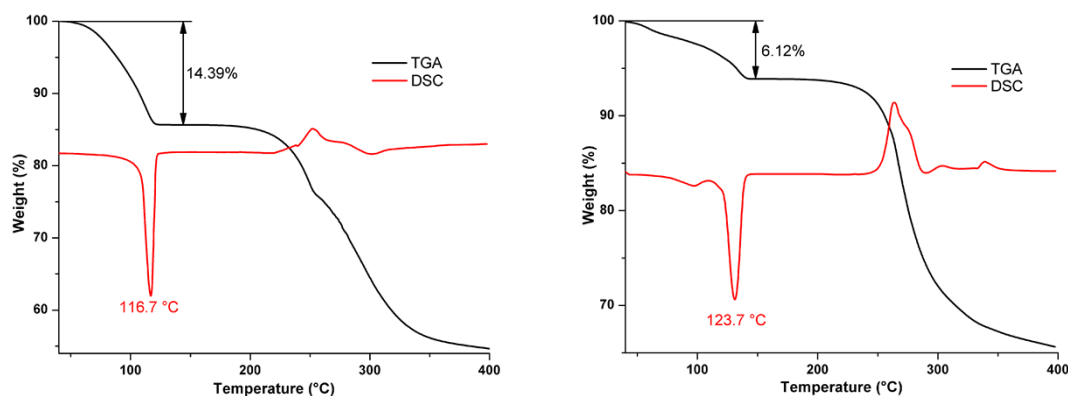


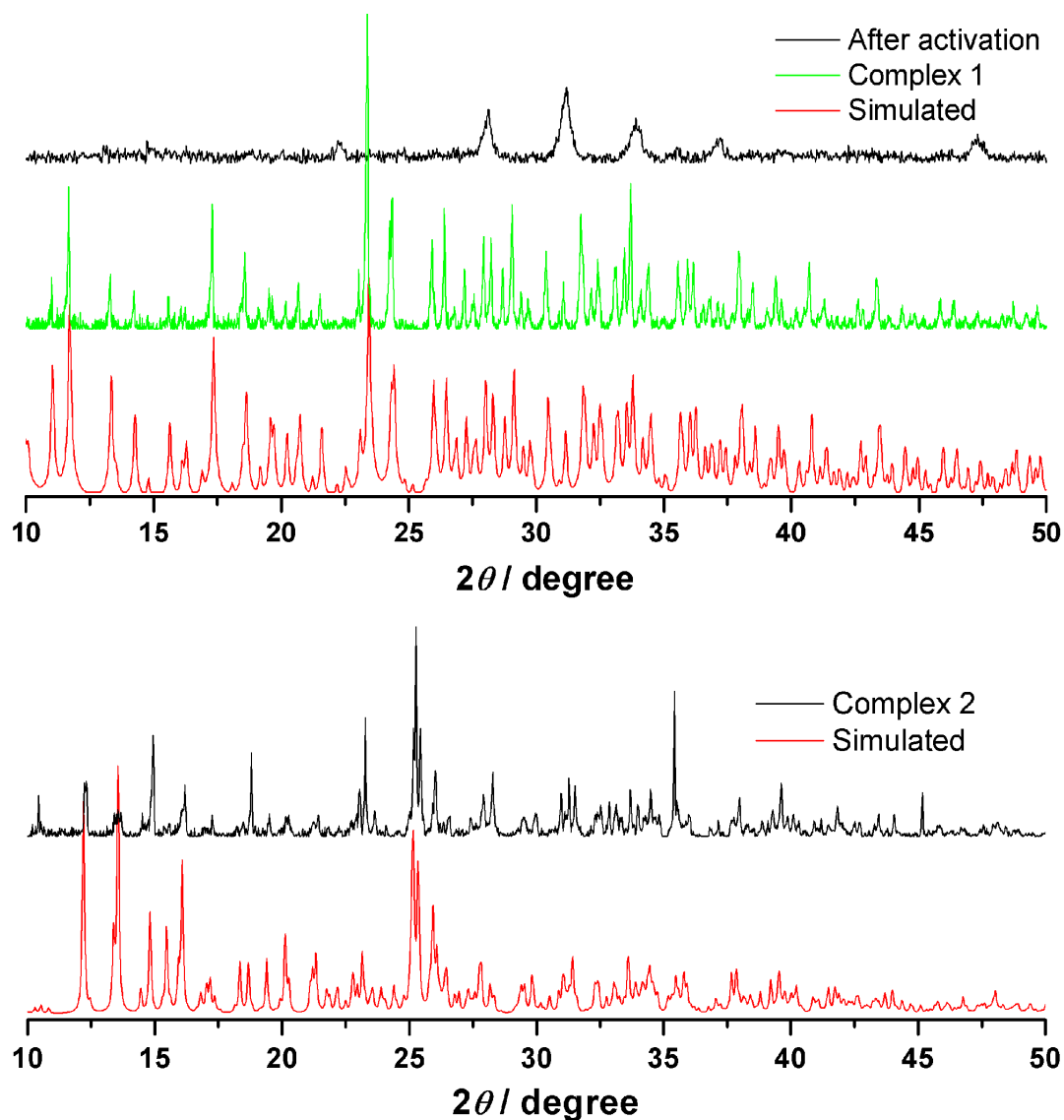
## Supplementary Information

### Determination of the structural formula of complex 1

The lattice water molecules within the big cavities of complex **1** are necessarily disordered, making it difficult to locate from Fourier difference maps, and the thermal vibration parameters (U value) of some of the located water molecules are accordingly relatively large. As a consequence, the refined structure only contains a part (45) of the 72 H<sub>2</sub>O molecules. On the other hand, the TGA weight loss of 14.39% at 116.7 °C (see Supporting information Figure S1) attributed to the release of guest water molecules indicates a hydration number of 74.24 in the structural formula, or  $(74.24 \times 8)/96 \cong 6.19$  water molecules in the asymmetric unit. Taking the structural formula as  $[\text{Ag}_{16}(\text{SO}_4)_8][\text{Ag}_4(\text{SO}_4)_2]_3(\text{L}_1)_{12} \cdot n\text{H}_2\text{O}$  ( $n = 72$ ), the calculated and observed elemental analysis results are C, 20.25 (20.49); H, 2.74 (2.64); N, 9.08 (9.20) %. Furthermore, structure refinement with the SQUEEZE procedure<sup>Ref 1</sup> ( $R_1 = 0.0544$ ,  $wR_2 = 0.1107$  for  $I > 2\sigma(I)$ ) indicated the presence of 6.32 independent guest water molecules in the asymmetric unit, which is also in good agreement with the value of 72 in the structural formula of complex **1**. Moreover, the absence of acetonitrile or other solvent in the framework was further confirmed from the measured IR spectra (Figure S3).

