

Supporting Information

Encapsulation of Unusual Nitrate-Water Cluster $[(\text{NO}_3)_4(\text{H}_2\text{O})_6]^{4-}$ Anions into Cages of a 3D Cationic Coordination Polymer

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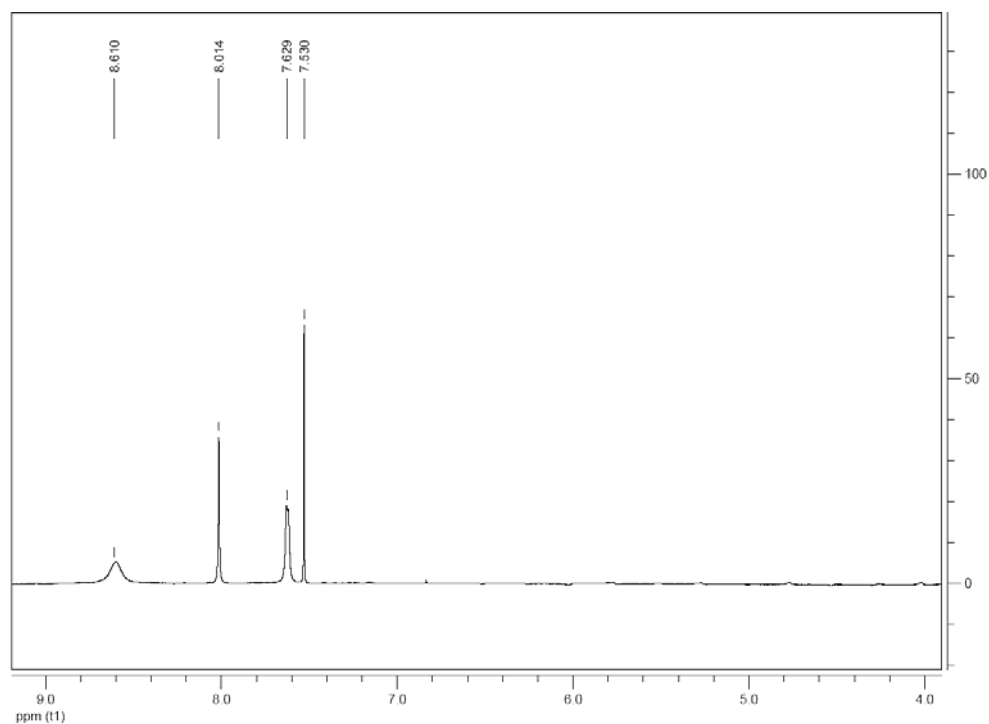
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(a)



(b)

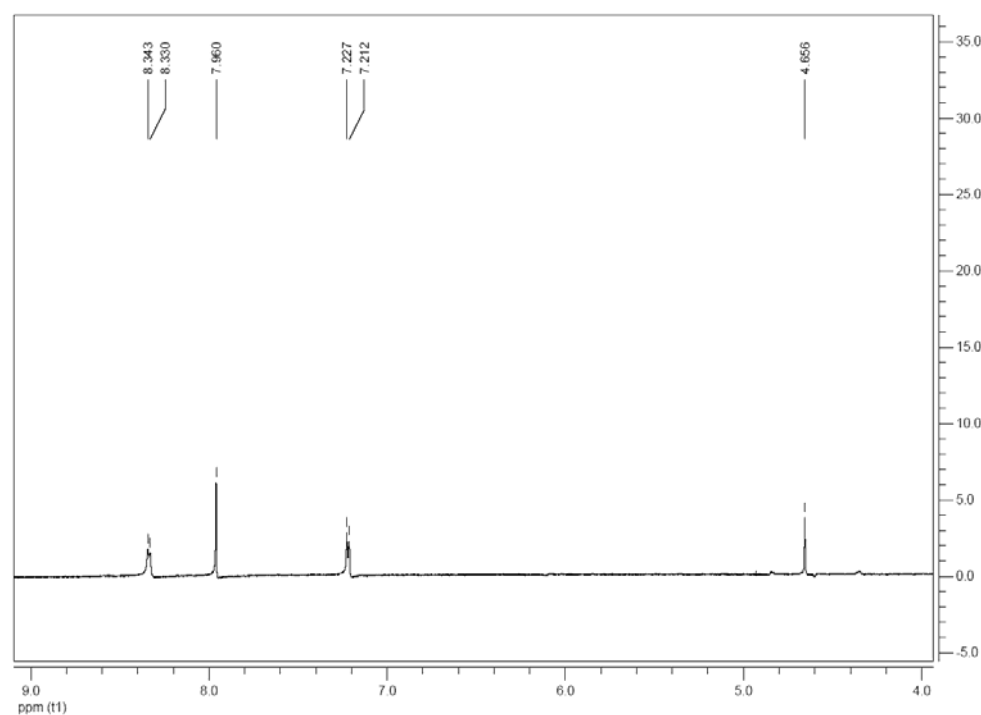


Figure S1. (a) The ¹H NMR spectrum of **1** in *d*₆-DMSO at ambient temperature. (b) The ¹H NMR spectrum of **1a** in *d*₆-DMSO at ambient temperature

