

Supporting Information

MOF-5-Polystyrene: Direct Production from Monomer, Improved Hydrolytic Stability, and Unique Guest Adsorption

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I. Experimental Procedures

Starting Reagents: Zinc nitrate hexahydrate (Fisher Scientific, ACS reagent), 1,4-benzenedicarboxylic acid (H₂BDC, Fisher Scientific, 98%), dichloromethane (CH₂Cl₂, Fisher Scientific, > 99.9%), xylenes (Sigma-Aldrich, > 98.5%, ACS reagent), tetrahydrofuran (THF, Fisher Scientific, ACS and HPLC grades), dimethylformamide (DMF, Fisher Scientific, > 99.5%), sodium hydroxide (NaOH, Fisher Scientific, ACS reagent), sodium chloride (NaCl, Fisher Scientific, ACS reagent), sodium sulfate, anhydrous (Na₂SO₄, Acros Organics, ACS reagent), and hydrochloric acid (HCl, 36.5–38.0% w/w, Fisher Scientific, certified ACS plus) were used as received without further purification. Diethylformamide (DEF, TCI America, > 99.0%) was purified by storing over activated carbon for ~1 month and subsequently passing through a column containing silica gel. Styrene (stabilized and N₂ flushed, Acros Organics, 99.5%) was purified by passing through a column of *t*-Butyl catechol remover (chromatographic packing, Scientific Polymer Products Inc.) and consequently filtering through a CHROMAFIL[®] Xtra PTFE-45/13 0.45 μm disposable syringe filter. Nile red (Acros Organics, 99%, pure) and methyl red (Acros Organics, pure, ACS reagent) organic dyes were used as purchased.

Synthesis:

Zinc nitrate tetrahydrate, Zn(NO₃)₂·4H₂O: Zinc nitrate tetrahydrate was prepared as previously described.¹

MOF-5: MOF-5 was synthesized based on a slightly modified previously published procedure.² H₂BDC (0.100 g, 0.602 mmol), Zn(NO₃)₂·4H₂O (0.500 g, 1.91 mmol), and 15 mL of DEF were

added to a 20 mL vial. The mixture was sonicated for 15 minutes until all the solid materials were dissolved and heated to 100 °C for 18–24 hours to obtain colorless cubic crystals of MOF-5. The DEF solution was decanted and MOF-5 crystals were washed with DEF ((i) 3 × 10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh DEF over 24 h) and CH₂Cl₂ ((i) 3 × 10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh CH₂Cl₂ over 24 h). The resultant MOF-5 crystals were activated by exposure to dynamic vacuum (10⁻² Torr) for 24 h and were stored in a glove box under an atmosphere of nitrogen.

MOF-5-PS-4–24 h: MOF-5 crystals (0.100 g) and purified styrene (10 mL) were added to a 20 mL vial and the mixture was heated at 65 °C for 4–24 h to obtain colorless MOF-5-PS-4–24 h composite crystals. Afterwards, the styrene solution was decanted and MOF-5-PS-4–24 h crystals were washed with THF ((i) 3 × 10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh THF over 24 h) and CH₂Cl₂ ((i) 3 × 10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh CH₂Cl₂ over 24 h). The resultant MOF-5-PS-4–24 h crystals were activated by exposure to dynamic vacuum (10⁻² Torr) for 24 h and were stored in a glove box under an atmosphere of nitrogen.

Extraction of polystyrene on MOF-5-PS-4–24 h composites:

Method 1: MOF-5-PS-4–24 h composite was vigorously shaken in 1 M NaOH (10 mL) for 5–10 min. and sonicated further for 5–10 min. The NaOH solution was decanted and the resultant material was washed with (i) saturated NaCl (2 × 10 mL), (ii) distilled H₂O (2 × 10 mL), and (iii) acetone (2 × 1 mL). The residual solvent was removed under reduced pressure and the resultant

partially degraded MOF-5-PS-4–24 h composite was kept in THF (1.8 mg/mL) for 5–10 min. and also sonicated for 5–10 min. The dispersed mixture obtained was filtered through a CHROMAFIL[®] Xtra PTFE-45/13 0.45 µm disposable syringe filter. Finally, a gel permeation chromatography (GPC) trace was obtained to determine the polymer molecular weight and dispersity (Đ).

Method 2: MOF-5-PS-4–24 h composite was ground until a uniform powder was obtained and then, this powder was vigorously shaken in 1 M NaOH (10 mL) for 5–10 min. and sonicated further for 5–10 min. Afterwards, the polymer was extracted to CH₂Cl₂ (10 mL) in a separatory funnel. This CH₂Cl₂ layer was separated from the aqueous layer and was washed with saturated NaCl (3 × 10 mL). Then, the CH₂Cl₂ layer was separated and dried with anhydrous Na₂SO₄. Finally, the dry CH₂Cl₂ layer was decanted and the solvent was removed under reduced pressure to obtain the extracted polystyrene. This polystyrene was dissolved in THF (1 mg/mL) and was filtered through a CHROMAFIL[®] Xtra PTFE-45/13 0.45 µm disposable syringe filter. A gel permeation chromatography (GPC) trace was obtained to determine the polymer molecular weight and Đ.

There was no significant difference in the measured polymer molecular weights and dispersities measured by the two different methods.

Determination of polystyrene retention:

(i) Polymer retention after the washing procedure:

(a) Analysis of the final (CH₂Cl₂) wash solution: The final CH₂Cl₂ solution (10 mL) that was used to wash MOF-5-PS crystals (0.100 g) over 24 h on the shaker was dried on the Schlenk line under reduced pressure. Then, the residue was dissolved in THF (1 mg/mL) and filtered through a CHROMAFIL[®] Xtra PTFE-45/13 0.45 µm disposable syringe filter. Finally, a GPC trace was collected and there was no polystyrene in the final (CH₂Cl₂) wash solution, which indicates there was no polymer coming off from the MOF-5-PS-24 h composite in to the CH₂Cl₂ washing solvent.

(b) Analysis of extracted polystyrene from MOF-5-PS-24 h after the washing procedure:

After the washing procedure mentioned in (a) and activation, the presence of polymer on the MOF-5-PS-24 h composite was confirmed using TGA and Raman Spectroscopy. The grafted polystyrene was studied by GPC after it was extracted from the digested MOF-5-PS-24 h composite using the above mentioned extraction method 2. Based on GPC, a polymer of 594 kDa was observed with a Đ of 1.35.

The observations in (a) and (b) indicate that the high molecular weight polymer was grafted and was not washed by the washing procedure with THF and CH₂Cl₂ mentioned above in the MOF-5-PS-24 h composite synthesis.

(ii) Polymer retention after heating in THF at 60 °C:

(a) Analysis of polymer after heating in THF at 60 °C: To a 20 mL vial, a sample of washed and activated MOF-5-PS-24 h composite (0.432 g) and THF (10 mL) was added and the mixture

was kept shaking at 60 °C on a Glas-Col[®] pulse vortex mixer/heater (Terre Haute, USA). Afterwards, the THF was decanted, allowed to come to room temperature, and was filtered through a CHROMAFIL[®] Xtra PTFE-45/13 0.45 µm disposable syringe filter. A GPC trace was obtained and there was no polymer, which indicated that no polymer was coming off from the MOF-5-PS-24 h composite in to THF at 60 °C.

