

Supporting Information

**Rapid Guest Exchange and Ultra-Low Surface Tension Solvents  
Optimize Metal–Organic Framework Activation**

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## Supporting Information for

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## 1. Reagents and instrumental analysis

### Reagents:

Zinc nitrate hexahydrate (Fisher Scientific, ACS grade), 1,4-benzenedicarboxylic acid (H<sub>2</sub>BDC, Fisher Scientific, 98%), 2,6-naphthalenedicarboxylic acid (H<sub>2</sub>NDC, TCI America, 98%), 4,4'-biphenyldicarboxylic acid (H<sub>2</sub>BPDC, Acros Organics, 98%), 2-bromoterephthalic acid (H<sub>2</sub>BDC-Br, Acros Organics, 95%), zinc perchlorate hexahydrate (Alfa Aesar, Reagent grade), 1,3,5-tris(4-carboxyphenyl)benzene (H<sub>3</sub>BTB, Alfa Aesar, 98%), 4,4'-bipyridine (Acros Organics, 98%), tetrafluoroboric acid solution (HBF<sub>4</sub>, Sigma-Aldrich, 48 wt% in H<sub>2</sub>O), N-Methyl-2-pyrrolidone (NMP, Fisher Scientific, Laboratory grade), dichloromethane (Fisher scientific, HPLC grade), perfluoropentane (Strem Chemicals, >98%), and dimethylformamide (DMF, Fisher Scientific, >99.5%) were used as received. Diethylformamide (DEF, TCI America, >99.0%) was purified by storing over activated charcoal for ~1 month and subsequently passing through a silica gel column. Anhydrous n-hexane (Fisher Scientific) was stored over activated 4 Å molecular sieves.

### Instrumental analysis:

#### Powder X-ray diffraction:

Powder X-ray diffraction (PXRD) data were collected on a Rigaku R-axis Spider diffractometer with an image plate detector and Cu-K $\alpha$  radiation (graphite monochromated, 1.5406 Å) operating at 40 kV and 44 mA in transmission mode. Images were collected with  $\chi$  fixed at 45° while the  $\phi$  was rotating at 10°/min and  $\omega$  oscillating between 5° and 50° to minimize effects of preferred orientation. The 1-D diffractogram was obtained by integration of the resulting two-dimensional images using the AreaMax (2.0) software package with a step size of 0.1° in  $2\theta$ .

#### Solvent evacuation instrumentation:

All MOFs were evacuated under dynamic vacuum for 2 hours using a duoseal vacuum pump (Welch, Model No. 1400B-1). The ultimate vacuum level reached is ~ 0.05 torr. Controlled evacuation experiments were carried out with specified evacuation rates using a needle valve coupled with a Digital Vacuum Regulator (J-KEM, Model No. DVR-200).

#### Gas sorption measurement:

Nitrogen gas sorption experiments were carried out using a NOVA 4200 surface area analyser from Quantachrome Instruments (Boynton Beach, Florida, USA). Ultra-high purity N<sub>2</sub> (99.999%) was purchased from Cryogenic Gases and used as received. Approximately 30-40 mg of samples in a sample cell soaked in desired exchange solvent were first evacuated under a dynamic vacuum (10<sup>-2</sup> torr) for 2 hours before transferring to the surface area analyzer. N<sub>2</sub> sorption experiments were carried out at 77K. The obtained isotherm was obtained and analysed using the NOVAwin software. The relative pressure range for calculating the surface area satisfies the criteria for applying BET theory<sup>1</sup>.

#### <sup>1</sup>H-NMR measurement:

All <sup>1</sup>H-NMR measurements are carried out on Varian Inova 500 spectrometer operating at 500 MHz at room temperature. See more details in sections below.

2. Synthesis of MOF-5, IRMOF-2, UMCM-9 and FJI-1

**MOF-5:**

MOF-5 was synthesized based on a published procedure.<sup>2</sup>

**IRMOF-2:**

IRMOF-2 was synthesized based on a slightly modified published procedure.<sup>2</sup> H<sub>2</sub>BDC-Br (0.147 g, 0.588 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O (0.512 g, 1.96 mmol), and 15 mL of DEF were added to a 20 mL vial. The mixture was sonicated for 15 minutes and heated to 100 °C for 24 hours. The obtained colorless cubic crystals were washed with DMF three times (3 × 20 mL) over 1 hour and soaked in DMF overnight before further usage.

**UMCM-9:**

UMCM-9 was synthesized based on a slightly modified published procedure.<sup>3</sup> H<sub>2</sub>NDC (28.7 mg, 0.132 mmol), H<sub>2</sub>BPDC (35.6 mg, 0.147 mmol), Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (23.8 mg, 0.798 mmol), 6.7 mL DEF and 13.3 mL NMP were added to a 20 mL vial. The mixture was sonicated for 15 minutes and heated at 85 °C for 7 days. The obtained light yellow cubic crystals were washed with DMF three times (3 × 20 mL) over 1 hour and soaked in DMF overnight before further usage.

