

## Supporting Information

### Photocatalytic water oxidation with cobalt-containing tungstobismutates: Tuning the metal core

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## 1. Crystallographic Information

**Table S1.** Crystallographic data and structural refinements for compounds **(1)**, **(2)** and **(3)**.

	<b>(1)</b>	<b>(2)</b>	<b>(3)</b>
Empirical formula	Na <sub>10</sub> Bi <sub>2</sub> Co <sub>3</sub> W <sub>19</sub> O <sub>113</sub> H <sub>90</sub>	Na <sub>8</sub> Bi <sub>2</sub> Co <sub>2.5</sub> W <sub>19.5</sub> O <sub>108</sub> H <sub>80</sub>	Na <sub>6</sub> Bi <sub>2</sub> Mn <sub>1.5</sub> W <sub>20.5</sub> O <sub>112</sub> H <sub>86</sub>
Formula weight (g.mol <sup>-1</sup> )	6215.71	6142.165	6285.09
Temperature	183 K	183 K	183 K
Radiation (λ/Å)	0.71073	0.71069	0.71069
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	13.1899(5)	12.827(5)	12.8784(4)
<i>b</i> (Å)	13.2965(4)	25.075(5)	25.2028(9)
<i>c</i> (Å)	18.0356(4)	15.881(5)	15.9495(7)
<i>α</i> (°)	70.908(2)	90	90
<i>β</i> (°)	85.482(2)	95.286(5)	95.594(3)
<i>γ</i> (°)	64.300(3)	90	90
<i>V</i> (Å <sup>3</sup> )	2686.00(16)	5086(3)	5152.1(3)
<i>Z</i>	1	1	1
ρ <sub>calc</sub> (g/cm <sup>3</sup> )	3.787	4.011	4.017
Crystal size	0.24 × 0.14 × 0.03	0.43 × 0.08 × 0.04	0.35 × 0.08 × 0.05
Reflections collected/unique	35147/16327 [R <sub>int</sub> = 0.0557]	87105/15497 [R <sub>int</sub> = 0.0580]	37047/12105 [R <sub>int</sub> = 0.0583]
Unique observed reflections	13638	13675	10033
θ range (°)	2.84-30.51	2.76-30.51	2.90-28.28
F(000)	2667	5337	5397
Data/restraints/parameters	13638/12/680	13675/0/662	10033/0/633
Goodness-of-fit	1.085	1.276	1.137
<i>R</i> <sub>1</sub> <sup>a</sup> [I > 2σ(I)]	0.0502	0.0493	0.0705
<i>wR</i> <sub>2</sub> <sup>b</sup>	0.1239	0.0963	0.1353
<i>R</i> <sub>1</sub> <sup>a</sup> [I > 2σ(I)] (all data)	0.0613	0.0583	0.0884
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1316	0.0991	0.1440

$$R_1 = \Sigma(F_o - F_c) / \Sigma F_o \text{ and } wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$$

**Table S2.** Selected bond distances for Co/Bi-POM (**1**).

<b>Bond</b>	<b>Distance (Å)</b>	<b>Bond</b>	<b>Distance (Å)</b>
W(1)-O(1) <sub>ter</sub>	1.739(7)	W(7)-O(7) <sub>ter</sub>	1.729(8)
W(1)-O(12) <sub>eq</sub>	1.925(7)	W(7)-O(21) <sub>eq</sub>	1.973(7)
W(1)-O(15) <sub>eq</sub>	1.906(8)	W(7)-O(22) <sub>eq</sub>	1.916(8)
W(1)-O(19) <sub>eq</sub>	1.866(8)	W(7)-O(28) <sub>eq</sub>	1.902(8)
W(1)-O(26) <sub>eq</sub>	1.931(7)	W(7)-O(29) <sub>eq</sub>	1.843(7)
W(1)-O(16) <sub>ax</sub>	2.278(6)	W(7)-O(17) <sub>ax</sub>	2.232(7)
W(2)-O(2) <sub>ter</sub>	1.738(8)	W(8)-O(8) <sub>ter</sub>	1.771(7)
W(2)-O(12) <sub>eq</sub>	1.887(8)	W(8)-O(9) <sub>eq</sub>	1.776(7)
W(2)-O(13) <sub>eq</sub>	1.878(8)	W(8)-O(23) <sub>eq</sub>	2.083(7)
W(2)-O(20) <sub>eq</sub>	1.931(8)	W(8)-O(24) <sub>eq</sub>	2.078(7)
W(2)-O(21) <sub>eq</sub>	1.950(7)	W(8)-O(30) <sub>eq</sub>	1.775(7)
W(2)-O(17) <sub>ax</sub>	2.259(7)	W(8)-O(18) <sub>ax</sub>	2.216(6)
W(3)-O(3) <sub>ter</sub>	1.726(8)	W(9)-O(11) <sub>ter</sub>	1.733(7)
W(3)-O(13) <sub>eq</sub>	1.985(7)	W(9)-O(10) <sub>eq</sub>	1.844(7)
W(3)-O(14) <sub>eq</sub>	1.929(7)	W(9)-O(25) <sub>eq</sub>	1.979(8)
W(3)-O(22) <sub>eq</sub>	1.913(7)	W(9)-O(26) <sub>eq</sub>	1.980(7)
W(3)-O(23) <sub>eq</sub>	1.857(7)	W(9)-O(38) <sub>eq</sub>	1.903(7)
W(3)-O(18) <sub>ax</sub>	2.320(7)	W(9)-O(16) <sub>ax</sub>	2.248(6)
W(4)-O(4) <sub>ter</sub>	1.734(8)	W(10) Co(2)-O(36)	1.893(9)
W(4)-O(14) <sub>eq</sub>	1.929(7)	W(10) Co(2)-O(10)	2.013(7)
W(4)-O(15) <sub>eq</sub>	1.938(7)	W(10) Co(2)-O(29)	2.007(7)
W(4)-O(24) <sub>eq</sub>	1.880(7)	W(10) Co(2)-O(30)	2.110(7)
W(4)-O(25) <sub>eq</sub>	1.871(8)	W(10) Co(2)-O(37)	1.917(11)
W(4)-O(18) <sub>ax</sub>	2.254(7)	W(10) Co(2)-O(9)	2.112(8)
W(5)-O(5) <sub>ter</sub>	1.746(8)	Co(1)-O(32)	2.030(7)
W(5)-O(19) <sub>eq</sub>	2.059(7)	Co(1)-O(8)	2.041(7)
W(5)-O(27) <sub>eq</sub>	1.919(7)	Co(1)-O(31)	2.070(7)
W(5)-O(31) <sub>eq</sub>	1.766(7)	Co(1)-O(33)	2.211(7)
W(5)-O(38) <sub>eq</sub>	1.956(7)	Co(1)-O(34)	2.112(7)
W(5)-O(16) <sub>ax</sub>	2.209(7)	Co(1)-O(35)	2.088(8)
W(6)-O(6) <sub>ter</sub>	1.758(7)	Bi(1)-O(16)	2.154(6)
W(6)-O(20) <sub>eq</sub>	2.009(8)	Bi(1)-O(17)	2.130(6)
W(6)-O(27) <sub>eq</sub>	1.922(7)	Bi(1)-O(18)	2.138(7)
W(6)-O(28) <sub>eq</sub>	1.986(7)		
W(6)-O(32) <sub>eq</sub>	1.801(7)		
W(6)-O(17) <sub>ax</sub>	2.228(7)		

