Supplementary material (ESI) for Daltopn Transactions

Electronic Supplementary Information

$[Re_2(\mu\text{-}1,2,4\text{-triazolate})_2(\mu\text{-}OH)(CO)_6]^-$: a novel metalloligand for the construction of flexible porous coordination networks

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Characterization and Physical Measurements.

Elemental (C,H,N) analyses were obtained at a CHNS/O Perkin Elmer 2400 analyzer and ^{1}H NMR spectra were recorded on a Bruker DRX400 spectrometer (University of Milan); thermogravimetric analyses were registered on a NETZSCH STA 409 PC/PG equipment, at heating rate of 20 ^{o}C min^{-1}, respectively (University of Insubria) in the presence of a dinitrogen atmosphere. Sorption isotherms were measured on a Micromeritics Tristar 3000 (University of Granada) volumetric instruments under continuous adsorption conditions. Prior to measurement, powder samples were heated at 60 °C for 2 h and outgassed to 10^{-3} Torr using a Micromeritics Flowprep. X-ray powder diffractometric experiments were performed on a Bruker AXS Advance D8 diffractometer (University of Milan), by employing a background free sample holder. Typically, a sequence of scans in the 5-40° 2θ range was performed.

General characterization:

$[Et_4N]$**2**. Anal. Calcd for $Re_2C_{18}H_{25}N_7O_7$: C, 26.24; H, 3.06; N, 11.90. Found: C, 26.18; H, 3.05; N, 12.25. ^{1}H NMR (CD_3CN, 298 K). δ (ppm) = 8.12 (s, 4 H); 3.18 (q, 8 H, J_{HH} = 7.3 Hz, CH_2CH_3); 1.23 (tt, 12 H, J_{HH} = 7.3 Hz, J_{HN}= 1.8 Hz, CH_2CH_3). IR (CH_3CN). ν (C=O, cm^{-1}) = 2019 (vw), 2007 (vs), 1900 (vs), 1886 (s).

Ag@2. Anal. Calcd for $AgRe_2C_{10}H_5N_6O_6{\cdot}(CH_3OH)_{0.33}$: C, 15.59; H, 0.80; N, 10.56. Found: C, 15.42; H, 0.80; N, 10.54.

Ag@2$_D$. Anal. Calcd for $AgRe_2C_{10}H_5N_6O_6{\cdot}((CH_2CH_2OH)_2O)_{1.5}$: C, 20.00; H, 2.10; N, 8.75. Found: C, 19.89; H, 2.17; N, 9.08.

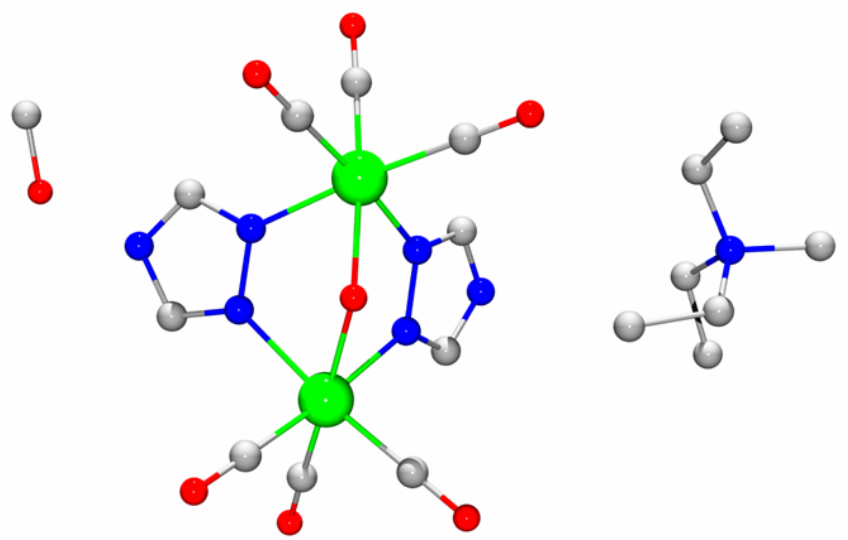

Fig. S1 Asymmetric unit in $\{[Et_4N][Re_2(\mu\text{-trz-}\kappa N^1{:}\kappa N^2)_2(\mu\text{-OH})(CO)_6]\}_n{\cdot}nCH_3OH$. Re (green), C (grey), N (blue), O (red).

