Synthesis and characterization of the interpenetrated MOF-5*

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Table S1 Attempted synthesis of the non-penetrated MOF-5 using DEF as solvent.

	Reactants in g (mmol) or ml (mmol) for DEF			Molar Ratios of Reactants	Reaction Temp.	Method of Removing Entrapped Solvent	Product and Surface Area of Product (m^2/g)	
1	$Zn(NO_3)_2{\cdot}4H_2O$ 3.14 (12.0)	H_2BDC 0.665 (4.00)	DEF 100 (890)	1:0.33:74	105℃, 24h	a	MOF-5-non 3362[1] (Langmuir) 3400[2](Langmuir)	*Published Work*[1-2]
2	$Zn(NO_3)_2{\cdot}6H_2O$ 0.628 (2.11)	H_2BDC 0.140 (0.843)	DEF[d] 20.0 (179)	1:0.40:85	105℃, 24h	b.	MOF-5-int 1052 (Langmuir) 797 (BET)	Product (71% yield) denoted as **B** PXRD shown in Figure 1(e) and Figure S1(a)
3	$Zn(NO_3)_2{\cdot}6H_2O$ 0.10 (0.34)	H_2BDC 0.040 (0.24)	DEF 20.0 (179)	1:0.72:540	100℃, 12 h	Heated at 300 ºC under vacuum.	MOF-5-non with pore volume of 0.95 cm^3/g	*Published Work*[3]
4	$Zn(NO_3)_2{\cdot}6H_2O$ 0.306 (1.03)	H_2BDC 0.140 (0.843)	DEF[e] 20.0 (178)	1:0.82:175	100℃, 41 h[c]	b.	MOF-5-int [d]	Figure S1(b)

a. After exchange with chloroform for 12 h[1] or 24 h[2], solvent in the products were removed under vacuum at 105ºC for 12 h[1] or 110 ºC for 16 h.[2] b. Product was immerged in dry chloroform for 3 d, chloroform had been changed for 3-4 times in between, and the resulted product was dried at 150 ºC for 12 h, c. By applying a 35 ml, heavy wall, pressure vessel, we observed that the product started to appear after 17 h. d. Identified by XRD power diffraction (Figure S1 in Supporting Information (SI)). d. used as received. e. dried over molecular sieves, the top clear solution was .

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* Electronic supplementary information (ESI) available: The PXRD patterns of the MOF-5 synthesized using DEF(Figure S1), the MOF-5-int before and after the adsorption measurement, the MOF-5 materials synthesized according to Huang's method at room temperature with and without adding H_2O_2 solution, the MOF-5-int prepared in a much diluted reactant mixture (1/4 of the original), the packing of the MOF-5-int structure, the N_2 adsorption isothermal plot and the pore size distribution.

