Metal-Organic Framework@Microporous Organic Network: Hydrophobic Adsorbents with a Crystalline Inner Porosity

Jiseul Chun,[†] Sungah Kang,[†] Nojin Park,[†] Eun Ji Park,[†] Xing Jin,[†] Kwang-Dae Kim,[†] Hyun Ook Seo,[†] Sang Moon Lee,[†] Hae Jin Kim,[‡] Woo Hyun Kwon,[§] Young-Kwon Park,[§] Ji Man Kim,*[,†] Young Dok Kim,*[,†]and Seung Uk Son*[,†]

[†] *Department of Chemistry and Department of Energy Science, Sungkyunkwan University, Suwon 440-746, Korea*
[‡] *Korea Basic Science Institute, Daejeon 350-333, Korea*
[§] *Graduate School of Energy and Environmental System Engineering, University of Seoul, Seoul 130-743, Korea*

Experimental Section

All SEM images were taken using a FE-SEM (JSM6700F). The TEM images were taken using a JEOL 2100F unit operated at 200kV. The solid phase ^{13}C-NMR spectrum was recorded on a Varian 600 MHz solid state NOVA600 spectrometer at the Korea Basic Science Institute (Daegu) and operated at 150.9 MHz Larmor frequency. A spinning speed of 9.5 kHz was applied and the repetition delay time was 6.5 sec. An adsorption-desorption isotherm for N_2 (77 K) was recorded using BELSORP II-mini volumetric adsorption equipment. Water and toluene adsorption isotherms were obtained at 25°C by a conventional volumetric technique using BELSORP II-mini. Before water adsorption isotherm measurement, the samples (50 mg) were treated at 100°C for 12 hours under vacuum. For measurement of toluene adsorption isotherm, the samples were treated at 160°C for 12 hours under vacuum. For measurement of time dependent toluene adsorption at 30°C, the samples (10 mg) were treated 100°C for 2 hours under vacuum. The TGA curve was obtained by Seiko Exstar 7300. Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku MAX-2200 and filtered Cu-Ka radiation. Elementary analysis was performed on a CE EA1110 elementary analysis instrument. The UV/vis absorption spectra were recorded using a JASCO V-630 spectrophotometer. For contact angle measurement, the pellets of powdery samples were prepared. The water contact angles of ACFs were measured using the Theta Optical Tensiometer model (KSV instruments, Ltd.) and lectrooptics comprising a CCTV camera connected to a computer (software Attension Theta).
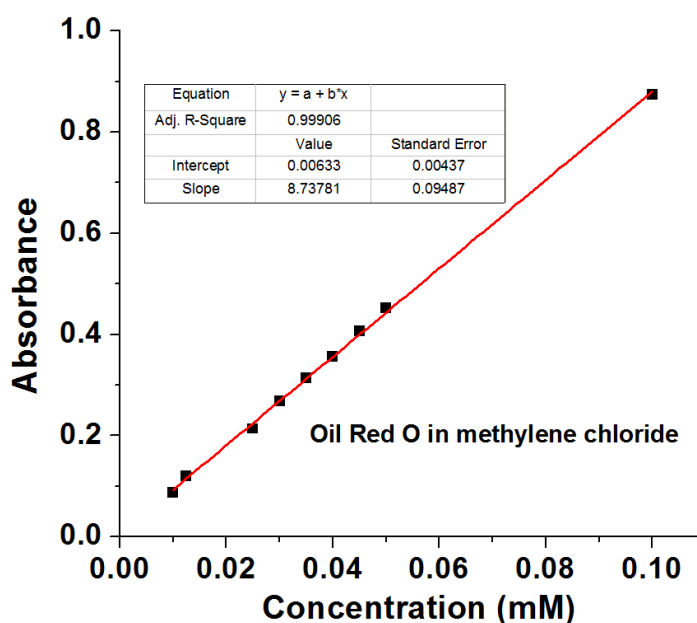
***Preparation of UiO-66-NH₂*:** The UiO-66-NH$_2$ was prepared following the procedure outlined in the literature (ref. 3 and 5 in text). In a 20 mL vial, 2-amino-terephthalic acid (0.13 g, 0.72 mmol), zirconium(IV) chloride (0.17 g, 0.72 mmol), and formic acid (0.8 mL) were dissolved in DMF (8 mL). After sealing the vial with Teflon tape and a cap, the reaction mixture was heated at 120 °C for 24 hours. During this process, the white powder gradually formed. The powder was retrieved by centrifugation, washed with methanol, and dried under vacuum.

