Supporting information for

Two organic-inorganic hybrid frameworks with unusual inorganic and organic connectivity

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Experimental Section

General Remarks. All of the chemicals are commercially available and used without further purification. Elemental analyses were determined using Elementar Vario EL elemental analyser. The IR spectra were recorded in the 4000 to 400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) was carried out on Netzsch TG-209 Thermogravimetry Analyzer in air atmosphere. The Powder X-ray diffraction patterns were recorded on D8 ADVANCE X-Ray Diffractometer. The single crystal data were collected on a Bruker Smart 1000 CCD diffractometer.

X-ray Crystallography. Single-crystal data for **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer, with Mo-Kα radiation (λ = 0.71073 Å). All empirical absorption corrections were applied using the SADABS program.[1] The structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. The disordered electron density of the guest DMF and H_2O molecules in **1** were

treated as a diffuse contribution using the program SQUEEZE.[2] The hydrogen atoms in **1** and **2** were placed in calculated position, with fixed isotropic thermal parameters and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs.[3]

Gas Sorption Measurements. The N_2 sorption experiment for **1** was measured with a BELSORP-max gas adsorption instrument in a relative pressure range from 10^{-4} to 1.0 atom. The cryogenic temperature of 77 K was controlled by liquid nitrogen. The initial outgassing process for the sample was carried out under a high vacuum (less than 10^{-6} mbar) at 80 ℃ for 10 hrs. The degassed sample and sample tube were weighed precisely and transferred to the analyzer.

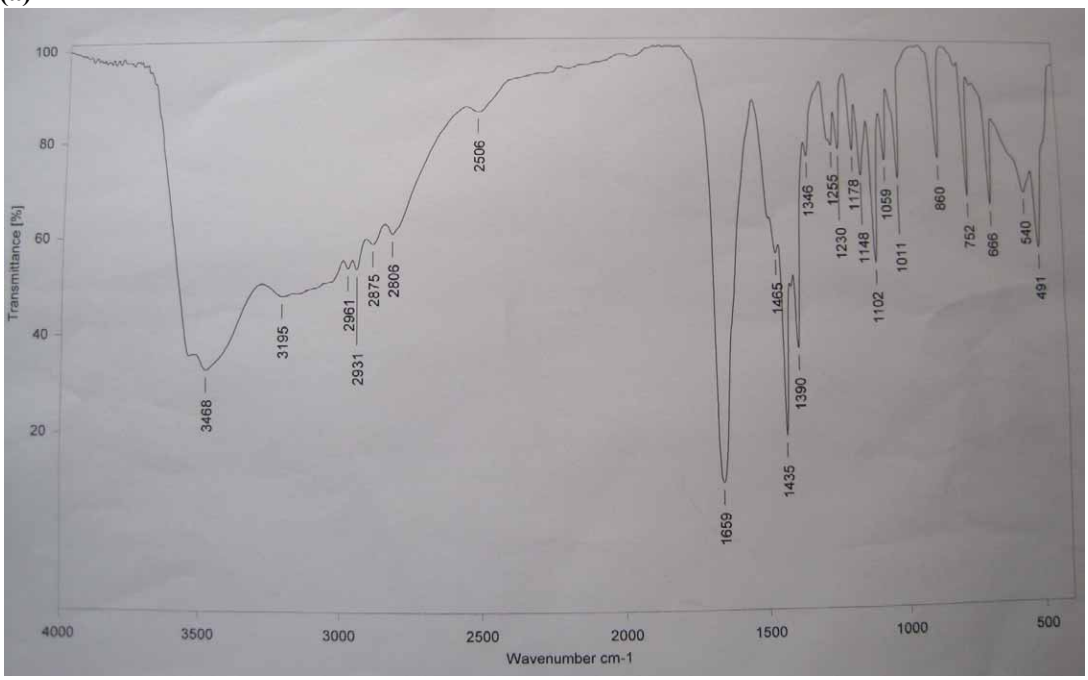
References

1 G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, 1996.

2 P. van der Sluis and A. L. Spek, *Acta Cryst.,* 1990, **A46**, 194.

3 G. M. Sheldrick, *SHELXS 97*, *Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, 1997.

(a)



