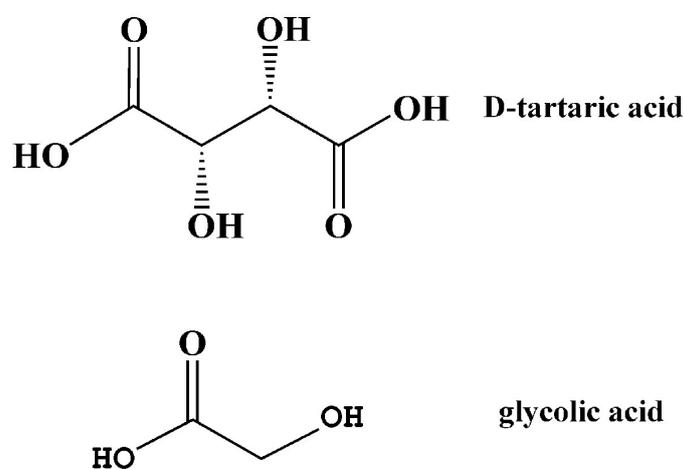


# Zr<sub>4</sub>-Substituted Polyoxometalate Dimers Decorated by D-Tartaric Acid/ Glycolic Acid: Syntheses, Structures and Optical/Electrochemical Properties

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Scheme S1. The ligands used in this work.

