Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Ring-size controllable Metallamacrocycles as Building Blocks for the Construction of Microporous Metal-Organic Frameworks

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Materials and Instrumentation. All reagents were purchased commercially and used without further purification. FT-IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range of 400~4000 cm^{-1}. All Powder X-ray diffraction (PXRD) analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 0.05°. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under an N_2 atmosphere. The adsorption experiments were performed on Micromeritics ASAP 2020 surface area and pore size analyzer.

Synthesis of $(dma)_3[Zn_3(btz)(btc)_2(DMF)]_3 \cdot 7(DMF)$ (1):
A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1000 g, 0.34 mmol), pyrazine(0.0300 g 0.37 mmol), 1H-Benzotriazole (Hbtz, 0.0500 g, 0.42 mmol), 1,3,5-Benzenetricarboxylic acid (1,3,5-BTC, 0.1000 g 0.48 mmol), and N,N-dimethylformamide (DMF, 8 mL) in a 23 mL Teflon-lined stainless steel vessel was heated at 120 ℃ for 72 hours, and then cooled to room temperature. The resulting colorless transparent crystals were obtained, washed with acetone, and dried at room temperature (Yield: 75 %).

Synthesis of $(tma)_4[Zn_3(btz)(btc)_2(H_2O)]_4 \cdot 15(DMF)$ (2):
A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1000 g, 0.34 mmol), pyrazine(0.0300 g 0.37 mmol), 1H-Benzotriazole (Hbtz, 0.0500 g, 0.42 mmol), 1,3,5-Benzenetricarboxylic acid (1,3,5-BTC, 0.0420 g 0.20 mmol), tetramethylammonium bromide (0.0300g 0.20 mmol), and N,N-dimethylformamide (DMF, 8 mL) in a 23 mL Teflon-lined stainless steel vessel was heated at 120 ℃ for 72 hours, and then cooled to room temperature. The resulting colorless transparent crystals were obtained, washed with acetone, and dried at room temperature (Yield: 83 %).

Synthesis of $(tma)_4[Zn_3(tz)(btc)_2(H_2O)]_4 \cdot x(DMF)$ (3):
A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1600 g, 0.54 mmol), pyrazine(0.0300 g 0.37 mmol), 1,2,3-1H-Triazole (1,2,3-tz, 0.0500 g, 0.73 mmol), 1,3,5-Benzenetricarboxylic acid (1,3,5-BTC, 0.0500 g 0.24 mmol), tetramethylammonium bromide (0.0300g 0.20 mmol), and N,N-dimethylformamide (DMF, 8 mL) in a 23 mL Teflon-lined stainless steel vessel was heated at 120 ℃ for 72 hours, and then cooled to room temperature. The resulting colorless transparent crystals were obtained, washed with acetone, and dried at room temperature. The final sample is not pure as characterized by powder XRD (Figure S12).

X-ray Crystallographic Study: Suitable single crystals of **1-3** were carefully selected under an optical microscope and glued to thin glass fibers. Single-crystal X-ray diffraction analyses were performed on a computer-controlled Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda_{Mo\ K\alpha}$=0.71073 Å) at T = 293.2 K. The structures were solved using the direct method and refined by full-matrix least-squares methods on F^2 by using the SHELX-97 program package. The crystallographic data and details of the structure for three compounds are listed in Table *S1*.

Table S1 Crystal data summary for all compounds.

Compound reference	**1**	**2**	**3**
Chemical formula	$C_{75}H_{34}N_{10}O_{37}Zn_9$	$C_{28}H_{22}N_4O_{13}Zn_3$	$C_{24}H_{20}N_4O_{13}Zn_3$
Formula Mass	2255.45	818.67	768.55
Crystal system	Orthorhombic	Tetragonal	Tetragonal
a/ Å	23.157(5)	22.000(10)	21.265(4)
b/ Å	27.317(7)	22.000(10)	21.265(4)
c/ Å	22.592(5)	23.000(10)	22.666(6)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	90.00
γ/°	90.00	90.00	90.00
Unit cell volume/ Å^3	14291(6)	11132(9)	10250(4)
Temperature/K	293(2)	293(2)	293(2)
Space group	*Pnnm*	*I*4/*m*	*I*4/*m*
No. of formula units per unit cell, *Z*	4	8	8
No. of reflections measured	85197	6807	18872
No. of independent reflections	12911	4831	2485
R_{int}	0.1179	0.0384	0.0771
Final R_1 values ($I > 2\sigma(I)$)	0.0518	0.0543	0.0781
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1461	0.1435	0.2141
Final R_1 values (all data)	0.0677	0.0739	0.0945
Final $wR(F^2)$ values (all data)	0.1543	0.1564	0.2374
Goodness of fit on F^2	0.928	0.992	1.060