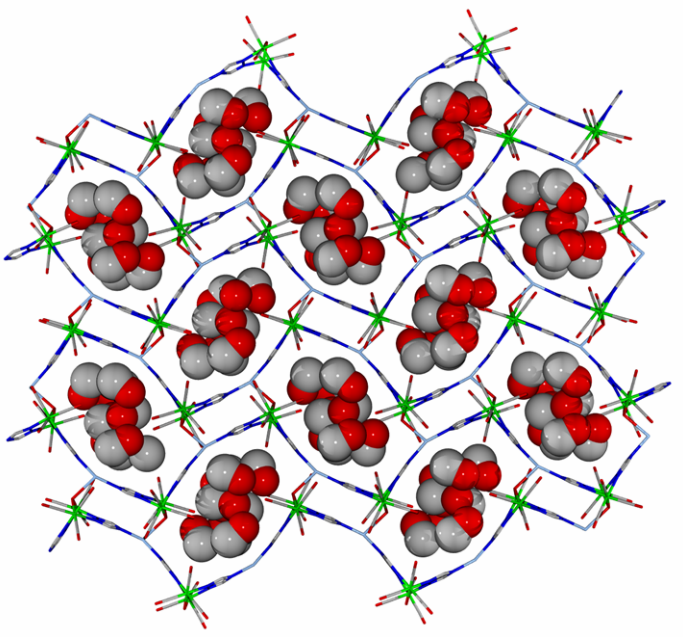

Fig. S2 Perspective view of one of the layers containing solvation MeOH molecules in the $Ag_4(Re_2)_4$ voids. Re (green), Ag (light blue), C (grey), N (blue), O (red).

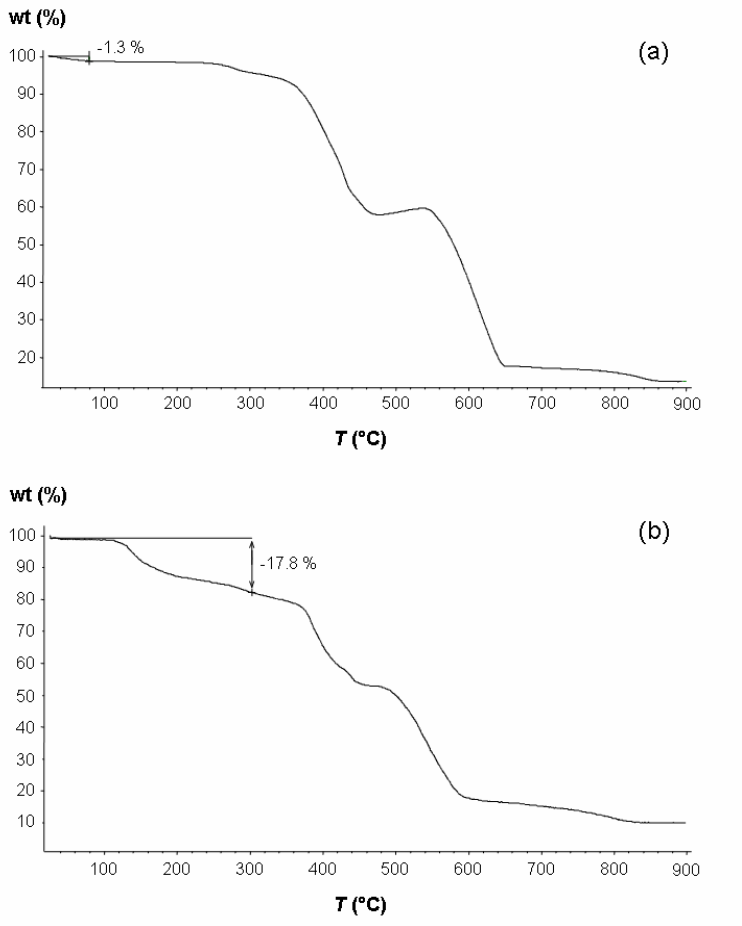

Fig. S3 TGA curves of (a) **Ag@2** (calc. per 0.33 MeOH molecules, -1.3 %; found, -1.3 %) and (b) **Ag@2$_D$** (calc. per 1.5 $(CH_2CH_2OH)_2O$) molecules, -16.6 %; found, -17.8 %).