(b) Analysis of extracted polystyrene from MOF-5-PS-24 h after heating in THF: After heating in THF at 60 °C as mentioned in (a) and activation, the presence of polymer on the corresponding MOF-5-PS-24 h composite was confirmed using TGA and Raman Spectroscopy. The grafted polystyrene was studied by GPC after it was extracted from the digested MOF-5-PS-24 h composite using the above mentioned extraction method 2. Based on GPC, a high molecular weight polymer of 541 kDa was observed with a \bar{M}_w of 1.41.

The observations in (a) and (b) indicate that the high molecular weight polymer was grafted and was not washed by heating in THF at 60 °C.

Feasibility of high molecular weight polystyrene entrapment in MOF-5:

To each of three 20 mL vials, high molecular weight polystyrene ($M_w = 280$ kDa, ~0.100 g) was added. Polystyrene was dissolved in (i) THF, (ii) Xylenes, or (iii) DCM (5 mL) by sonication in separate vials. Then, MOF-5 (~0.010 g) was added to each vial and the corresponding mixtures were heated at 65 °C for 24 h. Afterwards, the solutions were decanted and the resultant MOF-5 crystals were washed with THF ((i) 3×10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh THF over 24 h) and CH₂Cl₂ ((i) 3×10 mL; (ii) kept on an IKA[®] vibrax VXR basic shaker at 100 rpm in 10 mL of fresh CH₂Cl₂ over 24

h). These washed crystals were activated by exposure to dynamic vacuum (10^{-2} Torr). No polystyrene was observed based on Raman Spectroscopy, TGA, and GPC (after digestion of MOF-5 with the extraction method 2), which indicates that high molecular weight polymer does not directly graft onto, or otherwise become strongly associated with, MOF-5 crystals under the same conditions of MOF-5-PS-4–24 h composite synthesis. If there are physisorbed high molecular weight polymers with MOF-5 crystals, they get completely washed away during the washing procedure.

Study of hydrolytic stability:

The hydrolytic stability measurements were performed using saturated salt solutions of K_2CO_3 in distilled H_2O (in 20 mL vials) to provide an environment of 53% relative humidity (RH).³ To two 4 mL vials, MOF-5 (~0.020 mg) and MOF-5-PS-24 h (~0.020 mg) were added and then, they were quickly incorporated in to 20 mL vials with the saturated K_2CO_3 solution and sealed. After different time points, crystals of MOF-5 and MOF-5-PS-24 h were harvested and any effects on their crystallinity was analysed by powder X-ray diffraction (PXRD, Section IX, Figure S11 and S12, respectively). Based on the PXRD patterns, pristine MOF-5 degraded within 4 h whereas the MOF-5-PS-24 h composite was stable for > 3 months (12 weeks) at 53% RH, which indicates that grafting of polystyrene using this simple protocol results in a significant enhancement of the hydrolytic stability. For N_2 gas sorption results confirming maintenance of porosity see below (Section IX, Figure S13).

Dye sorption experiments:

Saturated methyl red and nile red dye solutions were prepared in CH₂Cl₂ (1–2 mL) using two 4 mL vials. The MOF-5-PS-24 h composite (~0.010 mg, after the CH₂Cl₂ wash, without activation) was added to each vial and the mixture was kept on an IKA[®] vibrax VXR basic shaker at 100 rpm for 24 h. Afterwards, the dye solutions were decanted and the dye adsorbed MOF-5-PS-24 h composites were washed with fresh CH₂Cl₂ (2 × 5 mL) and activated by exposure to dynamic vacuum (10⁻² Torr) for 24 h and were stored in a glove box under an atmosphere of nitrogen.

Instrumental analysis:

Powder X-ray diffraction: Powder X-ray diffraction (PXRD) data for MOF-5 and MOF-5-PS composites were collected on a Rigaku R-axis Spider diffractometer with an image plate detector and Cu-K α radiation (graphite monochromated, 1.5406 Å). The data collection was carried out operating at 40 kV and 44 mA in the transmission mode. Images were collected with χ fixed at 45° while the sample loop was rotated at 10°/min in ϕ on the goniometer and ω oscillating between 5° and 50° to minimize any effect of preferred orientation. Then, by integration of the resulting two-dimensional images using the AreaMax (2.0) software package with a step size of 0.1 in 2θ , the PXRD patterns were obtained.

Gas sorption measurements: Nitrogen gas sorption experiments of MOF-5 and MOF-5-PS composites were obtained using a NOVA *e*-series 4200 surface area analyser from Quantachrome Instruments (Boynton Beach, Florida, USA). Ultra-high purity N₂ (99.999%) was

purchased from Cryogenic Gases and used as received. N₂ sorption experiments were carried out at 77 K in a glass sample cell with approximately 15–20 mg of sample. The N₂ Sorption isotherms were obtained and analysed by applying the BET approximation using the NOVAwin software.

Argon and CO₂ sorption experiments were carried out using an AUTOSORB-1C gas sorption analyser from Quantachrome Instruments (Boynton Beach, Florida, USA). Liquid Argon (99.999%) and CO₂ (Bone Dry or 99.9%) were purchased from Cryogenic Gases and used as received. The argon sorption measurements were carried out at 87 K in a glass sample cell with approximately 10 mg of sample. The CO₂ sorption measurements were carried out at 298 K and 273 K in a glass sample cell with approximately 100 mg of sample. Pore size distributions of MOF-5 and MOF-5-PS composites were obtained by applying the non-local density functional theory (NLDFT) with a zeolite/silica equilibrium kernel using the cylindrical pore model by employing the ASWin software package (version 1.2).

Thermogravimetric Analysis (TGA): Thermogravimetric analyses of MOF-5 and MOF-5-PS composites were performed on a TA Instruments Q50 thermogravimetric analyser. The analyte was heated from room temperature (~25 °C) to 600 °C at a rate of 10 °C/min using platinum pans under a flow of nitrogen gas.

Gel permeation chromatography (GPC): Analyses of the polystyrene extracted from the MOF-5-PS composites were performed on a Shimadzu GPC with a molecular weight range coverage of 1,000,000 to 92 Da. THF was used as the solvent and the sample concentrations

were adjusted to be ~1–1.8 mg/mL. GPC was performed in the batch processing mode with a solvent flow rate of 1 mL/min and the spectra were obtained using a diode array UV-vis detector at 259 nm wavelength. These GPC analyses were performed and analysed using Shimadzu LCsolution software.

Raman Spectroscopy: Single point Raman spectra of MOF-5 and MOF-5-PS-4–24 h composites were obtained using a Renishaw inVia Raman microscope equipped with a RenCam CCD detector, Leica microscope, 633 nm laser, 1800 lines/mm grating, and 65 μm slit. Calibration of the instrument was performed using a silicon standard for all experiments. For collecting data, the extended scan mode was used in the range of 100–3200 cm^{-1} . The spectra were analysed using the Wire 3.4 software package.