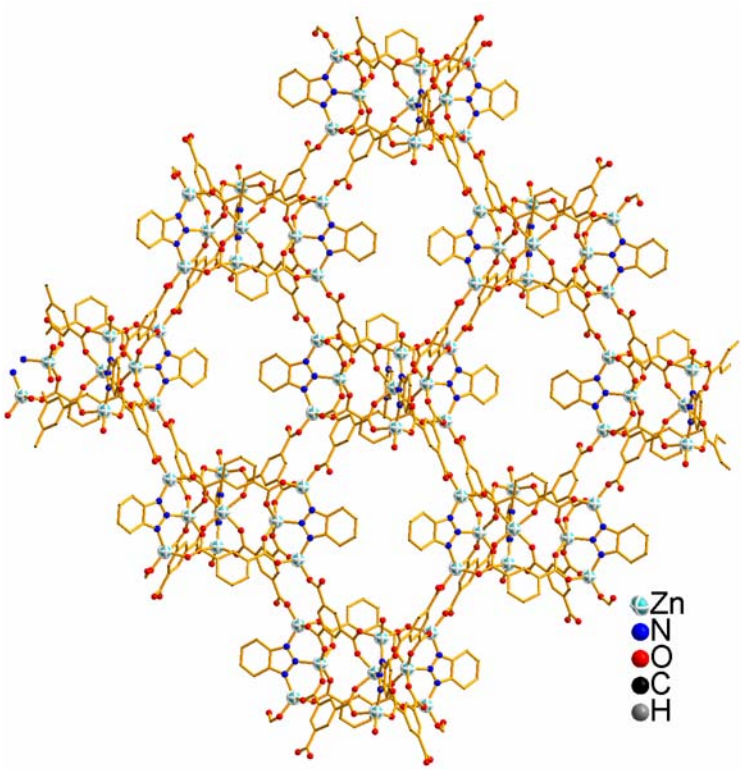

Figure S1. View of the 4^4 layer along the ac plane in **1**.

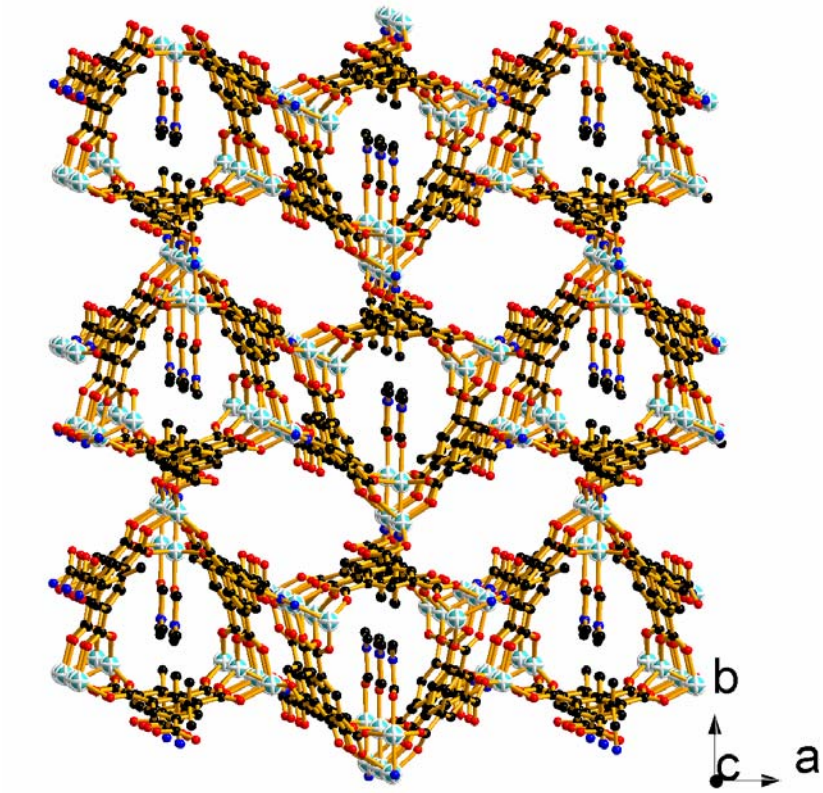

Figure S2. The 3D packing structure of **1**.

