

Supporting Information (SI)

A Heptanuclear $\text{Co}^{\text{II}}_5\text{Co}^{\text{III}}_2$ Cluster as Efficient Water Oxidation Catalyst

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Materials and General Methods.

All reagents are commercial available and used as received without any purifications. The amount of evolved O₂ dissolved in solution was measured *in situ* by a standard Clark-type oxygen electrode (Hansatech Instruments). The total amount of evolved O₂ was quantified by Techcomp 7890 II gas chromatography (GC) equipped with a 5 Å molecular sieve column using argon as carrier gas and thermal conductivity detector. FT-IR spectra were obtained with a PerkinElmer FT-IR Spectrometer Spectrum Two in the range of 4000 – 450 cm⁻¹. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/Max 2200PC diffractometer equipped with a graphite monochromator and Cu K α radiation ($\lambda = 1.5418$ Å) in the range of $2^\circ < 2\theta < 50^\circ$. Electrochemical measurements were carried out on a CHI 760e electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd) with a conventional three electrode arrangement. The High-Resolution Electrospray Mass Spectrometry was performed on an Agilent (Santa Clara, CA, USA) ESI-TOF mass spectrometer (6224). The instrument was calibrated with an Agilent tune mixture before mass analysis. The sample was introduced by a syringe pump (KDS-100, KD Scientific, Holliston, MA, USA) at a flow rate of 5 μ L/min. The nebulizing nitrogen gas pressure was 15 psi, the capillary voltage was 4 kV, the desolvation gas flow rate was 4 L/min, and the desolvation gas temperature was 100 °C around the MS-inlet capillary entrance.

Photocatalytic water oxidation

The amount of evolved O_2 dissolved in solution was measured *in situ* by a standard Clark-type oxygen electrode (Hansatech Instruments), the electrode was calibrated following standard procedure before measurement. In a typical experiment, each component was mixed in 2.0 mL buffer solution, and then the solution was degassed with argon for 30 min before measurement. The degassed solution was then irradiated by a 450 nm LED lamp and the amount of O_2 evolved in solution was measured *in situ*.

The total amount of evolved O_2 was quantified by gas chromatography (GC) analysis. The gas chromatography (GC) analysis was performed by Techcomp D7980 GC using argon as the carrier gas and a 5 Å molecular sieve column to separate O_2 , N_2 and CH_4 , then gases were detected with a thermal conductivity detector. In a typical experiment, a Pyrex tube was filled with borate buffer solution (10.0 mL, 0.2 M) which contains catalyst, $[Ru(bpy)_3]^{2+}$, and $K_2S_2O_8$. Then the tube was sealed with a rubber plug and the junction between the tube and the rubber plug was sealed with wax. Subsequently, the tube was flushed with argon for 60 min to remove the residual air. After degassing, 200 μ L CH_4 was injected into the tube as the internal standard. Then the tube was photolyzed with a 450 nm LED lamp. After photolysis, 200 μ L of the gas in the headspace was sampled by a Hamilton (1750 SL) gas-tight microliter syringe and then analyzed by GC. Contamination of the headspace caused by air in the degassed sample was nullified by measuring the N_2 peak on GC.

Synthesis and characterization of 1.

The sodium azide (0.086 mmol, 5.59 mg) and N-Methyldiethanolamine (0.35 mmol, 41.23 mg) were added to a acetonitrile solution (5 mL) of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.25 mmol, 91.48 mg), and stirred for 10 minutes, which caused the solution color change to black green. The solution was stirred for another 1.5 hours, then filtered to remove any solid. After 2 days, the dark green crystals were collected and washed with ethyl alcohol. Yield: 52% (based on Co). Elemental analysis calculated for $\text{C}_{32}\text{H}_{66}\text{N}_{16}\text{O}_{28}\text{Cl}_4\text{Co}_7$ (%): C 22.91, H 3.97, N 13.36; found: C 22.92, H 3.95, N 13.37. Selected IR peak (cm^{-1}): 3525(w), 2989(w), 2927(w), 2875(w), 2132(w), 2082 (m), 1636(w), 1459(w), 1300(w), 1067(s), 921(w), 749 (w), 673(m), 622(s), 536(m), 462 (m).

X-ray Crystallography

Single crystal of **1** with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collections. Single-crystal X-ray diffraction data were collected using a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromatic Mo K α radiation, $\lambda = 0.71073$ Å, ω -scans with a 0.5° step in ω). Indexing was performed using APEX2 (Difference Vectors method).^[1] Data integration and reduction were performed using Saint Plus 6.01.^[2] Absorption correction was performed by multi-scan method implemented in SADABS.^[3] Space groups were determined using XPREP implemented in APEX2.^[4] Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. The structure was examined using the Addsym subroutine of PLATON^[5] to assure that no additional symmetry could be applied to the models.

