

## Supplementary Information

### Removal and reintroduction of guest molecules

Crystalline sample of  $\text{Ag}_3[\text{Ag}_5(\mu_3\text{-}3,5\text{-Ph}_2\text{-tz})_6](\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  ( $\mathbf{1}(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was subjected to vacuum at  $100^\circ\text{C}$  for 1 hour. Elemental analysis shows that besides water,  $\text{HNO}_3$  has also been removed from the sample. The PXRD pattern for the sample after removal of the guest molecules is very similar to that calculated from X-ray data of  $\mathbf{1}$ , indicating the retention of framework structures after evacuation (Fig. S1).

Evacuated sample,  $\text{Ag}_3[\text{Ag}_5(\mu_3\text{-}3,5\text{-Ph}_2\text{-tz})_6](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ . If  $x = 0$ , Anal. Calcd. for  $\text{C}_{84}\text{H}_{60}\text{Ag}_8\text{N}_{20}\text{O}_6$ : C, 43.7; H, 2.6; N, 12.1%; if  $x = 2$ , Anal. Calcd. for  $\text{C}_{84}\text{H}_{60}\text{Ag}_8\text{N}_{20}\text{O}_6 \cdot 2\text{H}_2\text{O}$ : C, 43.0; H, 2.7; N, 11.9 %; Found: C, 42.9; H, 3.0; N, 11.9 %.

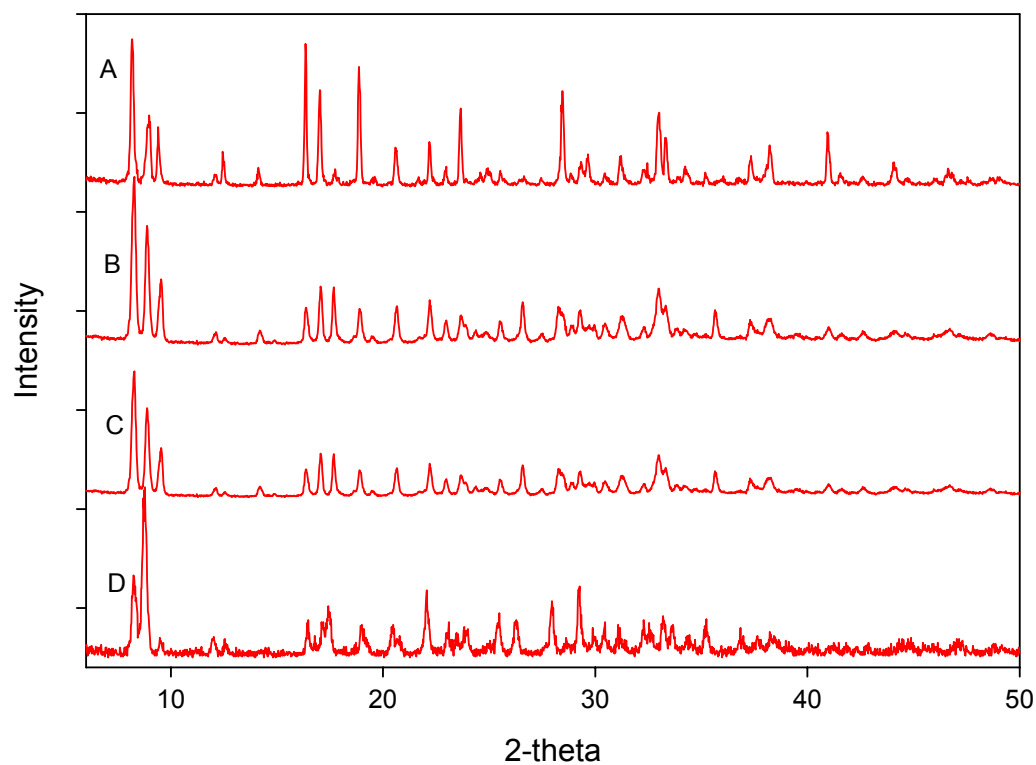
Solvents like hexane, cyclohexane, pentane, acetone, THF, acetyl acetate, 1-propanol etc. have been tested for the adsorption properties of  $\mathbf{1}$ . The dehydrated samples of  $\mathbf{1}$  were soaked in the above-mentioned solvents for 1 day, then filtered and washed by ethanol and ether. After air-dried for 2 hours, the solids were examined by IR and TGA (Fig. S2 and Fig. S3). The IR spectra show only non-polar solvents were adsorbed by dehydrated  $\mathbf{1}$ , as evident by the appearance of bands in  $2800\text{-}3000\text{ cm}^{-1}$ , corresponding to the symmetric and asymmetric bends of  $\text{CH}_2\text{-}$  or  $\text{CH}_3\text{-}$  groups. On the other hand, no bands corresponding to polar solvents were found in the IR spectra of  $\mathbf{1}$ . The PXRD pattern for the sample after adsorption of the solvents are similar to the one calculated from X-ray data of  $\mathbf{1}$ , indicating the retention of framework structures after the solvent adsorption (Fig. S1).