***Preparation of MOF@MONs*:** In a flame-dried 50 mL two neck Schlenk flask, UiO-66-NH$_2$ (100 mg) was well dispersed in a mixture of toluene (10 mL) and triethylamine (5 mL). The (PPh$_3$)$_2$PdCl$_2$ (1.7 mg, 2.4 μmol), and

CuI (0.50 mg, 2.6 μmol) were added. The mixture was stirred for 1 hour at 90 °C. Tetra(4-ethynylphenyl)methane (10 mg, 0.024 mmol) and 1,4-diiodobenzene (16 mg, 0.048 mmol) were added. The reaction mixture was refluxed at 90 °C for 24 hours. During this process, a yellow powder gradually formed. After cooling to room-temperature, the precipitates (**MOF@MON-1**) were retrieved by centrifugation, washed with methanol, and dried under vacuum. For the preparation of **MOF@MON-2** and **MOF@MON-3**, 20 mg and 30 mg of tetra(4-ethynylphenyl)methane and 2 eq. 1,4-diiodobenzne were used respectively, instead of 10 mg of tetra(4-ethynylphenyl)methane for **MON@MON-1**. For the preparation of **MOF@MON-4**, 4,4'-diiodobiphenyl (20 mg, 0.048 mmol) and 0.5 eq. tetra(4-ethynylphenyl)methane were used instead of 1,4-diiodobenzene for **MON@MON-1**.

MOF etching from MOF@MONs: The **MOF@MON** (0.30 g) was added to the HF solution (48%, 25 mL) in a Falcon tube. The reaction mixture was stirred at room temperature for 1 hour. The resultant powder was retrieved by centrifugation, washed with water, methanol, and acetone, and dried under vacuum.

Adsorption experiment: The Oil Red O (0.010 M) was dissolved in toluene. Well-dried adsorbent (30 mg) was added to the mixture of Oil Red O solution (0.010 M in toluene, 0.20 mL) and water (30 mL). After adsorption for 5 minutes, the water and un-adsorbed Oil Red O solution were removed. The remaining red colored powder was dried in vacuum oven for 3 hours. The Oil Red O in the collected powder was dissolved in dichloromethane (20 mL). A calibration curve (See the following Graph S1) was obtained from the UV/vis absorption spectra (λ_{max} = 518 nm) of the Oil Red O in methylene chloride with various concentrations. Using this, the amount of Oil Red O in adsorbents and volume of toluene were calculated. For example, in one experiment using **MOF@MON-1**, the absorbance of 0.615 was measured and corresponds to 0.139 mL toluene.


Equation	y = a + b*x	
Adj. R-Square	0.99906	
	Value	Standard Error
Intercept	0.00633	0.00437
Slope	8.73781	0.09487

Oil Red O in methylene chloride

Graph S1. Concentration dependent UV/vis absorbance (at λ_{max} = 518 nm) of Oil Red O in methylene chloride

**Table S1.** Physical and chemical properties of materials in this work.

Materials	S_{BET} (m^2/g)	Total Pore Volume (cm^3/g)	(cm^3/30 mg)	Adsorbate amount* (mL/30 mg)	Elemental Analysis N (%)	C (%)	H (%)
UiO-66-NH$_2$	1070	0.700	0.021	0.009	3.963	29.985	3.107
MOF@MON-1	795	0.380	0.011	0.150	3.376	34.386	4.113
MOF@MON-2	711	0.335	0.010	0.072	3.049	40.430	4.096
MOF@MON-3	703	0.334	0.010	0.041	2.923	42.439	4.118
MOF@MON-4	809	0.390	0.012	0.170	3.448	36.555	3.879
H-MON-1	1138	1.095	0.033	0.009	-	80.171	4.224
H-MON-4	866	0.690	0.021	0.012	-	76.866	4.142

*Some adsorbate amount exceeds the total pore volume of adsorbent, as commonly observed in literature (ref. 20~21 in text). The hydrophobic adsorbents for organic model pollutants in ref. 20-21 in text showed the 9~16 weight times of adsorption for aromatic adsorbates such as benzene, toluene and nitrobenzene.

