Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

A mononuclear cobalt complex with organic ligand acting as precatalyst for efficient visible light-driven water oxidation

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Experimental and calculation

Quantum yield calculation

Initial O_2 formation rate = 6.10 μmol·min^{-1} = 0.102 μmol·s^{-1}

Irradiation radius = 1 cm = 0.01 m

Photon flux = $\pi\times(0.01\text{m})^2\times1686\ \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1} = 0.529\ \mu\text{mol}\cdot\text{s}^{-1}$

$$\Phi_{\mathrm{QY(initial)}} = 2\times\frac{\text{initial O}_2\text{ formation rate}}{\text{photon flux}}\times100\%$$

$$=\frac{2\times0.102\ \mu\text{mol}\cdot\text{s}^{-1}}{0.529\mu\text{mol}\cdot\text{s}^{-1}}\times100\%$$

$$=38.6\%$$

Materials:

N,N'-Bis(salicylidene)ethylenediaminecobalt (II) (99 %) was purchased from Aldrich. 2, 2’, 2”-Triaminotriethylamine (TREN, 97%) was from STREM CHEMICALS. Meso-Tetra(4-carboxyphenyl)porphine (TCPP) was from the Frontier Scientific. Purified water (18.2 MΩ cm) for the preparation of solutions was obtained from a Milli-Q system (Millipore, Direct-Q 3 UV), and all other chemicals and salts used were of the highest purity available from commercial sources.

Preparation of different kinds of photosensitizers

Synthesis of $[Ru(bpy)_3]Cl_2\cdot6H_2O$

Commercial $RuCl_3\cdot xH_2O$ is dried in an oven at 120 °C for 3 h. It is then finely ground in a mortar and returned to the oven for a further 1h prior to use. It is convenient to store the “dried” $RuCl_3$ at this temperature.

“Dried” $RuCl_3$ (0.4 g, 1.93 mmol), 2, 2’-bipyridine (0.9 g, 5.76 mmol), and water (40 mL) are placed in a 100 mL flask fitted with a reflux condenser. Freshly prepared sodium phosphinate (sodium hypophosphite) solution (2 mL) is added and the mixture heated at the boil for 30 min. [The sodium phosphinate solution is prepared by the careful addition of sodium hydroxide pellets to about 2 mL of 31% phosphinic acid (hypophosphorous acid) until a slight cloudy precipitate is obtained. Phosphinic acid is then added dropwise, until the precipitate just redissolves.]

During reflux, the initial green solution changes to brown and finally orange. It is filtered to remove traces of undissolved material and potassium chloride (12.6 g) added to the filtrate to precipitate the crude product. The solution and solid are then heated at the boil to give a deep-red solution, which on cooling to room temperature yields beautiful, red plate-like crystals. These are filtered off, and air-dried. The yield is 1.05g (73%). The product could be recrystallized from boiling water (~2.8 $mL\cdot g^{-1}$) and then air-dried.

Properties: Aqueous solution of $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ have two characteristic absorption maxima at 428 nm (shoulder ε = 11,700 $dm^3\cdot mol^{-1}\cdot cm^{-1}$) and 452nm ($\varepsilon$ = 14,000 $dm^3\cdot mol^{-1}\cdot cm^{-1}$), which have been assigned to metal ligand charge-transfer transitions.

Synthesis of $[Ru(bpy)_3]SO_4$

$[Ru(bpy)_3]SO_4$ was synthesized according to reference 1. 1 equiv of Ag_2SO_4 was added to an aqueous solution of $[Ru(bpy)_3]Cl_2$ and stirred vigorously for 1 hour. Solid and liquid were separated by filtration. After evaporation of the aqueous solution under reduced pressure, orange solid photosensitizer was obtained.

Synthesis of $[Ru(bpy)_3](ClO_4)_2$

$[Ru(bpy)_3](ClO_4)_2$ was synthesized according to reference 2. $[Ru(bpy)_3](ClO_4)_2$ was prepared by adding 4 M $HClO_4$ to an aqueous solution of $[Ru(bpy)_3]Cl_2$ and then separated by filtration.

Synthesis of $[Ru(bpy)_3](ClO_4)_3$

$[Ru(bpy)_3](ClO_4)_3$ was prepared according to reference 3**.** The salt of $[Ru(bpy)_3](ClO_4)_2$ was dissolved in 0.5 M H_2SO_4. A scoop of PbO_2 was added, and the solution was stirred at room temperature and filtered through a fine frit. The perchlorate concentration of the filtrate was adjusted to ~ 2 M by the dropwise addition of $HClO_4$, and the solution was then cooled in an ice bath. Green crystals of $[Ru(bpy)_3](ClO_4)_3$ rapidly formed and were recrystallized from 4 M $HClO_4$ at 0 °C.

Preparation of various cobalt complexes

Syntesis of $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]\cdot 15H_2O$

The synthesis was seen reference 4. 19.8 g (0.06 mol) of $Na_2WO_4\cdot 2H_2O$ was dissolved in 40 mL of H_2O. This solution was adjusted to pH between 6.5 and 7.5 by the slow addition of 4 mL of glacial acetic acid before heated to near boiling. A solution containing 2.5 g (0.01 mol) of $Co(OAc)_2\cdot 4H_2O$ in 13 mL of H_2O was then added dropwise to the above system with stirring.

After the $Co(OAc)_2$ solution had been added, the mixture was heated to reflux for 10 min and then filtered while still hot to remove trace of insoluble material. This solution was heated to 80 ^{o}C, and 7 g of $K_2S_2O_8$ was slowly added in small amounts. During the addition, a large amount of gas generated instantaneously. When addition is completed, the solution was heated to boiling. The color changed from green to deep dark brown finally. The result mixture was boiled for 5 more minutes, filtered hot and then heated to boiling again. 25 mL of hot saturated KNO_3 solution was added. This mixture was then cooled in an ice bath, brown precipitate formed rapidly. Fine dark brown particle solid was obtained after filtered. This solid was added to a beaker containing appropriate amount of water and then heated in 90 ^{o}C hot water bath. The mixture was stirred for few minutes, filtered and filtrate was collected. Sludge solid continually precipitated from the filtrate solution in cooling process. Removing this sludge by filtration several times until a clear brown solution obtained. The well-formed dark brown cubic single crystals formed in two weeks after evaporation at room temperature. Yield: 2.5 g (15%). Single crystals suitable for X-ray crystallography were obtained by filtration. Thermogravimetric analysis (TGA) gave 15 water molecules of hydration. FT-IR (cm^{-1}): 953 (sh), 891 (s), 795 (s), 748 (m), 668 (m), 524 (w), 478 (w), 424 (sh). UV-Vis (H_2O, pH 7.0): λ_{max}, 387 nm (ε_{387} = 1580 dm^{3}·mol^{-1}·cm^{-1}). Elemental analysis calculated (%) for $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]\cdot15H_2O$: K, 8.23; Co, 3.54; W, 60.80. Found: K, 8.18; Co, 3.56; W, 60.12.

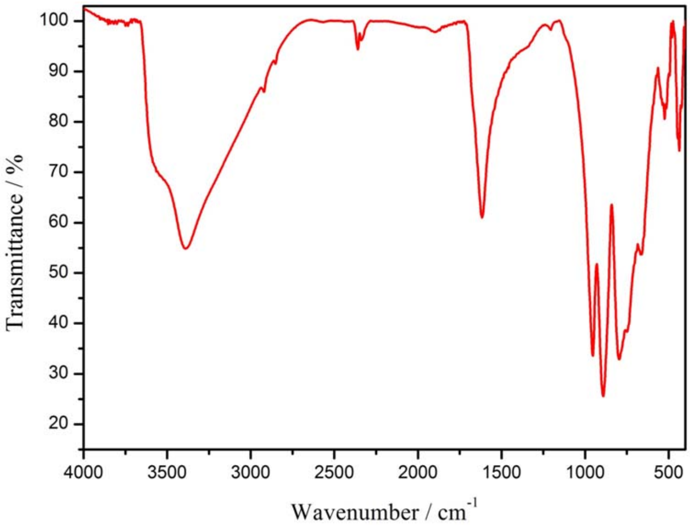


Fig. S1 FT-IR spectrum of $K_7[Co^{III}Co^{II}(H_2O)W_{11}O_{39}]\cdot15H_2O$.

Synthesis of $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]\cdot25H_2O$

$Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ was synthesized according to reference 5. $Na_2WO_4\cdot2H_2O$

(35.62 g, 0.108 mol), $Na_2HPO_4{\cdot}7H_2O$ (3.22 g, 0.012 mol), and $Co(NO_3)_2{\cdot}6H_2O$ (6.98 g, 0.024 mol) were mixed in 100 mL water. After adjusting the pH from 9 to 7, this purple suspension was then refluxed at 100 °C for 3 hours. A dark purple solution resulted within minutes of heating. After reflux, the solution was saturated with NaCl and allowed to cool to room temperature. The resulting purple crystals were collected, quickly washed with approximately 40 mL of water, and recrystallized from hot water (31% mass yield based on Co). Thermogravimetric analysis gave 25 water molecules of hydration. FT/IR (cm^{-1}): 1039 (m), 941 (m), 890 (w), 807 (w), 750 (w). UV-Vis (H_2O, pH 3.5 to 9): λ_{max}, 580 nm (ε_{579} = 330 $dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}$). Elemental analysis calculated (%) for $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]{\cdot}25H_2O$: Co, 4.36; Na, 4.25; P, 1.14; W, 61.15. Found: Co, 4.33; Na, 4.18; P, 1.20; W, 60.48.

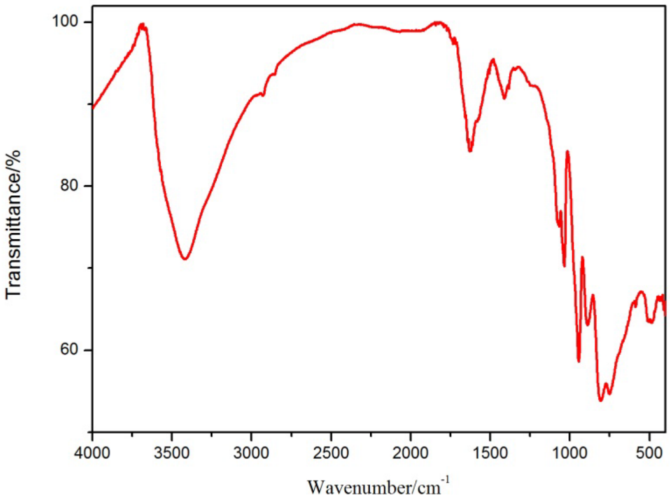
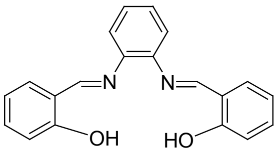


Fig. S2 FT-IR spectrum of $Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]{\cdot}25H_2O$.