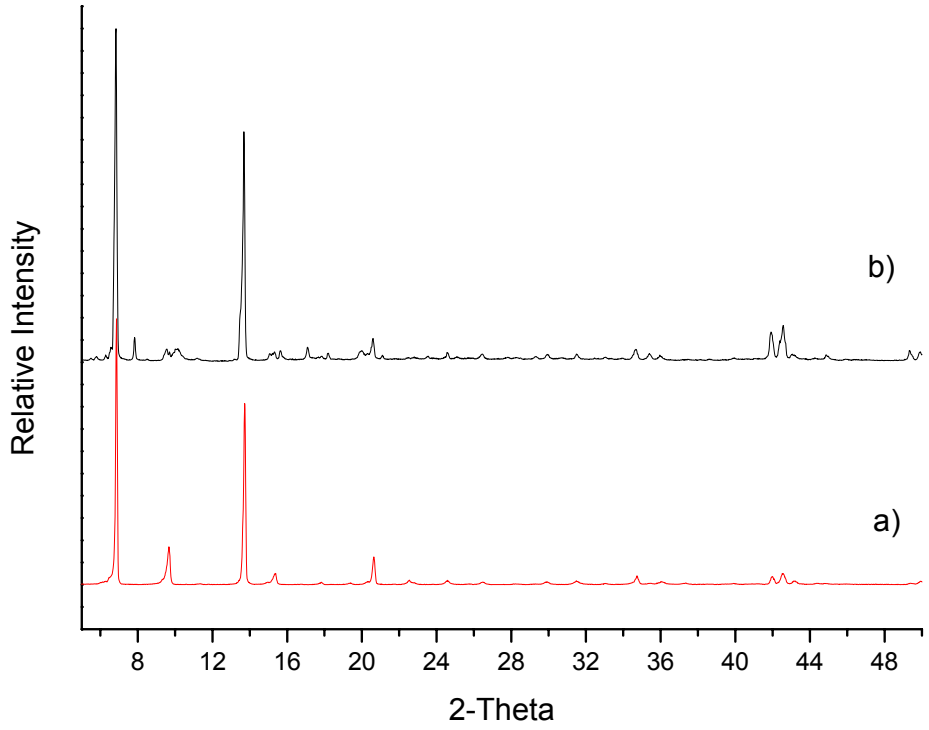


Figure S1 PXRD patterns of MOF-5-int synthesized using DEF. Synthetic conditions: a) The MOF-5-int material **B** (No. 2 in Table S1), b) No. 4 in Table S1.

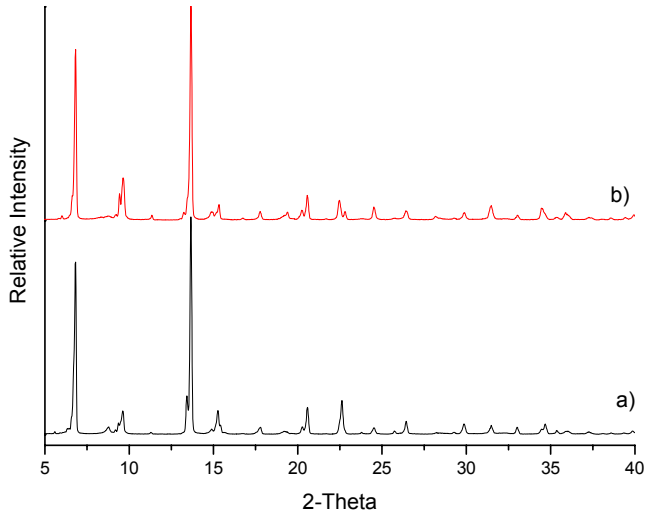


Figure S2. The PXRD patterns of the MOF-5-int material **A** synthesized using DMF as solvent. a) Product dried at 150 ºC for 3h ,BET SSA of 724.5 m^2/g, Langmuir Surface Area : 953.8 m^2/g, pore volume (H-K analysis): 0.31 cm^3/g, the mean pore width (H-K) method: 5.7 Å, the intensity ratio of peaks at 6.8, 9.7 and 13.8 = 1 : 0.14 : 1.3; b) Sample (a) after adsorption measurement during which (a) had been activated at 250 ºC for 20 h, the intensity ratio of peaks at 6.8, 9.7 and 13.8 = 0.25 : 1 : 1.3. (001-807)

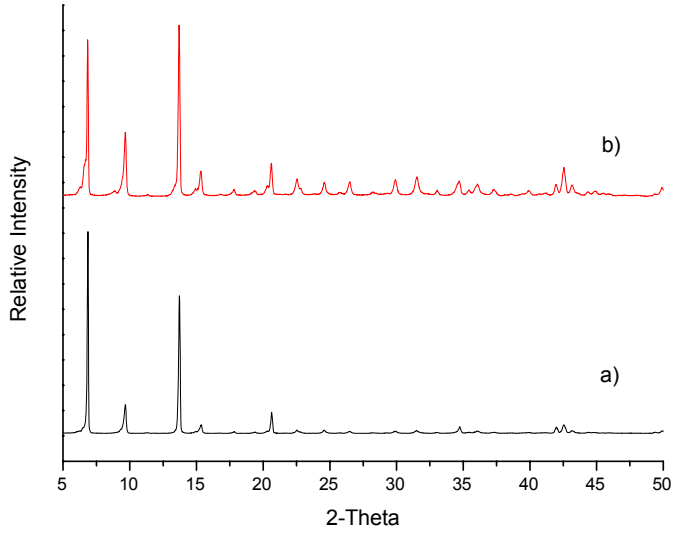


Figure S3. The PXRD patterns of the MOF-5-int material **B** synthesized using DEF as solvent. a) Product dried at 150 ºC for 12 h, BET SSA of 797 m^2/g, Langmuir Surface Area : 1052 m^2/g, pore volume (H-K analysis): 0.40 cm^3/g, the mean pore width (H-K) method: 5.25 Å the intensity ratio of peaks at 6.8, 9.7 and 13.8 = 1 : 0.14: 0.68; b) Sample (a) after adsorption measurement during which (a) had been activated at 250 ºC for 6 h, the intensity ratio of peaks at 6.8, 9.7 and 13.8 = 1: 0.40 : 1.1 (CB-165-2) .