ter = terminal oxygen; eq = equatorial oxygen; ax = axial oxygen

**Table S3.** Selected bond distances for Co/Bi-POM (**2**).

<b>Bond</b>	<b>Distance (Å)</b>	<b>Bond</b>	<b>Distance (Å)</b>
W(1)-O(5) <sub>ter</sub>	1.714(8)	W(8)-O(25) <sub>ter</sub>	1.756(8)
W(1)-O(1) <sub>eq</sub>	1.878(8)	W(8)-O(13) <sub>eq</sub>	2.068(8)
W(1)-O(4) <sub>eq</sub>	1.918(8)	W(8)-O(14) <sub>eq</sub>	2.067(9)
W(1)-O(10) <sub>eq</sub>	1.912(8)	W(8)-O(29) <sub>eq</sub>	1.780(9)
W(1)-O(11) <sub>eq</sub>	1.968(9)	W(8)-O(32) <sub>eq</sub>	1.794(9)
W(1)-O(20) <sub>ax</sub>	2.261(7)	W(8)-O(17) <sub>ax</sub>	2.198(7)
W(2)-O(6) <sub>ter</sub>	1.725(8)	W(9)-O(26) <sub>ter</sub>	1.718(10)
W(2)-O(1) <sub>eq</sub>	1.975(8)	W(9)-O(15) <sub>eq</sub>	1.948(9)
W(2)-O(2) <sub>eq</sub>	1.945(8)	W(9)-O(16) <sub>eq</sub>	1.948(9)
W(2)-O(12) <sub>eq</sub>	1.885(8)	W(9)-O(19) <sub>eq</sub>	1.908(9)
W(2)-O(13) <sub>eq</sub>	1.862(8)	W(9)-O(34) <sub>eq</sub>	1.827(9)
W(2)-O(17) <sub>ax</sub>	2.301(8)	W(9)-O(18) <sub>ax</sub>	2.244(8)
W(3)-O(7) <sub>ter</sub>	1.721(9)	W(10)-O(30)	1.840(16)
W(3)-O(2) <sub>eq</sub>	1.924(8)	W(10)-O(33)	1.856(14)
W(3)-O(3) <sub>eq</sub>	1.972(8)	W(10)-O(31)	1.988(12)
W(3)-O(14) <sub>eq</sub>	1.853(8)	W(10)-O(34)	2.007(12)
W(3)-O(15) <sub>eq</sub>	1.883(9)	W(10)-O(32)	2.120(11)
W(3)-O(17) <sub>ax</sub>	2.295(8)	W(10)-O(29)	2.124(12)
W(4)-O(8) <sub>ter</sub>	1.731(9)	Co(1)-O(33)	1.89(3)
W(4)-O(3) <sub>eq</sub>	1.877(8)	Co(1)-O(30)	1.95(3)
W(4)-O(4) <sub>eq</sub>	1.904(8)	Co(1)-O(31)	1.98(3)
W(4)-O(9) <sub>eq</sub>	1.912(9)	Co(1)-O(34)	1.99(3)
W(4)-O(16) <sub>eq</sub>	1.926(9)	Co(1)-O(32)	2.01(3)
W(4)-O(18) <sub>ax</sub>	2.273(8)	Co(1)-O(29)	2.08(3)
W(5)-O(21) <sub>ter</sub>	1.720(8)	W(11)-O(37)	1.94(2)
W(5)-O(9) <sub>eq</sub>	1.999(9)	W(11)-O(27)	1.98(2)
W(5)-O(19) <sub>eq</sub>	1.968(8)	W(11)-O(35)	1.98(2)
W(5)-O(22) <sub>eq</sub>	1.918(8)	W(11)-O(28)	2.13(2)
W(5)-O(27) <sub>eq</sub>	1.822(8)	W(11)-O(25)	2.14(2)
W(5)-O(18) <sub>ax</sub>	2.211(8)	W(11)-O(36)	2.15(2)
W(6)-O(23) <sub>ter</sub>	1.746(8)	Co(2)-O(36)	1.99(2)
W(6)-O(10) <sub>eq</sub>	2.006(8)	Co(2)-O(37)	2.00(3)
W(6)-O(22) <sub>eq</sub>	1.922(8)	Co(2)-O(28)	2.05(2)
W(6)-O(24) <sub>eq</sub>	1.977(8)	Co(2)-O(35)	2.07(2)
W(6)-O(28) <sub>eq</sub>	1.810(9)	Co(2)-O(25)	2.08(2)
W(6)-O(20) <sub>ax</sub>	2.200(8)	Co(2)-O(27)	2.12(2)
W(7)-O(38) <sub>ter</sub>	1.740(9)	Bi(1)-O(17)	2.122(8)
W(7)-O(11) <sub>eq</sub>	1.961(9)	Bi(1)-O(18)	2.135(7)
W(7)-O(12) <sub>eq</sub>	1.959(8)	Bi(1)-O(20)	2.147(7)
W(7)-O(24) <sub>eq</sub>	1.919(8)		
W(7)-O(31) <sub>eq</sub>	1.847(9)		
W(7)-O(20) <sub>ax</sub>	2.233(8)		

ter = terminal oxygen; eq = equatorial oxygen; ax = axial oxygen

**Table S4.** Selected bond distances for Mn/Bi-POM (**3**).

Bond	Distance (Å)	Bond	Distance (Å)
W(1)-O(1) <sub>ter</sub>	1.710(13)	W(7)-O(28) <sub>ter</sub>	1.704(16)
W(1)-O(2) <sub>eq</sub>	1.854(14)	W(7)-O(16) <sub>eq</sub>	1.897(14)
W(1)-O(3) <sub>eq</sub>	1.985(13)	W(7)-O(24) <sub>eq</sub>	1.924(17)
W(1)-O(4) <sub>eq</sub>	1.870(14)	W(7)-O(26) <sub>eq</sub>	1.861(14)
W(1)-O(5) <sub>eq</sub>	1.945(14)	W(7)-O(27) <sub>eq</sub>	1.859(13)
W(1)-O(6) <sub>ax</sub>	2.299(13)	W(7)-O(14) <sub>ax</sub>	2.248(13)
W(2)-O(8) <sub>ter</sub>	1.722(15)	W(8)-O(29) <sub>ter</sub>	1.709(16)
W(2)-O(4) <sub>eq</sub>	1.973(13)	W(8)-O(5) <sub>eq</sub>	1.922(13)
W(2)-O(9) <sub>eq</sub>	1.926(14)	W(8)-O(25) <sub>eq</sub>	1.960(14)
W(2)-O(10) <sub>eq</sub>	1.928(14)	W(8)-O(27) <sub>eq</sub>	1.869(15)
W(2)-O(11) <sub>eq</sub>	1.889(14)	W(8)-O(30) <sub>eq</sub>	1.868(15)
W(2)-O(7) <sub>ax</sub>	2.254(14)	W(8)-O(6) <sub>ax</sub>	2.291(13)
W(3)-O(15) <sub>ter</sub>	1.740(13)	W(9)-O(32) <sub>ter</sub>	1.739(14)
W(3)-O(12) <sub>eq</sub>	2.036(15)	W(9)-O(2) <sub>eq</sub>	2.050(13)
W(3)-O(13) <sub>eq</sub>	1.795(13)	W(9)-O(30) <sub>eq</sub>	2.056(16)
W(3)-O(16) <sub>eq</sub>	1.977(15)	W(9)-O(31) <sub>eq</sub>	1.784(15)
W(3)-O(17) <sub>eq</sub>	1.935(14)	W(9)-O(33) <sub>eq</sub>	1.806(14)
W(3)-O(14) <sub>ax</sub>	2.219(12)	W(9)-O(6) <sub>ax</sub>	2.181(13)
W(4)-O(18) <sub>ter</sub>	1.708(16)		
W(4)-O(3) <sub>eq</sub>	1.865(13)	W(10) Mn(1)-O(34)	1.76(2)
W(4)-O(10) <sub>eq</sub>	1.974(15)	W(10) Mn(1)-O(35)	1.785(17)
W(4)-O(19) <sub>eq</sub>	1.897(15)	W(10) Mn(1)-O(11)	1.969(14)
W(4)-O(20) <sub>eq</sub>	1.916(14)	W(10) Mn(1)-O(26)	2.000(13)
W(4)-O(7) <sub>ax</sub>	2.240(12)	W(10) Mn(1)-O(33)	2.118(14)
W(5)-O(21) <sub>ter</sub>	1.722(15)	W(10) Mn(1)-O(31)	2.140(15)
W(5)-O(9) <sub>eq</sub>	1.998(15)		
W(5)-O(17) <sub>eq</sub>	1.907(15)	W(11) Mn(2)-O(36)	1.996(18)
W(5)-O(20) <sub>eq</sub>	2.007(15)	W(11) Mn(2)-O(38)	2.07(2)
W(5)-O(22) <sub>eq</sub>	1.827(15)	W(11) Mn(2)-O(22)	2.096(14)
W(5)-O(7) <sub>ax</sub>	2.214(12)	W(11) Mn(2)-O(37)	2.111(19)
W(6)-O(23) <sub>ter</sub>	1.711(17)	W(11) Mn(2)-O(13)	2.133(13)
W(6)-O(12) <sub>eq</sub>	1.874(14)	W(11) Mn(2)-O(32)	2.186(13)
W(6)-O(19) <sub>eq</sub>	1.917(15)		
W(6)-O(24) <sub>eq</sub>	1.928(16)	Bi(1)-O(14)	2.131(13)
W(6)-O(25) <sub>eq</sub>	1.888(14)	Bi(1)-O(6)	2.142(13)
W(6)-O(14) <sub>ax</sub>	2.271(14)	Bi(1)-O(7)	2.147(12)