Synthesis of N,N'-disalicylal-1,2-phenylenediamine: Salophen (Slp) ligand



The synthesis was according to reference 6. *o*-Phenylenediamine (108 mg, 1 mmol) and salicyaldehyde (256 mg, 2.1 mmol) were refluxed for 5 h at 78 °C in 100 mL of absolute ethanol in the presence of a few drops of acetic acid. The mixture turned orange immediately. The product was collected by filtration as orange crystals after the mixture evaporated to a smaller volume under reduced pressure. (77% yield). ^1H NMR: ($CDCl_3$) 6.90−7.39 (m, 12H), 8.64 (s, 2H), 13.07

(s, 2H).

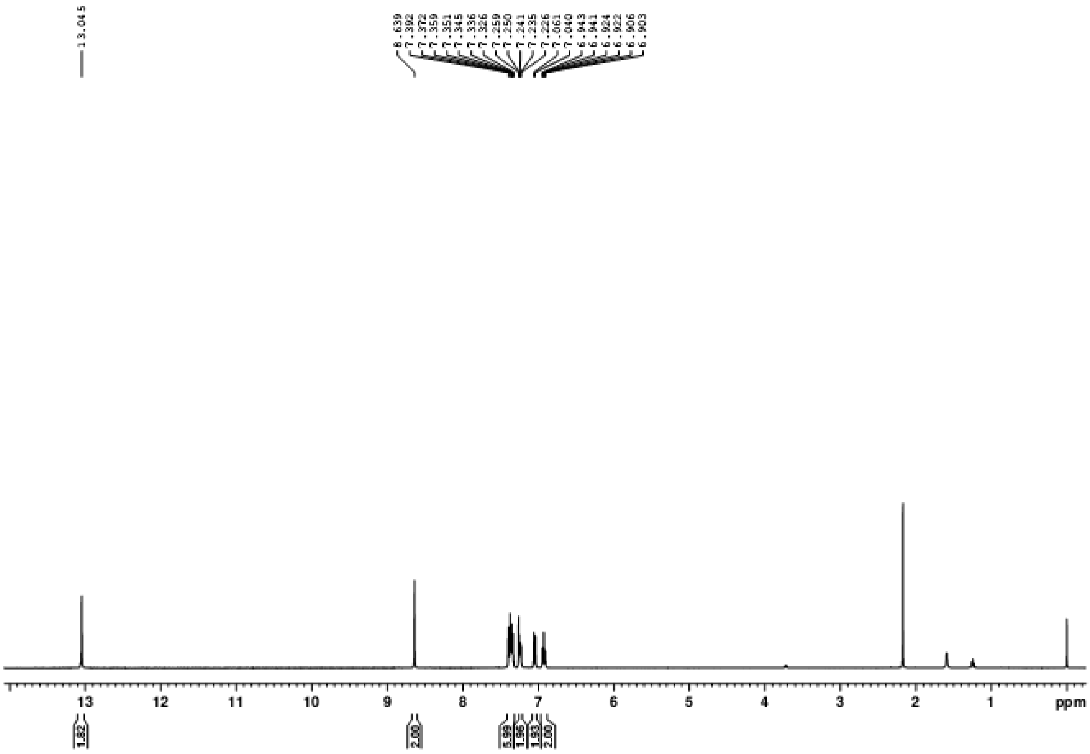
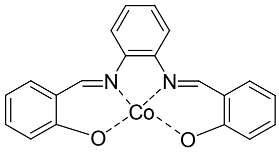


Fig. S3 ^{1}H NMR spectrum of **Slp.**

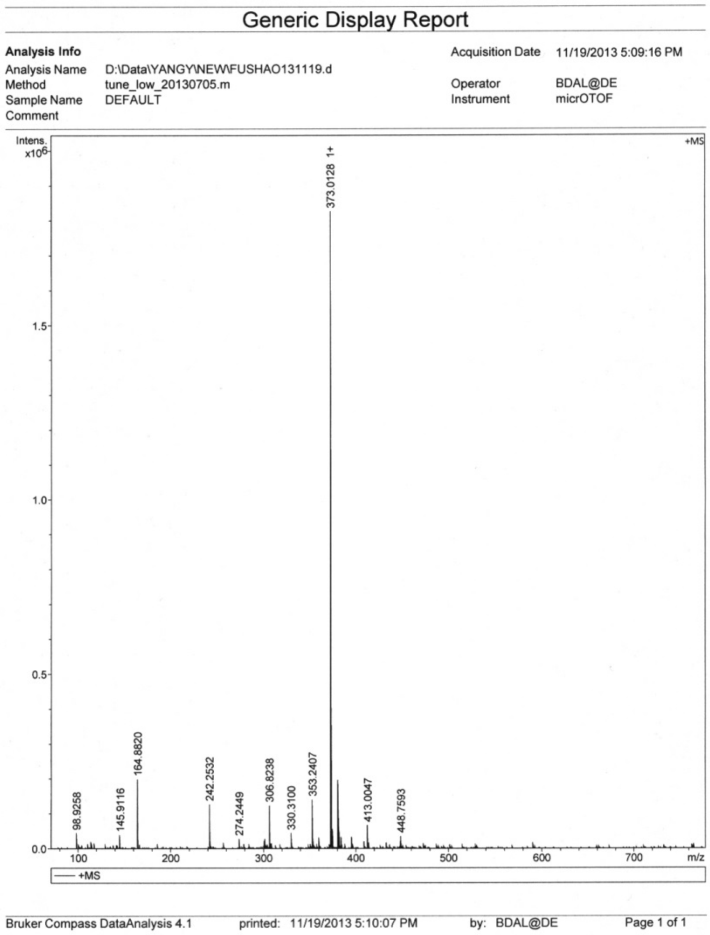
Synthesis of Co-Salophen (CoSlp)



CoSlp was synthesized according to reference 7. In a 50 mL round-bottom flask 240 mg (0.759 mmol) of Slp was dissolved in 18 mL of methanol. To this solution, 189 mg (0.76 mmol) of $Co(OAc)_2 \cdot 4H_2O$ was added and an immediate color change in the solution from pale orange to dark brown was observed. The mixture was stirred for 3 hours at room temperature, when diethyl ether (12 mL) were added to induce the formation of a precipitate; this was filtered and washed with diethyl ether and recrystallized from chloroform to obtain a brownish orange solid (70 % yield).

ESI-MS (H_2O, m/z): 373 $[\{Co(C_{20}H_{14}N_2O_2)\}H]^+$.

FT-IR (KBr, cm^{-1}): 1623 (s), 1581(s), 1543 (m), 1465 (m), 1312(s), 1194 (s), 756 (s), 573 (w), 470 (w). UV-Vis (phosphate buffer 20 mM at pH 7): λ_{max} = 447 nm (ε_{max} = 3300 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$).



Generic Display Report

Analysis Info

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Operator BDAL@DE
Instrument micrOTOF

Bruker Compass DataAnalysis 4.1 printed: 11/19/2013 5:10:07 PM by: BDAL@DE Page 1 of 1

Fig. S4 ESI/MS of **CoSlp** in H_2O.

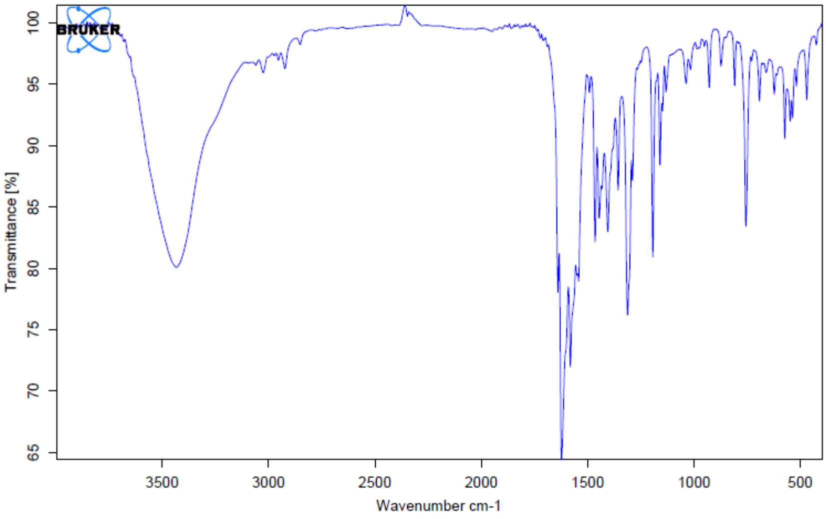


Fig. S5 FT-IR spectrum of **CoSlp.**

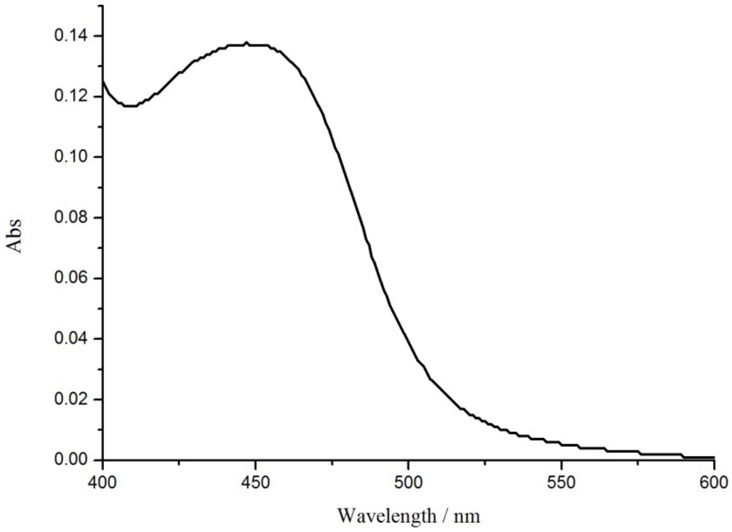
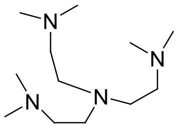


Fig. S6 UV-Vis spectra of a fresh 0.5 mM **CoSlp** solution in buffer phosphate 20 mM (pH 7).

Synthesis of Tris[2-(dimethylamino)ethyl]amine (Me_6-TREN)



Me_6-TREN was synthesized according to reference 8. Aqueous formaldehyde (25.0 mL, 330 mmol, 37 wt%) was added to a solution of 1.50 mL (10.9 mmol) of tren and 65 mL of acetic acid in acetonitrile (300 mL) and allowed to stir for 1 h. Subsequently, the reaction mixture was cooled to 0 ^{o}C and 5.0 g (132 mmol) of sodium borohydride slowly added. After being stirred for 48 h, all solvents were removed, and the residue was made strongly basic with 3 M aqueous sodium hydroxide, and extracted several times with DCM. The DCM extracts were combined, dried ($MgSO_4$), and the solvent removed. The residue was dissolved in pentane, filtered, and the filtrate reduced to dryness to give target compound as pale yellow oil (2.18 g, 95%). ^{1}H NMR ($CDCl_3$): δ 2.60 (m, 6H), 2.36 (m, 6H), 2.21 (s, 18H).

