Electronic Supplementary Information

A mesoporous aluminium metal-organic framework with 3 nm open pores

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Structural Modeling and Powder X-Ray Diffraction Analysis.

The theoretical model of CYCU-3 was carried out using the Materials Studio 5.5.[S1] Initially, only the Al atoms were included using the fractional coordinates found in MIL-68(V). The unit cell was elongated accordingly by the experimental lattice constants. Finally, the atoms of the 4,4'-stilbenedicarboxylate linker without hydrogen atoms were inserted. The geometry optimizations converged to give finally a plausible crystal structure by adjusts the bond length of aluminum to oxygen atoms bond angles of O-Al-O. The calculated and measured powder X-ray diffraction patterns are in good agreement (Fig. S2). The export res file was further examined by *PLATON*[S2] software by the Addsym command. This would produce a new suitable res file for the further use on the structure analysis. The models were used as a starting point for the Rietveld refinement.

The structure of CYCU-3 was solved from the powder XRD pattern of the activated sample, heated at 150 ^{o}C, to prevent re-absorption of water. The lab and synchrotron powder X-ray diffraction were measured for further considerations. Due to higher ratio of intensity to noise of CYCU-3 in the measurement results by synchrotron radiation, the lab-machine measurements were used for the profile analysis. Extractions of the peak positions, pattern indexing and Rietveld refinements were carried out with the GSAS program.[S3] For CYCU-3, the symmetric *Cmcm* space group was chosen to solve the structure. The experimental powder X-ray diffraction pattern was indexed as an orthorhombic system with a lattice constant of a=33.776, b=59.003, and c=6.742 Å. The final Rietveld plot corresponds to the crystal structure model and profile factors were display in Fig. S1. Tables S1 and S2 are list the crystallographic data and atomic coordinates.