Figure S1. (a) PXRD patterns, (b) solid phase ^{13}C NMR spectra (red asterisks: major peaks from MON, blue asterisks: major peaks from MOF), (c) N_2 adsorption/desorption isotherm curves at 77K (The N_2 sorption isotherms of **MOF@MON-2** and **H-MON-1** were omitted for clarity. See Table S1 in the SI), and (d) pore size distribution diagrams by the DFT method of UiO-66-NH$_2$, **MOF@MON-1**, **MOF@MON-2**, **MOF@MON-3**, **MOF@MON-4, H-MON-1** and **H-MON-4**. (e) TGA curves of materials in this work.
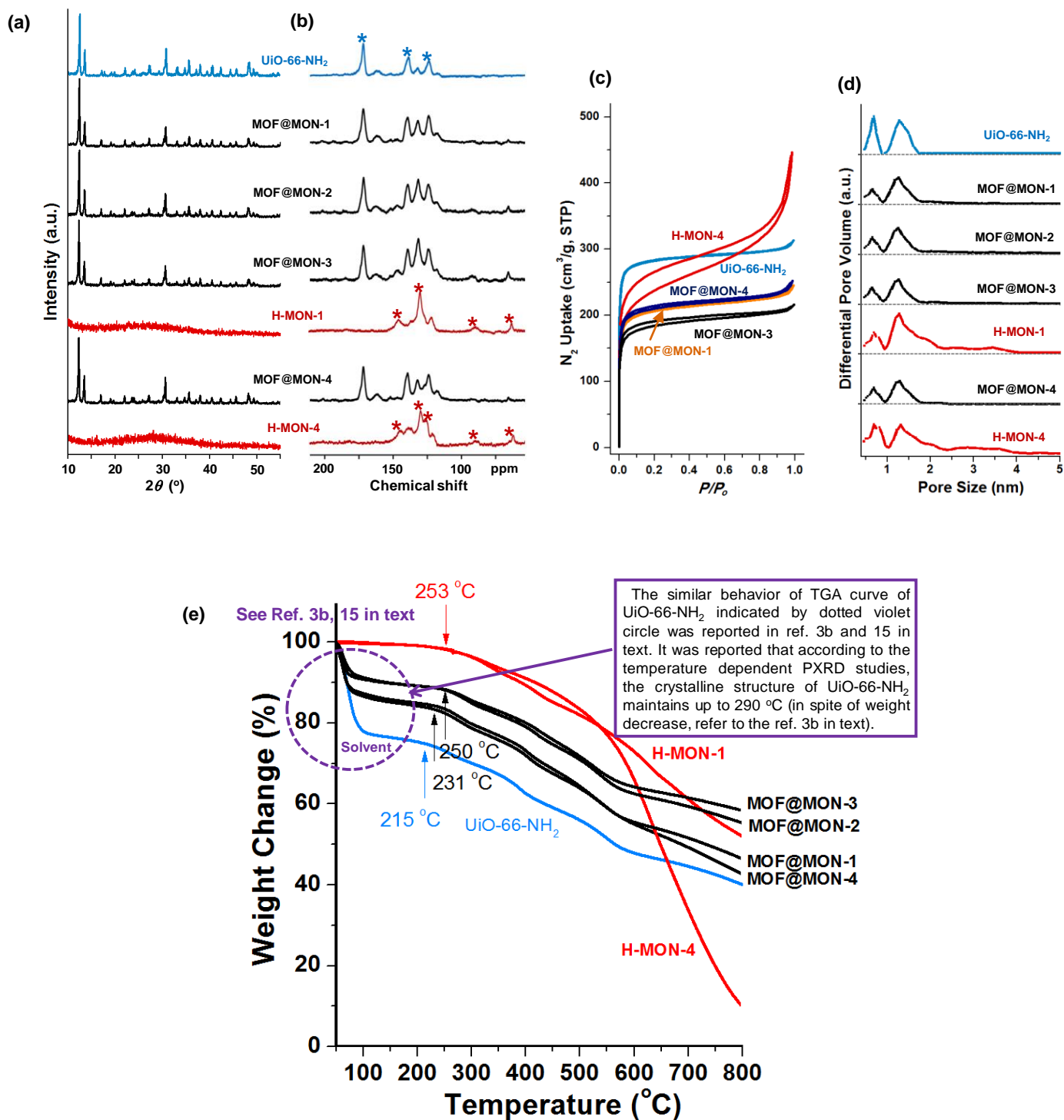
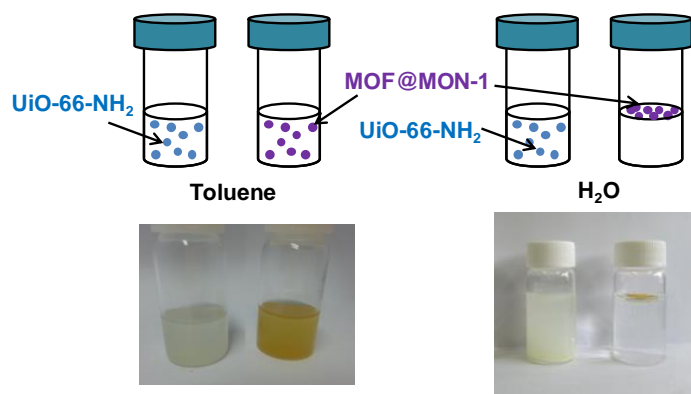**Figure S2.** Nanopore distribution (by DFT method) of **H-MON-1** and **H-MON-4**.
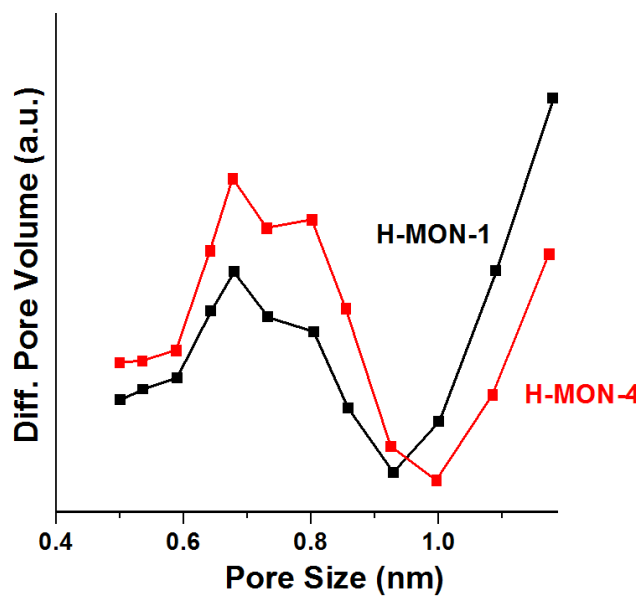