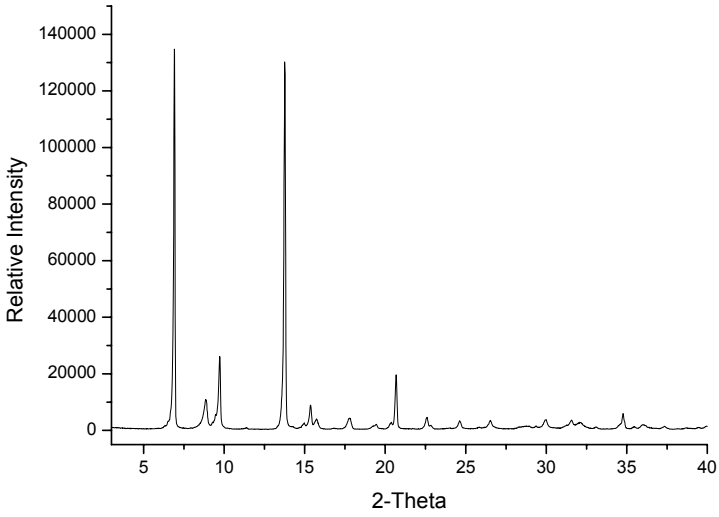
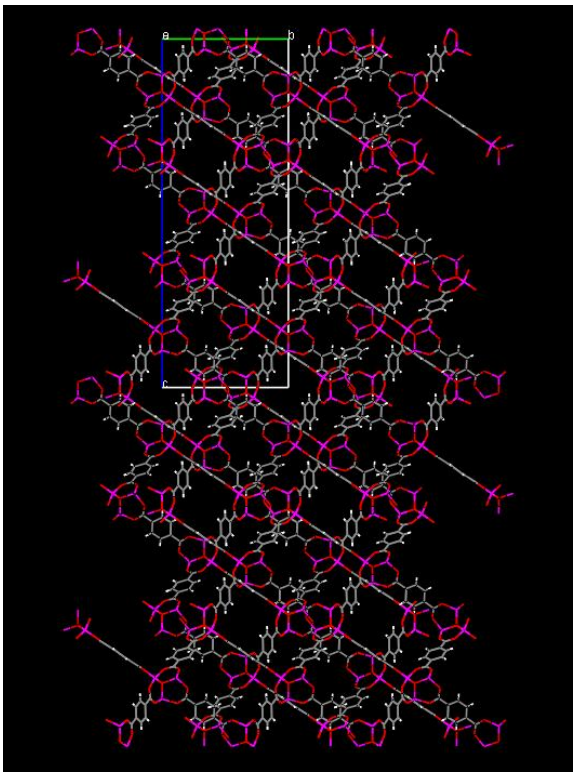
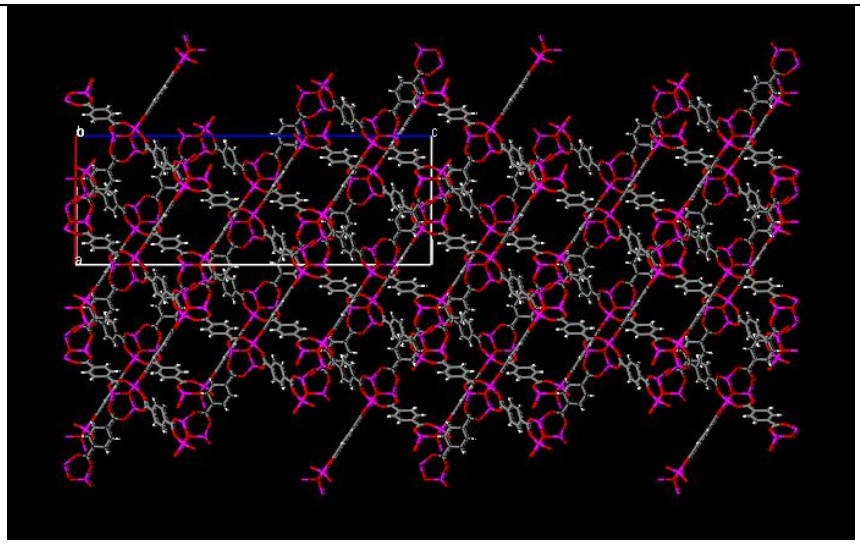