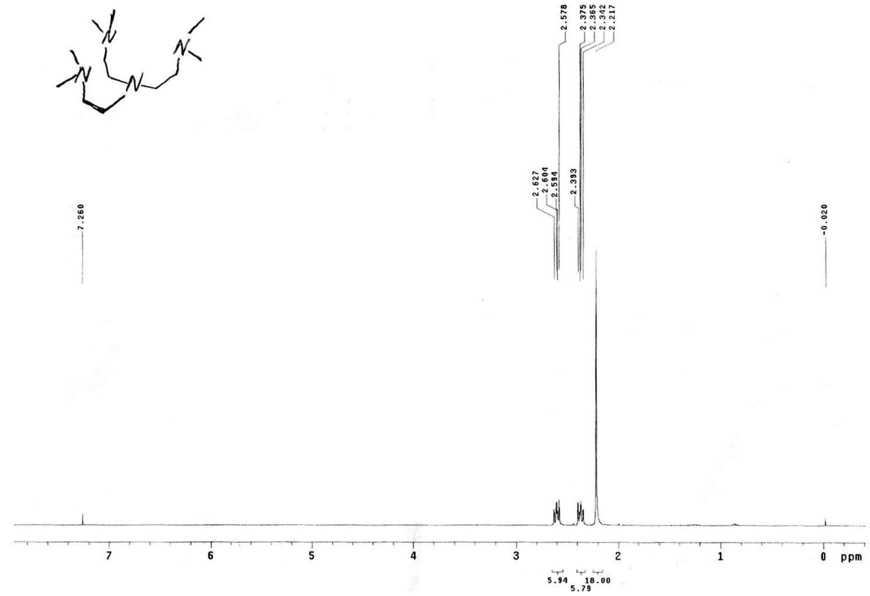
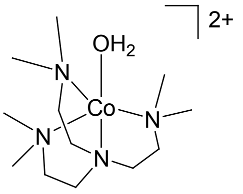


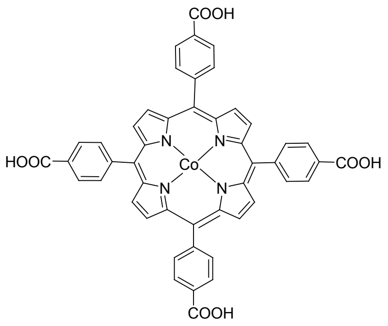
Fig. S7 ^{1}H NMR spectrum of **Me$_6$tren**.

Synthesis of [Co(Me$_6$tren)(OH$_2$)](ClO$_4$)$_2$



[Co(Me$_6$tren)(OH$_2$)](ClO$_4$)$_2$ was synthesized according to reference 9. To a hot solution of 2.5 mmol of Co(ClO$_4$)$_2$•6H$_2$O in 10mL of absolute ethanol was added slowly a solution of 2.5 mmol (0.57 g) of Me$_6$tren in 5 mL of ethanol. The perchlorate complex [Co(Me$_6$tren)](ClO$_4$)$_2$ separated from the reaction mixture to yield green solids, which was filtered and dried in Ar gas. The green crystalline solids were recrystallized from ethanol. Yield: 52%. ESI-MS in CH$_3$CN: *m*/*z* 388.2 for [Co(Me$_6$tren)(ClO$_4$)]$^+$; *m*/*z* 432.5 for [Co(Me$_6$tren)(OH$_2$)$_6$Cl)]$^+$.

Synthsis of CoTCPP ([[*meso*-tetra(4-carboxyphenyl)porphyrinato]cobalt(III)]Cl)·7H$_2$O



CoTCPP was synthesized according to reference 10. CoCl$_2$·6H$_2$O (90 mg, 0.378 mmol), and meso-Tetra(4-carboxyphenyl)porphine (TCPP)(90 mg, 0.11 mmol) were dissolved in DMSO (25 mL), followed by refluxing for 24 h. After the solution was cooled to room temperature, ca.75 mL 1 M HCl was added to the solution to cause deposition of the crude product as a purple solid, which was collected by filtration, washed with water, and dried in vacuo. This was redissolved in 0.1 M NaOH (ca. 20 mL) followed by addition of 1 M HCl (ca. 40 mL), which caused deposition of the product as a purple solid. This was collected by filtration and dried in vacuo. Yield: 79 mg (0.08 mmol, 80%). Elemental analysis of CoTCPP calcd. (%) for $C_{48}H_{28}N_4O_8ClCo{\cdot}7H_2O$: C 57.12, H 4.19, N 5.55. Found: C 56.21, H 3.83, N 5.46.

Oxygen Evolution Quantified by GC

Photocatalytic water oxidation was performed as follows. The desired concentration of catalyst (1.2–2.4 μM) was prepared by dissolving the appropriate amount of catalyst to a buffer solution (80 mM, pH 7.0–10.0 for borate buffer; 80 mM, pH 9.0 for phosphate and carbonate buffer) containing $[Ru(bpy)_3](ClO_4)_2$ (1.0mM) and $Na_2S_2O_8$ (5.0 mM). The above solution was deaerated by purging with Ar gas for 5 min in a flask (23 mL) sealed with a rubber septum (the total volume of reaction solution was 10 mL). The reaction was then started by irradiating the solution with a LED light source (light intensity 16 mW, beam diameter 2 cm) through a transmitting glass filter ($\lambda \geq 420$ nm) at room temperature. After each sampling time, 100 μL of Ar was injected into the flask and then the same volume of gas sample in the headspace of the flask was withdrawn by a SGE gas-tight syringe and analyzed by gas chromatography (GC). The O_2 in the sampled gas was separated by passing through a 2 m × 3 mm packed molecular sieve 5A column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD)(Shimadzu GC-9A). The total amount of evolved O_2 was calculated based on the concentration of O_2 in the headspace gas. Contamination of the head-space with air was corrected by measuring of N_2 concentration present in the head-space. The solution pH was monitored after the reaction by a METTLER TOLEDO FEP20 pH meter.

The quantum yields of O_2 evolution were determined for the photocatalytic water oxidation under the following conditions. A quartz flask containing a borate buffer solution (80 mM, pH 9.0, 10 mL) with **1** (1.6 μM), $[Ru(bpy)_3](ClO_4)_2$ (1 mM) and $Na_2S_2O_8$ (5 mM) was irradiated by an interference filtered (Asahi spectra SV 490) from a LED source ($420 < \lambda < 490$ nm) described above. The photon flux of the incident light was determined using a Ray virtual radiation actinometer (FU 100, silicon ray detector, light spectrum, 400 –700 nm; sensitivity, 10–50 μV $\mu mol^{-1} \cdot m^{-2} \cdot s^{-1}$), affording a value to be 1686 $\mu mol\ m^{-2} \cdot s^{-1}$.

Dark water oxidation reaction

A round-bottom flask with a total volume of 23 mL was used to hold 5 mL of aqueous $[Ru(bpy)_3]^{3+}$ (3.0 mM) solution. 5 mL of the catalyst **1** (3.2 μM) in buffered solution was held in a tube. Both containers were capped with a rubber stopper and deaerated by purging with Ar gas for 5 min. The catalyst solution in the tube was then quickly transferred into the round-bottom flask using a syringe. The method used for the detection of the produced O_2 was the same as that described in the photocatalytic water oxidation section.

^{18}O-Labeling Experiments

The 10.8 atom % $H_2{}^{18}O$ of borate buffer solution (pH 9.0, 80 mM) containing **1** (1.6 μM), $[Ru(bpy)_3]^{2+}$ (1 mM), $Na_2S_2O_8$ (5 mM) was deaerated with Helium gas before irradiation by LED light (λ ≥ 420 nm) in a quartz flask that is sealed with a rubber septum. After 10 min, 50 μL of gas sample was withdrawn using a gas-tight syringe for gas analysis. An Agilent Series 7890A model chromatograph interfaced with an Agilent Series 5975C model mass spectrometer operating in electron impact ionization mode was used to collect mass spectrometric data. The MS detector was tuned for maximum sensitivity (quadrupole temperature, 150 °C; ion source temperature, 230 °C). Single ion mode was used to scan for the ions m/z = 28, 32, 34, 36 with a dwell time of 100 ms, resulting in 8.3 cycles per second. Ions in the m/z range from 30 to 50 were also scanned in order to observe the abundance change of $^{16}O^{18}O$ and $^{18}O^{18}O$, which evolved from $H_2{}^{16}O$ and $H_2{}^{18}O$, respectively. The total flow rate into the spectrometer was limited to 0.6 $mL \cdot min^{-1}$. The GC was equipped with a molecular sieve column (30 m × 0.32 mm × 15 um), and the vaporizing chamber temperature and column temperature was set for 100 °C and 35 °C, respectively.

CO_2 detection Experiment

A buffer solution (pH 9.0, 10 mL) containing $Na_2S_2O_8$ (25 mM), $[Ru(bpy)_3](ClO_4)_2$ (0.25 mM) and cobalt catalysts (0–0.5 mM) was sealed in a flask with a rubber septum. The above solution was deaerated by purging with Ar gas for 5 min in a flask. The reaction was then started by irradiating the solution with a LED light source through a transmitting glass filter (λ ≥ 420 nm) at room temperature. The CO_2 in the sampled gas was separated by passing through a 2 m × 3 mm packed propak-Q column with an Ar carrier gas and quantified by a Thermal Conductivity Detector (TCD) (Shimadzu GC-9A).

Spectroscopic Measurements

Dynamic light scattering (DLS) measurements were carried out using a Zatasizer Nano 3600 instrument (Malvern Instruments Ltd.) for reaction solutions. UV-vis absorption spectra were recorded on a TU-1810 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.) equipped with a photomultiplier tube detector. ^{1}H NMR spectrum was recorded on an AVANCE III 400 MHz NMR spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. Chemical shifts were recorded in ppm (δ) relative to $CDCl_3$ on 7.26 for ^{1}H NMR. Electrospray ionization (ESI) spectrum was performed with an esquire 6000 ESI-ION TRAP (Bruker Daltonics) with ESI source.

Electrochemical Measurements

Cyclic voltammetry (CV) was recorded on a CHI600D electrochemical analyser with a glassy carbon, Ag/AgCl and Pt wire electrode as the working, reference and auxiliary electrodes, respectively, in buffer solutions (pH 9.0, 80 mM) containing 1 M KCl as a supporting electrolyte at room temperature with a scanning rate of 20 $mV\cdot s^{-1}$ or 100 $mV\cdot s^{-1}$.

