

Supporting Information

Two highly-connected, chiral, porous coordination polymers featuring novel heptanuclear metal carboxylate clusters

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Materials and Measurements:

All solvents and starting materials for synthesis were purchased commercially and were used as received. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer in the 400-4000 cm⁻¹ region. Elemental analysis (C, H, N) was performed on a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analysis (TGA) was performed at a rate of 10 °C/min under N₂ using a NETZSCH TG 209 system. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (CuK α , 1.5418 Å). The samples for liquid sorption experiments were obtained through placing the desolvated samples in vapor diffusion chambers for 48 hrs. The samples for solvothermal resistance experiments were prepared through soaking the desolvated samples in H₂O, CH₃OH, benzene for 24 hrs at room temperature and 24 hrs in boiling benzene, CH₃OH and 1 hr in boiling H₂O.

Synthesis of 1, MCF-24. A mixture of benzene-1,3,5-tribenzoic acid (H₃BTB, 0.033 g, 0.075 mmol),¹ Zn(NO₃)₂·6H₂O (0.067 g, 0.225 mmol) and NaNO₃ (0.013 g, 0.15 mmol) in *N,N'*-dimethylformamide (DMF) (5 mL), ethanol (2 mL) and water (1 mL) was placed in a Teflon-lined stainless steel vessel (12 mL) and heated at 90 °C for 48 hrs, and then cooled to room temperature at a rate of 0.1 °C/min. The resulting yellow microcrystalline precipitate of **1**, isolated by

washing with DMF/ethanol, and dried in vacuo. The yield was ~42 mg (74%, based on H₃BTB). Yellow single crystals for X-ray single-crystal diffraction were prepared by heating a solution of H₃BTB (0.033 g, 0.075 mmol), cyclohexene-1,4-dicarboxylic acid (0.012 g, 0.075 mmol), Zn(NO₃)₂·6H₂O (0.067 g, 0.225 mmol) and NaNO₃ (0.013 g, 0.15 mmol) in DMF (5 mL), ethanol (2 mL) and water (1 mL) in a Teflon-lined stainless steel vessel at 90 °C for 48 hrs, and then cooled to room temperature at a rate of 0.1 °C/min. The yield was ~15 mg (26%, based on H₃BTB). Anal. Calc. for C₉₉H₁₁₃Na_{0.50}Zn_{4.75}N₅O₃₇: C, 51.99; H, 4.98; N, 3.06. Found: C, 52.35; H, 4.88; N, 3.12%. IR (KBr, cm⁻¹): 3407m, 2934w, 1660s, 1610s, 1532s, 1391vs, 1256w, 1100w, 861w, 781m,

Synthesis of 2, MCF-24 (K). A mixture of H₃BTB (0.033 g, 0.075 mmol), Zn(NO₃)₂·6H₂O (0.067 g, 0.225 mmol) and KNO₃ (0.015 g, 0.15 mmol) in DMF (5 mL), ethanol (2 mL) and water (1 mL) was placed in a Teflon-lined stainless steel vessel (12 mL) and heated at 90 °C for 48 hrs, and then cooled to room temperature at a rate of 0.1 °C/min. The resulting yellow single crystals for X-ray single-crystal diffraction of **2** can be collected by filtration. The yield was ~22 mg (42%, based on H₃BTB). Anal. Calc. for C₉₉H₁₁₇N₅K_{0.50}Zn_{4.75}O₃₉: C, 51.01; H, 5.06; N, 3.00. Found: C, 51.09; H, 4.98; N, 2.96%. IR (KBr, cm⁻¹): 3405m, 2930w, 1660s, 1609s, 1549s, 1390vs, 1252w, 1097w, 862w, 782m.

Sorption Measurements. The sorption isotherm for N₂ gas was measured by using BELmax 00027 adsorption equipment (BEL Japan) at 77 K. The as-synthesized samples (weight 110 mg) were soaked in CH₃OH for 48 hrs and then placed in a quartz tube and dried under high vacuum at 423 K for 12 hrs to remove the solvated molecules prior to measurements. The BET surface area was calculated from a line regression plot of 1/($W((P_0/P) - 1)$) vs. P/P_0 (where W is the total volume absorbed at particular P/P_0 point and P_0 is 1 atm pressure).