### Anion exchange experiment:

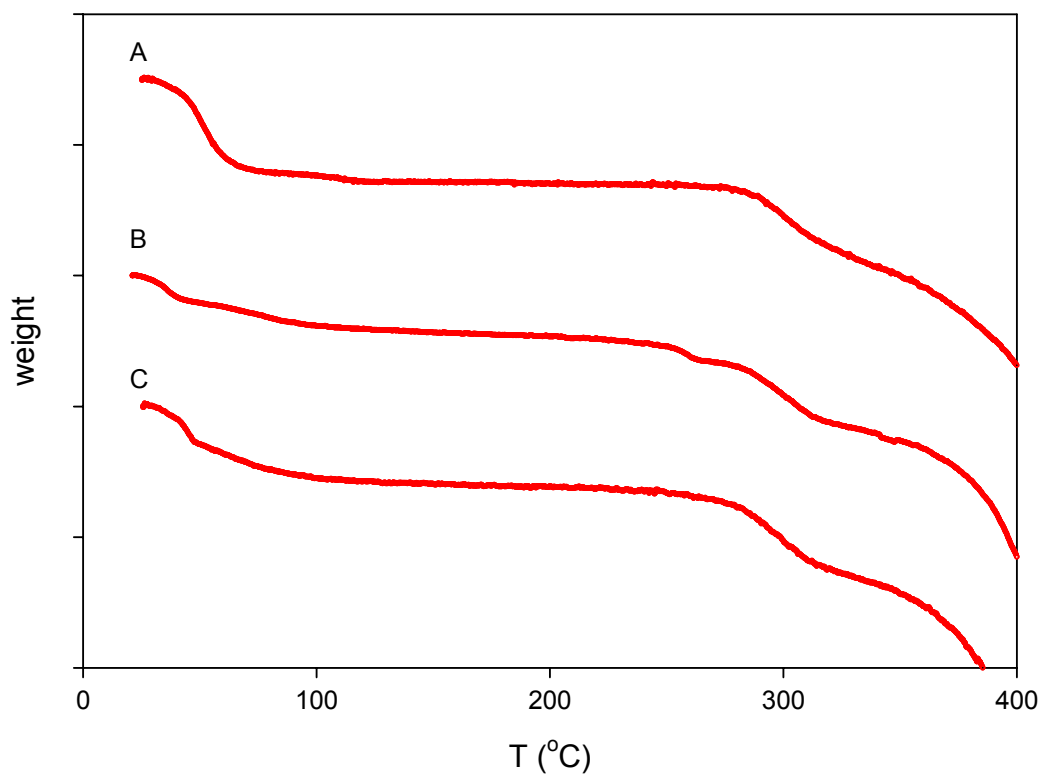
Well-ground powder of  $\mathbf{1}(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (40 mg) was suspended in a solution of  $\text{NaClO}_4$  (2 g) in 20 mL of water, and the mixture was stirred for two days at room temperature, then filtered, washed with water, then ethanol and finally ether to give white powder. IR spectra show the disappearance of intense  $\text{NO}_3^-$  band ( $1386\text{ cm}^{-1}$ ) and appearance of a new strong  $\text{ClO}_4^-$  band ( $1088\text{ cm}^{-1}$ ), indicating the anions have been exchanged (See Fig. S4). However, the XPRD pattern of the anion-exchanged sample

shows some peaks have been slightly shifted, indicative of subtle structural change after anion exchange (Fig. S1). Elemental analysis of the anion-exchanged sample suggests a formula of  $\text{Ag}_3[\text{Ag}_5(\mu_3\text{-}3,5\text{-Ph}_2\text{-tz})_6](\text{ClO}_4)(\text{OH})\cdot 12\text{H}_2\text{O}$ . A further anion-exchange experiment was carried out by suspending this sample in an aqueous solution of  $\text{NaNO}_3$ . An IR spectrum shows the disappearance of intense  $\text{ClO}_4^-$  band and appearance of  $\text{NO}_3^-$  band. XPRD pattern of the further anion-exchanged sample is identical to that obtained from the sample containing  $\text{ClO}_4^-$ . Therefore, the structural change remains invariable upon further anion-exchange processes.