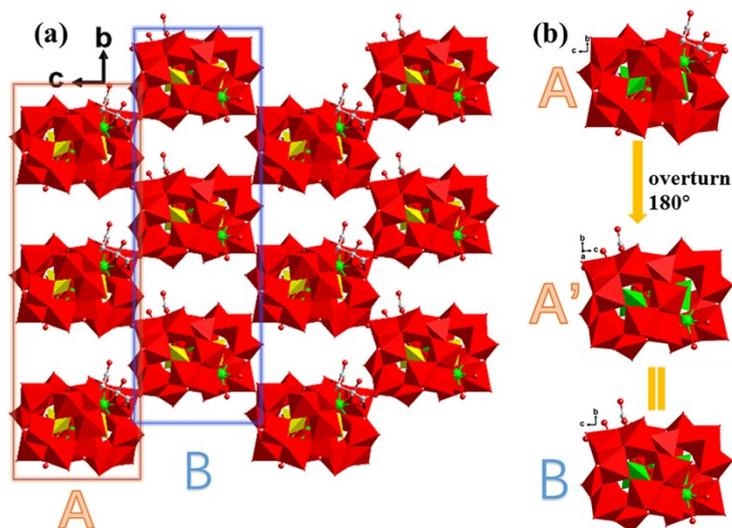
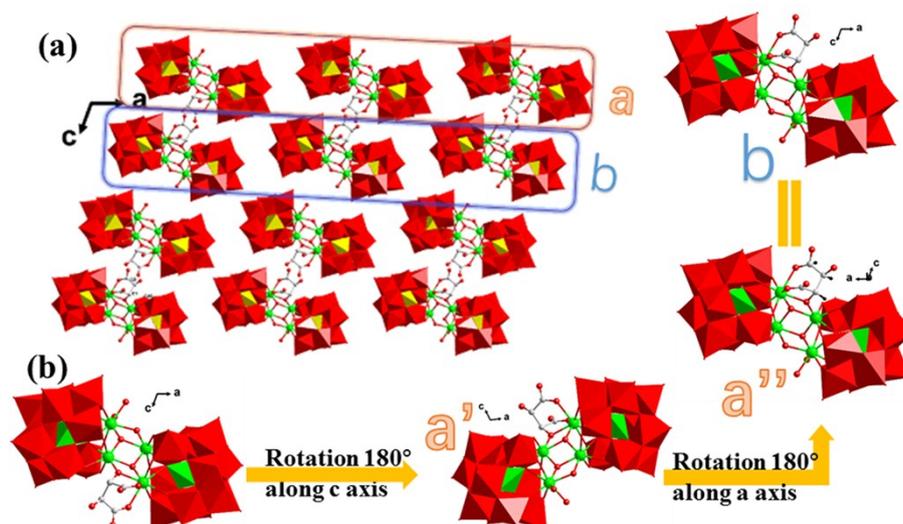
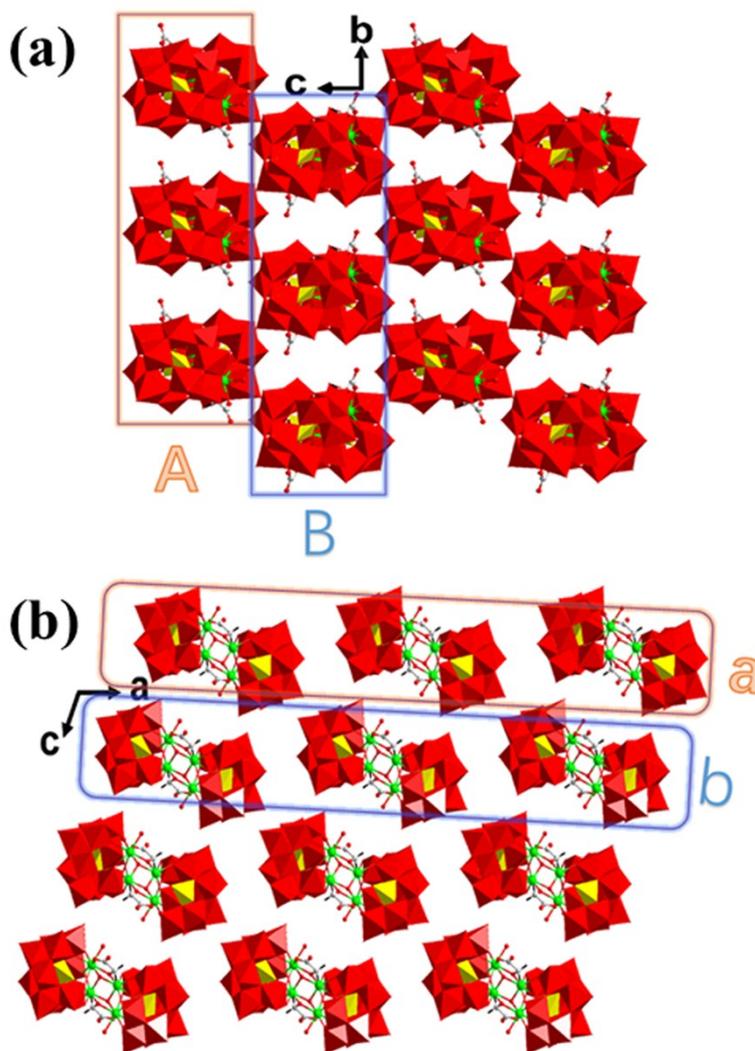


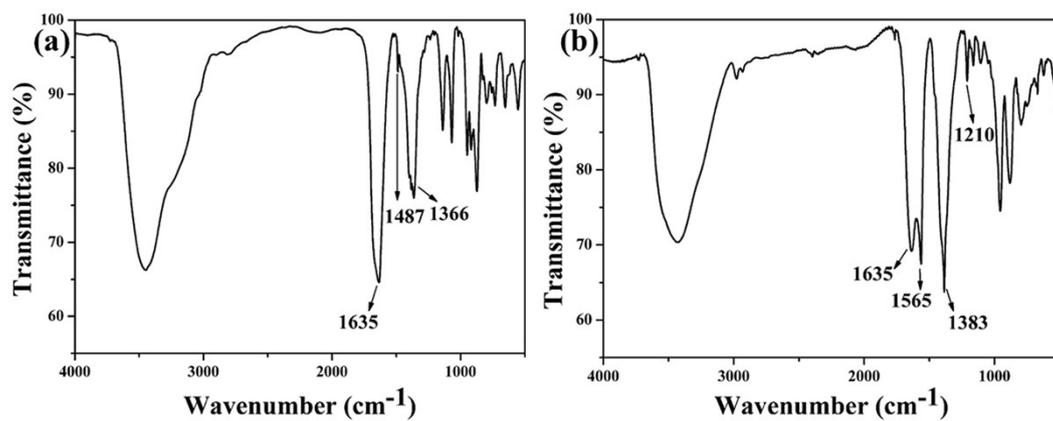
Fig. S1. (a) The stacking of the polyanions in **1** along the *a*-axis. (b) The relationship between A and B of **1**. Color codes: WO<sub>6</sub> red; GeO<sub>4</sub> yellow; Zr green; O red; C gray.



