**Zr₄-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.](image)

**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: WO₆ red; GeO₄ 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: WO$_6$ red; 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: WO$_6$ red; 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 1000ºC under air atmosphere with the heating rate of 10ºC/min.
Fig. S7. (a) Cyclic voltammograms of 2 in 0.5 mol·L⁻¹ Na₂SO₄ + H₂SO₄ solution (pH = 4.92) at a scan rate of 80 mV·s⁻¹; (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⁻¹); (c) Variation of the cathodic peak current (II) with the scan rate for 2; (d) Cyclic voltammograms of 2 containing various concentrations of H₂O₂.