Crystallography. The diffraction data were collected at 293(2) K with a Bruker AXS SMART CCD area detector diffractometer using ω rotation scans with a scan width of 0.3° and MoK α radiation (λ = 0.71073 Å). Absorption corrections were carried out utilizing SADABS routine.² The structures were solved by the direct methods and refined by full-matrix least-squares refinements based on F^2 .³ All non-hydrogen atoms except for disordered solvent molecules were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The hydrogen atoms of the coordinated water molecules could not be located from the electron density. Selected

phenyl group C-C bond lengths were restrained using DFIX 1.39 0.01, C(sp²)-C(sp²) bond lengths were restrained using DFIX 1.50 0.01 [C(1)-C(2), C(66)-C(68) in **1** and C(10)-C(14) in **2** are still slightly long at 1.53 Å] and the geometry of the phenyl rings C(29)~C(34) in **1** and C(68)~C(73) in **2** were constrained using AFIX 66. The thermal displacement parameters of various atoms were restrained using DELU and SIMU. Due to the presence of large cavities in the structure and heavily disordered solvent molecules in the cavities, the crystals of **1** and **2** scattered weakly and only low-angle data could be detected even when using long exposure times. An attempt to locate and refine the solvent molecules failed. Thus the SQUEEZE routine of PLATON⁴ was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine. Crystal data: Both **1** and **2** belong to the tetragonal space group *I*₄22 (No. 91) with *Z* = 16 at *T* = 293(2) K. For **1**: C₈₁H₄₉Na_{0.5}Zn_{4.75}O_{20.5}, *M* = 1672.20, *a* = 32.4729(7), *c* = 47.6641(18) Å, *V* = 50261(2) Å³, *ρ* = 0.884 g cm⁻³, *μ* = 0.940 mm⁻¹, 80929 reflections measured, 24575 unique (*R*_{int} = 0.1136) which were used in all calculations, final *R*₁ = 0.0592 and *wR*₂ = 0.1128 for *I* > 2σ[*I*], and *S* = 0.945 (after SQUEEZE), Flack parameter = 0.06(1), (*R*₁ = 0.0943 and *wR*₂ = 0.2250 (*I* > 2σ[*I*]), and *S* = 1.189 without employing PLATON/SQUEEZE). For **2**: C₈₁H₄₉K_{0.5}Zn_{4.75}O_{20.5}, *M* = 1680.26, *a* = 32.441(2), *c* = 47.814(3) Å, *V* = 50320(4) Å³, *ρ* = 0.887 g cm⁻³, *μ* = 0.954 mm⁻¹, 79454 reflections measured, 22182 unique (*R*_{int} = 0.1177) which were used in all calculations, final *R*₁ = 0.0594 and *wR*₂ = 0.1273 for *I* > 2σ[*I*], *S* = 0.947, Flack parameter = 0.03(1), (*R*₁ = 0.0942 and *wR*₂ = 0.2474 (*I* > 2σ[*I*]), and *S* = 0.999 without employing PLATON/SQUEEZE).

The final formulas for these two complexes were determined by combining single-crystal structure, elemental microanalysis and TGA.

References

- 1 J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239.
- 2 Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, 2002.
- 3 G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.
- 4 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

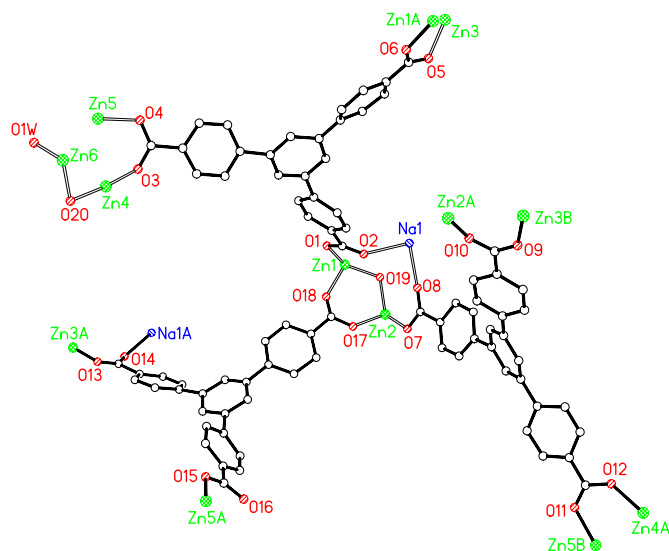


Fig. S1 Asymmetric unit of **1** with the bridging modes of BTB ligands, the hydrogen atoms and solvent molecules are omitted.

