## Postsynthetic Modification at Orthogonal Reactive Sites on Mixed, Bifunctional Metal-Organic Frameworks

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# SUPPORTING INFORMATION

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### **General Methods for Metal-Organic Frameworks Experiments.**

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz for <sup>1</sup>H/ 100 MHz for <sup>13</sup>C). Carbon nuclear magnetic resonance spectroscopy was fully decoupled by broad band decoupling. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d= doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz (Hz).

### General Methods for Aerosol Time-of-Flight Mass Spectrometry Experiments.

Dry UiO materials were aerosolized using sonication and were drawn into an ATOFMS where they were accelerated to their terminal aerodynamic velocity. The particles pass through two continuous wave diode pumped 532 nm lasers beams (Crystal Laser, Reno, NV) whose positions are 6 cm apart. The time between the two scattering signals and the known distance are used to calculate the particle's velocity, which were converted to aerodynamic size using a calibration curve. The particle's velocity is also used to time the firing of a 266 nm laser desorption ionization laser pulse (Nd:YAG, Quantel, Newbury, UK, Ultra CFR ) at ~1 mJ (~10<sup>8</sup> W/cm<sup>2</sup>). The pulse ablates the particle and ions are detected using a dual polarity reflection time of flight mass spectrometer.<sup>1</sup> Rates of particle sampling were reported in Hz. ATOFMS sizes were calibrated using polystyrene latex spheres, sizes 0.23, 0.27, 0.33, 0.42, 0.61, 0.72, 0.81, 0.99, 1.50, 1.70, and 2.4  $\mu$ m (Invitrogen). UiO-66 classifications were assigned by identifying the presence of the ions CN<sup>-</sup>, Br<sup>-</sup>, or both in the negative ion spectrum of the particle. Typical spectra of UiO-66-NH<sub>2</sub>, UiO-66-Br, and UiO-66-(Br)(NH<sub>2</sub>) are given in Figures S1-S3, respectively. Particles with no negative ion spectra were removed from this analysis.

## **Experimental Procedure for Dry Aerosol Generation.**

Approximately 100 mg of dry UiO material was placed in a 1 L volumetric flask. Aerosol was generated by constant sonication using a Bransonic 3510R-MTH sonicator. ~1-2 lpm of dry N<sub>2</sub> flowed into the volumetric flask carrying the MOF into a dilution chamber (~7900 cm<sup>3</sup>). A constant 1 lpm was brought into the ATOFMS for analysis at ~10-12 Hz. Between sample runs the dilution chamber was purged with dry N<sub>2</sub> until no aerosol particles were observed (<0.001Hz).

#### **Experimental Procedures for MOFs Synthesis.**

*UiO-66-NH<sub>2</sub>, UiO-66-Br Synthesis.* UiO-66-NH<sub>2</sub>, and UiO-66-Br were prepared and activated as previously described.<sup>2</sup>

*Mixed UiO-66-(Br)(NH<sub>2</sub>) Synthesis.* 2-Amino-1,4-benzenedicarboxylic acid (NH<sub>2</sub>-BDC, 32 mg, 0.175 mmol), 2-bromo-1,4-benzenedicarboxylic acid (Br-BDC, 43 mg, 0.175 mmol), ZrCl<sub>4</sub> (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 °C for 24 h. The microcrystalline powders were then isolated by centrifugation. The solids were washed three times with 10 mL of MeOH, and after the last wash, the material was transferred to a clean vial containing 10 mL of MeOH and was left to soak in MeOH overnight. The solid material was then rinsed with 10 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solid was isolated by centrifugation, air dried, and then dried at 120 °C in an oven.

### **Experimental Procedures for Postsynthetic Modification**

Acylation on UiO-66-(Br)(NH<sub>2</sub>) or UiO-66-(CN)(NH<sub>2</sub>).<sup>2</sup> Fully dried UiO-66-(Br)(NH<sub>2</sub>) or UiO-66-(CN)(NH<sub>2</sub>) (64 mg or 61 mg, 0.1 mmol of NH<sub>2</sub>) was treated with 1 mL solution of CHCl<sub>3</sub> containing acetic anhydride (11 mg, 0.11 mmol) and heated at 55 °C for 24 h. After cooling to room temperature, the sample was washed with 10 mL of CHCl<sub>3</sub> by centrifugation, and dried in a isothermal oven at 120 °C for 6 h. The cycle of exposure to acetic anhydride, centrifugation, and

drying, was repeated a total of three times to achieve full conversion to the amide.