[1] Bruker APEX2; Bruker AXS, Inc.: Madison, WI, **2010**.

[2] *Bruker SAINT, Data Reduction Software*; Bruker AXS, Inc.: Madison, WI, **2009**.

[3] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction*; University of Gottingen: Gottingen, Germany, **2008**.

[4] a) G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal*; University of Gottingen: Gottingen, Germany, **1997**. b) G. M. Sheldrick, *Acta Crystallogr.* **1990**, A46, 467. c) G. M. Sheldrick, *Acta Crystallogr.* **2008**, A64, 112.

[5] A. L. Spek, *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1998**.

Table S1. Crystallographic data of 1.

Empirical formula	C ₃₂ H ₆₆ Cl ₄ Co ₇ N ₁₆ O ₂₈
Formula weight	1677.32
Temperature/K	298.15
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	11.723(2)
b/Å	23.448(4)
c/Å	12.930(2)
α/°	90.00
β/°	116.1675(15)
γ/°	90.00
Volume/Å ³	3189.8(10)
Z	2
ρ _{calc} /cm ³	1.746
μ/mm ⁻¹	2.032
F(000)	1702.0
Crystal size/mm ³	0.2 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.94 to 50
Index ranges	-13 ≤ h ≤ 13, -27 ≤ k ≤ 26, -15 ≤ l ≤ 15
Reflections collected	12209
Independent reflections	5583 [R _{int} = 0.0300]
Data/restraints/parameters	5583/161/463
Goodness-of-fit on F ²	1.030
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0556, wR ₂ = 0.1536
Final R indexes [all data]	R ₁ = 0.0711, wR ₂ = 0.1702
Largest diff. peak/hole / e Å ⁻³	1.22/-1.62

Table S2. Selected bond lengths (Å) and angles (°).

Co1—O9	2.069 (4)	Co3—O9 ⁱ	2.033 (3)
Co1—O11 ⁱ	1.974 (4)	Co3—O9	2.033 (3)
Co1—O12 ⁱ	2.254 (4)	Co3—O10 ⁱ	2.132 (4)
Co1—N1	2.128 (6)	Co3—O10	2.132 (4)
Co1—N2	2.146 (6)	Co3—O12 ⁱ	2.111 (3)
Co1—N3	2.116 (6)	Co3—O12	2.111 (3)
Co2—O1W	2.142 (5)	Co4—O10	1.910 (4)
Co2—O9	2.069 (4)	Co4—O11	1.884 (4)
Co2—O10	2.251 (4)	Co4—O12	1.911 (4)
Co2—O13	1.978 (4)	Co4—O13	1.887 (4)
Co2—N3	2.105 (5)	Co4—N7	2.027 (5)
Co2—N6	2.146 (6)	Co4—N8	2.022 (5)
O9—Co1—O12 ⁱ	80.58 (13)	N6—Co2—O10	108.8 (2)
O9—Co1—N1	91.67 (19)	O9 ⁱ —Co3—O10	94.97 (14)
O9—Co1—N2	164.3 (2)	O9 ⁱ —Co3—O10 ⁱ	85.03 (14)
O9—Co1—N3	79.29 (18)	O9—Co3—O10 ⁱ	94.97 (14)
O11 ⁱ —Co1—O9	98.77 (16)	O9—Co3—O10	85.03 (14)
O11 ⁱ —Co1—O12 ⁱ	72.11 (14)	O9—Co3—O12 ⁱ	84.96 (14)
O11 ⁱ —Co1—N1	92.3 (2)	O9 ⁱ —Co3—O12	84.96 (14)
O11 ⁱ —Co1—N2	96.8 (2)	O9 ⁱ —Co3—O12 ⁱ	95.04 (14)
O11 ⁱ —Co1—N3	163.79 (19)	O9—Co3—O12	95.04 (14)
N1—Co1—O12 ⁱ	161.1 (2)	N8—Co4—N7	105.3 (2)
N1—Co1—N2	85.5 (2)	O12 ⁱ —Co3—O10	105.24 (14)
N2—Co1—O12 ⁱ	106.5 (2)	O12 ⁱ —Co3—O10 ⁱ	74.76 (14)
N3—Co1—O12 ⁱ	91.73 (18)	O12—Co3—O10 ⁱ	105.24 (14)
N3—Co1—N1	103.8 (2)	O12—Co3—O10	74.76 (14)
N3—Co1—N2	86.4 (2)	O13—Co4—N8	84.5 (2)
O1W—Co2—O10	160.83 (19)	O10—Co4—O12	84.79 (15)
O1W—Co2—N6	85.7 (2)	O10—Co4—N7	86.51 (18)
O9—Co2—O1W	87.53 (17)	O10—Co4—N8	163.11 (19)
O9—Co2—O10	81.22 (13)	O11—Co4—O10	98.10 (17)
O9—Co2—N3	79.55 (18)	O11—Co4—O12	82.37 (17)
O9—Co2—N6	164.6 (2)	O11—Co4—O13	179.58 (19)
O13—Co2—O1W	95.3 (2)	O11—Co4—N7	84.5 (2)
O13—Co2—O9	101.73 (16)	O11—Co4—N8	95.1 (2)
O13—Co2—O10	72.11 (14)	O12—Co4—N7	163.06 (18)
O13—Co2—N3	161.5 (2)	O12—Co4—N8	86.6 (2)
O13—Co2—N6	92.7 (2)	O13—Co4—O10	82.29 (17)
N3—Co2—O1W	103.2 (2)	O13—Co4—O12	97.49 (17)
N3—Co2—N6	88.5 (2)		
Symmetry code: (i) $-x+1, -y+1, -z+2$.			