Characterization of Particles

X-ray photoelectron spectra (XPS) were measured by ESCALAB250Xi with X-Ray monochromatisation. Scanning electron microscope (SEM) images of particles were observed by a Hitachi S-4800, with scanning voltage at 5000 V.

Table S1. TON, $TOF_{initial}$ and quantum yield of photocatalytic water oxidation catalyzed by different catalysts [a].

Catalyst	Representative reaction conditions	TON	TOF	$\Phi_{QY(initial)}$ %	Ref.
1	LED lamp ($\lambda \geq 420$ nm), 1.6 μM catalyst, 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (pH 9.0).	854	6.4 s^{-1}	38.6	This work
$Na_{10}[Co_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2]$	Xe lamp (420–470 nm), 5 μM catalyst, 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (pH 8.0).	224	No data	30	11
$K_{10.2}Na_{0.8}[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]$	Xe lamp (420–520 nm), 10 μM catalyst, 1.0 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 25 mM sodium borate buffer (pH 9.0).	80	0.1 s^{-1}	No data	12
$(NH_4)_3[CoMo_6O_{24}H_6]$	300 W Xe lamp (400–800 nm), 0.4 mM $[Ru(bpy)_3](NO_3)_2$, 3 mM $Na_2S_2O_8$, 0.1 M borate buffer solution (pH 8.0).	107 (Based on 3.6 μM catalyst)	0.11 s^{-1} (Based on 20 μM catalyst)	54	13
$(NH_4)_6[Co_2Mo_{10}O_{38}H_4]$	300 W Xe lamp (400–800 nm), 0.4 mM $[Ru(bpy)_3](NO_3)_2$, 3 mM $Na_2S_2O_8$, 0.1 M borate buffer solution (pH 8.0).	154 (Based on 1.9 μM catalyst)	0.16 s^{-1} (Based on 10 μM catalyst)	42	13
Trans-$[Co^{II}(qpy)(OH_2)_2](ClO_4)_2$	500 W mercury arc lamp (457 nm), 0.2 μM catalyst, 128 μM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 15 mM borate buffer solution (pH 8.0).	355 (Reaction time = 1.5 h)	No data	No data	14
$[Co^{II}(Me_6tren)(OH_2)](ClO_4)_2$	500 W Xe lamp ($\lambda > 420$ nm), 5.0 μM catalyst, 0.5 mM $[Ru(bpy)_3](ClO_4)_2$, 10 mM $Na_2S_2O_8$, 100 mM borate buffer solution (pH 9.0).	420 (Decomposed to $Co(OH)_x$)	No data	32	2
$[Co^{III}(Cp^*)(bpy)(OH_2)](PF_6)_2$	500 W Xe lamp ($\lambda > 420$ nm), 5.0 μM catalyst, 0.5 mM $[Ru(bpy)_3](ClO_4)_2$, 10 mM $Na_2S_2O_8$, 100 mM borate buffer solution (pH 9.0).	320 (Decomposed to $Co(OH)_x$)	No data	30	2
$Co^{III}_4O_4(OAc)_4$	250 W high power Arc lamp (450 nm),	40	0.02 s^{-1}	No data	15

$(py)_4$	41.5 μM catalyst, 0.5 mM $[Ru(bpy)_3]Cl_2$, 10.5 mM $Na_2S_2O_8$, HCO_3^- buffer (pH 7.0).				
$K_{10}H_2[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})_2]$	455 nm LED light (17 mW, beam diameter ~0.5 cm), 1.0 mM $[Ru(bpy)_3]Cl_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer with initial pH 8.0, total volume 2.0 mL.	60 (Based on 2 μM catalyst)	1 s^{-1}(the first 10 Seconds)	3.8	16
$Cs_9[(\gamma\text{-}PW_{10}O_{36})_2Ru_4O_5(OH)(H_2O)_4$	Xe lamp, 420–520 nm bandpass filter, 1.0 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 20 mM Na_2SiF_6 buffer pH 5.8, 5.1 μM catalyst total solution volume in each reaction, 8 mL.	120	0.13 s^{-1}	No data	17
$\alpha\text{-}K_6Na[\{Ru_3O_3(H_2O)Cl_2\}(SiW_9O_{34})$	LED lamp, 470 nm; 1 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, 50 μM catalyst, Na_2SiF_6 buffer pH 5.8(20 mM), total solution volume in each reaction:13 mL.	23	0.7 s^{-1}	No data	18
$\alpha\text{-}K_{11}Na_1[Co_4(H_2O)_2(SiW_9O_{34})_2]$	LED lamp, 470 nm; 1 mM $[Ru(bpy)_3]Cl_2$, 5 mM $Na_2S_2O_8$, Na_2SiF_6 buffer pH 5.8 (20 mM), total solution volume in each reaction: 13 mL.	24 (Based on 20μM catalyst)	0.4 s^{-1} (Based on 42μM catalyst)	No data	18
$Ru^{II}(hqc)(pic)_3$	A xenon lamp (500 W) with a λ > 400 nm filter, 10 mL of pH 7.2 phosphate buffer (20 mM), 0.55 mL of acetonitrile, 55.0 μM catalyst, 550 μM $[Ru(bpy)_3]^{2+}$, and $[S_2O_8^{2-}]$ = 10 mM.	< 5	No data	No data	19
	A xenon lamp (500 W) with a λ > 400 nm filter, 10 mL of pH 7.2 phosphate buffer (20 mM), 0.55 mL of acetonitrile, 55.0 μM catalyst, 550 μM $[Ru(bpy)_2(dcbpy)]^{2+}$, and $[S_2O_8^{2-}]$ = 10 mM.	42	No data	No data	19
	A xenon lamp (500 W) with a λ > 400 nm filter, 10 mL of pH 7.2 phosphate buffer (20 mM), 0.55 mL of acetonitrile, 55.0 μM catalyst, 550 μM $[Ru(bpy)(dcbpy)_2]^{2+}$, and $[S_2O_8^{2-}]$ = 10 mM.	61	No data	9	19
$Fe(mcp)Cl_2$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ =	194	No data	No data	20

	0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.				
$[Fe(bpy)_2Cl_2]Cl$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.	157	No data	No data	20
$[Fe(tpy)_2]Cl_2$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.	376	No data	No data	20
$[Fe(cyclen)Cl_2]Cl$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.	412	No data	No data	20
$Fe(tmc)Br_2$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.	364	No data	No data	20
$Fe(ClO_4)_3$	[Catalyst] = 1.0 mM, $[Ru(bpy)_3Cl_2]$ = 0.2 mM, $[Na_2S_2O_8]$ = 2 mM in 15 mM borate buffer (pH 8.5) at 23 ^oC, $\lambda > 420$ nm.	436	No data	No data	20
$Fe(BQEN)(OTf)_2$	A xenon lamp (500 W) with a $\lambda > 400$ nm filter, 5.0 μM catalyst, 0.25 mM $[Ru(bpy)_3]SO_4$, 5.0 mM $Na_2S_2O_8$, 100 mM sodium borate buffer (pH 9.0).	259	No data	No data	21
$Fe(BQCN)(OTf)_2$	A xenon lamp (500 W) with a $\lambda > 400$ nm filter, 5.0 μM catalyst, 0.25 mM $[Ru(bpy)_3]SO_4$, 5.0 mM $Na_2S_2O_8$, 100 mM sodium borate buffer (pH 9.0).	No data	No data	No data	21
$[NiL_3](ClO_4)_2$	$[Ru(bpy)_3](ClO_4)_2$ (0.12 mM), catalyst (0.6 μM), and $Na_2S_2O_8$ (2.5 mM) in 30 mM borate buffer (pH 8.0), T = 23 ^oC 500 W Xe lamp ($\lambda = 457$ nm).	855			22

[a] $TOF_{initial} = TON_{initial}$ /60 s, $TON_{initial}$ = Molar of oxygen produced in 1 minute /Molar of **1**, Φ_{QY}(quantum yield) = [(initial O_2 formation rate) / (photon flux)].

Table S2. TON, TOF$_{initial}$ thermal water oxidation catalyzed by different catalysts using $[Ru(bpy)_3](ClO_4)_3$ as oxidant.

Catalyst	$[Ru(bpy)_3](ClO_4)_3$ concentration (mM)	Yield (%)	TON	TOF$_{nitial}$ (s^{-1})	Ref.
1	1.5	83	194	2.0	This work
$Rb_8K_2[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]\cdot 25H_2O$	1.2	59			23
$Na_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$	1.5	67	78	>5	5
$K_{14}[(IrCl_4)KP_2W_{20}O_{72}]\bullet 23H_2O$	1.4	30			24
$K_{10}H_2[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})]\cdot 34H_2O$	1.0	42	1.3		16
$Fe(mcp)Cl_2$	0.75	9			20
$[Fe(bpy)_2Cl_2]Cl$	0.75	49	95	3.6	20
$[Fe(tpy)_2]Cl_2$	0.75	16	19	1.5	20
$[Fe(cyclen)Cl_2]Cl$	0.75	54	108	4.4	20
$Fe(tmc)Br_2$	0.75	48	93	4.6	20
$Fe(ClO_4)_3$	0.75	71	147	9.6	20

Table S3. Water oxidation catalyzed without **1** or $Ru(bpy)_3^{2+}$ or persulfate

Entry	$[Ru(bpy)_3](ClO_4)_2$ (mM)	$Na_2S_2O_8$ (mM)	Catalyst (μM)	O_2 (μmol)
1	1	5	0	0.8
2	1	0	1.6	0
3	0	5	1.6	0

Conditions: LED lamp (≥ 420 nm), 80 mM sodium borate buffer (initial pH 9.0), total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

Table S4. GC data

[cat.] /µM	No. of experiment	area O_2	$n(O_2)$/ µmol
0	(1)	1294.852	0.85
1.2	(1)	13056.550	12.61
	(2)	12946.661	12.50
	(3)	13116.787	12.67
1.6	(1)	14957.000	14.51
	(2)	14936.600	14.49
	(3)	15010.600	14.56
2.0	(1)	15040.051	14.59
	(2)	15166.834	14.72
	(3)	14846.270	14.40
2.4	(1)	15478.300	15.03
	(2)	15657.123	15.21
	(3)	15176.986	14.73

Head space of reaction flask is 11.5 mL. Temperature: 291 K. 1 mol of gas is around 26.30 L at 291 K. Sample volume for GC analysis: 100 µL. Retention time of the O_2 peak: 1.39 min. Conditions: LED lamp (≥ 420 nm), 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0), total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

Table S5. XPS binding energy values for compound containing cobalt

Complexes based on cobalt	Spectral region	Binding energy (eV)	Reference
SalenCo(II)	Co2p3/2	780.5, 785.9, 795.7	25
CoO	$Co2p_{3/2}$	780.5	26
	$Co2p_{1/2}$	796.3	
$Co(OH)_2$	Co2p3/2	781.3	26
	Co2p1/2	797.3	
CoOOH	Co2p3/2	786.5	26
	Co2p1/2	802.4	
$Co(OH)_3$ nanobelts	Co2p3/2	785.7	26
	Co2p1/2	801.9	

Table S6. Photocatalytic water oxidation catalyzed by Salen Co (**1**) and other cobalt oxide/hydroxide [a]

Entry	Catalyst	Concentration	O_2 yield (%)
1	Salen Co (**1**)	1.6 μmol/L	54.6
2	Precipitate from **1**	1.43×10^{-4} g/L	40.9
3	Co_3O_4	1.28×10^{-4} g/L	4.3
4	Co_2O_3	1.33×10^{-4} g/L	4.5
5	$Co(OH)_2$	1.49×10^{-4} g/L	31.9

Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

All compounds contained the same amount of cobalt atoms (1.6×10^{-8} mol).

