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Supporting Information

A hybrid polyoxometalate-organic molecular catalyst for visible light driven water oxidation

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Materials and methods

All reagents were commercially available and used without further purification. $[Co(bpy)_3](ClO_4)_2$ was synthesized according to the literature.[1] The mixture of $[Co(bpy)_3]^{2+}$, $[Co(bpy)_2]^{2+}$ and $[Co(bpy)]^{2+}$ was synthesized according the literature,[2] and the stoichiometric ratio was validated by the ^1H NMR spectrum ($[Co(bpy)_3]^{2+}$: $[Co(bpy)_2]^{2+}$: $[Co(bpy)]^{2+}$ = 1:9:1, See **Fig. S12**).

Elemental analyses of Co, Mo were performed on a PLASMA-SPEC (I) inductively coupled plasma (ICP) atomic emission spectrometer. Thermogravimetric analyses were performed on a SHIMADZU TGA-50 instrument in air atmosphere with a heating rate of 10 °C·min^{-1}. IR spectra were recorded in the range of 400–4000 cm^{-1} on a Nicolet 330 FT-IR Spectrophotometer with pressed KBr pellets. Cyclic voltammograms were obtained at room temperature in buffered solutions using CHI-660e electrochemistry workstation. Reference electrode: Ag/AgCl (saturated KCl), work electrode: glassy carbon disk electrode (dia 5mm) Single crystal data were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å). Suitable crystals were mounted in a thin-glass tube and transferred to the goniostat. The structure of **1** was solved by direct methods and refined by the full-matrix least-squares fit on F^2 using the SHEL-97 and olex2 GUI crystallographic software package.[3, 4] The photocatalytic water oxidation was carried out in 20 mL 80mM pH=9.0 borate buffer with 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff). The sample was treated by supersonication before illumination. The reaction solution was first degassed by ultrasonication and added to the photosensitizer, sacrificial electron acceptor and then evacuated to ensure complete air removal. The generated O_2 was analyzed by gas chromatography with a GC-D7900P instrument with a thermal conductivity detector and a 5 Å molecular sieve column (3mm × 2m) using Ar gas as carrier gas.

Syntheses of **1**: A mixture of $Na_2MoO_4{\cdot}2H_2O$ (0.5 g, 2.07 mmol), $Co(Ac)_2{\cdot}4H_2O$ (0.05g, 0.201 mmol), 2,2'-bipyridine (0.05g, 0.31mmol), 4, 4'-bis(phosphonomethyl) biphenyl (0.05 g, 0.15 mmol), $Na_2HPO_4{\cdot}4H_2O$ (0.2 g, 0.56 mmol), and 85% H_3PO_4 (150 μL) in 12 mL of distilled water was stirred for 30 min. The mixture was then transferred to a 25 mL Teflon-lined stainless steel autoclave and kept at 220 ^oC for 3days and then slowly cooled to ambient temperature at 8 ^oC/ h. Black block crystals of **1** were collected by filtering, washing with distilled water, and drying in air. Yield: 0.43g (35% based on 2, 2'-bipyridine). Anal. Calcd. (%) for **1**: C 25.81, H 2.00, N 6.02, Mo 36.65, Co 6.10; found C 25.93, H 2.08, N 5.98, Mo 36.78, Co 6.14. Selected FT-IR data (KBr pellets, **Fig. S8**, ESI): $\tilde{\nu}$= 3489 (S, Br), 1637 (m), 1569 (m), 1412 (w), 1057 (s), 1010 (w), 921 (s), 884 (w), 821 (s), and 748(s) cm^{-1}.

Table S1 Crystal data for **1.**

	1
Empirical formula	$C_{130}H_{97}Co_{6.5}Mo_{24}N_{26}O_{88}P_2$
Formula weight	6178.88
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	29.607(4)
b/Å	26.660(3)
c/Å	24.133(3)
α/°	90.00
β/°	108.178(2)
γ/°	90.00
Volume/$Å^3$	18097(4)
Z	4
$\rho_{calc}mg/mm^3$	2.268
m/mm^{-1}	2.294
F(000)	11906.0
Crystal size/mm^3	0.3 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	1.44 to 50°

Index ranges	$-21 \leq h \leq 35, -31 \leq k \leq 31, -28 \leq l \leq 28$
Reflections collected	91307
Independent reflections	31824 [$R_{int} = 0.0654$, $R_{sigma} = 0.0896$]
Data/restraints/parameters	31824/52/2497
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	$R_1 = 0.0690$, $wR_2 = 0.1732$
Final R indexes [all data]	$R_1 = 0.1007$, $wR_2 = 0.1866$
Largest diff. peak/hole / e Å^{-3}	1.89/-1.32

Table S2 Bond valence sum (BVS) results.