Table S3. BVS calculations for the Co atoms in 1

Atom	Co ^{II}	Co ^{III}
Co1	<u>2.417</u>	2.440
Co2	<u>1.969</u>	1.992
Co3	<u>2.049</u>	2.094
Co4	3.508	<u>3.558</u>

The underlined value is the one closest to the charge for which it was calculated. The oxidation state can be taken as the integer nearest to the underlined value.

Figure S1. The IR of 1

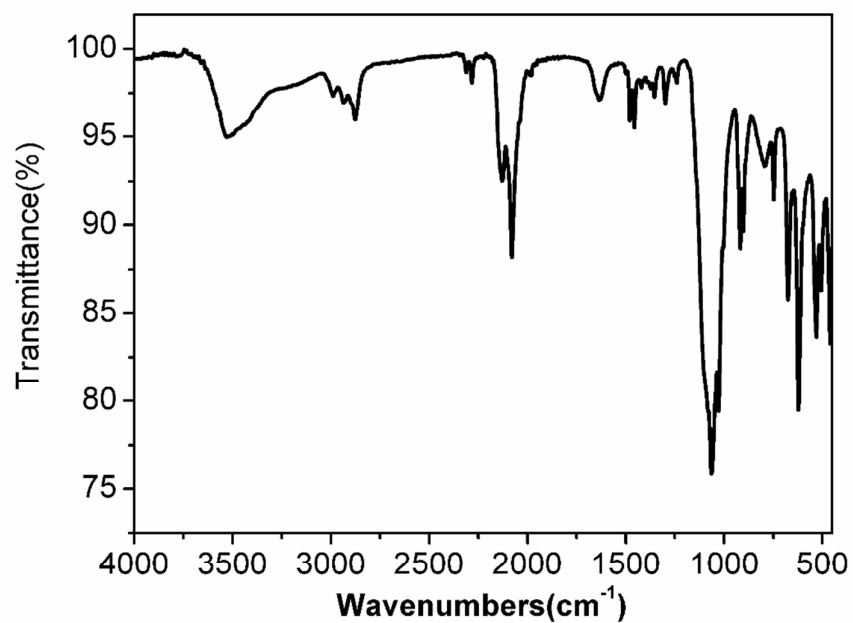


Figure S2. The TGA of 1

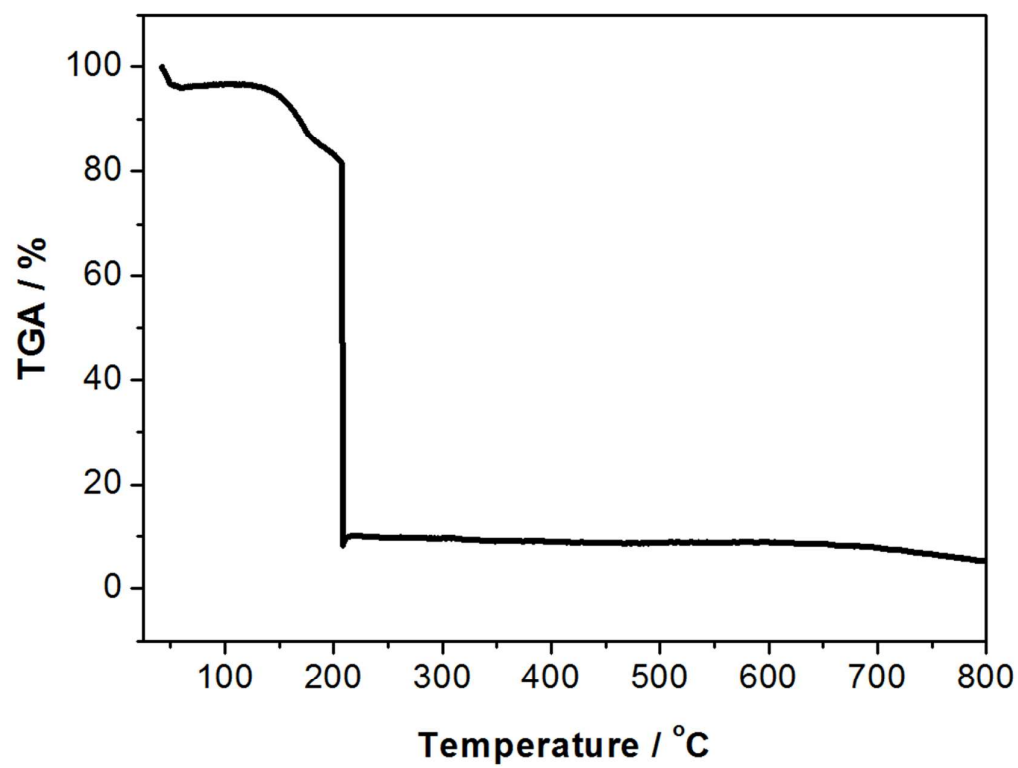


Figure S3. Solid state UV-Vis spectrum of 1.

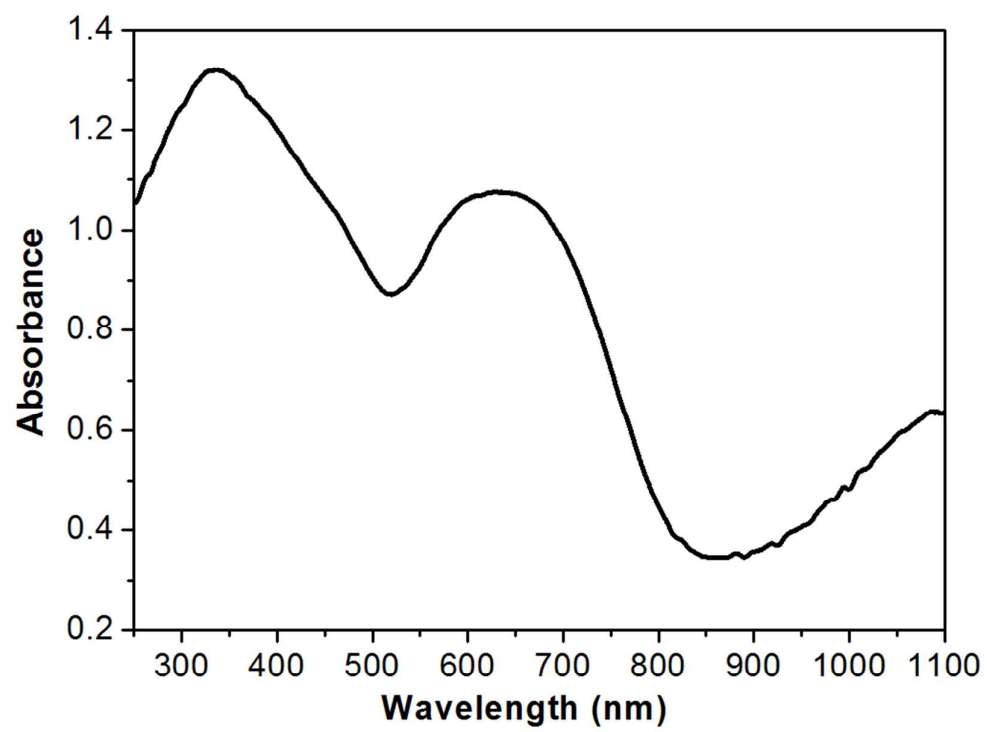


Figure S4. Experimental and simulated powder XRD patterns of **1**.