Table S7. CO_2 evolution under different photocatalytic conditions

Salen Co (mM)	$[Ru(bpy)_3](ClO_4)_2$ (mM)	$Na_2S_2O_8$ (mM)	Reaction time (min)	CO_2 amounts (μmol)
no	0.25	25	30	0.8
0.5	0.25	25	30	7.5

Conditions: LED lamp (≥ 420 nm), 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

Table S8. Photocatalytic water oxidation catalyzed using **1** and recovered catalyst from **1**(true catalytic active species) [a]

catalyst	catalyst Concentration(μM)	TON[b]	O_2 yield (%)[c]
Salen Co(Ⅱ) (**1**)	1.6	854	54.6
Particles from **1**[b]	1.43×10^{-4} g/L		40.9

[a] Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

[b] The preparation of particles derived from salen Co: a solution containing 0.2 mM **1**, 2.4 mM of $[Ru(bpy)_3](ClO_4)_2$ and 5.0 mM of $Na_2S_2O_8$ in a borate buffer (80 mM) at pH 9.0 was irradiated under visible light for 6 min at room temperature. Solid precipitates were obtained after

irradiation.

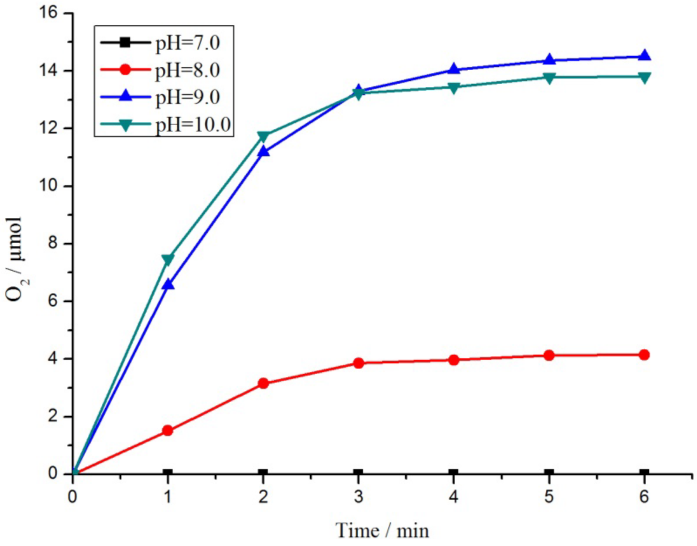


Fig. S8 Kinetics of O_2 formation in the photocatalytic system under various pH conditions (pH = 9.0, 80 mM NaBi, blue; pH = 10.0, 80 mM NaBi, green; pH = 8.0, 80 mM NaBi, red; pH = 7.0, 80 mM NaBi, black).

Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.6 μM salen Co, 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$; total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

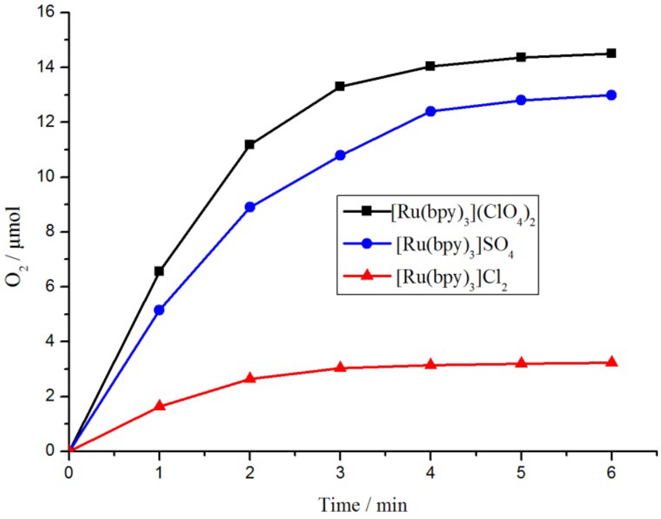


Fig. S9 Kinetics of O_2 formation in the photocatalytic system using different photosensitizers ($[Ru(bpy)_3](ClO_4)_2$, black; $[Ru(bpy)_3]SO_4$, blue; $[Ru(bpy)_3]Cl_2$, red).

Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.6 μM salen Co; 1.0 mM photosensitizer, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

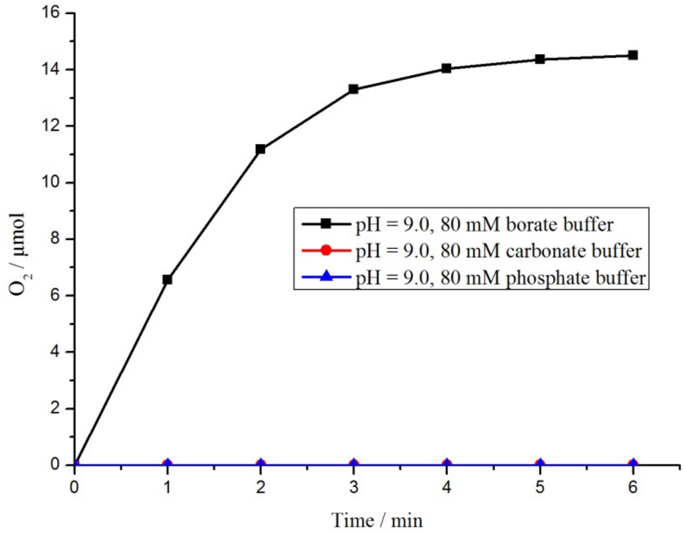


Fig. S10 Kinetics of O_2 formation in the photocatalytic system using different kinds of buffers (pH = 9.0, 80 mM borate buffer, black; pH = 9.0, 80 mM carbonate buffer, red; pH = 9.0, 80 mM phosphate buffer, blue).

Conditions: LED lamp (≥ 420 nm), 15.8 mW; catalyst 1.6 μM; 1.0 mM [Ru(bpy)$_3$](ClO$_4$)$_2$, 5.0 mM $Na_2S_2O_8$, 80 mM buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

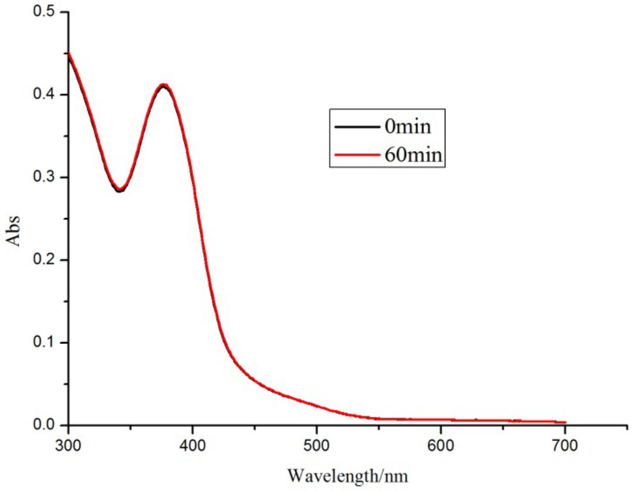


Fig. S11 Time-dependent UV-vis absorption spectra of **1** (75.0 μM) over 60 min, in borate buffer solution (80 mM, pH 9.0).

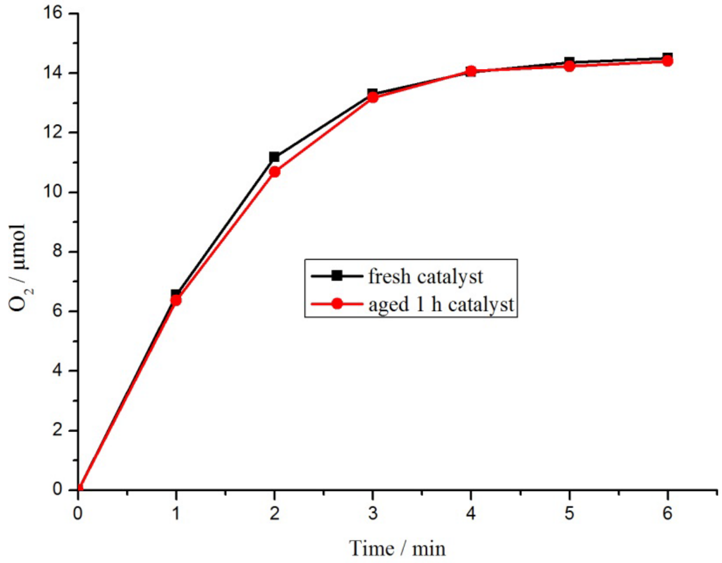


Fig. S12 Kinetics of O_2 formation in the photocatalytic system using fresh **1** (black) and **1** aged for 1 h. Conditions: LED lamp (≥ 420 nm), 15.8 mW; catalyst 1.6μM; 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

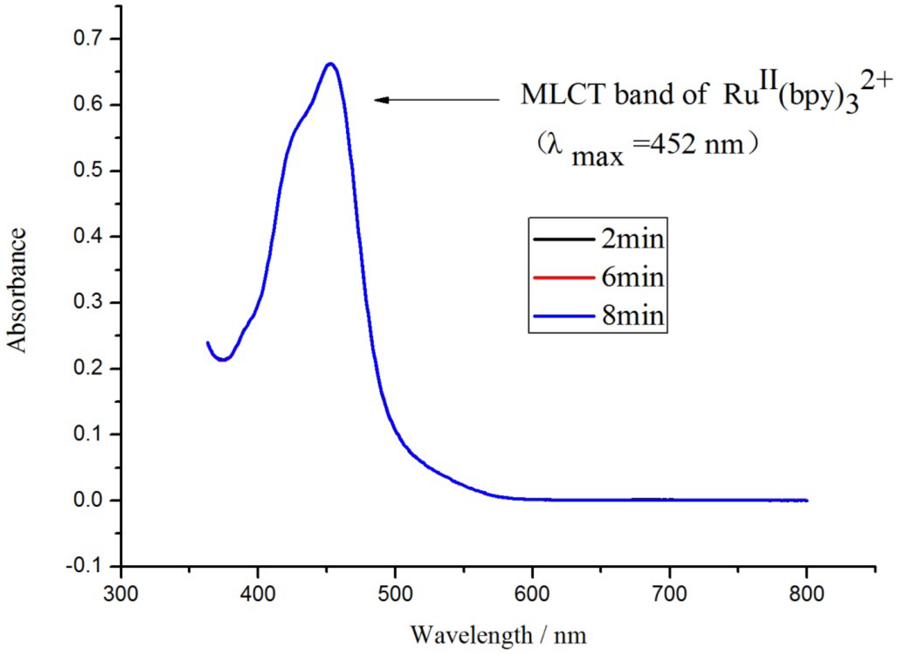


Fig. S13 Time-dependent UV-vis absorption spectra after mixing a 5 μM of **1** in borate buffer solution and a 50 μM $[Ru(bpy)_3]^{3+}$ aqueous solution.

