Supporting Information

Improving the mechanical stability of zirconium-based metal-organic frameworks by incorporation of acidic modulators

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SI-1: Modulated sample characterization
SI-2: Powder X-ray Diffraction
SI-3: Scanning Electron Microscopy Infrared Spectroscopy
SI-4: Modulator Removal from UiO-66m TFA
SI-5: Gas Sorption and Pore Distribution Analysis
SI-6: Thermogravimetric Analysis
SI-7: IR Spectroscopy
Figure S1. Additional thermogravimetric analyses were performed to analyze the linker deficiency of each UiO-66 material by heating the samples at 3°C/min under an oxygen containing atmosphere. Weights were normalized with respect to the ZrO$_2$ residue left after heating up to 550°C.
Figure S2a. Powder X-ray diffraction patterns of MIL-140A after milling for the indicated lengths of time.

Figure S2b. Powder X-ray diffraction patterns of MIL-140B after milling for the indicated lengths of time.
**Figure S2c.** Powder X-ray diffraction patterns of MIL-140C after milling for the indicated lengths of time.

**Figure S2d.** Powder X-ray diffraction patterns of MIL-140D after milling for the indicated lengths of time.
Figure S2e. Powder X-ray diffraction patterns of UiO-66 after milling for the indicated lengths of time.

Figure S2f. Example of profile fitting for crystalline UiO-66.
Figure S2g. Powder X-ray diffraction patterns of UiO-66m TFA after milling for the indicated lengths of time.

Figure S2h. Powder X-ray diffraction patterns of ZIF-8 after milling for the indicated lengths of time.
Figure S2i. Powder X-ray diffraction patterns of UiO-66mh after milling for the indicated lengths of time.

Figure S2j. Powder X-ray diffraction patterns of UiO-66m ClA after milling for the indicated lengths of time.
Figure S2k. Powder X-ray diffraction patterns of UiO-66m AA after milling for the indicated lengths of time.

Figure S2l. Evolution of the integral breadth of the last remaining diffraction peak for MIL-140A-D.
Figure S3a. SEM images of samples of MIL-140A. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S3b. SEM images of samples of MIL-140B. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S3c. SEM images of samples of MIL-140C. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S3d. SEM images of samples of MIL-140D. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
**Figure S3e.** SEM images of samples of UiO-66. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S3f. SEM images of samples of UiO-66m TFA. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S3g. SEM images of samples of ZIF-8. Top – crystalline, middle – after ten minutes of ball-milling and bottom – after 25 minutes of ball-milling.
Figure S4a. Normalized FTIR spectra of UiO-66m TFA at 50°C (blue) and UiO-66m TFA at 350°C (black). The stars indicate typical vibrational signals for trifluoroacetate.

By treating UiO-66m TFA for several hours at 350°C, TFA is removed from the cluster. The material is designated as UiO-66mh, and was as well subjected to the milling treatment. The infrared spectra indicate the removal of TFA for the most characteristic peaks after a thermal treatment at 350°C as indicated by the red stars.
SI-5: N$_2$ physisorption and pore size distribution analysis

It is important to note that the pore-size distributions were calculated with the Tarazona NLDFT model using a regularization factor 0.00100. This model is not specific for MOF structures, however the qualitative analysis of the PSD’s is correct.

**Figure S5a.** N$_2$ physisorption isotherms for the crystalline MIL-140(A-D), UiO-66, UiO-66m TFA and ZIF-8.

**Figure S5b.** Pore size distributional analysis for crystalline (black) and amorphized (red) MIL-140A.
**Figure S5c.** Pore size distributional analysis for crystalline (black) and amorphized (red) MIL-140B.

**Figure S5d.** Pore size distributional analysis for crystalline (black) and amorphized (red) MIL-140C.
Figure S5e. Pore size distributional analysis for crystalline (black) and amorphized (red) MIL-140D.

Figure S5f. Pore size distributional analysis for crystalline (black) and amorphized (red) UiO-66.
Figure S5g. Pore size distributional analysis for crystalline (black) and amorphized (red) ZIF-8.
SI-6: Thermogravimetric Analysis

MIL-140A

MIL-140B

MIL-140C

MIL-140D

UiO-66

UiO-66m TFA

ZIF-8

UiO-66m AA
Figure S6a. Thermogravimetric (TGA) traces under N$_2$ atmosphere (solid lines) and derivative TGA curves (dashed lines) of crystalline (black) and amorphous (red) samples of the zirconium containing frameworks studied, along with ZIF-8.
SI-7: IR spectroscopy

All samples were outgassed at 50°C under vacuum unless otherwise indicated. The absorbance is normalised for all spectra. Slight variance from the results in Figure 5 arises from slightly different outgassing procedures.

Figure S7a. Infra-red spectroscopy spectra for MIL-140A and the amorphized framework for the regions (top) 400-800 cm\(^{-1}\), (middle) 1600-1800 cm\(^{-1}\) and (bottom) 3100-3800 cm\(^{-1}\).
**Figure S7b.** Infra-red spectroscopy spectra for UiO-66 and the amorphized framework for the regions (top) 400-800 cm\(^{-1}\), (middle) 1600-1800 cm\(^{-1}\) and (bottom) 3100-3800 cm\(^{-1}\).

**Figure S7c.** Infra-red spectroscopy spectra for UiO-66m TFA and the framework after 25 minutes of ball-milling for the regions (top) 400-800 cm\(^{-1}\), (middle) 1600-1800 cm\(^{-1}\) and (bottom) 3100-3800 cm\(^{-1}\).