	BVS	
Mo1	5.786124	Mo^{VI}
Mo2	5.876053	Mo^{VI}
Mo3	5.320183	Mo^{V}
Mo4	5.75744	Mo^{VI}
Mo5	5.368372	Mo^{V}
Mo6	5.778328	Mo^{VI}
Mo7	5.275168	Mo^{V}
Mo8	5.368472	Mo^{V}
Mo9	5.81212	Mo^{VI}
Mo10	5.714077	Mo^{VI}
Mo11	5.896063	Mo^{VI}
Mo12	5.937218	Mo^{VI}
Mo13	5.830258	Mo^{VI}
Mo14	5.781164	Mo^{VI}
Mo15	5.86393	Mo^{VI}
Mo16	5.904925	Mo^{VI}
Mo17	5.329022	Mo^{V}
Mo18	5.277404	Mo^{V}
Mo19	5.319688	Mo^{V}
Mo20	5.375735	Mo^{V}
Mo21	5.846347	Mo^{VI}
Mo22	5.890628	Mo^{VI}

Mo23	5.781774	Mo^{VI}
Mo24	5.91979	Mo^{VI}
Co1	1.836536	Co^{II}
Co2	1.822622	Co^{II}
Co3	1.911072	Co^{II}
Co4	1.846738	Co^{II}
Co5	1.745866	Co^{II}
Co6	1.64087	Co^{II}
Co7	2.145588	Co^{II}

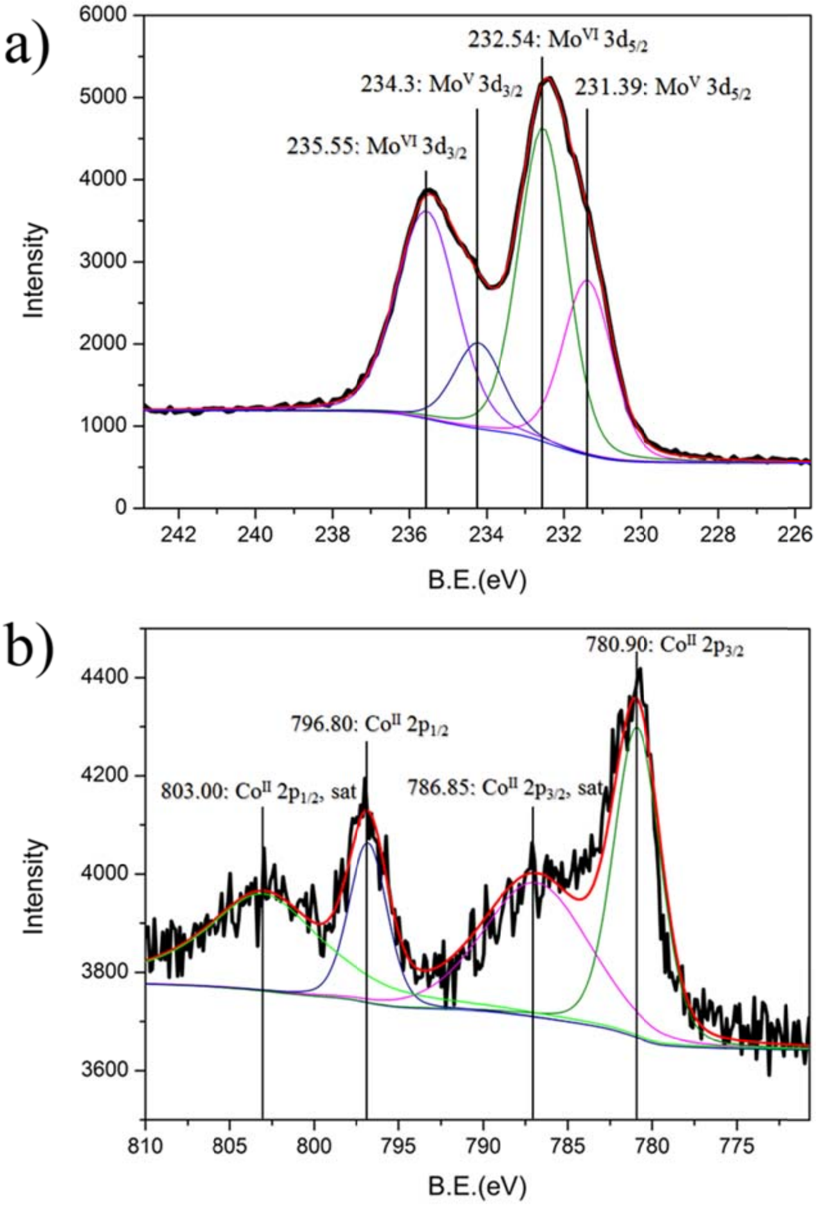

Fig. S1 XPS spectra of a) Mo 3d region and b) Co 2p region for **1**.

