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

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

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>ligands</th>
<th>cubane-type topologies</th>
<th>TON$^b$</th>
<th>TOF$^c$</th>
<th>Ref</th>
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<tbody>
<tr>
<td>$<a href="%5Cgamma%5Ctext%7B-SiW%7D_%7B10%7D%5Ctext%7BO%7D_%7B36%7D">\text{Ru}_4\text{O}_4(\text{OH})_2(\text{H}_2\text{O})_4</a>_{2}]^{10−}$</td>
<td>$\gamma\text{-SiW}<em>{10}\text{O}</em>{36}$</td>
<td>Ru$_4$O$_4$ core</td>
<td>500</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>$[\text{Co}^{III}_4\text{O}_4(\text{OAc})_4(\text{py})_4]$</td>
<td>py; OAc</td>
<td>Co$^{III}_4$O$_4$ cubane</td>
<td>40</td>
<td>0.02</td>
<td>2</td>
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<tr>
<td>$[\text{Co}^{III}_4\text{O}_4(\text{OAc})_4(p\text{-C}_5\text{H}_4\text{X})_4]$</td>
<td>$p\text{-C}_5\text{H}_4\text{X}$; OAc</td>
<td>Co$^{III}_4$O$_4$ cubane</td>
<td>140</td>
<td>0.07</td>
<td>3</td>
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<tr>
<td>$[\text{Co}^{II}_4(\text{hmp})_4(\mu\text{-OAc})_2(\mu\text{-2-OAc})_2(\text{H}_2\text{O})_2]$</td>
<td>hmp; OAc</td>
<td>Co$^{II}_4$O$_4$ cubane</td>
<td>40</td>
<td>7</td>
<td>4</td>
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<tr>
<td>$[\text{Co}_3\text{Ln}(\text{hmp})_4(\text{OAc})_5\text{H}_2\text{O}]$ (Ln = Ho, Er, Tm, Yb)</td>
<td>hmp; OAc</td>
<td>Co$^{II}_3$Ln cubane</td>
<td>160</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Mn$^{III}_3\text{Mn}^{IV}_4\text{O}_3\text{(CH}_3\text{COO)}<em>2(\text{SiW}<em>9\text{O}</em>{34})</em>{2}]^{6−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; OAc</td>
<td>Mn$^{III}_3$Mn$^{IV}_3$O$_3$ quasi-cubane</td>
<td>5</td>
<td>-</td>
<td>6</td>
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<tr>
<td>$[\text{Mn}_4\text{V}_2\text{O}_7(\text{OAc})_3]^{3−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; OAc</td>
<td>Mn$_4$O$_7$ cubane</td>
<td>1150</td>
<td>1.75</td>
<td>7</td>
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<tr>
<td>$([\text{Co}_4\text{OH}_3(\text{PO}<em>4)<em>4]</em>{4}\text{(SiW}<em>9\text{O}</em>{34})</em>{4}]^{12−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; PO$_4^{3−}$</td>
<td>Co$_4$O$_4$ cubane</td>
<td>44.5</td>
<td>0.053</td>
<td>8</td>
</tr>
<tr>
<td>$([\text{SiW}<em>9\text{O}</em>{34}]_2\text{Co}_8(\text{OH})_6(\text{H}_2\text{O})_2(\text{CO}_3)_2)]^{16−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; CO$_3^{2−}$</td>
<td>Co$_8$O$_6$ quasi-cubane (double)</td>
<td>1436</td>
<td>10</td>
<td>9</td>
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<tr>
<td>$[\text{Ni}_{12}\text{(OH)}_3(\text{CO}_3)_3(\text{PO}_4)<em>4(\text{SiW}<em>9\text{O}</em>{34})</em>{3}]^{24−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; PO$_4^{3−}$; CO$_3^{2−}$</td>
<td>Ni$_{12}$O$_4$ quasi-cubane</td>
<td>128.2</td>
<td>0.2</td>
<td>10</td>
</tr>
<tr>
<td>$[\text{Ni}_{13}\text{(H}_2\text{O})_3(\text{OH})_8(\text{PO}_4)_4(\text{SiW}<em>9\text{O}</em>{34})_8]^{25−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; PO$_4^{3−}$; CO$_3^{2−}$</td>
<td>Ni$_{13}$O$_4$ cubane</td>
<td>147.6</td>
<td>0.25</td>
<td>10</td>
</tr>
<tr>
<td>Ni$_{25}(\text{H}_2\text{O})<em>2\text{OH}</em>{18}(\text{CO}_3)_2(\text{PO}_4)<em>8(\text{SiW}<em>9\text{O}</em>{34})</em>{6}]^{30−}$</td>
<td>α-SiW$<em>9$O$</em>{34}$; PO$_4^{3−}$; CO$_3^{2−}$</td>
<td>Ni$<em>{25}$O$</em>{14}$ cubane (double)</td>
<td>204.5</td>
<td>0.34</td>
<td>10</td>
</tr>
<tr>
<td>1$^a$</td>
<td>α-SiW$<em>9$O$</em>{34}$; AsO$_3^{2−}$; OAc; imidazole; amino acid residues</td>
<td>Co$^{II}_6$O$_6$ “fused” double-quasi-cubane</td>
<td>115.2</td>
<td>0.14</td>
<td>this work</td>
</tr>
<tr>
<td>PS II</td>
<td>CaMn$_4$O$_3$ cubane</td>
<td></td>
<td>10$^7$</td>
<td>500</td>
<td>11</td>
</tr>
</tbody>
</table>

