Functionalization of Zr-based MOFs with alkyl and perfluoroalkyl groups: effect on the water sorption behavior

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1. Synthesis

Ligands synthesis

2-Methyl-,¹ 2,5-dimethyl-, 2-trifluoromethyl-² and 2,5-bis(trifluoromethyl)¹ terephthalic acids were synthesized according to the reported procedures.

2,5-bis(diethyl) terephthalic acid was synthesized in three steps from the commercially available 1,4diethylbenzene. A three-necked round bottomed flask was loaded with 1,4-diethylbenzene (5.0 g, 37.2 mmol) which was then cooled to 0 °C. In the absence of light, I₂ (44 mg, 0.17 mmol) was added and after 10 min, Br₂ (12.19 g, 76.2 mmol) via a dropping funnel over a period of 30 min. The ice bath was removed and after 24 h at room temperature, 20% aqueous KOH (30 mL) was introduced until total discoloration occurred. The aqueous phase was removed and the crude mixture was crystallized in EtOH (200 mL) to give rise to pure 1,4-dibromo-2,5-diethylbenzene (6.5 g, 60%). ¹H NMR (300 MHz, CDCl₃): δ = 7.37 (s, 2H), 2.70 (q, J = 7.5 Hz, 4H), 1.22 (t, J = 7.6 Hz, 6H). 13C NMR (75 MHz, CDCl₃): δ = 142.54, 133.04, 123.01, 28.7, 13.86. A solution of 1,4-dibromo-2,5-diethylbenzene (8.7 g, 30 mmol) and CuCN (8.1 g, 90 mmol) was refluxed in N,N'-dimethylformamide (DMF; 100 mL) for 2 days under argon. The reaction mixture was poured into a saturated solution of NH₄OH (250 mL) yielding a brown precipitate. The solid was filtered off, washed with NH₄OH (250 mL) and water (500 mL), and left open to air-dry. The solid was then hot-extracted with acetone in a Soxhlet apparatus, to yield a yellow solid after removal of the acetone. The residual copper was removed by rapid filtration on a silica gel (dichloromethane (DCM) as solvent) to obtain pure 1,4-dibromo-2,5dicyanobenzene (2.5 g, 45%). ¹H NMR (300 MHz, CDCl₃): δ = 7.58 (s, 2H), 2.89 (q, J = 7.6 Hz, 4H), 1.32 (t, J = 7.7 Hz, 6H). A solution of the dicyano compound (1 g, 5.5 mmol) and KOH (1 g, 17.8 mmol) in diethylene glycol (15 mL) was refluxed overnight. The reaction mixture was then diluted with water (25 mL) and acidified to pH 1 with 10% HCl. A brown solid was filtered off and left to air-dry overnight. The solid was then dissolved in 10% NaOH, and the resulting solution was decolorized with charcoal. The solution was then acidified and filtered to give rise to the 2,5-bis(diethyl) terephthalic acid (0.6 g, 50%). ¹H NMR (300 MHz, DMSO): δ = 7.64 (s, 1H), 5.00-3.20 (bs, 2H), 2.87 (q, J = 7.4 Hz, 4H), 1.13 (t, J = 7.4 Hz, 6H). ¹³C NMR (75 MHz, DMSO-d6) δ = 168.4, 141.7, 133.2, 131.3, 26.06, 15.82.