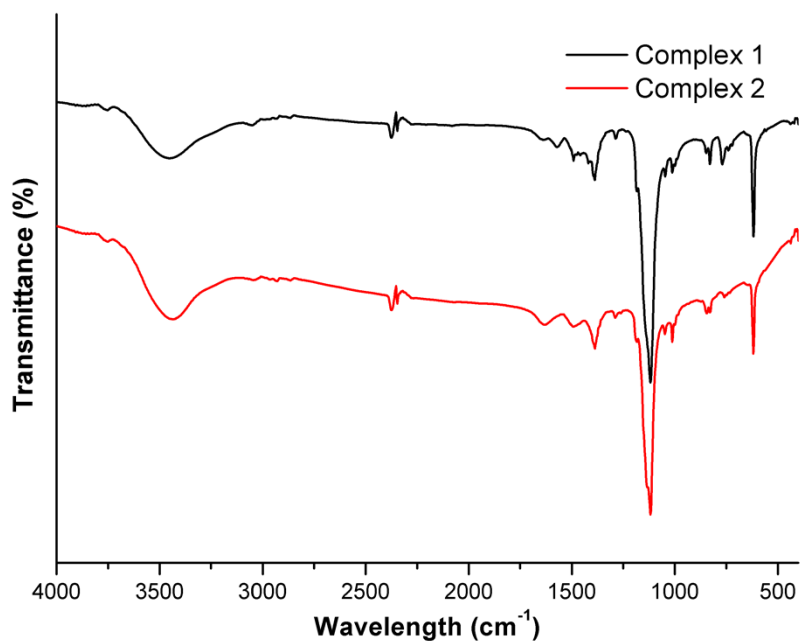


**Figure S1.** TGA and DSC curves for  $[\text{Ag}_{16}(\text{SO}_4)_8][\text{Ag}_4(\text{SO}_4)_2]_3(\text{L}_1)_{12} \cdot n\text{H}_2\text{O}$  ( $n = 72$ ) (**1**) (left part) and  $[\text{Ag}_{10}(\text{SO}_4)_5(\text{L}_2)_4(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$  (right part).



**Figure S2.** Powder X-Ray diffraction patterns of complexes **1** and **2**.

Measurement of the N<sub>2</sub> adsorption isotherm of [Ag<sub>16</sub>(SO<sub>4</sub>)<sub>8</sub>][Ag<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>]<sub>3</sub>(L<sub>1</sub>)<sub>12</sub> · *n*H<sub>2</sub>O (*n* = 72) (**1**) at 77 K revealed virtually no N<sub>2</sub> uptake, which can be attributed to loss of porosity of the original framework during activation. The markedly different PXRD patterns of a sample recorded before and after activation showed the collapse of the porous host network structure (Figure S4).



**Figure S3.** IR spectra of complexes **1** and **2**.

## References

- Ref 1. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands., 2005.
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