ter = terminal oxygen; eq = equatorial oxygen; ax = axial oxygen

**Table S5.** BVS calculations for Co/Bi-POM (1).

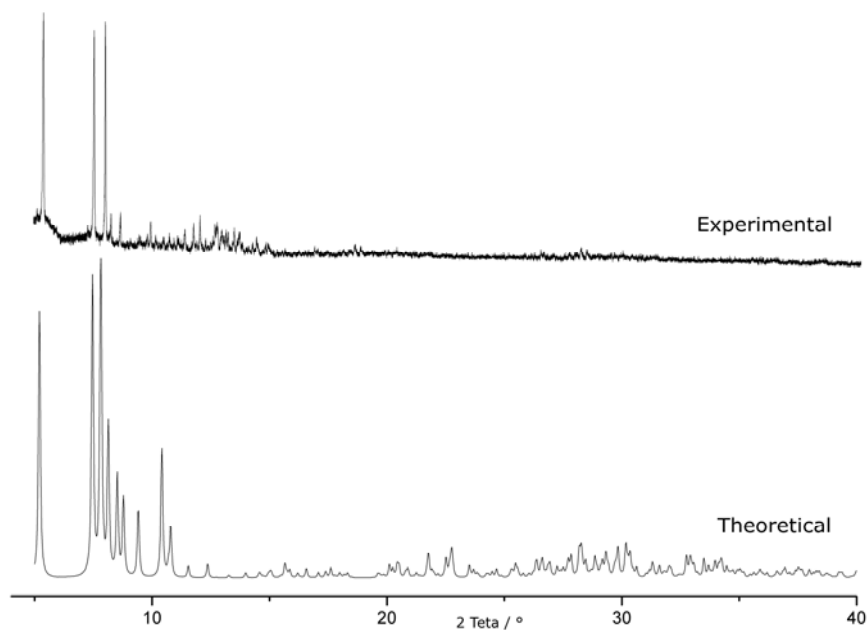
W(1)	5.9929	W(2)	5.9727	W(3)	5.8875	W(4)	6.0752	W(5)	5.9927
W(6)	5.8375	W(7)	6.0995	W(8)	5.9719	W(9)	5.8709	Co(1)	1.6795
W(10)	3.4270	Co(2)	1.7701						
O(1)	1.5200	O(2)	1.5244	O(3)	1.5712	O(4)	1.5439	O(5)	1.5026
O(6)	1.4588	O(7)	1.5698	O(8)	1.4049	O(9)	1.4468	O(10)	1.3165
O(11)	1.5457	O(12)	2.0356	O(13)	1.9459	O(14)	1.9105	O(15)	1.9750
O(16)	2.0764	O(17)	2.1376	O(18)	2.0451	O(19)	1.8128	O(20)	1.7381
O(21)	1.7744	O(22)	2.0285	O(23)	1.7996	O(24)	1.7439	O(25)	1.9792
O(26)	1.8046	O(27)	1.9974	O(28)	1.8559	O(29)	1.9223	O(30)	1.9556
O(31)	1.8507	O(32)	1.8380	O(33)	0.2828	O(34)	0.3230	O(35)	0.3384
O(36)	0.8020	O(37)	0.7389	O(38)	1.9167	Bi(1)	3.0553		

**Table S6.** BVS calculations for Co/Bi-POM (2).

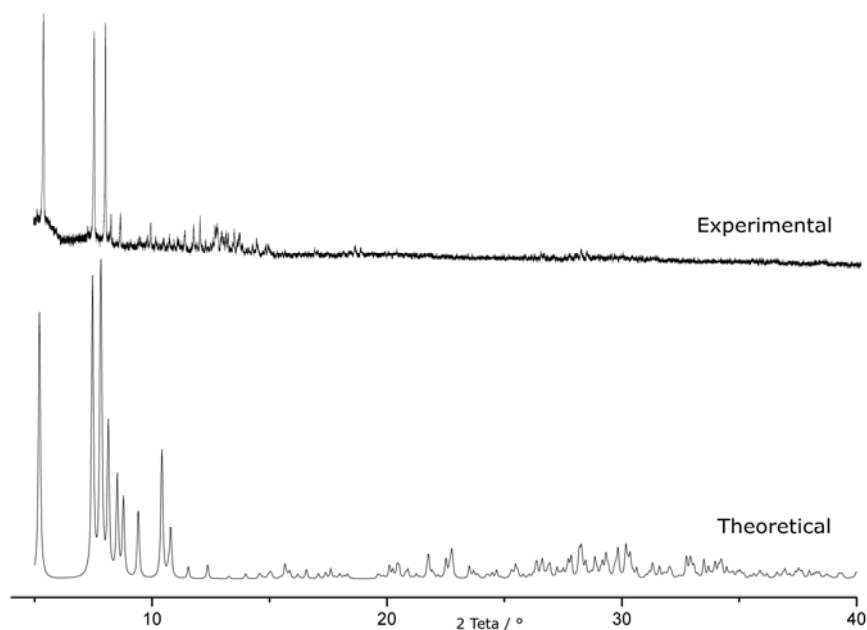
W(1)	5.9919	W(2)	5.9550	W(3)	6.0653	W(4)	6.0514	W(5)	5.9978
W(6)	5.9173	W(7)	5.9282	W(8)	6.0387	W(9)	6.1403		
O(1)	1.9715	O(2)	1.8872	O(3)	1.9769	O(4)	2.0096	O(5)	1.6580
O(6)	1.7484	O(7)	1.6012	O(8)	1.5565	O(9)	1.8132	O(10)	1.8023
O(11)	1.7640	O(12)	1.9987	O(13)	1.9724	O(14)	1.8450	O(15)	2.0266
O(16)	1.8880	O(17)	2.0758	O(18)	2.1200	O(19)	1.8890	O(20)	2.1338
O(21)	1.7609	O(22)	2.0051	O(23)	1.7037	O(24)	1.8435	O(25)	1.9203
O(26)	1.6300	O(27)	1.8069	O(28)	1.8301	O(29)	1.9658	O(30)	0.8556
O(31)	1.9466	O(32)	1.9459	O(33)	0.8930	O(34)	1.9793	O(35)	0.6812
O(36)	0.4661	O(37)	0.5844	O(38)	1.5320	Bi(1)	3.1871		

