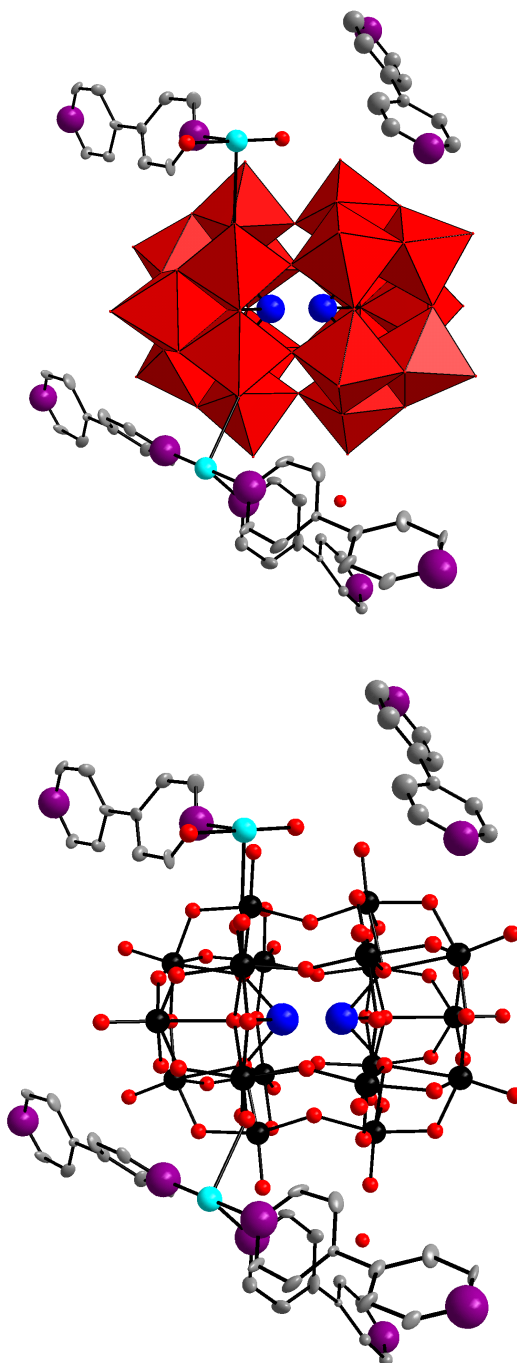
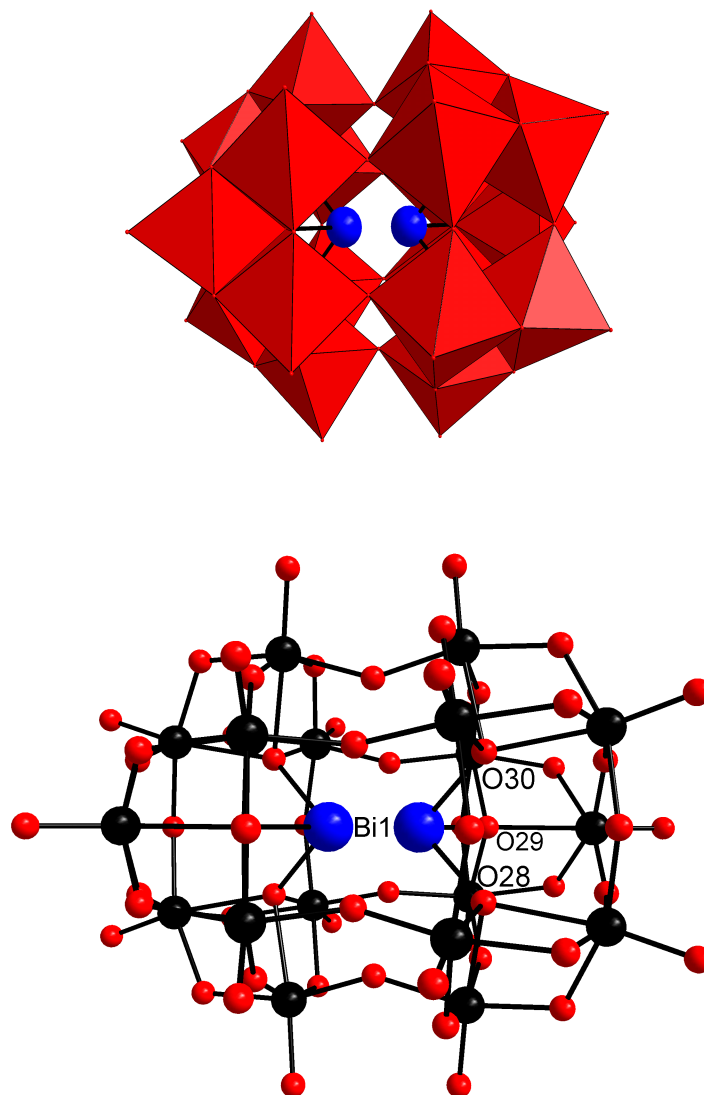