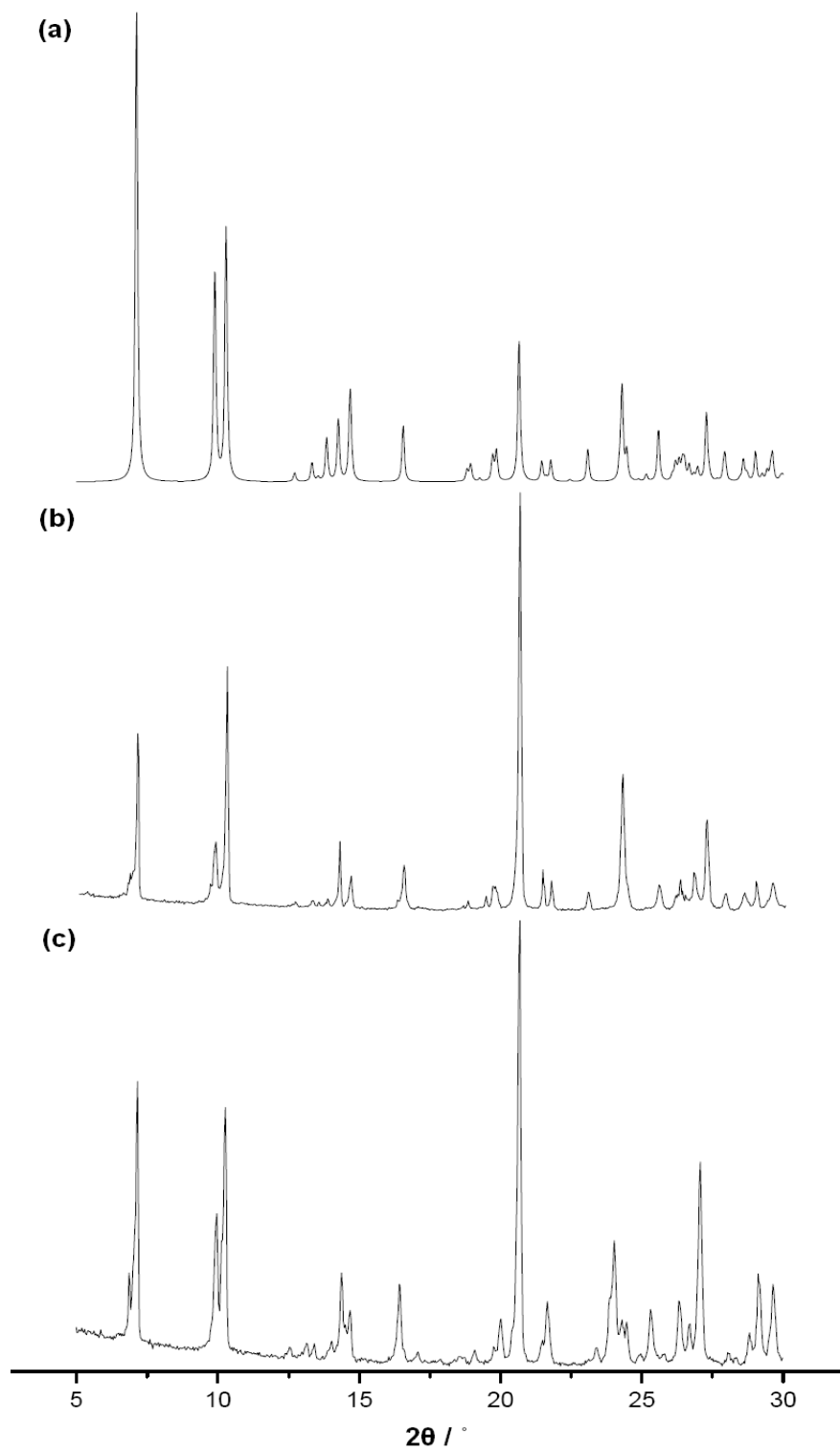
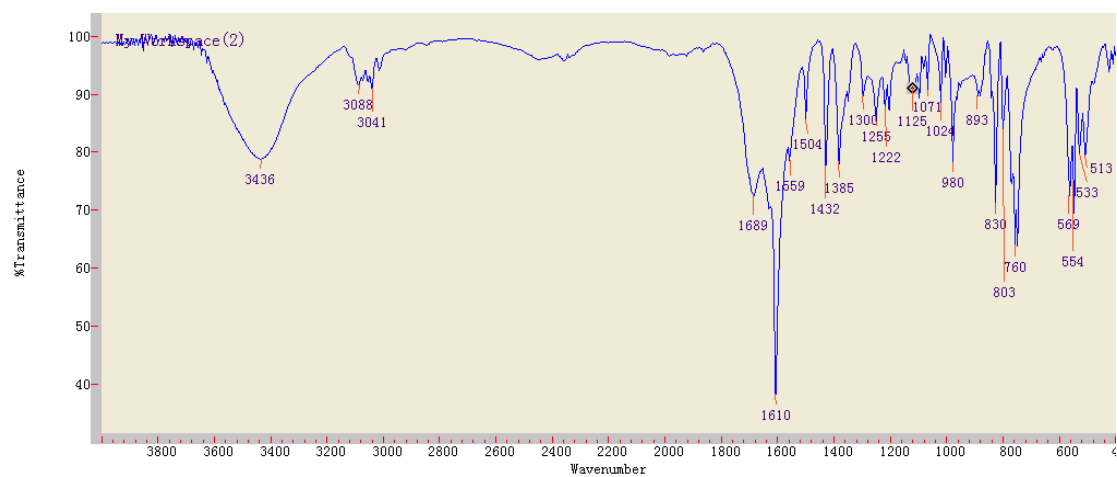