(b)

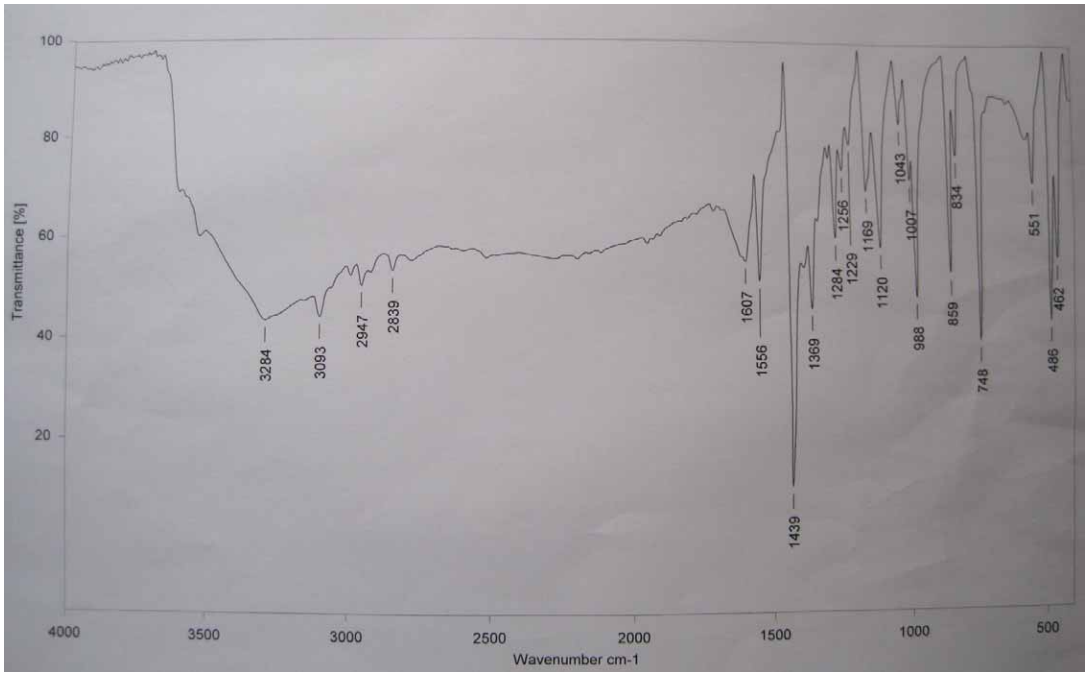


Fig. S1 The infrared spectra for **1** (a) and **2** (b).

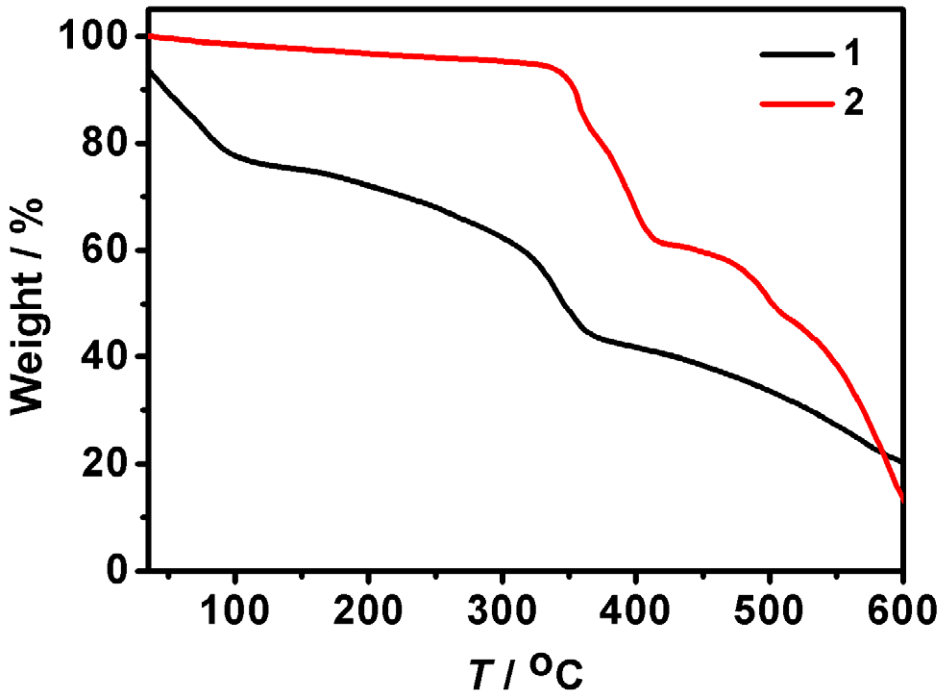


Fig. S2 The TGA curves for **1** and **2**.