[a] Conditions: 300W Xe lamp equipped with a long-pass filter (420 nm cutoff); catalysts concentration (1 μM), [Ru(bpy)$_3$]$^{2+}$ (1.0 mM), Na$_2$S$_2$O$_8$ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5 × 10$^3$ rpm). [b] TON = mol of O$_2$/mol of catalyst. [c] TOF = mol of O$_2$/(mol of catalyst × 300 s).
References:


Section 2 Structures of 1
**Synthesis of 1**

CoCl$_2$·6H$_2$O (0.25 g, 1.05 mmol) was dissolved in 40 mL of distilled water. Na$_{10}$[4-α-SiW$_9$O$_{34}$]·18H$_2$O (1.18 g, 0.40 mmol) was added, and the mixture was stirred until a clear, purple solution was obtained. NaAsO$_2$ (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 $\nu$/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).

**Table S2.** Crystal Data and Structure Refinements for 1.
Empirical formula  \( \text{H}_{22}\text{As}_{6}\text{Co}_{7}\text{Na}_{12}\text{O}_{91}\text{Si}_{2}\text{W}_{18} \)

\[ M = 5981.57 \]
\[ \lambda/\text{\AA} = 0.71073 \]
\[ T/\text{K} = 296(2) \]

Crystal system  Triclinic

Space group  \( P\overline{1} \)

\[ a/\text{\AA} = 13.7347(6) \]
\[ b/\text{\AA} = 20.3688(10) \]
\[ c/\text{\AA} = 23.0951(11) \]
\[ \alpha/^{\circ} = 107.1840(10) \]
\[ \beta/^{\circ} = 94.8450(10) \]
\[ \gamma/^{\circ} = 92.0890(10) \]

\[ V/\text{\AA}^3 = 6137.8(5) \]

\[ Z = 2 \]

\[ D_c/\text{Mg m}^{-3} = 3.237 \]

\[ \mu/\text{mm}^{-1} = 19.459 \]

\[ F(000) = 5258 \]

\[ \theta \text{ Range}^{\circ} = 0.93–25.00 \]

Measured reflections  35622

Independent reflections  21578

\[ R_{int} = 0.0385 \]

after SQUEEZE

Goodness-of-fit on \( F^2 \)  1.007

\[ R_1 (I > 2\sigma(I))^a = 0.0421 \]

\[ wR_2 \text{ (all data)}^b = 0.1280 \]

\[ ^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|. \]
\[ ^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}. \]

**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 MoK\(\alpha\) radiation (\( \lambda = 0.71073 \) Å) at 296(2) K. Absorption corrections
were applied using multiscan technique and performed by using the SADABS program\textsuperscript{1}. The structures of 1 was solved by direct methods and refined on \( F^2 \) by full-matrix leastsquares methods by using the SHELXL package\textsuperscript{2}. 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 SQUEEZE\textsuperscript{3}. (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 eÅ\(^3\) and the deepest hole is -2.188 eÅ\(^3\).

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:


Table S3. Selected As-O bond lengths for 1.

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

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

<table>
<thead>
<tr>
<th>Oxygen Code</th>
<th>Bond Valence</th>
<th>Protonation Degree</th>
<th>Oxygen Code</th>
<th>Bond Valence</th>
<th>Protonation Degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_{77}$</td>
<td>1.431</td>
<td>1</td>
<td>O$_{9}$</td>
<td>1.320</td>
<td>1</td>
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<tr>
<td>O$_{7}$</td>
<td>1.344</td>
<td>1</td>
<td>O$_{11}$</td>
<td>1.326</td>
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<tr>
<td>O$_{12}$</td>
<td>1.392</td>
<td>1</td>
<td>O$_{48}$</td>
<td>1.405</td>
<td>1</td>
</tr>
</tbody>
</table>