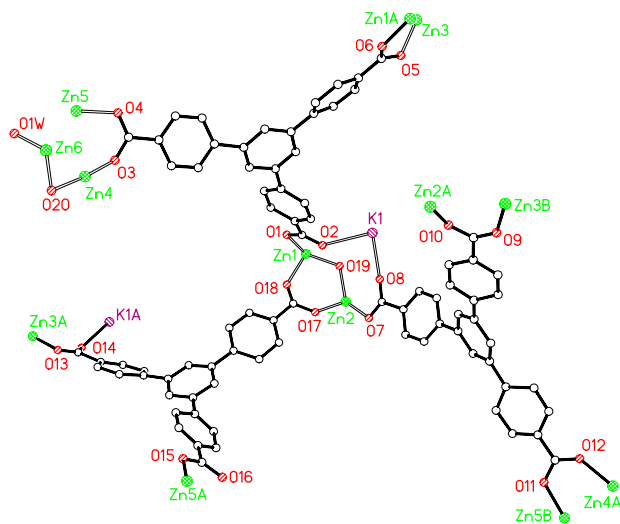


Fig. S2 Asymmetric unit of **2** with the bridging modes of BTB ligands, hydrogen atoms and solvent molecules are omitted.

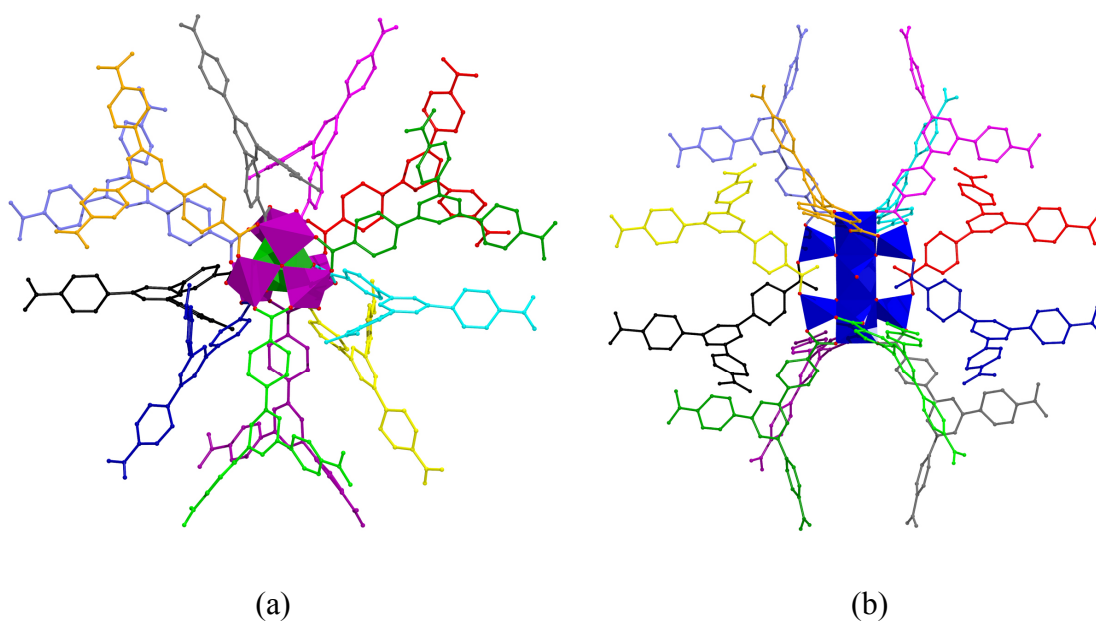


Fig. S3 Ball-and-stick diagrams showing two kinds of heptanuclear clusters $[\text{NaZn}_6(\mu_3\text{-OH})_2(\text{O}_2\text{C-})_{12}]$ SBU1(a) and $[\text{Zn}_7(\mu_3\text{-OH})_4(\text{H}_2\text{O})_2(\text{O}_2\text{C-})_8(\text{HO}_2\text{C-})_4]$ SBU2 (b) in **1** ligated by twelve BTB ligands. SBU1: Na green polyhedron, Zn purple polyhedron; SBU2: Zn blue polyhedron.