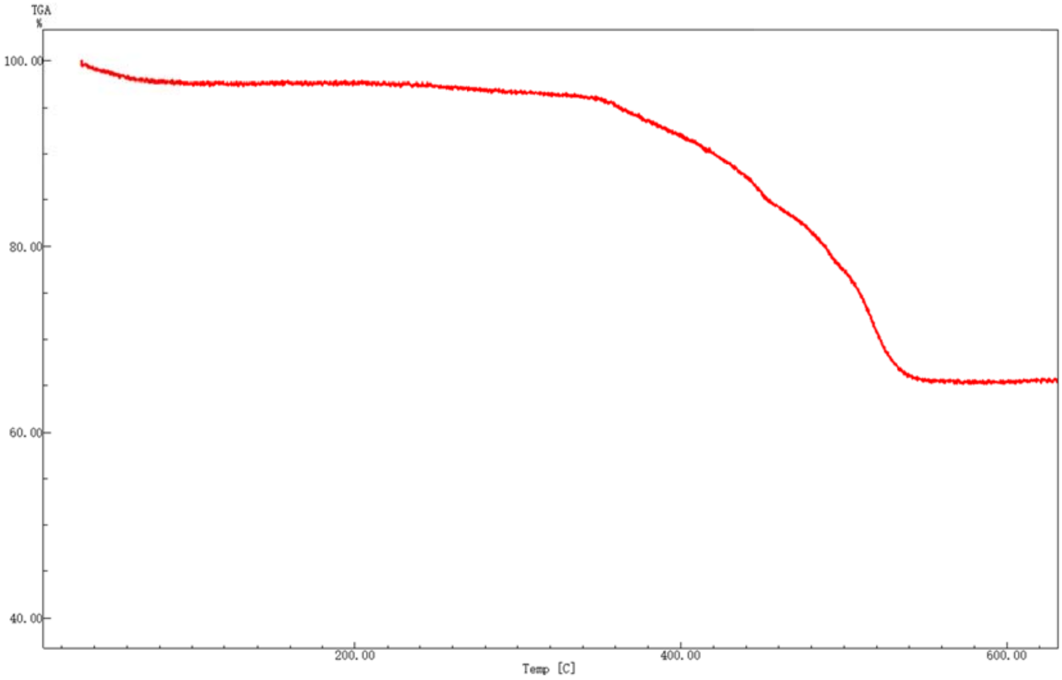

Fig. S2 TGA curve of **1**.

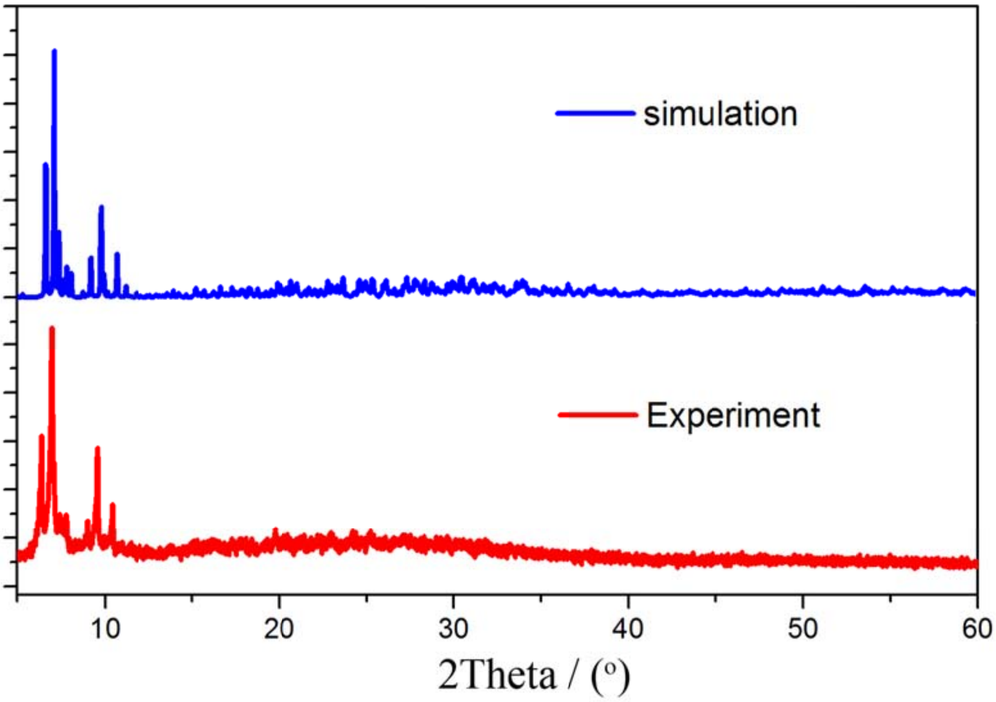

Fig. S3 Comparison of the simulated and experimental XRPD patterns of **1**.