**FJI-1:**

FJI-1 was synthesized based on a published procedure.<sup>4</sup>

### 3. T1 relaxation measurement for DMF in CH<sub>2</sub>Cl<sub>2</sub>

T1 relaxation experiments were performed on 20  $\mu$ l of DMF in 600  $\mu$ l of CH<sub>2</sub>Cl<sub>2</sub> to determine relaxation time of the methyl protons. The T1 experiments were performed on a Varian INOVA 500 using standard inversion recovery method at room temperature. Relaxation times were probed through the range of 0.5 s to 10 s with an automatically assigned distribution of delays. Data analysis was performed using MestReNova 5.3.1. The determined T1 relaxation time for DMF methyl peak at 2.55 ppm is 3.9 s and methyl peak at 2.46 ppm is 5.2 s.

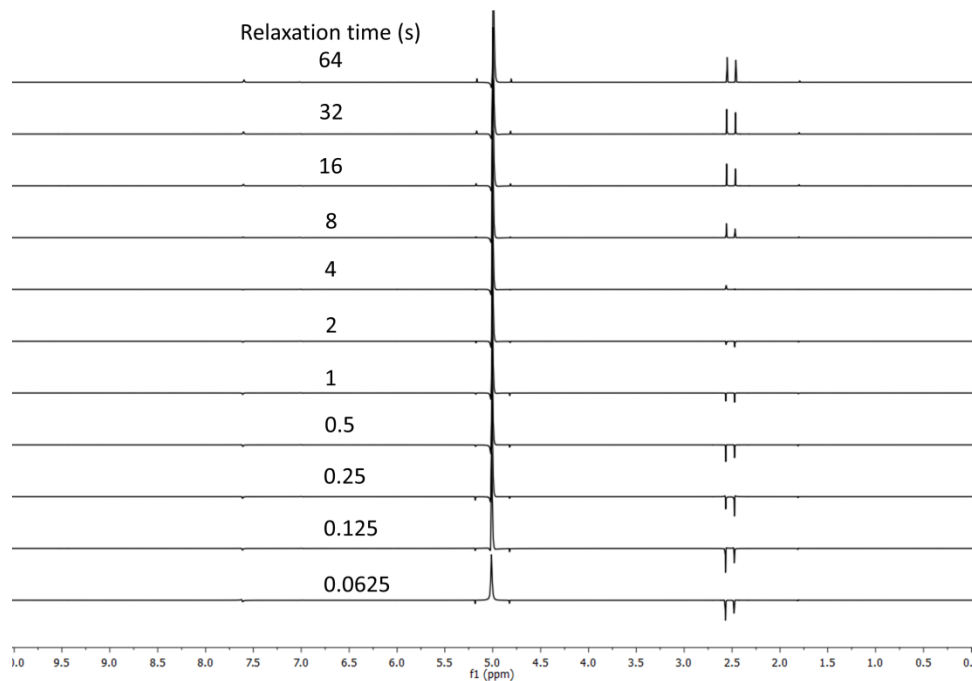


Figure S1. T1 relaxation measurement for DMF in CH<sub>2</sub>Cl<sub>2</sub>.

#### 4. Monitoring of solvent exchange in MOF-5 and IRMOF-2 by $^1\text{H-NMR}$

$\sim 50$  mg of MOF-5 or IRMOF-2 soaked in DMF were transferred to a 5 mm NMR tube. A 5 mm NMR tube with 600  $\mu\text{L}$  of  $\text{CH}_2\text{Cl}_2$  and  $\sim 50$  mg MOF-5 was first loaded in the Varian Inova 500 spectrometer to pre-shim the magnet. Due to the short interval between each data point, the following acquisition parameters were chosen and applied to give relatively accurate integration and good signal to noise ratio for the kinetics data: steady state scan (ss) = -1, acquisition time (at) = 5 s, relaxation delay (dl) = 5 s, number of transient (nt) = 2. The total relaxation time is 10s which is  $\sim 2.5$  T1 of methyl proton in DMF at 2.55 ppm. Once the acquisition parameter is set and the pre-shimming of the magnet is completed, 600  $\mu\text{L}$  of  $\text{CH}_2\text{Cl}_2$  was introduced into the NMR tube with MOF-5 crystals and the sample was immediately loaded with acquisitions of spectra every 30s for 20 mins. The obtained raw spectra were phase corrected and baseline corrected before integration of the proton peak in the  $\text{CH}_2\text{Cl}_2$  and DMF methyl peak ( $(\text{CH}_3)_2\text{NC}(\text{O})\text{H}$ ) at 2.55 ppm in MestReNova 5.3.1. The DMF concentration was then calculated based on the amount of  $\text{CH}_2\text{Cl}_2$  and the ratio between the integration area of DMF methyl peak and  $\text{CH}_2\text{Cl}_2$  proton peak.