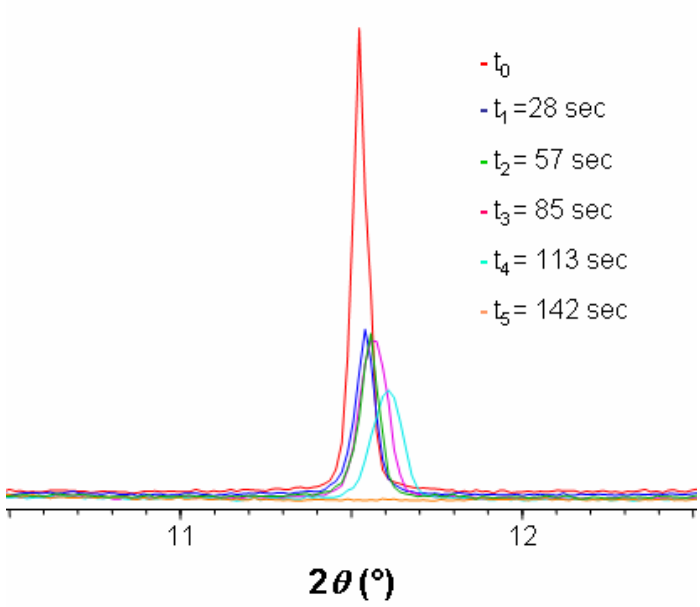

Fig. S4 Evolution of the XRPD traces of **Ag@2$_M$** during desolvation in the 10.5-12.5° range, collected using a Position Sensitive Detector with a window of 2° on a drop of **Ag@2$_M$** slurry deposited on a free background sample holder. It can be observed that the 020 reflection of the solvated phase disappears in only 2.5 minutes.

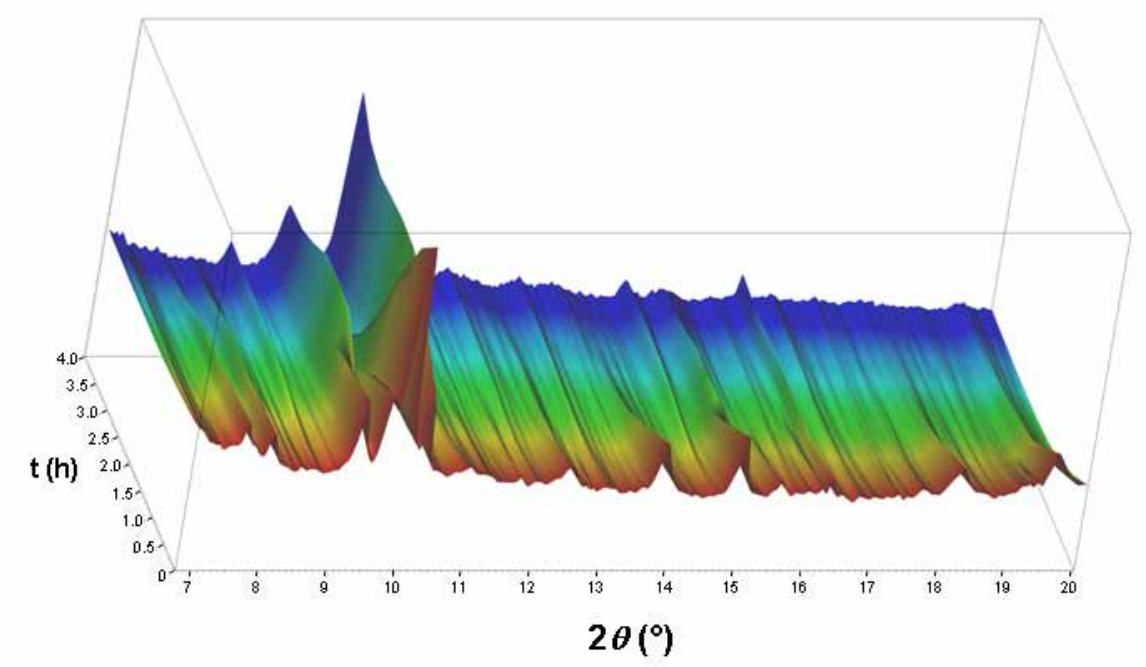

Fig. S5 Evolution of the XRP diffractograms during the **Ag@2$_E$** ↔ **Ag@2'** transformation. In this case, it should be noted that the desolvation process occurs in a few hours and not in a few seconds as in **Ag@2$_M$** A drop of **Ag@2$_E$** slurry was deposited on a free background sample holder and, then, we started to record a set of XRPD patterns (5-40° 2θ, step 0.02°, 1s per step). The t_0 diffractogram corresponds to the first trace lacking of the solvent bump.

