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Supporting Information

A Carbon-Free Polyoxometalate Molecular Catalyst with Cobalt-Arsenic Core for Visible Light-Driven Water Oxidation

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Section 1 Survey of WOCs with quasi-cubane- and cubane-type cores

Catalysts	ligands	cubane-type topologies	TON ^{[b}]	$TOF^{[c}]$ [s ⁻¹]	Ref
$[\{Ru_4O_4(OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$	$\gamma\text{-}SiW_{10}O_{36}$	Ru ₄ O ₄ core	500	0.1	1
$[\mathrm{Co}^{\mathrm{III}_4}\mathrm{O}_4(\mathrm{OAc})_4(\mathrm{py})_4]$	py; OAc	Co ^{III} ₄ O ₄ cubane	40	0.02	2
$[Co^{III}_4O_4(OAc)_4(p-C_5H_4X)_4]$ (X = H, Me, t-Bu, OMe, Br, COOMe, CN)	<i>p</i> -C ₅ H ₄ X; OAc	Co ^{III} ₄ O ₄ cubane	140	0.07	3
$[Co^{II}_4(hmp)_4(\mu\text{-OAc})_2(\mu_2\text{-OAc})_2(H_2O)_2]$	hmp; OAc	Co ^{II} ₄ O ₄ cubane	40	7	4
$[Co_{3}Ln(hmp)_{4}(OAc)_{5}H_{2}O]$ $(Ln = Ho, Er, Tm, Yb)$	hmp; OAc	Co ^{II} ₃ Ln cubane	160	9	5
$Mn^{III}_{3}Mn^{IV}O_{3}(CH_{3}COO)_{3}(SiW_{9}O_{34})]^{6-}$	α-SiW ₉ O ₃₄ ; OAc	Mn ^{III} ₃ Mn ^{IV} O ₃ quasi- cubane	5	-	6
$[Mn_4V_4O_{17}(OAc)_3]^{3-}$	[V ₄ O ₁₃] ⁶⁻ ; OAc	Mn ₄ O ₄ cubane	1150	1.75	7
$[\{Co_4(OH)_3(PO_4)\}_4(SiW_9O_{34})_4]^{32-}$	α-SiW ₉ O ₃₄ ; PO ₄ ³⁻	Co ^{II} ₄ O ₄ cubane	44.5	0.053	8
$[(SiW_9O_{34})_2Co_8(OH)_6(H_2O)_2(CO_3)_3]^{16-}$	α-SiW ₉ O ₃₄ ; CO ₃ ²⁻	$Co^{II}_4O_3$ quasi- cubane (double)	1436	10	9
$[Ni_{12}(OH)_9(CO_3)_3(PO_4)(SiW_9O_{34})_3]^{24-}$	α-SiW ₉ O ₃₄ ; PO ₄ ³⁻ ; CO3 ²⁻	Ni ^{II} ₃ O ₄ quasi- cubane	128.2	0.2	10
$[Ni_{13}(H_2O)_3(OH)_9(PO_4)_4(SiW_9O_{34})_3]^{25-}$	α-SiW ₉ O ₃₄ ; PO ₄ ³⁻	${\rm Ni}^{{\rm II}}_4{\rm O}_4$ cubane	147.6	0.25	10
$Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-1}$	α-SiW ₉ O ₃₄ ; PO ₄ ³⁻ ; CO ₃ ²⁻	Ni ^{II} ₄ O ₄ cubane (double)	204.5	0.34	10
1 ^[a]	α-SiW ₉ O ₃₄ ; AsO ₃ ²⁻	Co ^{II} ₇ O ₆ "fused" double-quasi-cubane	115.2	0.14	this work
PS II	OAc; imidazole; amino acid residues	CaMn ₄ O ₅ cubane	107	500	11

Table S1. Survey of WOCs with quasi-cubane- and cubane-type cores

[a] Conditions: 300W Xe lamp equipped with a long-pass filter (420 nm cutoff); catalysts concentration (1 μ M), [Ru(bpy)₃]²⁺ (1.0 mM), Na₂S₂O₈ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5 × 10³ rpm). [b] TON = mol of O₂/mol of catalyst. [c] TOF = mol of O₂/(mol of catalyst × 300 s).