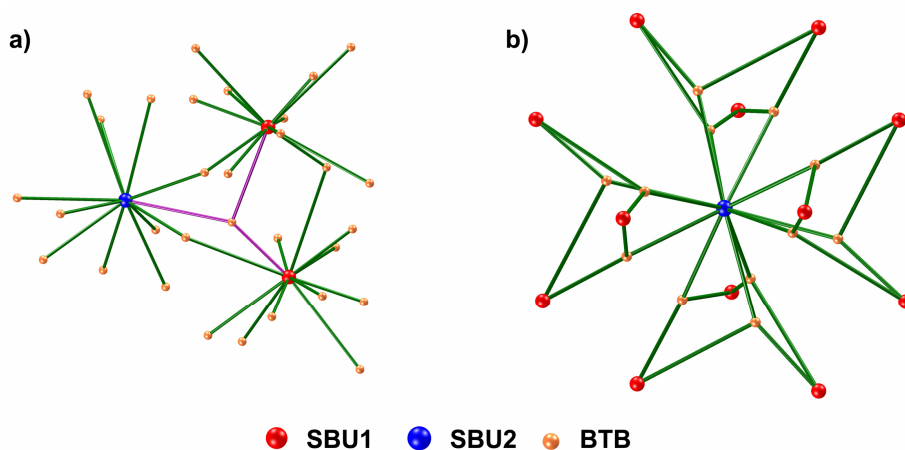


Fig. S4 The simplified topological representation of the 3-connected BTB ligand and 12-connected heptanuclear SBU in **1**.

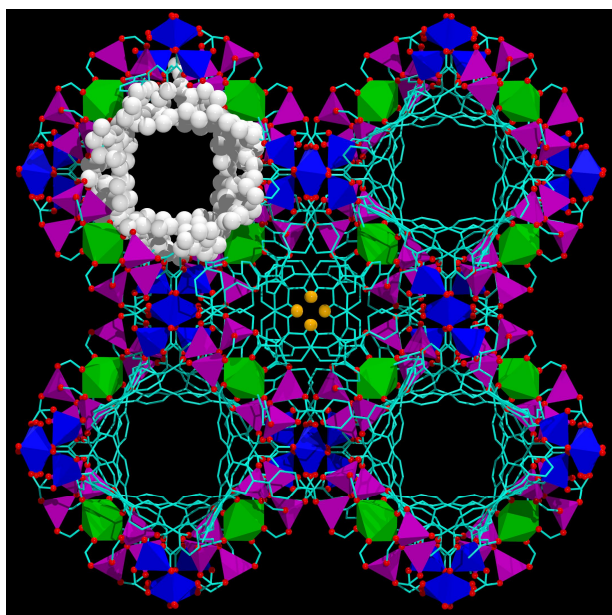


Fig. S5 3D porous network of **1** viewed along the [001] direction with two types of hydrophobic channels are highlighted (white C, yellow H), the small channels are surrounded by phenyl H atoms. SBU1, purple (Zn) and green (Na) polyhedrons; SBU2, blue (Zn) polyhedron.

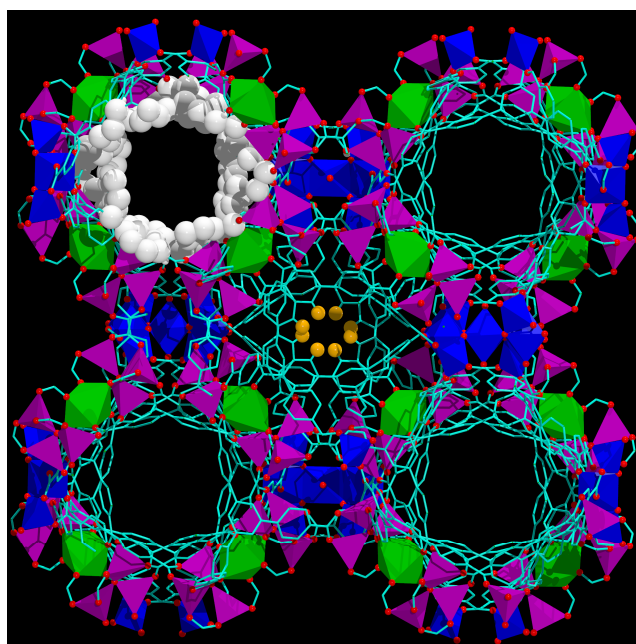


Fig. S6 3D porous network of **1** viewed along the [110] direction with two kinds of hydrophobic channels are highlighted (white C, yellow H), the small channels are surrounded by phenyl H atoms.