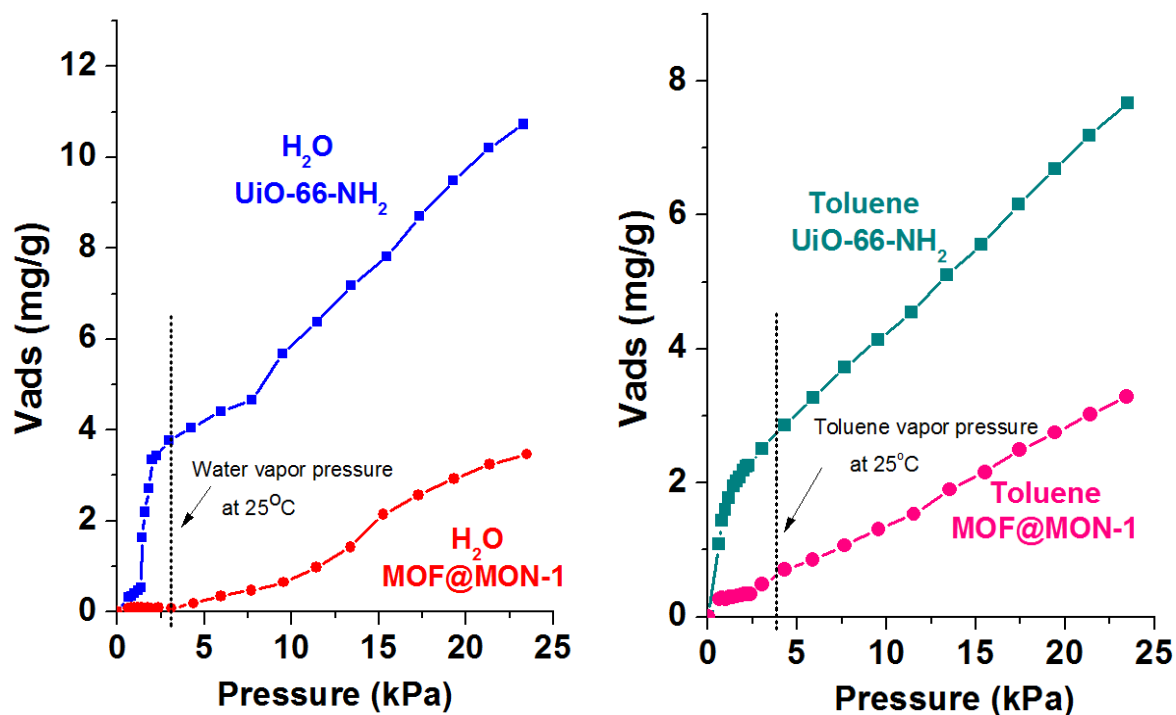**Figure S3.** Dispersion behaviors of **MOF@MON-1** in water and in mixtures of (1/1, v/v) MeOH/H$_2$O and (1/1, v/v) THF/H$_2$O.
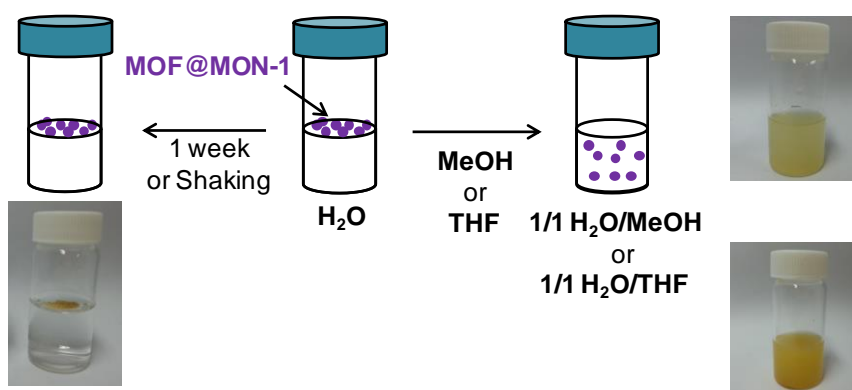
**Figure S4.** PXRD patterns of **MOF@MON-**1 depending on the water exposure time.
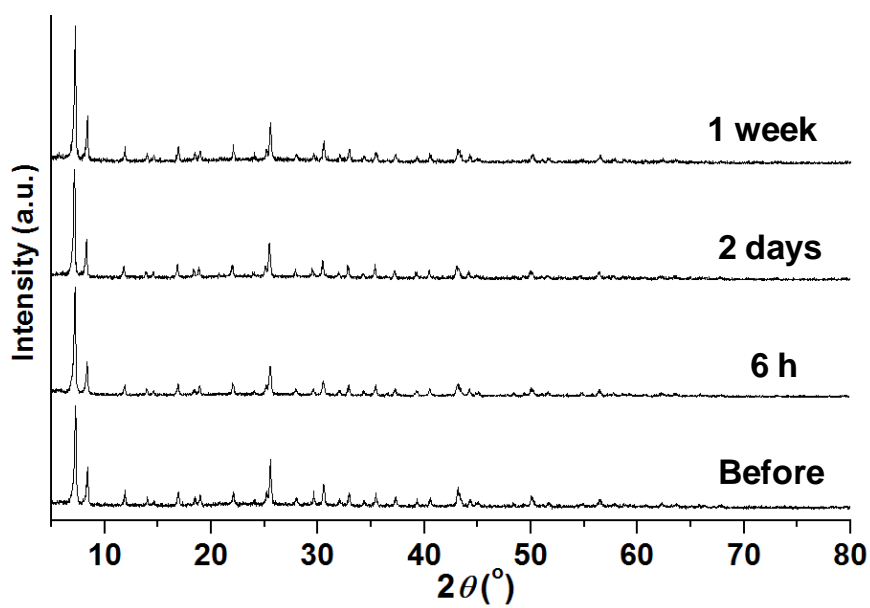
**Figure S5.** Dispersion behavior of UiO-66-NH$_2$ and **MOF@MON-1** in toluene and water.

