Supporting Information

Auxiliary ligand induced structural allomorphism in nanotubular microporous metal–organic frameworks based on discrete magnesium clusters

Hai-Ning Wang, Xing Meng, Xin-Long Wang*, Guang-Sheng Yang and Zhong-Min Su*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

E-mail address: zmsu@nenu.edu.cn; wangxl824@nenu.edu.cn.

Tel.: (+86)-431-85099108.

Synthesis of complex 1: A solution of $Mg(OAc)\cdot 4H_2O$ (0.105g), 5-H_2aip (0.09g), isophthalic acid (0.1 g) in DMA (5 mL), ethanol (2 mL) and water (1mL) was heated at 110 °C for 3 days. The resulting pink crystals were collected, washed with ethanol, and dried at room temperature. Elemental analysis for $C_{48}H_{66}Mg_3N_8O_{24}$ (1212.02) (%): calcd. C 47.57 H 5.49 N 9.25; found C 47.42 H 5.39 N 9.13%.

Synthesis of complex 2:

The preparation of **2** was similar to that of **1** except that 2'2-bpy (0.06g) was used at. Pink block crystals of **2** were collected in 75% yield based on $Mg(OAc)\cdot 4H_2O$. Elemental Anal. Calcd for $C_{48}H_{66}Mg_3N_8O_{24}$ (1211.49): C, 47.57; H, 5.49; N, 9.25. Anal. Found: C, 47.62; H, 5.54; N, 9.36%.

Synthesis of complex 3:

The preparation of **3** was similar to that of **1** except that 4'4-bpy (0.06g) was used at. Pink block crystals of **3** were collected in 60% yield based on $Mg(OAc)\cdot 4H_2O$. Elemental Anal. Calcd for $C_{48}H_{66}Mg_3N_8O_{24}$ (1211.49): C, 47.57; H, 5.49; N, 9.25. Anal. Found: C, 47.49; H, 5.36; N, 9.04%.

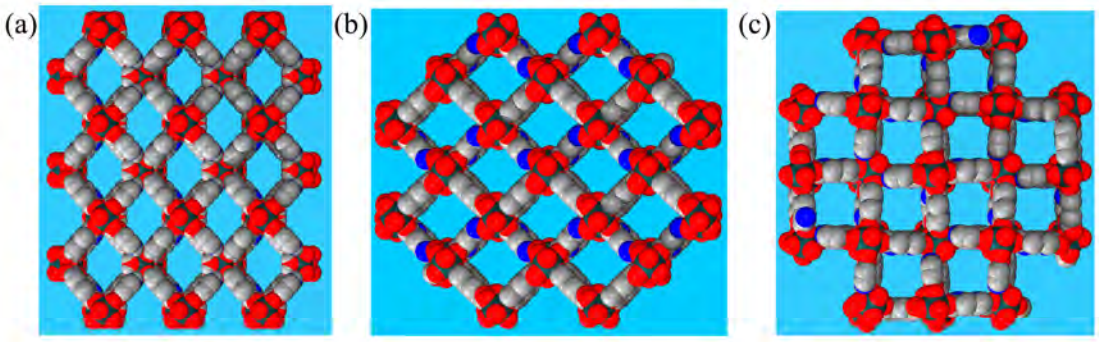

Fig. S1 (a) The channel of **1** along *b* direction; (b) The channel along *a* direction; (c) The channel along *b* direction.

The structural difference of three allomorphs: The hexagon-like channel of **1** run along *b* direction; the rhombus-like channels of **2** run along *a* direction; the square-like channels of **3** run along *b* direction.

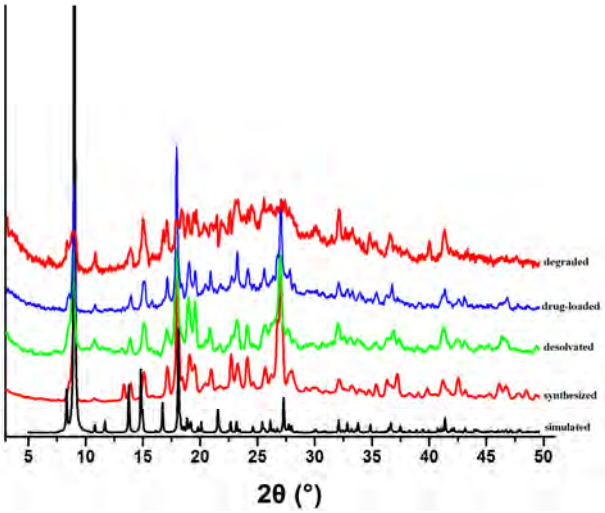

Fig. S2 Experimental and simulated powder X-Ray diffraction patterns for **1**.

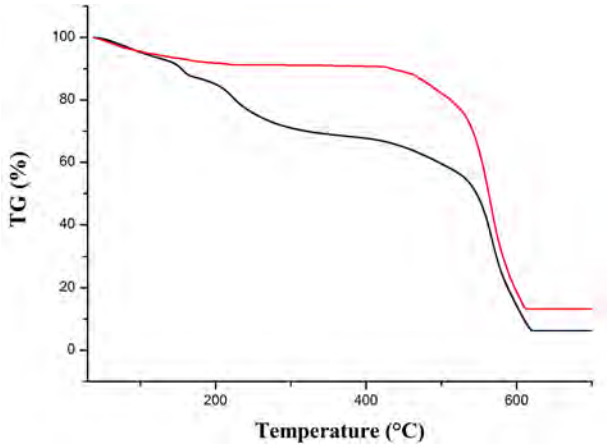

Fig. S3 TG profiles of **1** (black) and evacuated **1** (red).

Preparation of desolvated 1

The bulky crystals of **1** were immersed in the dichloromethane. After 24 h, the CH_2Cl_2 was decanted from the vial and fresh CH_2Cl_2 was added. The solution was replaced with fresh CH_2Cl_2 every 24 h for a total of 3 days and the crystals were stored in CH_2Cl_2 until further used. Finally, the sample was heated at 120 °C for 24 hours in vacuum.

Drug Loading Dissolving 5-FU (20 mg) and desolvated **1** (20 mg) in ethanol (5 mL) three days yielded heterogeneous pink solution. The precipitation was isolated by centrifuging and washed with ethanol. The 5-FU content was calculated using UV method (λ = 266 nm).

Dissolving Ibuprofen (30 mg) and **1** (30 mg) in ethanol (5 mL) three days yielded heterogeneous pink solution. The precipitation was isolated by centrifuging and washed with ethanol. The 5-FU content was calculated using UV method (λ = 222 nm).

Drug Release 7 mg of drug-loaded **1** was dissolved into 1.5 mL of PBS buffer solution (pH 7.4), and loaded into a dialysis bag, which was dialyzed against 5 mL of deionized water at 37°C. During each time interval, about 1 mL of the solution was pulled out to test, and decanted back when the test was over. The content of 5-FU in the samples taken out was monitored by fluorometry, in which the detection wavelength was 453 nm.

7 mg of drug-loaded **1** was dissolved into 1.5 mL of PBS buffer solution (pH 7.4), and loaded into a dialysis bag, which was dialyzed against 5 mL of deionized water at 37°C. During each time interval, about 1 mL of the solution was pulled out to test, and decanted back when the test was over. The content of ibuprofen in the samples taken out was monitored by fluorometry, in which the detection wavelength was 289 nm.