Electric Supplemental Information for:

Two Novel Zipper-like Compounds of the Usual and Bivanadyl Capped Keggin Clusters Connected by Propeller-shaped Complexes

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Chart S1. Structure of ligand L.

Table S1 The bond valence sum calculations for V atoms in compound **2**.

Compound	Atoms	BVS
2	V1	4.394
	V2	4.378
	V3	4.665
	V4	4.819

Fig. S1. View of the assembly process of the 1D poly-pendant infinite chain in **1**.

Fig. S2. The schematic view of the spherical diameters of PMo_{12} and PMo_8V_6 polyoxoanions.

Fig. S3. XPS of compound **1** and **2**.

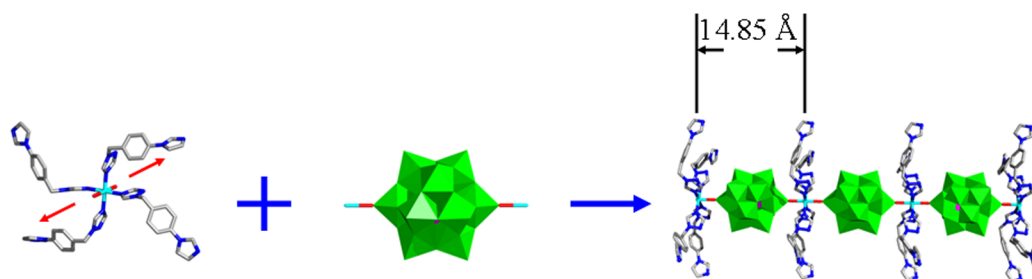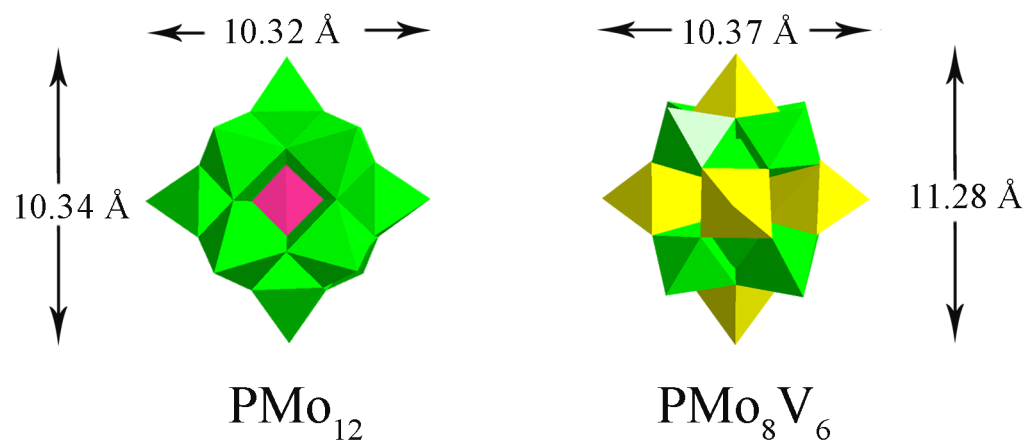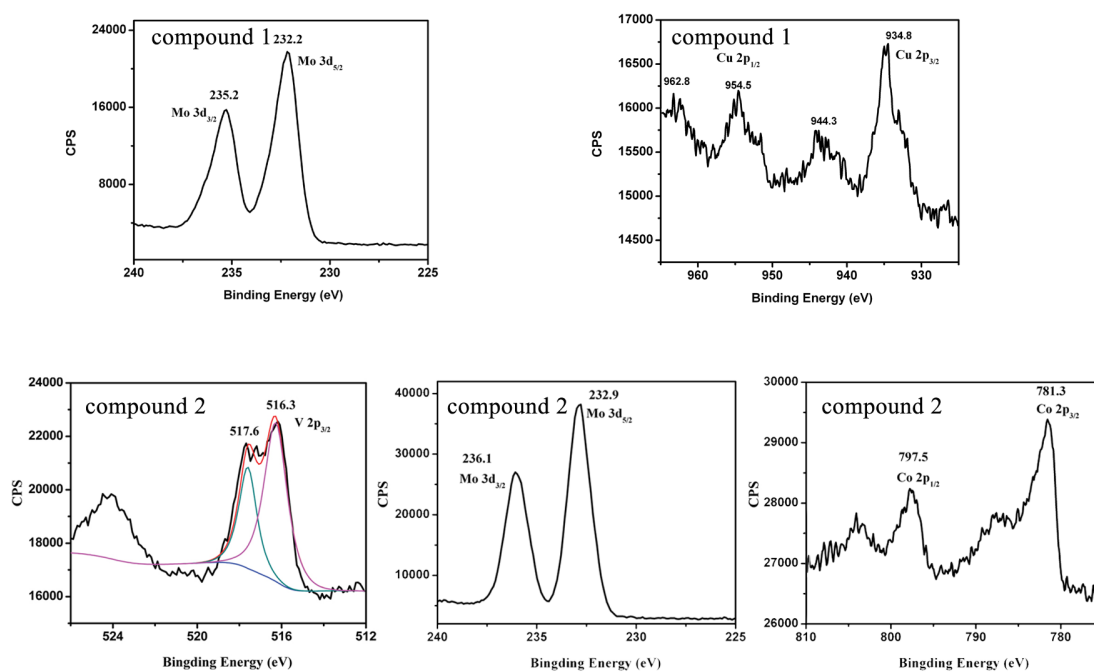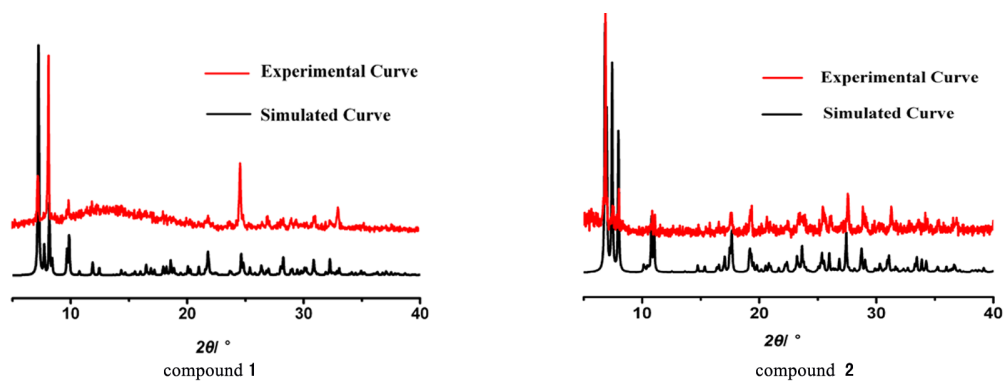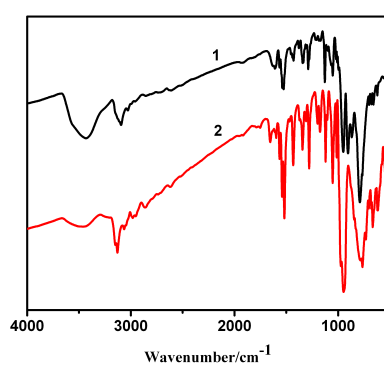**Fig. S4.** PXRD patterns for compounds **1** and **2**.