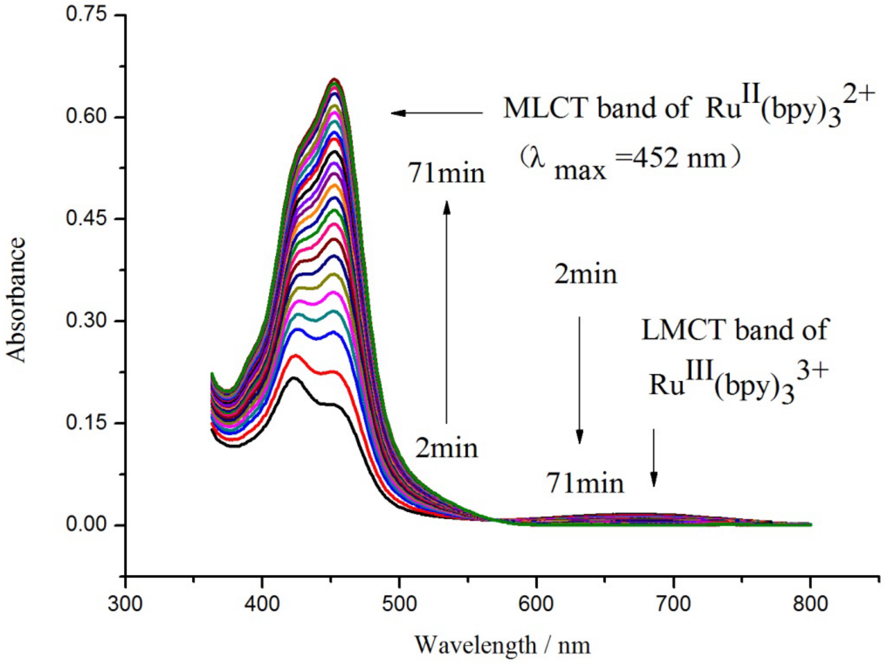


Fig. S14 Time-dependent UV-vis absorption spectra of a 50 μM $[Ru(bpy)_3]^{3+}$ aqueous solution.

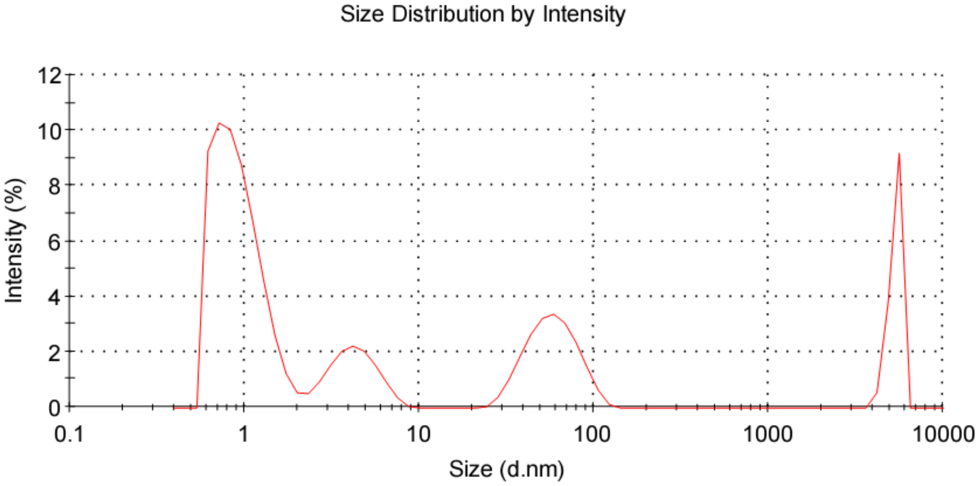


Fig. S15 DLS measurement of a water oxidation reaction solution after 6 min of irradiation shows that different sizes of particles exist in photocatalytic water oxidation system.

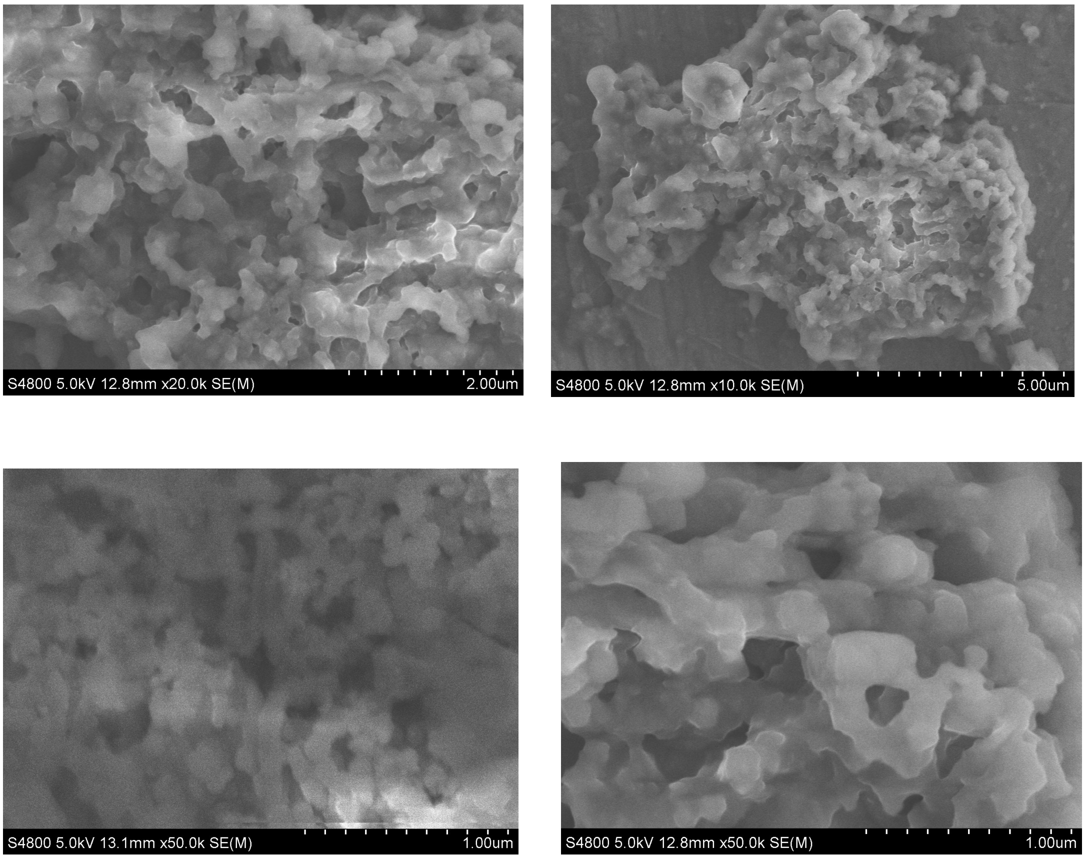


Fig. S16 SEM images of particles derived from **1**.

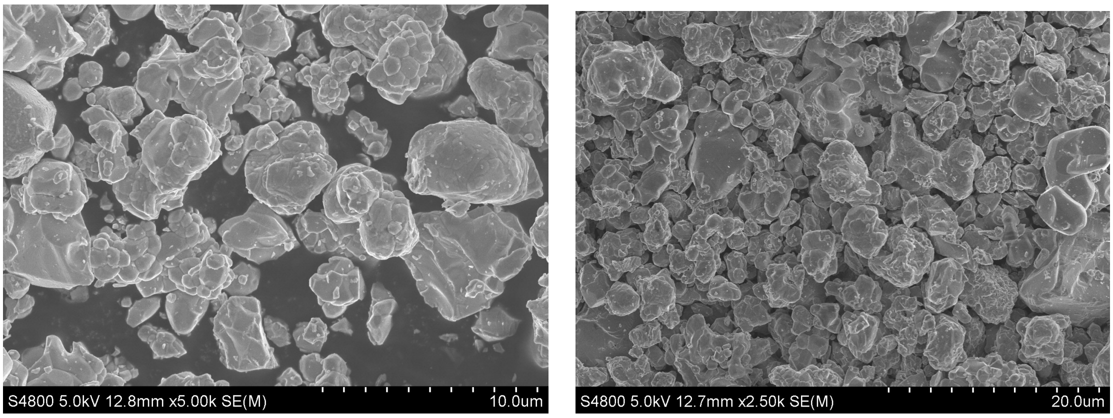
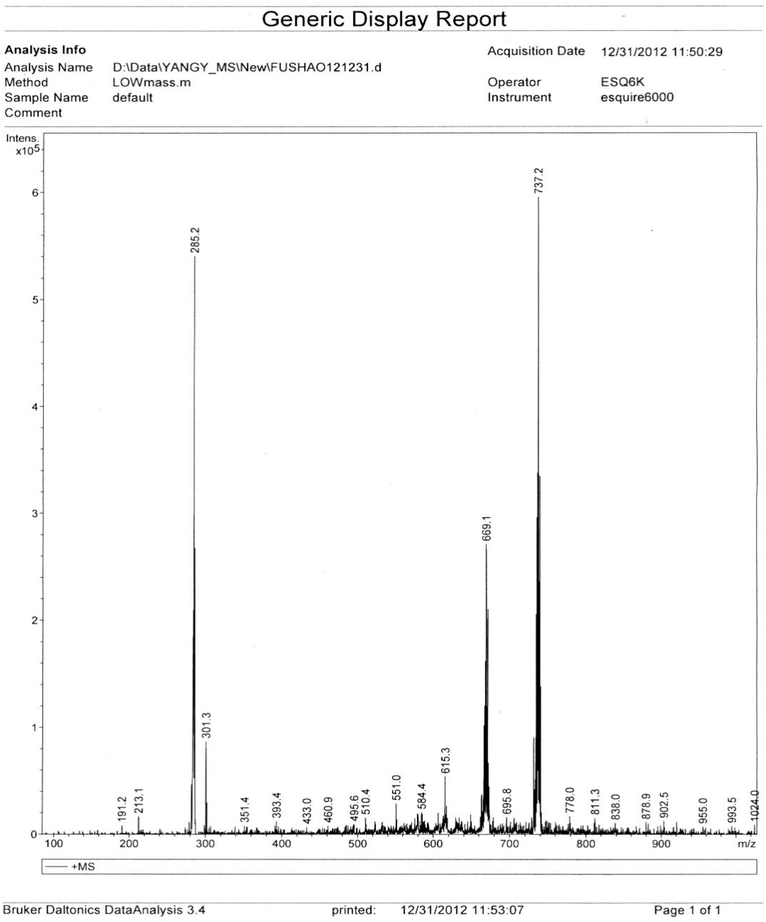


Fig. S17 SEM images of Co_3O_4.