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Section 2 Structures of 1

Synthesis of 1

CoCl₂·6H₂O (0.25 g, 1.05 mmol) was dissolved in 40 mL of distilled water. Na₁₀[A- α -SiW₉O₃₄]·18H₂O (1.18 g, 0.40 mmol) was added, and the mixture was stirred until a clear, purple solution was obtained. NaAsO₂ (0.10 g, 0.77 mmol) was then added, while a pH of 8.0 was maintained with 2.0 M HCl (aq). The resulting solution was stirred for 3 h at room temperature, and then filtered. The filtrate was kept in a 50 mL beaker to allow slow evaporation at room temperature. After five weeks, light-violet crystals suitable for X-ray crystallography were obtained, washed with cold water, and air-dried to give 120 mg of **1** (13.4% yield base on Co). IR (KBr disk ν /cm⁻¹): 3431(w), 1615(s), 937(m), 887(s), 812(w), 764(w). Elemental anal. Calcd (%) (found): Co 6.90 (7.05), Na 4.61 (4.53), W 55.32 (56.11).

	1
Empirical formula	$H_{22}As_6Co_7Na_{12}O_{91}Si_2W_{18}\\$
M	5981.57
λ /Å	0.71073
T/K	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	13.7347(6)
$b/{ m \AA}$	20.3688(10)
$c/{ m \AA}$	23.0951(11)
$\alpha /^{\circ}$	107.1840(10)
$eta/^{\circ}$	94.8450(10)
$\gamma/^{\circ}$	92.0890(10)
$V/\text{\AA}^3$	6137.8(5)
Ζ	2
$D_c/Mg \text{ m}^{-3}$	3.237
μ/mm^{-1}	19.459
<i>F</i> (000)	5258
θ Range/°	0.93-25.00
Measured reflections	35622
Independent reflections	21578
<i>R_{int}</i> after SQUEEZE	0.0385
Goodness-of-fit on F^2	1.007
$R_1 (I > 2\sigma(I))^a$	0.0421
wR_2 (all data) ^b	0.1280
$aR_1 = \sum F_0 - F_c / \sum F_0 . \ ^b wR_2 =$	$\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$

Single-crystal X-ray diffraction: Single-crystal X-ray diffraction data for 1 was recorded on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 296(2) K. Absorption corrections

were applied using multiscan technique and performed by using the SADABS program¹. The structures of **1** was solved by direct methods and refined on F^2 by full-matrix leastsquares methods by using the SHELXTL package². The numbers of lattice water molecules and counter cations for **1** was estimated by the results of elemental analyses, TG curves, and calculations of electron count in the voids with SQUEEZE³. (CCDC 1475602)

During the refinement, all the non-H atoms were refined anisotropically. Since most O atoms on the polyanion and solvent water molecules, as well as some Na atoms exhibit obvious ADP and NPD problems with the anisotropic parameters, they are just refined isotropically. But this treatment didn't influence the precise of the polyanion structure and the final R values, the 'isor' command were used to restraint the non-H atoms with ADP and NPD problems, which led to a relative high restraint value 477 but cannot be avoided. The 'omit -3 50' command was used to omit the weak reflections above 50 degree.

In the crystal structure, no H atoms on these O atoms could be found from the difference Fourier map. All H atoms on solvent water molecules were included into the formula directly.

The highest residue peak 3.223 eA³ and the deepest hole is -2.188 eA³.

About 8 solvent water molecules, 9 Na+ cations were found from the Fourier maps, however, there are still a very large accessible solvent voids in the crystal structure caculated by SQUEEZE subroutine of PLATON software, indicating that some more water molecules or cations should exist in the structure, but cannot be found from the weak residual electron peaks. Based on the TGA curve and elemental analyses, another 3 Na⁺ cations and 8 H⁺ were included into the molecular formula directly. References:

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			0 00000000		
bond	d (Å)	bond	d (Å)	bond	d (Å)
As(1)-O(77)	1.751(11)	As(3)-O(45)	1.752(10)	As(5)-O(12)	1.757(10)
As(1)-O(25)	1.761(10)	As(3)-O(48)	1.765(10)	As(5)-O(8)	1.771(10)
As(1)-O(45)	1.793(10)	As(3)-O(28)	1.774(10)	As(5)-O(13)	1.814(11)
As(2)-O(9)	1.778(10)	As(4)-O(11)	1.758(11)	As(6)-O(13)	1.765(10)
As(2)-O(19)	1.780(10)	As(4)-O(19)	1.809(9)	As(6)-O(7)	1.778(10)
As(2)-O(14)	1.787(11)	As(4)-O(10)	1.815(9)	As(6)-O(15)	1.840(10)

Table S3. Selected As-O bond lengths for 1

Table S4. The BVS calculation results of the mono-protonated oxygen atoms in 1.