Raman mapping of a sectioned MOF-5-PS-24 h composite embedded in epoxy, was performed on a Renishaw inVia Raman microscope equipped with a Renishaw 1” CCD array detector, Leica microscope, 785 nm laser, and a 65 μm slit in the streamline image acquisition mode. A region of the cross-section that includes the sectioned MOF-5-PS-24 h crystal and the epoxy background were selected for analysis. The spectra were collected using a static scan mode in the range of 555–1679 cm^{-1} . The mapping image was analysed using the Wire 4.2 software package.

Solid-state UV-visible (UV-vis) spectroscopy: UV-vis spectra of methyl red and nile red dye adsorbed MOF-5 and MOF-5-PS-24 h composite were performed on a double beam Varian Cary 5000 UV-vis-NIR spectrophotometer in the reflectance mode (%R). Spectra were scanned at a

rate of 600 nm/min within the wavelength range of 200–2500 nm. Instrument baseline was set to zero using powdered barium sulphate (BaSO_4). The dye adsorbed MOF-5 and MOF-5-PS-24 h crystals (~10 mg) were mixed with BaSO_4 (~20 mg) and ground together to obtain a homogeneous solid mixture for analysis. The spectral data obtained in the reflectance mode were converted to transmission mode, $F(R)$ using the Kubelka-Munk theory of reflectance by employing the Varian Cary WinUV Scan software version 3.0.

II. PXRD patterns of pristine MOF-5 and MOF-5-PS-24 h composite

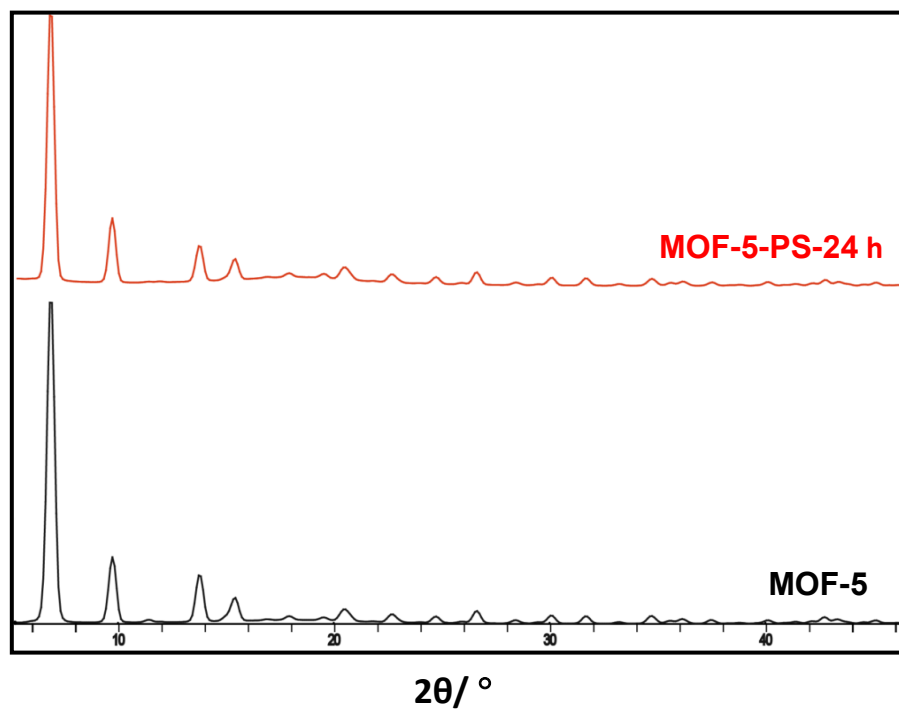


Figure S1. PXRD patterns of pristine MOF-5 and MOF-5-PS-24 h composite

III. Thermogravimetric analysis

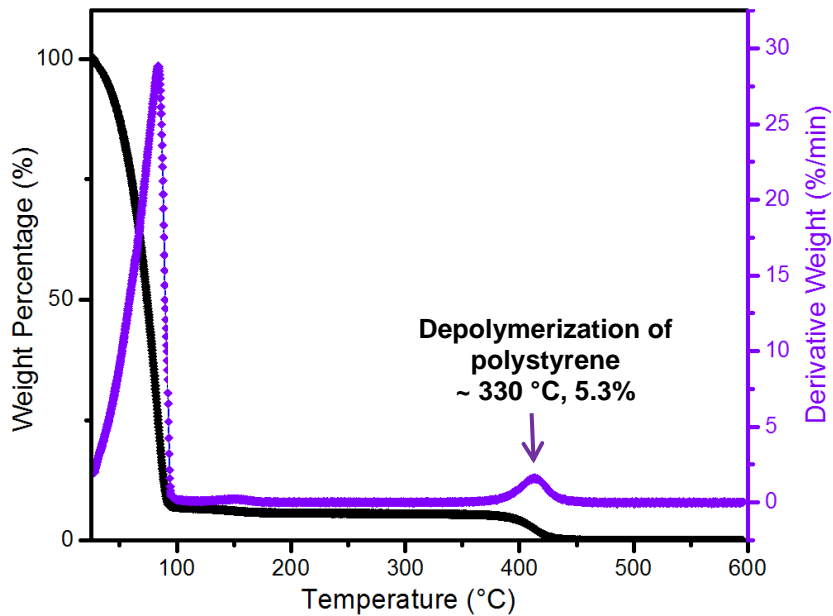


Figure S2. TGA weight loss (black) and differential weight loss (purple) curves of styrene after heating at 65 °C for 24 h

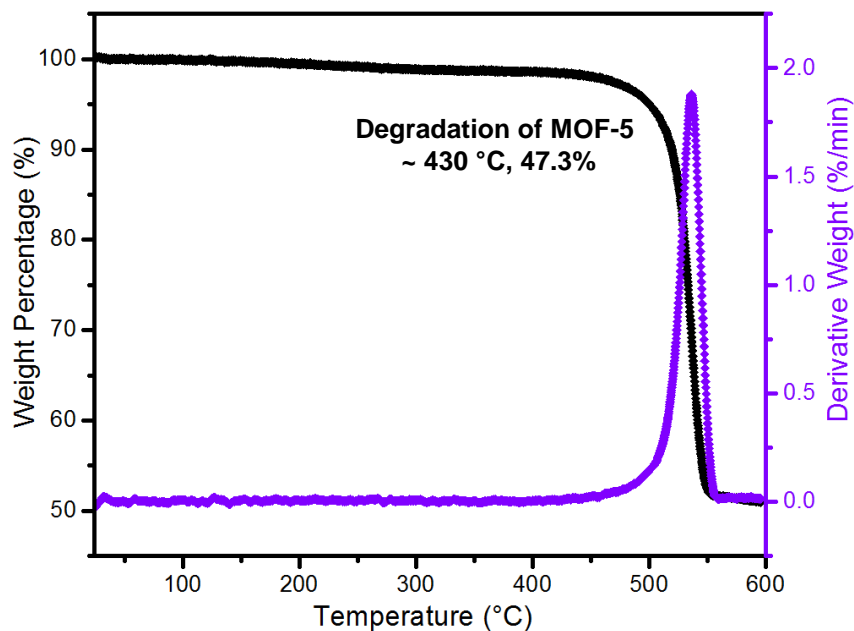


Figure S3. TGA weight loss (black) and differential weight loss (purple) curves of pristine MOF-5