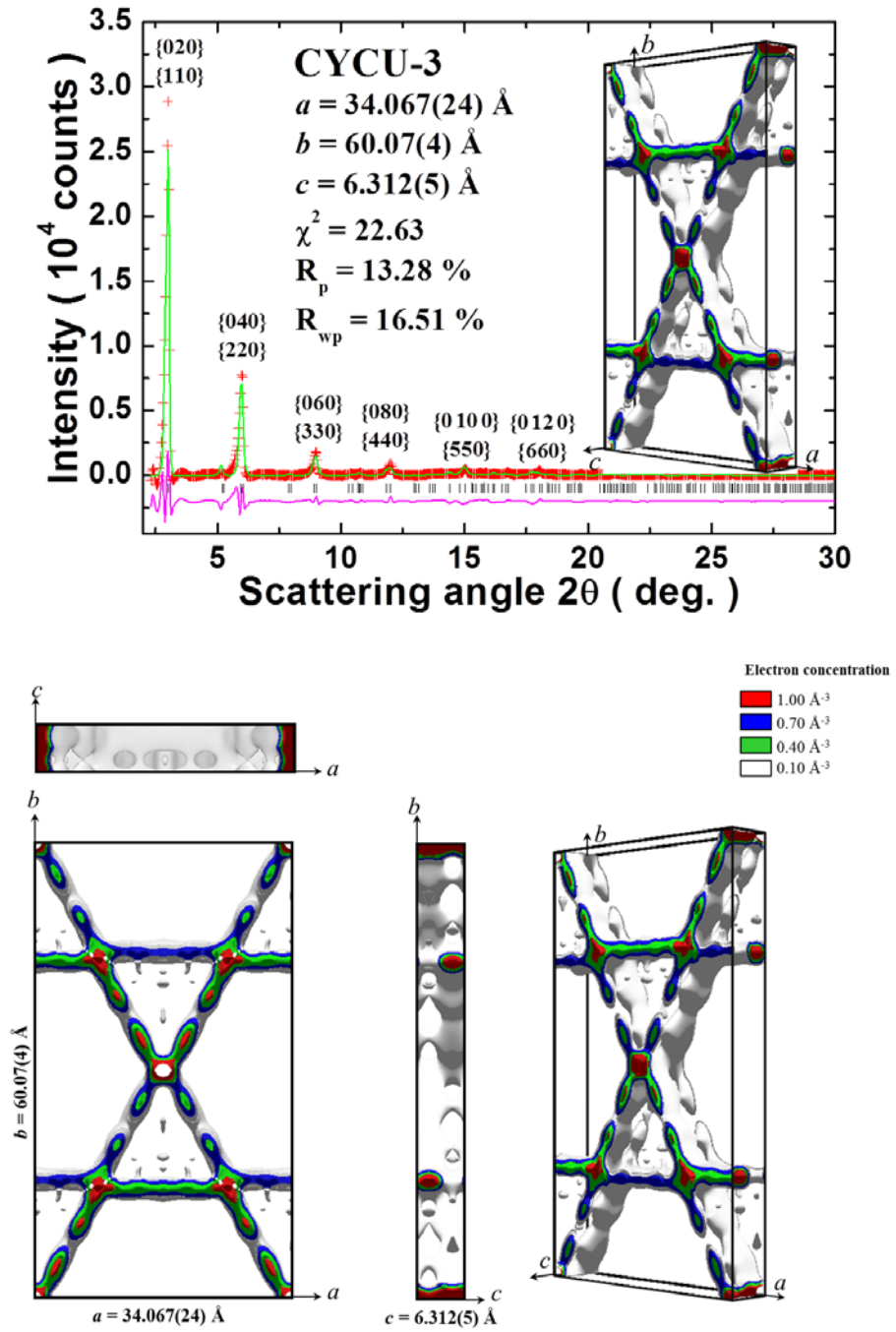


Fig. S1. The plots of electron density from X-ray powder diffraction pattern for the CYCU-3.