Oxygen Code	Bond Valence	Protonation Degree	Oxygen Code	Bond Valence	Protonation Degree	
O ₇₇	1.431	1	O9	1.320	1	
O_7	1.344	1	O ₁₁	1.326	1	
O ₁₂	1.392	1	O_{48}	1.405	1	
Total 6 protons per cluster						

Table S5. Bond Valence Sum (BVS) of the Co and As atoms.

Atom	BVS value
Co1	1.875
Co2	1.844
Co3	1.794
Co4	1.881
Co5	1.901
Co6	1.987
Co7	1.813
As1	3.176
As1	3.060
As1	3.214
As1	2.967
As1	3.075
As1	2.968

 Table S6. Selected Co-O bond lengths for 1.

bond	d (Å)						
Co(1)-O(22)	2.012(11)	Co(3)-O(15)	2.123(11)	Co(5)-O(33)	2.027(11)	Co(7)-O(14)	2.067(11)
Co(1)-O(46)	2.069(10)	Co(3)-O(10)	2.132(10)	Co(5)-O(25)	2.090(10)	Co(7)-O(37)	2.085(10)
Co(1)-O(28)	2.079(10)	Co(3)-O(28)	2.136(10)	Co(5)-O(16)	2.098(10)	Co(7)-O(41)	2.085(10)
Co(1)-O(77)	2.186(10)	Co(3)-O(14)	2.139(10)	Co(5)-O(15)	2.113(11)	Co(7)-O(25)	2.157(10)
Co(1)-O(10)	2.190(10)	Co(3)-O(8)	2.150(10)	Co(5)-O(48)	2.179(10)	Co(7)-O(11)	2.183(11)
Co(1)-O(53)	2.255(10)	Co(3)-O(25)	2.153(11)	Co(5)-O(69)	2.231(11)	Co(7)-O(18)	2.271(11)
Co(2)-O(23)	2.031(10)	Co(4)-O(70)	2.030(10)	Co(6)-O(34)	1.993(10)		
Co(2)-O(8)	2.087(9)	Co(4)-O(61)	2.062(11)	Co(6)-O(10)	2.033(10)		
Co(2)-O(52)	2.119(12)	Co(4)-O(15)	2.087(10)	Co(6)-O(21)	2.064(10)		
Co(2)-O(7)	2.140(11)	Co(4)-O(12)	2.125(11)	Co(6)-O(8)	2.147(10)		
Co(2)-O(28)	2.172(9)	Co(4)-O(14)	2.164(10)	Co(6)-O(9)	2.164(10)		
Co(2)-O(43)	2.264(11)	Co(4)-O(66)	2.330(12)	Co(6)-O(57)	2.272(11)		

 Table S7. Selected metal-metal distances for the Co centers in 1.

	Bond dista	the natura	l OEC		
Co1 ••• Co3	3.051	Co3 ••• Co7	3.072	Mn2•••Mn3	2.9
Co1 ••• Co2	3.788	Co3 ••• Co5	3.069	Mn2•••Mn1	2.8
Co1 ••• Co6	3.736	Co3 ••• Co4	3.060	Mn3•••Mn1	3.3
Co2 ••• Co6	3.755	Co5 ••• Co3	3.787	Mn3•••Mn4	3.0
Co3 ••• Co2	3.074	Co5 ••• Co4	3.786	Mn1•••Mn4	5.0
Co3 ••• Co6	3.063	Co4 ••• Co7	3.773	Mn2•••Mn4	5.4



Fig. S1. W, Co and As XPS spectra of 1.

Section 3 Water Oxidation Experimental Section

Materials and Methods

Na₁₀[A- α -SiW₉O₃₄]·18H₂O was synthesized according to the literature method. (G. Hervé, A. Tézé, *Inorg. Chem.* **1977**, *16*, 2115-2117) All commercially obtained reagent, including CoCl₂·6H₂O, NaAsO₂, HCl, [Ru(bpy)₃]Cl₂·6H₂O and Na₂S₂O₈ were purchased from Aldrich and used without further purification. Deionized water was used throughout the study. A pHS-25B pH meter was used for pH measurements. Elemental analyses of Co, W and Na were performed on a PLASMA-SPEC (I) inductively coupled plasma (ICP) atomic emission spectrometer. Water contents were determined by TG analyses on a PerkinElmer TGA7 instrument in flowing N₂ with a heating rate of 10 °C min⁻¹. UV/Vis absorption spectra were obtained by using a 752 PC UV/Vis spectrophotometer. XRD studies were performed with a Rigaku D/max-IIB X-ray diffractometer at a scanning rate of 1° min⁻¹ with Cu_{Ka} radiation ($\lambda = 1.5418$ Å). Electrospray ionization mass spectrometry was carried out on a Bruker Micro TOF-QII instrument, the solution of the investigated systems were prepared in water.