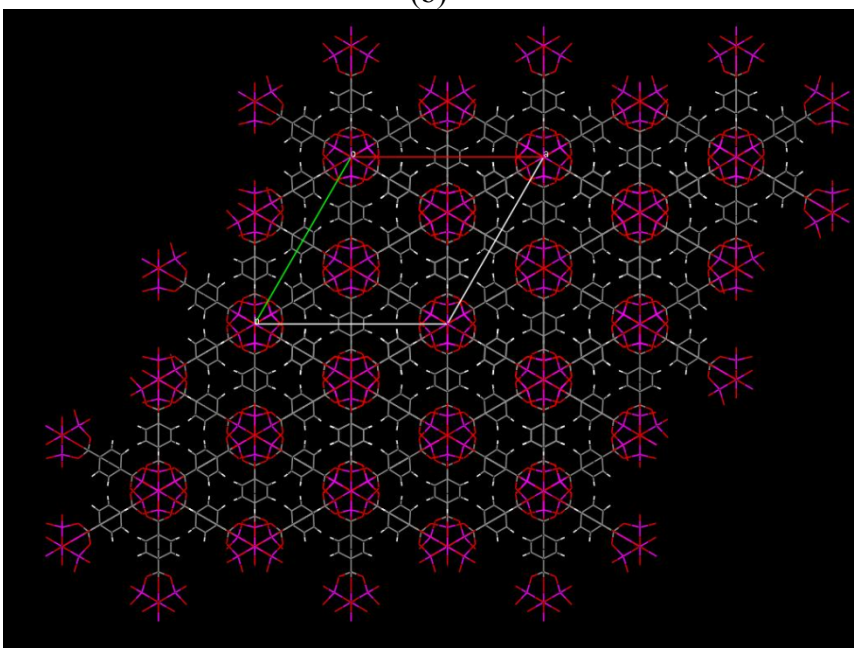
Figure S4 The PXRD pattern of the product prepared by a much diluted solution. The molar ratio of $Zn(NO_3)_2$: H_2BDC: H_2O: DMF =1:0.75:11.0: 665 (about 1/4 of the normal concentration).



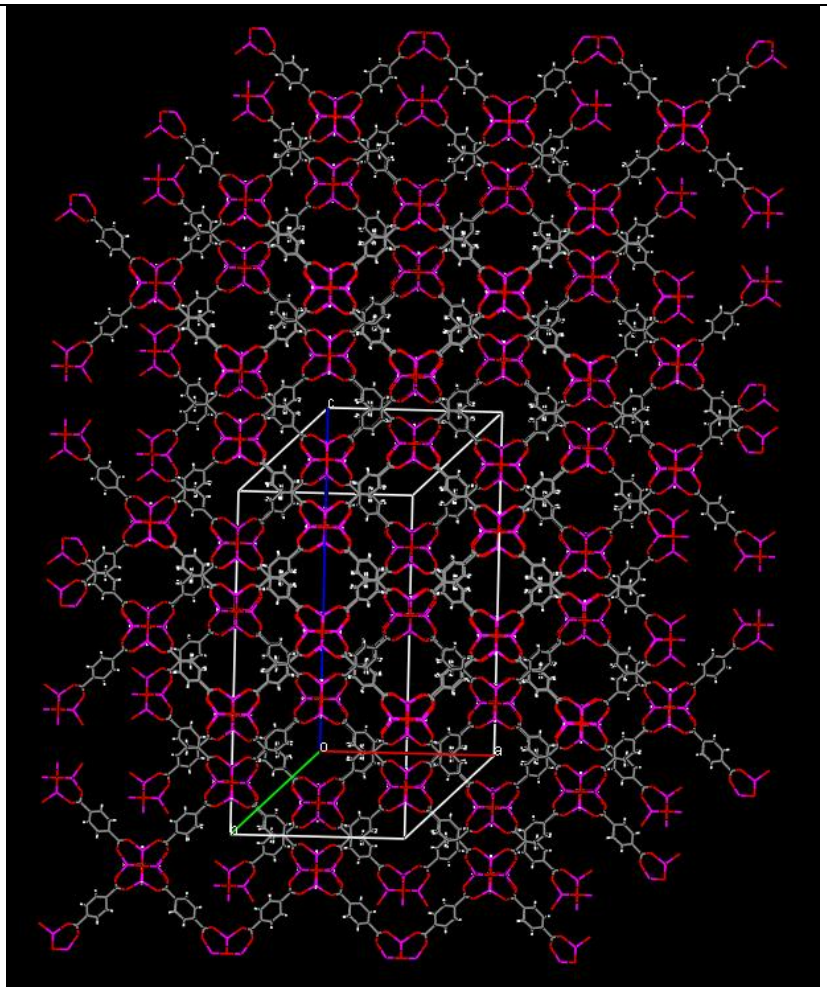
(a)