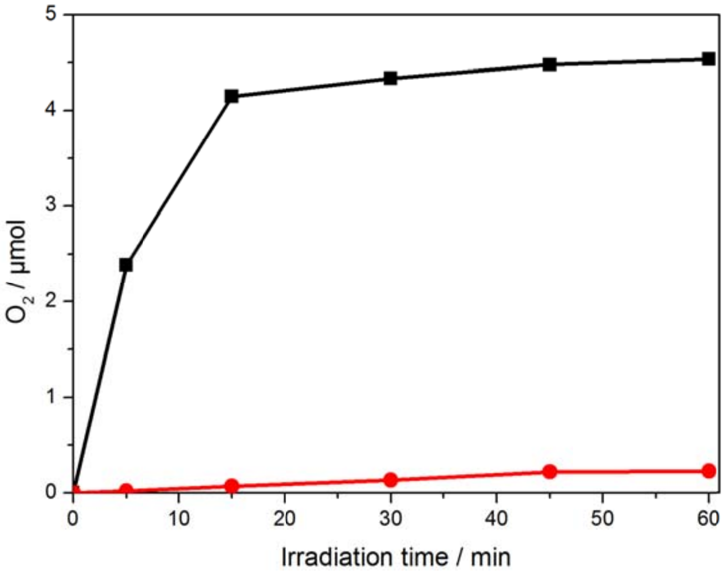

Fig. S4 The photocatalytic water oxidation activity of 5 μM **1** (black) and 20μM $Co(bpy)_3(ClO_4)_2$. Other conditions: pH=9 borate buffer solutions, 5 μM **1**, 1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0 mM $Na_2S_2O_8$; 300W Xe lamp, 420-800 nm; total reaction volume 20mL; vigorous stirring (1.5×10^3 rpm).

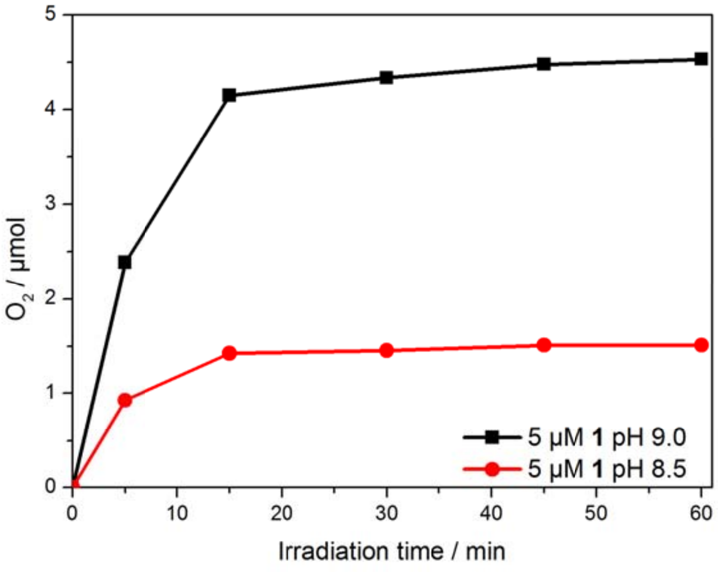

Fig. S5 Photochemical O_2 production in borate buffer solutions at pH=8.5 and pH=9. Other conditions: 5 μM **1**, 1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0 mM $Na_2S_2O_8$; 300W Xe lamp, 420-800 nm; total reaction volume 20mL; vigorous stirring (1.5×10^3 rpm).