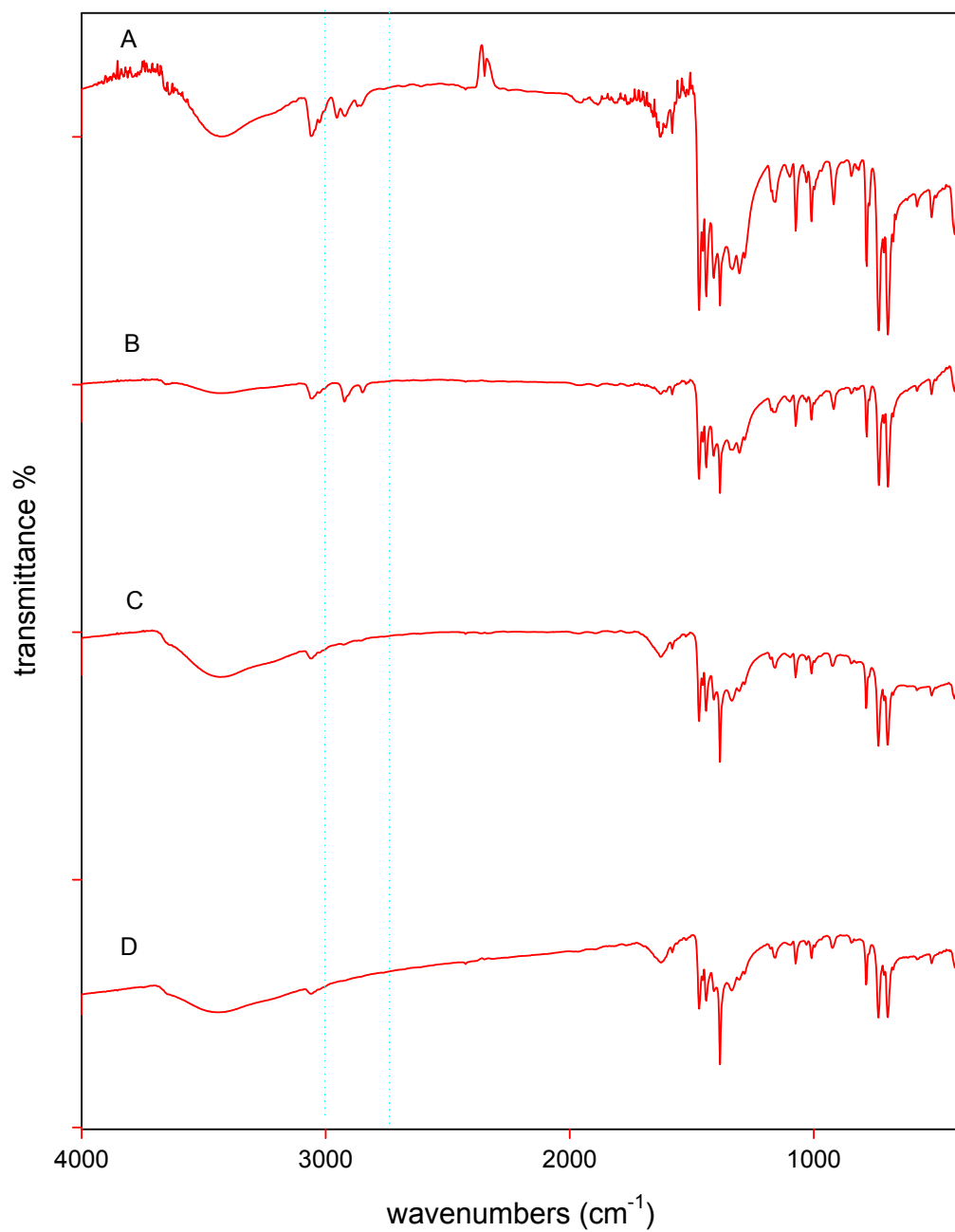
$\text{Ag}_3[\text{Ag}_5(\mu_3\text{-}3,5\text{-Ph}_2\text{-tz})_6](\text{ClO}_4)(\text{OH})\cdot 12\text{H}_2\text{O}$  Anal. Calcd. for  $\text{C}_{84}\text{H}_{61}\text{Ag}_8\text{N}_{18}\text{O}_5\text{Cl}\cdot 12\text{H}_2\text{O}$ :  
C, 40.1; H, 3.4; N, 10.0; Cl, 1.4% Found: C, 39.3; H, 3.2; N, 9.8; Cl, 1.4%.