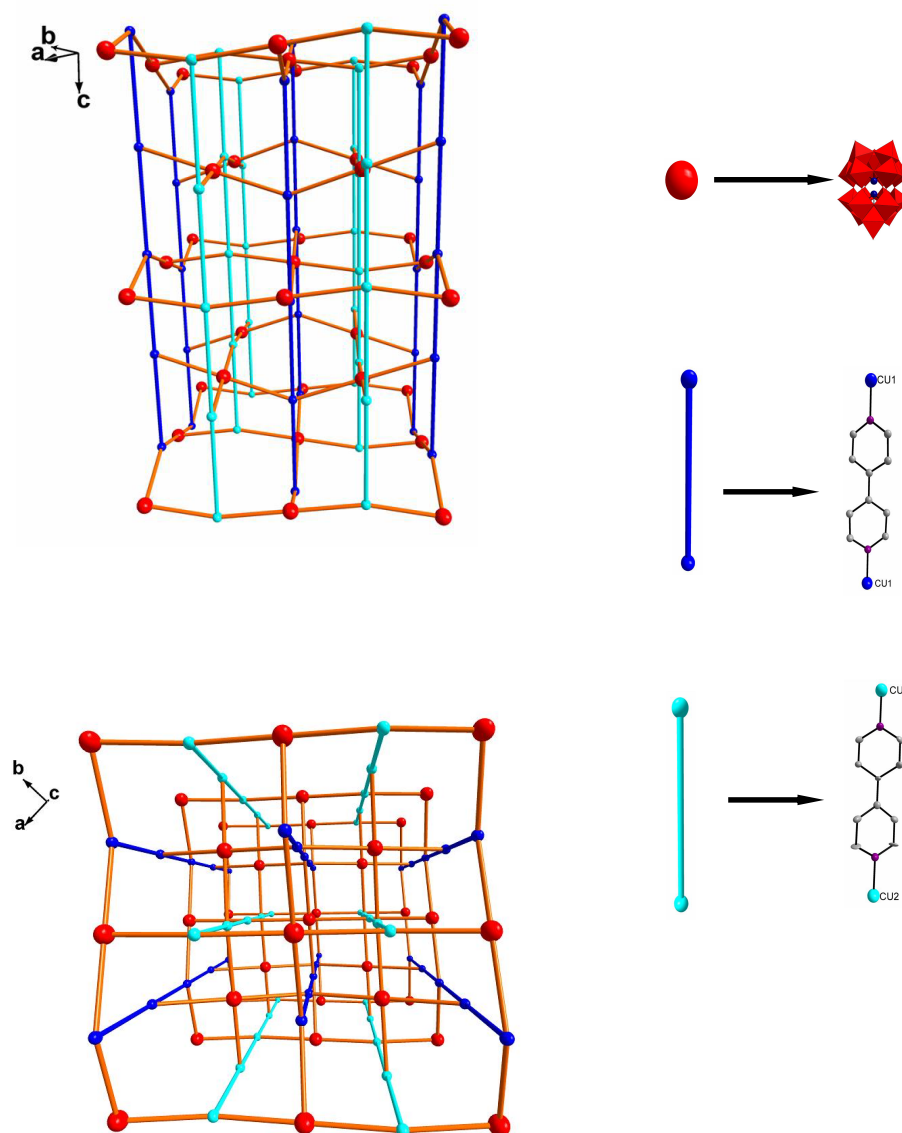
## Supporting Information



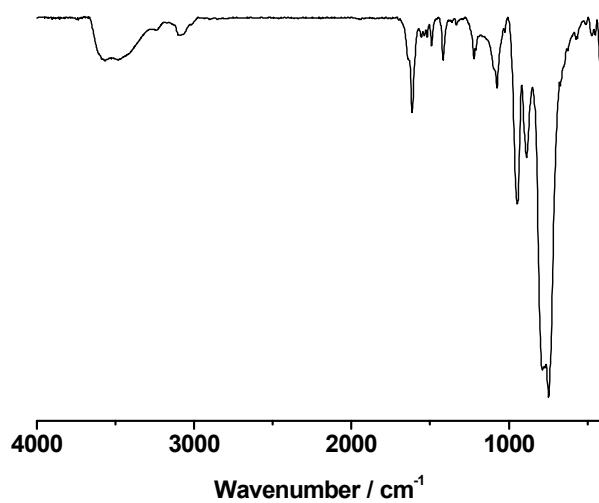
**Fig. S11.** (top) Combined polyhedral/ball-and-stick representation of compound **1a**. Color code: W, red; Bi, blue; Cu, cyan; N, purple; C, gray. (bottom) ball-and-stick representation of compound **1a**. Color code: W, black. Hydrogen atoms are omitted for clarity.



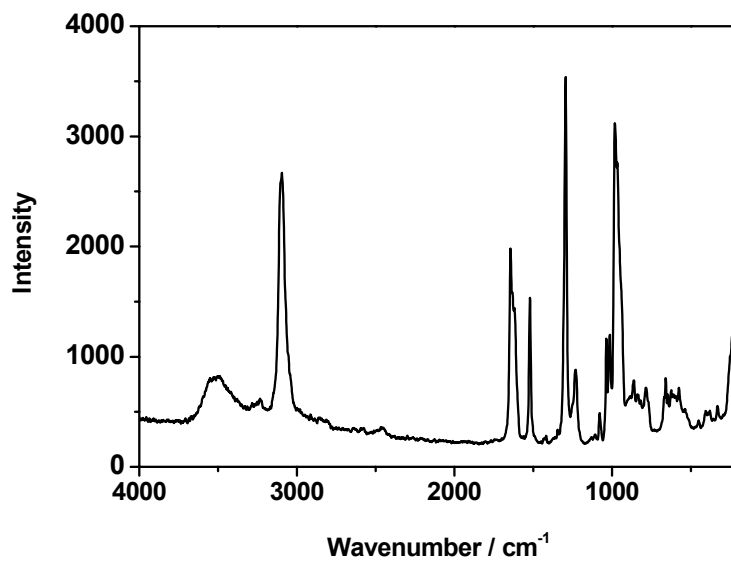
**Fig. SI2.** (top) Combined polyhedral/ball-and-stick representation of  $\text{BiW}_{18}$ . Color code: W, red; Bi, blue. (bottom) Partial labeling ball-and-stick representation of  $\text{BiW}_{18}$ . Color code: W, black; Bi, blue; O, red.