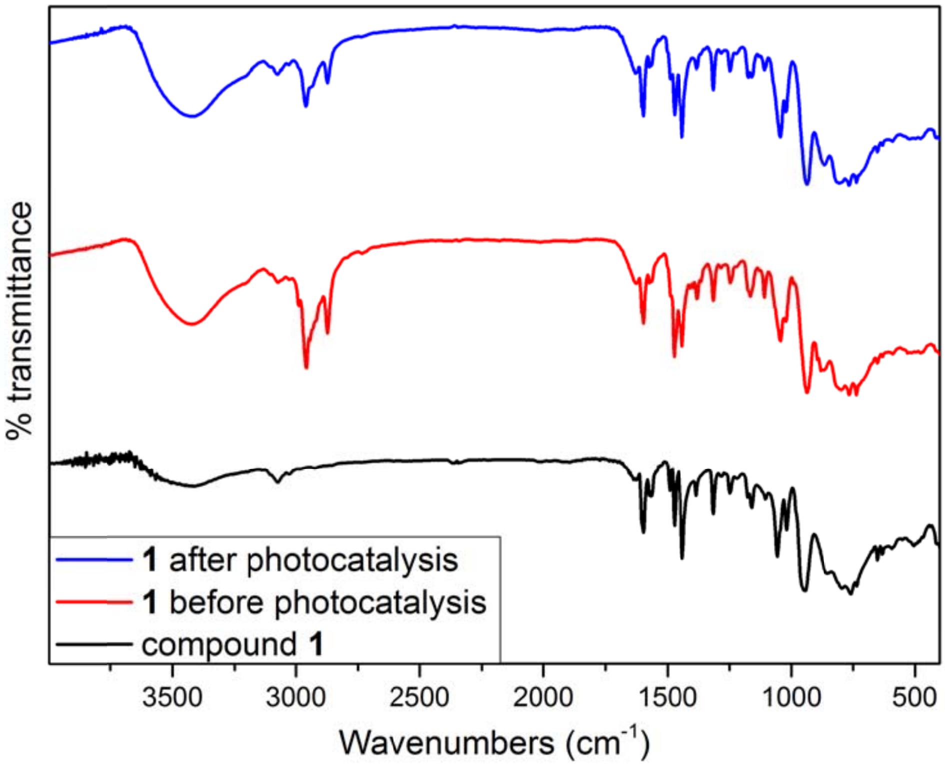

Fig. S6 FT-IR spectrum of **1** and extractions from the WOC system before and after light illumination.

Table S3 FT-IR assignment for **1.**

Cm^{-1}	**Assignment**
1598,1571	υ (C=C)
1490, 1471, 1440	υ (C=C, C=N)
1058, 1020	υ (P-O)
944, 856, 800, 760	υ (Mo-O)