**Table S7.** BVS calculations for Mn/Bi-POM (3).

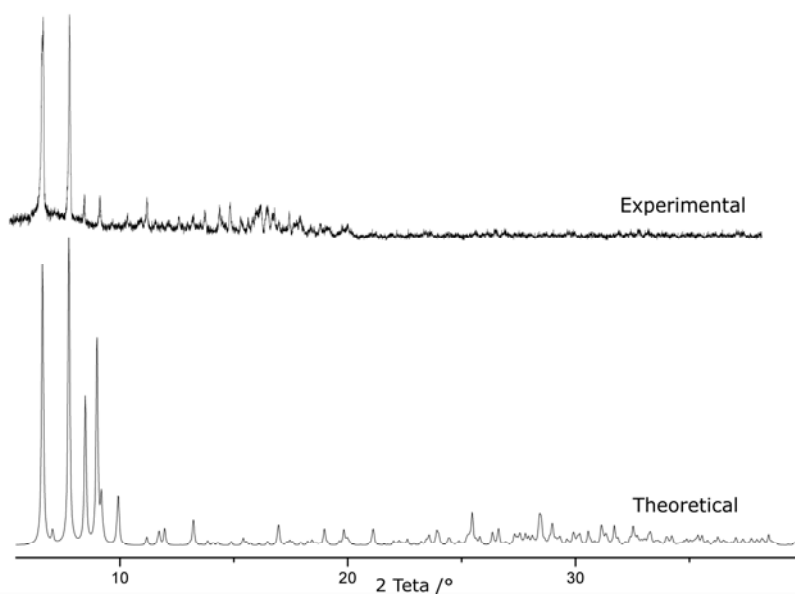
W(1)	6.0647	W(2)	5.8833	W(3)	5.8648	W(4)	6.1044	W(5)	5.9232
W(6)	6.1583	W(7)	6.1585	W(8)	6.1359	W(9)	6.1237		
O(1)	1.6365	O(2)	1.8674	O(3)	1.9795	O(4)	2.0054	O(5)	1.8918
O(6)	2.0622	O(7)	2.1167	O(8)	1.6024	O(9)	1.7684	O(10)	1.8262
O(11)	2.0320	O(12)	1.8315	O(13)	1.8622	O(14)	2.1179	O(15)	1.5245
O(16)	1.8882	O(17)	1.9983	O(18)	1.6470	O(19)	2.0299	O(20)	1.7770
O(21)	1.5933	O(22)	1.8188	O(23)	1.6365	O(24)	1.9362	O(25)	1.9694
O(26)	2.0424	O(27)	2.0426	O(28)	1.6725	O(29)	1.6405	O(30)	1.8219
O(31)	2.0178	O(32)	1.9216	O(33)	1.9774	O(34)	1.4063	O(35)	1.3195
O(36)	0.6106	O(37)	0.4507	O(38)	0.4970	Bi(1)	3.1644		



**Figure S1.** X-ray powder diffraction pattern of bulk Co/Bi-POM (1) vs. calculated pattern. Intensity differences may be due to preferred orientation of the powder sample.



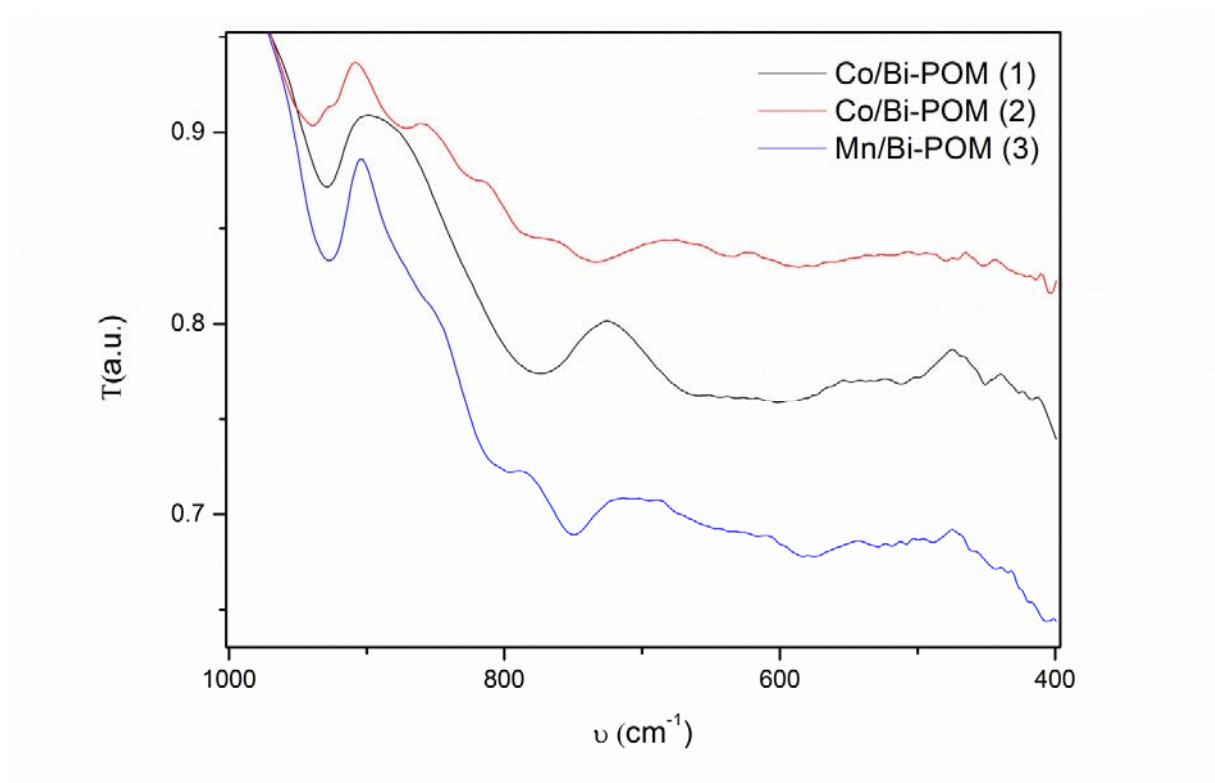
**Figure S2.** X-ray powder diffraction pattern of bulk Co/Bi-POM (2) vs. calculated pattern. Intensity differences may be due to preferred orientation of the powder sample.



**Figure S3.** X-ray powder diffraction pattern of bulk Co/Bi-POM (**3**) vs. calculated pattern. Intensity differences may be due to preferred orientation of the powder sample.