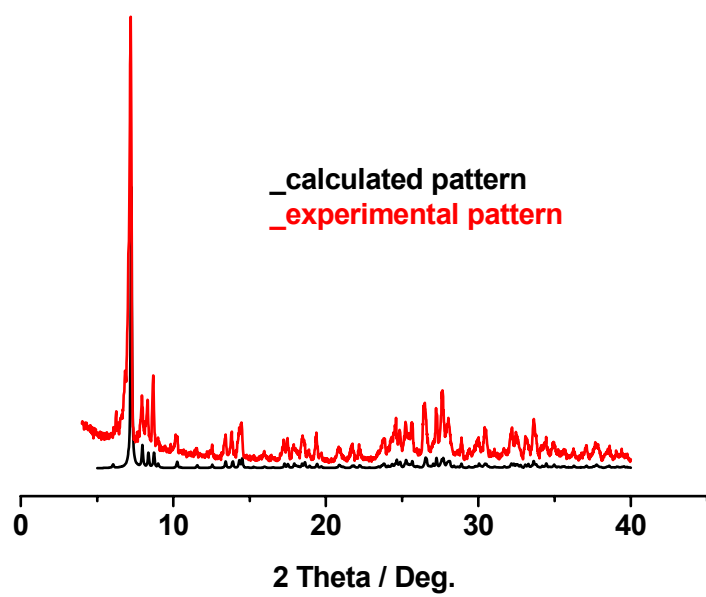
**Fig. SI3.** Schematic representation of 3D **supramolecular** framework of compound **1a**. Color code:  $[\text{H}_3\text{BiW}_{18}\text{O}_{60}]^{6-}$  anion, red ball; Cu1, blue; Cu2, cyan; **bipy** ligands coordinated to Cu1 atoms, blue stick; **bipy** ligands coordinated to Cu2 atoms, cyan stick; W-O-Cu bonds, orange stick. The **bipy** ligands coordinated to Cu1, **diprotonated**  $[\text{H}_2\text{bipy}]^{2+}$  ion, lattice water and all H atoms are omitted for clarity.