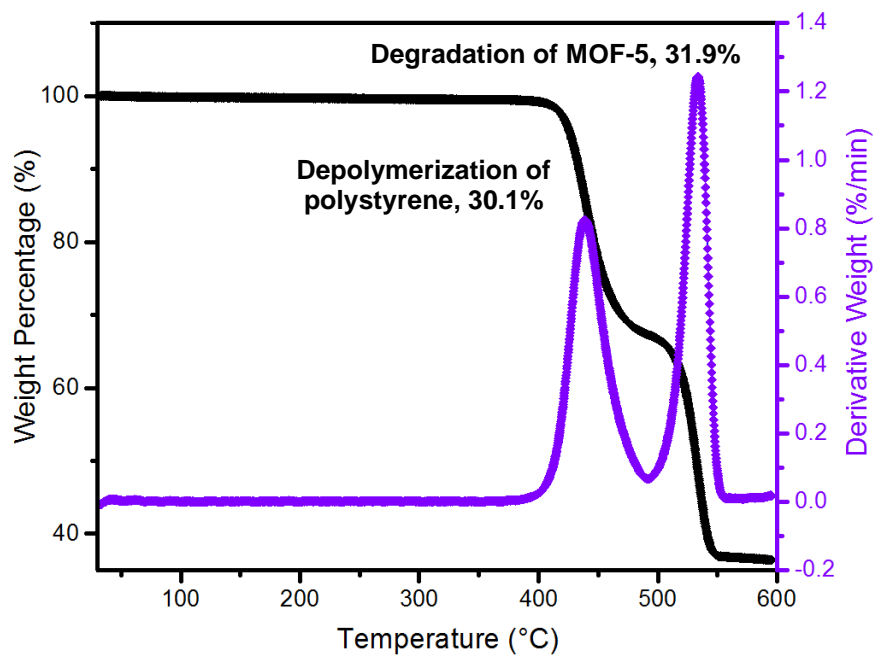


Figure S4. TGA weight loss (black) and differential weight loss (purple) curves of MOF-5-PS-24 h composite where depolymerization of polystyrene is well separated from decomposition of MOF-5

IV. Analysis of N₂ sorption data of the MOF-5-PS-4-24 h composites

Correlation of BET surface area of the MOF-5-PS-4-24 h composites to the duration of heating MOF-5 in styrene and percentage of MOF-5:

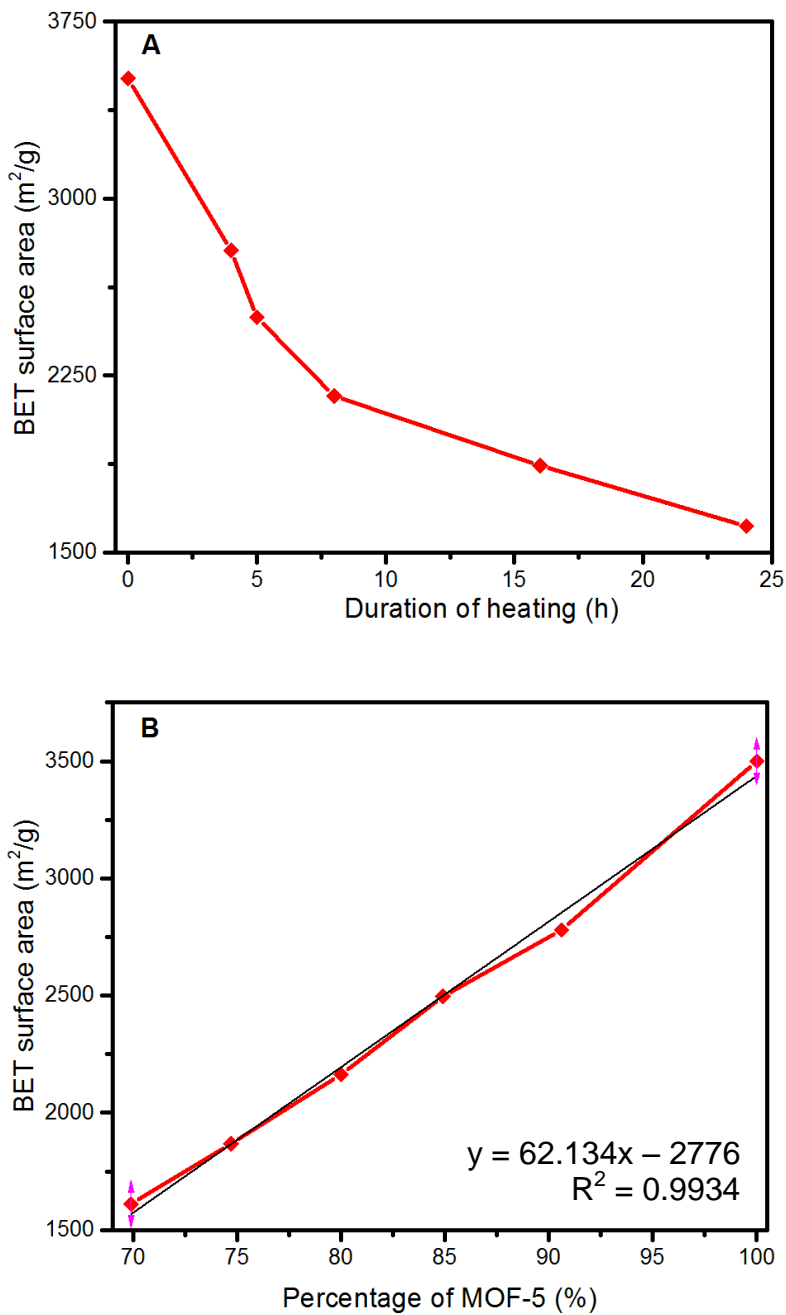


Figure S5. Correlation graphs: (A) BET surface area versus duration of heating and (B) BET surface area versus percentage of MOF-5 in the MOF-5-PS-4-24 h composites