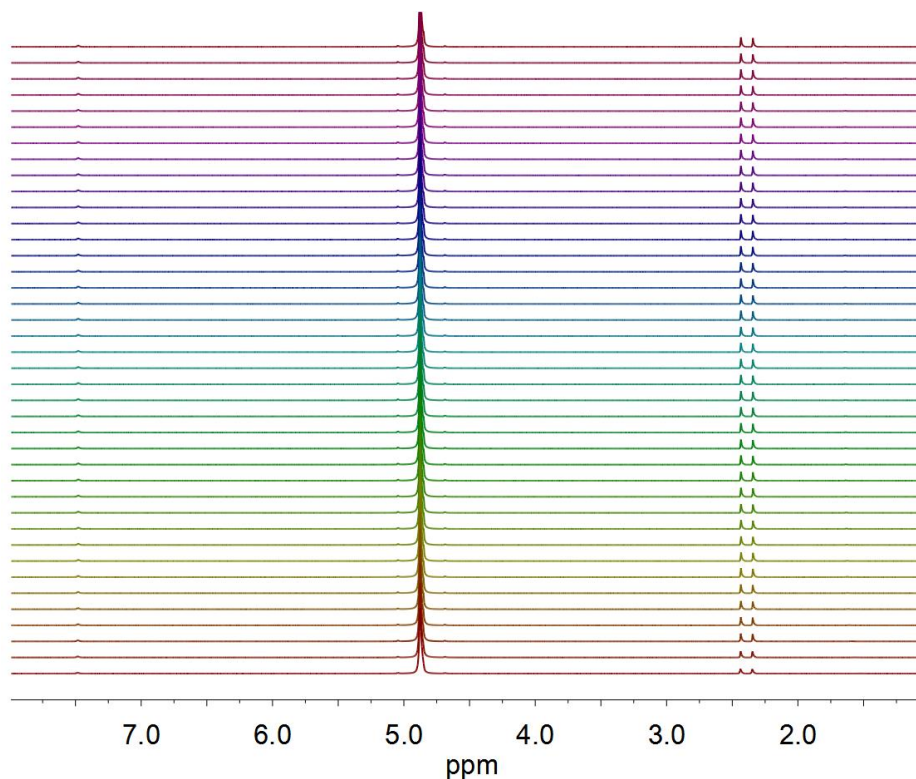


Figure S2. Raw spectra of MOF-5 first-time exchange from DMF to  $\text{CH}_2\text{Cl}_2$  monitored with  $^1\text{H-NMR}$ . The spectra are overlaid sequentially from bottom to the top with the bottom being the first spectrum taken and the top one being the 40<sup>th</sup>.

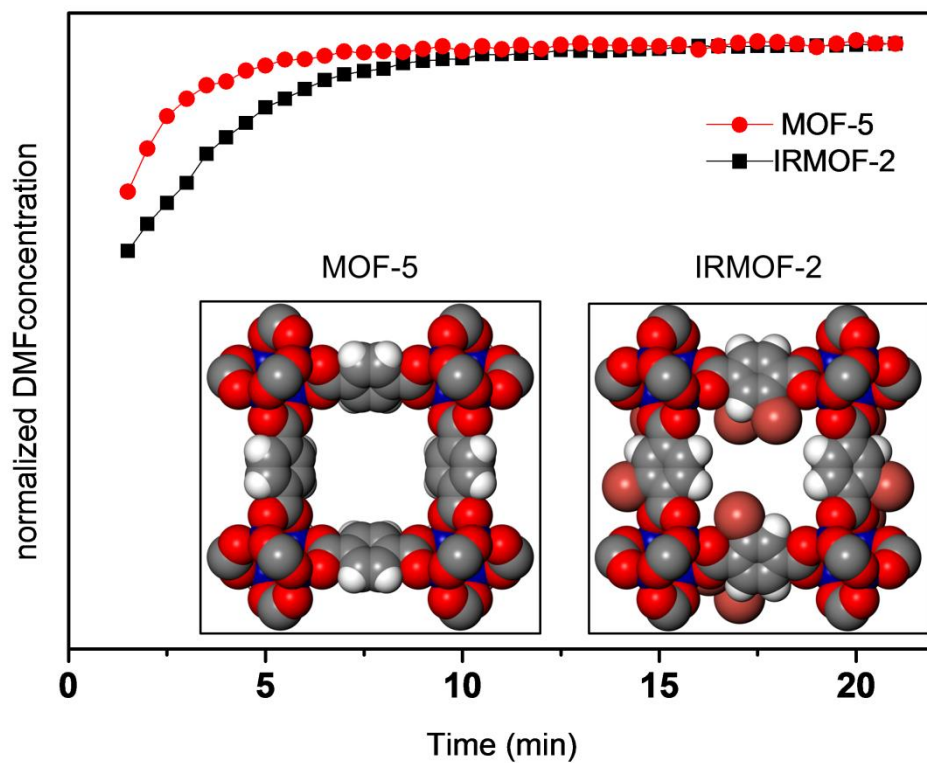


Figure S3.  $^1\text{H-NMR}$  spectroscopy monitoring of the amount of DMF diffusing into  $\text{CH}_2\text{Cl}_2$  for MOF-5 and IRMOF-2 during the first solvent exchange process. Concentration of DMF has been normalized for comparison. Inset: structures of MOF-5 and IRMOF-2 (space filling representation, color code: white, H; grey, C; red, O; blue, Zn; maroon, Br)

### 5. N<sub>2</sub> isotherm measurement and digestion of MOF-5 after multiple solvent exchanges

~ 40 mg of MOF-5 were exchanged with 10 mL CH<sub>2</sub>Cl<sub>2</sub> 1, 2 or 3 times. Each time crystals were soaked in CH<sub>2</sub>Cl<sub>2</sub> for 20 min before solvent decanted and replenished with fresh CH<sub>2</sub>Cl<sub>2</sub>. After the desired number of solvent exchanges, MOF-5 crystals were evacuated under a dynamic vacuum (~ 0.05 torr) for 2 hours before N<sub>2</sub> isotherm measurements. After the N<sub>2</sub> measurement was done, MOF-5 crystals were digested in a mixture of 550  $\mu$ L DMSO-d<sub>6</sub> (99.96 atm % D, Sigma Aldrich) and 50  $\mu$ L DCI (35 wt% in D<sub>2</sub>O, 99 atm % D, Sigma Aldrich). The samples were then subjected to <sup>1</sup>H-NMR spectroscopy to quantitatively determine DMF content per unit cell. Relaxation delay time was set to 25 s to ensure the complete relaxation of methyl proton in DMF.