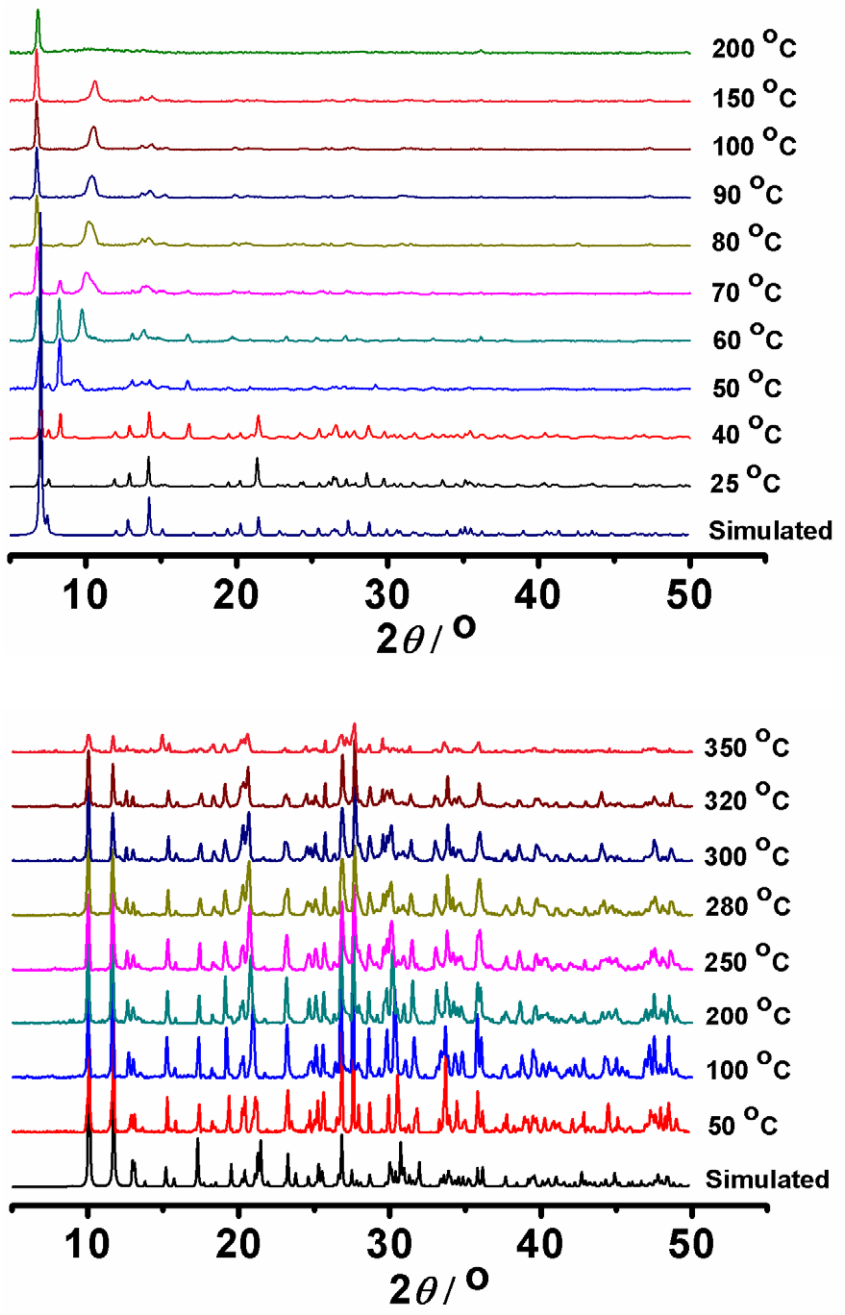


Fig. S3 The variable temperature PXRD patterns for **1** and **2**.