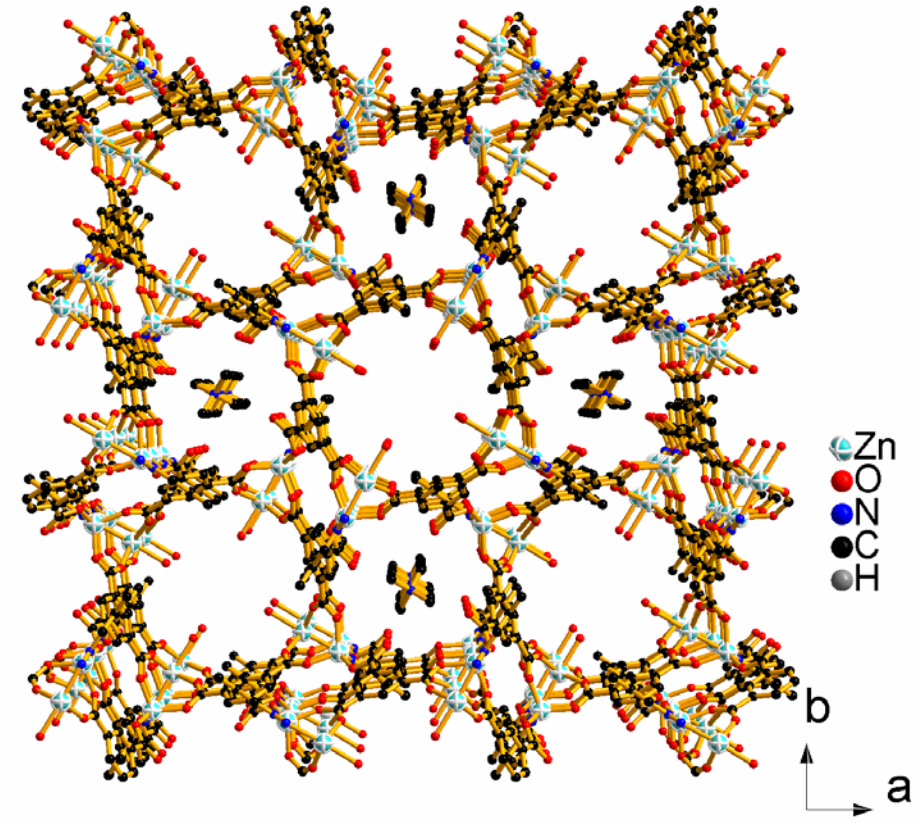

Figure S3. The 3D packing structure of **2**, showing the location of the tma cation in the center of the channels.