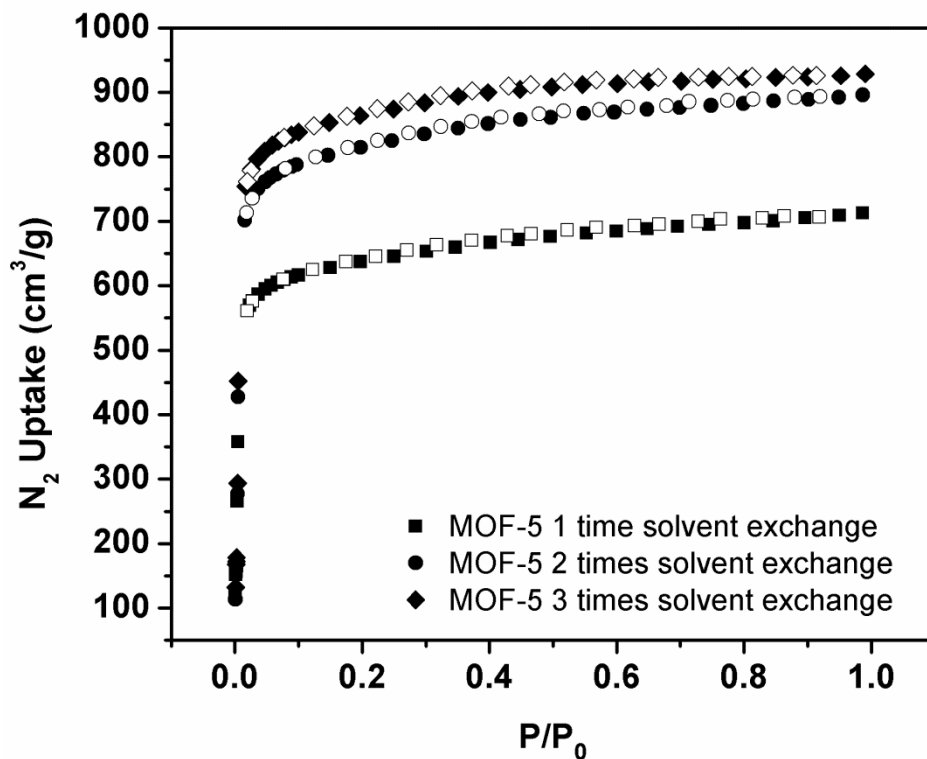


Figure S4. N<sub>2</sub> isotherm plot of MOF-5 after 1 (BET SA = 2650  $\pm$  20 m<sup>2</sup>/g), 2 (BET SA= 3410  $\pm$  30 m<sup>2</sup>/g) or 3 (BET SA= 3640  $\pm$  40 m<sup>2</sup>/g) times solvent exchange.



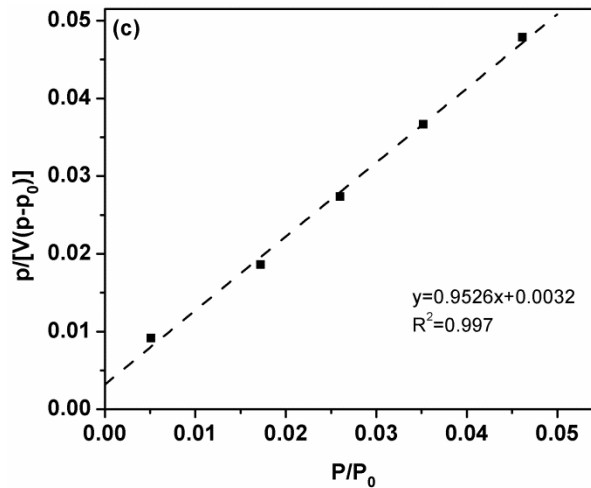
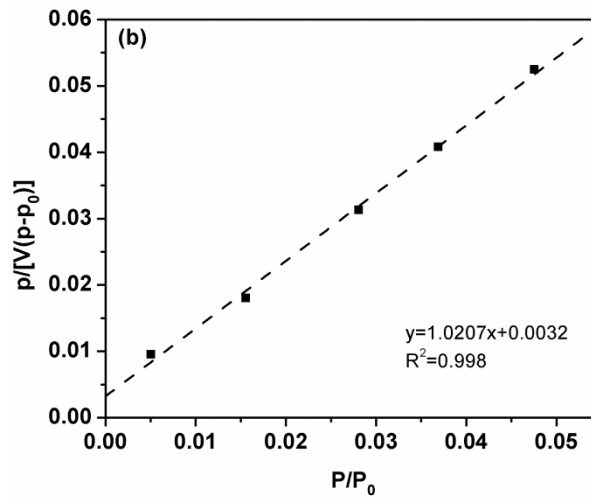
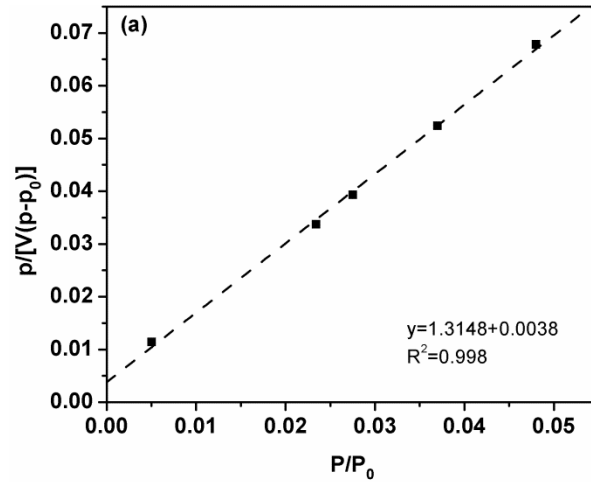


