Supporting Information

Spray drying for making Covalent Chemistry: Post-Synthetic Modification of Metal-Organic Frameworks

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S1
**Section S1: Materials, methods and synthetic procedures**

**Materials and methods**

Zirconium chloride, zinc acetate hexahydrate, 2-aminoterephthalic acid, 4-pyridinecarboxaldehyde, 2-pyridinecarboxaldehyde, salicylaldehyde, trimethylamine, butylamine and hexamethylenediamine were purchased from Sigma Aldrich. 2-imidazolecarboxaldehyde was obtained from TCI. Dimethylformamide was obtained from Fisher Chemical. Ethanol absolute was purchased from Scharlab S.L. All the reagents were used without further purification. Deionised water was obtained with a Milli-Q® system (18.2 MΩ·cm).

ESI-MS spectra were recorded on a microTOF-Q Bruker Daltoniks spectrometer. X-ray powder diffraction (XRPD) patterns were collected on an X'Pert PRO MPDP analytical diffractometer (Panalytical) at 45 kV, 40 mA using CuKα radiation (λ = 1.5419 Å). Nitrogen adsorption and desorption measurements were done at 77 K using an Autosorb-IQ-AG analyser (Quantachrome Instruments). Field-Emission Scanning Electron Microscopy (FESEM) images were collected on a FEI Magellan 400L scanning electron microscope at an acceleration voltage of 2.0 KV, using aluminium as support. TEM images were collected on a Transmission Electron Microscopy (TEM; FEI Tecnai G2 F20) at 200 KV. Fourier transform infra-red (FT-IR) spectra were recorded on a Bruker Tensor 27FTIR spectrometer equipped with a Golden Gate diamond attenuated total reflection (ATR) cell, in transmittance mode at room temperature. Static contact angle measurements were performed on hand-packed powders using a Krüss DSA 100 drop shape analyzer. A 4-μL droplet of deionized water was placed onto the sample surface in sessile mode at a speed of 135.2 μL/min. $^{13}$C($^1$H) cross-polarization (CP-MAS) experiments were performed at room temperature on a Bruker Avance III 9.4T spectrometer equipped with a double channel 4.0 mm MAS probe. Sample spinning was set to 12 kHz in all experiments. $^1$H NMR experiments of the imine molecules and of the digested ZIFs samples were carried out on a Bruker Avance DRX-250 spectrometer. $^1$H-NMR spectra of the digested UiO-66s were collected on a 400MHz Bruker AVANCE III spectrometer.

**Synthesis of Imines**

**Synthesis of 2-((pyridin-4-ylmethylene)amino)terephthalic acid**

\[
\begin{align*}
\text{HO} & \quad \text{NH}_2 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{N} \\
\text{HO} & \quad \text{OH}
\end{align*}
\]

2-aminoterephthalic acid (0.150 g, 0.828 mmol) was dispersed in 15 mL of ethanol by sonication for 10 min. Then, 80 µL, 160 µL or 240 µL of 4-pyridinecarboxaldehyde (0.85, 1.70 or 2.55 mmol, respectively) was added to the dispersion at room temperature and stirring for 5 min. The resulting
reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min (Conversion for 1:3 eq bdc-NH₂:4PC: 92 %). ¹H NMR (250 MHz, DMSO-d₆): δ (ppm) = 8.76 – 8.69 (m, 2H), 8.18 (d, J = 2.1 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.55 (d, J = 1.5 Hz, 1H), 7.42 (dd, d, = 8.2, 1.6 Hz, 1H). ¹³C NMR (63 MHz, DMSO-d₆): δ (ppm) = 169.05, 166.45, 162.62, 150.23, 148.41, 144.49, 136.80, 130.26, 122.15, 121.88, 119.58, 116.86. m/z (ESI) calculated for [C₁₄H₁₀N₂O₄-H]: 269.0568; found 269.0562 [M-H]⁻.