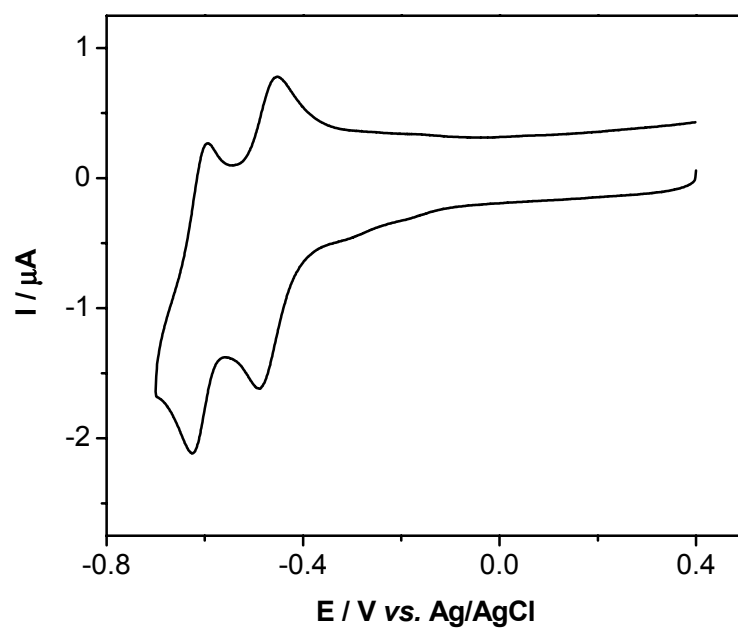
**Fig. SI4.** IR spectrum of **1a**.



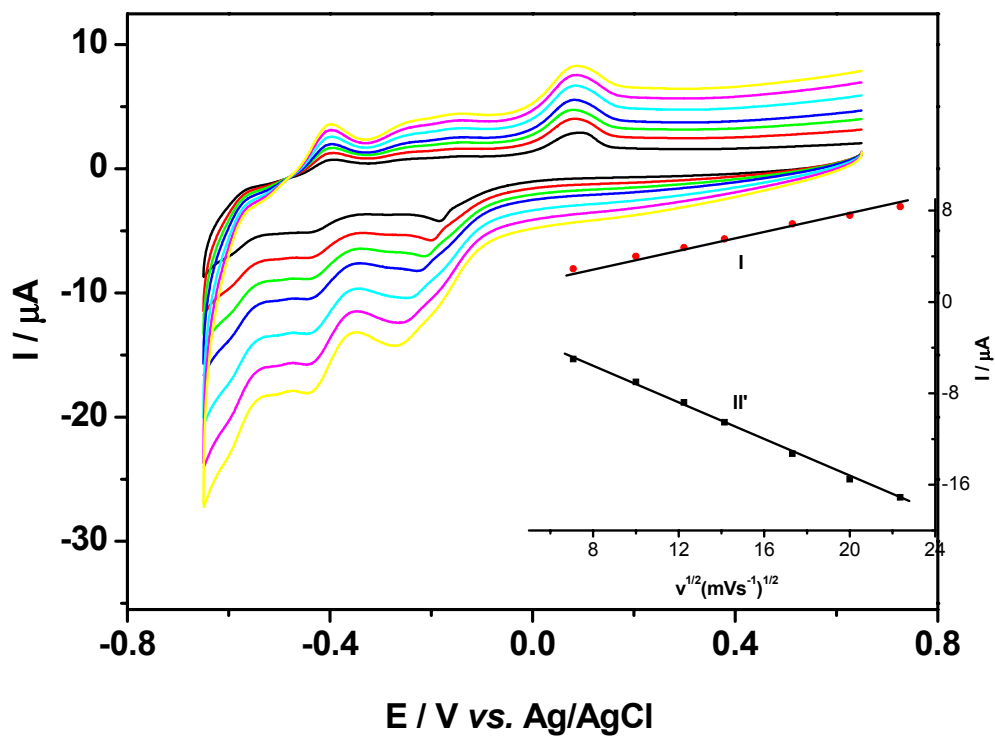
**Fig. SI5.** Raman spectrum of **1a**.