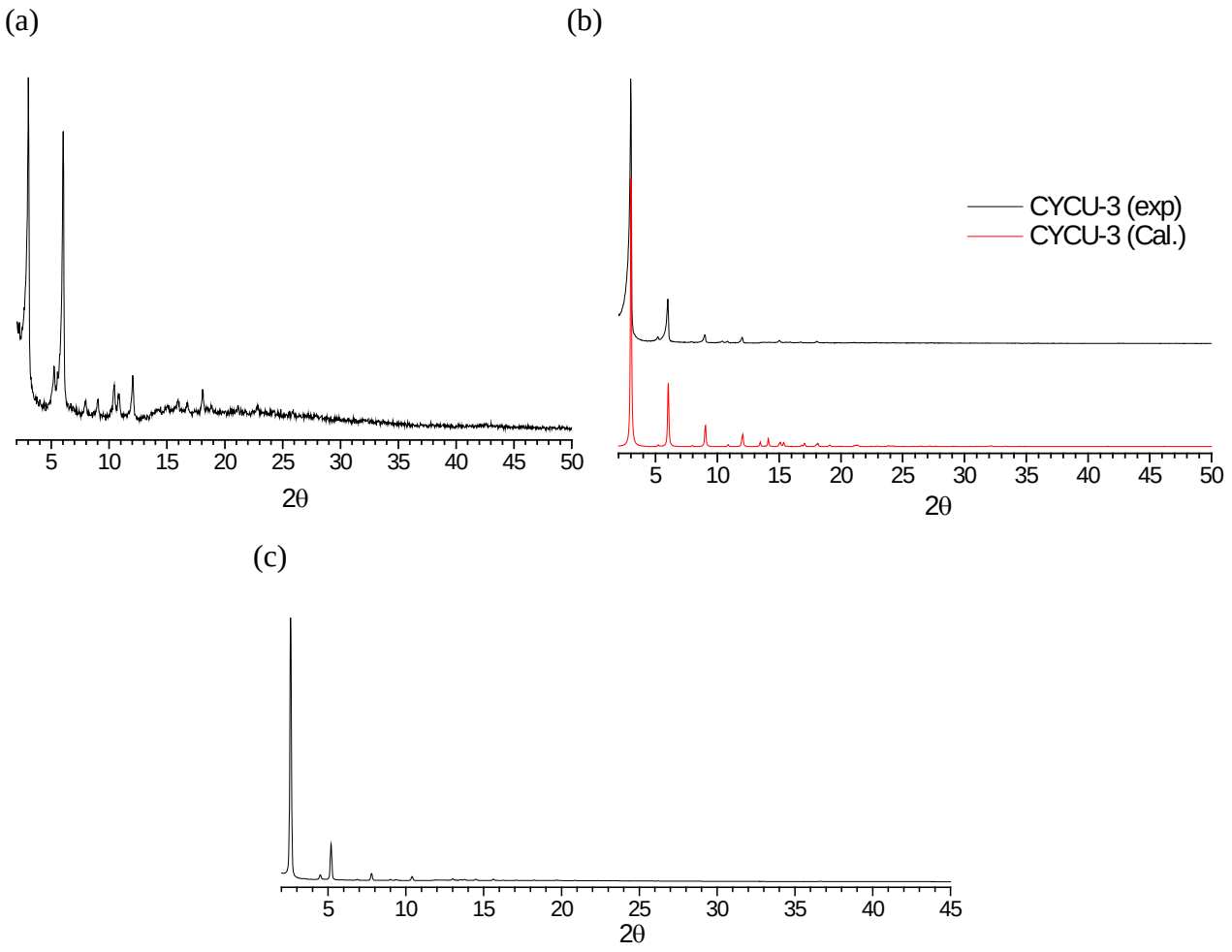


Fig. S2. Powder XRD patterns of: (a) as-synthesized CYCU-3; (b) desolvated CYCU-3; (c) desolvated CYCU-3 (measured by synchrotron radiation).

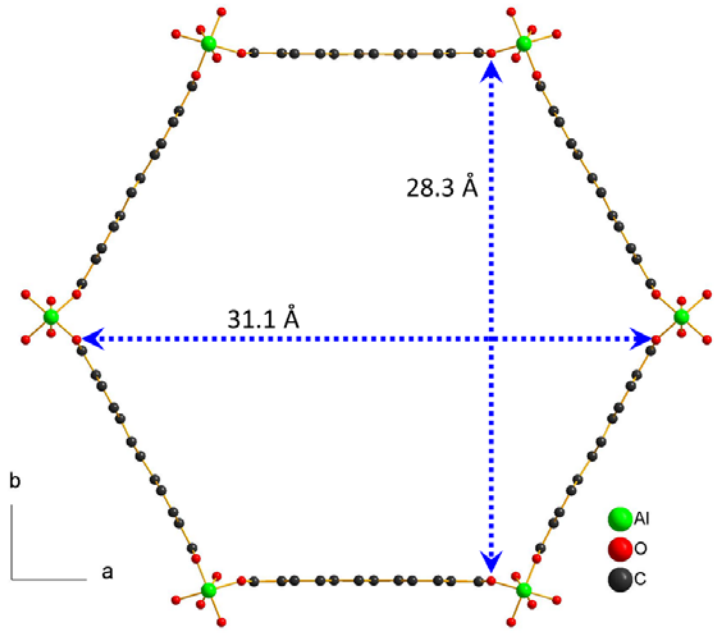


Fig. S3. The hexagonal pore sizes of CYCU-3.

