Supporting Information for

Water oxidation catalyzed by a new tetracobalt-substituted polyxometalate complex: $[\{Co_4(\mu\text{-}OH)(H_2O)_3\}(Si_2W_{19}O_{70})]^{11-}$

Guibo Zhu[a], Yurii V. Geletii[a], Paul Kögerler[b], Helmut Schilder[b], Jie Song[a], Sheri Lense[a], Chongchao Zhao[a], Kenneth I. Hardcastle[a], Djamaladdin G. Musaev[c], and Craig L. Hill[a]*

[a]Department of Chemistry, Emory University, Atlanta, GA 30322, USA. [b]Institut für Anorganische Chemie, RWTH Aachen University, D-52074 Aachen, Germany. [c]Cherry L. Emerson Center for Scientific Computation, Emory University, Atlanta, GA 30322. Fax: 404-727-6076; Tel: 404-727-6611; E-mail: chill@emory.edu.

Table of Contents

Fig. S1 X-Ray structure of **polyanion** $[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{Co(H_2O)_4\}(Si_2W_{18}O_{66})]^{11-}$ **(3)**.

Fig. S2 IR spectra of $K_{10.2}Na_{0.8}$-**2** (upper) and $K_{10}Na$-**3** (lower).

Fig. S3 Thermogravimetric Analysis (TGA) of crystalline $K_{10.2}Na_{0.8}$-**2**.

Fig. S4 TGA of crystalline $K_{10}Na$-**3**

Fig. S5 Cyclic voltammograms of 160 mM sodium borate buffer solution at pH 9 and of 1 mM **2** in the same solution.

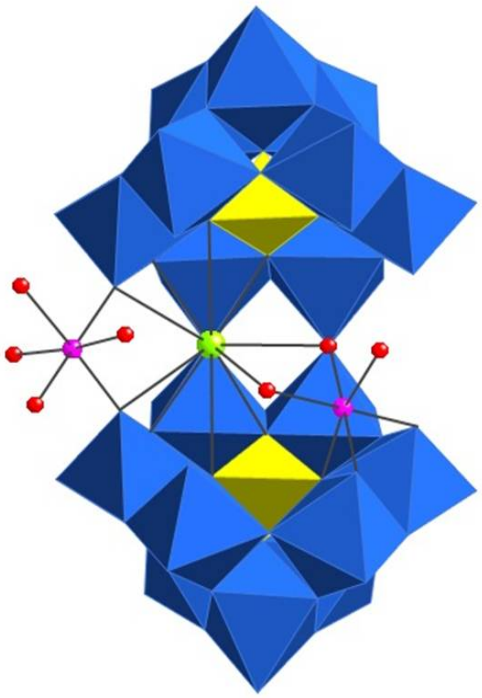

Fig. S1 X-Ray structure of polyanion $[\{Co(H_2O)\}(\mu\text{-}H_2O)_2K\{Co(H_2O)_4\}(Si_2W_{18}O_{66})]^{11-}$ (**3**). The cobalt atoms (purple) and the potassium atom (green) are in ball-and-stick notation and the rest of the polyoxometalate framework is in polyhedral notation (WO_6 octahedra: blue, SiO_4 tetrahedra: yellow). Hydrogen atoms are omitted for clarity.