Synthesis of 2-((pyridin-2-ylmethylene)amino)terephthalic acid

2-aminoterephthalic acid (0.150 g, 0.828 mmol) was dispersed in 15 mL of ethanol by sonication for 10 min. Then, 2-Pyridinecarboxaldehyde (0.24 mL, 2.52 mmol) was added to the dispersion at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min (Conversion: 87 %). ¹H NMR (250 MHz, DMSO-d₆) δ (ppm) = 8.67 (d, J = 4.8 Hz, 1H), 8.20 (s, 1H), 7.96 (dd, J = 7.8, 1.7 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.72 (dd, d, = 7.5, 1.4 Hz, 1H), 7.60 (d, J = 1.7 Hz, 1H), 7.52 (ddd, J = 7.7, 4.8, 1.4 Hz, 1H), 7.39 (dd, d, = 6.9, 1.5 Hz, 1H). ¹³C NMR (63 MHz, DMSO-d₆) δ (ppm) = 169.05, 167.07, 162.85, 150.26, 149.12, 148.39, 137.69, 135.15, 131.41, 128.44, 124.86, 121.68, 119.17, 117.56. m/z (ESI) calculated for [C₁₄H₁₀N₂O₄-H]: 269.0568; found 269.0562 [M-H]⁻.

Synthesis of 2-((2-hydroxybenzylidene)amino)terephthalic acid

2-aminoterephthalic acid (0.150 g, 0.828 mmol) was dispersed in 15 mL of ethanol by sonication for 10 min. Then, salicylaldehyde (0.265 mL, 2.49 mmol) was added to the dispersion at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min (Conversion: 87 %). ¹H NMR (250 MHz, DMSO-d₆) δ (ppm) = 8.67 (d, J = 4.8 Hz, 1H), 8.20 (s, 1H), 7.96 (dd, J = 7.8, 1.7 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.72 (dd, d, = 7.5, 1.4 Hz, 1H), 7.60 (d, J = 1.7 Hz, 1H), 7.52 (ddd, J = 7.7, 4.8, 1.4 Hz, 1H), 7.39 (dd, d, = 6.9, 1.5 Hz, 1H). ¹³C NMR (63 MHz, DMSO-d₆) δ (ppm) = 169.05, 167.07, 162.85, 150.26, 149.12, 148.39, 137.69, 135.15, 131.41, 128.44, 124.86, 121.68, 119.17, 117.56. m/z (ESI) calculated for [C₁₄H₁₀N₂O₄-H]: 269.0568; found 269.0562 [M-H]⁻.
Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). An orange powder was collected after 5 min (Conversion: 75 %). $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ (ppm) = 8.95 (S, 1H), 7.94 (d, $J = 7.2$ Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.66 (m, 1H), 7.38 (s, 1H), 7.07 – 6.91 (m, 3H). $^{13}$C NMR (63 MHz, DMSO-$d_6$) $\delta$ (ppm) = 169.05, 167.08, 166.42, 160.71, 151.19, 135.15, 131.42, 129.18, 119.48, 119.10, 117.56, 117.22, 114.60, 112.53. $m/z$ (ESI) calculated for [C$_{15}$H$_{11}$NO$_5$-H]$^-$: 284.0553; found 284.05620[M-H]$^-$.

Synthesis of UiO-66-NH$_2$

UiO-66-NH$_2$ was synthesized following a previously reported method. In a typical synthesis, 11.652 g (0.05 mol) of ZrCl$_4$ was dissolved in 250 mL of DMF at room temperature under stirring for 15 min. In a separate flask, NH$_2$-bdc (9.058 g, 0.05 mol) was dissolved in 250 mL of DMF at room temperature under stirring for 15 min. The yellow NH$_2$-bdc solution obtained was added to the ZrCl$_4$ solution, followed by addition of 35 mL of HCl 37% under stirring. The resulting mixture was heated at 120 °C under stirring for 2 h. The obtained solid was collected by centrifugation at 9000 rpm for 5 min, washed two times with 100 mL of DMF for 12 h at 120 °C and three times with 100 mL of absolute ethanol for 12 h at 60 °C. Finally, the resulting powder was dried at 85 °C overnight. (Yield = 75 %).