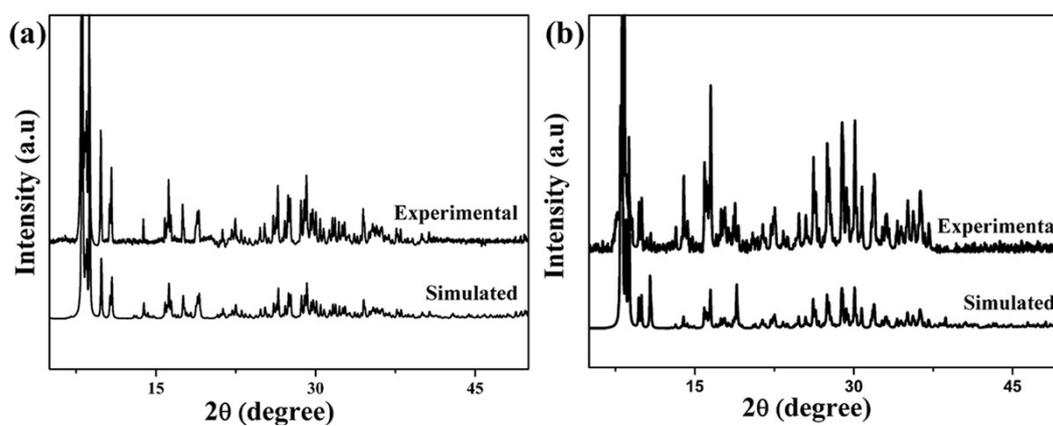
**Fig. S2.** (a) The stacking of polyanion in **1** along the  $b$ -axis. (b) The relationship between  $a$  and  $b$  of **1**. Color codes:  $\text{WO}_6$  red;  $\text{GeO}_4$  yellow; Zr green; O red; C gray.



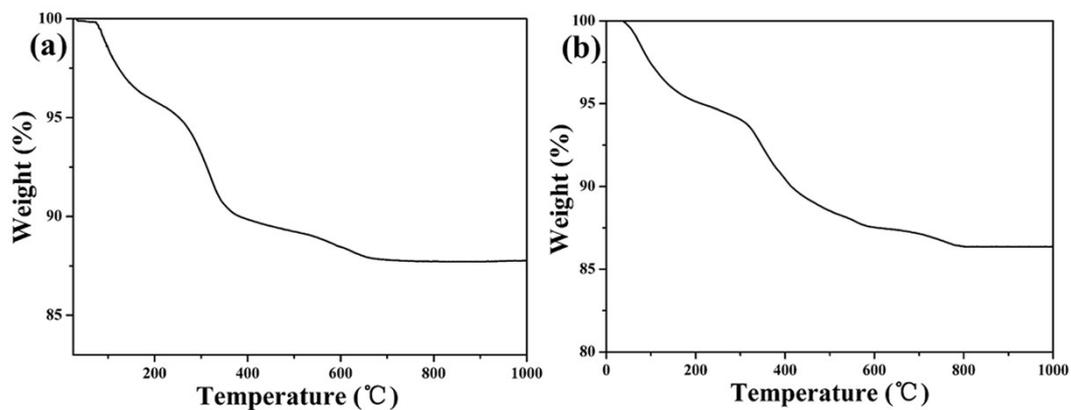
**Fig. S3.** (a,b) The stacking of polyanion in **2** along the  $a$ -axis and  $b$ -axis, respectively. Color codes:  $\text{WO}_6$  red;  $\text{GeO}_4$  yellow; Zr green; O red; C gray.