Fig. S5. IR spectra of compounds **1** and **2**.
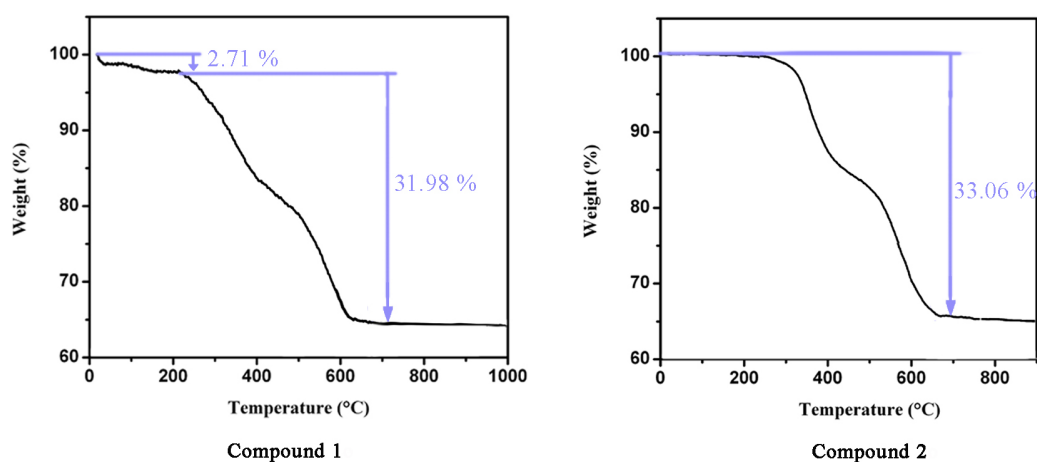

Fig. S6. TG curves of **1** and **2**.
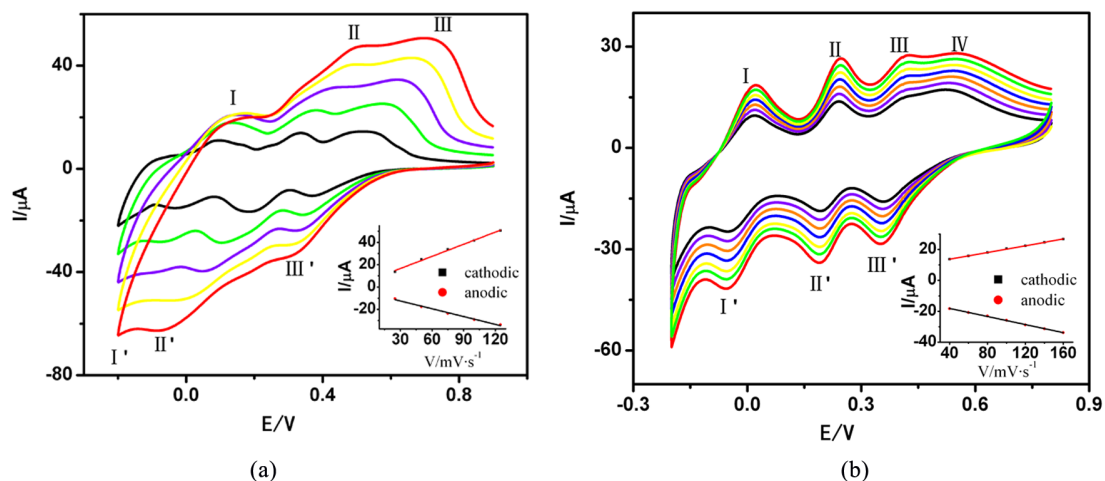
Fig. S7. (a) Cyclic voltammograms of the **1**-CPE in 0.5M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 25, 50, 75, 100, 125mV/s) in the potential range of +900 to −200 mV. The inset shows plots of the anodic and the cathodic peak currents for III against scan rates. (b) Cyclic voltammograms of the **2**-CPE in 0.5M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 60, 80, 100, 120, 140, 160mV/s). in the potential range of +800 to −200 mV. The inset shows plots of the anodic and the cathodic peak currents for II against scan rates. Potentials vs Ag/AgCl.

Fig. S8. Reduction of IO_3^- (a) and oxidation of AA (b) for **1**-CPE in 0.5 M H_2SO_4 solution containing IO_3^- and AA: 0.0, 0.2, 0.4, 0.6, 0.8 mM. Scan rate: 50 mV/s. In the potential range of +900 to −200 mV and +800 to −200 mV, respectively. Potentials vs Ag/AgCl.

