## SUPPLEMENTARY INFORMATION

## WATER SORPTION STUDIES WITH MESOPOROUS MULTIVARIATE MONOLITHS BASED ON UiO-66

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**Figure S1:** Representative SEM images for the monoliths (a)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B and (b)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A, contrasting the smoothness of the surface of the monolith before thermolysis (a) compared to after thermolysis (b).



**Figure S2:** Representative low magnification SEM images for the monoliths (a)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B and (b)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A, contrasting the smoothness of the surface of the monolith before thermolysis (a) compared to after thermolysis (b).



Figure S3: Representative low magnification TEM images of (a)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B and (b)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A.



Figure S4: Representative TEM images of (a)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B and (b)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A.



Figure S5: SEM-EDX plot for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B. Inset: Area scanned. The sample was sputter-coated with Cr for analysis.



**Figure S6:** EDX elemental mapping showing how the elements are dispersed in  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B: (a) carbon, (b) oxygen, (c) composite map, (d) zirconium. All the elements are evenly dispersed throughout the monolith, as shown in (c).



Figure S7: SEM-EDX plot for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A. Inset: Area scanned. The sample was sputter-coated with Cr for analysis.



**Figure S8:** EDX elemental mapping showing how the elements are dispersed in  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A: (a) carbon, (b) oxygen, (c) composite map, (d) zirconium, and (e) chlorine. All the elements are evenly dispersed throughout the monolith, as shown in (c).



**Figure S9:** <sup>1</sup>H NMR spectrum of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B (500.200 MHz). Spectrum recorded at 27 °C, using DMSO-d<sub>6</sub> solvent after sample was initially digested in concentrated D<sub>2</sub>SO<sub>4</sub>. Inset: Expansion of the region  $\delta$  8.2-7.3 ppm.



**Figure S10:** <sup>1</sup>H NMR spectrum of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A (500.200 MHz). Spectrum obtained at 27 °C, using DMSO-d<sub>6</sub> solvent after sample was initially digested in concentrated D<sub>2</sub>SO<sub>4</sub>. Inset left: Expansion of the region  $\delta$  8.5-0.0 ppm. Inset right: Expansion of the aromatic region suggesting non-zero levels of BDC-NH<sub>2</sub> after thermolabilization.



**Figure S11:** <sup>13</sup>C(<sup>1</sup>H) NMR spectrum of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B (125.775 MHz). Spectrum obtained at 27 °C, using DMSO-d<sub>6</sub> solvent after sample was initially digested in concentrated D<sub>2</sub>SO<sub>4</sub>.



**Figure S12:** <sup>13</sup>C(<sup>1</sup>H) NMR spectrum of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A (125.775 MHz). Spectrum obtained at 27 °C, using DMSO-d<sub>6</sub> solvent after sample was initially digested in concentrated D<sub>2</sub>SO<sub>4</sub>.



**Figure S13:** Stacked <sup>13</sup>C(<sup>1</sup>H) NMR spectra of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B (blue) and  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A (red) shown in Figures S11-S12.

**Table S1:** Nanoindentation data for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B and  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A. The average values and standard deviations were determined from 32 measurements.

SAMPLE	MAX DEPTH (NM)	INDENTATION MODULUS (GPa)	HARDNESS (MPa)
<sub>mono</sub> UiO-66-NH <sub>2</sub> -30%-B	1000	$6.09\pm0.18$	185 ± 10
	2000	$5.98\pm0.24$	180 ± 14
monoUiO-66-NH2-30%-A	1000	$4.80 \pm 0.25$	169 ± 16
	2000	$4.58 \pm 0.20$	155 ±13



**Figure S14**: Low pressure  $N_2$  gas adsorption data for isotherms measured at 77 K for (a)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B (solid triangles represent adsorption, and open triangles denote desorption); (b)  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A (solid squares represent adsorption, and open squares denote desorption).



**Figure S15:** Load-displacement (*P-h*) nanoindentation data for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B. 2 sets of 16 indents were performed in different areas, setting the maximum indentation depth to 1000 nm. The highly reproducible *P-h* data reflect the homogeneity of the sample tested.



**Figure S16:** Hardness of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged hardness was determined using data collected over the 500-1000 nm indentation depth range, yielding 185 ± 10 MPa.



**Figure S17:** Indentation modulus,  $E^*$ , of <sub>mono</sub>UiO-66-NH<sub>2</sub>-30%-B plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged indentation modulus was determined using data collected over the 500-1000 nm indentation depth range, yielding 6.09  $\pm$  0.18 GPa.



**Figure S18:** Load-displacement (*P-h*) nanoindentation data for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B. 2 sets of 16 indents were performed in different areas, setting the maximum indentation depth to 2000 nm. The highly reproducible *P-h* data reflect the homogeneity of the sample tested.



**Figure S19:** Hardness of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged hardness was determined using data collected over the 500-2000 nm indentation depth range, yielding  $180 \pm 14$  MPa.



**Figure S20:** Indentation modulus,  $E^*$ , of <sub>mono</sub>UiO-66-NH<sub>2</sub>-30%-B plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged indentation modulus was determined using data collected over the 500-2000 nm indentation depth range, yielding 5.98 ± 0.24 GPa.



**Figure S21:** Load-displacement (*P-h*) nanoindentation data for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A. 2 sets of 16 indents were performed in different areas, setting the maximum indentation depth to 1000 nm. The highly reproducible *P-h* data reflect the homogeneity of the sample tested.



**Figure S22:** Hardness of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged hardness was determined using data collected over the 500-1000 nm indentation depth range, yielding 169 ± 16 MPa.



**Figure S23:** Indentation modulus,  $E^*$ , of <sub>mono</sub>UiO-66-NH<sub>2</sub>-30%-A plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged indentation modulus was determined using data collected over the 500-1000 nm indentation depth range, yielding 4.80  $\pm$  0.25 GPa.



**Figure S24:** Load-displacement (*P-h*) nanoindentation data for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A. 2 sets of 16 indents were performed, setting the maximum indentation depth to 2000 nm. The highly reproducible *P-h* data reflect the homogeneity of the sample tested.



**Figure S25:** Hardness of  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged hardness was determined using data collected over the 500-2000 nm indentation depth range, yielding 155 ± 13 MPa.



**Figure S26:** Indentation modulus,  $E^*$ , of <sub>mono</sub>UiO-66-NH<sub>2</sub>-30%-A plotted as a function of indentation depth. 2 sets of 16 indents were performed. Averaged indentation modulus was determined using data collected over the 500-2000 nm indentation depth range, yielding 4.58  $\pm$  0.20 GPa.



**Figure S27:** DVS water sorption kinetics over three isotherm cycles for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B using Intrinsic-DVS instrument at 27 °C. The sample was heated for 6 h at 40 °C and 0% RH between cycles.



**Figure S28:** Triplicated DVS water sorption isotherms for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-B using Intrinsic-DVS instrument at 27 °C. The sample was heated for 6 h at 40 °C and 0% RH between cycles.



**Figure S29**: Triplicated DVS water sorption isotherms for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A at 27 °C. The sample was heated for 6 h at 40 °C and 0% RH between cycles.



**Figure S30:** DVS water sorption kinetics over three isotherm cycles for  $_{mono}$ UiO-66-NH<sub>2</sub>-30%-A at 27 °C. The sample was heated for 6 h at 40 °C and 0% RH between cycles.