Ultraviolet photoelectron spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) was performed by using a VG Scienta R3000 spectrometer in ultrahigh vacuum with a base pressure of 0.02 Pa. The measurement chamber was equipped with an ultraviolet source providing photons with 21.22 eV.

Cyclic Voltammetry

Electrochemical measurement was carried out on a CHI 660 electrochemical workstation at room temperature. Thrice-distilled water was used throughout the experiments. All solutions were deaerated by bubbling high pure argon prior to the experiments and the electrochemical cell was kept under an argon atmosphere

throughout the experiment. A conventional three-electrode system was used with a 1.5 mm glassy carbon working electrode, an Ag/AgCl reference electrode used as electrode, and a platinum wire counterelectrode. The glassy carbon working electrodes were polished with alumina on polishing pads, rinsed with distilled water, and sonicated in H₂O before each experiment. The scan rate was 100 mV s⁻¹. All potentials were measured and reported versus Ag/AgCl. Solution **1** in sodium buffer solution (pH 8.0, 80 mM) was used.

FTIR Spectroscopy

IR spectra were recorded on an Alpha Centauri FTIR spectrophotometer on pressed KBr pellets in the range 400~4000 cm⁻¹. A 20 mL reaction solution was prepared with $[Ru(bpy)_3]Cl_2$ (1 mM), Na₂S₂O₈ (5 mM), **1** (0.2 mM) in 80 mM sodium borate buffer (pH 8.0). The above solution was deaerated by purging vacuum for 15 min. The reaction was then started by irradiating the solution with a 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff) for 60 min. The complex (dye–POM conjugate) was precipitated from the post-reaction solution by adding 3 mL of concentrated $[Ru(bpy)_3]^{2+}$ solution.

X-ray photoelectron spectroscopy

XPS was performed on a VG ESCALABMKII spectrometer with an Mg_{*Ka*} (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis. A 20 mL reaction solution was prepared with [Ru(bpy)₃]Cl₂ (1 mM), Na₂S₂O₈ (5 mM), **1** (0.2 mM) in 80 mM sodium borate buffer (pH 8.0). The above solution was deaerated by purging vacuum for 15 min. The reaction was then started by irradiating the solution with a 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff) for 60 min. The complex (dye–POM conjugate) was precipitated from the post-reaction solution by adding acetone.

Dynamic light scattering measurements

DLS measurements were done by using a Zetasizer NanoZS (Malvern Instruments). Contact angles were measured on a KRÜSS DSA20MK2 Drop Shape Analysis System.

SEM analysis

The morphology of dye–POM conjugate was characterized with SEM (FESEM; XL30, FEG, FEI Company). Energy dispersive X-ray spectroscopy (EDS) was obtained from FEI Quanta 200F microscope. A 20 mL reaction solution was prepared with $[Ru(bpy)_3]Cl_2$ (1 mM), $Na_2S_2O_8$ (5 mM), 1 (40 μ M) in 80 mM sodium borate buffer (pH 8.0). After irradiating the solution for 60 min, the complex (dye–POM conjugate) was precipitated from the post-reaction solution.

THpANO₃ toluene extraction

Synthesis of tetraheptylammonium nitrate (THpANO₃) and extraction of **1** from postreaction solution. (J. W. Vickers, H.-J. Lv, J. M. Sumliner, G.-B. Zhu, Z. Luo, D. G. Musaev, Y. V. Geletii, C. L. Hill, *J. Am. Chem. Soc.* **2013**, *135*, 14110-14118.)

Visible Light-Driven Water Oxidation

Visible light-driven water oxidation was performed in an external illumination type reaction vessel (total volume 50 mL) with a magnetic stirrer for vigorous stirring and analyzed by using an automatic O_2 monitoring system at room temperature. The vessel was filled with 20 mL of reaction solution with different concentrations of **1** (0–40 μ M), sacrificial electron acceptor Na₂S₂O₈ (5 mM), and photosensitizer [Ru(bpy)₃]Cl₂ (1 mM) in 80 mM sodium buffer solution (pH 8.0). Before irradiation, the reaction solution was first degassed by ultrasonication and added to the photosensitizer [Ru(bpy)₃]Cl₂, then evacuated in the dark to ensure complete air removal. The photoirradiation was performed using a 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff). The produced O₂ was automatically analyzed by gas

chromatography with a GC7890T instrument with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column (2 m \times 3 mm) using Ar as carrier gas.