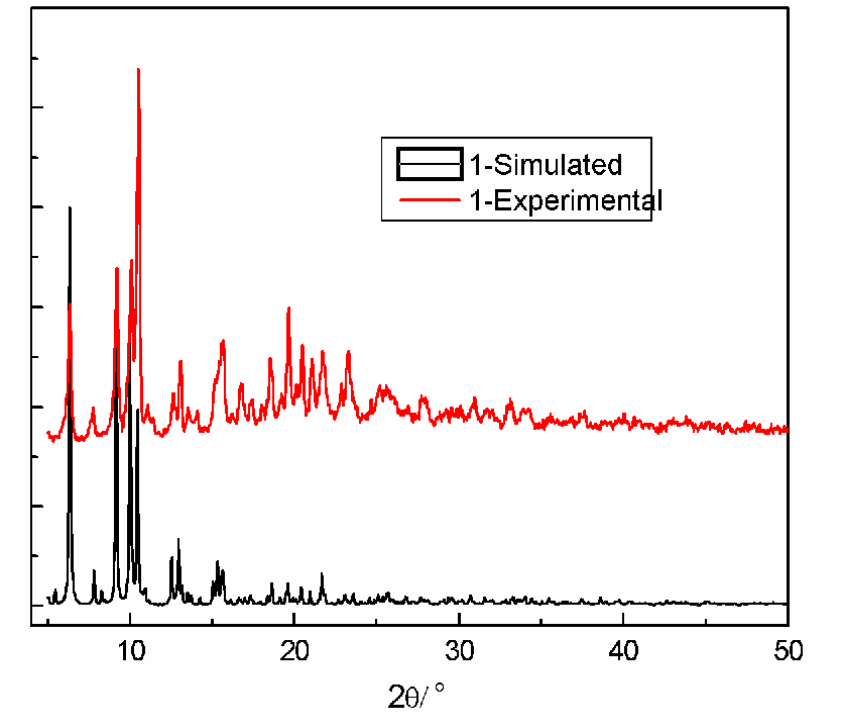

Figure S4. The Powder X-ray diffraction patterns of **1**.

To evaluate the thermal behavior, thermalgravimatric analysis (TGA) of **1** were performed under N_2 atmosphere with a heating rate of 10 ℃·min^{-1} in the temperature range 30-700 ℃ (Figure S5). The TGA curve for 1 reveals that the solvents on the sample surface are gradually removed in proceeding from 30 ℃ to 100 ℃. The weight losses from 100 to 250 ℃ corresponds to the removal of the coordinated and free guest molecules. The observed weight loss of 22.1% is in agreement with the calculated value of 20%. The third weight losses from 250 ℃ to 400 ℃ may correspond to the release of the charge-balancing dimethylamine(dma) cations. The observed weight loss of 5.1% is in agreement with the calculated value of 4.6%.Above 400 ℃, the weight loss is due to the decomposition of the organic ligands, accompanying the collapse of the whole framework.

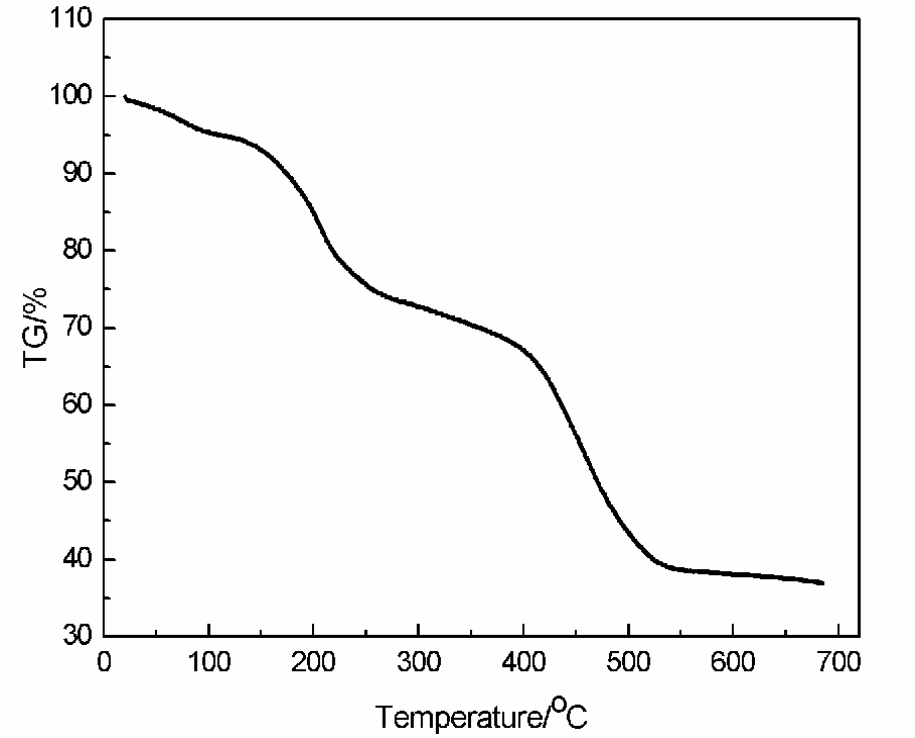

Figure S5. The TGA plot of **1**.