SBU1, purple (Zn) and green (Na) polyhedrons; SBU2, blue (Zn) polyhedron.

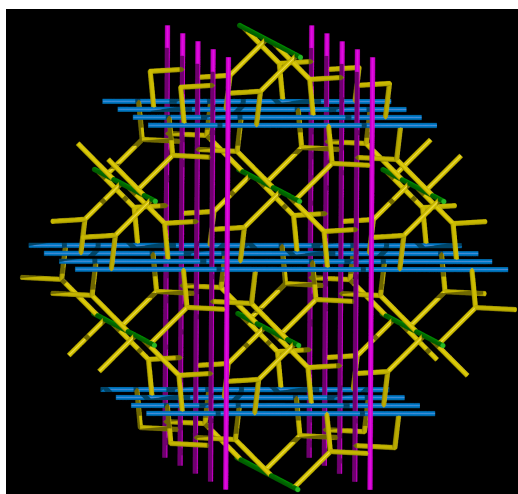


Fig. S7 3-Connected 3D porous network in **1** and **2** with three channels along the $[001]$, $[110]$ and $[1\bar{1}0]$ directions (green, azury and purple rods, respectively) kneaded by 3-connected cavities (yellow rod).

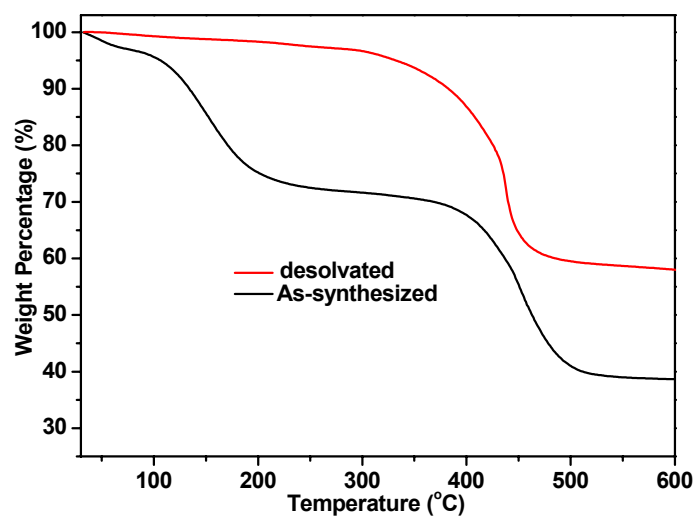


Fig. S8 TGA plots of the as-synthesized and desolvated samples of **1**.

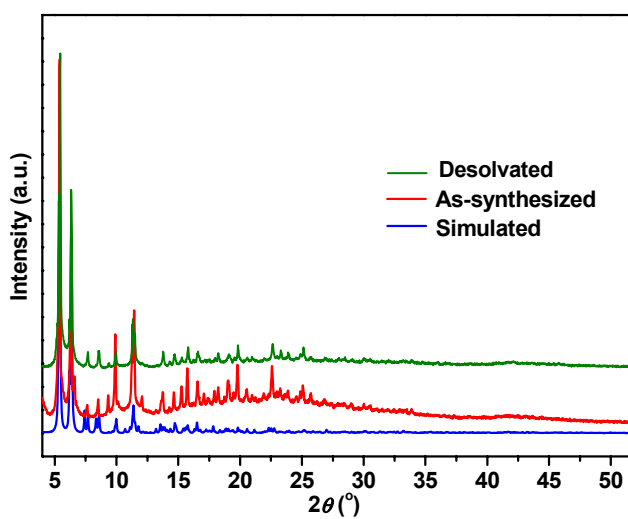


Fig. S9 PXRD patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized and desolvated samples of **1**.