Synthesis of (UiO-66-4PC)$_x$

0.150 g (0.085 mmol) of UiO-66-NH$_2$ was dispersed in ethanol (15 mL) by sonication for 10 min. Then, 144 µL, 240 µL, 480 µL or 720 µL of 4-pyridinecarboxaldehyde was added to the dispersion at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min$^{-1}$ and a flow rate of 336 mL·min$^{-1}$ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 5 min. This process was repeated four times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

Synthesis of (UiO-66-2PC)$_x$

0.150 g (0.085 mmol) of UiO-66-NH$_2$ was dispersed in ethanol (15 mL) by sonication for 10 min. Then, 144 µL, 240 µL, 480 µL or 720 µL of 2-pyridinecarboxaldehyde was added to the dispersion at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min$^{-1}$ and a flow rate of 336 mL·min$^{-1}$ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 5 min. This process was repeated four times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

Synthesis of (UiO-66–Sal)$_x$

0.150 g (0.085 mmol) of UiO-66-NH$_2$ was dispersed in ethanol (15 mL) by sonication for 10 min. Then, 160 µL, 240 µL, 540 µL or 810 µL of salicylaldehyde was added to the dispersion at room
temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 5 min. This process was repeated four times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

Synthesis of ZIF-90 (Nanoparticles)

ZIF-90 was synthesized following a previously reported method.² In a typical synthesis, 0.200 g (2.10 mmol) of imidazolate-2-carboxyaldehyde was dissolved in 150 mL of DMF at 100 °C under stirring for 1 h and then cooled to room temperature. In a separate flask, 0.223 g (0.75 mmol) of Zn(NO₃)₂·6H₂O was dissolved in 50 mL of DMF at room temperature. The resulting solution was added to the imidazolate-2-carboxyaldehyde solution under stirring, followed by addition of 0.27 mL of trimethylamine (1.96 mmol). The resulting mixture was stirred for 1 min at room temperature and then 100 mL of ethanol was added. The particles were collected by centrifugation at 9000 rpm for 8 min, washed five times with ethanol, and finally, dried at 70 °C overnight. (Yield = 70 %).

Synthesis of ZIF-90-BAₙ

ZIF-90 (0.100 g, 0.39 mmol) was dispersed in 15 mL of ethanol by sonication for 10 min. Then, 230 µL, 770 µL or 1200 µL of butylamine was added to the dispersion of ZIF-90 at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 8 min. This process was repeated five times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

Synthesis of ZIF-90-HMDA

ZIF-90 (0.100 g, 0.39 mmol) was dispersed in 15 mL of ethanol by sonication for 10 min. Then, hexamethylenediamine (0.45 g, 3.9 mmol) was added to a dispersion of ZIF-90 at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min⁻¹ and a flow rate of 336 mL·min⁻¹ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 8 min. This process was repeated five times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

Synthesis of ZIF-90 (Crystals)

ZIF-90 was synthesized following a previously reported method.³ In a typical synthesis, a solid mixture of 0.384 g (4.00 mmol) of imidazolate-2-carboxyaldehyde, 0.296 g (1.00 mmol) of Zn(NO₃)₂·6H₂O and 0.068 g (1.00 mmol) of sodium formate was dissolved in 40 mL of methanol at room temperature by sonication. The resulting solution was placed in a Teflon-lined stainless steel
autoclave and heated at 85 °C for 24 h. The crystals were isolated by centrifugation at 9000 rpm for 7 min, washed three times with methanol and finally, dried at room temperature for 24 h.

**Synthesis of (ZIF-90-BA)$_{15}$**

ZIF-90 crystals (0.090 g, 0.35 mmol) were dispersed in 15 mL of ethanol by sonication for 20 min. Then, 1080 µL of butylamine was added to the dispersion of ZIF-90 at room temperature and stirring for 5 min. The resulting reaction mixture was then spray-dried at an inlet temperature of 130 °C, a feed rate of 3.0 mL·min$^{-1}$ and a flow rate of 336 mL·min$^{-1}$ using a Mini Spray Dryer B-290 (BUCHI Labortechnik; spray cap: 0.5-mm-hole). A yellow powder was collected after 5 min. The resulting solid was then dispersed in 20 mL of ethanol and precipitated by centrifugation at 9000 rpm for 8 min. This process was repeated five times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