(b)

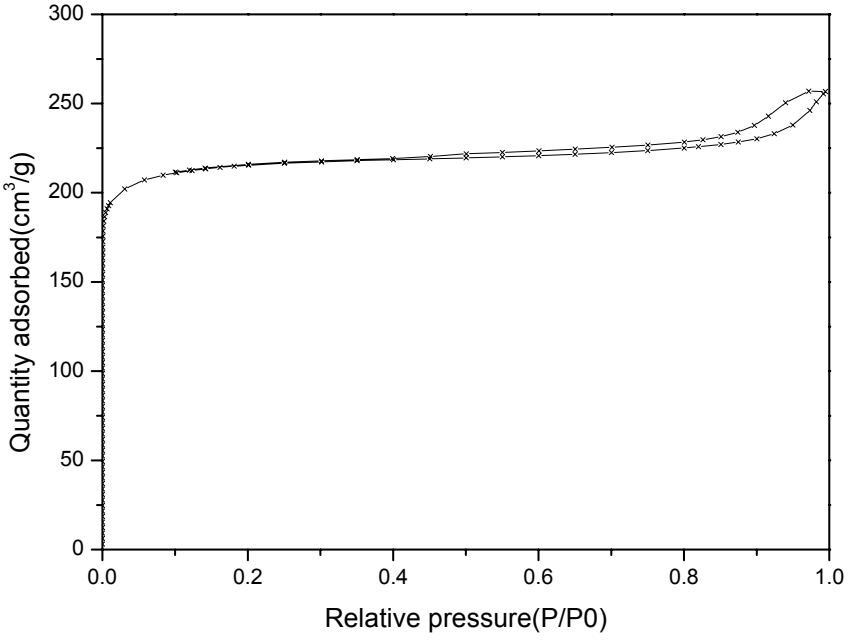


(c)

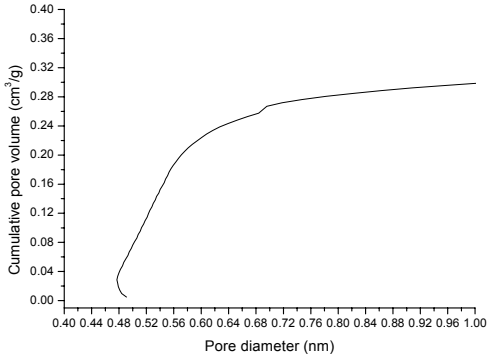


(d)

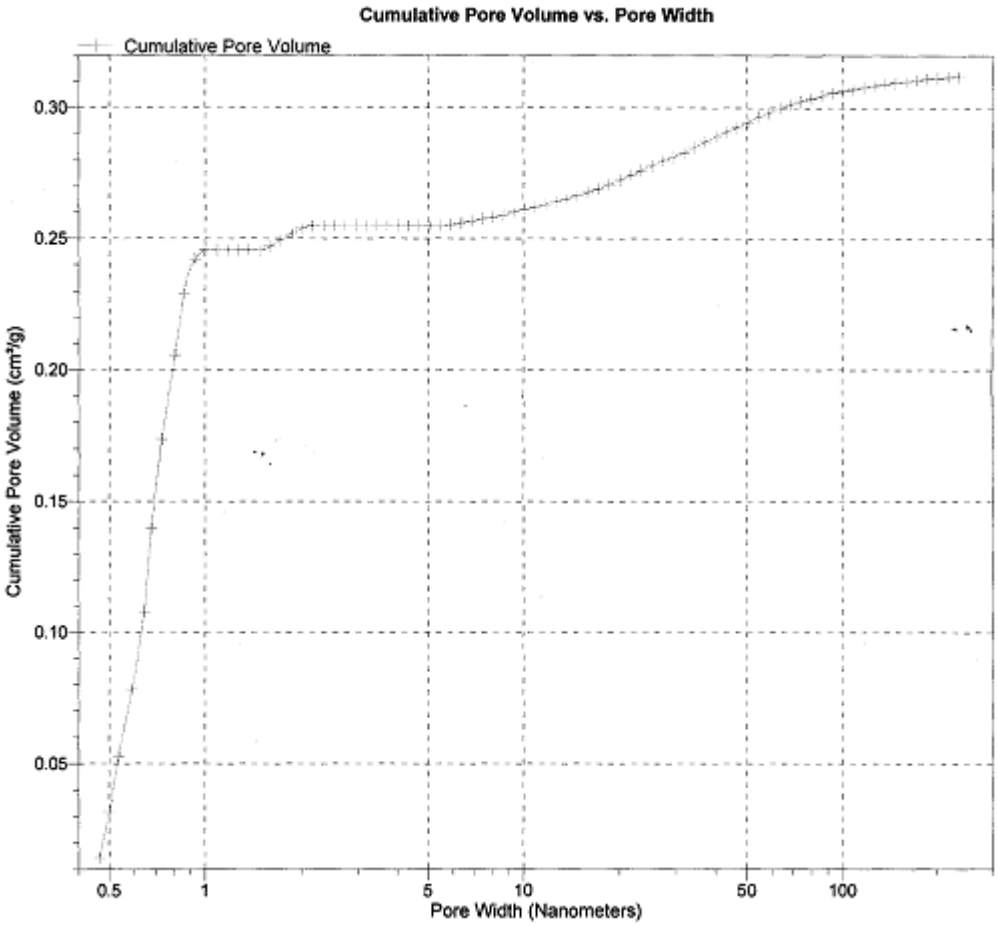
Figure S5. Wireframe diagrams of the MOF-5-int **A** viewed along a (a), b (b),c (c), other directions (d), showing different types of pores. C is gray, Zn is pink, O is red and H is white.