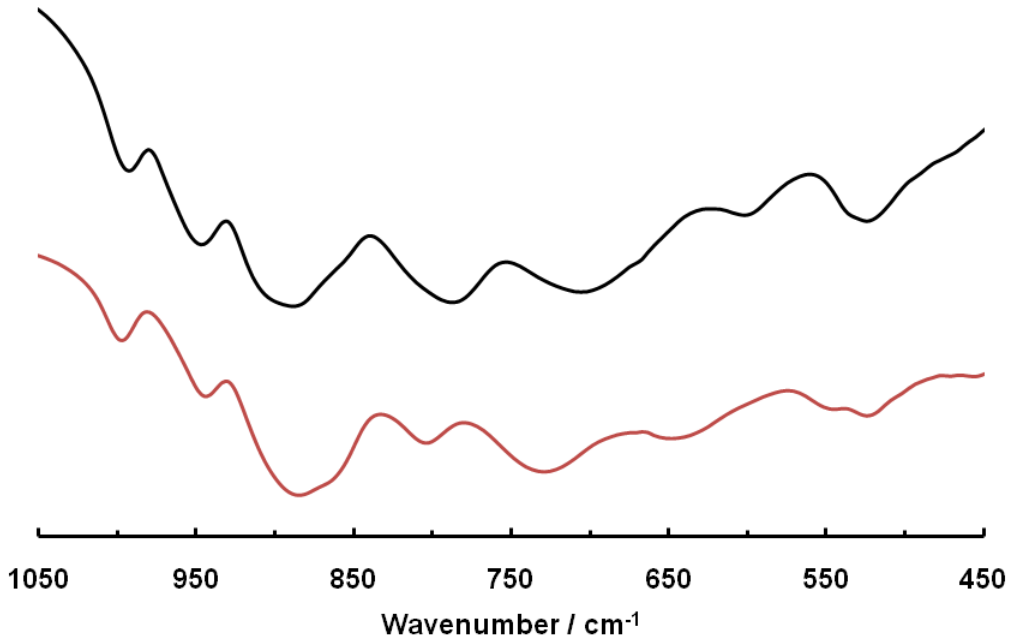

Fig. S2 IR spectra of $K_{10.2}Na_{0.8}$-**2**(upper) and $K_{10}Na$-**3** (lower).

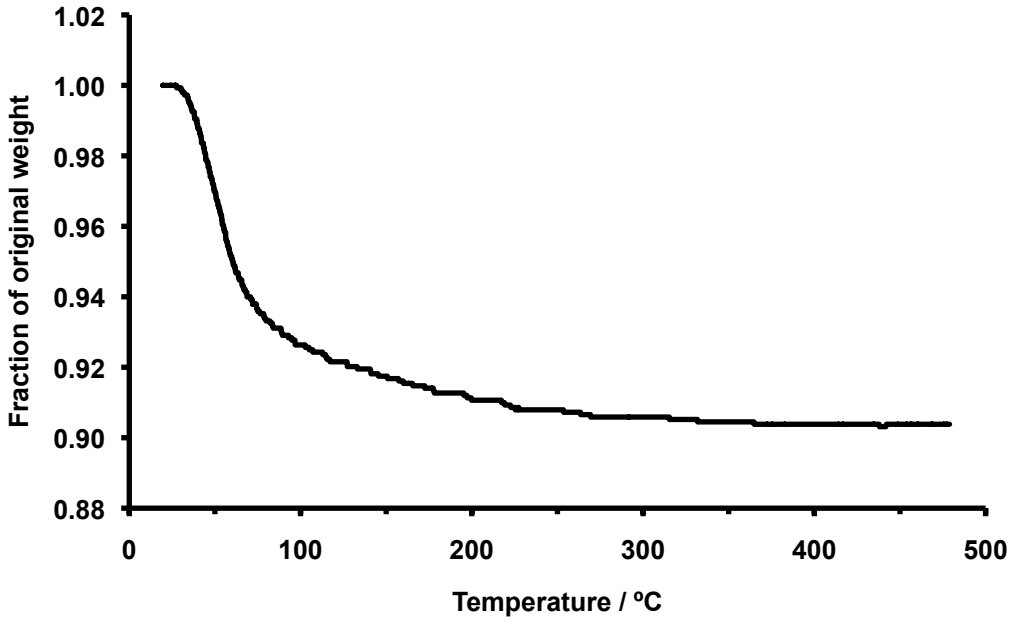

Fig. S3 Thermogravimetric Analysis (TGA) of crystalline $K_{10.2}Na_{0.8}$-**2**.

