# SUPPORTING INFORMATION

# Using water adsorption measurements to access the chemistry of defects in the metal-organic framework UiO-66.

Stefano Dissegna,<sup>a</sup> Rifan Hardian,<sup>b</sup> Konstantin Epp,<sup>a</sup> Gregor Kieslich,<sup>a</sup> Marie-Vanessa Coulet,<sup>b</sup> Philip Llewellyn<sup>b</sup> and Roland A. Fischer<sup>a</sup>

a. Chair of Inorganic and Metal-Organic Chemistry, Faculty of Chemistry and Catalysis Research Center, Technical University of Munich, Lichtenbergstraße 4, 85748 Garching, Germany. E-mail: roland.fischer@tum.de Tel: +49 (0)89 289 13081;Fax: +49 (0)89 289 13194.

b. Aix-Marseille Univ, CNRS, MADIREL (UMR 7246), Centre de St. Jérôme, 13397 Marseille cedex 20.

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# **Experimental section**

**Materials:** All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Acros Organics and others) and used without further purification.

**Characterization Methods:** Powder X-ray diffraction (PXRD) measurements for AA samples were recorded in flat mode with an X'Pert Empyrean series 2 PANalytical equipment in Bragg–Brentano geometry, with a PIXcel position sensitive detector and a CuK $\alpha$  radiation source ( $\lambda$  = 1.54178 Å) at room temperature. Instead, TFA samples were recorded in capillary mode. FTIR spectra were measured with a Bruker Alpha FTIR spectrometer equipped with a single-reflection platinum ATR module under inert gas conditions. Nitrogen sorption measurements were performed with a Quantachrome NovaTouch instrument with nitrogen gas at 77 K. Prior to the measurements, all samples were evacuated in dynamic vacuum (p =  $10^{-3}$  mbar) at 150 °C for 12 h. Thermogravimetric analysis was performed with a Mettler Toledo TGA/STA 409 PC apparatus with a continuous heating ramp of 10 °C/min applied under inert conditions in Ar flow. 3-5 mg of sample were used in a temperature range from 30 to 1000°C.

Water isotherms were measured on a BEL Japan BELSORP. Prior to the measurements, samples were activated to 170°C under secondary vacuum for 16 hours. Prior to performing water adsorption, water (analyte) was flash frozen with liquid nitrogen and then evacuated under dynamic vacuum 3 times in order to remove dissolved gases from the water reservoir. The measurement temperature was controlled with a water bath at 25 °C and with the dosing manifold controlled at 40°C to avoid unwanted condensation effects. Helium was used to estimate the dead volume prior to the water adsorption-desorption measurements. Adsorption equilibrium was assumed when the variation of the cell pressure was 0.5% for a minimum period of 300 seconds.

# Synthesis of defect free UiO66 and defective UiO66 samples

## **Reference UiO-66**

The reference sample (UiO-66 ref) was synthesized with a slightly modified procedure of Shearer et al.. Typically 0,945 g of  $ZrCl_4$  1.34 g of terephthalic acid and 0,715 ml of HCl were mixed in 24,35 ml of DMF. The solution was kept in a oven for 24 h at 180°C in a 50 ml teflon liner autoclave. The resulting material were then collected via centrifugation washed 3 times with fresh DMF (3 x 30 ml) and solvent exchange with MeOH (3 x 30 ml). The product was heated under vacuum at 250°C overnight, at 300°C for two hours and then stored in a glovebox.

## Defective UiO-66 (Acetic acid modulation)

Briefly, for the AA modulation, 169 mg of  $ZrCl_4$  (0,73 mmol) and either 121 mg of terephthalic acid (0,73mmol) were dissolved in 38ml of DMF. For each sample 16AA, 32AA, 64AA, 100AA, 200AA we added a different amount of acetic acid: 0.7, 1.4, 2.8, 4,2 and 8,4 ml, respectively. All the samples were kept in a glass jar in the oven at 120°C for 24h. The resulted materials were collected by centrifugation, washed three times with DMF (3 x 30 ml) and solvent exchange with MeOH (3 x 30 ml) in three days. Finally, the solids were activated at 250°C overnight under dynamic vacuum (  $\approx 10^{-3}$  mbar) and stored in a glovebox.