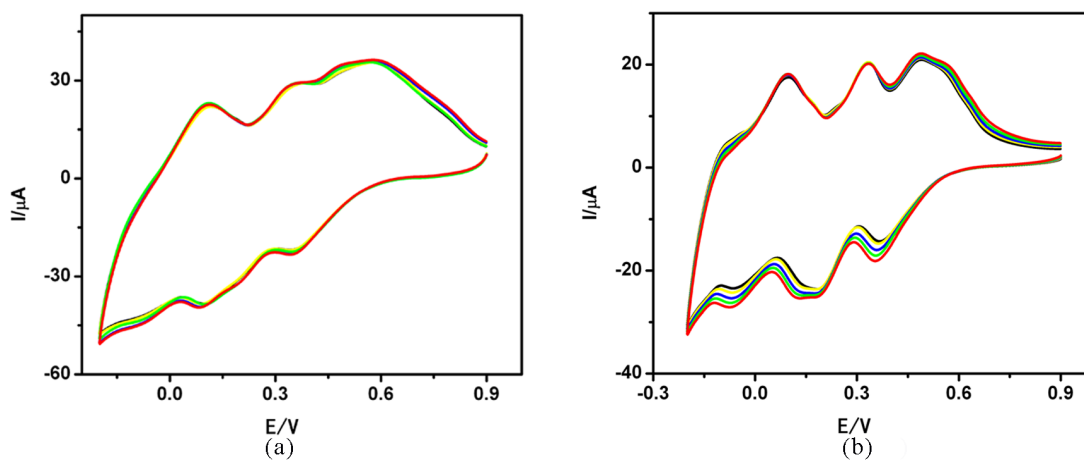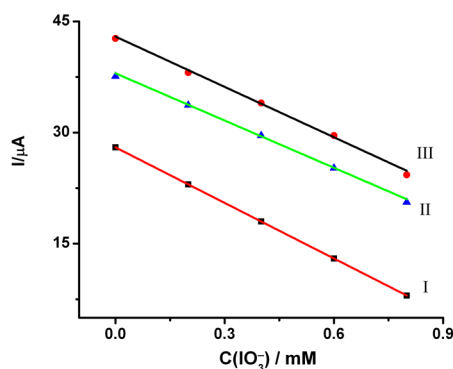**Fig. S9.** A linear dependence of the anodic current peaks of **2**-CPE with iodated concentration. Potentials vs Ag/AgCl. Scan rate: 100 mV/s.

A discussion for CVs.

Part I. Both CPEs toward different scan rate

As shown in Fig. S7, in the potential range +900 to −200 mV, with scan rate varying from 25 to 125 mV·s^{-1} for **1**-CPE, the peak currents increased, and cathodicpeak potentials (Epc) shifted slightly to negative potential values and the anodic peak potentials (Epa) shifted slightly to positive potential values, which is consistent with a reversible but non-ideal redox process[1]. Taking the peak III as a representative, the linear relationships of the peaks current with the scan rate were analyzed. The linear regression equations for the peak current with the scan rate are $I_{a3}(\mu A) = 0.3624 \ (mV·s^{-1}) + 5.72$, $R^2_{a3} = 0.9963$ for anodic peak, and $I_{c3}(\mu A) = -0.2332 \ (mV·s^{-1}) - 5.47$, $R^2_{c3} = 0.9926$ for cathodic peak, respectively, which indicates that the redox process is surface-controlled. In the potential range +800 to −200 mV, with scan rate varying from 40 to 160 mV·s^{-1} for **2**-CPE, the currents for second couple waves increased gradually and the peak potentials were almost unchanged. The linear relationships of the peak current with scan rate were studied from the CVs data. The linear regression equations for the peak current with scan rate are $I_{a2}(\mu A) = 0.1089 \ (mV·s^{-1}) + 9.3643$, $R^2_{a2} = 0.9989$, and $I_{c2}(\mu A) = -0.1309 \ (mV·s^{-1}) - 12.882$, $R^2_{c2} = 0.9997$, respectively. The results indicat that the peak current of **2** exhibit a linear dependence on scan rate between 40 and 160 mV·s^{-1}. The clear linear relationship indicates that the redox process is surface-controlled.