**Control synthesis of (UiO-66-4PC)$_{15}$**

0.075 g (0.043 mmol) of UiO-66-NH$_2$ was dispersed in ethanol (7.5 mL) by sonication for 10 min. Then, 360 µL of 4-pyridinecarboxaldehyde was added to the dispersion at room temperature and stirring for 5 min. The resulting reaction mixture was then heated at 130 °C for 5 min. The yellow powder was isolated by centrifugation at 9000 rpm for 5 min and then dispersed in 10 mL of ethanol and precipitated by centrifugation at 9000 rpm for 5 min. This process was repeated four times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

**Control synthesis of (ZIF-90-BA)$_{15}$**

ZIF-90 (0.050 g, 0.20 mmol) were dispersed in 7.5 mL of ethanol by sonication for 10 min. Then, 600 µL of butylamine was added to the dispersion of ZIF-90 at room temperature and stirring for 5 min. The resulting reaction mixture was then heated at 130 °C for 5 min. The yellow powder was isolated by centrifugation at 9000 rpm for 8 min and then dispersed in 10 mL of ethanol and precipitated by centrifugation at 9000 rpm for 8 min. This process was repeated five times. The final product was washed one time with acetone and centrifuged again at 9000 rpm and dried for 12 h at 85 °C.

**Activation protocol**

All washed samples (with ethanol and acetone and then dried at 85 °C overnight) were degassed at 200 °C for 12 h under vacuum. In the case of UiO-66-NH$_2$-based samples, FT-IR spectra were collected after heating at 85 ° to confirm the removal of the unreacted aldehydes prior to the N$_2$ sorption measurement at 77 K.
Section S2: Characterization of 2-((pyridin-4-ylmethylene)amino)terephthalic acid

FIGURE S1: $^1$H NMR spectrum of 2-((pyridin-4-ylmethylene)amino)terephthalic acid synthesized using NH$_2$-bdc:4PC molar ratios of 1:1 (red), 1:2 (green) and 1:3 (blue) in DMSO-$d_6$.

FIGURE S2: $^{13}$C NMR spectrum of 2-((pyridin-4-ylmethylene)amino)terephthalic acid in DMSO-$d_6$. 
FIGURE S3: ESI-MS spectrum of 2-((pyridin-4-ylmethylene)amino)terephthalic acid.

Chemical Formula: C_{14}H_{12}N_{2}O_{4}
Calcd. for [M-nH]^+\#: 269.0568
Section S3: Characterization of 2-((pyridin-2-ylmethylene)amino)terephthalic acid

FIGURE S4: $^1$H NMR spectrum of 2-((pyridin-2-ylmethylene)amino)terephthalic acid synthesized using NH$_2$-bdc:2PC molar ratio of 1:3 in DMSO-$d_6$.

FIGURE S5: $^{13}$C NMR spectrum of 2-((pyridin-2-ylmethylene)amino)terephthalic acid in DMSO-$d_6$. 
FIGURE S6: ESI-MS spectrum of 2-((pyridin-2-ylmethylene)amino)terephthalic acid.

Chemical Formula: $C_{14}H_{10}N_2O_4$

calcd. for [M-nH]$^+$: 269.0568
Section S4: Characterization of 2-((2-hydroxybenzylidene)amino)terephthalic acid

FIGURE S7: $^1$H NMR spectrum of 2-((2-hydroxybenzylidene)amino)terephthalic acid synthesized using NH$_2$-bdc:Sal molar ratio of 1:3 in DMSO-$d_6$.

FIGURE S8: $^{13}$C NMR spectrum of 2-((2-hydroxybenzylidene)amino)terephthalic acid in DMSO-$d_6$. 
FIGURE S9: ESI-MS spectrum of 2-((2-hydroxybenzylidene)amino)terephthalic acid.
Section S5: Characterization of UiO-66-NH$_2$

FIGURE S10: Simulated (black) and synthesized (red) XRPD patterns of UiO-66-NH$_2$.

FIGURE S11: N$_2$ adsorption isotherm and BET linear fit of synthesized UiO-66-NH$_2$.

BET surface area: 914.070 m$^2$/g  
Slope: 3.805 g/cm$^3$ STP  
Intercept: 5.085e-03 g/cm$^3$ STP  
Correlation coefficient: 0.999965  
C constant: 749.221  
Molecular cross-sectional area: 0.1620 nm$^2$
FIGURE S12: $^{13}$C MAS-NMR spectra of UiO-66-NH$_2$. 