**Total 6 protons per cluster**

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

<table>
<thead>
<tr>
<th>Atom</th>
<th>BVS value</th>
</tr>
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<tbody>
<tr>
<td>Co1</td>
<td>1.875</td>
</tr>
<tr>
<td>Co2</td>
<td>1.844</td>
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<tr>
<td>Co3</td>
<td>1.794</td>
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<tr>
<td>Co4</td>
<td>1.881</td>
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<tr>
<td>Co5</td>
<td>1.901</td>
</tr>
<tr>
<td>Co6</td>
<td>1.987</td>
</tr>
<tr>
<td>Co7</td>
<td>1.813</td>
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<tr>
<td>As1</td>
<td>3.176</td>
</tr>
<tr>
<td>As1</td>
<td>3.060</td>
</tr>
<tr>
<td>As1</td>
<td>3.214</td>
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<td>As1</td>
<td>2.967</td>
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<td>As1</td>
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<td>As1</td>
<td>2.968</td>
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Table S6. Selected Co-O bond lengths for 1.

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<th>bond</th>
<th>d (Å)</th>
<th>bond</th>
<th>d (Å)</th>
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<tbody>
<tr>
<td>Co(1)-O(22)</td>
<td>2.012(11)</td>
<td>Co(3)-O(15)</td>
<td>2.123(11)</td>
<td>Co(5)-O(33)</td>
<td>2.027(11)</td>
<td>Co(7)-O(14)</td>
<td>2.067(11)</td>
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<tr>
<td>Co(1)-O(46)</td>
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<td>Co(3)-O(10)</td>
<td>2.132(10)</td>
<td>Co(5)-O(25)</td>
<td>2.090(10)</td>
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<td>2.085(10)</td>
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<td>2.136(10)</td>
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<td>2.098(10)</td>
<td>Co(7)-O(41)</td>
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<td>2.139(10)</td>
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<td>2.157(10)</td>
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<td>Co(7)-O(11)</td>
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<td>Co(4)-O(70)</td>
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<td>Co(2)-O(52)</td>
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<td>Co(6)-O(21)</td>
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<td>Co(2)-O(43)</td>
<td>2.264(11)</td>
<td>Co(4)-O(66)</td>
<td>2.330(12)</td>
<td>Co(6)-O(57)</td>
<td>2.272(11)</td>
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</table>

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

<table>
<thead>
<tr>
<th>Bond distances (Å) in 1</th>
<th>the natural OEC</th>
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<tr>
<td>Co1 ••• Co3</td>
<td>3.051</td>
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<td>3.788</td>
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<tr>
<td>Co1 ••• Co6</td>
<td>3.736</td>
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<tr>
<td>Co2 ••• Co6</td>
<td>3.755</td>
</tr>
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<td>Co3 ••• Co2</td>
<td>3.074</td>
</tr>
<tr>
<td>Co3 ••• Co6</td>
<td>3.063</td>
</tr>
<tr>
<td>Co3 ••• Co7</td>
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</tr>
<tr>
<td>Co3 ••• Co5</td>
<td>3.069</td>
</tr>
<tr>
<td>Co3 ••• Co4</td>
<td>3.060</td>
</tr>
<tr>
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<td>3.787</td>
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<tr>
<td>Co5 ••• Co4</td>
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<td>Mn2•••Mn4</td>
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</table>

Fig. S1. W, Co and As XPS spectra of 1.
Section 3 Water Oxidation Experimental Section

Materials and Methods

Na$_{10}$[\(\text{\(A\)-\(\alpha\)-SiW}_{9\text{O}_{34}\)}]\(\cdot\)18H$_2$O was synthesized according to the literature method. (G. Hervé, A. Tézé, Inorg. Chem. 1977, 16, 2115-2117) All commercially obtained reagent, including CoCl$_2$$\cdot$6H$_2$O, NaAsO$_2$, HCl, [Ru(bpy)$_3$]Cl$_2$$\cdot$6H$_2$O and Na$_2$S$_2$O$_8$ 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 N$_2$ 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$_{K\alpha}$ 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]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 3 mL of concentrated [Ru(bpy)₃]²⁺ solution.

**X-ray photoelectron spectroscopy**

XPS was performed on a VG ESCALABMKII spectrometer with an MgKα (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$_2$S$_2$O$_8$ (5 mM), 1 (40 μM) 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.

$\text{THpANO}_3$ toluene extraction


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 μM), sacrificial electron acceptor Na$_2$S$_2$O$_8$ (5 mM), and photosensitizer [Ru(bpy)$_3$]Cl$_2$ (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)$_3$]Cl$_2$, 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 O$_2$ 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 × 3 mm) using Ar as carrier gas.