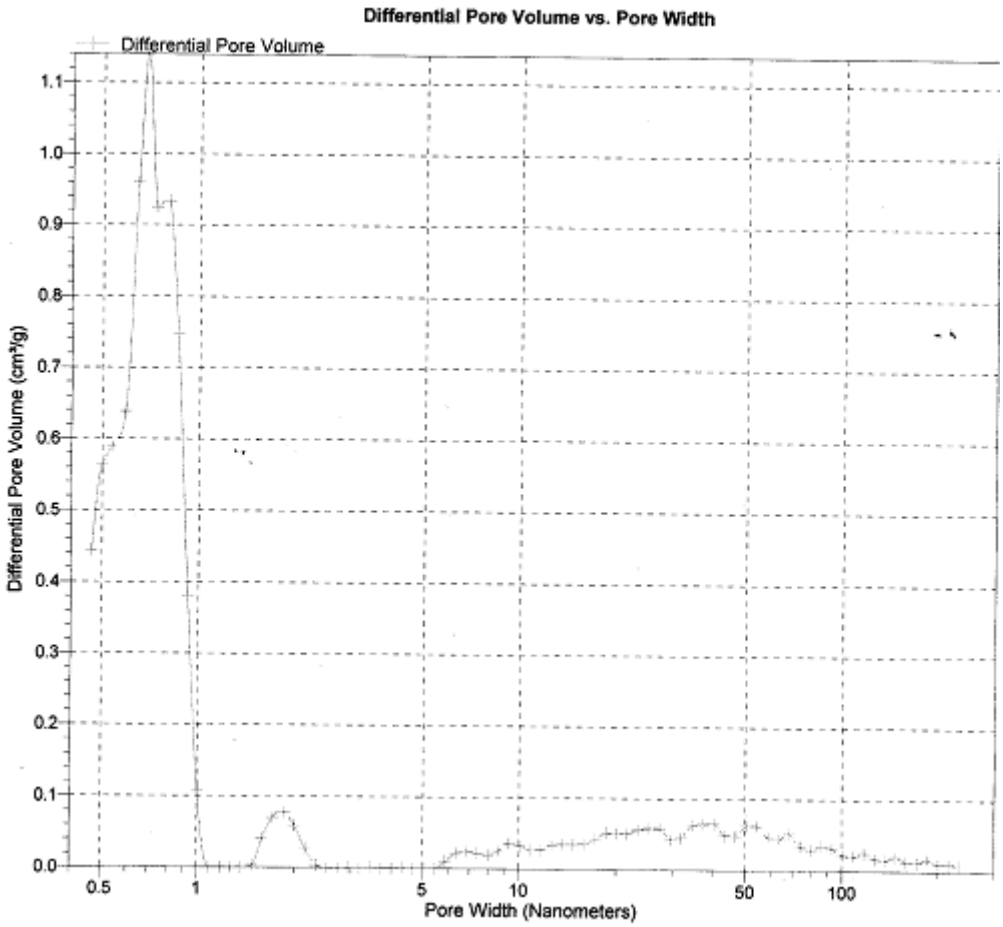
(a) N_2 adsorption/desorption isothermal plot



(b) Cumulative pore volume versus pore diameter calculated by H-K method. 4.8-6.84 Å: 0.26 cm^3/g; 6.78-7.00 Å: 0.013 cm^3/g.