## 2. Spectroscopic characterization



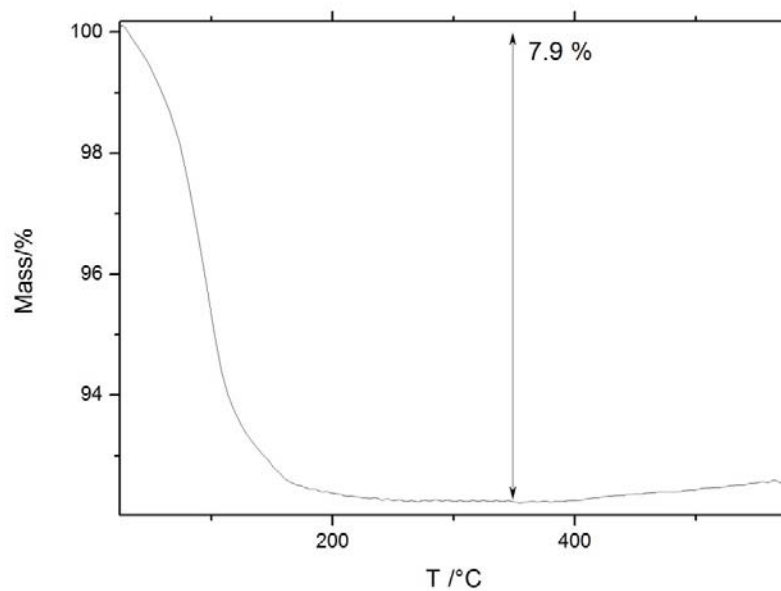
**Figure S4.** FT-IR spectra of pristine Co/Bi-POM **(1)** (black), Co/Bi-POM **(2)** (red) and Mn/Bi-POM **(3)** (blue).

The FT-IR spectrum of Co/Bi-POM **(1)** (Fig. S4) has one absorption band at  $930\text{ cm}^{-1}$  (s) attributed to the characteristic vibration  $\nu(\text{W-O(d) stretching})$ , and one broad band centered at  $775\text{ cm}^{-1}$  assigned to the  $\nu(\text{Co-O-W})$  stretch vibration of the tetrahedral Co(II) site. The lower energetic and less defined transitions at  $664\text{ cm}^{-1}$ , and  $425\text{ cm}^{-1}$  are assigned to the  $\nu(\text{Co-O-W})$  stretching vibrations and the  $589\text{ cm}^{-1}$  band is assigned to the  $\nu(\text{Co-O-W bending})$  vibration mode.

The FT-IR spectrum of Co/Bi-POM **(2)** shows differences compared to Co/Bi-POM **(1)** (see Fig. 4): the vibration bands  $\nu(\text{W-O(d) stretch})$  and  $\nu(\text{O(b)-W-O(b)}$  (or W-O-W stretch) are shifted to higher energy ( $938\text{ cm}^{-1}$  (s) with a shoulder at  $953\text{ cm}^{-1}$  (w)), and a series of weak bands appeared at  $875\text{ cm}^{-1}$  (s),  $823\text{ cm}^{-1}$  (s),  $789\text{ cm}^{-1}$  (s) and  $733\text{ cm}^{-1}$  (w) assigned to the  $\nu(\text{Co-O-W})$  stretching vibrations.

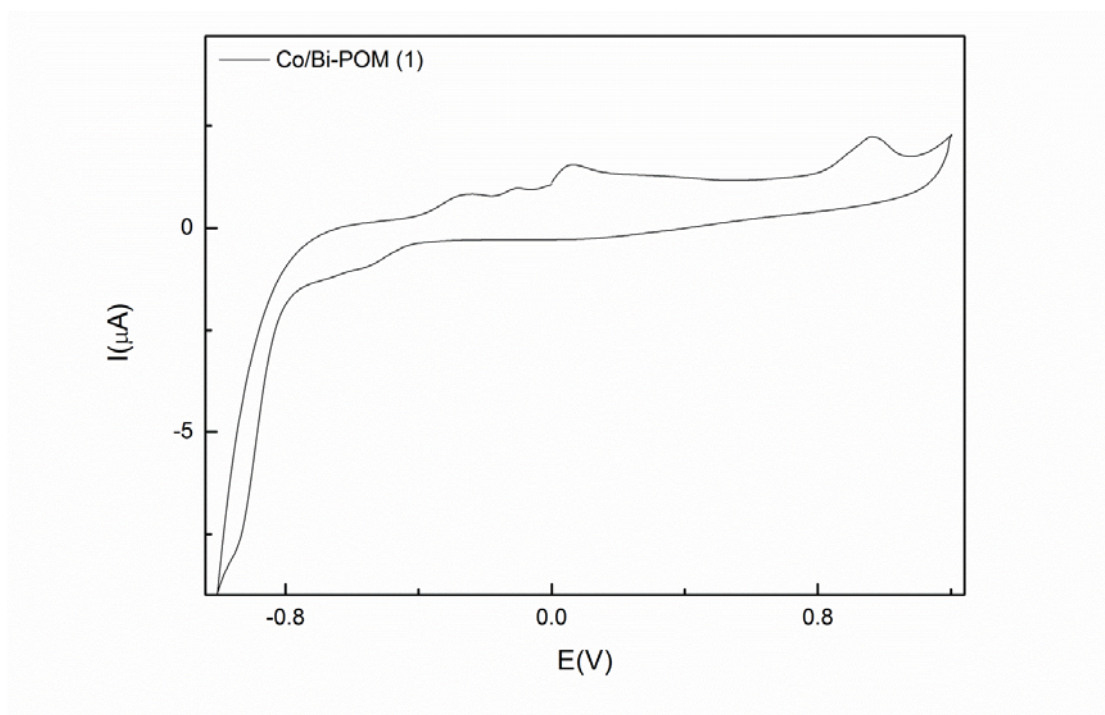
The FT-IR spectrum of Mn/Bi-POM **(3)** (Fig. S4) displays one absorption at  $926\text{ cm}^{-1}$  (s), another band centered at  $870\text{ cm}^{-1}$  (s) and a more defined peak at  $759\text{ cm}^{-1}$  (w) attributed to the characteristic vibration bands  $\nu(\text{W-O(d) stretching})$  and  $\nu(\text{O(b)-W-O(b)}$  (or W-O-W stretching). The transition at  $578\text{ cm}^{-1}$  (w) is assigned to the  $\nu(\text{Mn-O-W bending})$  of the tetrahedral Mn(II).

### 3. Thermogravimetric analyses (TGA)

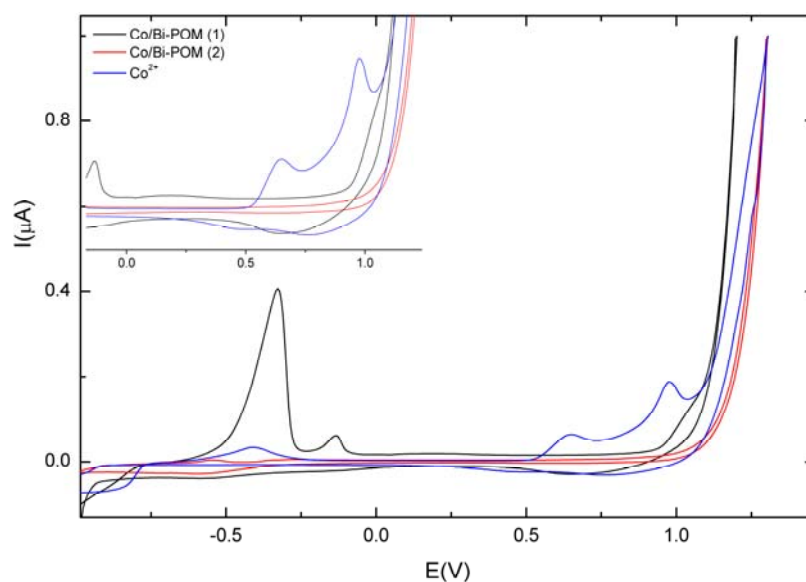


**Figure S5.** TG analysis of pristine Mn/Bi-POM (**3**) (air, Al<sub>2</sub>O<sub>3</sub> crucible, heating rate 10 K/min).