Fig. S2. (a) UPS photoemission spectrum of 1. The red lines are the tangents of the curve. (Inset: $(\alpha hv)^{1/2}$ versus hv curve of 1. The red dashed line is the tangent of the curve. The intersection value is the band gap of 1.) (b) The band gap structures of 1. $\Delta E = \text{HOMO} (\text{Ru}(\text{bpy})_3) - \text{HOMO} (\text{POMs}).$

The ultraviolet photoelectron spectroscopy (UPS) measurement of **1** was carried out to gain more insight into the energy levels. As shown in Fig. 2a, the work function (W_F) of **1** is calculated to be about 2.89 eV by subtracting the width of the secondary electron cutoff (18.33 eV) from the excitation energy (21.22 eV). The ionization energy (I_E , the onset of the band of occupied orbital) of **1** is about 3.32 eV, and then

the highest occupied molecular orbital (HOMO) of **1** with respect to vacuum level can be caculated from $-(W_F+I_E)$, which is -6.21 eV. On the basis of the UPS and UV-vis spectrum results (the HOMO–LUMO energy gap is 2.29 eV), the lowest unoccupied molecular orbital (LUMO) of **1** is -3.92 eV. After converting to electrochemical energy potentials according to the reference standard *versus* RHE as shown in Fig. 2b, the HOMO of **1** is +1.71 V, which lays between the oxidation level for H₂O to O₂ and HOMO of Ru(bpy)₃. The potential difference (ΔE = HOMO (Ru(bpy)₃) – HOMO (POMs)) between Ru(bpy)₃ and **1** indicates that **1** could be easily oxidized by Ru(bpy)₃ for water oxidation.



Fig. S3. Cyclic voltammogram (CV) of 80 mM sodium borate buffer solution at pH 8.0 without **1** (black) and with 0.5 mM **1** (red). The relationship between potentials in RHE and in Ag/AgCl is given as followings: V(RHE) = V(Ag/AgCl) + 0.0591 * pH + 0.197 V. The cyclic voltammetry of **1** was tested in 80 mM sodium borate buffer solution (pH 8.0). The onset potential for water oxidation is 0.98 V (*vs.* Ag/AgCl), after converting to RHE according to the aforementioned formula, the onset potential for water oxidation is 1.65 V (*vs.* RHE).



Observed	Calculated	Chargo	Molecular	Delverion
m/z	m/z	Charge	mass	Polyanion
1408.2	1408.8	-4	5635.3	$\{Na_{3}H_{5}[\{Co^{II}_{7}As^{III}_{6}O_{9}(OH)_{6}\}(\alpha\text{-}SiW_{9}O_{34})_{2}]\}^{4\text{-}}$
1414.0	1414.3	-4	5657.3	$\{Na_{4}H_{4}[\{Co^{II}_{7}As^{III}_{6}O_{9}(OH)_{6}\}(\alpha\text{-}SiW_{9}O_{34})_{2}]\}^{4\text{-}}$
1419.0	1419.8	-4	5679.3	$\{Na_{5}H_{3}[\{Co^{II}_{7}As^{III}_{6}O_{9}(OH)_{6}\}(\alpha\text{-}SiW_{9}O_{34})_{2}]\}^{4\text{-}}$
1425.2	1425.3	-4	5701.3	$\{Na_{6}H_{2}[\{Co^{II}_{7}As^{III}_{6}O_{9}(OH)_{6}\}(\alpha\text{-}SiW_{9}O_{34})_{2}]\}^{4\text{-}}$
1430.4	1430.8	-4	5723.3	$\{Na_7H[\{Co^{11}_7As^{111}_6O_9(OH)_6\}(\alpha\text{-}SiW_9O_{34})_2]\}^{4\text{-}}$

 Table S8. Assignment of peaks of 1.



Scheme S1. Photochemical water oxidation cycle in presence of catalyst, photosensitizer, and electron acceptor.

Entry	Catalysts	рН	Catalyst concentration (µM)	O ₂ Yield ^[b] (%)	TON ^[c]	TOF ^[d] [s ⁻¹]
1	1 [a]	8.0	20	38.4	48.2	0.037
2	1	7.5	20	26.9	33.7	0.024
3	1	7.0	20	16.4	20.6	0.014
4	1	8.0	0	0.4	-	-
5	1	8.0	1	4.6	115.2	0.14
6	1	8.0	2	6.9	86.7	0.093
7	1	8.0	3	7.9	66.1	0.063
8	1	8.0	5	9.6	48.3	0.042
9	1	8.0	10	19.2	48	0.028
10	1	8.0	15	28.9	48.6	0.027
11	1	8.0	30	32.8	27.3	0.016
12	1 (aged 8 h)	8.0	5	9.6	48.3	0.042
13	1 (aged 24 h)	8.0	5	9.5	47.2	0.044
14	$Co(NO_3)_2$	8.0	140	28.3	5.0	0.0034
15	Co8POM ^[e]	8.0	1	5.1	128.1	0.12
16	Co8POM ^[e]	8.0	5	10.0	50.5	0.034
16	Co8POM ^[e]	8.0	20	19.8	24.7	0.0168
17	Co-V-POM ^[f]	8.0	20	20.2	25.5	0.025
18	NaAsO ₂	8.0	120	0.44	0.55	0.00086
19	Co(NO ₃) ₂ +NaAsO ₂	8.0	140+120	28.3	-	-
20	1 (second run) ^[g]	8.0	20	20.0	25.0	0.028

