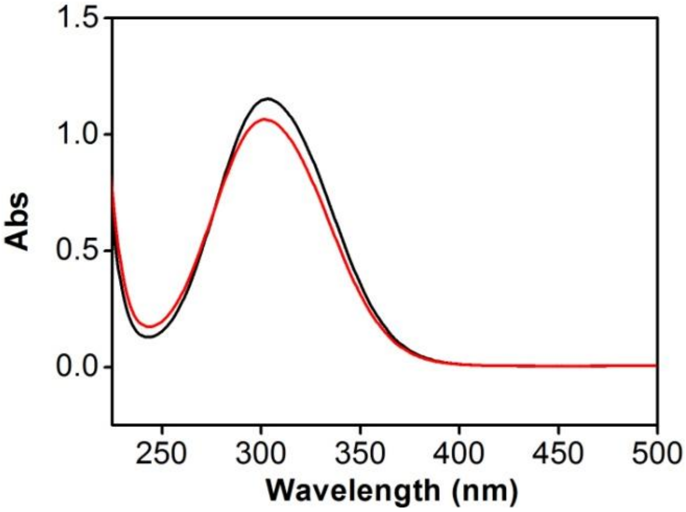

Figure S10. UV-visible spectra of **1** before (black) and after (red) 4 hours electrolysis at 1.64 V in 0.1 M pH 7 phosphate buffer containing 1.0 mM catalyst.

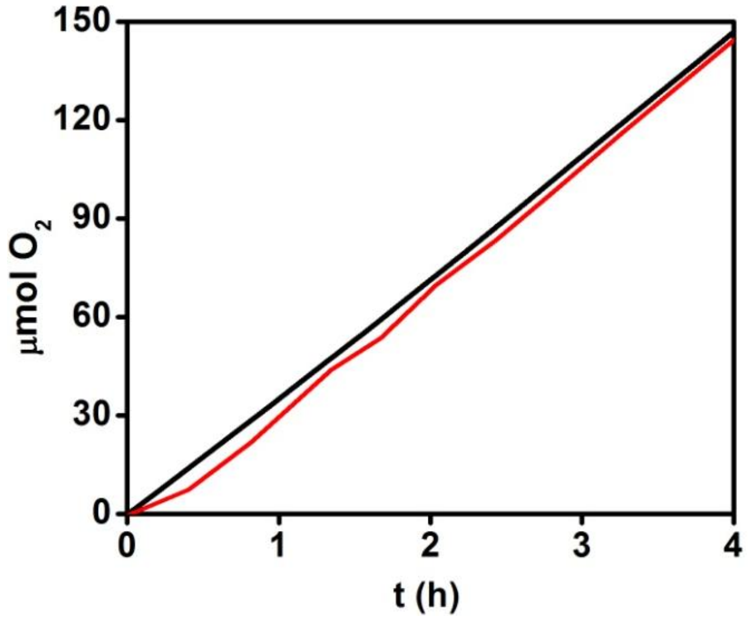

Figure S11. Determination of the Faradic efficiency of **1** modified carbon cloth electrode measured in 0.1 M pH 7 phosphate buffer under gently stirring. Black line: Theoretical amount of oxygen as assumed by charge passed with 100% Faradic efficiency. Red line: The amount of evolved oxygen measured by GC.

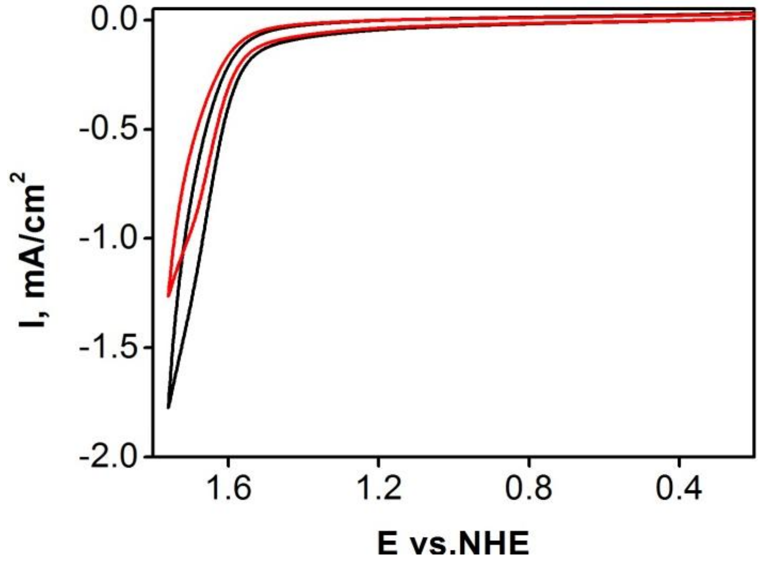

Figure S12. CV curves of **1** in H_2O (black) and D_2O (red) phosphate buffer with glassy carbon as working electrode at a scan rate 100mV/s.

Table S1. Crystallographic data and processing parameters for complex **1**.

Complex	[Cu(TMC)(H_2O)](NO_3)$_2$
Formula	$C_{14}H_{34}CuN_6O_7$
Formula weight	461.18
Crystal system	Triclinic
space group	P-1
Z	2
a/Å	9.4885(3)
B/Å	10.1789(3)
c/Å	11.6397(4)
alpha/deg	85.237(2)
beta/deg	74.9220(10)
gamma/deg	77.7440(10)
Volume/$Å^3$	1060.29(6)
D_{calcd}/mg/m^3	1.504
Absorption coefficient/mm^{-1}	1.083
Crystal size/mm	0.21 x 0.18 x 0.17
θ Range/deg	2.27 to 25.00
Reflns collected/Indep	6913 / 3721
F(000)	510
GOF on F^2	1.014
Final $R1$ ($I > 2\sigma(I)$)	0.0384
Final $wR2$ ($I > 2\sigma(I)$)	0.1001
max. peak/hole / e $Å^{-3}$	0.807, -0.874

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$

(1) X. J. Su, M. Gao, L. Jiao, R. Z. Liao, P. E. Siegbahn, J. P. Cheng, M. T. Zhang, *Angew. Chem. Int. Ed*. **2015**, *54*, 4909-4914.

(2) E. K. Barefield, F. Wagner, *Inorg. Chem*. **1973**, *10*, 2435-2439.

(3) F. Yu, F. Li, B. Zhang, H. Li, L. Sun, *ACS Catal*. **2015**, *5*, 627-630.