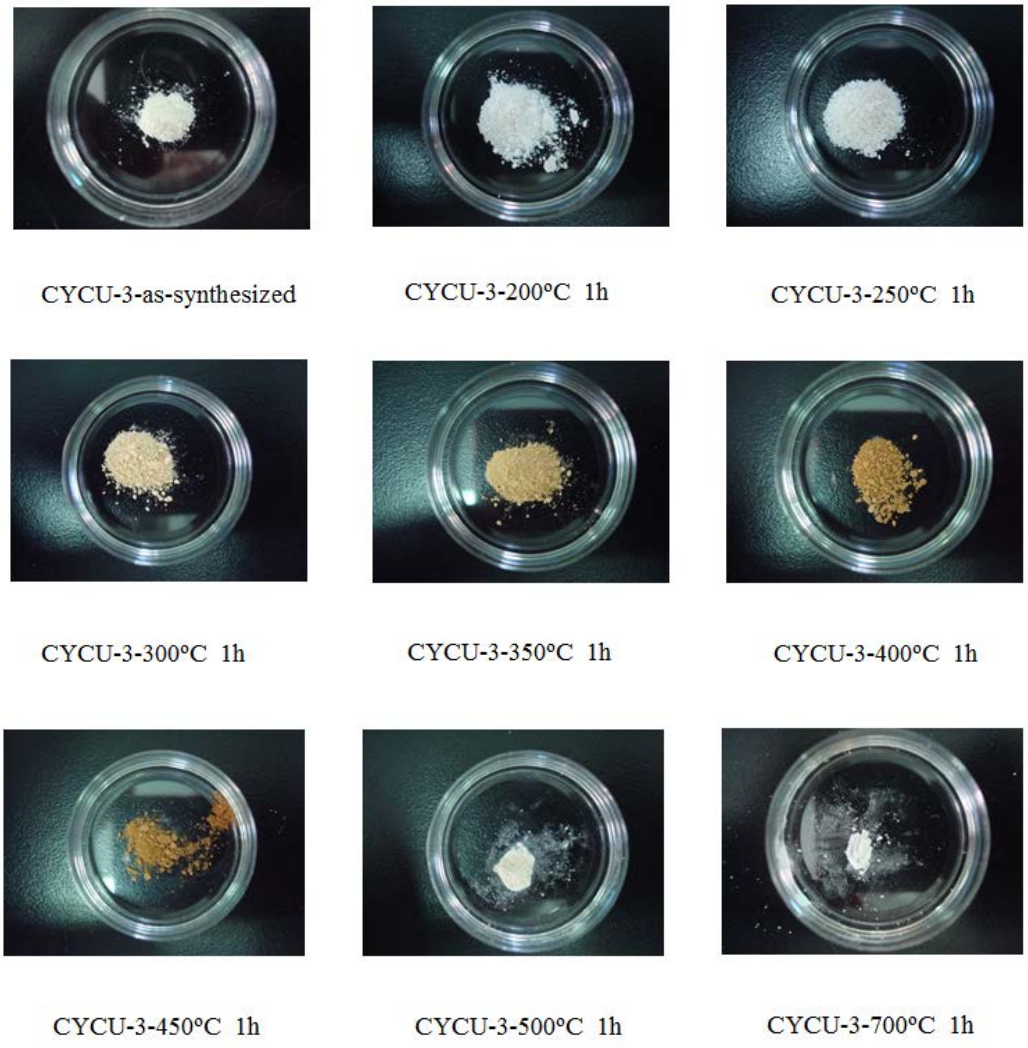


Fig. S4. Photographs of the corresponding samples with the specific thermal treatments of CYCU-3.