V. Gel permeation chromatography (GPC)

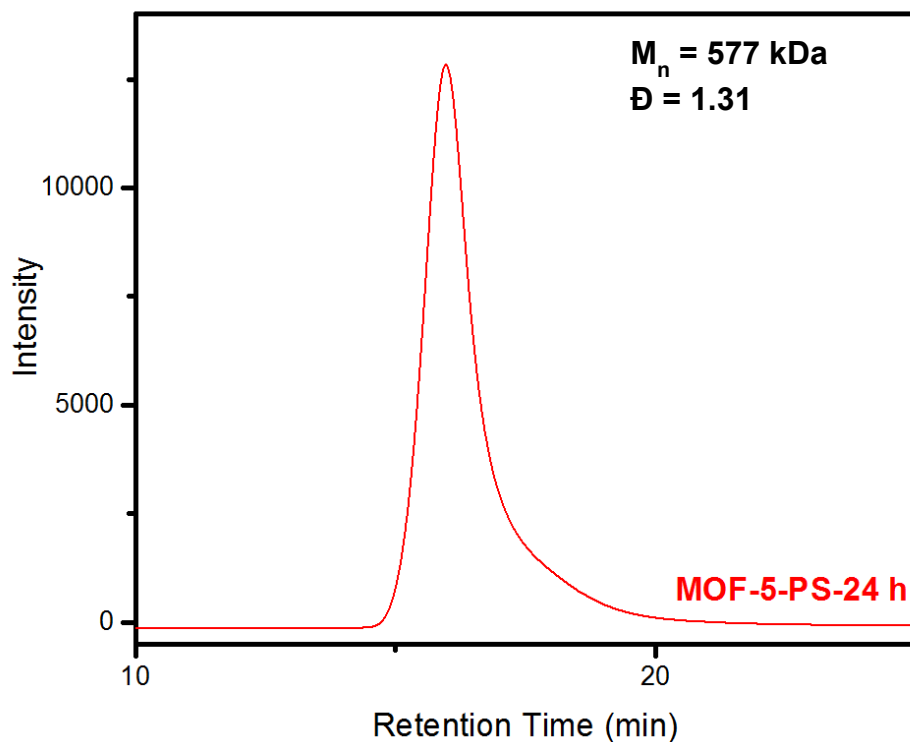


Figure S6. A representative GPC trace of high molecular weight polystyrene extracted from MOF-5-PS-24 h

Table S1. GPC data for polystyrene extracted after digestion of the MOF-5-PS-4–24 h composites

Composite	M _n	M _w	Đ
MOF-5-PS-4 h	481828	618424	1.28
MOF-5-PS-5 h	513819	689742	1.34
MOF-5-PS-8 h	541955	703823	1.30
MOF-5-PS-16 h	555162	715539	1.29
MOF-5-PS-24 h	576805	758366	1.31

VI. Calculation of the distribution of polystyrene through the MOF-5 network

(i) **The number of repeating units (n) of bulk polystyrene that fit a single pore of MOF-5**

- Bulk density of polystyrene = 1.04 g/mL
- MOF-5 pore diameter based on the argon pore size distribution measurements = 1.25 nm
- Molecular weight of styrene = 104.1 g/mol

The number of repeating units that fit a single pore of MOF-5 at maximum density, n , is given by;

$$\frac{n \times 104.1 \text{ g/mol}}{1.04 \text{ g/cm}^3} \times \frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{10^{21} \text{ nm}^3}{1 \text{ cm}^3} = (1.25 \text{ nm})^3$$

$$n \approx 12$$

(ii) **The number of pores of MOF-5 filled by bulk polystyrene of $M_n = 577$ kDa**

The volume of bulk polystyrene of $M_n = 577$ kDa is given by;

$$\frac{577,000 \text{ g/mol}}{1.04 \text{ g/cm}^3} \times \frac{1}{6.022 \times 10^{23} \text{ mol}^{-1}} \times \frac{10^{21} \text{ nm}^3}{1 \text{ cm}^3} = 921 \text{ nm}^3$$

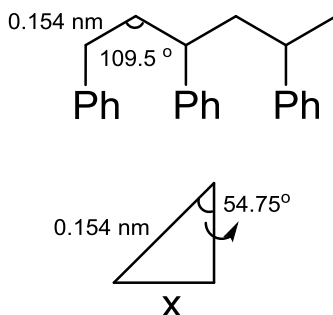
Thus, the diameter (d) of bulk polystyrene of $M_n = 577$ kDa is given by;

$$d = 2 \left(\frac{921 \text{ nm} \times 3}{4\pi} \right)^{1/3} = 12 \text{ nm}$$

The number of pores of MOF-5 filled by bulk polystyrene of $M_n = 577$ kDa is given by;

$$\frac{921 \text{ nm}^3}{(1.25 \text{ nm})^3} \approx 472$$

(iii) The number of repeating units of polystyrene that is stretched to a totally linear conformation that can fit a single pore of MOF-5



$$\sin 54.75^\circ = x/0.154 \text{ nm}$$

$$X = 0.126 \text{ nm}$$

The length of each repeating unit = $2x = 0.252 \text{ nm}$

The number of repeating units that can fit a single pore of MOF-5 = $1.25/0.252 \approx 5$

(iv) The number of pores of MOF-5 that can be filled by polystyrene of $M_n = 577 \text{ kDa}$ that is stretched to a totally linear conformation

The number of repeating units in polystyrene of $M_n = 577 \text{ kDa}$ is given by;

$$\frac{577,000}{104.1} = 5543$$

Based on (iii), the length of each repeating unit = 0.252 nm

Thus, the length of the stretched polystyrene = $5543 \times 0.252 = 1397 \text{ nm}$

Hence, the number of pores of MOF-5 that can be filled = $1397/1.25 \text{ nm} = 1117$

VII. Raman Spectra of pristine MOF-5 and MOF-5-PS-4-24 h composites

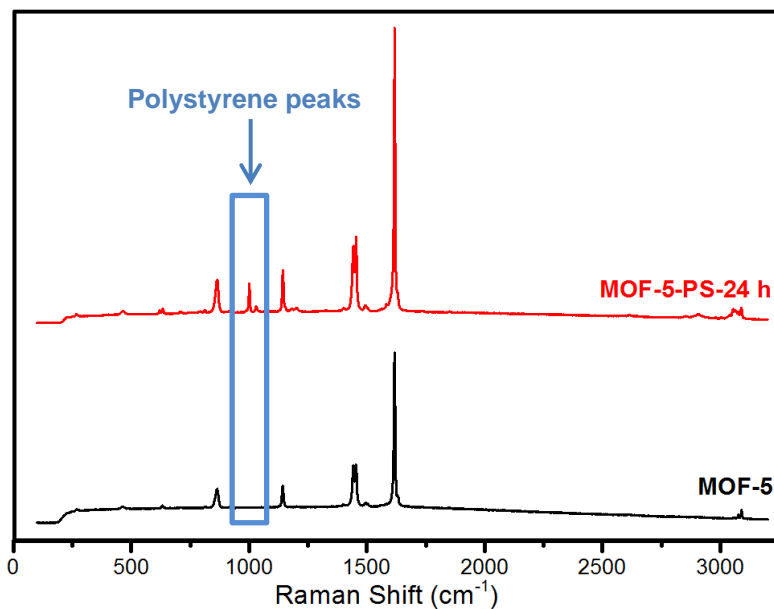


Figure S7. Raman spectra of pristine MOF-5 and MOF-5-PS-24 h with additional peaks of 1001 and 1030 cm⁻¹ from polystyrene