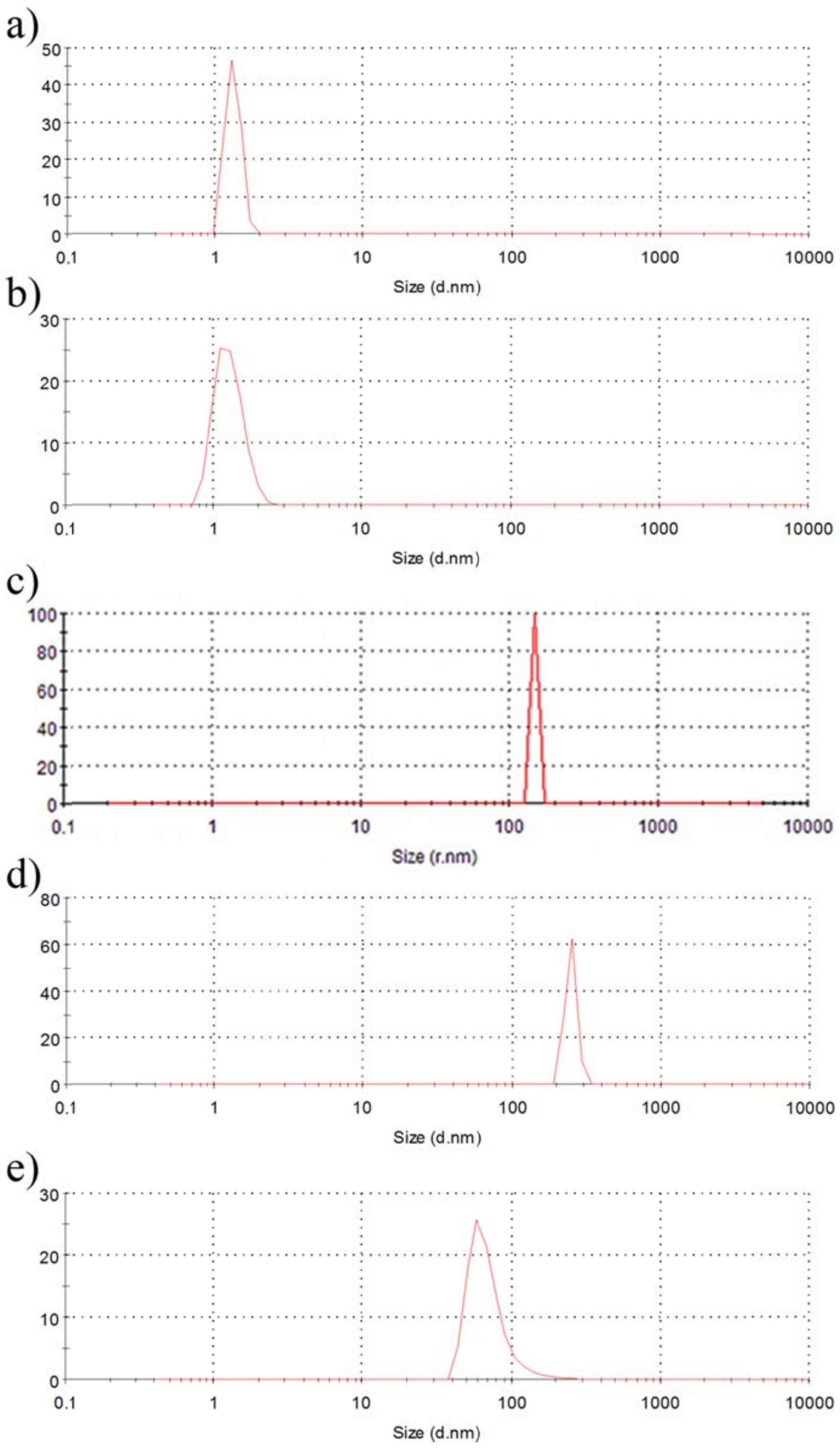

Fig. S7 DLS measurements of (a) 5μM **1** before irradiation; (b) 5μM **1** after irradiation; (c) 20μM $Co(NO)_3 \cdot 6H_2O$ after irradiation; (d) 2.7μM $Co(NO)_3 \cdot 6H_2O$ after irradiation; (e) 35μM mixture of $[Co(bpy)]^{2+}$ and $[Co(bpy)_2]^{2+}$ after irradiation. Other condition: 80mM borate buffer solution (pH 9.0, 20 mL); 1mM irradiation time $[Ru(bpy)_3]^{2+}$; 5mM $Na_2S_2O_8$; 300W Xe lamp (420-800nm); Irradiation time: 1h.

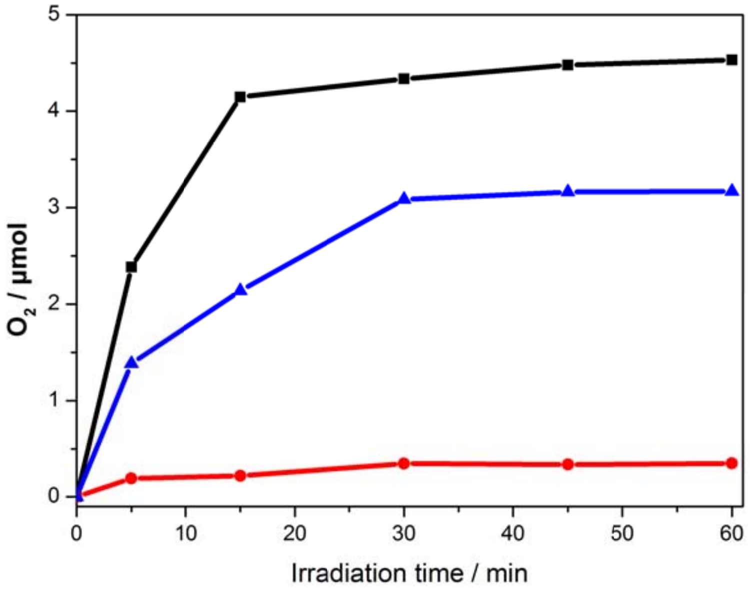

Fig. S8 Photochemical O_2 production of 1.76 μM mixture of $Co(bpy)_3^{2+}$, $Co(bpy)_2^{2+}$ and $Co(bpy)^{2+}$ (contains 1.6μM $Co(bpy)^{2+}$ and $Co(bpy)_2^{2+}$, red), 38.5 μM mixture of $Co(bpy)_3^{2+}$, $Co(bpy)_2^{2+}$ and $Co(bpy)^{2+}$ (contains 35 μM $Co(bpy)^{2+}$ and $Co(bpy)_2^{2+}$, blue) and 5 μM **1** (black). Other conditions: 80 mM borate buffer solution (pH 9.0, 80 mL); 1 mM irradiation time $[Ru(bpy)_3]^{2+}$; 5mM $Na_2S_2O_8$; 300W Xe lamp (420-800 nm); Irradiation time: 1h.