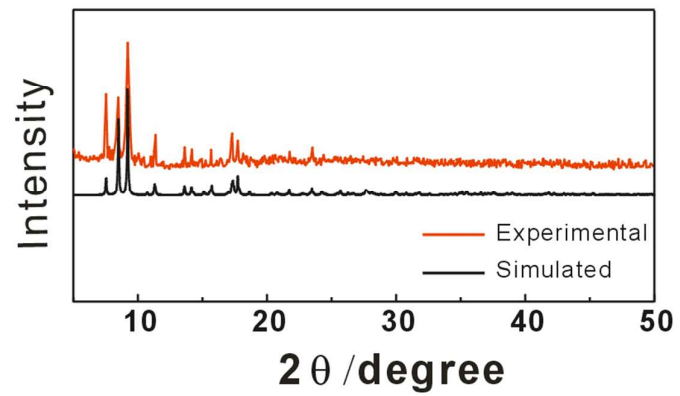
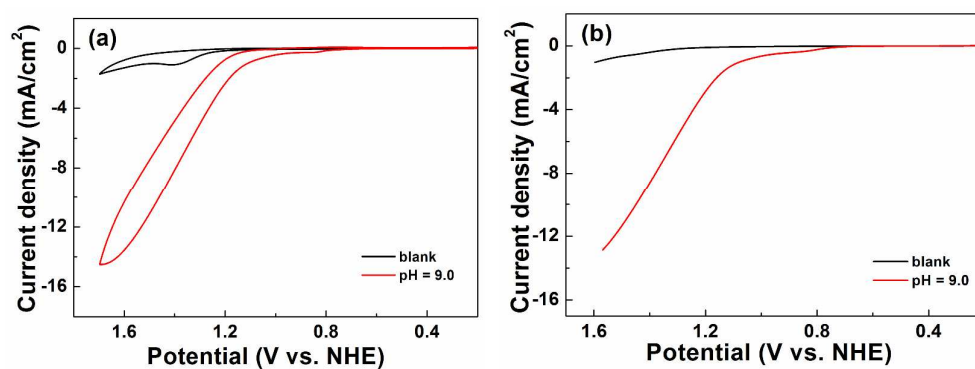
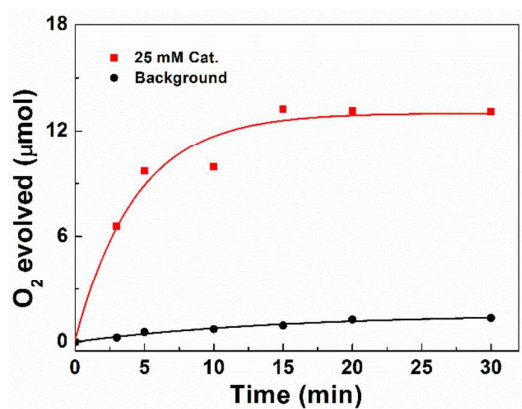


Figure S5. (a) Cyclic voltammograms (CV) and (b) Linear sweep voltammetry (LSV) of 0.5 mM 1 in 0.2 M borate buffer (pH 9.0).



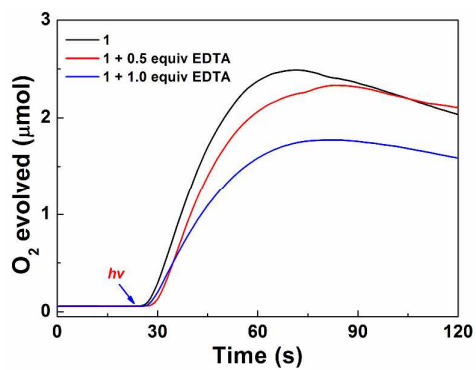
Conditions: scan rate: 100 mV s⁻¹; GC working electrode, Ag/AgCl (3.0 M KCl) reference electrode, and Pt wire counter electrode.

Figure S6. O₂ evolution catalyzed by 1 from scaled up reaction system.



Conditions: 25 μM catalyst, 1.0 mM [Ru(bpy)₃]Cl₂, 9.0 mM K₂S₂O₈, 0.2 M borate buffer (10.0 mL, initial pH 9.0), irradiated by a 450 nm LED light source.

Figure S7. O₂ evolution catalyzed by 1 in the presence of EDTA.



Conditions: 1.0 mM [Ru(bpy)₃]Cl₂, 9 mM K₂S₂O₈, 25 μM catalyst, 0-1 equivalent EDTA, 0.2 M borate buffer (2.0 mL, initial pH 9.0), and irradiated by a 450 nm LED light source.