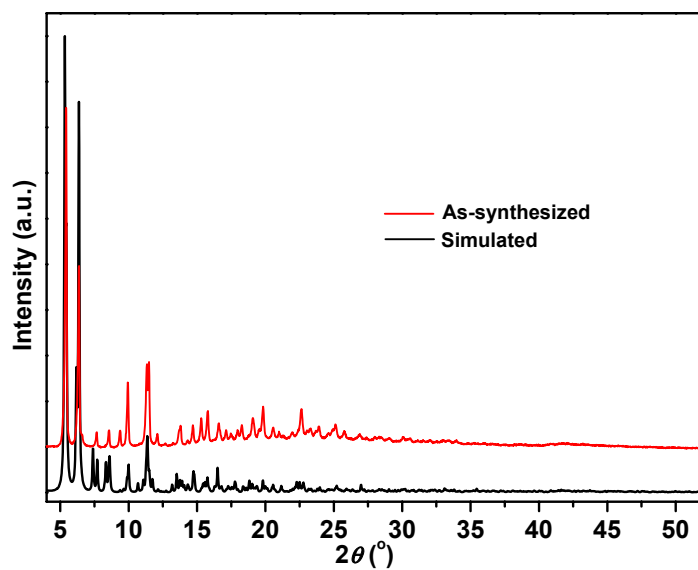


Fig. S10 PXRD patterns of **2** simulated from the X-ray single-crystal structure and as-synthesized samples of **2**.

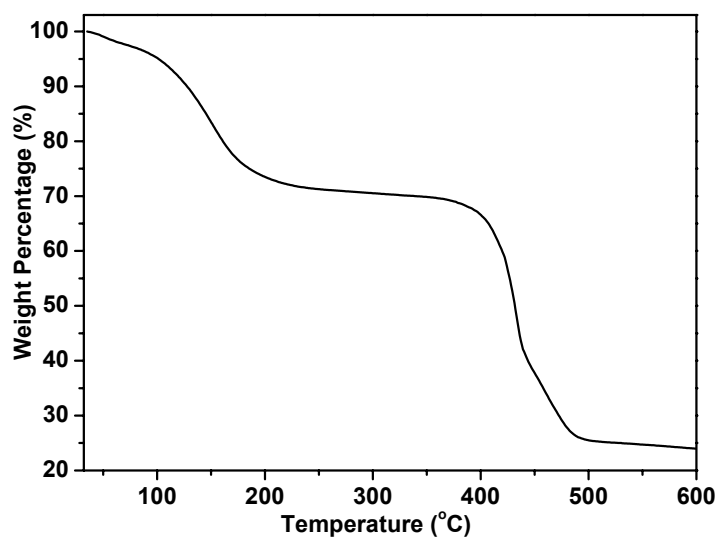


Fig. S11 TGA plot of the as-synthesized samples of **2**, showing a weight loss of 28.0% before 225 °C corresponding to the removal of 12 free H₂O, 1.5 EtOH and 5 DMF guest molecules (calc. 27.9%), and no further weight loss before the decomposition at 350 °C.

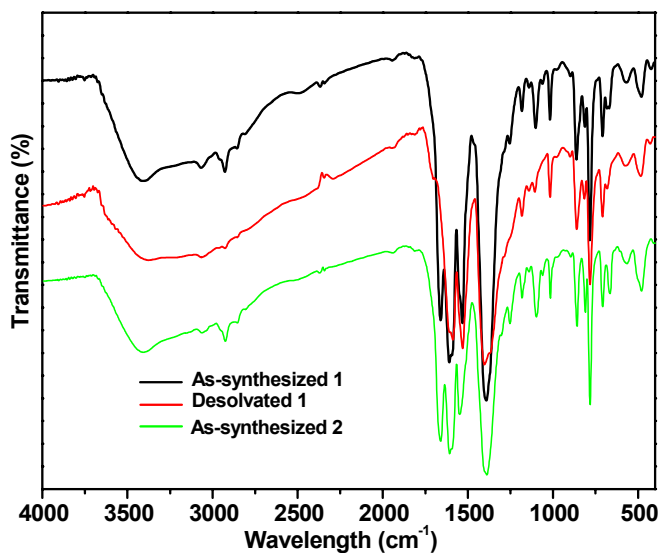


Fig. S12 IR spectra of the as-synthesized, desolvated samples of **1** and **2**.