#### 4. Electrochemical characterization



**Figure S6.** Cyclic voltammogram of Co/Bi-POM (1) (15.8 mM) in H<sub>2</sub>SO<sub>4</sub> (0.4 M) at pH 3 (red line), scan rate: 10 mV/s, (vs. Ag/AgCl).



**Figure S7.** Cyclic voltammograms of Co/Bi-POM (1), Co/Bi-POM (2) (both 15.8 mM) and Co(NO<sub>3</sub>)<sub>2</sub> (50 mM) in Na<sub>2</sub>SiF<sub>6</sub>/NaHCO<sub>3</sub> buffer (20 mM, pH=5.8); scan rate: 10 mV/s, (vs. Ag/AgCl). Insert: magnification of 0-1 V range.

## 5. Water oxidation catalysis tests

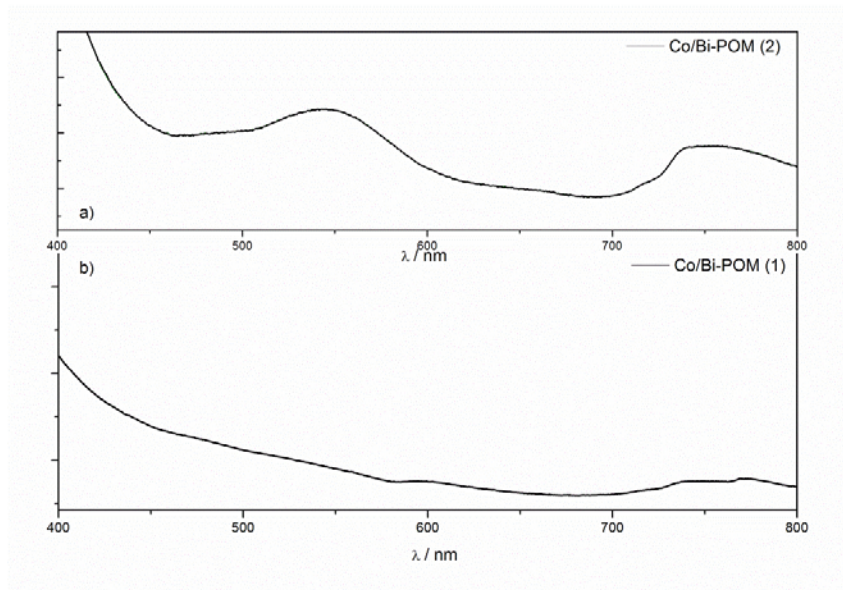
### 5.1. Experimental procedure for WOC activity tests

Water oxidation performance for all compounds has been monitored simultaneously using Clark electrodes and GC equipment. After the degassing process, first 100  $\mu\text{L}$  of headspace were injected into the GC to monitor the efficiency of the He-purging. The  $\text{O}_2/\text{N}_2$  ratio was evaluated and subtracted by the mean of the calibration line. Note that no He-injection in the headspace has been performed in order to re-balance the lower pressure caused by the GC injection.

After evaluation of the purging process, the Clark-electrode was lifted down in the catalytic vial, first in the headspace and once it showed constant voltage, it was moved down into the solution. After 30'' of equilibration time at controlled 500 rpm, the irradiation was started and the oxygen evolution kinetics were recorded.

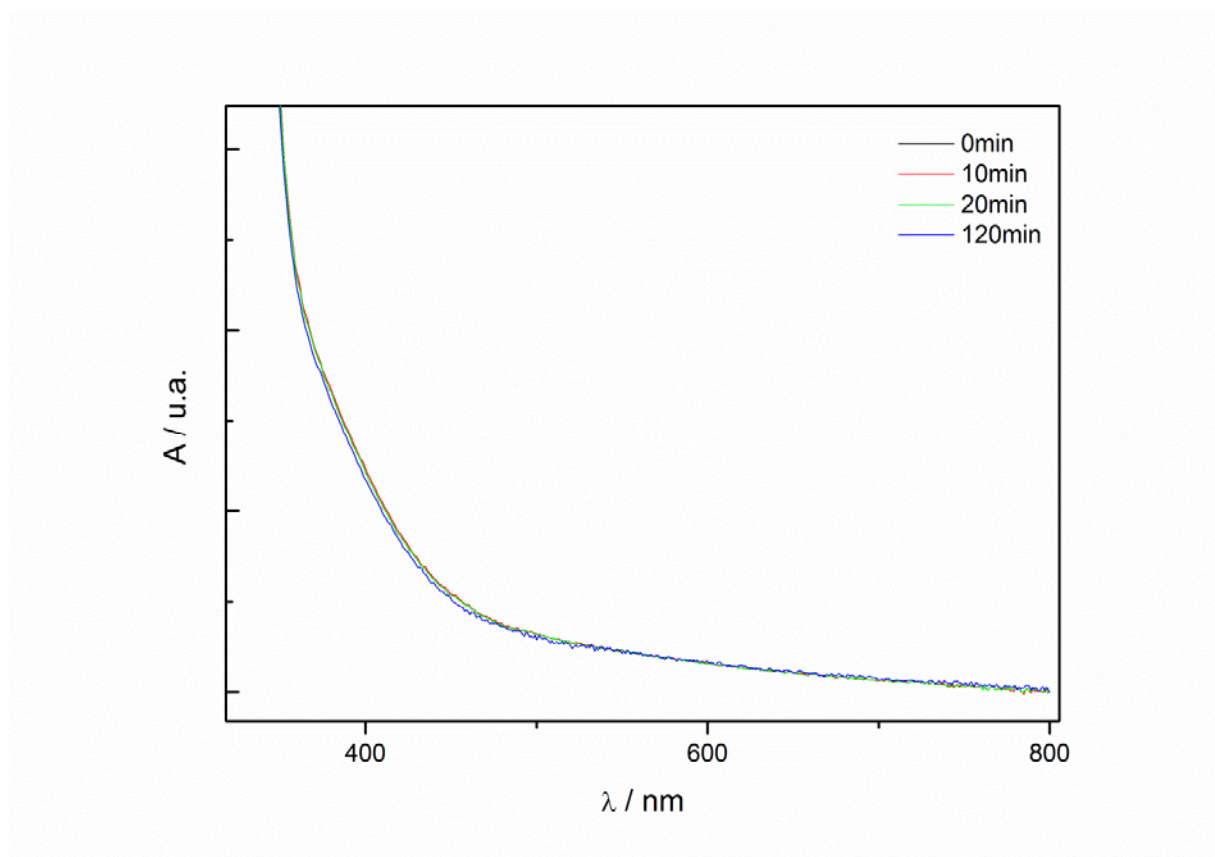
For Co/Bi-POM (**1**), maximum amounts of  $\text{O}_2$  dissolved in solution was obtained after 30 min of Clark electrode monitoring; no GC injection was performed up to this point. GC injection was initiated 1 h after the reaction had started to evaluate the final  $\text{O}_2$  yield of the catalytic process (Fig. S10).