[1] (*a*) S. P. Liu, F. Y. Li, W. H. Guo, Y. Xing, Z. X. Sun, *Electrochim. Acta*, 2011, **56**, 8156; (*b*)
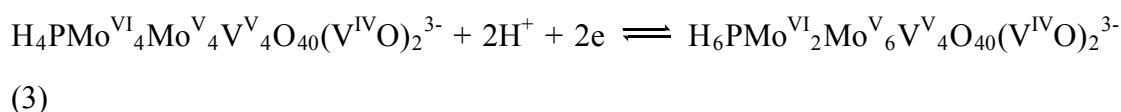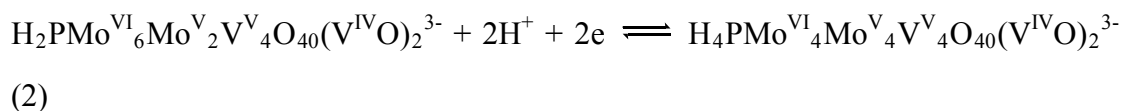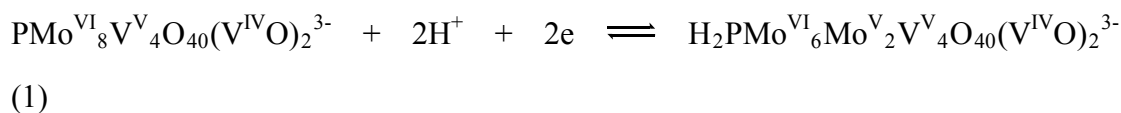
S. Q. Liu, D. G. Kurth, B. Bredenkötter, D. Volkmer, *J. Am. Chem. Soc.*, 2002, **124**, 12279.

Part II. The mechanisms of electrocatalytic activities for 2-CPE toward iodated (IO_3^-) and ascorbic acid (AA)
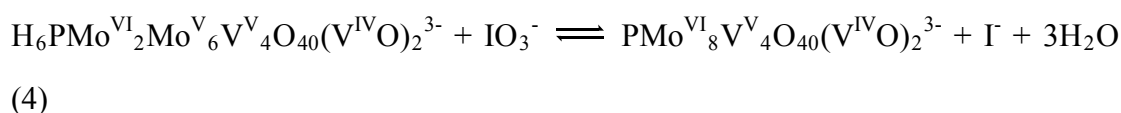
In the potential range of +800 to −150 mV, with addition of KIO_3, the reduction peak currents I', II' and III' of **2**-CPE, increase gradually while the corresponding oxidation peak currents decrease.

The reaction mechanism of **2**-CPE toward IO_3^- can be described by the following equations[2]:
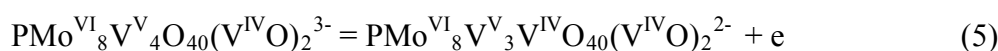
Electrochemical reactions:

$$PMo^{VI}_8V^V_4O_{40}(V^{IV}O)_2^{3-} + 2H^+ + 2e \rightleftharpoons H_2PMo^{VI}_6Mo^V_2V^V_4O_{40}(V^{IV}O)_2^{3-}$$

(1)

$$H_2PMo^{VI}_6Mo^V_2V^V_4O_{40}(V^{IV}O)_2^{3-} + 2H^+ + 2e \rightleftharpoons H_4PMo^{VI}_4Mo^V_4V^V_4O_{40}(V^{IV}O)_2^{3-}$$