![Diagram](image)

**Fig. S2.** (a) UPS photoemission spectrum of **1**. The red lines are the tangents of the curve. (Inset: (dνhν)½ versus hν 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**. 

$\Delta E = \text{HOMO (Ru(bpy)₃)} - \text{HOMO (POMs)}$.

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 calculated 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 H\(_2\)O to O\(_2\) and HOMO of Ru(bpy)\(_3\). The potential difference (\(\Delta E = \text{HOMO (Ru(bpy)\(_3\))} - \text{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).

Fig. S4. ESI–MS of 1 in H₂O.
Table S8. Assignment of peaks of 1.

<table>
<thead>
<tr>
<th>Observed m/z</th>
<th>Calculated m/z</th>
<th>Charge</th>
<th>Molecular mass</th>
<th>Polyanion</th>
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<tr>
<td>1408.2</td>
<td>1408.8</td>
<td>-4</td>
<td>5635.3</td>
<td>{Na_3H_5<a href="%CE%B1-SiW_%7B9%7DO_%7B34%7D">(Co^{II}<em>{7}As^{III}</em>{6}O_9(OH)_6</a>_2]}^{4-}</td>
</tr>
<tr>
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<td>1414.3</td>
<td>-4</td>
<td>5657.3</td>
<td>{Na_4H_4<a href="%CE%B1-SiW_%7B9%7DO_%7B34%7D">(Co^{II}<em>{7}As^{III}</em>{6}O_9(OH)_6</a>_2]}^{4-}</td>
</tr>
<tr>
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<td>-4</td>
<td>5679.3</td>
<td>{Na_5H_3<a href="%CE%B1-SiW_%7B9%7DO_%7B34%7D">(Co^{II}<em>{7}As^{III}</em>{6}O_9(OH)_6</a>_2]}^{4-}</td>
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<tr>
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<td>1430.8</td>
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</tbody>
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Scheme S1. Photochemical water oxidation cycle in presence of catalyst, photosensitizer, and electron acceptor.
Table S9. Catalytic water oxidation activity of 1 under various pH and concentration conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>pH</th>
<th>Catalyst concentration (μM)</th>
<th>O$_2$ Yield$^b$ (%)</th>
<th>TON$^c$</th>
<th>TOF$^d$ [s$^{-1}$]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1$^a$</td>
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<td>16.4</td>
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<td>4.6</td>
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<td>48.6</td>
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<td>28.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>1 (second run)$^g$</td>
<td>8.0</td>
<td>20</td>
<td>20.0</td>
<td>25.0</td>
<td>0.028</td>
</tr>
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</table>

[a] Conditions: 300 W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts 1 concentration 1-30 μM, [Ru(bpy)$_3$]$^{2+}$ (1.0 mM), Na$_2$S$_2$O$_8$ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10$^3$ rpm). [b] O$_2$ Yield = 2 × mole of O$_2$ per mole of Na$_2$S$_2$O$_8$. [c] TON = mole of O$_2$/mole of catalyst. [d] TOF$_{initial}$ = mole of O$_2$/mole of catalyst × 300 s, based on the amount of O$_2$ produced after 5 min of irradiation. [e] Conditions: 300 W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts Co$_8$POM concentration 1, 5 and 20 μM, [Ru(bpy)$_3$]$^{2+}$ (1.0 mM), Na$_2$S$_2$O$_8$ (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10$^3$ rpm). [f]
Conditions: 300 W Xe lamp equipped with a longpass filter (420 nm cutoff); catalysts Co-V-POM concentration 20 μM, [Ru(bpy)_3]^{2+} (1.0 mM), Na_2S_2O_8 (5.0 mM), sodium borate buffer (80 mM, pH 8.0), total reaction solution volume: 20 mL; vigorous stirring (1.5×10^3 rpm). [g] After completion of the first run, 5 mM of Na_2S_2O_8 was added to the reaction and the system started producing oxygen again.

Fig. S5. TON (left) or TOF_{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 $O_2$ production in the photocatalytic system by 20 μM 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)$_3$]Cl$_2$, 5.0 mM Na$_2$S$_2$O$_8$; total reaction volume 20 mL; vigorous stirring ($1.5 \times 10^3$ rpm).