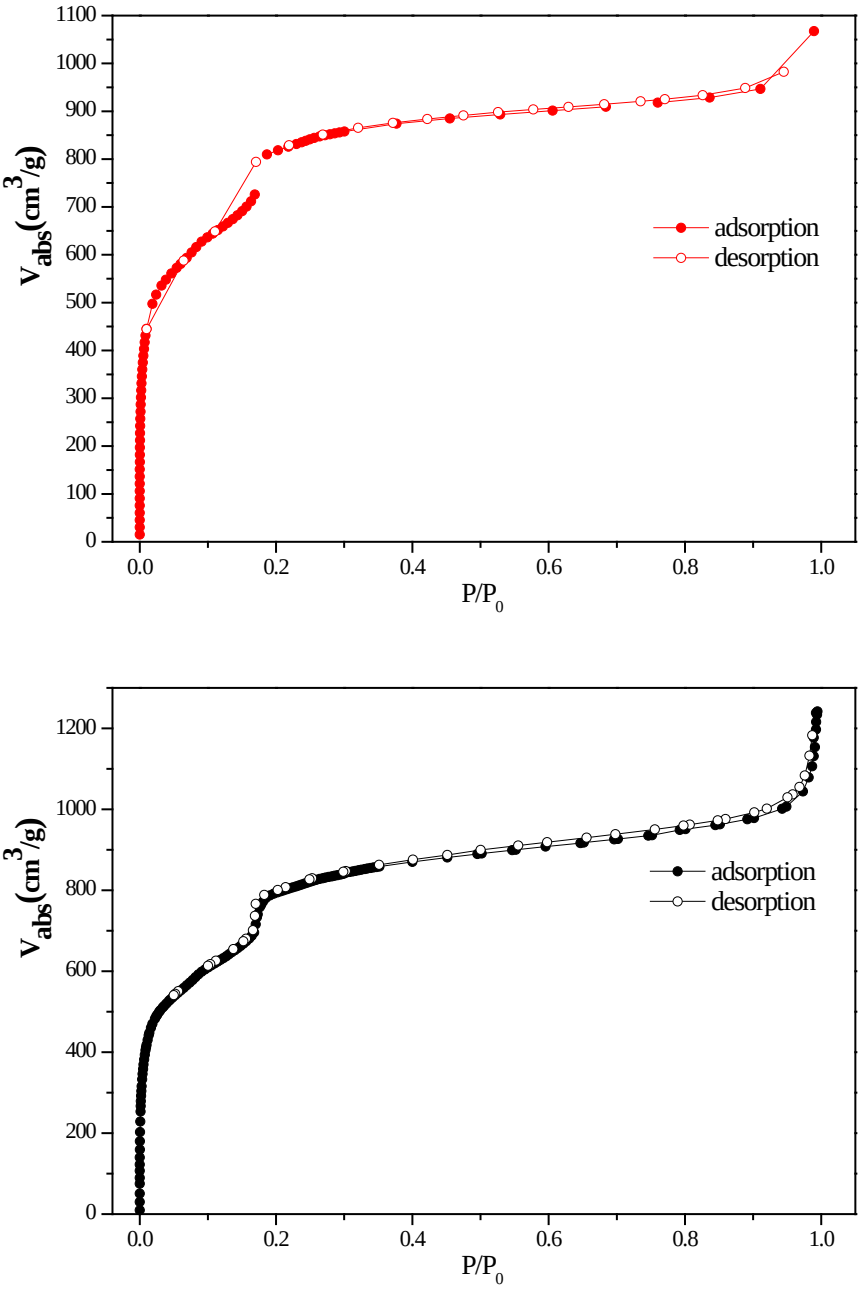


Fig. S5. Nitrogen sorption isotherms of CYCU-3 at 77K measured by ASAP 2020 (top) and Autosorp-iQ (bottom).

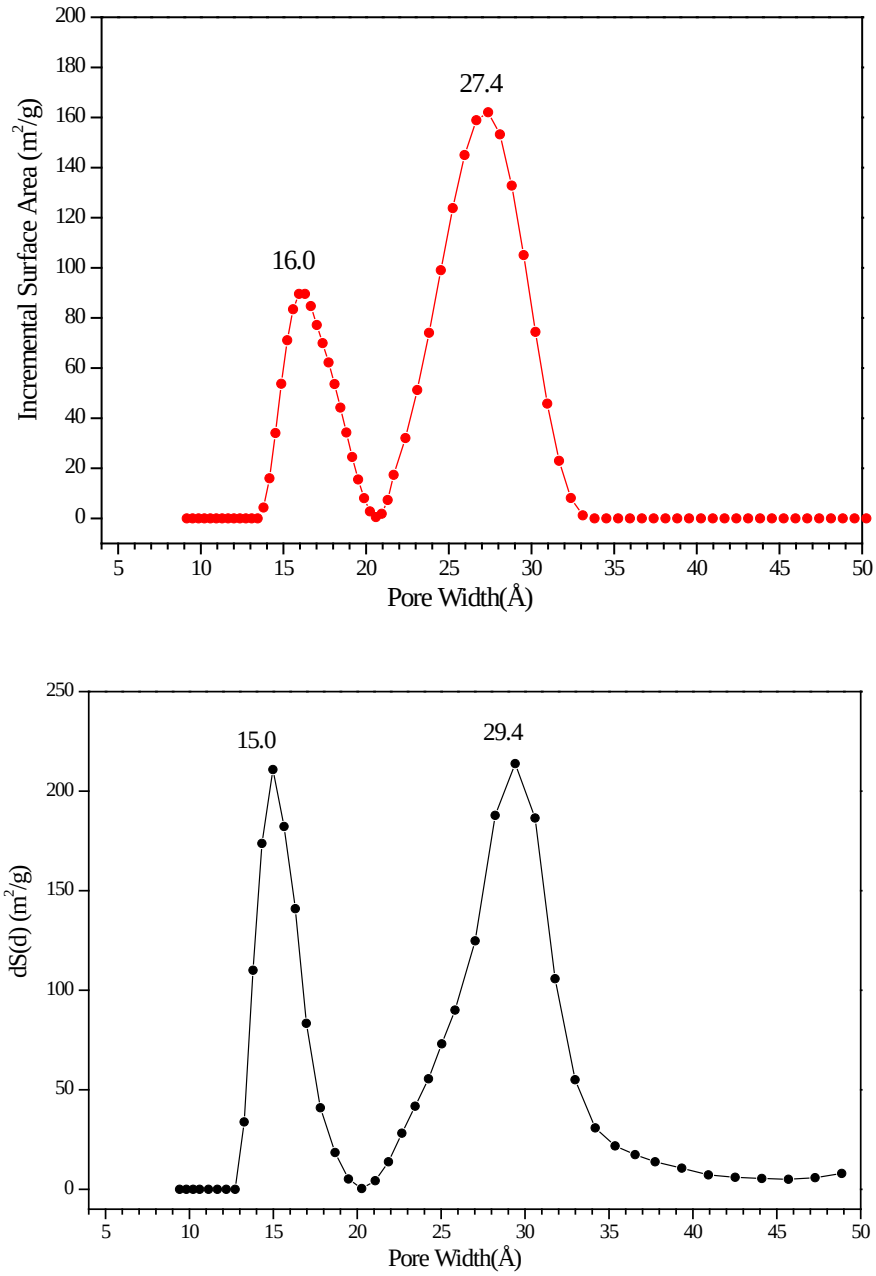


Fig. S6. The DFT pore size distribution of CYCU-3 analyzed from nitrogen sorption isotherms at 77K measured by the instruments of ASPA 2020 (top) and Autosorp-iQ (bottom).