### 5.2. WOC stability tests



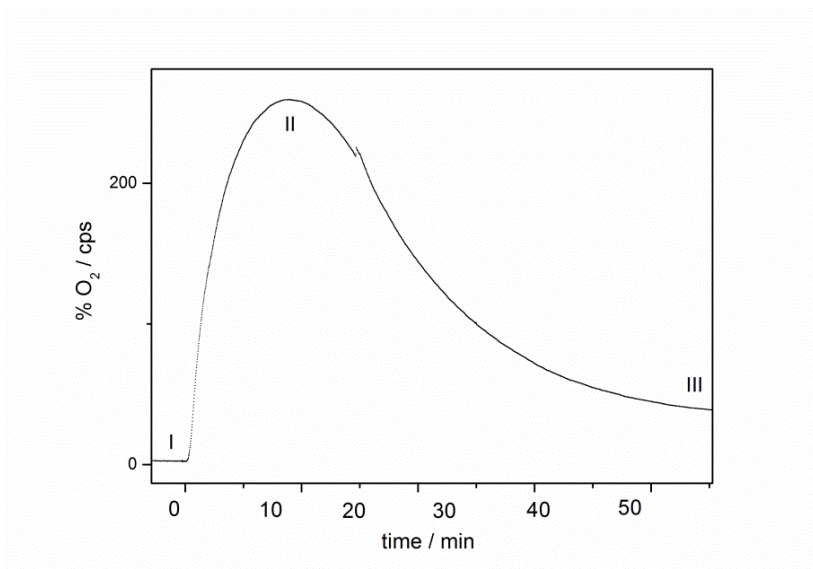
**Figure S8.** UV/Vis absorption spectra of Co/Bi-POM (**1**) (50  $\mu\text{M}$ , bottom) and Co/Bi-POM (**2**) (70 mM, top) in NaPi (40 mM) buffer at pH=8.



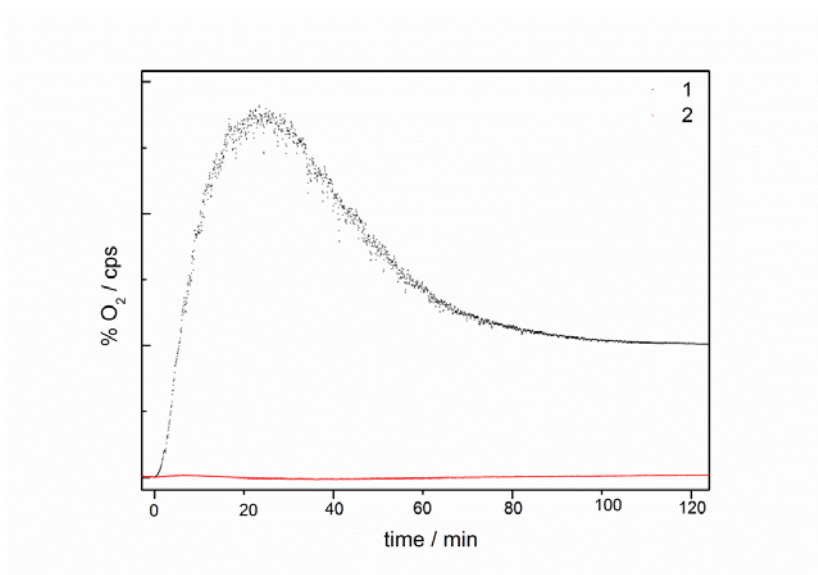


**Figure S9.** UV/Vis absorption spectrum of Mn/Bi-POM (**3**) (50 mM) in Na<sub>2</sub>SiF<sub>6</sub>/NaHCO<sub>3</sub> buffer (20 mM, pH=5.8).

### 5.3. Clark electrode tests for visible light driven water oxidation

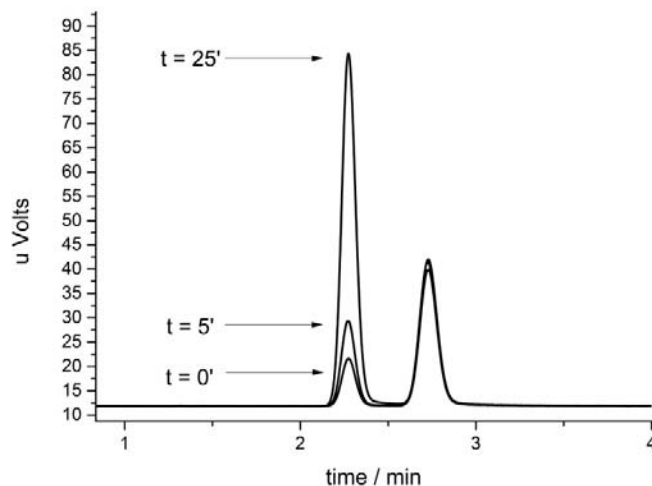


**Figure S10.** Clark-electrode kinetics for visible-light-driven  $O_2$  formation with Co/Bi-POM (**1**). Conditions: LED lamp, 470 nm; 1 mM  $[Ru(bpy)_3]Cl_2$ , 5 mM  $Na_2S_2O_8$ ,  $Na_2SiF_6/NaHCO_3$  buffer (20 mM, pH=5.8). At time **I** the first GC control-injection is performed, and irradiation was started after complete purging. At time **II**, usually after 20-25 min, the oxygen evolution reached the maximum value after  $O_2$  in solution and headspace were equilibrated, i.e. equilibrium between  $O_2$  (solution) and  $O_2$  (headspace) is reached. The last GC injection was performed after monitoring point **III** with the Clark electrode.

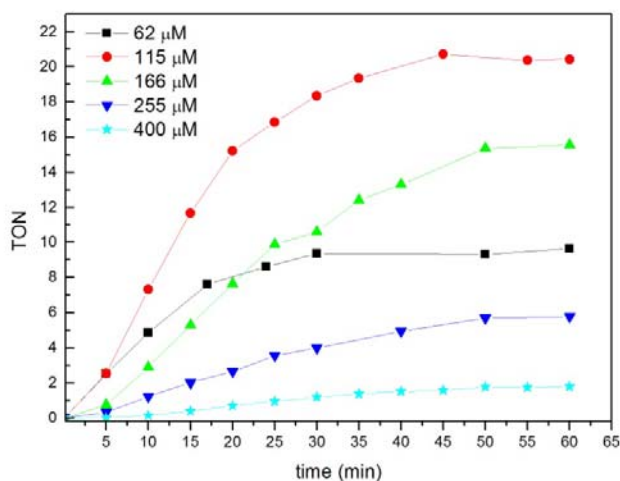


**Figure S11.** Clark-electrode kinetics of visible-light-driven  $O_2$  evolution for Co/Bi-POM (**1**) (black) and Co/Bi-POM (**2**) (red). Conditions: LED lamp, 470 nm; 1 mM  $[Ru(bpy)_3]Cl_2$ , 5 mM  $Na_2S_2O_8$ ,  $Na_2SiF_6/NaHCO_3$  buffer (20 mM, pH=5.8).

#### 5.4. GC tests for visible-light-driven water oxidation



**Figure S12.** Representative GC kinetics traces of headspace injection of Co/Bi-POM (**1**) after 0, 5 and 25 min of illumination with LED lamp, 470 nm (conditions: 1 mM  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 5 mM  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$  buffer (20 mM, pH=5.8)).  $\text{N}_2$  area is in line with the manual injection.<sup>1</sup> Referring to Fig. S11, injection at 0 min corresponds to time **I**, injection at 5 min corresponds to a range time between time **I**–**II** and GC injection at 25 min corresponds to a time after **III**.