Figure S5. BET fit for the  $N_2$  adsorption isotherm of MOF-5 after (a) 1, (b) 2 or (c) 3 times of exchange. The relative pressure range ( $0.005 \leq P/P_0 \leq 0.05$ ) for calculating the surface area satisfies the criteria for applying BET theory.<sup>1</sup>

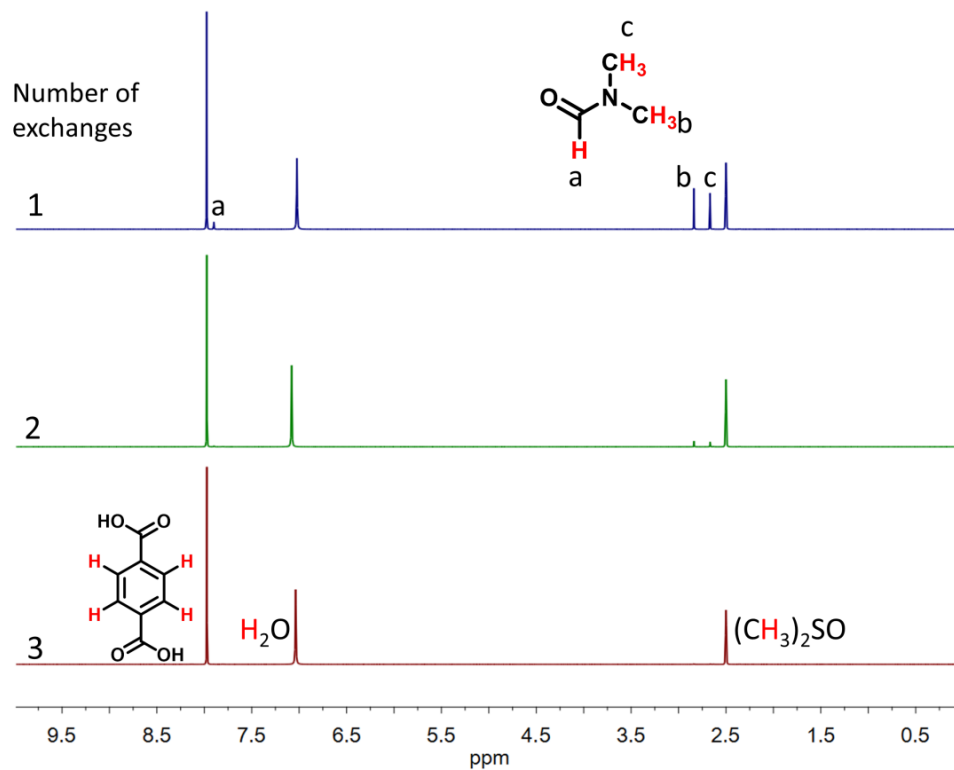


Figure S6. DMF content in MOF-5 after multiple solvent exchanges determined by  $^1\text{H-NMR}$

Exchange repeat time	X in $\text{Zn}_4\text{O}(\text{BDC})_3(\text{DMF})_x$	DMF weight percentage
1	0.78	6.9%
2	0.12	1.1%
3	0.014	0.13%

Table S1. DMF content per unit cell after each solvent exchange determined by  $^1\text{H-NMR}$  spectroscopy.

#### 6. Solvent exchange procedures for UMCM-9 and FJI-1 before evacuation

##### Solvent exchange procedures for UMCM-9 from DMF to n-hexane

Because n-hexane is not miscible with DMF, a two-step exchange procedure is carried out. UMCM-9 (~40 mg) initially washed with DMF ( $3 \times 20$  mL) was first exchanged with  $\text{CH}_2\text{Cl}_2$ . The crystals were soaked in 20 mL of  $\text{CH}_2\text{Cl}_2$  3 times over 1 hour (20 minutes each). The crystals were then immersed in 20 mL of dry n-hexane over 1 hour replacing the solvent every 20 minutes. The material was soaked in n-hexane before solvent evacuation.