Generic Display Report

Analysis Info		Acquisition Date	12/31/2012 11:50:29
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Sample Name	default	Instrument	esquire6000
Comment			

Bruker Daltonics DataAnalysis 3.4 printed: 12/31/2012 11:53:07 Page 1 of 1

Fig. S18 ESI/MS of a CH_2Cl_2 solution that was used to extract precipitate derived from **1.** Water oxidation conditions: 0.2 mM **1**, 2.4 mM of $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM of $Na_2S_2O_8$, 80 mM borate buffer (pH = 9.0); irradiation with LED lamp (≥ 420 nm) for 6 min at 25 ºC. The precipitate formed during the illumination was separated from the reaction solution by centrifugation. Then, CH_2Cl_2 was used to extract the above solid.

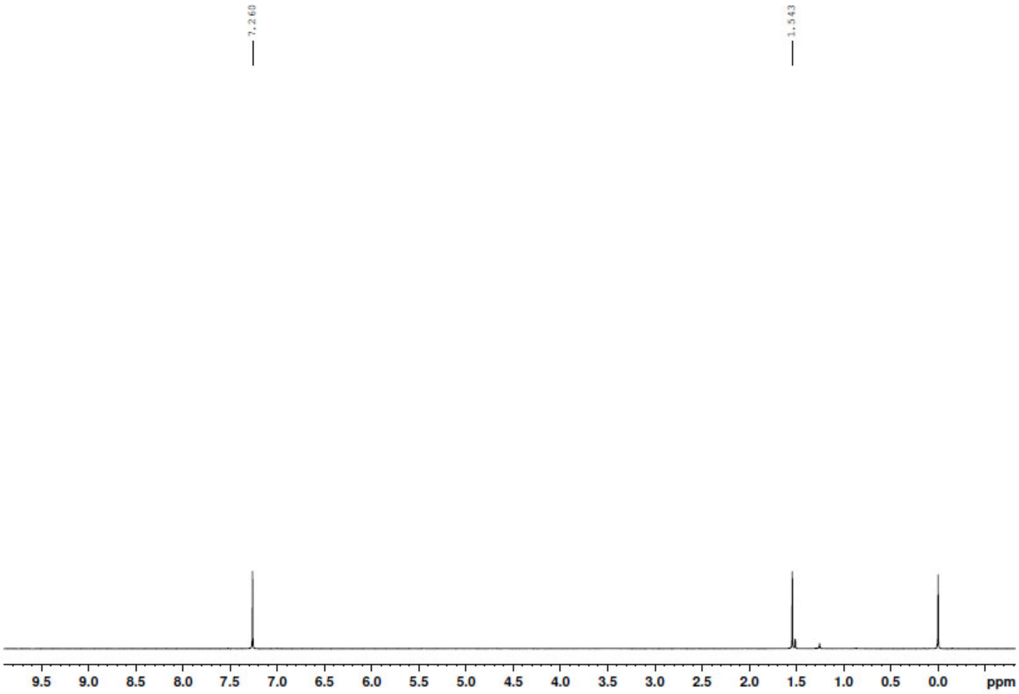
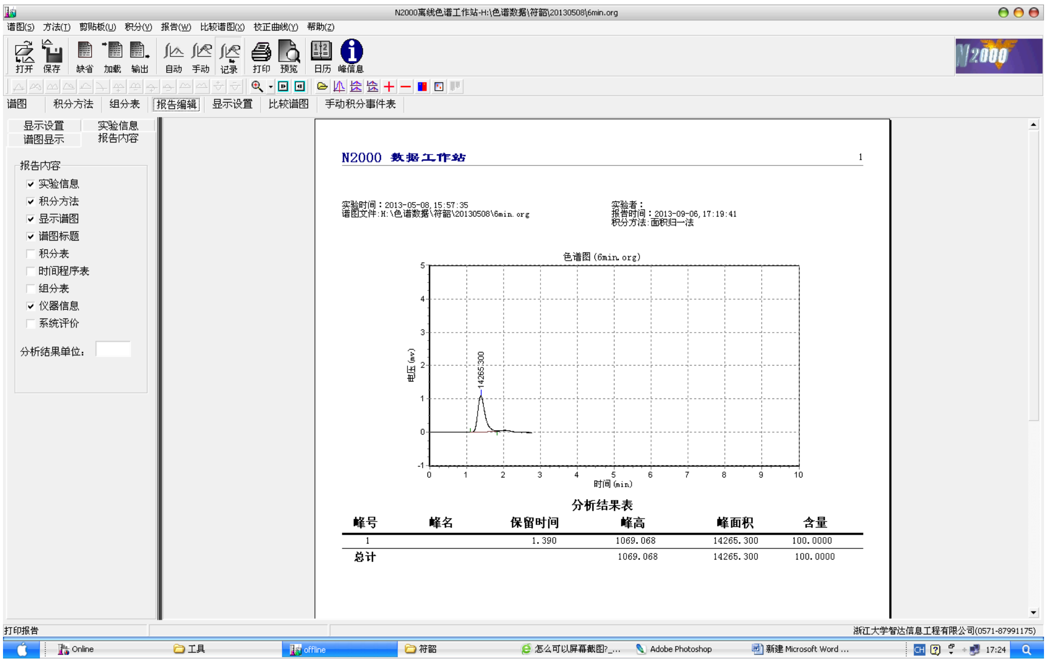


Fig. S19 ^{1}H NMR spectrum of a $CDCl_3$ solution that was used to extract precipitate derived from **1.** Water oxidation conditions: 0.2 mM **1**, 2.4 mM of $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM of $Na_2S_2O_8$, 80 mM borate buffer (pH = 9.0); irradiation with LED lamp (≥ 420 nm) for 6 min at 25 ºC. Some precipitates were formed after illumination, then separated from the reaction solution by centrifugation and washed by pure water repeatedly. The obtained solid then was dried up overnight at 50 ºC. $CDCl_3$ was used to extract the above precipitates and then was analyzed by HNMR.

Note: 0, 1.543, 7.260 ppm are the ^{1}H NMR signals of tetramethylsilane (TMS), H_2O and $CHCl_3$, respectively.



报告内容

☑ 实验信息
☑ 积分方法
☑ 显示谱图
☑ 谱图标题
☐ 积分表
☐ 时间程序表
☐ 组分表
☑ 仪器信息
☐ 系统评价

分析结果单位：

N2000 数据工作站 1

实验时间：2013-05-08, 15:57:35
谱图文件：H:\色谱数据\符韶\20130508\6min.org

实验者：
报告时间：2013-09-06, 17:19:41
积分方法：面积归一法

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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总计			1069.068	14265.300	100.0000

Fig. S20 Typical GC traces of a head space in the reaction of water oxidation with **1**.

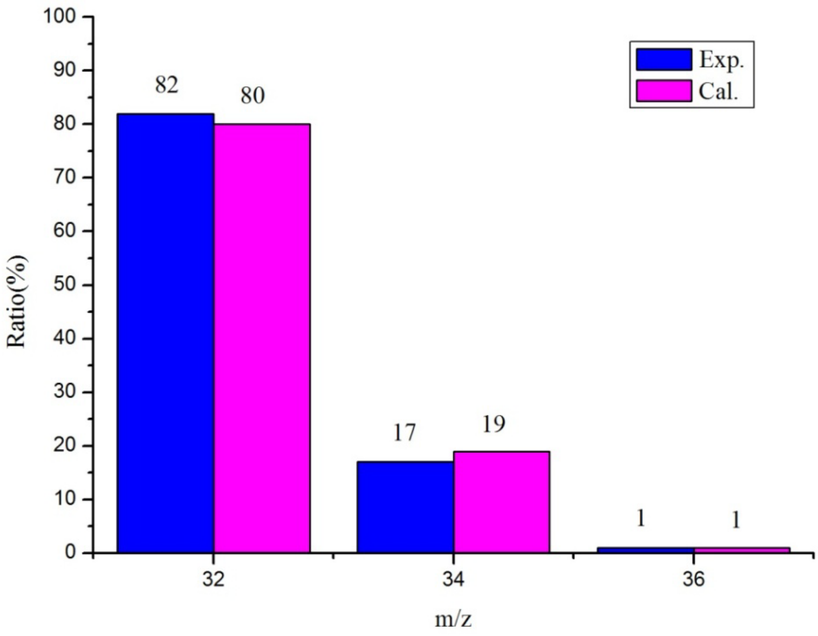


Fig. S21 Observed and theoretical relative abundances of ^{18}O-labeled and unlabeled oxygen evolved during the photocatalytic oxidation of a buffer solution (5.0 mL) prepared with $H_2{}^{18}O$-enriched water (10.8% $H_2{}^{18}O$) containing **1** (1.6 μM), $[Ru(bpy)_3]^{2+}$ (1 mM) and $Na_2S_2O_8$ (5 mM) (blue, detected mass intensity; magenta, calculated values assuming that evolved O_2 results exclusively from water).

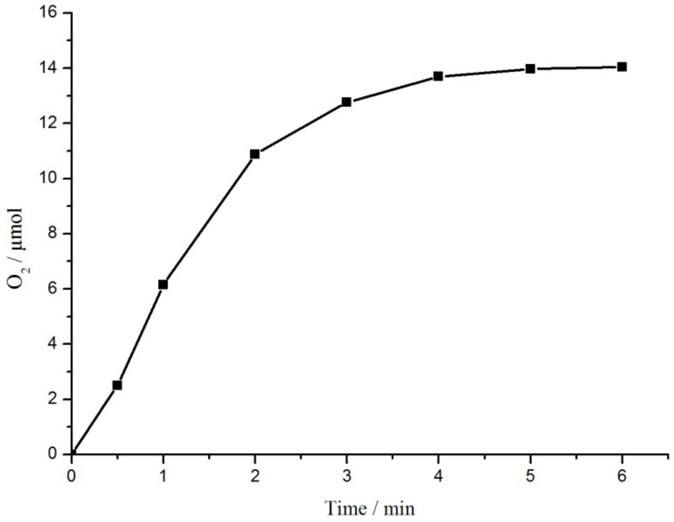


Fig. S22 Kinetics of O_2 formation in the photocatalytic system using salen Co (1.6 μM) , Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.0 mM [Ru(bpy)$_3$](ClO$_4$)$_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer. An induction period can be seen in 1 minute reaction.