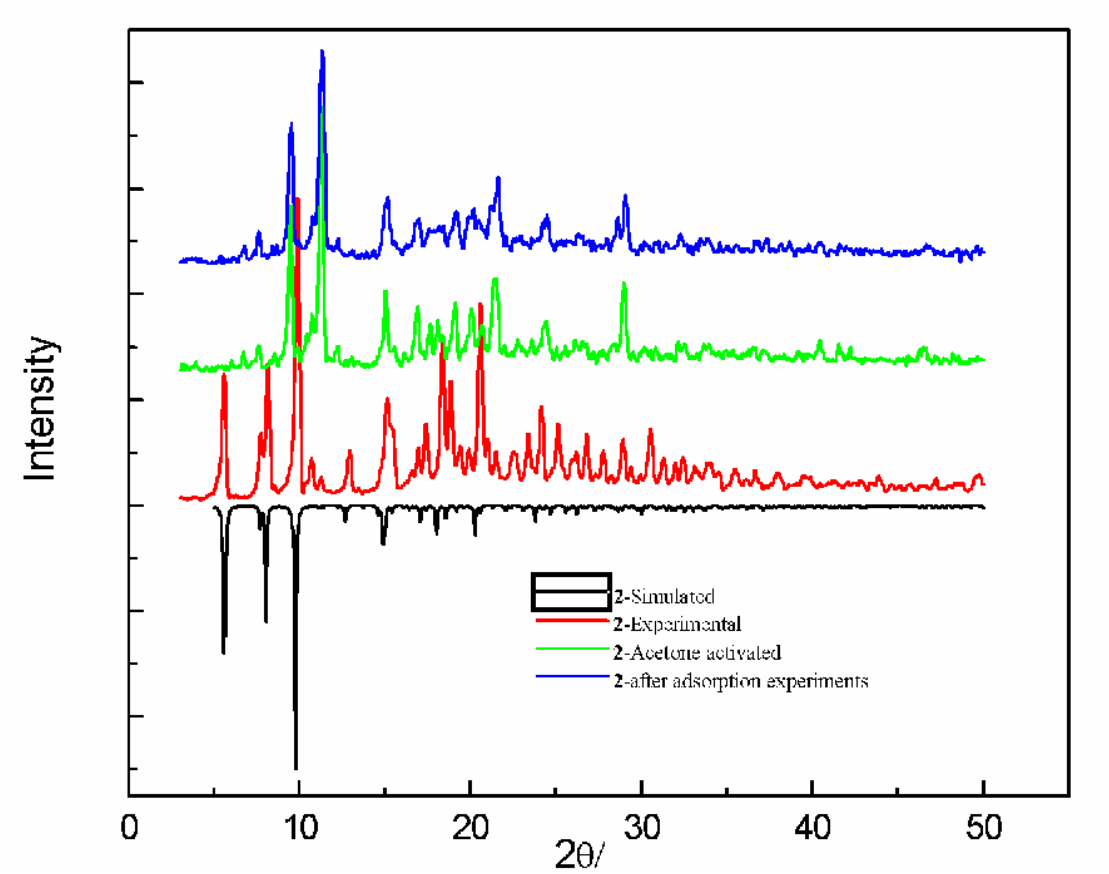

Figure S6. The Powder XRD patterns of **2**.

To evaluate the thermal behavior, thermalgravimatric analysis (TGA) of **2** were performed under N_2 atmosphere with a heating rate of 10 ℃·min^{-1} in the temperature range 20-650 ℃ (Figure S7). The TGA curve for 2 reveals that the solvents on the sample surface are gradually removed in proceeding from 20 ℃ to 85 ℃.The observed weight loss of 24.6% (calcd 25.5%) from 85 to 350 ℃ corresponds to the removal of the coordinated and free guest molecules. Above 350 ℃, the weight loss is due to the release of the charge-balancing tetramethylammonium (tma) cations and the decomposition of the organic ligands, accompanying the collapse of the whole framework.