##### Solvent exchange procedures for FJI-1 from DMF to perfluoropentane

Because perfluoropentane is not miscible with most organic solvents, a multiple step exchange procedure is carried out below. FJI-1 (~40 mg) initially washed with DMF ( $3 \times 20$  mL) was first exchanged with  $\text{CH}_2\text{Cl}_2$ . The crystals were soaked in 20 mL of  $\text{CH}_2\text{Cl}_2$  3 times over 1 hour (20 minutes each). The crystals were then immersed in 20 mL of dry n-hexane over 1 hour replacing the solvent every 20 minutes. FJI-1 crystals were finally soaked in 20 mL of perfluoropentane 3 times over 1 hour (20 minutes each) before solvent evacuation.

## 7. Powder X-ray Diffraction of UMCM-9 and FJI-1

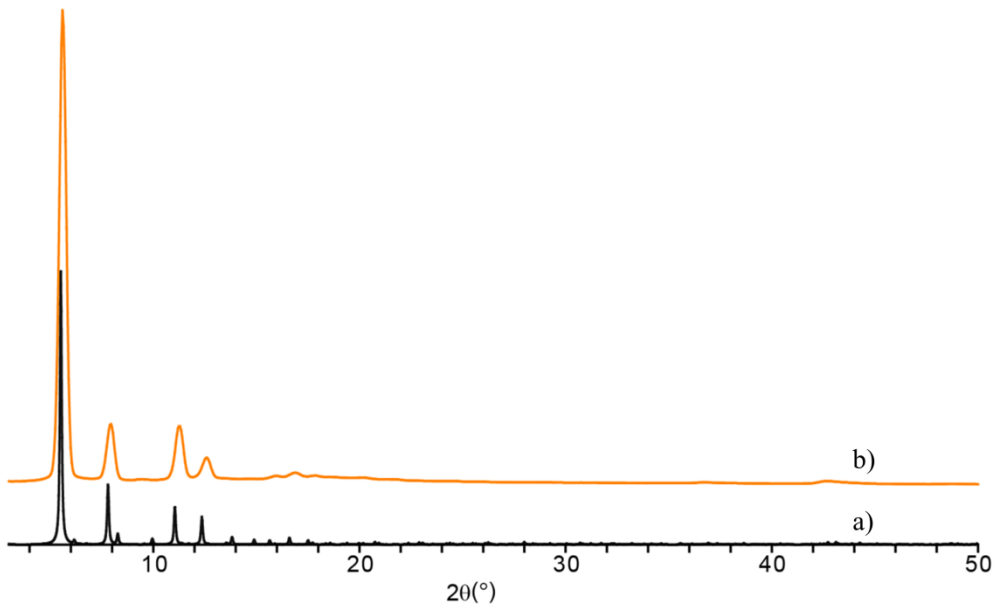


Figure S7. PXRD patterns of UMCM-9. a) Simulated, b) conventional solvent exchange activation from n-hexane.

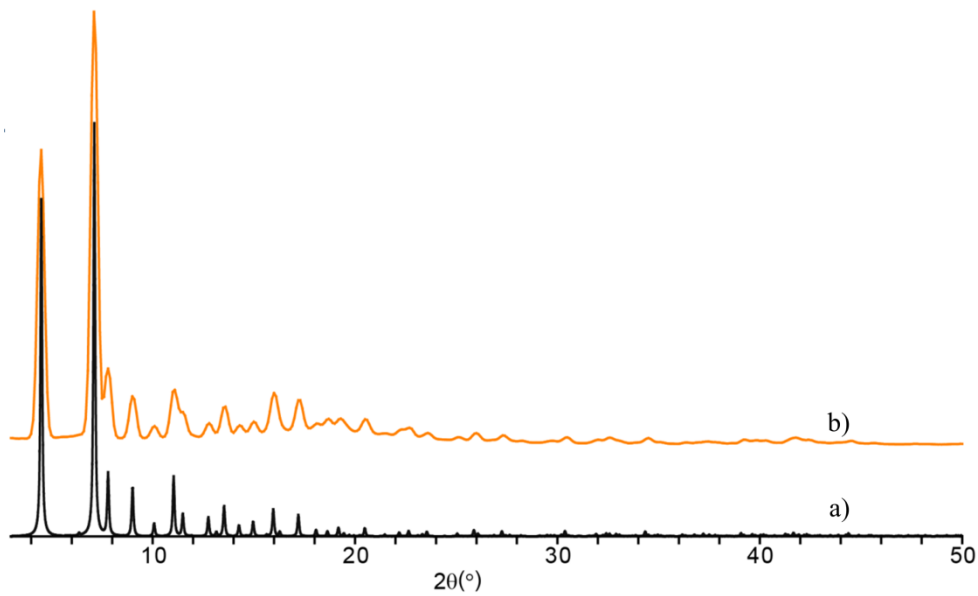


Figure S8. PXRD patterns of FJI-1. a) Simulated, b) conventional solvent exchange activation from perfluoropentane.