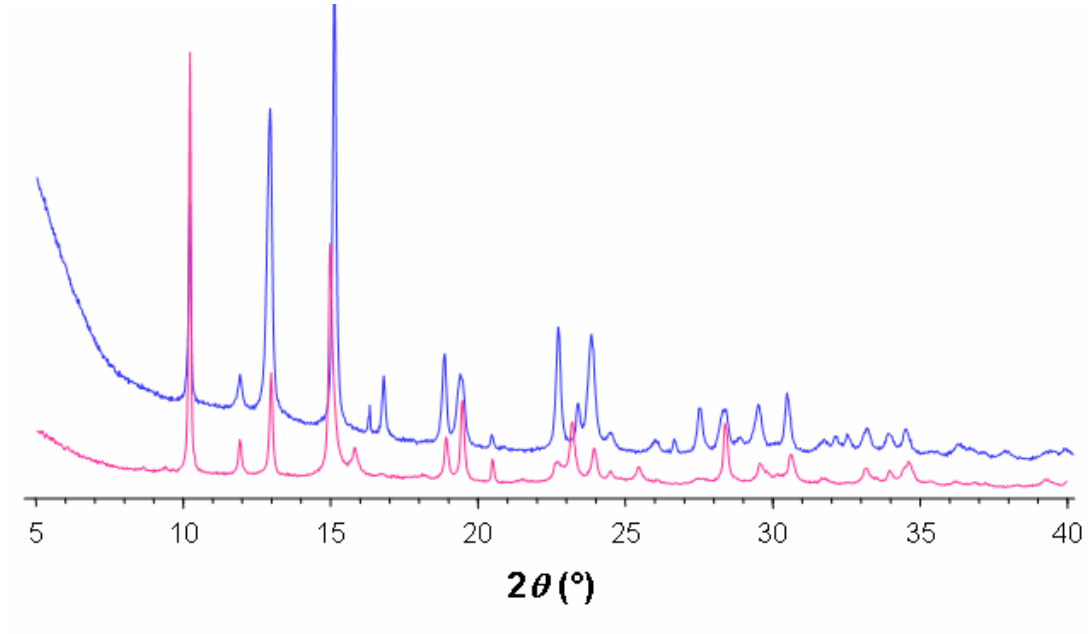

Fig. S6 XRPD traces of the desolvated **Ag@2** (blue) and **Ag@2'** (pink) phases.

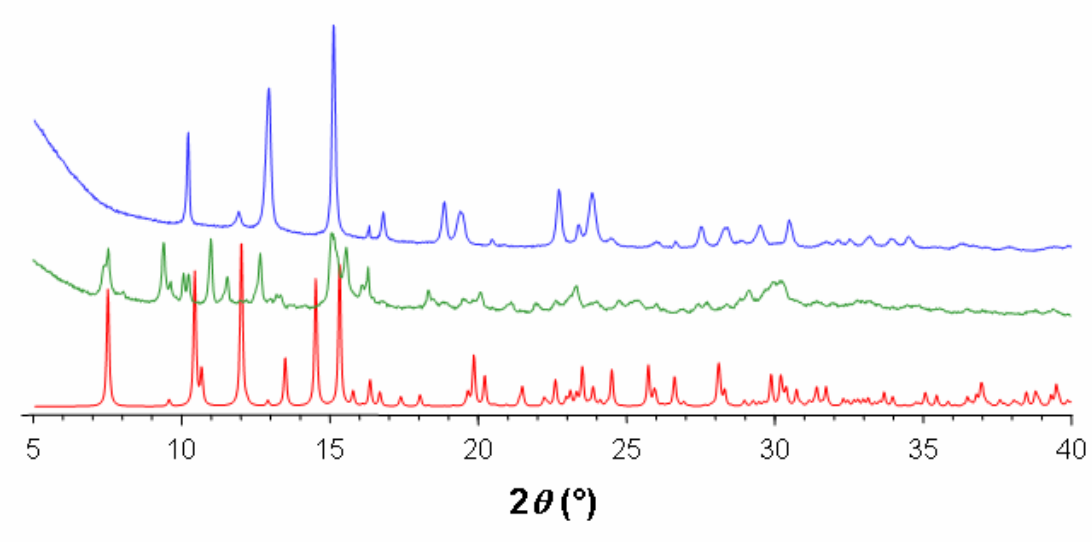

Fig. S7 XRP diffractogram of **Ag@2$_D$** (green) in comparison with the XRPD traces of the **Ag@2** phase (blue) and the simulated spectrum of **Ag@2$_M$** (red).