Yield for UiO-66-(Br)(NH<sub>2</sub>) to UiO-66-(Br)(AM1): >95% by <sup>1</sup>H NMR from three independent samples.

Yield for UiO-66-(CN)(NH<sub>2</sub>) to UiO-66-(CN)(AM1):  $75\pm6\%$  by <sup>1</sup>H NMR from three independent samples.

*Cyanation on UiO-66-(Br)(NH<sub>2</sub>) or UiO-66-(Br)(AM1).*<sup>3</sup> Fully dried UiO-66-(Br)(NH<sub>2</sub>) or UiO-66-(Br)(AM1) (51 mg or 48 mg, 0.075 mmol of Br) and copper cyanide (9 mg, 0.0975 mmol) were suspended in 1 mL of NMP in a microwave tube. The mixture was heated in a microwave reactor at 170 °C for 10 min without stirring (Maximum power = 200 W). After cooling to room temperature, the suspension was diluted with 10 mL of DMF and the solids were isolated by centrifugation. After centrifugation, 10 mL of 0.01 M KCN was added to remove remaining copper and the solids were isolated by centrifugation again. The solids were washed three times with 10 mL of MeOH, and after the last wash, the material was transferred to a clean vial containing 10 mL of MeOH and left to soak in MeOH overnight. The solid material was then rinsed with 10 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solid was isolated by centrifugation, air dried, and then dried at 120 °C in an oven.

Yield for UiO-66-(Br)(NH<sub>2</sub>) to UiO-66-(CN)(NH<sub>2</sub>): >95% by <sup>1</sup>H NMR from three independent samples.

Yield for UiO-66-(Br)(AM1) to UiO-66-(CN)(AM1): >95% by <sup>1</sup>H NMR from three independent samples.

*Digestion and Analysis by* <sup>1</sup>*H NMR*. Approximately 10 mg of UiO-66 material was dried under vacuum at 100 °C and digested with sonication in 580  $\mu$ L of CD<sub>3</sub>OD and 20  $\mu$ L of HF (48% aqueous solution).

Mass Spectrometry Analysis. Electrospray ionization mass spectrometry (ESI-MS) was performed

using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite. Approximately 5 mg of the sample was digested with sonication in 1 mL of MeOH and 10  $\mu$ L of HF (48% aqueous solution).

*Thermal Analysis.* Approximately 10-15 mg of exchanged UiO-66 series was used for TGA measurements. Samples were analyzed under a stream of  $N_2$  using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.

*PXRD Analysis.* Approximately 20-30 mg of UiO-66 series was dried at 120 °C prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka (l = 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02° in 20, and a 20 range of 5-55°.

*BET Surface Area Analysis*. Approximately 50 mg of UiO-66 series was evacuated on a vacuum line overnight at room temperature. The sample was then transferred to a pre-weighed sample tube and degassed at room temperature on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. The sample tube was re-weighed to obtain a consistent mass for the degassed UiO-66 series. BET surface area ( $m^2/g$ ) measurements were collected at 77 K by N<sub>2</sub> on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.

*Scanning Electron Microscopy.* Approximately 5 mg of UiO-66 material was evacuated on a vacuum line overnight at room temperature. Half of the sample was then transferred to carbon black on a sample holder disk. The sample was coated using a Cr-sputter coating to preventing the image from being too bright. A Philips XL30 ESEM instrument was used for acquiring images using a 5 kV-30 kV energy source under vacuum. Around 18000× scale images were collected.

*Dynamic Light Scattering*. Dynamic Light Scattering (DLS) size distribution was performed using a Zeta Sizer from Malvern. Approximately 5 mg of UiO-66 material was placed in 995  $\mu$ L of water (0.5 wt% water solution) and the sample was sonicated for 1 min. Approximately 100  $\mu$ L of sample solution was transferred to disposable cuvette cell to acquire the measurements.



**Fig. S1** Thermogravimetric analysis of activated (after BET analysis) UiO-66-Br, UiO-66-NH<sub>2</sub>, and UiO-66-(Br)(NH<sub>2</sub>).