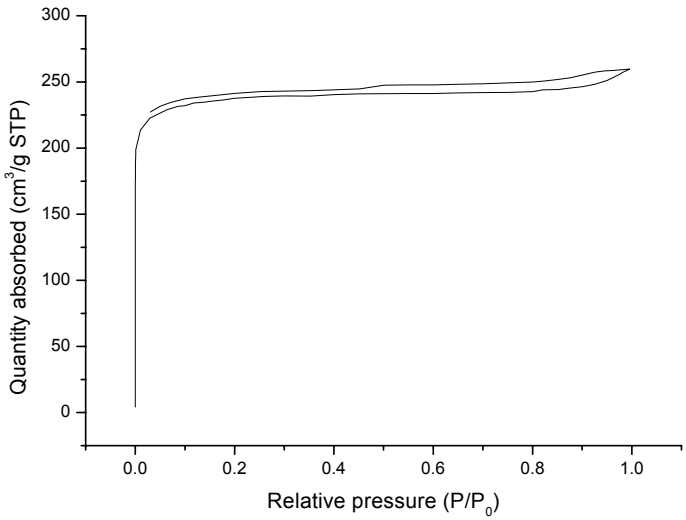


(c) Cumulative pore volume versus pore diameter calculated by DFT method

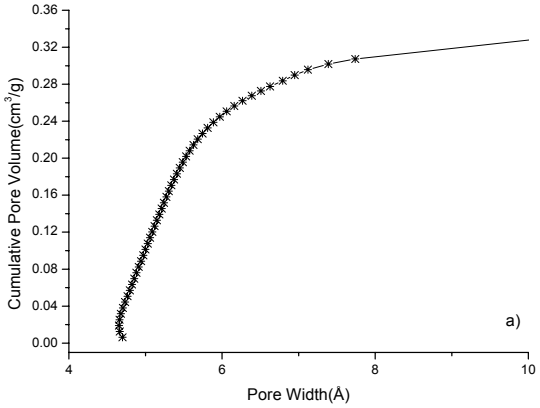


(d) Pore distribution calculated by DFT method

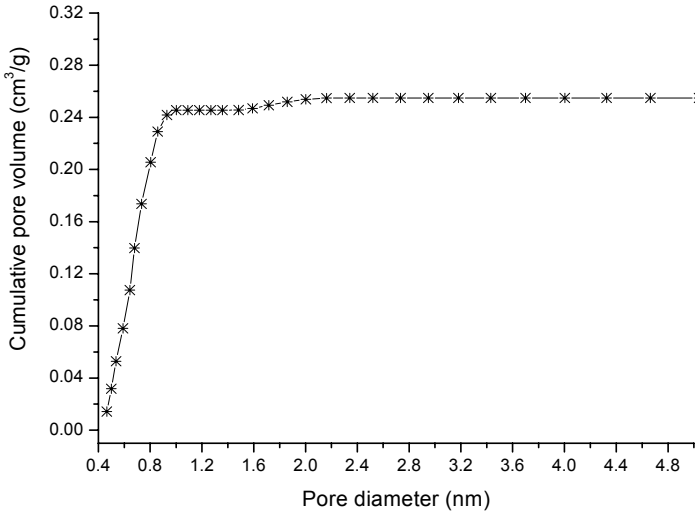
Figure S6. N_2 adsorption/desorption results of the MOF-5-int material **A** (001-807)



(a)N_2 adsorption/desorption isothermal plot

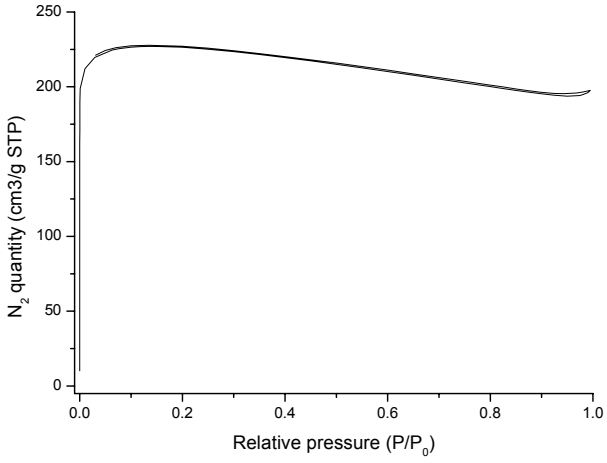


(b) Cumulative pore volume versus pore diameter calculated by H-K method. 4.8-6.64 Å: 0.278 cm^3/g; 6.64-7.04: 0.018 Å; <1.0 Å：0.327.