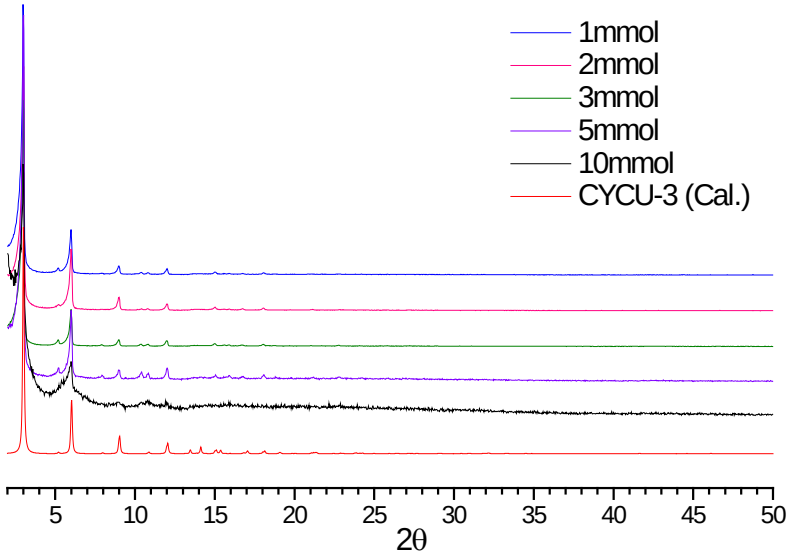


Fig. S7. Powder XRD patterns of **CYCU-3** synthesized under various molarity of acetic acid.

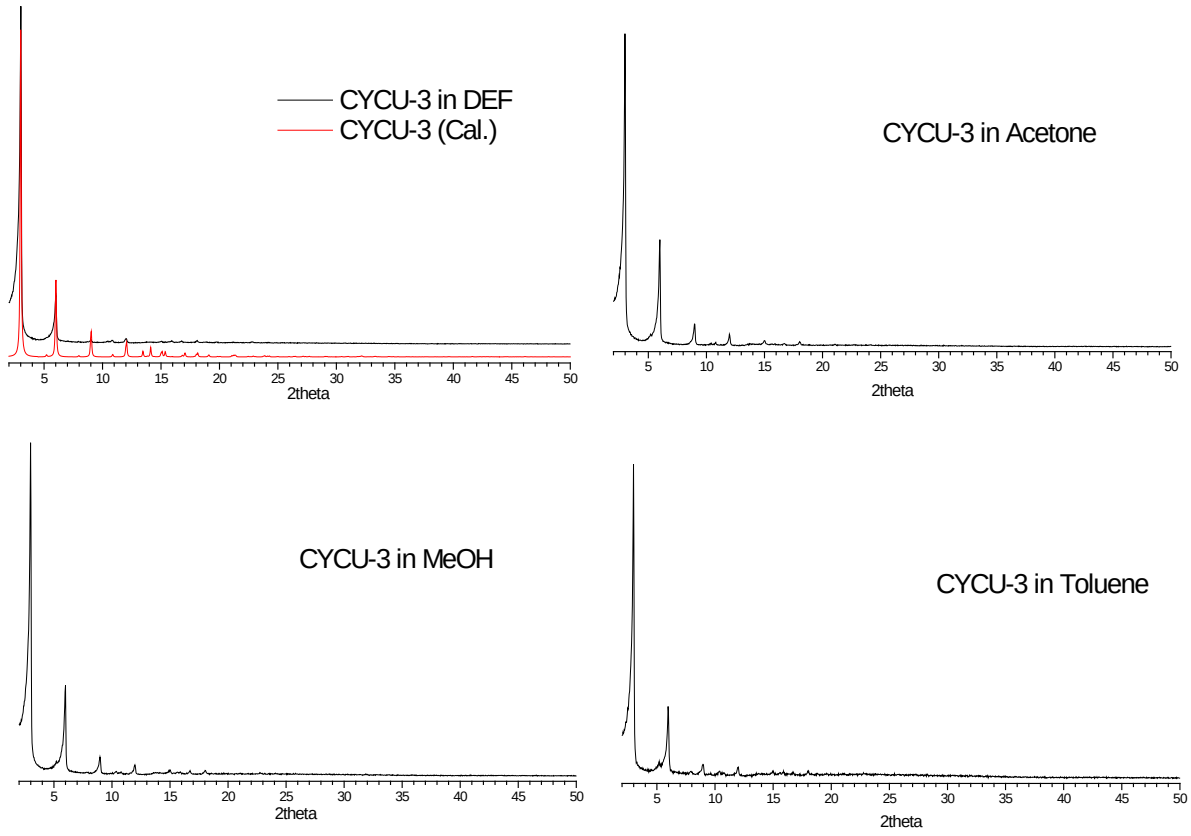
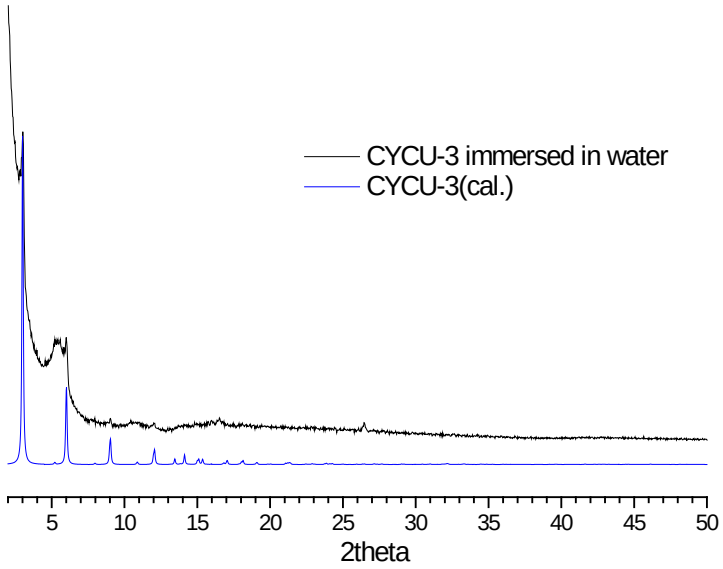