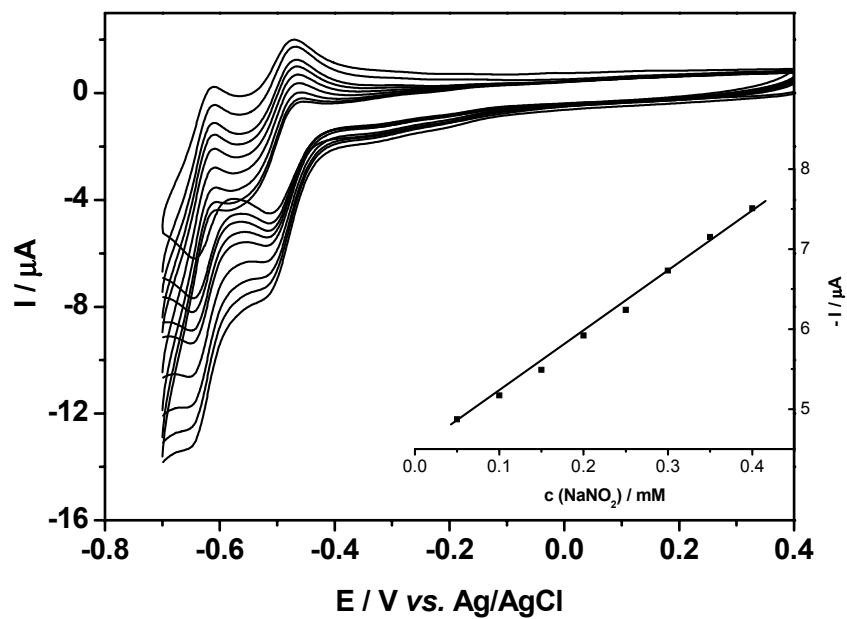
**Fig. SI6.** The calculated and experimental powder XRD patterns of compound **1a**.



**Fig. SI7.** CV of 0.19 mM BiW<sub>18</sub> in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 2.5) with scan rate of 50 mV · s<sup>-1</sup>.

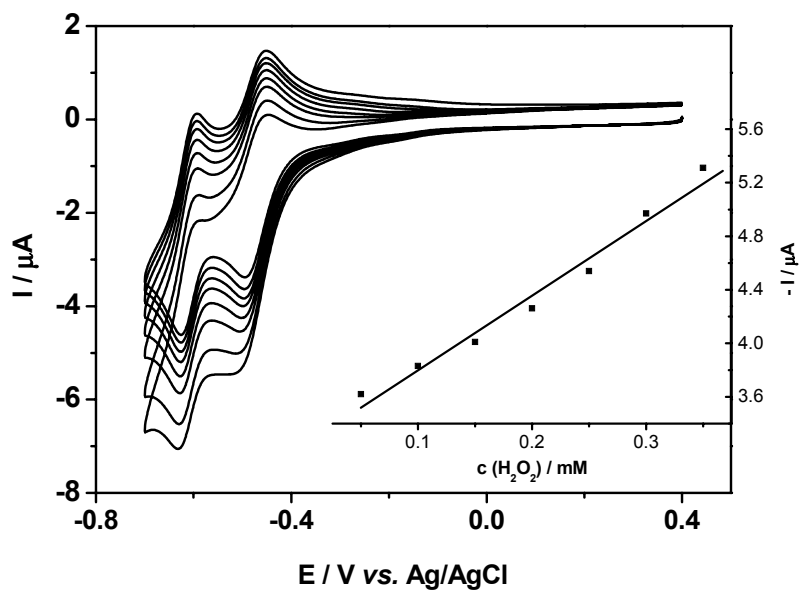


**Fig. SI8.** CVs of 0.16 mM **1a** in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 2.5) at scan rates of 50, 100, 150, 200, 300, 400 and 500  $\text{mV} \cdot \text{s}^{-1}$ . The inset shows the relationship of the square roots of the scan rates *vs.* the oxidation peak currents of Cu(I) and reduction peak currents of W (II').



**Figure SI9.** CVs of 0.15 mM **1a** in 0.5 M  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH 2.5) at  $20 \text{ mV} \cdot \text{s}^{-1}$  in the presence of  $\text{NO}_2^-$ . The inset shows the catalytic currents caused by the first cathodic **peak** of  $\text{W}^{\text{VI}}$  vs. concentrations of  $\text{NO}_2^-$  at various concentrations: 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35 and 0.40 mM.





**Figure SI10.** CVs of 0.19 mM **1a** in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 2.5) at 20 mV·s<sup>-1</sup> in the presence of H<sub>2</sub>O<sub>2</sub>. The inset shows the catalytic currents caused by the first cathodic peak of W<sup>VI</sup> vs. concentrations of H<sub>2</sub>O<sub>2</sub> at various concentrations: 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 mM.