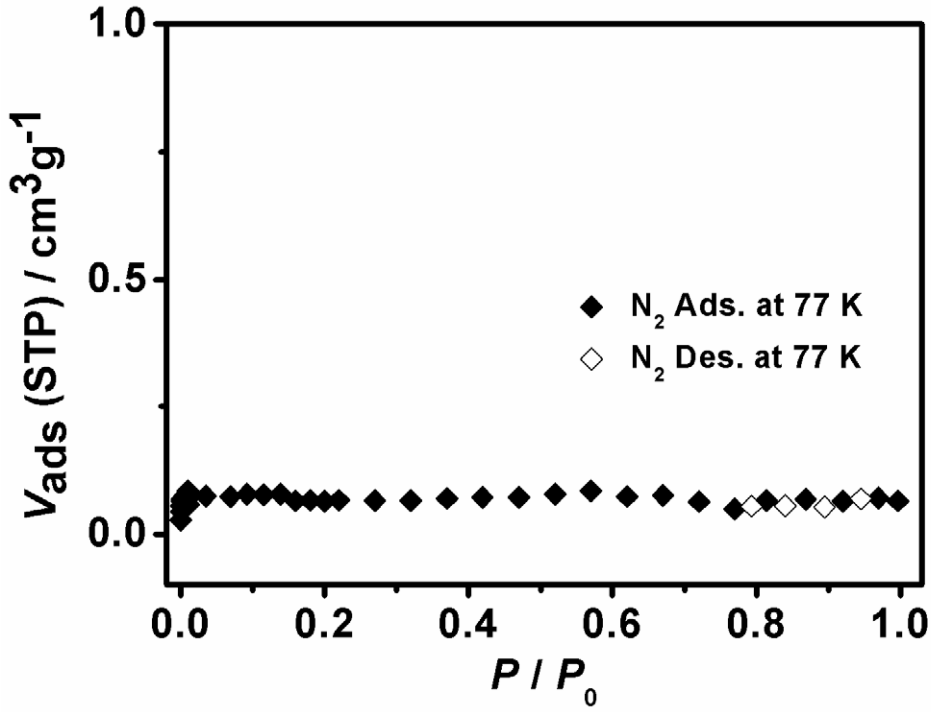


Fig. S4 Nitrogen isotherm measurement of the desolvated **1**, indicating the desolvated **1** becomes non-porous after removing the guest DMF and water molecules.

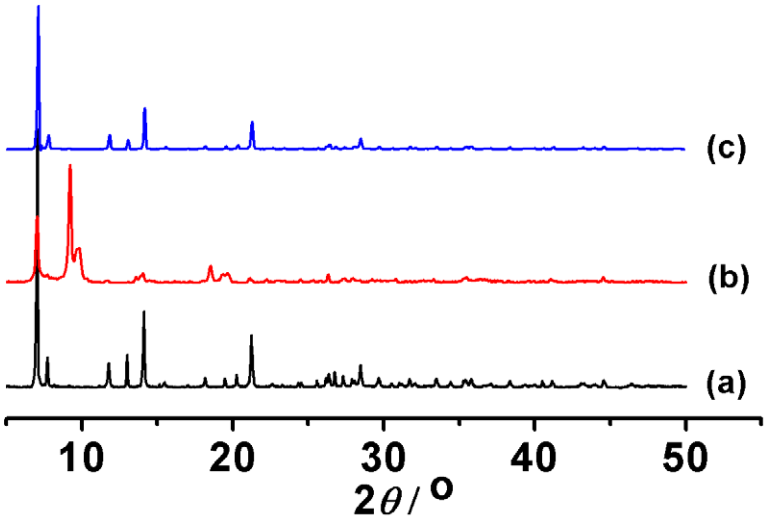


Fig. S5 The PXRD patterns for (a) **1**, (b) the desolvated **1**, and (c) the desolvated **1** immersed in 1:1 (*v*/*v*) DMF/H_2O for one day.