![13C MAS-NMR spectra of UiO-66-NH$_2$.](image)
Section S6: FESEM images of UiO-66-NH$_2$, (UiO-66-4PC)$_x$, (UiO-66-2PC)$_x$ and (UiO-66-Sal)$_x$

**Section S7:** XRPD patterns of (UiO-66-4PC)$_x$, (UiO-66-2PC)$_x$, and (UiO-66-Sal)$_x$.

**FIGURE S14:** XRPD patterns of (UiO-66-4PC)$_x$ (Blue: $x = 3$; Pink: $x = 5$; Orange: $x = 10$; Green: $x = 5$), in comparison to the activated UiO-66-NH$_2$ (red) and the simulated powder pattern of UiO-66 (black).

**FIGURE S15:** XRPD patterns of (UiO-66-2PC)$_x$ (Blue: $x = 3$; Pink: $x = 5$; Orange: $x = 10$; Green: $x = 5$), in comparison to the activated UiO-66-NH$_2$ (red) and the simulated powder pattern of UiO-66 (black).
**FIGURE S16**: XRPD patterns of (UiO-66-Sal)$_x$ (Blue: $x = 3$; Pink: $x = 5$; Orange: $x = 10$; Green: $x = 5$), in comparison to the activated UiO-66-NH$_2$ (red) and the simulated powder pattern of UiO-66 (black).
Section S8: $^{13}C$ MAS-NMR spectra of (UiO-66-4PC)$_{15}$, (UiO-66-2PC)$_{15}$ and (UiO-66-Sal)$_{15}$

**FIGURE S17:** $^{13}C$ MAS-NMR spectrum of (UiO-66-4PC)$_{15}$.

**FIGURE S18:** $^{13}C$ MAS-NMR spectrum of (UiO-66-2PC)$_{15}$. 
FIGURE S19: $^{13}$C MAS-NMR spectrum of (UiO-66-Sal)$_{15}$.
Section S9: $^1$H NMR spectra of the digested $(\text{UiO-66-4PC})_x$, $(\text{UiO-66-2PC})_x$, and $(\text{UiO-66-Sal})_x$ in HF/DMSO-$d_6$.

FIGURE S20: $^1$H NMR spectra of the digested UiO-66-NH$_2$ in HF/DMSO-$d_6$. 

![NMR spectrum of UiO-66-NH$_2$]
FIGURE S21: $^1$H NMR spectra of the digested (UiO-66-4PC)$_3$ in HF/DMSO-$d_6$.

FIGURE S22: $^1$H NMR spectra of the digested (UiO-66-4PC)$_5$ in HF/DMSO-$d_6$. 
FIGURE S23: $^1$H NMR spectra of the digested (UiO-66-4PC)$_{10}$ in HF/DMSO-$d_6$.

FIGURE S24: $^1$H NMR spectra of the digested (UiO-66-4PC)$_{15}$ in HF/DMSO-$d_6$. 
FIGURE S25: $^1$H NMR spectra of the digested (UiO-66-2PC)$_3$ in HF/DMSO-$d_6$.

FIGURE S26: $^1$H NMR spectra of the digested (UiO-66-2PC)$_5$ in HF/DMSO-$d_6$. 
FIGURE S27: $^1$H NMR spectra of the digested (UiO-66-2PC)$_{10}$ in HF/DMSO-$d_6$.

FIGURE S28: $^1$H NMR spectra of the digested (UiO-66-2PC)$_{15}$ in HF/DMSO-$d_6$. 
FIGURE S29: $^1$H NMR spectra of the digested (UiO-66-Sal)$_3$ in HF/DMSO-$d_6$.

FIGURE S30: $^1$H NMR spectra of the digested (UiO-66-Sal)$_5$ in HF/DMSO-$d_6$. 
FIGURE S31: $^1$H NMR spectra of the digested (UiO-66-Sal)$_{10}$ in HF/DMSO-$d_6$.