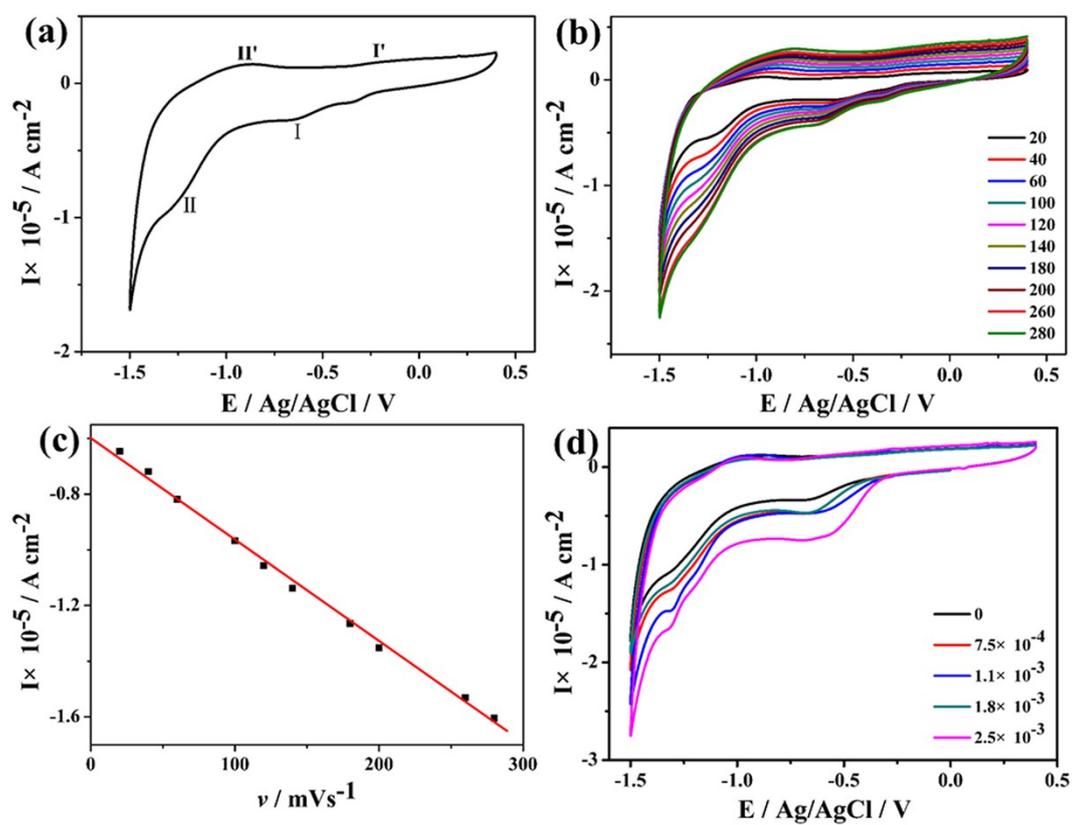
**Fig. S4.** The FT-IR spectra of **1** and **2**, respectively.



**Fig. S5.** Comparison of the experimental and simulated PXRD patterns of (a) **1** and (b) **2**.



**Fig. S6.** The thermogravimetric (TG) curves of **1** and **2** measured from ambient temperature to 1000°C under air atmosphere with the heating rate of 10°C/min.



**Fig. S7.** (a) Cyclic voltammograms of **2** in 0.5 mol·L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> solution (pH = 4.92) at a scan rate of 80 mV·s<sup>-1</sup>; (b) Cyclic voltammograms of **2** at varied scan speeds (from inner to outer: 20, 40, 60, 100, 120, 140, 180, 200, 260, and 280 mV·s<sup>-1</sup>); (c) Variation of the cathodic peak current (II) with the scan rate for **2**; (d) Cyclic voltammograms of **2** containing various concentrations of H<sub>2</sub>O<sub>2</sub>.