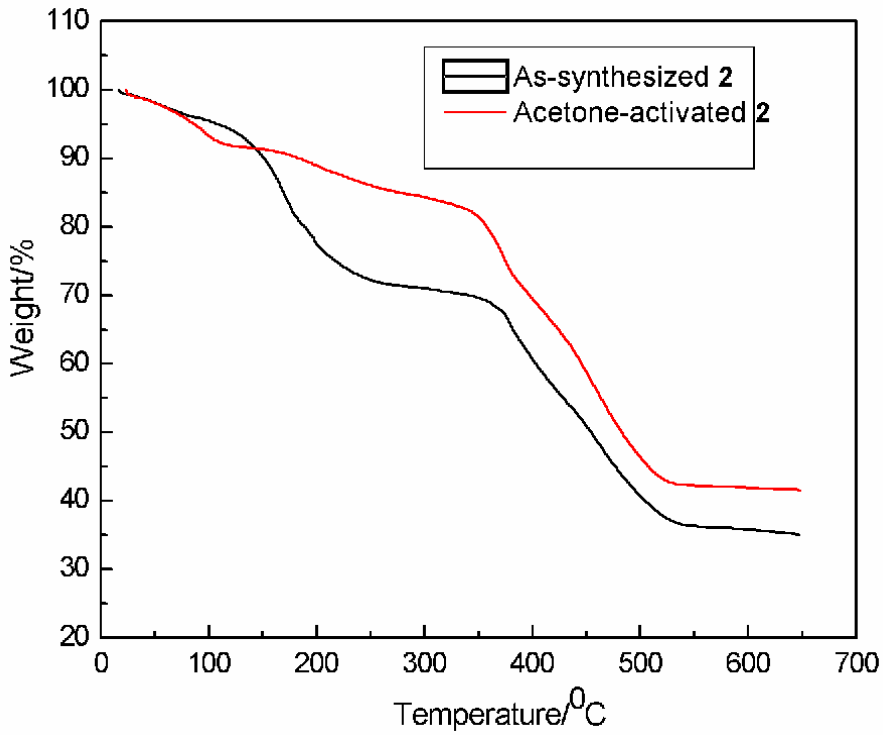

Figure S7. The TGA plots of **2**.

The activated sample of **2** was prepared by exchanging the solvent in as-synthesized 2 with acetone, followed by evacuation at room temperature. The gas-adsorption measurements (N_2, CO_2, and H_2) of **2** were performed on a Micromeritics ASAP 2020 surface-area and pore-size analyzer (Figure S8).

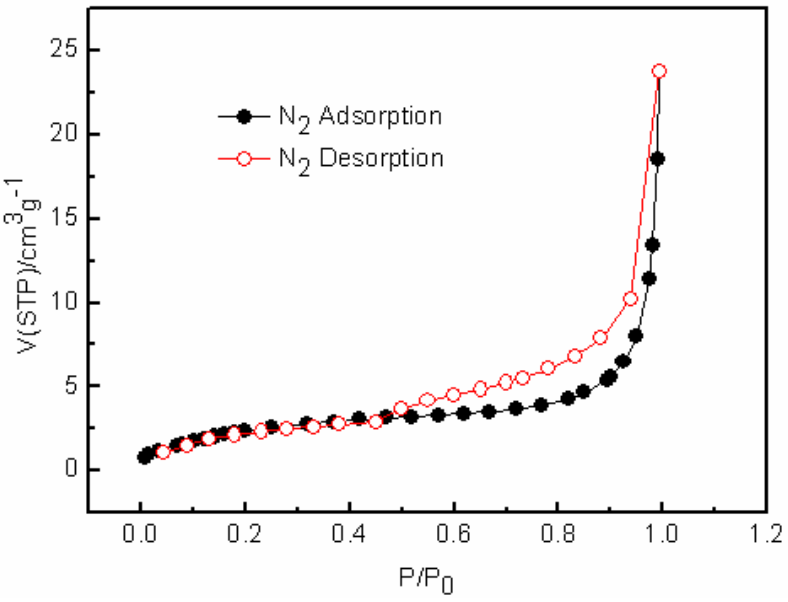

Figure S8. The N_2 (●: adsorption, ○: desorption) isotherms at 77 K for **1**.