2-pentafluoroethylterephthalic acid was prepared from known 2-iodoterephthalic acid³ according to the procedure described by Yagupolskii et al.⁴ A mixture of Zn(CF₃)Br·2DMF (5.40 g, 15 mmol) and copper(I) bromide (4.30 g, 30 mmol) in DMF (60 mL) was stirred at room temperature for 30 min, then heated at 50 °C for 4 h. The 2-iodoterephthalic acid (1.60 g, 5 mmol) was added and the reaction mixture was stirred overnight at 85 °C. The mixture was poured into 15% aqueous ammonia (100 mL) and extracted with diethyl ether (3 X 100 mL). The combined organic phases were washed with a solution of 5% NaHCO₃ (3 X 100 mL), dried over MgSO₄ and concentrated under reduced pressure. The crude mixture was purified by flash chromatography with pure DCM to afford the dimethyl 2-(pentafluoroethyl)terephthalate (1.1 g, 70%). ¹H NMR (200 MHz, CDCl₃): δ = 8.30 (s, 1H), 8.28 (d, J = 7.7 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H). ¹⁹F NMR (188 MHz, CDCl₃): δ = - 83.1 (m, 3F), 109.1 (m, 2F). ¹³C NMR (75 MHz, CDCl₃): δ = 167.4, 164.8, 136.7 (t, J = 3.0 Hz), 132.8, 132.1, 129.3, 129.4 (t, J = 5.8 Hz), 126.5 (t, J = 24.1 Hz), 53.0, 52,7. HRMS: calcd. for C₁₃H₉F₅O₄: 313.0499, found 313.0497. A solution of the afore mentioned diester (3.5 mmol) in 45% aqueous KOH (3 mL) was heated at 115 °C for 1 h. The reaction mixture was cooled down and acidified with HCl to pH 1. The precipitate was filtered, washed with water and dried to give rise to the desired compound (0.7 g, 70%). ¹H NMR (200MHz, acetone-d6): δ = 8.40 (d, J=8.9 Hz, 1H), 8.30 (s, 1H), 7.91 (d, J=8.1 Hz, 1H). ¹⁹F NMR (188 MHz, acetone-d6): δ = -83.8, (m, 3F), -109.1 (m, 2F). ¹³C NMR (75 MHz, acetone-d6) : δ = 168.2, 165.7, 138.7 (t, J = 3.3 Hz), 134.3, 133.4, 130.5, 129.8 (t, J = 6.1 Hz), 126.1 (t, J = 24.0 Hz). HRMS: calcd. for C₁₁H₅F₅O₄: 285.0186, found 285.0025

2,2'-bistrifluoromethyl-4,4'-azobenzenedicarboxylic acid was synthesized following a procedure derived from the one used to prepare 4,4'-azobenzenedicarboxylic acid.⁵ 2-trifluoromethyl-4nitrobenzoic acid (1.0 g, 4.2 mmol) and NaOH (2.9 g, 73 mmol) were mixed in water (12 mL) and heated at 50°C; a hot (~70°C) aqueous solution of glucose (5.7 g in 8.5 mL of water) was then added, leading to a dark brown coloration. The mixture was stirred for 5 h and acidified with a 5 M HCl solution down to pH = 1. The resulting light brown-pink precipitate was recovered by filtration, and redissolved in 20 mL of a 2 M NaOH solution. 10 mL of a 30 wt% H₂O₂ solution were added, and the solution stirred for 12 h. A 5 M HCl solution was added until the pH reached 1. The resulting pink precipitate was recovered by filtration, washed with water and dried in air. ¹H NMR (200 MHz, DMSO-d₆): δ = 8.31 (s, 2H), 8.28 (d, J = 8.5 Hz, 2 H,), 8.06 (d, J = 8.0 Hz, 2 H). ¹⁹F NMR (188 MHz, DMSO-d₆): δ -58.4. ¹³C NMR (75 MHz, DMSO-d₆, 323 K): δ = 167.3, 152.7, 135.5, 131.8, 128.6 (q, J = 32 Hz), 127.0, 123.0, (q, J = 271.7 Hz, CF₃), 121.2, (q, J = 5,4 Hz).

MOFs synthesis

UiO-66 solids were prepared according to the following general procedure. $ZrCl_4$ (233 mg, 1 mmol), the terephthalic acid derivative (1 mmol) and DMF (3 mL) were added into a 23 mL teflon-lined Paar autoclave. In the case of UiO-66-C₂F₅, 85 µL of a 12 M HCl solution was also added. The mixture was heated to 100 °C for 24 h. After cooling down to room temperature, the product was filtered off, washed with DMF overnight, and then washed twice with MeOH for 8 h, and further dried in air.