Table S9. Catalytic water oxidation activity of 1 under various pH and concentration conditions.

[a] Conditions: 300W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts **1** concentration 1-30 μ M, [Ru(bpy)₃]²⁺ (1.0 mM), Na₂S₂O₈ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10³ rpm). [b] O₂ Yield = 2 × mole of O₂ per mole of Na₂S₂O₈. [c] TON = mole of O₂/mole of catalyst. [d] TOF_{initial} = mole of O₂/(mole of catalyst × 300 s), based on the amount of O₂ produced after 5 min of irradiation. [e] Conditions: 300 W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts Co8POM concentration 1, 5 and 20 μ M, [Ru(bpy)₃]²⁺ (1.0 mM), Na₂S₂O₈ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10³ rpm). [f]

Conditions: 300 W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts Co-V-POM concentration 20 μ M, [Ru(bpy)₃]²⁺ (1.0 mM), Na₂S₂O₈ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10³ rpm). [g] After completion of the first run, 5 mM of Na₂S₂O₈ was added to the reaction and the system started producing oxygen again.



Fig. S5. TON (left) or $\text{TOF}_{\text{initial}}$ (right) *vs*. catalyst concentration for **1** after 60 min illumination with a 300W Xe lamp equipped with a long-pass filter (420 nm cut-off).



Fig. S6. Image of reaction solutions of 1 with different concentration. Conditions: 1.0 mM $[Ru(bpy)_3]Cl_2$ and 5.0 mM $Na_2S_2O_8$ in 80 mM sodium borate buffers (pH 8.0), total reaction volume 20 mL.



Fig. S7. Kinetics of O₂ production in the photocatalytic system by 20 μ M 1 under different pH conditions in 80 mM sodium borate buffers (red curve at pH 8.0, blue curve at pH 7.5 and black curve at pH 7.0). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; total reaction volume 20 mL; vigorous stirring (1.5 × 10³ rpm).



Fig. S8. O₂ formation kinetics of the first run (black) and the second run (red) from an aqueous sodium borate buffer solution (80 mM, pH 8.0, 20 mL) containing $Ru(bpy)_3^{2+}$ (1.0 mM), $Na_2S_2O_8$ (5.0 mM), and 20 μ M **1** by using a 300 W Xe lamp

equipped with a long-pass filter (420 nm cut-off). After completion of the first run, another 5 mM of $Na_2S_2O_8$ was added to the reaction solution.

After the first completion of catalytic experiment, the reuse of catalyst 1 was carried out by addition of another 5 mM of Na₂S₂O₈ (sacrificial electron acceptor) to the reaction solution. In the second run, the O₂ evolution amount decreased to 10.0 µmol for 1 (Fig. S8 in the Supporting Information). DLS measurements showed the absence of any particles after the second run of photocatalytic water oxidation. The decline of the O₂ evolution activity after the first run suggests that such a photocatalytic reaction system is influenced by a combination of several factors (such as pH value changes, partial decomposition of the photosensitizer [Ru(bpy)₃]²⁺) of the complicated solution environment. Furthermore, after completion of the first run, 0.25 mM of the photosensitizer was added to reaction system together with another 5 mM of Na₂S₂O₈, and then photocatalytic water oxidation was run by the same operation as the first run. The O_2 evolution amount was similar to that of adding only 5 mM of $Na_2S_2O_8$ after the first run (Fig. S8 in the Supporting Information). Further, the pH value of sodium borate buffer decreased after the photocatalytic experiments (from 8.00 to about 7.70). A high pH is thermodynamically favorable for water oxidation (*Phys. Chem. Chem.* Phys. 2012, 14, 5753-5760). So we performed another second run of photocatalytic reaction by the addition of Na₂B₄O₇ to adjust the pH value of the reaction solution back to 8.0. The O₂ evolution amount was a litter higher than the red curve in Fig. S8 in the Supporting Information. These results indicate that the loss of the O₂ evolution activity after the first reaction run is influenced by a combination of several factors of the complicated solution environment after photocatalysis, such as Na₂S₂O₈ consumption, degradation of the photosensitizer, decrease in the pH value, the change of ionic strength, liquid electrolyte, etc.. This phenomenon is often observed in other POM-based WOCs: such as J. Am. Chem. Soc. 2011, 133, 2068-2071, J. Am. Chem. Soc. 2009, 131, 7522-7523, Energy Environ. Sci. 2013, 6, 1170-1184, Chem. Commun. 2015, 51, 17443-17446, etc..