Fig. S8. $O_2$ 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$_2$S$_2$O$_8$ (5.0 mM), and 20 μM 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$_2$S$_2$O$_8$ 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 Na$_2$S$_2$O$_8$ (sacrificial electron acceptor) to the reaction solution. In the second run, the O$_2$ 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 O$_2$ 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 Na$_2$S$_2$O$_8$, 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$_2$S$_2$O$_8$ 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 Na$_2$B$_4$O$_7$ to adjust the pH value of the reaction solution back to 8.0. The O$_2$ 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 O$_2$ evolution activity after the first reaction run is influenced by a combination of several factors of the complicated solution environment after photocatalysis, such as Na$_2$S$_2$O$_8$ 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(NO₃)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 O₂ evolution of the photocatalytic system with 1, Co(NO₃)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 $O_2$ evolution rate vs (a) $[\text{Ru(bpy)}_3^{2+}]$ ($[\text{S}_2\text{O}_8^{2-}] = 5 \text{ mM}$, $[\mathbf{1}] = 20 \mu\text{M}$) and (b) $[\text{S}_2\text{O}_8^{2-}]$ ($[\text{Ru(bpy)}_3^{2+}] = 1 \text{ mM}$, $[\mathbf{1}] = 20 \mu\text{M}$) for $\mathbf{1}$.

Fig. S12. Kinetics of $O_2$ evolution of the photocatalytic system with $\mathbf{1}$ (1 $\mu$M) and Co8POM (1 $\mu$M). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM $[\text{Ru(bpy)}_3\text{Cl}_2$, 5.0 mM $\text{Na}_2\text{S}_2\text{O}_8$; total reaction volume 20 mL; 80 mM sodium borate buffer solution (pH 8.0); vigorous stirring ($1.5 \times 10^3$ rpm).
Fig. S13. Kinetics of $O_2$ evolution of the photocatalytic system with 1 (20 μM) and Co-V-POM (20 μM). Conditions: 300 W Xe lamp equipped with a long-pass filter (420 nm cutoff); 1.0 mM [Ru(bpy)$_3$]Cl$_2$, 5.0 mM $Na_2S_2O_8$; total reaction volume 20 mL; 80 mM sodium borate buffer solution (pH 8.0); vigorous stirring ($1.5 \times 10^3$ 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) (3μM) or Co(NO$_3$)$_2$·6H$_2$O (b) (20 μM) with [Ru(bpy)$_3$]$^{2+}$ (1 mM), Na$_2$S$_2$O$_8$ (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)$_3$]Cl$_2$, 5.0 mM Na$_2$S$_2$O$_8$; total reaction volume 20 mL; vigorous stirring (1.5 × 10$^3$ rpm).
Fig. S17. Solid-state FT-IR spectra of pristine 1 (blue), [Ru(bpy)$_3$]Cl$_2$ (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 μM), [Ru(bpy)$_3$]$^{2+}$ (1 mM), Na$_2$S$_2$O$_8$ (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 μM), [Ru(bpy)$_3$]$^{2+}$ (1 mM), Na$_2$S$_2$O$_8$ (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 μM), [Ru(bpy)$_3$]$^{2+}$ (1 mM), Na$_2$S$_2$O$_8$ (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).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time (min)</th>
<th>Concentration of catalysts (μM)</th>
<th>Elements</th>
<th>Co, W after extraction (μM)</th>
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<tbody>
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<td>0</td>
<td>10</td>
<td>Co</td>
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</tr>
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THpANO$_3$ toluene extraction experiment was performed to quantitatively extract 1 from the aqueous solution. Before the photocatalytic water oxidation reaction, 10 μM of 1 in 80 mM pH 8.0 sodium borate buffer, followed by the extraction technique, yielded a concentration of cobalt at 0.16 μM remaining in the reaction solution. Thus, the mole of the Co$^{2+}$ in the solution: 0.16 * 10$^{-6}$ * 20 * 10$^{-3}$ = 3.20 * 10$^{-9}$ mol. While the total mole of the Co$^{2+}$ in 10 μM of 1: 10 * 10$^{-6}$ * 20 * 10$^{-3}$ * 7 = 1.4 * 10$^{-6}$ mol. The percentage of decomposed Co$^{2+}$ 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 Co$^{2+}$ 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 Co$^{2+}$ 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 Co$^{2+}$ ions could be responsible for the observed photocatalytic water oxidation activity of 1, the catalytic reaction with 1 $\mu$M Co(NO$_3$)$_2$·6H$_2$O under the same catalytic conditions have been performed (Fig. S7 in the Supporting Information), which can only produce a very small amount of O$_2$ ($< 5\%$ of those produced by 1).

After 120 min, 240 min and 360 min of irradiation, THpANO$_3$ 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 Ni$^{2+}$ ions in the borate buffer.

Thus, THpANO$_3$ 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 $\nu_{(W-O)}$. 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 °C) and then the structure begins to decompose.)