8. BET fit for N<sub>2</sub> isotherm of UMCM-9 and FJI-1

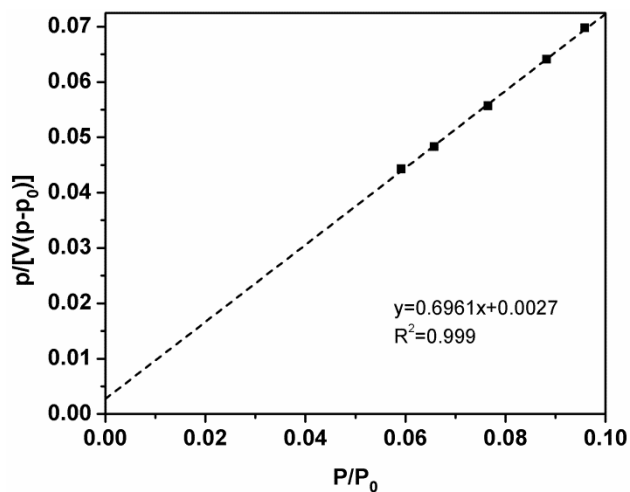


Figure S9. BET fit for the N<sub>2</sub> adsorption isotherm of UMCM-9 activated from n-hexane (BET SA= 4980 ± 50 m<sup>2</sup>/g). The relative pressure range (0.05 ≤ P/P<sub>0</sub> ≤ 0.1) for calculating the surface area satisfies the criteria for applying BET theory.<sup>1</sup>

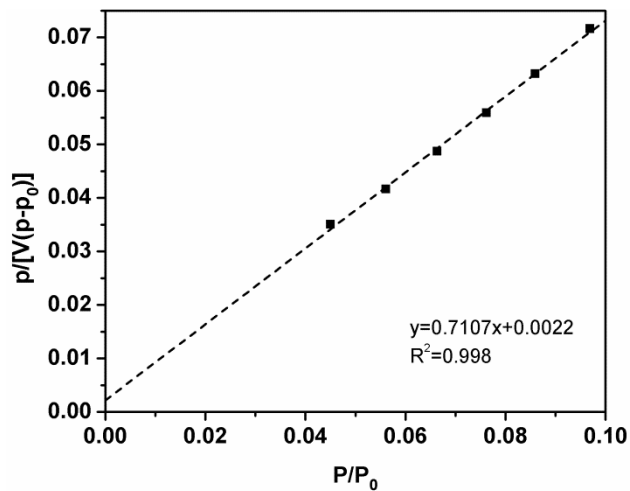


Figure S10. BET fit for the N<sub>2</sub> adsorption isotherm of FJI-1 activated from perfluoropentane (BET SA= 4890 ± 50 m<sup>2</sup>/g). The relative pressure range (0.04 ≤ P/P<sub>0</sub> ≤ 0.1) for calculating the surface area satisfies the criteria for applying BET theory.<sup>1</sup>

9. Pressure profile for UMCM-9 under different evacuation rate

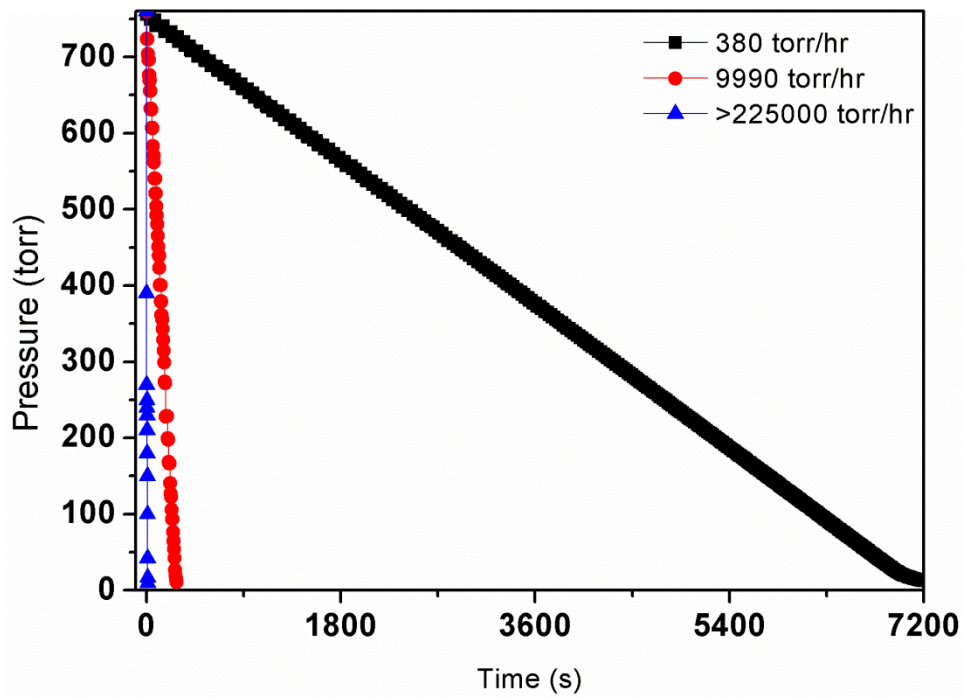


Figure S11. Pressure profiles (1<sup>st</sup> stage: from 760 torr to 1 torr) for evacuation of UMCM-9 from n-hexane with different evacuation rate.