Figure S6. Water and toluene adsorption isotherms of UiO-66-NH$_2$ and **MOF@MON-1** at 25°C.

Figure S7. Experimental set up and toluene adsorption curves of UiO-66-NH$_2$ and **MOF@MON-1**. (Total flow: 20 sccm, gas: N$_2$ + toluene, toluene gas concentration: 40 and 110 ppm)
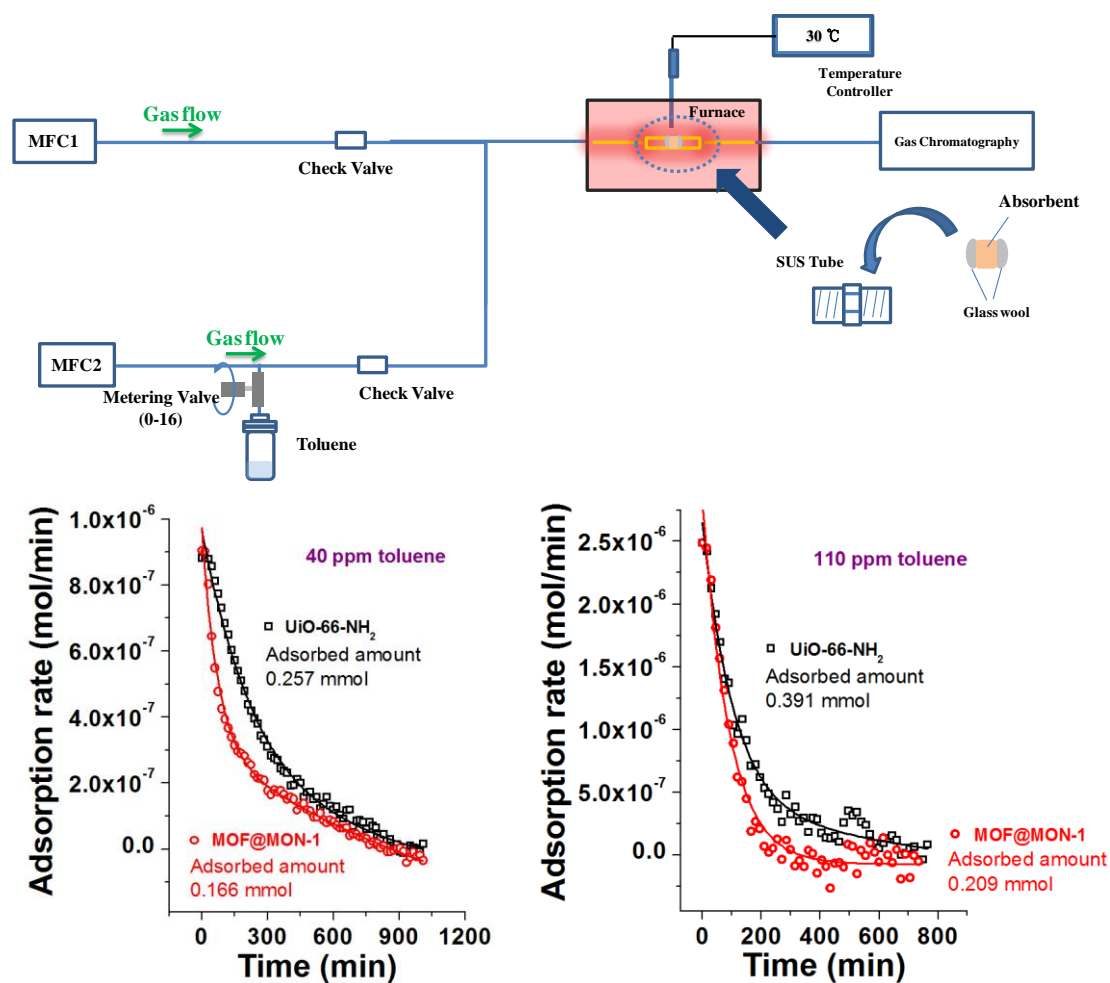
Figure S8. Post synthetic approach for **MOF@MON-1**. (The 50 mg of MOF@MON-1 was treated with 12 mmol anhydride