Fig. S8. Powder XRD patterns of **CYCU-3** treated with various solvents after desolvation.

(a)



(b)

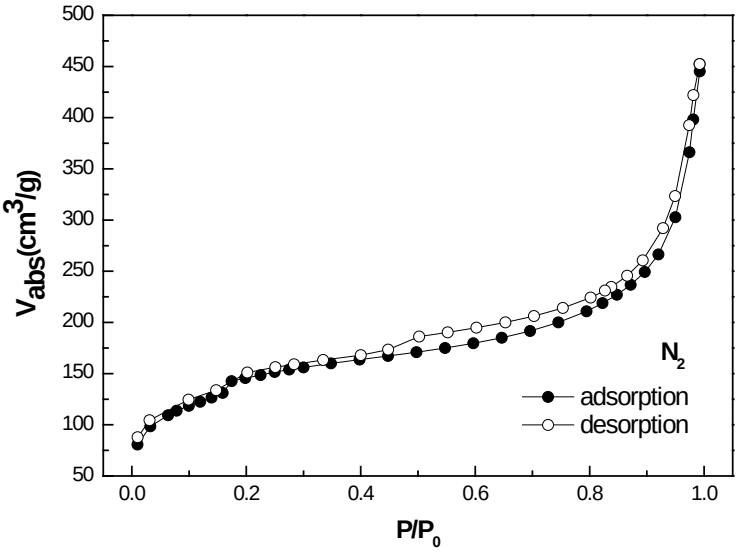
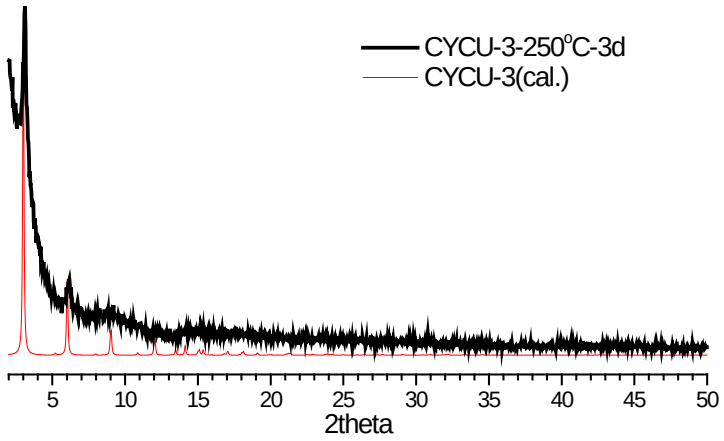


Fig. S9. (a) Powder XRD patterns of CYCU-3 sample after immerse in water for 7 day; (b) the nitrogen adsorption and desorption isotherms at 77 K of CYCU-3 after immersed in water and washed with water and hot DMF.