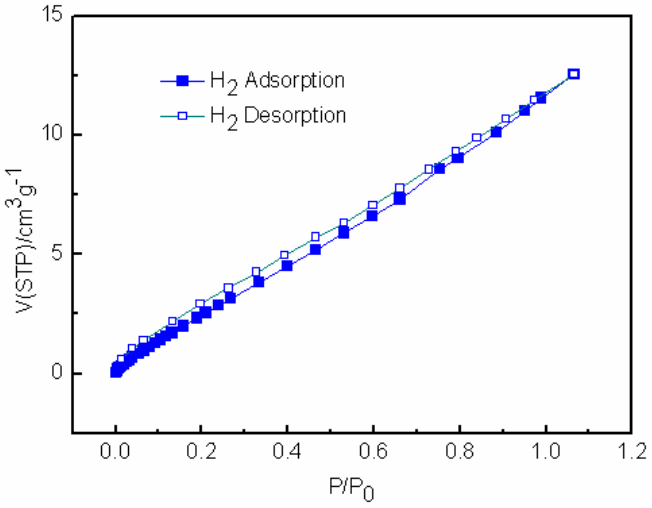

Figure S9. The H_2 (■: adsorption, □: desorption) isotherms at 77 K for **1**.

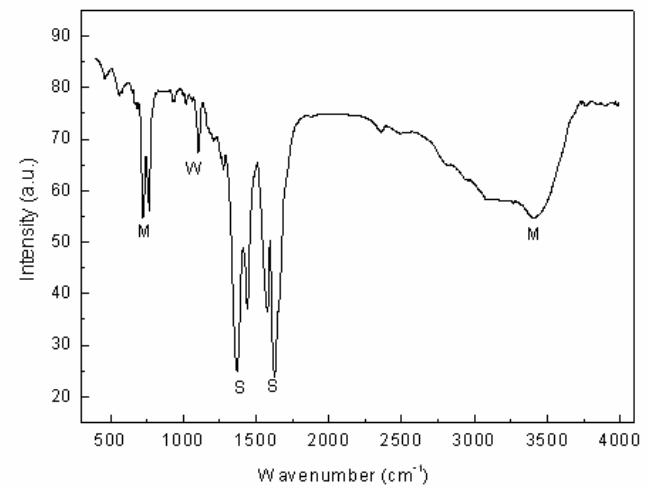

Figure S10. Infra-red spectra of compound **1.**

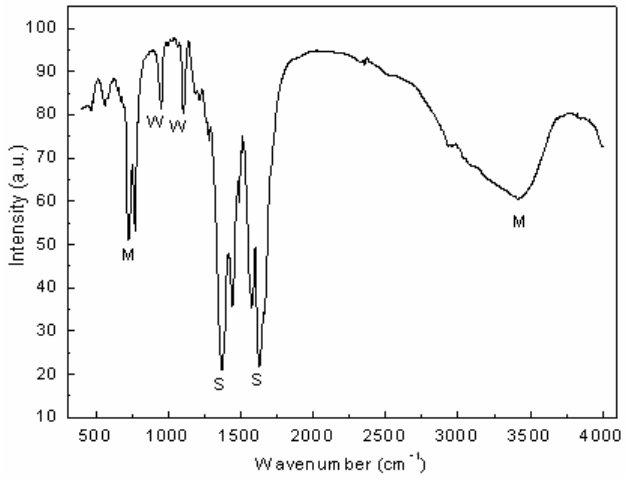

Figure S11. Infra-red spectra of compound **2.**

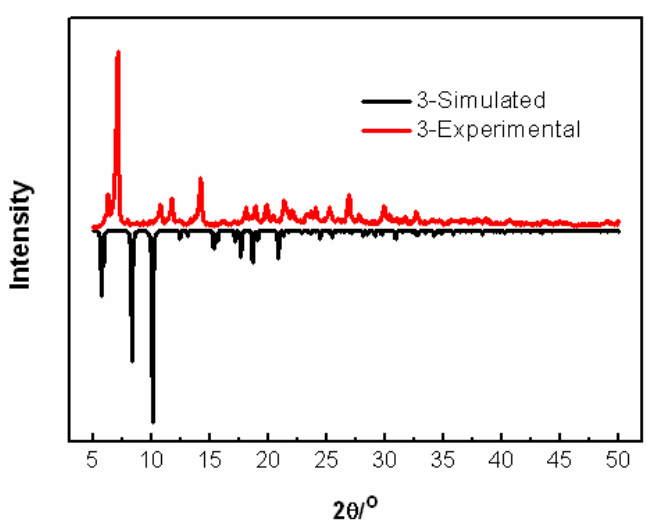

Figure S12. The Powder XRD patterns of impure compound 3.