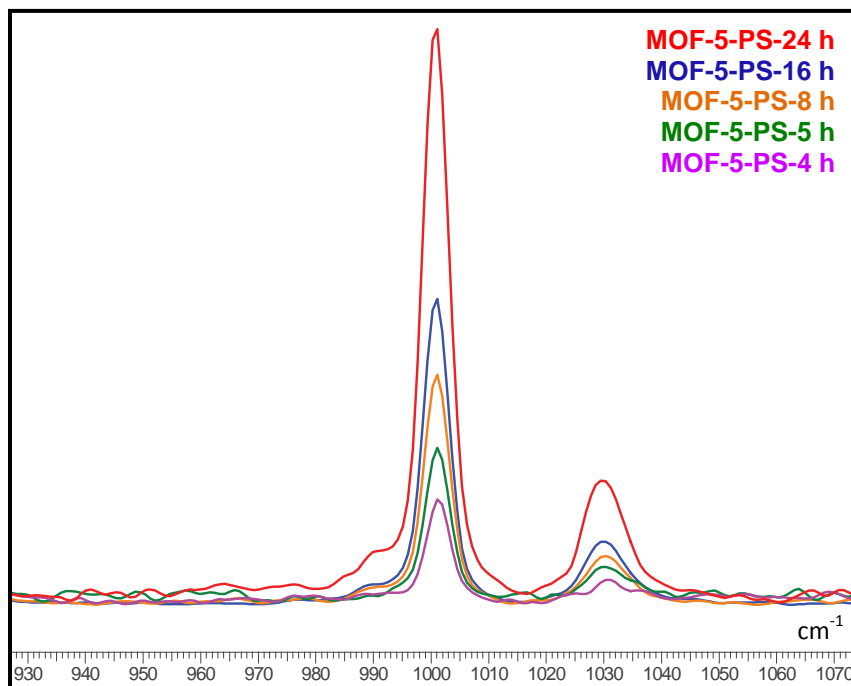


Figure S8. Raman peaks at 1001 and 1030 cm⁻¹ from MOF-5-PS-4-24 h composites after normalization of the MOF-5 peak at 1617 cm⁻¹

VIII. Argon pore size distribution analysis

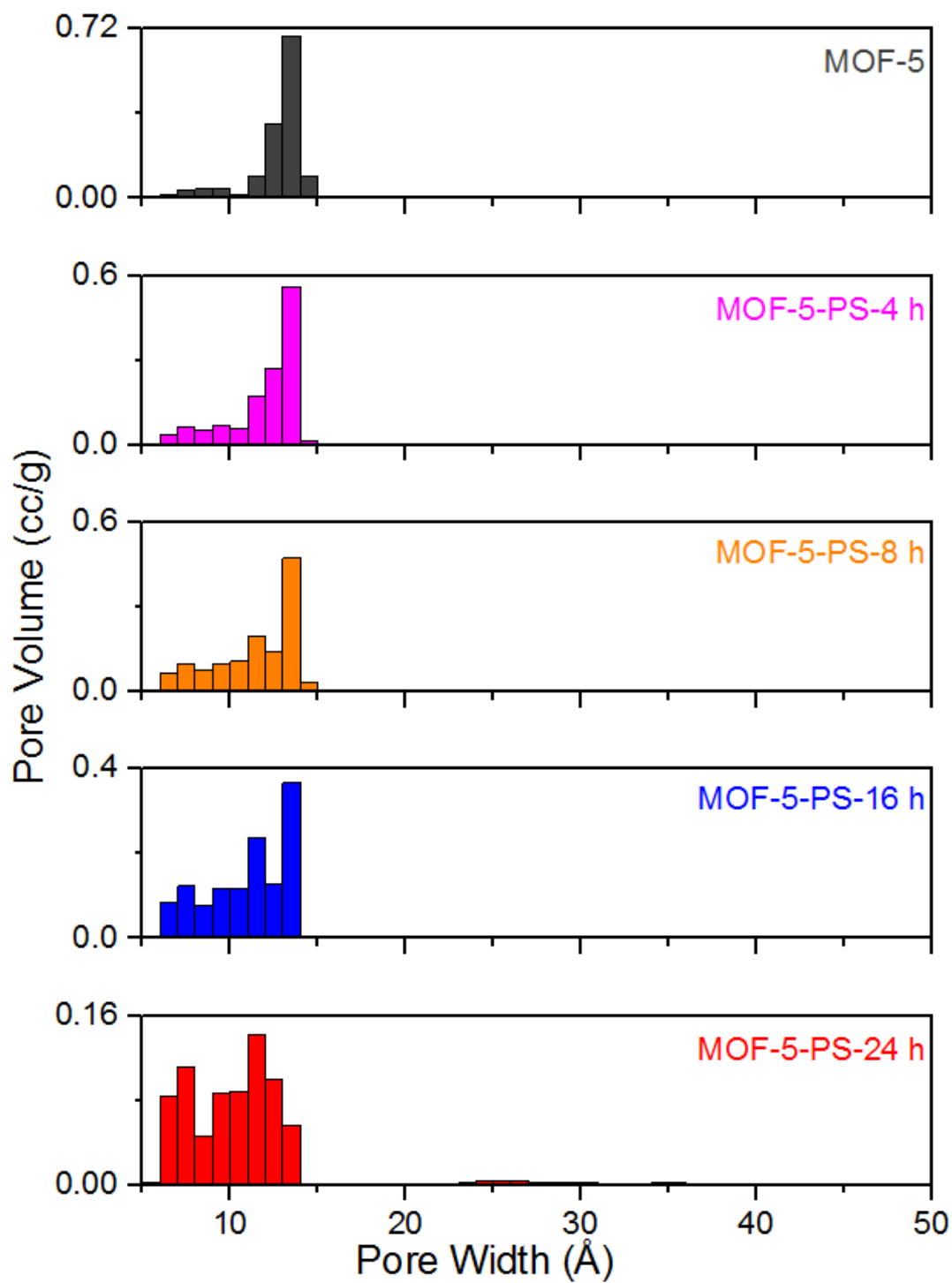


Figure S9. Pore volume histograms of pristine MOF-5 and MOF-5-PS-4, -8, -16, and -24 h composites