10. Gas-sorption data of UMCM-9 activated under different evacuation rate

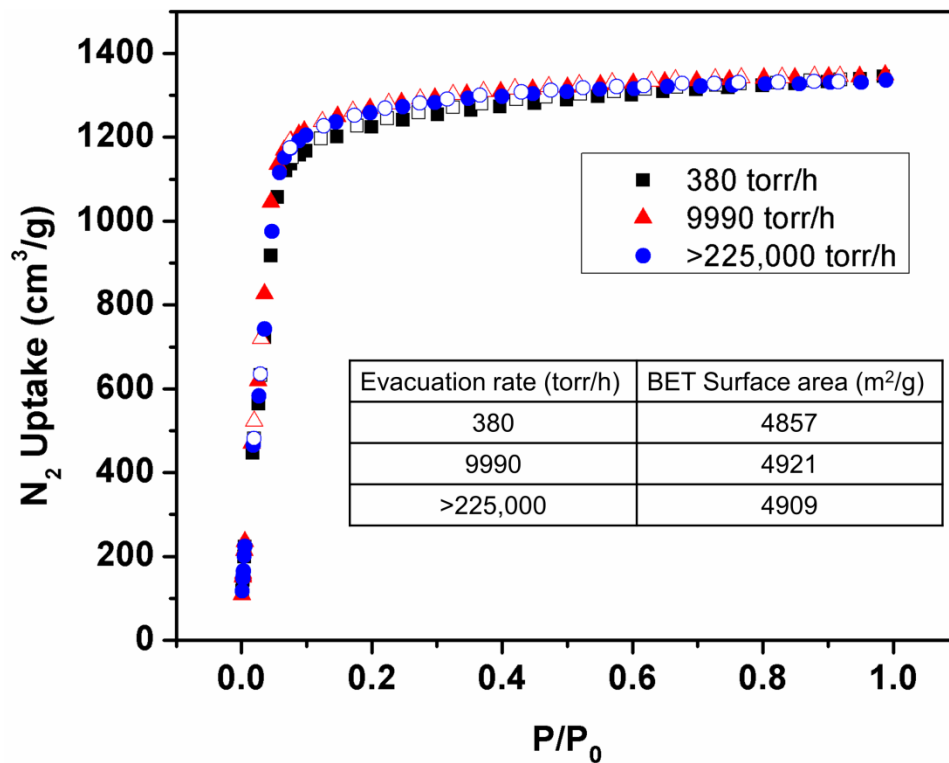


Figure S12. N<sub>2</sub> isotherm plot of UMCM-9 activated from n-hexane under different evacuation rates. Inset: BET surface area of activated UMCM-9 with different evacuation rates.

11. Summary of surface tension values for solvents used in this paper and other common solvents used in the conventional solvent exchange activation.

Solvent	Surface tension (25°C unless otherwise specified) mN/m
Dimethyl sulfoxide (DMSO)	42.7 <sup>5</sup>
N-Methyl-2-pyrrolidone (NMP)	41.8 <sup>6</sup>
Dimethylformamide (DMF)	36.0 <sup>7</sup>
Dichloromethane (CH <sub>2</sub> Cl <sub>2</sub> )	27.2 <sup>8</sup>
Chloroform (CHCl <sub>3</sub> )	26.6 <sup>9</sup>
Methanol (CH <sub>3</sub> OH)	22.1 <sup>10</sup>
n-Hexane	17.9 <sup>11</sup>
Pentane	16.2(20 °C) <sup>12</sup>
Perfluoropentane	9.42 <sup>13</sup>



**References:**

1. Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, 129, 8552
2. Gamage, N.D. H.; Mcdonald, K. A.; Matzger, A. J. *Angew. Chem.* **2016**, 128, 12278
3. Koh, K.; Oosterhout, J. D. V.; Roy, S.; Wong-Foy, A. G.; Matzger, A. J. *Chem. Sci.* **2012**, 3, 2429.
4. Han, D.; Jiang, F. L.; Wu, M.Y.; Chen, L.; Chen, Q. H.; Hong, M. C. *Chem. Commun.* **2011**, 47, 9861.
5. Kinart, C. M.; Kinart, W. J.; Bald, A. *Phys. Chem. Liq.* **1999**, 37, 317
6. Granzhan, V.A.; Kirillova, O.G. *Zh. Prikl. Khim.* **1970**, 43, 1875
7. Wadewitz, T. diploma thesis, Martin-Luther-Universitaet Halle-Wittenberg **1995**
8. Aracil, J.; Luengo, G.; Almeida, B.S.; Telo da Gama, M.M.; Rubio, R.G.; Diaz Pena, M. *J.Phys.Chem.* **1989**, 93, 3210
9. Migal, P.K.; Belotskii, D.P. *Zh. Obshch. Khim.* **1955**, 25, 1908
10. Teitel'baum, B.Y.; Gortalova, T.A.; Ganelina, S.G. *Kolloidn. Zh.* **1950**, 12, 294
11. Teitel'baum, B.Y.; Gortalova, T.A.; Sidorova, E.E. *Zh. Fiz. Khim.* **1951**, 25, 911
12. Aguila-Hernandez, J.; Hernandez, I.; Trejo, A. *Int. J. Thermophys.* **1995**, 16, 45
13. Rohrback, G.H.; Cady, G.H. *J. Am. Chem. Soc.* **1949**, 71, 1938