FIGURE S32: $^1$H NMR spectra of the digested (UiO-66-Sal)$_{15}$ in HF/DMSO-$d_6$. 
Section S10: FT-IR spectra of (UiO-66-4PC)$_x$, (UiO-66-2PC)$_x$ and (UiO-66-Sal)$_x$

FIGURE S33: FT-IR spectra of (UiO-66-4PC)$_{15}$ before (red) and after (blue) activation, in comparison to the spectrum of 4PC (black). The region of the band corresponding to the C=O stretch of the aldehyde is highlighted.

FIGURE S34: FT-IR spectra of (UiO-66-2PC)$_{15}$ before (red) and after (blue) activation, in comparison to the spectrum of 2PC (black). The region of the band corresponding to the C=O stretch of the aldehyde is highlighted.
FIGURE S35: FT-IR spectra of (UiO-66-Sal)$_{15}$ before (red) and after (blue) activation, in comparison to the spectrum of Sal (black). The region of the band corresponding to the C=O stretch of the aldehyde is highlighted.
Section S11: $N_2$ adsorption isotherms and BET linear fits of $(\text{UiO-66-4PC})_x$, $(\text{UiO-66-2PC})_x$ and $(\text{UiO-66-Sal})_x$

FIGURE S36: $N_2$ adsorption isotherm and BET linear fit of $(\text{UiO-66-4PC})_3$.

- BET surface area: 736.709 m²/g
- Slope: 4.724 g/cm³ STP
- Intercept: 5.442e-03 g/cm³ STP
- Correlation coefficient: 0.999987
- C constant: 1363.292
- Molecular cross-sectional area: 0.1620 nm²

FIGURE S37: $N_2$ adsorption isotherm and BET linear fit of $(\text{UiO-66-4PC})_5$.

- BET surface area: 712.017 m²/g
- Slope: 4.888 g/cm³ STP
- Intercept: 3.009e-03 g/cm³ STP
- Correlation coefficient: 0.999992
- C constant: 1625.250
- Molecular cross-sectional area: 0.1620 nm²
**FIGURE S38**: N\textsubscript{2} adsorption isotherm and BET linear fit of (UiO-66-4PC\textsubscript{10}).

- BET surface area: 621.852 m\textsuperscript{2}/g
- Slope: 5.597 g/cm\textsuperscript{3} STP
- Intercept: 3.017e-03 g/cm\textsuperscript{3} STP
- Correlation coefficient: 0.999994
- C constant: 1856.203
- Molecular cross-sectional area: 0.1620 nm\textsuperscript{2}

**FIGURE S39**: N\textsubscript{2} adsorption isotherm and BET linear fit of (UiO-66-4PC\textsubscript{15}).

- BET surface area: 572.622 m\textsuperscript{2}/g
- Slope: 6.077 g/cm\textsuperscript{3} STP
- Intercept: 4.975e-03 g/cm\textsuperscript{3} STP
- Correlation coefficient: 0.999990
- C constant: 1222.484
- Molecular cross-sectional area: 0.1620 nm\textsuperscript{2}
**FIGURE S40:** N₂ adsorption isotherm and BET linear fit of (UiO-66-2PC)₃.

- BET surface area: 698.985 m²/g
- Slope: 4.979 g/cm³ STP
- Intercept: 3.305e-03 g/cm³ STP
- Correlation coefficient: 0.999992
- C constant: 1507.634
- Molecular cross-sectional area: 0.1620 nm²

**FIGURE S41:** N₂ adsorption isotherm and BET linear fit of (UiO-66-2PC)₅.

- BET surface area: 624.509 m²/g
- Slope: 5.571 g/cm³ STP
- Intercept: 5.337e-03 g/cm³ STP
- Correlation coefficient: 0.999985
- C constant: 1044.848
- Molecular cross-sectional area: 0.1620 nm²
FIGURE S42: N₂ adsorption isotherm and BET linear fit of (UiO-66-2PC)₁₀.

- BET surface area: 585.293 m²/g
- Slope: 5.942 g/cm³ STP
- Intercept: 8.365e-03 g/cm³ STP
- Correlation coefficient: 0.999966
- C constant: 711.311
- Molecular cross-sectional area: 0.1620 nm²

FIGURE S43: N₂ adsorption isotherm and BET linear fit of (UiO-66-2PC)₁₅.