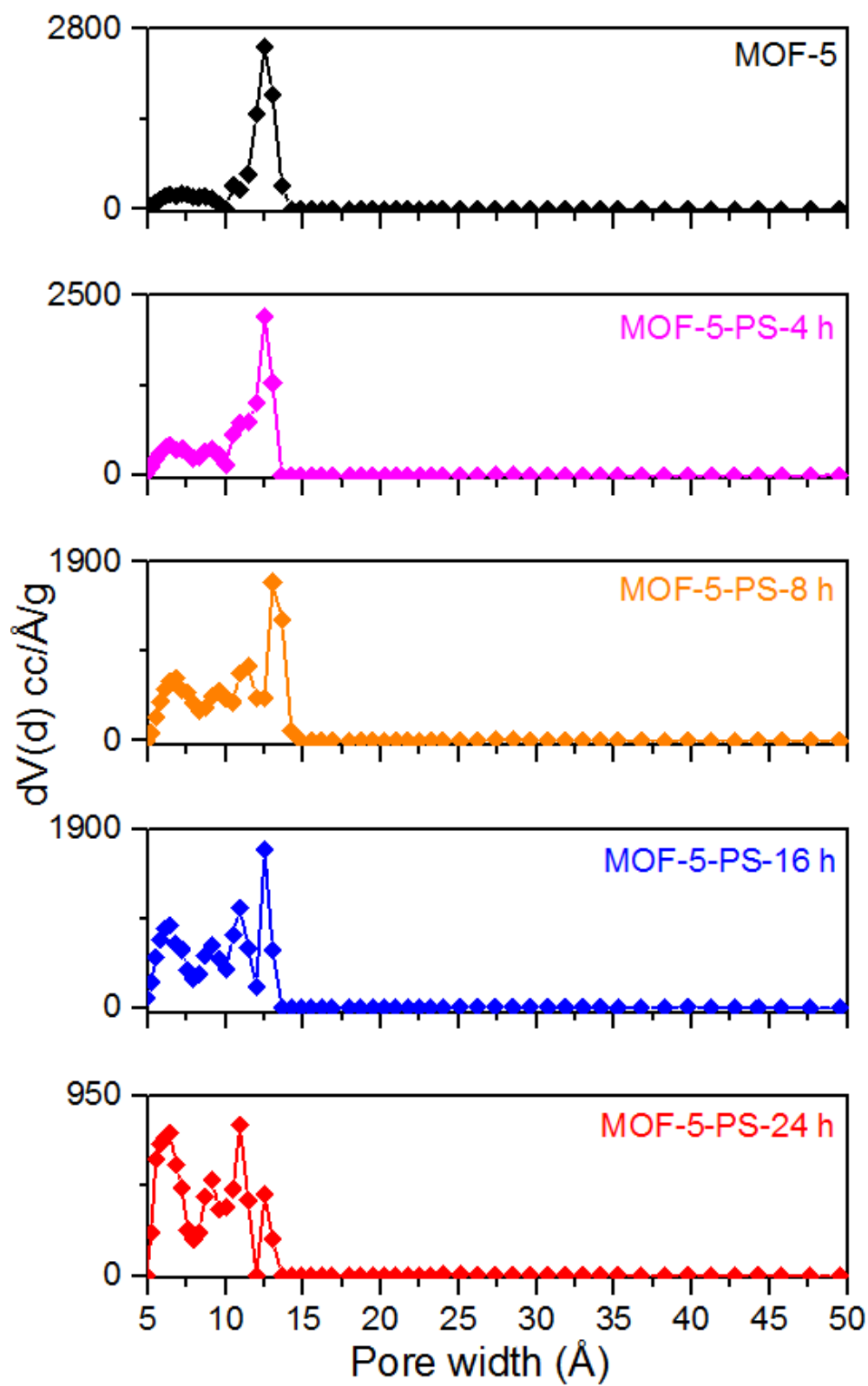


Figure S10. Differential pore volume distribution plots of MOF-5 and MOF-5-PS-4, -8, -16, and -24 h composites

IX. Stability of MOF-5-PS-24 h to humid air

(i) PXRD patterns of pristine MOF-5 and MOF-5-PS-24 h before and after exposing to 53% RH

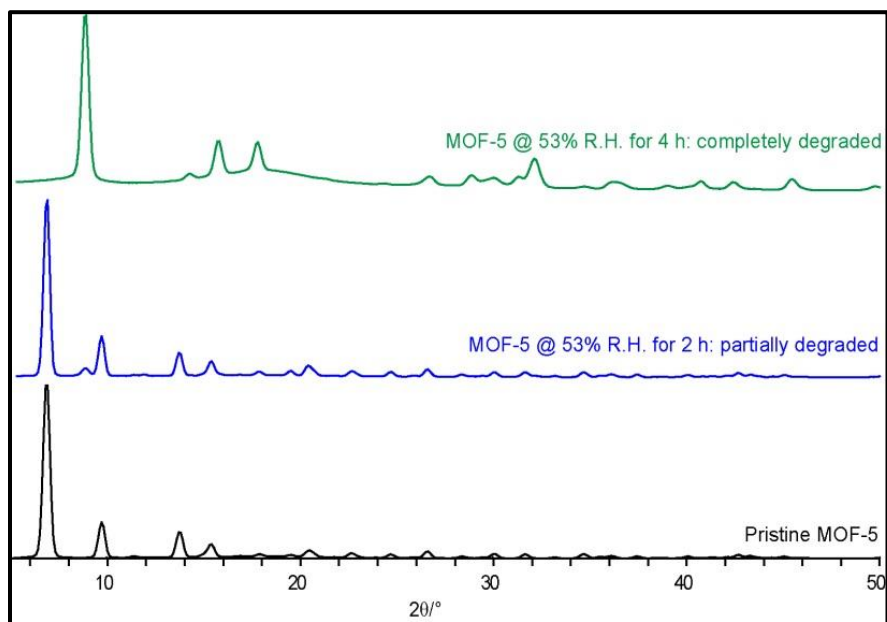


Figure S11. PXRD patterns of pristine MOF-5 and MOF-5 crystals after exposing to 53% RH

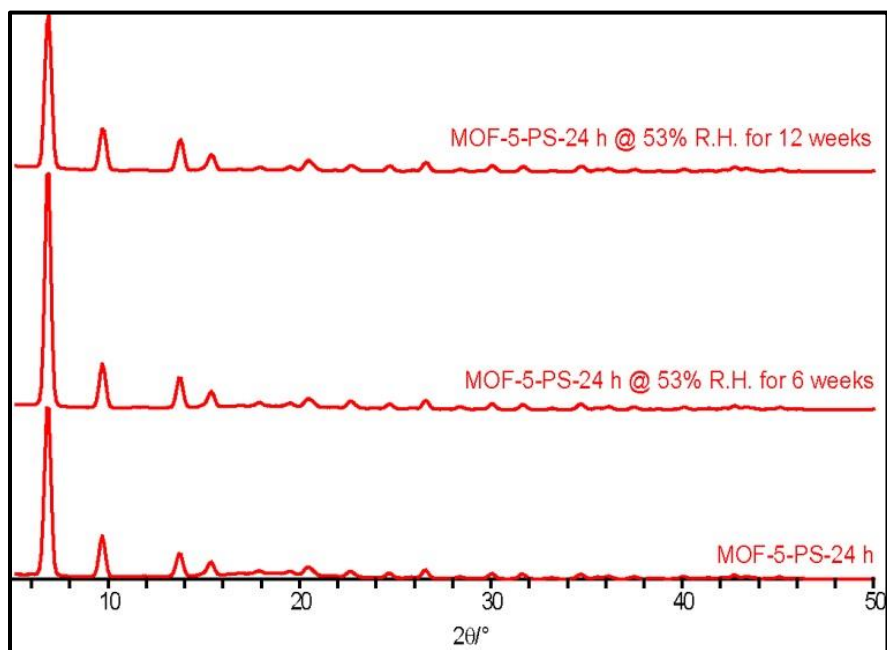


Figure S12. PXRD patterns of pristine MOF-5-PS-24 h and MOF-5-PS-24 h crystals after exposing to 53% RH