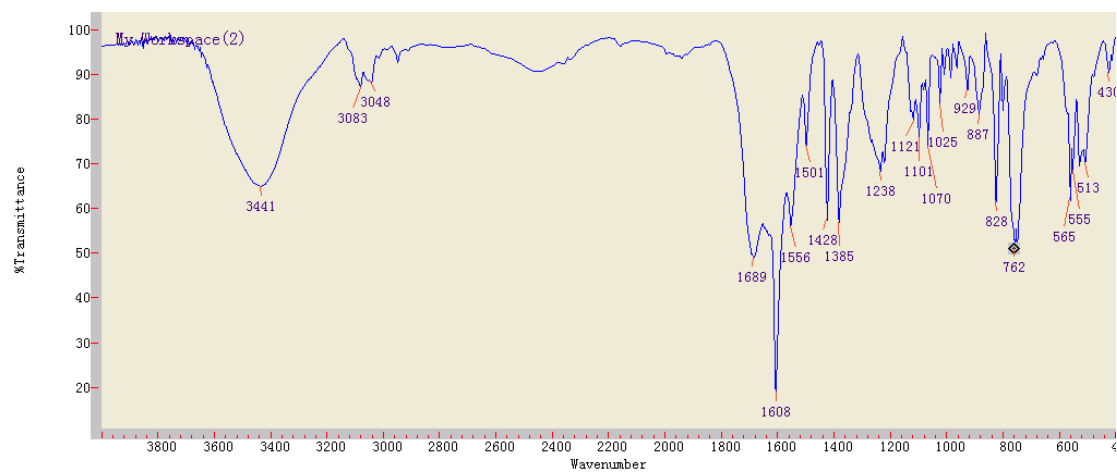