- BET surface area: 516.215 m²/g
- Slope: 6.740 g/cm³ STP
- Intercept: 6.121e-03 g/cm³ STP
- Correlation coefficient: 0.999984
- C constant: 1102.155
- Molecular cross-sectional area: 0.1620 nm²
**FIGURE S44**: N$_2$ adsorption isotherm and BET linear fit of (UiO-66-Sal)$_3$.

BET surface area: 760.923 m$^2$/g  
Slope: 4.574 g/cm$^3$ STP  
Intercept: 2.398e-03 g/cm$^3$ STP  
Correlation coefficient: 0.999994  
C constant: 1908.173  
Molecular cross-sectional area: 0.1620 nm$^2$

**FIGURE S45**: N$_2$ adsorption isotherm and BET linear fit of (UiO-66-Sal)$_5$.

BET surface area: 709.865 m$^2$/g  
Slope: 4.904 g/cm$^3$ STP  
Intercept: 1.990e-03 g/cm$^3$ STP  
Correlation coefficient: 0.999995  
C constant: 2465.505  
Molecular cross-sectional area: 0.1620 nm$^2$
**FIGURE S46:** $N_2$ adsorption isotherm and BET linear fit of $(\text{UiO-66-Sal})_{10}$.

BET surface area: 665.192 m²/g  
Slope: 5.233 g/cm³ STP  
Intercept: 2.748e-03 g/cm³ STP  
Correlation coefficient: 0.999997  
C constant: 1904.883  
Molecular cross-sectional area: 0.1620 nm²

**FIGURE S47:** $N_2$ adsorption isotherm and BET linear fit of $(\text{UiO-66-Sal})_{15}$.

BET surface area: 616.220 m²/g  
Slope: 5.649 g/cm³ STP  
Intercept: 2.652e-03 g/cm³ STP  
Correlation coefficient: 0.999997  
C constant: 2131.140  
Molecular cross-sectional area: 0.1620 nm²
Section S12: Characterization of ZIF-90

**FIGURE S48:** XRPD pattern of simulated (black) and synthesized (red) ZIF-90.

**FIGURE S49:** N$_2$ adsorption isotherm and BET linear fit of ZIF-90.

BET surface area: 1071.640 m$^2$/g
Slope: .3.249 g/cm$^3$ STP
Intercept: 5.715e-04 g/cm$^3$ STP
Correlation coefficient: 0.999999
C constant: 5686.229
Molecular cross-sectional area: 0.1620 nm$^2$
FIGURE S50: FESEM images of ZIF-90. Scale bars: 2 µm (a) and 200 nm (b).
Section S13: Characterization of (ZIF-90-BA)$_x$

FIGURE S51: FESEM and TEM images of a-b) ZIF-90, c-d) (ZIF-90-BA)$_3$, e-f) (ZIF-90-BA)$_{10}$, g-h) (ZIF-90-BA)$_{15}$. Scale bars correspond to 200 nm (FESEM images) and to 50 nm (TEM images).
FIGURE S52: XRPD patterns of (ZIF-90-BA)$_x$ (Blue: $x = 3$; orange: $x = 10$; and green: $x = 15$), in comparison to the as synthesized ZIF-90 (red) and the simulated powder pattern of ZIF-90 (black).
FIGURE S53: a) $^1$H-NMR spectrum of the digested (ZIF-90-BA)$_3$ in CD$_3$CO$_2$D. b) ESI-MS spectrum of the digested (ZIF-90-BA)$_3$ in CH$_3$CO$_2$H.
FIGURE S54: a) $^1$H-NMR spectrum of the digested (ZIF-90-BA)$_{10}$ in CD$_3$CO$_2$D. b) ESI-MS spectrum of the digested (ZIF-90-BA)$_{10}$ in CH$_3$CO$_2$H.
FIGURE S55: a) $^1$H-NMR spectrum of the digested (ZIF-90-BA)$_{15}$ in CD$_3$CO$_2$D. b) ESI-MS spectrum of the digested (ZIF-90-BA)$_{15}$ in CH$_3$CO$_2$H.
FIGURE S56: $^1$H NMR spectrum of the digested ZIF-90 in DCl/DMSO-d$_6$.