(a)



(b)

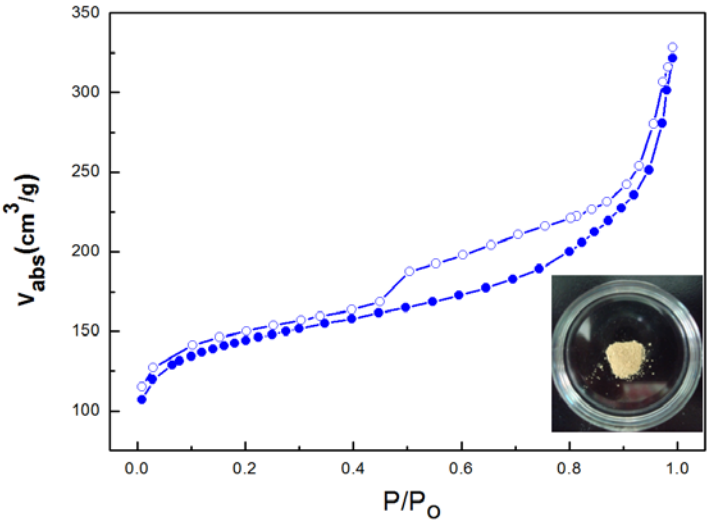


Fig. S10. (a) The powder XRD patterns for thermal treated samples of CYCU-3 by 250 ^{o}C and 3 days. (b) The N_2 sorption isotherms at 77K and photos of CYCU-3 after heated at 250^{o}C and 3 days (solid circles, adsorption; open circles, desorption).

Table S1 Results and relevant information for the Rietveld refinement of CYCU-3.

	CYCU-3
Formula	$Al_4O_{20}C_{64}H_{44}$
Formula weight	1240.2
Temperature (K)	298
Wavelength (Å)	1.54056
Pattern range (°, 2θ)	2– 30
Space group	*Cmcm* (No. 63)
a (Å)	34.067(24)
b (Å)	60.07(4)
c (Å)	6.312(5)
V (Å^3)	12916.9 (28)
Z	16
χ^2	22.63
R_p	0.1328
R_{wp}	0.1651

Table S2 Atomic coordinates and equivalent isotropic displacement parameters (Å^3).

CYCU-3

	x	y	z	U_{iso}	Occupancy
Al1	0.2500	-0.2500	-0.5000	0.1	0.25
Al2	0.0000	0.0000	-1.0000	0.1	1
O1	0.2311	-0.2224	-0.5766	0.1	1
O2	0.0389	-0.0192	-0.9199	0.1	1
O3	0.2988	-0.2411	-0.5822	0.1	1
O4	0.2398	-0.2604	-0.7500	0.1	1
O5	0.0000	0.0120	-0.7500	0.1	1
C1	0.2249	-0.2128	-0.7500	0.1	1
C2	0.2042	-0.1900	-0.7500	0.1	1
C3	0.1944	-0.1793	-0.5724	0.1	1
C4	0.1748	-0.1586	-0.5725	0.1	1
C5	0.1640	-0.1479	-0.7500	0.1	1
C6	0.1416	-0.1271	-0.6782	0.1	0.5
C7	0.0474	-0.0292	-0.7500	0.1	1
C8	0.0697	-0.0515	-0.7500	0.1	1
C9	0.0790	-0.0616	-0.9276	0.1	1
C10	0.0984	-0.0818	-0.9274	0.1	1
C11	0.1088	-0.0920	-0.7500	0.1	1
C12	0.1275	-0.1140	-0.8224	0.1	0.5
C13	0.3185	-0.2417	-0.7500	0.1	1
C14	0.3631	-0.2413	-0.7500	0.1	1
C15	0.3833	-0.2408	-0.5711	0.1	1
C16	0.4244	-0.2409	-0.5696	0.1	1
C17	0.4462	-0.2405	-0.7500	0.1	1
C18	0.4882	-0.2408	-0.6714	0.1	1

Reference

S1. Accelrys, *Materials Studio Release Notes*, 5.5, Accelrys Software, Inc., San Diego, 2008.

S2. A. L. Spek, *PLATON*; The University of Utrecht: Utrecht, The Netherlands, 1999.

S3. A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory, USA, 1994.