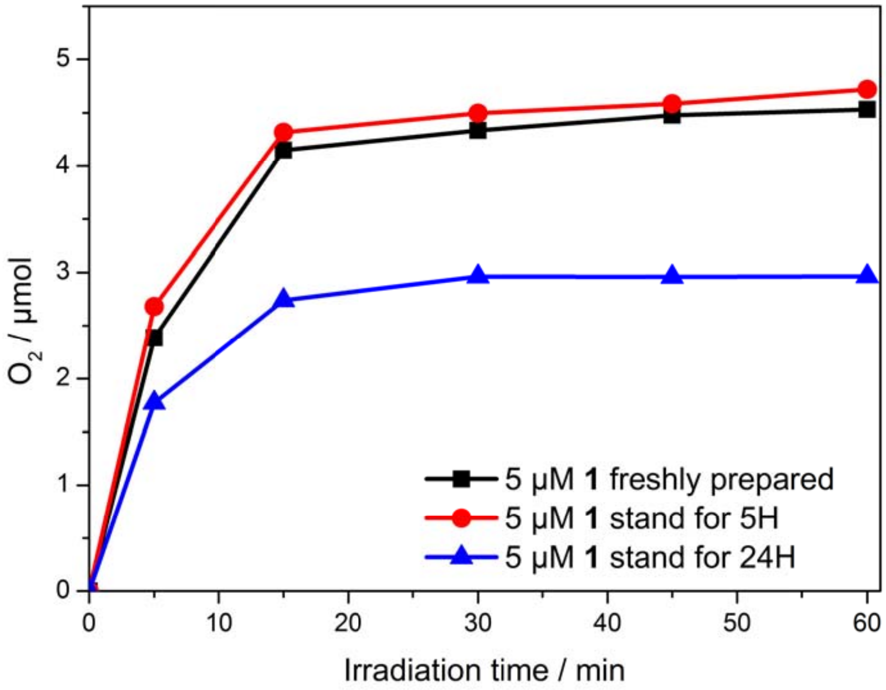

Fig. S9 The photocatalytic water oxidation activity of 5 μM **1** after being aged for 0 h, 5 h and 24 h. Other conditions: 80 mM borate buffer solution (pH 9.0, 80 mL); 1 mM irradiation time $[Ru(bpy)_3]^{2+}$; 5mM $Na_2S_2O_8$; 300W Xe lamp (420-800 nm); Irradiation time: 1h.

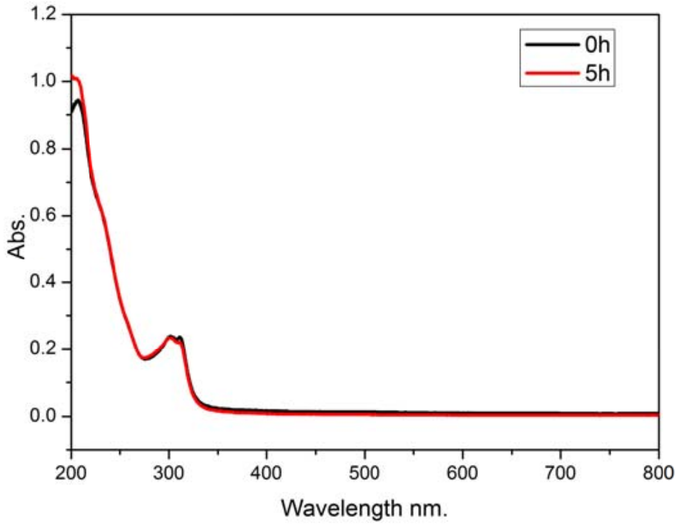

Fig. S10 UV-Vis curves of **1** after being aged for 0h (black curve) and 5h (red curve). Other conditions: 80 mM pH 9.0 borate buffer solution.