UiO-66D was synthesized according to the reported procedure.⁶

UiO-66D-(CF₃)₂ was prepared from a mixture of 0.5 mmol (116 mg) of $ZrCI_4$, 1 mmol of 2,2'bistrifluoromethyl-4,4'-azobenzenedicarboxylic acid and 285 µL of acetic acid in 5 mL of DMF. The mixture was placed into a 23 ml teflon-lined Paar autoclave and heated at 120°C for 16 h. The resulting solid was recovered by filtration, thoroughly rinsed with DMF, washed overnight once with DMF (50 mL), once with MeOH and further dried under vacuum.

2. XRPD analysis.

XRPD data were collected at 293 K on a Siemens D5000 diffractometer by using CuK α radiation (λ = 1.5418 Å). The patterns were scanned over an angular range 4-50° (2 θ) with a step length of 0.02° (2 θ). XRPD patterns were indexed by means of the computer program DICVOL04⁷ from the first ten lines, with an absolute error in peak positions of 0.03° (2 θ). Subsequent Le Bail structure-independent fits were performed using FullProf⁸ software integrated in the WinPlotr suite.⁹

Solid	possible space group	a (Å)	V (Å ³)
UiO-66-CH ₃	Pm-3m	20.737(3)	8917(2)
UiO-66-2CH ₃	Fm-3m	20.774(1)	8964.8(8)
UiO-66-2C ₂ H ₅	Fm-3m	20.781(1)	8974.6(6)
UiO-66-CF ₃	Fm-3m	20.713(3)	8886(2)
UiO-66-2CF ₃	Fm-3m	20.789(3)	8985(2)
UiO-66-C ₂ F ₅	Fm-3m	20.779(5)	8971(4)
UiO-66D	Fm-3m	29.514(2)	25710(2)
UiO-66D-2CF ₃	Fm-3m	29.577(3)	25873(4)

Table S1. Unit-cells parameters of the UiO-66 and UiO-66D series.







Figure S2. From bottom to top: XRPD patterns of UiO-66- C_2F_5 , UiO-66- CH_3 , UiO-66- $(CH_3)_2$ and UiO-66- $(C_2H_5)_2$ after a long term storage (> 2 years) under ambient air. These diagrams are similar to the ones of the fresh samples shown in Figure 1.



Figure S3. XRPD pattern of UiO-66D-(CF_3)₂ before (bottom) and after (top) the water sorption experiment.