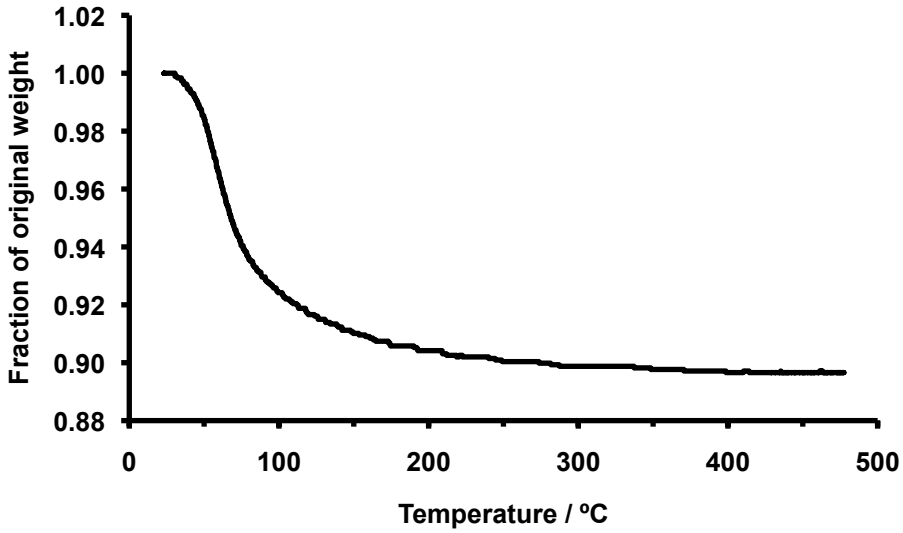

Fig. S4 TGA of crystalline $K_{10}Na$-**3**.

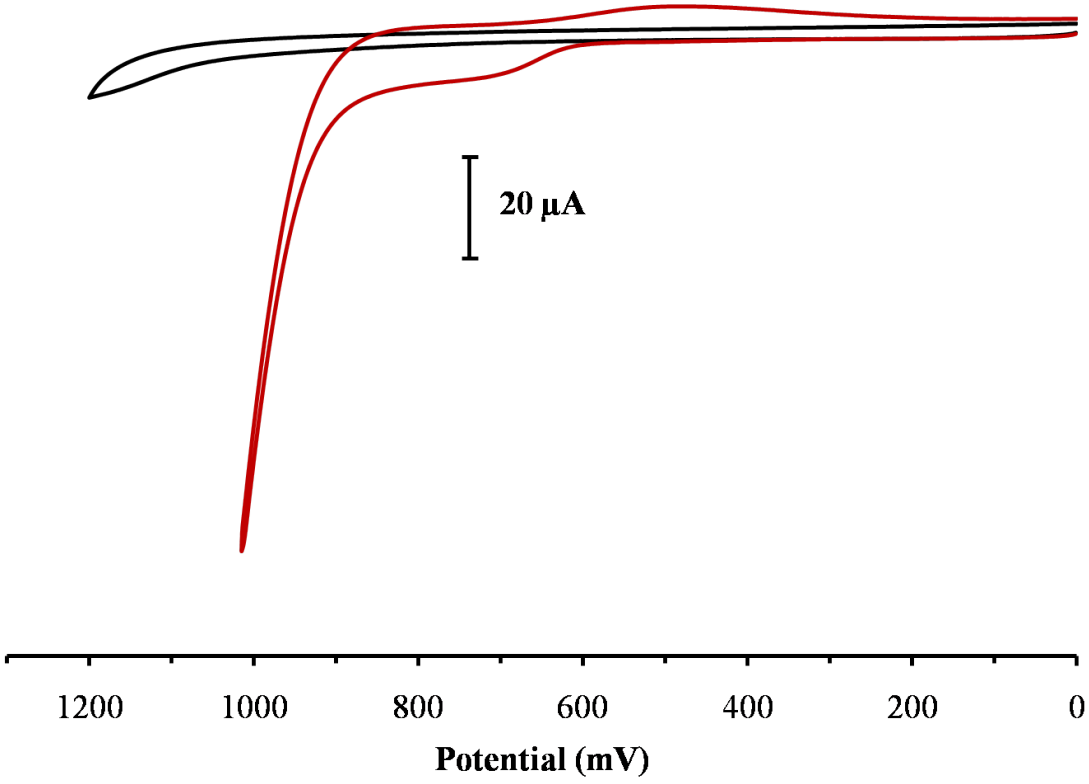

Fig. S5 Cyclic voltammograms of 160 mM sodium borate buffer solution at pH 9 (black curve) and of 1 mM **2** (red curve) in the same solution. Scan rate 100 mV/s. Cyclic voltammetry of 1 mM **2** shows a large catalytic current with a low overpotential for the water oxidation.