Hydrophobicity and dielectric properties across an isostructural family of MOFs: a duet or a duel?

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Materials and methods.

Experimental details

The dielectric constants were determined through impedance spectroscopy, carried out with a Solartron impedance/Gain-Phase analyzer ModulabXM equipped with XM MFRA 1 MHz and XM MAT 1 MHz control modules. A 12962A sample holder was used with dried powder pellet samples with a diameter of 13 mm prepared by applying a force of ca. 15 kN (corresponding to a pressure of ca. 0.1 GPa). The measurement parameters were controlled with the ModulabXM software. A fixed mode generator voltage level of 0 V with amplitude of 100 mV was applied with a frequency sweep from 1 Hz to 1 MHz. All pellets were activated at 120 °C for 8 h at 10^{-2} mbar and loaded into the sample holder in a glovebox under N₂ atmosphere. After the initial measurements at time t₀, all the pellets were expose to a stable air humidity of ca. 60% and the dielectric constant was measured after 24 h of air exposition. For each sample, we performed at least two measurements, and the reported results are the averaged values.

X-ray powder diffraction patterns on the sample pellets were recorded with a Bruker D2-Phaser, equipped with a Cu K α X-ray tube, working at 30 kV and 10 mA.

Synthesis of UiO-66-X and UiO-66-X-PDMS (X = H, NH₂, NO₂, and (F)₄). UiO-66-X (X = H, NH₂, NO₂) derivatives were synthesized following the defect-controlled synthesis method reported by DeStefano *et al.*,¹ while UiO-66-(F)₄ was prepared following the original literature from Hu *et al.*²

We reproduce the four UiO-66-X-PDMS (X = H, NH₂, NO₂, (F)₄) derivatives following the post-synthetic polydimethylsiloxane (PDMS) treatment procedure reported by Zhang *et al.* (see detailed characterisation: Figures S1-S4 in the supporting information).³

Fourier Transform Attenuated Total Reflectance (FT-ATR). The FT-ATR spectra were obtained on a Fourier-transform spectrophotometer Perkin-Elmer Spectrum 100 in the range 4000–400 cm⁻¹.

Scanning electron microscopy (SEM) measurements. SEM images are obtained with a NVision40 (Carl Zeiss AG) field emission scanning electron microscope, with an accelerating voltage of 5 kV and a working distance of 7.2 mm.

Thermogravimetric analysis (TGA). TGA measurements were conducted on a Netzsch TG-DSC STA 449 F5 in a temperature range from 25 °C to 800 °C with a heating rate of 10 K min⁻¹ under argon flow (flow rate: 20 mL min⁻¹). It should be noted that the sample is briefly (few seconds) exposed to air before the measurement when the aluminium oxide pan is transferred from the Ar filled transport vial to the pan holder stage.

Water vapour adsorption isotherm measurements. Water vapour adsorption measurements were conducted on a Belsorp-Max porosimeter (Microtrac Bel) equipped with a cryostat to maintain the temperature of the sample cell at 298 K during the measurements. The measurements were conducted with deionized water, which was degassed by three freeze-pump-thaw cycles via the solvent degassing-routine of the instrument. For each measurement around 50 mg of sample were pre-treated by heating to 120 °C in dynamic vacuum overnight (10^{-3} mbar).

Static contact angle measurements. Static water contact angles were recorded angles were measured on pressed sample pellets (after subjecting solid samples to mechanical pressure of *ca*. 1.5 ton press, each) with a Krüss EasyDrop Kys DAS 10 MK2 contact angle meter, followed by Krüss Advance software based analysis (Young-Laplace Fit using "Sessile Drop Analysis" method). The analysis is based on the fitting of the Young–Laplace equation to the droplet image data (droplet shape analysis), by using 10 μ L of distilled water, with an accuracy of ± 0.5°.

 N_2 adsorption isotherms and surface area determination. Ultra-high-purity grade N_2 was used for nitrogen adsorption isotherm experiments at 77 K. Adsorption experiments (up to 1 bar) were recorded on Micromeritics 3Flex surface area and pore size analyzer. About 200 mg of activated samples were used for each measurement. Liquid nitrogen was used to maintain constant temperature in the bath throughout the duration of these experiments. Samples were degassed on a Smart VacPrep prior to the analysis. BETSI.exe was used to determine the BET surface areas.⁴



Figure S1. A) Powder X-ray diffractograms collected on A) pellets of UiO-66-X and UiO-66-X-PDMS, that are subsequently used for recording the dielectric measurements. B) UiO-66-X and UiO-66-X-PDMS (X = H, (F)₄, NO₂ and NH₂) powders after synthesis, plotted alongside the simulated UiO-66 powder X-ray pattern reported in Cambridge Structural Database Refcode RUBTAK03.⁵



Figure S2. FT-ATR spectra collected for UiO-66-X (X = H, (F)₄, NO₂, NH₂) and the corresponding PDMS protected ones. Signals from PDMS are found to overlap with those from the MOFs, such as the most characteristic signal due to the bonds Si-O-Si at 1120-1000 cm⁻¹.



Figure S3. FE-SEM morphologies for UiO-66, UiO-66-NO₂, UiO-66-NH₂, UiO-66-(F)₄: A, C, E, G, respectively, and those for the corresponding PDMS protected UiO-66-PDMS, UiO-66-NO₂-PDMS, UiO-66-NH₂-PDMS, UiO-66-(F)₄-PDMS: B, D, F, H, respectively.



Figure S4. Thermogravimetric analysis profiles for UiO-66-X (X = H, (F)₄, NO₂, NH₂) (A), and the corresponding PDMS protected ones (B).



Figure S5. N₂ adsorption isotherms recorded at 77 K for UiO-66-X and UiO-66-X-PDMS (X = H, (F)₄, NO₂ and NH₂).



Figure S6. Comparison of H₂O vapour adsorption isotherms (recorded at 298 K) for all the four UiO-66-X MOFs (X = H, (F)₄, NO₂ and NH₂) before and after the PDMS treatment (only the X label is shown).



Figure S7. Dielectric constant trends plotted in logarithmic scale, for UiO-66-X (X = H, (F)₄, NO₂, NH₂) and the corresponding PDMS protected ones at $t_0 = 0$, and t = 24 h of air exposure to 60% of relative humidity.



Figure S8. BETSI fitting and BET area calculations for UiO-66.



Figure S9. BETSI fitting and BET area calculations for UiO-66-(F)₄.



Figure S10. BETSI fitting and BET area calculations for UiO-66-NH₂.



Figure S11. BETSI fitting and BET area calculations for UiO-66-NO₂.

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