(2)

$$H_4PMo^{VI}_4Mo^V_4V^V_4O_{40}(V^{IV}O)_2^{3-} + 2H^+ + 2e \rightleftharpoons H_6PMo^{VI}_2Mo^V_6V^V_4O_{40}(V^{IV}O)_2^{3-}$$

(3)

Catalytic chemical steps:

$$H_6PMo^{VI}_2Mo^V_6V^V_4O_{40}(V^{IV}O)_2^{3-} + IO_3^- \rightleftharpoons PMo^{VI}_8V^V_4O_{40}(V^{IV}O)_2^{3-} + I^- + 3H_2O$$
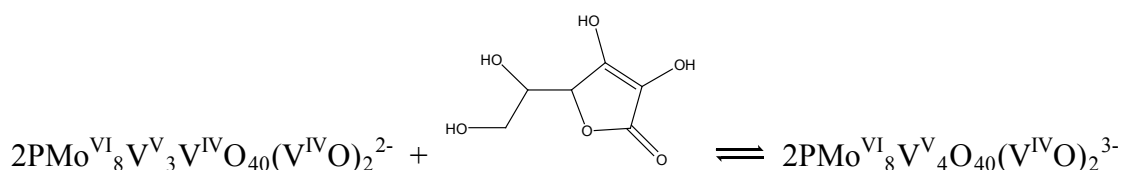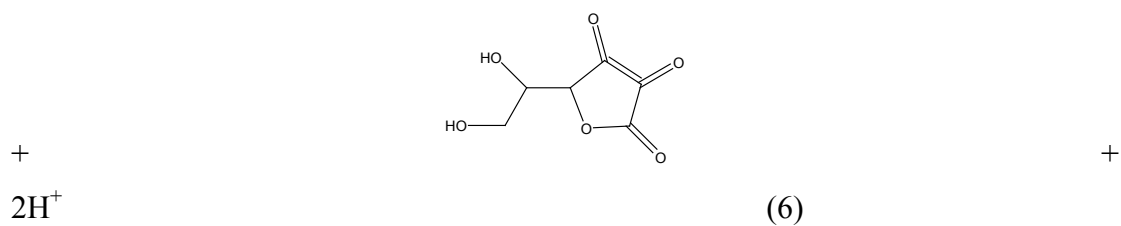
(4)

The electrocatalytic behavior of **2**-CPE toward ascorbic acid can be explained by the following mechanism[3]:

Electrochemical reactions:

$$PMo^{VI}_8V^V_4O_{40}(V^{IV}O)_2^{3-} = PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2^{2-} + e \qquad (5)$$

Catalytic chemical steps:

$$2PMo^{VI}_8V^V_3V^{IV}O_{40}(V^{IV}O)_2^{2-} + \text{[ascorbic acid]} \rightleftharpoons 2PMo^{VI}_8V^V_4O_{40}(V^{IV}O)_2^{3-}$$

+

+

$2H^+$ (6)
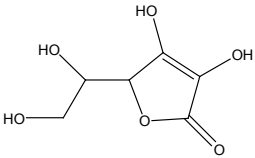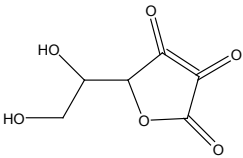
The ⟨structure⟩ is AA and the ⟨structure⟩ is the decomposition products of the AA.

[2] (*a*) X. Q. Lin and C. M. Jiang, *Anal. Sci.*, 2006, 22, 697; (*b*) M. Sadakane and E. Steckhan, *Chem. Rev.,* 1998, **98**, 219; (*c*) D. M. Fernandes, C. M. A. Brett, A. M. V. Cavaleiro, *J Solid State Electr.*, 2011, **15**, 811.

[3] (*a*) P. Wang, X. P. Wang, X. Y. Jing and G. Y. Zhu, *Anal. Chim. Acta*, 2000, **424**, 51; (*b*) S. Li, H. Y. Ma, K. P. O'Halloran, H. J. Pang, H. R. Ji, C. L. Zhou, *Electrochim. Acta*, 2013, 108, 717.