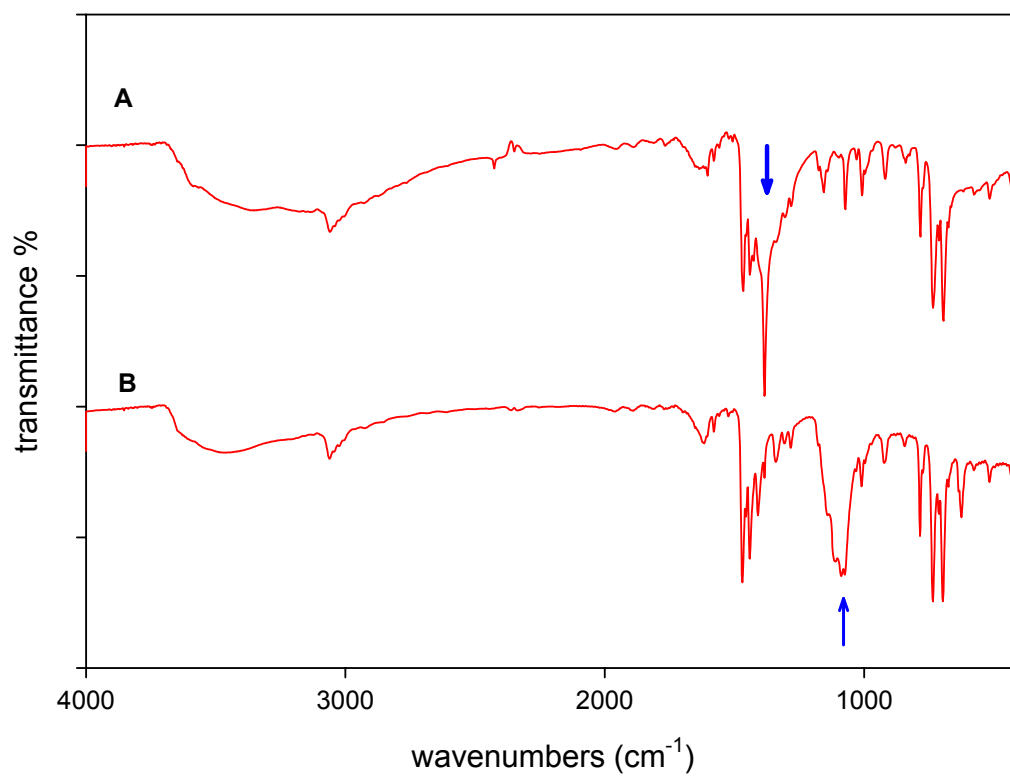
**Figure S1** The XPRD pattern of as-synthesized  $\mathbf{1}(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (A), evacuated sample  $\mathbf{1}(\text{NO}_3)_2$  (B), evacuated sample  $\mathbf{1}(\text{NO}_3)_2$  after adsorption of hexane (C) and well-ground  $\mathbf{1}(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  after anion-exchange with  $\text{ClO}_4^-$  (D).



**Figure S2.** TGA curves of  $\mathbf{1}(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (A), dehydrated sample  $\mathbf{1}(\text{NO}_3)_2$  + hexane (B) and dehydrated sample  $\mathbf{1}(\text{NO}_3)_2$  + cyclohexane.



**Figure S3.** IR spectra of evacuated samples of **1**(NO<sub>3</sub>)<sub>2</sub> after soaked in hexane (A), cyclohexane (B), THF (C) and acetone (D).



**Figure S4.** IR spectra of  $1(\text{H}_3\text{O})(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (A) and the sample exchanged with  $\text{ClO}_4^-$  (B).