 Table S1 BET surface areas of UiO-66 series; reference numbers of mono-functionalized UiO-66

 values (left),<sup>2,3</sup> and bifunctionalized UiO-66 values (right).

Monofunctionalized MOF	BET $(m^2/g)$	Bifunctionalized MOF	BET (m <sup>2</sup> /g)
UiO-66-Br	851	UiO-66-(Br)(NH <sub>2</sub> )	923±22
UiO-66-NH <sub>2</sub>	1112	UiO-66-(Br)(AM1)	763±28
UiO-66-CN	661	UiO-66-(CN)(NH <sub>2</sub> )	984±55
UiO-66-AM1	818	UiO-66-(CN)(AM1)	827±21



**Fig. S2** <sup>1</sup>H NMR spectra of ratio-controlled UiO-66-(Br)<sub>x</sub>(NH<sub>2</sub>)<sub>y</sub> after digestion. 50  $\mu$ L of DMSO-*d*<sub>6</sub> was employed during NMR sample preparation for better peak separation.

**Table S2** Ratio of ligands used in the synthesis of mixed UiO-66 materials compared to the ratio of ligands found in the crystalline products as determined by <sup>1</sup>H NMR analysis upon digestion.



Entry	Br-BDC	NH <sub>2</sub> -BDC	Br-BDC <sup>a</sup>	NH <sub>2</sub> -BDC <sup>a</sup>
	m	n	X	У
1	4	1	3.7	1
2	2	1	1.8	1
3	1	1	1	1.1
4	1	2	1	2.4
5	1	4	1	4.1

<sup>*a*</sup> Ratio of Br-BDC and NH<sub>2</sub>-BDC were determined by <sup>1</sup>H NMR integral analysis after MOF digestion (see Fig. S2).



Fig. S3 ESI-MS analysis of digested UiO-66-(Br)(NH<sub>2</sub>).



Fig. S4 ATOFMS positive ion (top) and negative ion (bottom) mass spectra of UiO-66-NH<sub>2</sub>.

0

0



Fig. S5 ATOFMS positive ion (top) and negative ion (bottom) mass spectra of UiO-66-Br.

-40

-60

m/z

-80

-20

-120

.....

-100



Fig. S6 ATOFMS positive ion (top) and negative ion (bottom) mass spectra of mixed UiO-66-(Br)(NH<sub>2</sub>).



Fig. S7 Powder X-ray diffraction spectra of ratio-controlled UiO-66-(Br)<sub>x</sub>(NH<sub>2</sub>)<sub>y</sub>.



**Fig. S8** Full range <sup>1</sup>H NMR spectra of UiO-66-(Br)(NH<sub>2</sub>), UiO-66-(Br)(AM1), UiO-66-(CN)(NH<sub>2</sub>), and UiO-66-(CN)(AM1).



Fig. S9 Powder X-ray diffraction spectra of MOFs after PSM.



**Fig. S10** Thermogravimetric analysis of activated (after BET analysis) UiO-66-(Br)(NH<sub>2</sub>), UiO-66-(Br)(AM1), UiO-66-(CN)(NH<sub>2</sub>), and UiO-66-(CN)(AM1).



**Fig. S11** <sup>1</sup>H NMR spectra of direction synthesized UiO-66-(Br)(AM1) (red), UiO-66-(CN)(NH<sub>2</sub>) (blue), and UiO-66-(CN)(NH<sub>2</sub>) (green).



**Fig. S12** Power X-ray diffraction patterns of direct synthesized UiO-66-(Br)(AM1) (red), UiO-66-(CN)(NH<sub>2</sub>) (blue), and UiO-66-(CN)(AM1) (green).



Fig. S13 Scanning electron microscope (SEM) images of bifunctional UiO-66 series; a) UiO-66-(Br)(AM1) from PSM, b) UiO-66-(Br)(AM1) from direct synthesis, c) UiO-66-(CN)(NH<sub>2</sub>) from PSM, d) UiO-66-(CN)(NH<sub>2</sub>) from direct synthesis, e) UiO-66-(CN)(AM1) from PSM, f) UiO-66-(CN)(AM1) from direct synthesis.



**Fig. S14** Dynamic light scattering (DLS) size distribution of bifunctional UiO-66 prepared via PSM route (solid lines) versus direct solvothermal syntheses (dotted lines).

## Reference

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