3. Solid state NMR.

All magic-angle spinning (MAS) NMR experiments were recorded on an Avance Bruker 500 spectrometer (Larmor frequencies of 500.1, 470.3 and 125.7 MHz for ¹H, ¹⁹F and ¹³C, respectively). For the fluorinated MOFs, a triple-channel ¹H-¹⁹F-X 2.5 mm probe,^{10, 11} allowing simultaneous irradiation/reception on the ¹H and ¹⁹F channels, was used at MAS of 25 kHz. The ¹³C NMR spectra were acquired using $({}^{1}\text{H}-{}^{19}\text{F}) \rightarrow {}^{13}\text{C}$ triple cross-polarization (TCP) experiment, 12 in which both the ${}^{1}\text{H}$ and ¹⁹F magnetization are transferred to the carbon atoms (Figure 3). The radiofrequency (RF) field on ¹³C was set to 70 kHz, and the ¹H and ¹⁹F RF field was adjusted to optimize the CP transfer around the n + 1 Hartmann-Hahn matching condition. ¹H small-phase incremental alternation (SPINAL-64¹³ and ¹⁹F swept-frequency two pulse phase modulated (SW(f)-TPPM)^{14, 15} decoupling schemes were applied with ~ 100 kHz RF fields on each channel. The recycle delay was 3 s for all samples and the contact time was set to 2 ms. 1024 to 5120 transients were co-added for each 1D spectrum, depending on the sample. The ¹H and ¹⁹F MAS NMR spectra were recorded using a rotorsynchronized Hahn-echo experiment, with 90° pulse length of 2.5 µs and recycle delays between 1 and 3 s depending on the sample. 16 to 32 transients were accumulated for each sample. The ${}^{19}F \rightarrow {}^{1}H$ CP-HETCOR NMR spectrum of UiO-66(Zr)-C₂F₅ (see Figure S4) was recorded using 1 ms contact time and 100 kHz RF field on ¹H and ¹⁹F. The States procedure was applied to obtain a phase sensitive spectrum. 64 t1 slices with 32 transients each were co-added. For the non-fluorinated MOFs, the ¹³C NMR spectra were recorded using a classical ${}^{1}H \rightarrow {}^{13}C$ CPMAS NMR experiment at MAS 10 kHz. The ${}^{13}C$ RF field was set to 50 kHz. ¹H SPINAL-64 decoupling was applied during the signal acquisition. The ¹H and ¹³C chemical shifts are referenced to TMS, the ¹⁹F chemical shifts are referenced to C₆F₆. The spectra were analyzed using the DMfit software.¹⁶

Figure S4. ¹⁹F MAS NMR spectra of the fluorinated studied MOFs. Unlabeled resonances are spinning sidebands.



Figure S5. ¹H MAS NMR spectra of the fluorinated studied MOFs. Unlabeled resonances are spinning sidebands.



Figure S6. ¹⁹F \rightarrow ¹H CPMAS HETCOR spectrum of UiO-66-C₂F₅, showing the spatial proximities between the fluorine and the protons (linker and hydroxyl) of the framework. The resonances are assigned.



Figure S7. ¹⁹F \rightarrow ¹H CPMAS HETCOR spectrum of UiO-66-C₂F₅, ₅, showing the spatial proximities between the fluorine and the protons (linker and hydroxyl) of the framework The resonances are assigned.



4. Nitrogen sorption measurements

The UiO-66 solids were heated overnight at 200 °C (160°C in the case of UiO-66D-(CF_3)₂) under primary vacuum (BEL Japan, BELSORP Prep) before recording nitrogen sorption isotherms at 77 K using a BEL Japan Belsorp Mini apparatus. Adsorption-desorption isotherms are shown in Figure S6.

Figure S8. Nitrogen sorption isotherms.



Table S2. BET surface areas and pore volumes extracted from nitrogen sorption experiments carriedout at 77 K.

Solid	S _{BET} (m ² g ⁻¹)	Vp (cm ³ g ⁻¹)
UiO-66-C ₂ F ₅	570	0.26
UiO-66-(CF ₃) ₂	630	0.30
UiO-66-CF ₃	815	0.36
$UiO-66-(C_2H_5)_2$	340	0.16
UiO-66-(CH ₃) ₂	790	0.35
UiO-66-CH ₃	760	0.32
$UiO-66D-(CF_{3})_{2}$	2180	0.88

5. Water sorption measurements

The water adsorption-desorption isotherms at 298 K were carried out using a gravimetric device (Q5000SA TA Instruments), which combines a high-sensitivity thermobalance and a humidity control chamber. Approximately 10 mg of sample was used. Prior to each experiment, the sample was outgassed *in situ* at 80°C (maximum temperature allowed by the device) under inert gas (N₂) flow for 5 h. The water adsorption isotherms were performed from 5% to 95% relative humidity (R. H.) at 298 K.

Moreover, in order to evaluate the stability and regenerability of the solid UiO-66D- $(CF_3)_2$ with respect to humidity, a second water adsorption run was performed at 298 K, without thermal regeneration between the two runs.

Figure S9. Successive water sorption isotherms for UiO-66D-(CF_3)₂, highlighting the instability of this solid towards moisture.



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