FIGURE S57: $^1$H NMR spectrum of the digested (ZIF-90-BA)$_3$ in DCl/DMSO-d$_6$. 
FIGURE S58: $^1$H NMR spectrum of the digested sample (ZIF-90-BA)$_{10}$ in DCl/DMSO-$d_6$.

FIGURE S59: $^1$H NMR spectrum of the digested sample (ZIF-90-BA)$_{15}$ in DCl/DMSO-$d_6$. 
**FIGURE S60:** $N_2$ adsorption isotherm and BET linear fit of (ZIF-90-BA)$_3$.

BET surface area: 669.762 m²/g  
Slope: 5.194 g/cm³ STP  
Intercept: 5.525e-03 g/cm³ STP  
Correlation coefficient: 0.999993  
C constant: 941.127  
Molecular cross-sectional area: 0.1620 nm²

**FIGURE S61:** $N_2$ adsorption isotherm and BET linear fit of (ZIF-90-BA)$_{10}$.

BET surface area: 483.124 m²/g  
Slope: 7.202 g/cm³ STP  
Intercept: 6.715e-03 g/cm³ STP  
Correlation coefficient: 0.999997  
C constant: 1073.387  
Molecular cross-sectional area: 0.1620 nm²
FIGURE S62: N\textsubscript{2} adsorption isotherm and BET linear fit of (ZIF-90-BA)\textsubscript{15}.

BET surface area: 423.638 m\textsuperscript{2}/g
Slope: 8.204 g/cm\textsuperscript{3} STP
Intercept: 1.689e-02 g/cm\textsuperscript{3} STP
Correlation coefficient: 0.999995
C constant: 486.720
Molecular cross-sectional area: 0.1620 nm\textsuperscript{2}
FIGURE S63: Contact angle measurements on pressed pellet disks of: a) ZIF-90, b) (ZIF-90-BA)$_3$, c) (ZIF-90-BA)$_{10}$ and d) (ZIF-90-BA)$_{15}$. 

a) 90.4°  
b) 93.3°  
c) 96.1°  
d) 99.3°
Section S14: Characterization of ZIF-90 crystals and (ZIF-90-BA)$_{15}$

Figure S64: XRPD pattern of simulated (black) and synthesized (red) ZIF-90 crystals.

Figure S65: FESEM images of ZIF-90 crystals. Scale bars: 20 µm (a) and 5 µm (b).
Figure S66: $^1$H NMR spectrum of the digested sample (ZIF-90-BA)$_{25}$ in DCl/DMSO-$d_6$. 
Section S15: Characterization of (ZIF-90-HMDA)$_5$

FIGURE S67: FESEM and TEM images of a-b) ZIF-90 and c-d) (ZIF-90-HMDA)$_5$. Scale bars correspond to 200 nm (FESEM images) and to 50 nm (TEM images).
FIGURE S68: XRPD patterns of the simulated ZIF-90 (black), as-synthesized ZIF-90 (red) and (ZIF-90-HMDA)$_5$ (blue).
FIGURE S69: a) $^1$H NMR spectrum of the digested (ZIF-90-HMDA)$_5$ in CD$_3$CO$_2$D. b) ESI-MS spectrum of the digested (ZIF-90-HMDA)$_5$ in CH$_3$CO$_2$H.
FIGURE S70: $^1$H NMR spectrum of the digested (ZIF-90-HMDA)$_5$ in DCl/DMSO-$d_6$. 
**FIGURE S71**: N₂ adsorption isotherm and BET linear fit of \((\text{ZIF-90-HMDA})_5\).

- BET surface area: 68.945 m²/g
- Slope: 49.119 g/cm³ STP
- Intercept: 1.392 g/cm³ STP
- Correlation coefficient: 0.999943
- C constant: 36.278
- Molecular cross-sectional area: 0.1620 nm²
Section S16: Characterization of control synthesis of (UiO-66-4PC)$_{15}$ and (ZIF-90-BA)$_{15}$

Figure S72: $^1$H NMR spectra of the digested control experiment of (UiO-66-4PC)$_{15}$ in HF/DMSO-d$_6$.

Figure S73: $^1$H NMR spectra of the digested control experiment of (ZIF-90-BA)$_{15}$ in DCl/DMSO-d$_6$.

Section S17: References