Fig. S9. Kinetics of O₂ evolution of the photocatalytic system with **1** and $Co(NO_3)_2$ ·6H₂O. Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; sodium borate buffer solution (80 mM, pH 8.0); total reaction volume 20 mL; vigorous stirring (1.5 × 10³ rpm).



Fig. S10. Kinetics of O_2 evolution of the photocatalytic system with **1**, $Co(NO_3)_2$, and NaAsO₂. Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; sodium borate buffer solution (80 mM, pH 8.0); total reaction volume 20 mL; vigorous stirring (1.5 × 10³ rpm).



Fig. S11. Initial O₂ evolution rate vs (a) $[Ru(bpy)_3^{2+}]$ ($[S_2O_8^{2-}] = 5 \text{ mM}$, $[1] = 20 \text{ }\mu\text{M}$) and (b) $[S_2O_8^{2-}]$ ($[Ru(bpy)_3^{2+}] = 1 \text{ }m\text{M}$, $[1] = 20 \text{ }\mu\text{M}$) for 1.



Fig. S12. Kinetics of O₂ evolution of the photocatalytic system with **1** (1 μ M) and Co8POM (1 μ M). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; total reaction volume 20 mL; 80 mM sodium borate buffer solution (pH 8.0); vigorous stirring (1.5 × 10³ rpm).



Fig. S13. Kinetics of O₂ evolution of the photocatalytic system with **1** (20 μ M) and Co-V-POM (20 μ M). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; total reaction volume 20 mL; 80 mM sodium borate buffer solution (pH 8.0); vigorous stirring (1.5 × 10³ rpm).



Fig. S14. The UV spectra of **1** in the pH 7.0 (a), 7.5 (b) and 8.0 (c) sodium borate buffer solution. The UV curves remained unchanged with time.



Fig. S15. DLS measurement of a water oxidation reaction solution of **1** (a) $(3\mu M)$ or $Co(NO_3)_2 \cdot 6H_2O$ (b) $(20 \ \mu M)$ with $[Ru(bpy)_3]^{2+}$ (1 mM), $Na_2S_2O_8$ (5 mM) in a 80 mM sodium borate buffer solution (pH 8.0) after 60 min of irradiation.



Fig. S16. The photocatalytic water oxidation activity of 1 after being aged for 8 h and 24 h was similar to that of the fresh catalyst. Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)₃]Cl₂, 5.0 mM Na₂S₂O₈; total reaction volume 20 mL; vigorous stirring $(1.5 \times 10^3 \text{ rpm})$.



Fig. S17. Solid-state FT-IR spectra of pristine **1** (blue), [Ru(bpy)₃]Cl₂ (red), dye–POM conjugate complex (black) retrieved after water oxidation reaction.



Fig. S18. XPS spectra of 1 showing the region of Co $2p_{3/2}$ and Co $2p_{1/2}$ peaks before (red) and after (black) the reaction.



Fig. S19. SEM images of the precipitate formed from 1. Photocatalytic water oxidation conditions: 1 (40 μ M), [Ru(bpy)₃]²⁺ (1 mM), Na₂S₂O₈ (5 mM) in a 80 mM sodium borate buffer solution (pH 8.0) after 60 min of irradiation.



Fig. S20. EDX analysis of the precipitate obtained from the photocatalytic water oxidation solution of **1**. Photocatalytic water oxidation conditions: **1** (40 μ M), [Ru(bpy)₃]²⁺ (1 mM), Na₂S₂O₈ (5 mM) in a 80 mM borate buffer solution (pH 8.0) after 60 min of irradiation.

Table S10. Inductively coupled plasma mass spectrometry for solution with 1 before and after the photocatalytic water oxidation reaction (Conditions: 1 (10 μ M), [Ru(bpy)₃]²⁺ (1 mM), Na₂S₂O₈ (5 mM) in a 80 mM sodium borate buffer solution (pH 8.0) after 60 min, 120 min, 240 min and 360 min of irradiation).