**Figure S13.** GC kinetics for visible-light-driven  $\text{O}_2$  formation from water oxidation for Co/Bi-POM (**1**) with persulfate as a sacrificial electron acceptor. Conditions: LED lamp, 470 nm; 1 mM  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 5 mM  $\text{Na}_2\text{S}_2\text{O}_8$ ,  $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$  buffer (20 mM, pH=5.8). [light blue: 400  $\mu\text{M}$ , black: 62  $\mu\text{M}$ , blue: 255  $\mu\text{M}$ , green: 166  $\mu\text{M}$ , red : 115  $\mu\text{M}$ ].

<sup>1</sup> P. E. Car, M. Guttentag, K. K. Baldrige, R. Alberto and G. R. Patzke, *Green Chem.*, 2012, **14**, 1680-1688.

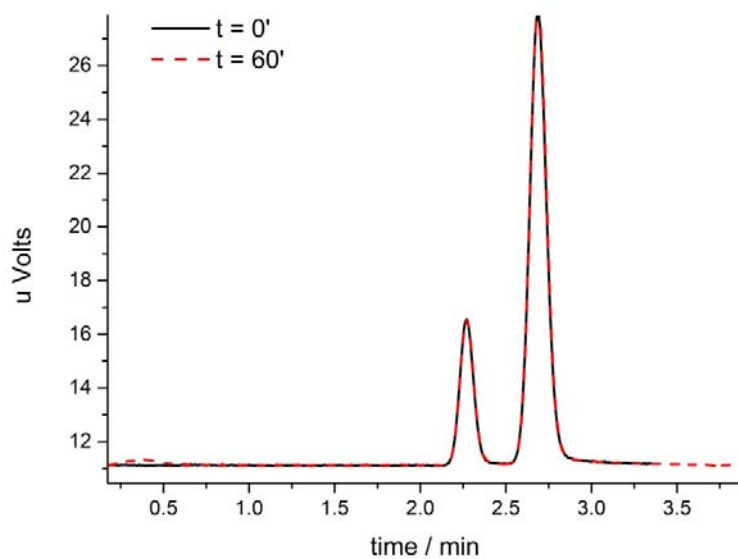
**Table S8.** Influence of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  and  $\text{Na}_2\text{S}_2\text{O}_8$  on WOC performance of Co/Bi-POM (**1**) under different catalytic conditions (top: 1 mM  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ , 166  $\mu\text{M}$  (**1**) and different amounts of  $\text{Na}_2\text{S}_2\text{O}_8$  in  $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$  buffer (20 mM, pH = 5.8).

$\text{Na}_2\text{S}_2\text{O}_8$ (mM)	$\text{O}_2$ ( $\mu\text{mol}$ )	Yield (%)
0	0	0
2	9.2	62.5
5	29.7	96.6
7	21.3	48.3
9	14	23.6

$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ (mM)	$\text{O}_2$ ( $\mu\text{mol}$ )	Yield (%)
0	0	0
0.5	13.1	40.5
1	28.7	96.6
2	14.4	44.2

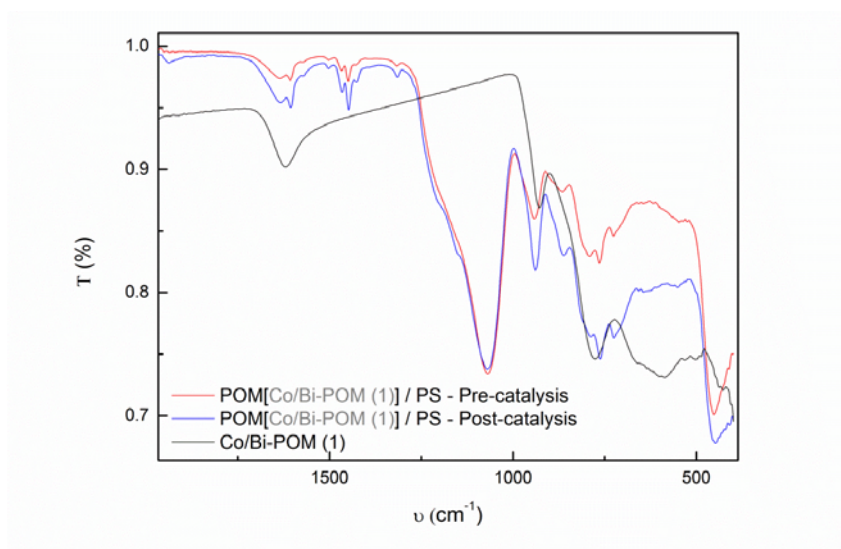




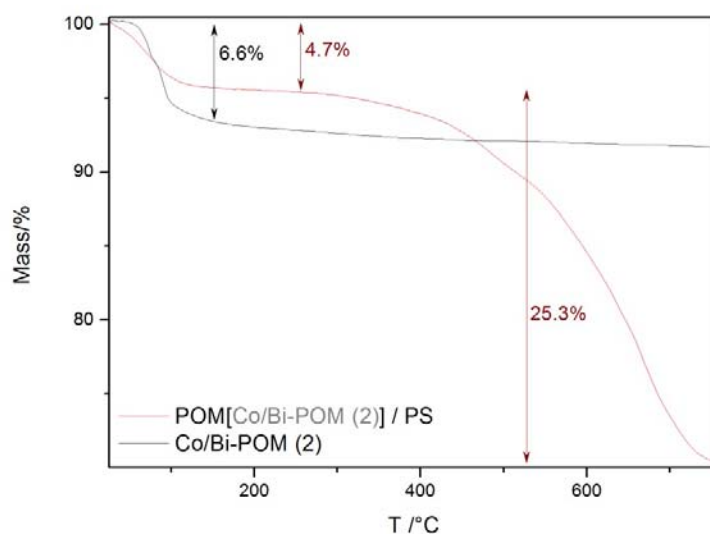
**Figure S14.** Representative GC kinetics traces of headspace injection of Co/Bi-POM (**2**) after 0 and 60 min of irradiation (conditions: 470 nm LED, 1 mM [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, 5 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Na<sub>2</sub>SiF<sub>6</sub>/NaHCO<sub>3</sub> buffer (20 mM, pH = 5.8) and 100 μM of Co/Bi-POM (**2**) as representative concentration). N<sub>2</sub> area is in line with the manual injection.<sup>2</sup>

<sup>2</sup> P. E. Car, M. Guttentag, K. K. Baldrige, R. Alberto and G. R. Patzke, *Green Chem.*, 2012, **14**, 1680-1688.

### 5.5. Investigation of POM/PS complexes



**Figure S15.** FT-IR spectra of of pristine Co/Bi-POM (1) (black), Co/Bi-POM (1)/PS complex obtained from  $\text{Na}_2\text{SiF}_6$  before catalysis (red), Co/Bi-POM (1)/PS complex obtained from  $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$  buffer (20 mM, pH=5.8) recovered from the second catalytic test (blue).



**Figure S16.** TG curves of pristine Co/Bi-POM (2) (black) and Co/Bi-POM (2)/PS complex obtained from  $\text{Na}_2\text{SiF}_6/\text{NaHCO}_3$  buffer (20 mM, pH=5.8) after catalytic test (air,  $\text{Al}_2\text{O}_3$  crucible, heating rate 10 K/min).