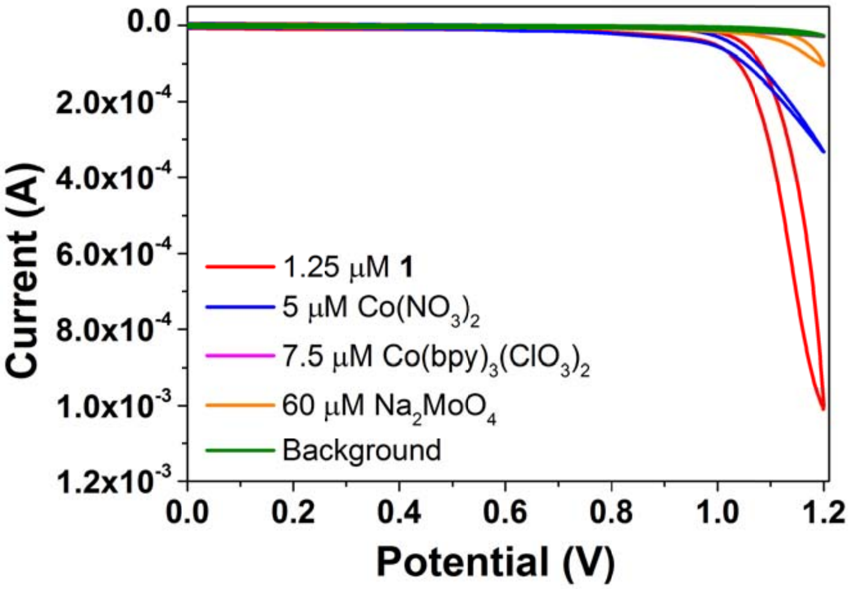

Fig. S11 CV curves of 1.25 μM **1** (red curve) and its control experiments in 80 mM pH 9.0 borate buffer. The oxidation onset potential was determined from the intersection of the two tangents drawn at the current decrease and background charging current of the CV.[5] The CV curve of 1 showed large, irreversible oxidative waves that correspond to catalytic water oxidation with an onset potential of ~0.98 V (vs. Ag/AgCl). Meanwhile, the reversible redox potential of $[Ru(bpy)_3]^{3+}$ / $[Ru(bpy)_3]^{2+}$ are located at +1.25V (pH 9.0, vs. Ag/AgCl).[6] Our proposed mechanism of $[Ru(bpy)_3]^{3+}$ oxidizing cobalt(II) in compound 1 into cobalt(III) is thus thermodynamically feasible.

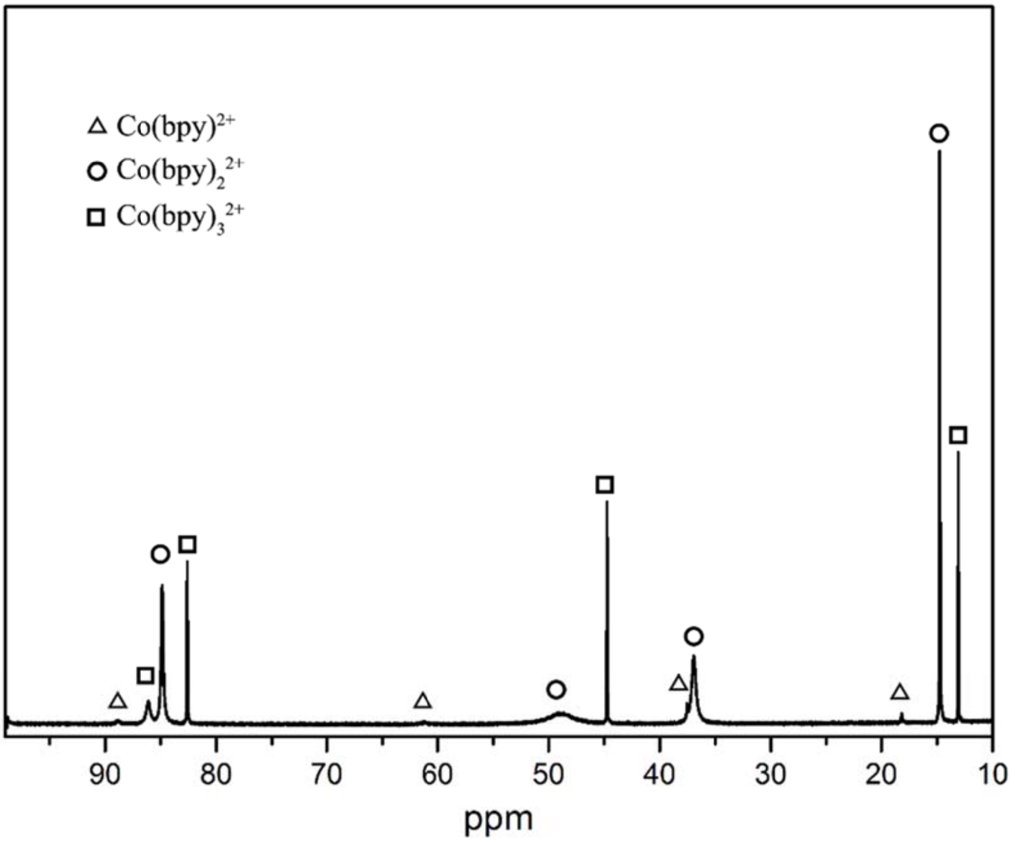

Fig. S12 ^{1}H NMR of the mixture of $[Co(bpy)_3]^{2+}$, $[Co(bpy)_2]^{2+}$ and $[Co(bpy)]^{2+}$ in CD_3OD solutions.

References

1. F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570–3579.
2. F. Qu, T. Q. Nguyen, and A. F. Janzen, *J. Fluor. Chem.*, 1999, **94**, 15–26
3. G.M. Seldrick, *Acta Crystallogr. A*, 1990, **64**, 467-473
4. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.*, **42**, 339-341.
5. W. Alhalash and R. Holze, J. *Solid State Electrochem.*, 2007, **11**, 1605.
6. (a) W. W. Brandt and G. F. Smith, *Anal. Chem.*, 1949, **21**, 1313–1319. (b) X. Chen, C. Q. Yi, M. J. Li, Z. Li, X. R. Wang, *Acta Chim. Sin.*, 2002, **60**, 1662–1667.