(ii) Effect on BET surface area of MOF-5-PS-24 h after exposure to 53% RH for 3 months:

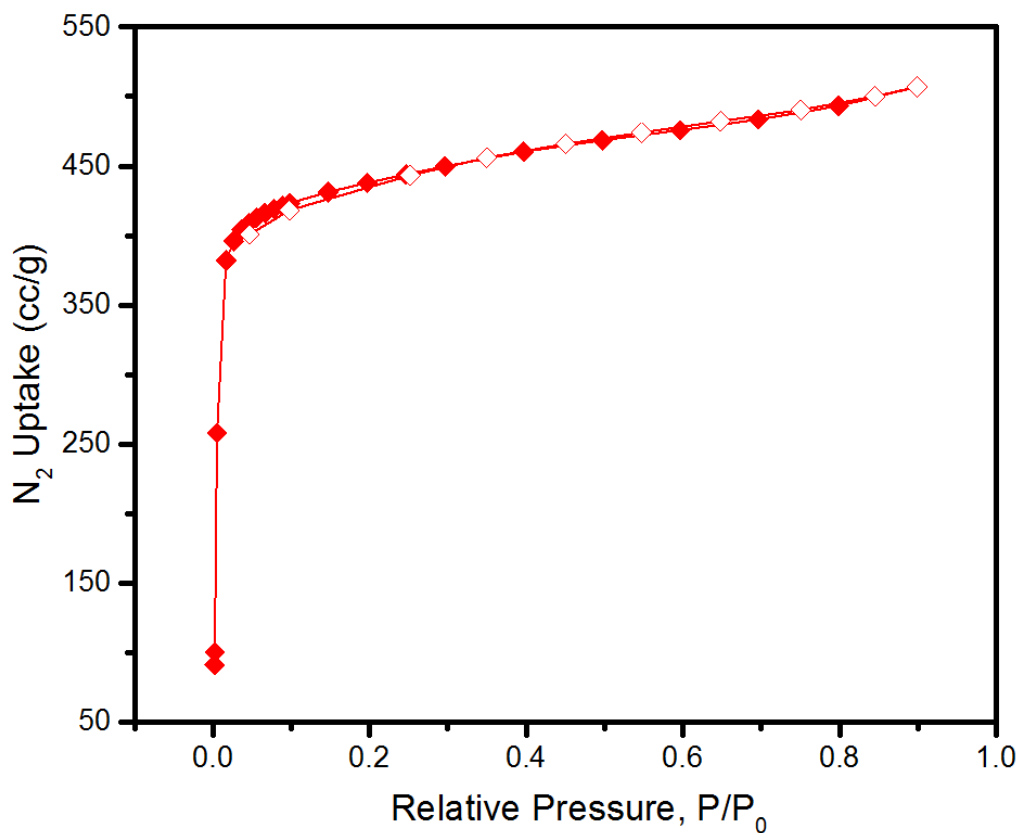


Figure S13. N_2 sorption isotherm of MOF-5-PS-24 h composite after exposure to 53% RH for 3 months. (BET surface area obtained: $1556 \text{ m}^2/\text{g}$)

Based on the BET surface area obtained from the N_2 isotherm ($1556 \text{ m}^2/\text{g}$), there is no significant reduction of surface area from the initial MOF-5-PS-24 h composite ($1611 \text{ m}^2/\text{g}$). Thus, the MOF-5-PS-24 h composite is hydrolytically stable for 3 months at 53% RH.

X. Solid-state UV-visible spectral data of MOF-5 and MOF-5-PS-24 h composite

Table S2. Peak maxima of the solid-state UV-visible spectra of methyl red and Nile red dye adsorbed on pristine MOF-5 and MOF-5-PS-24 h composite

Dye	Peak Maxima in MOF-5-PS-24 h (nm)	Peak Maxima in MOF-5 (nm)
Methyl red	566.8	575.6
	538.2	
Nile red	600.0	607.5
		631.7

XI. CO₂ adsorption data of MOF-5 and MOF-5-PS-24 h composite

Table S3. CO₂ adsorption capacities of pristine MOF-5 and MOF-5-PS-4, 8, and 24 h composites at 1 atm and 298 and 273 K

Sample	Temperature (K)	Uptake (cc/g)
MOF-5	298	16.6
	273	28.3
MOF-5-PS-4 h	298	19.9
	273	34.0
MOF-5-PS-8 h	298	21.2
	273	41.0
MOF-5-PS-24 h	298	18.8
	273	36.6

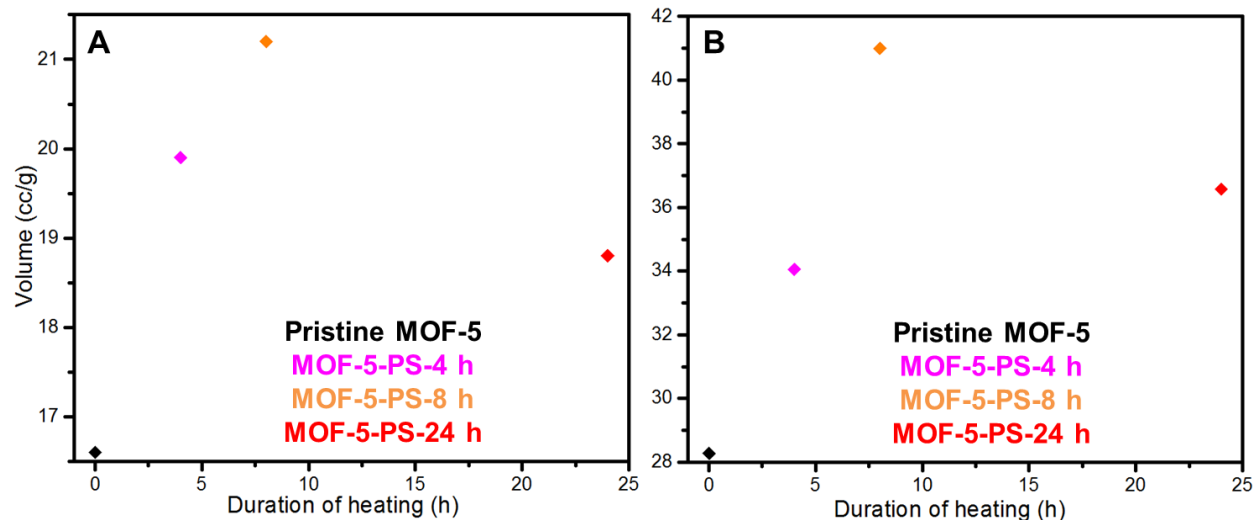


Figure S14. CO₂ adsorption capacities of MOF-5-PS-4, -8, and -24 h versus duration of heating styrene at 1 atm and 298 K (A) and 273 K (B)

XII. Disclaimer:

This work was prepared as an account of work sponsored by the Department of Energy (DOE), an agency of the United States Government, under grant number DE-SC0004888. Neither the United States or any agency thereof, nor any of their employees, makes any warranty, express or implied, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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