in 5 mL toluene for 24 hours at room temperature. After digesting using HF in DMSO-d^6 solvent, the organic compounds were analyzed by ^{1}H NMR. Refer to the procedure in *Chem. Commun.* **2010**, 46, 7700)
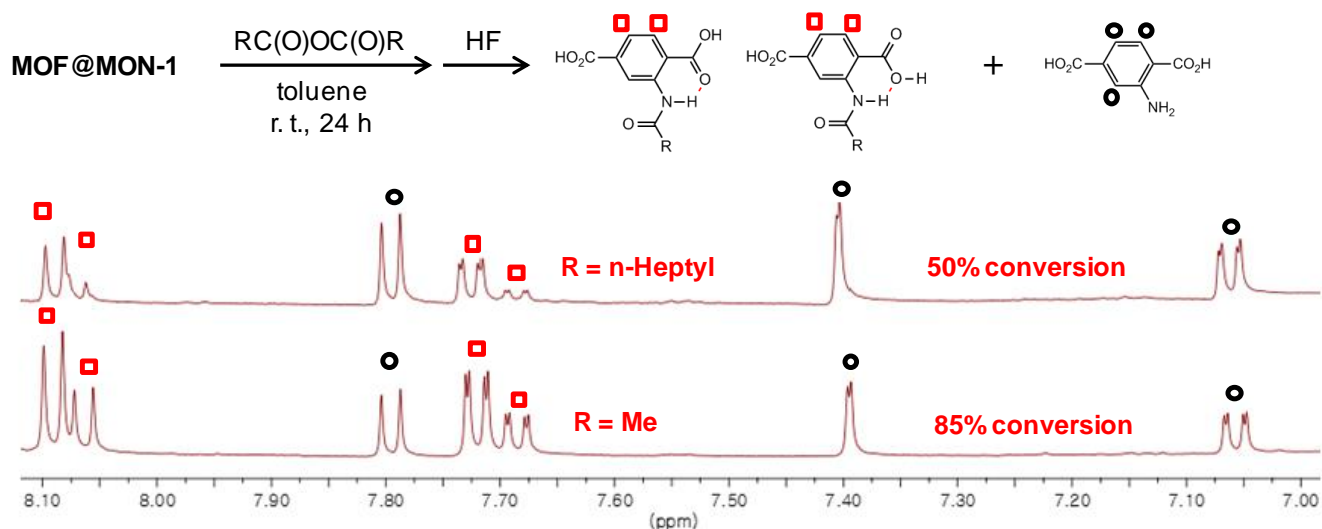
Figure S9. SEM and TEM images of UiO-66-I, **UiO-66-I@MON**, and MON hollows. (The same synthetic procedure for **MOF@MON-1** was applied using UiO-66-I instead of UiO-66-NH$_2$.)