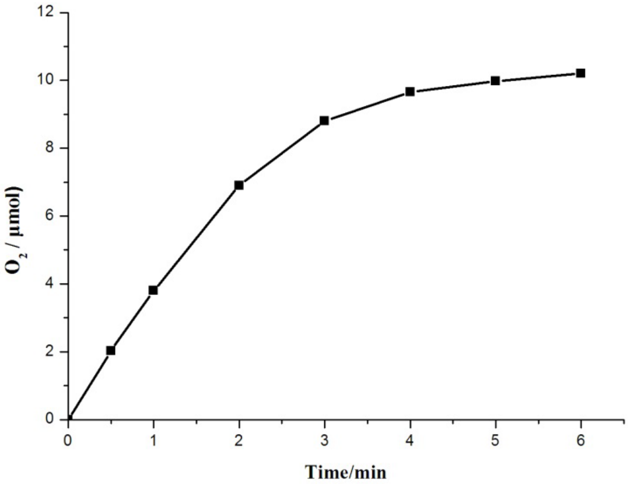


Fig. S23 Kinetics of O_2 formation in the photocatalytic system using precipitate derived from salen Co. Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.43×10^{-4} g/L catalyst, 1.0 mM [Ru(bpy)$_3$](ClO$_4$)$_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction solution volume is 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

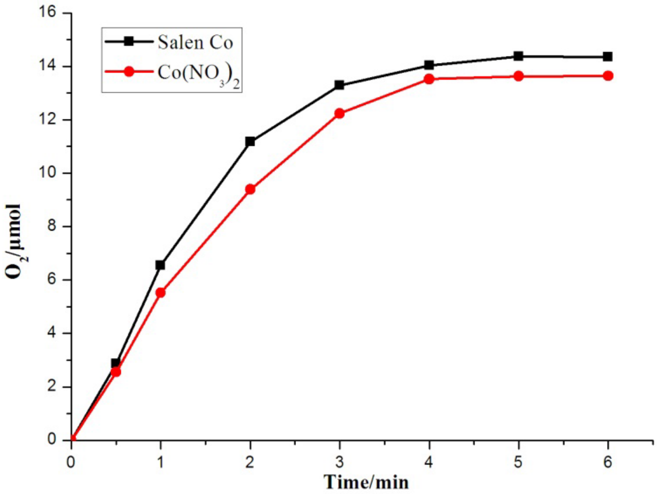
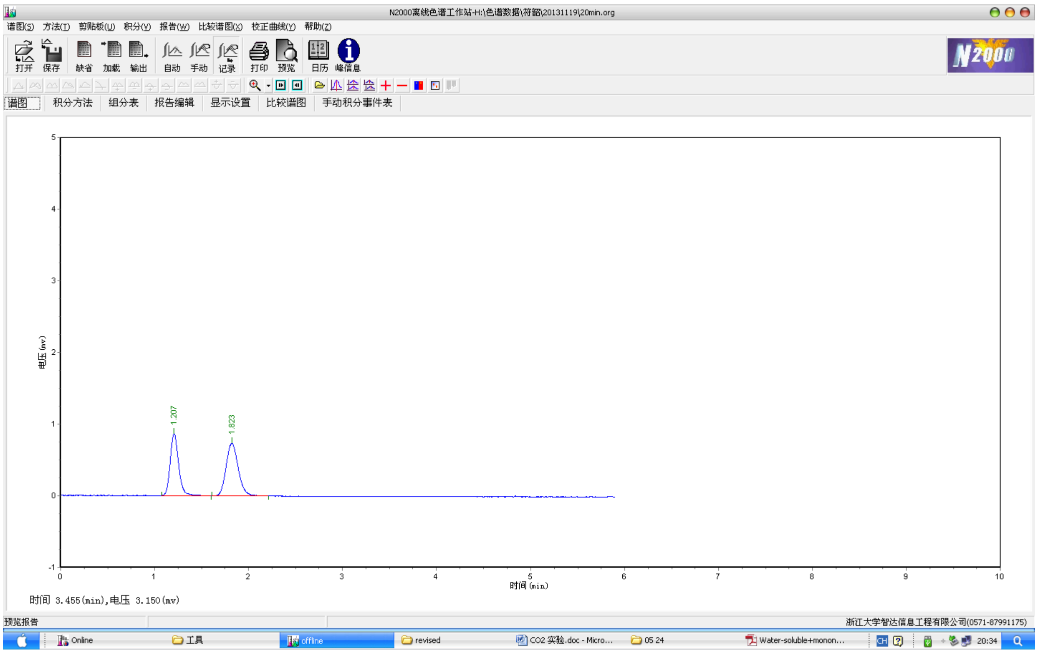


Fig. S24 Kinetics of O_2 formation in the photocatalytic system using salen Co and $Co(NO_3)_2$. Conditions: LED lamp (≥ 420 nm), 15.8 mW; 1.6 μM catalyst, 1.0 mM $[Ru(bpy)_3](ClO_4)_2$, 5.0 mM $Na_2S_2O_8$, 80 mM sodium borate buffer (initial pH 9.0); total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.



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时间 3.455(min),电压 3.150(mv)

Fig. S25 CO_2 evolution under photoirradiation for 30 min. Conditions: LED lamp (≥ 420 nm), 80 mM sodium borate buffer (initial pH 9.0); $[Ru(bpy)_3]$ $(ClO_4)_2$ (0.25 mM), $Na_2S_2O_8$ (25 mM) and salen Co (0.5 mM) ; total reaction volume 10 mL; overall volume ~23 mL; vigorous agitation using a magnetic stirrer.

Note: The peaks with retention times of 1.2 min and 1.8 min represent N_2 and CO_2, respectively.

References

1. D. Hong, S. Mandal, Y. Yamada, Y.-M. Lee, W. Nam, A. Llobet and S. Fukuzumi, *Inorg. chem.*, 2013, **52**, 9522-9531.
2. D. Hong, J. Jung, J. Park, Y. Yamada, T. Suenobu, Y.-M. Lee, W. Nam and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 7606-7616.
3. P. K. Ghosh, B. S. Brunschwig, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1984, **106**, 4772-4783.
4. F. Song, Y. Ding, B. Ma, C. Wang, Q. Wang, X. Du, S. Fu and J. Song, *Energy Environ. Sci.*, 2013, **6**, 1170-1184.
5. Q. Yin, J. M. Tan, C. Besson, Y. V. Geletii, D. G. Musaev, A. E. Kuznetsov, Z. Luo, K. I. Hardcastle and C. L. Hill, *Science*, 2010, **328**, 342-345.
6. J. Cheng, K. Wei, X. Ma, X. Zhou and H. Xiang, *J. Phys.Chem. C*, 2013, **117**, 16552-16563.
7. M. N. Erica Pizzolato, Bianca Posocco, Valentin, MarilenaáDi, Marcella Bonchio, Franco Scandola and Andrea Sartorel, *Chem. Commun.*, 2013, **49**, 9941-9943.
8. G. J. Britovsek, J. England and A. J. White, *Inorg.chem.*, 2005, **44**, 8125-8134.
9. M. Ciampolini and N. Nardi, *Inorg.chem.*, 1966, **5**, 41-44.
10. T. Nakazono, A. R. Parent and K. Sakai, *Chem. Commun.*, 2013, **49**, 6325-6327.
11. Z. Huang, Z. Luo, Y. V. Geletii, J. W. Vickers, Q. Yin, D. Wu, Y. Hou, Y. Ding, J. Song, D. G. Musaev, C. L. Hill and T. Lian, *J. Am. Chem. Soc.*, 2011, **133**, 2068-2071.
12. G. Zhu, Y. V. Geletii, P. Kogerler, H. Schilder, J. Song, S. Lense, C. Zhao, K. I. Hardcastle, D. G. Musaev and C. L. Hill, *Dalton Trans.*, 2012, **41**, 2084-2090.
13. S. Tanaka, M. Annaka and K. Sakai, *Chem. Commun.*, 2012, **48**, 1653-1655.
14. C.-F. Leung, S.-M. Ng, C.-C. Ko, W.-L. Man, J. Wu, L. Chen and T.-C. Lau, *Energy Environ. Sci.*, 2012, **5**, 7903-7907.
15. N. S. McCool, D. M. Robinson, J. E. Sheats and G. C. Dismukes, *J. Am. Chem. Soc.*, 2011, **133**, 11446-11449.
16. G. Zhu, E. N. Glass, C. Zhao, H. Lv, J. W. Vickers, I. Geletii, D. G. Musaev, J. Song and C. L. Hill, *Dalton Trans.*, 2012, **41**, 13043-13049.

17. C. Besson, Z. Huang, Y. V. Geletii, S. Lense, K. I. Hardcastle, D. G. Musaev, T. Lian, A. Proust and C. L. Hill, *Chem. Commun.*, 2010, **46**, 2784-2786.

18. P. E. Car, M. Guttentag, K. K. Baldridge, R. Alberto and G. R. Patzke, *Green Chem.*, 2012.

19. L. Tong, Y. Wang, L. Duan, Y. Xu, X. Cheng, A. Fischer, M. r. S. Ahlquist and L. Sun, *Inorg. Chem.*, 2012, **51**, 3388-3398.

20. G. Chen, L. Chen, S. M. Ng, W. L. Man and T. C. Lau, *Angew. Chem. Int. Ed.*, 2013, **52**, 1789-1791.

21. D. Hong, S. Mandal, Y. Yamada, Y. M. Lee, W. Nam, A. Llobet and S. Fukuzumi, *Inorg. Chem.*, 2013.

22. G. Chen, L. Chen, S. M. Ng and T. C. Lau, *ChemSusChem*, 2013, **10.1002/cssc.201300561**.

23. Y. V. Geletii, B. Botar, P. Kogerler, D. A. Hillesheim, D. G. Musaev and C. L. Hill, *Angew. Chem., Int. Ed.*, 2008, **47**, 3896-3899.

24. R. Cao, H. Ma, Y. V. Geletii, K. I. Hardcastle and C. L. Hill, *Inorg. Chem.*, 2009, **48**, 5596-5598.

25. I. Bar-Nahum, H. Cohen and R. Neumann, *Inorg. chem.*, 2003, **42**, 3677-3684.

26. J. Yang, H. Hyodo, K. Kimura and T. Sasaki, *Nanotechnology*, 2010, **21**, 045605.