Enter	Reaction time	Concentration of	Flomenta	Co, W after
Entry	(min)	catalysts (µM)	Elements	extraction (µM)
1	0	10	Со	0.16
1	0	10	W	0.33
2	2 60	10	Co	0.94
2		10	W	1.24
3	120	10	Co	1.05
	120	10	W	1.84
4 240	240	10	Co	1.74
	240	10	W	3.06
5	260	10	Co 1.97	
	500	10	W	3.48

THpANO₃ toluene extraction experiment was performed to quantitatively extract **1** from the aqueous solution. Before the photocatalytic water oxidation reaction, 10 μ M of **1** in 80 mM pH 8.0 sodium borate buffer, followed by the extraction technique, yielded a concentration of cobalt at 0.16 μ M remaining in the reaction solution. Thus, the mole of the Co²⁺ in the solution: 0.16 * 10⁻⁶ * 20 * 10⁻³ = 3.20 * 10⁻⁹ mol. While the total mole of the Co²⁺ in 10 μ M of **1**: 10 * 10⁻⁶ * 20 * 10⁻³ * 7 = 1.4 * 10⁻⁶ mol. The percentage of decomposed Co²⁺ ions: 3.20 * 10⁻⁹ / 1.4 * 10⁻⁶ = 0.23 %. The POM extraction and ICP-MS analysis results thus indicated that only 0.23 % of POMs could be decomposed to release Co²⁺ ions in the sodium borate buffer before the photocatalytic water oxidation reaction. After the photocatalytic water oxidation reaction with 60 min of irradiation, the POM extraction and ICP-MS analysis results indicated that only 1.34% of POMs could be decomposed to release Co²⁺ ions in the sodium borate buffer before the photocatalytic water oxidation the POM extraction and ICP-MS analysis results indicated that only 1.34% of POMs could be decomposed to release Co²⁺ ions in the photocatalytic water oxidation reaction with 60 min of irradiation, the POM extraction and ICP-MS analysis results indicated that only 1.34% of POMs could be decomposed to release Co²⁺ ions in the photocatalytic water oxidation reaction with 60 min of irradiation, the POM extraction and ICP-MS analysis results indicated that only 1.34% of POMs could be decomposed to release Co²⁺ ions in the photocatalytic water oxidation reaction with 60 min of irradiation, the POM extraction and ICP-MS analysis results indicated that only 1.34% of POMs could be decomposed to release Co²⁺ ions in the

sodium borate buffer. About 1.11% (\approx 1%, 1.34% – 0.23% = 1.11%) of **1** was decomposed in the sodium borate buffer during the photocatalytic water oxidation reaction. This phenomenon is often observed in other POM-based WOCs: for example, *Chem. Commun.* 2015, **51**, 17443-17446; *J. Am. Chem. Soc.* 2015, **137**, 5486-5493, etc.. In addition, to rule out that the dissociated Co²⁺ ions could be responsible for the observed photocatalytic water oxidation activity of **1**, the catalytic reaction with 1 μ M Co(NO₃)₂·6H₂O under the same catalytic conditions have been performed (Fig. S7 in the Supporting Information), which can only produce a very small amount of O₂ (< 5% of those produced by **1**).

After 120 min, 240 min and 360 min of irradiation, THpANO₃ toluene extraction experiments (Table S10 in the Supporting Information) show that 1.50%, 2.48% and 2.81% of 1 (< 3%) was decomposed. Thus we can say a very small amount of Co species can be detected as time goes on as reported in *Journal of Catalysis* 338 (2016) 168-173. These results are in line with previous reported POM-based WOCs (*J. Am. Chem. Soc.* 2015, 137, 5486-5493): these POM extraction and ICP-MS analysis results indicated that less than < 4.7% of POMs could have decomposed to release Ni²⁺ ions in the borate buffer.

Thus, THpANO₃ toluene extraction experiment is an efficient method to confirm that the polyanion unit itself is the dominant active catalyst.

Section 4 Supplementary Physical Characterizations



Fig. S21. IR spectrum of **1**: The characteristic peaks at 937, 887, 812, and 764 cm⁻¹ are ascribed to vibrations of $v_{(W-O)}$. The broad peak at 3431 cm⁻¹ and the strong peak at 1615 cm⁻¹ are attributed to the lattice water molecules and aqua ligands.



Fig. S22. The XRPD patterns for as-synthesized (b) and simulated (a)



Fig. S23. TG curve of 1. (The first step weight loss is corresponding to the loss of lattice water molecules (from 25 to ca. 400 $^{\circ}$ C) and then the structure begans to decompose.)