## Defective UiO-66 (trifluoro acetic acid modulation)

In a typical synthesis, 3,5 g of  $ZrCl_4$  as well as 2,5 g of terephthalic acid with 1,5 ml of HCl were mixed in 155 ml of DMF. Instead of AA, 1 eq (1,15 ml) and 10 eq (11,5 ml) of trifuoro acetic acid (TFA) were used as modulator respect to the amount of zirconium. The resulted materials were collected by centrifugation, washed three times with DMF (3 x 30 ml) and solvent exchange with MeOH (3 x 30 ml) in three days. Then the samples were activated at 250°C for 12 h and at 320°C for 3 h under dynamic vacuum. All the samples were stored inside a glovebox.

#### **Catalytic experiments**

In a typical catalytic experiment  $62\mu$ L (0.5 mmol) trimethylsilylcyanide (TMSCN), 25  $\mu$ L (0.25 mmol) benzaldehyde and ~3mg solid catalyst were stirred (~500 rpm) in a finger schlenk under Ar atmosphere at 40 °C in 1 mL DCM. The reaction was followed by taken aliquots at given time intervals that were analyzed by GC and GC-MS. For the analysis by GC the catalyst were filtered of by the use of syringe filters.

#### **1. CLASSICAL CHARACTERIZATION TECHNIQUES**



Fig. S1: Left panel: powder X-ray diffraction patterns of defect free UiO-66 (black), 16AA (red), 33AA(blue), 67AA (orange) and 100AA (olive green) of AA. Right panel: powder X-ray diffraction patterns of defect free UiO-66 (black), 1TFA (green), 10TFA (blue) of TFA.



Fig. S2: Left panel: N<sub>2</sub> adsorption measurements (77K) of defect free UiO-66 (black), 16AA (red), 33AA(blue), 67AA (orange) and 100AA (olive green) of AA. Right panel: N<sub>2</sub> adsorption measurements (77K) of defect free UiO-66 (black), 1TFA (green), 10TFA (blue) of TFA. Close and open symbols for each sample are for adsorption and desorption respectively.



Fig.S3: Left panel: Thermogravimetric analysis measured under Ar atmsphere (TGA) of of defect free UiO-66 (black), 16AA (red), 33AA(blue), 67AA (orange) and 100AA (olive green) of AA. Right panel: Thermogravimetric analysis (TGA) measured under synthetic air of defect free UiO-66 (black), 1TFA (green), 10TFA (blue) of TFA.

#### 2. WATER ADSORPTION PART



S4. Correlation between pore volume and concentration of acetic acid. Pore volume is determined with nitrogen sorption at 77K (blue circle) and with water sorption at 298K (orange circle).



S5. Correlation between maximum water uptake and concentration of acetic acid. Maximum water uptake is determined at p/p°~1.



S6. Correlation between BET area and concentration of acetic acid.



Fig. S7. Water adsorption isotherm of unmodulated UiO-66 (top), AA-modulated UiO-66 (middle), TFA-modulated UiO-66(bottom).



Fig. S8. Determination of Henry's Constant

#### **3. CATALYTIC PART**



Fig. S9: Powder X-ray diffractograms of the solid catalyst samples after two catalytic runs.

sample	Yield [%] After reaction	Yield [%] Recycled once	Yield [%] Recycled twice	
UiO-66 ref	90	91	88	Table
1TFA	95	95	93	\$1:
10TFA	96	95	93	Reusa bility

studies for UiO-66 ref, 1TFA and 10TFA which were used as catalysts in the cyanosilylation of benzaldehyde at T = 40  $^{\circ}$ C in CH<sub>2</sub>Cl<sub>2</sub> as solvent. Yield was obtained after 20 h reaction time.



Fig. S10: Hot filtration test conducted for UiO-66 ref, 1TFA and 10TFA catalysts. The inserted line indicates the time of the hot filtration.

Sample	Proposed Sum formula
16AA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>5.98</sub> (AA) <sub>0.02</sub>
33AA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>5.98</sub> (AA) <sub>0.02</sub>
67AA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>5.98</sub> (AA) <sub>0.02</sub>
100AA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>5.7</sub> (AA) <sub>0.3</sub>
1TFA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>5.1</sub> (TFA) <sub>0.9</sub>
10TFA	Zr <sub>6</sub> O <sub>4</sub> (OH) <sub>4</sub> (BDC) <sub>4.85</sub> (TFA) <sub>1.15</sub>

Table S2: Proposed sum formula for the defective UiO-66 samples.

The sum formula of the obtained materials are calculated from TGA data based on the method proposed by Valenzano et al..<sup>1</sup> Due to low incorporated amount of modulator and small differences in the TGA curves in the first three AA samples (16AA, 33AA, 67AA) the sum formula is considered the same.

#### **References:**

1. L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M. H. Nilsen, S. Jakobsen, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2011, **23**, 1700–1718.