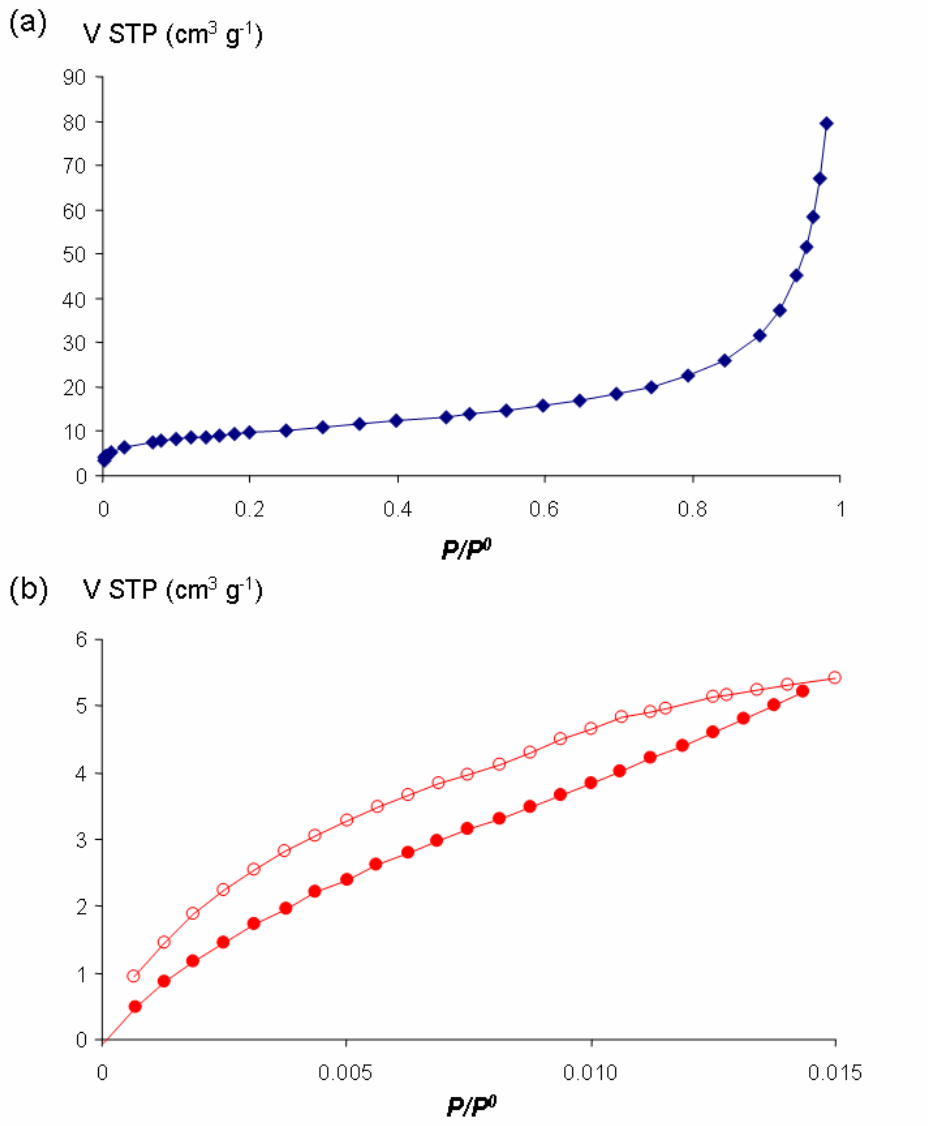

Fig. S8 N_2 (a) and CO_2 (b) sorption isotherms of **Ag@2** measured at 77 and 293 K, respectively. The open symbols denote desorption.