Figure S2. Powder XRD patterns of (a) simulated $\{[\text{Ag}_2(\text{bpe})_2](1,4\text{-BDC})\cdot(1,4\text{-H}_2\text{BDC})\}_n$ (**1**) from single crystal analysis and experimental; (b) $\{[\text{Ag}_2(\text{bpe})_2](1,4\text{-BDC})\cdot(1,4\text{-H}_2\text{BDC})\}_n$ (**1**) (as synthesized); (c) $\{[\text{Ag}_2(4,4'\text{-tpcb})_2](1,4\text{-BDC})\cdot(1,4\text{-H}_2\text{BDC})\}_n$ (**1a**) (UV irradiation form **1**).

(a)



(b)



(c)

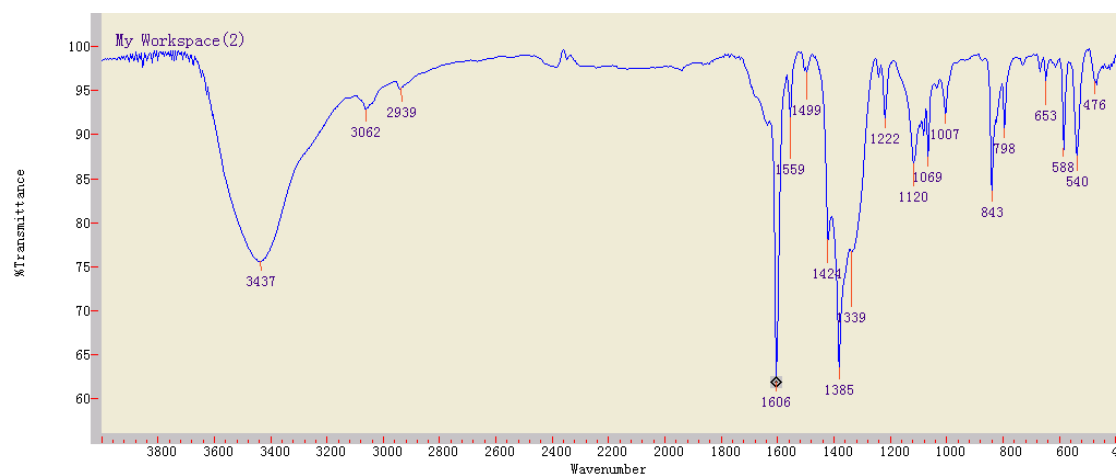


Figure S3. (a) The IR spectrum of **1**. (b) The IR spectrum of **1a**. (c) The IR spectrum of **2**.

Notes: Strong bands in the region of $1440\text{--}1315\text{ cm}^{-1}$, especially those at $1424/1339\text{ cm}^{-1}$ of the IR spectrum of **2** indicate the existence of NO_3^- .^{1a} Bands at $653/588\text{ cm}^{-1}$ are also characteristic bands of NO_3^- .^{1b,1c}

1. (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**, pp. 254-257; b) González Lebrero, M. C.; Bikiel, D. E.; Dolores Elola, M.; Estrin, D. A.; Roitberg, A. E. *J. Chem. Phys.* **2002**, *117*, 2718-2725 (c) Bianco, R.; Wang, S. Z.; Hynes, J. T. *J. Phys. Chem. A* **2008**, *112*, 9467–9476.

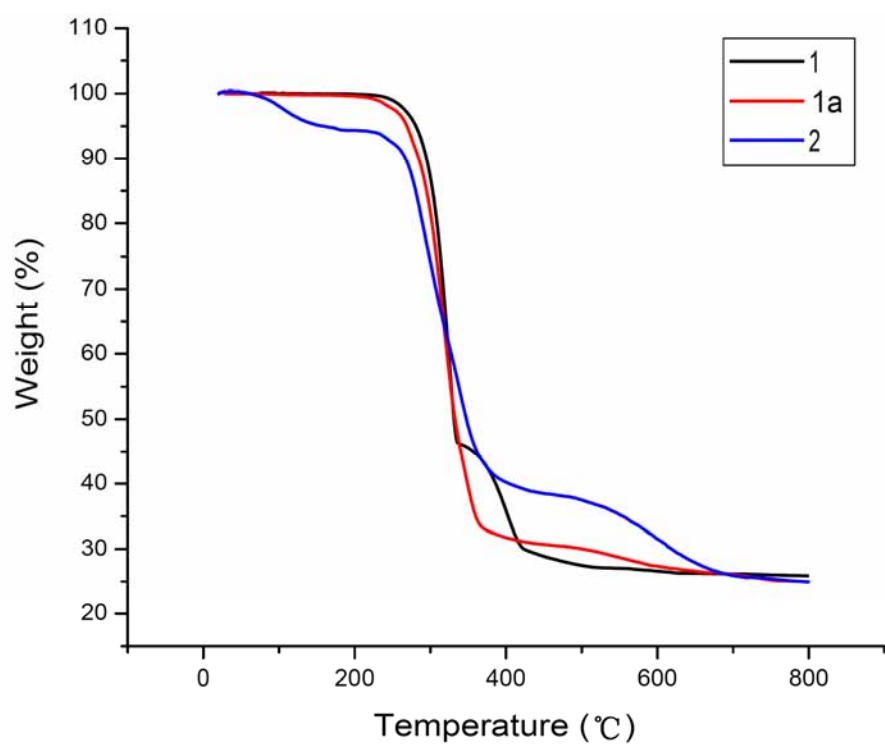


Figure S4. The TGA curves for **1** (black), **1a** (red) and **2** (blue).

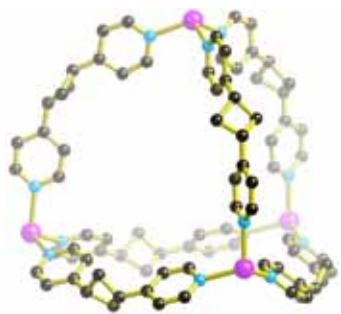


Figure S5. An adamantane-type unit within a single network of $[\text{Ag}(4,4'\text{-tpcb})_{0.75}]_n^{n+}$ in **2**.

Hydrogen atoms have been omitted for clarity.