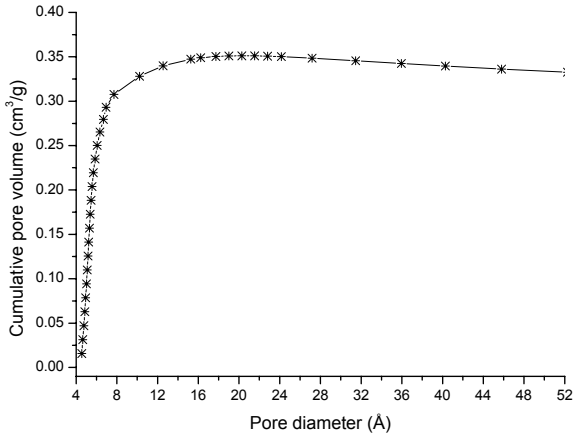


(c) Cumulative pore volume versus pore diameter (DFT method). Total: 0.33cm^3/g; 4.7-8.0 Å: 0.21; <1.0 Å : 0.25 cm^3/g; 1.0-5.0: 0.01 cm^3/g; 5-234: 0.06 cm^3/g

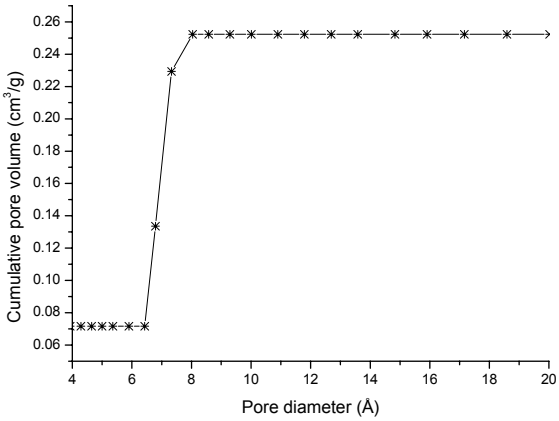
Figure S7 N_2 adsorption/desorption results of the MOF-5-int material **B**（CB-165-2）.



(a) N_2 adsorption/desorption isothermal plot



(b) Cumulative pore volume versus pore diameter calculated by H-K method. 4.8-8.0 Å: 0.31 cm^3/g; 8.0-16 Å : 0.04 cm^3/g.



(c) Cumulative pore volume versus pore diameter (DFT method). Total: 0.25cm^3/g; <6.4 Å: 0.07; <7.3 Å : 0.23 cm^3/g; <8.05 Å: 0.25 cm^3/g

Figure S8 N_2 adsorption/desorption results of the MOF-5-int material **C**（CB-170）.

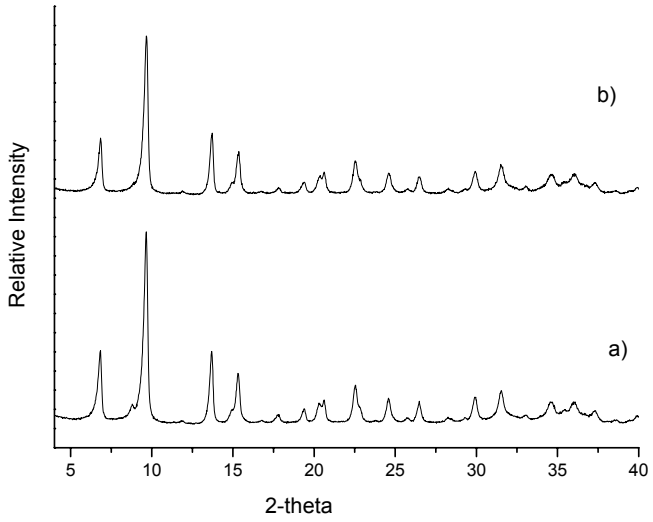


Figure S9. The MOF-5 material synthesized according to Huang's method at room temperature. (a) Without adding any acid；(b) adding 3 drops of H_2O_2 solution (30%).

References

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3 J. Gonzalez, R. N. Devi, D. P. Tunstall, P. A. Cox, P. A. Wright, *Micropor. Mesopor. Mater*, 2005, **84**, 97.