Supplementary Information

Thermo-temporal physisorption in Metal-Organic Frameworks probed by Cyclic Thermo-Ellipsometry

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Experimental section

Fabrication of the MOF films MIL-101(Cr) nanoparticles were synthesized using a microwave-assisted hydrothermal synthesis, following a procedure reported in the literature.¹ The resulting colloidal solution was applied by spin coating on a silicon wafer with a speed of 3500 rpm for 20s.

The ZIF-8 colloidal solution was synthesized using the rapid procedure described in the literature, using a slight modification of the protocol reported by Cravillon and $al.^2$ To prepare the solution, $Zn(NO_3)_2.6H_2O$ (1.47 g, 4.94 mmol) was dissolved in 100 mL of methanol and added to 2-Methylimidazole (3.24 g, 39.46 mmol) diluted in 100 mL of methanol. The solution was then allowed to cool and gently stirred. Within seconds, the mixture turned turbid, and after 7 minutes, centrifugation was performed multiple times to separate the nanoparticles from the dispersion. The resulting nanoparticles were then diluted with methanol and spin-coated on a silica wafer at 3500 rpm for 20s.

Characterization After coating, films were directly placed and characterized with UV-visible-NIR Woollam spectroscopic Ellipsometer (SE) (from 240 to 1700nm). The ellipsometer is equipped with a programmable heating stage (-80°C to 600°C) and an environmentally controlled chamber in which the local environment of the films can be controlled in terms of relative humidity or vapor pressure. Data measurement and analyses were performed with CompleteEASE by fitting the raw data curves by a Cauchy model for not absorbing materials. A mass flow controller is used to manage the vapor P/P₀ by combining two gas flows: (i) dry air flow with solvent P/P₀=0, and (ii) air flow that has gone through a bubbler containing liquid isopropyl alcohol (IPA) or water to obtain a saturated vapor P/P₀=1. The structural properties of the films were determined by SEM on a SU-70 Hitachi FESEM.

Calculation of the porous volume

Starting from the values of refractive index associated to the three states E, MF and F we can evaluate the porous volume by using the Bruggemann effective medium approximation (BEMA) model (eq 1). First, by taking the dielectric constant ε of the film in the empty (E) and filled state (F), this model allows the estimation of the dielectric constant of solid wall of the MIL-101 material (ε_{MOF}). In the empty and full states the BEMA model can be written as follows:

$$f_{MOF} \frac{\tilde{\varepsilon}_{MOF} - \tilde{\varepsilon}}{\tilde{\varepsilon}_{MOF} + 2\tilde{\varepsilon}} + f_A \frac{\tilde{\varepsilon}_A - \tilde{\varepsilon}}{\tilde{\varepsilon}_A + 2\tilde{\varepsilon}} = 0$$
 E state (1)

$$f_{MOF} \frac{\tilde{\varepsilon}_{MOF} - \tilde{\varepsilon}}{\tilde{\varepsilon}_{MOF} + 2\tilde{\varepsilon}} + f_W \frac{\tilde{\varepsilon}_W - \tilde{\varepsilon}}{\tilde{\varepsilon}_W + 2\tilde{\varepsilon}} = 0$$

F state (2)

being f_{MOF} , f_w and f_A and ε_{MOF} , ε_W , ε_A the relative volumetric fractions and dielectric constants of three compounds MOF, W (Water) and A (Air). We consider the dielectric constants to be the square of refractive index values (real part of the dielectric constants). This assumption can be made for media that are not adsorbing light in the considered range of wavelengths (typically 400-1000nm). It has to be noted, MIL101 (Cr) present a green color typical chromium based MOFs. However, the density of absorbing sites for a given volume in these very porous films is very low and the absorption contribution is negligible when performing ellipsometric measurements. For this reason, Cauchy model for "transparent" materials is generally employed to fit MIL-101(Cr) films. ¹ According with the scheme in Figure (1b), in the Filled state (F) all the air that was initially present in the film (porosity of the MOF + interparticle void) is replaced with water. We can thus assume that:

$$f_w = f_A \tag{3}$$

that also corresponds to the total porous volume. According to Figure (1c), the refractive indices of the empty and filled states are 1.16 and 1.43 respectively. Considering the refractive indices of water and air equal to 1.34 and 1 respectively, the porous volume and the ε_{MOF} (and the refractive index) can be calculated by combining equations (1), (2) and (3).

Following this calculations, the refractive index of the MIL-101(Cr) wall is deduced to be equal to 1.72 while the total porous volume is 74%. By knowing these values, we can calculate the percentage of porosity associated to each family of mesopores by applying a 3 phase BEMA relation for intemediate states:

$$f_{MOF} \frac{\tilde{\varepsilon}_{MOF} - \tilde{\varepsilon}}{\tilde{\varepsilon}_{MOF} + 2\tilde{\varepsilon}} + f_A \frac{\tilde{\varepsilon}_A - \tilde{\varepsilon}}{\tilde{\varepsilon}_A + 2\tilde{\varepsilon}} + f_W \frac{\tilde{\varepsilon}_W - \tilde{\varepsilon}}{\tilde{\varepsilon}_W + 2\tilde{\varepsilon}} = 0 \qquad \text{E} < \text{state} < \text{F}$$
(4)

In which:

$$f_{MOF} + f_A + f_W = 1 \tag{5}$$

Since f_{MOF} is equal to 0.74 this relationship can be rewritten as follows

$$f_W = 0.26 - f_A \tag{6}$$

and introduced in equation (4). From this calculation, the small cages, larges cages and interparticle mesoporosities represent around the 8%, 12% and 80% of the total porosity.

Capillary condensation in MIL101

The Kelvin equation relates the equilibrium vapor pressure of a liquid in a curved surface to the vapor pressure of the bulk liquid. The equation is given by:

$$\ln\left(\frac{P}{P_0}
ight) = \frac{2\gamma V_m}{RTr}$$

- P is the equilibrium vapor pressure of the liquid at a given curvature r,
- P_0 is the vapor pressure of the bulk liquid,
- γ is the surface tension of the liquid,
- V_m is the molar volume of the liquid,
- R is the gas constant
- T is the temperature.

From the Kelvin equation, we can see that as the radius of curvature r decreases, the term $\frac{2\gamma V_m}{RT_r}$ becomes more negative. This means that capillary condensation occurs at lower P/P₀ values, as smaller pores (corresponding to smaller radii of curvature) induce greater curvature, leading to higher vapor pressures within the pores.

In our experiment, decreasing the temperature results in gradually increase of P/P_0 in the film (see Figure S1) leading to the capillary condensation of the small cages first and of the large cages after.



Figure S1 Schematic evolution local gradients of temperature, saturated vapor pressure and relative vapor pressure as function of the temperature in the film.



Figure S2 XRD pattern of a MIL-101(Cr) colloidal film.



Figure S3 Thickness evolutions as function of the temperature in presence of $0.5 P/P_0$ of water vapor: adsorption and desorption isobars determined by in-situ ellipsometry.

Figure S3 displays the thickness evolution of the film associated to the thermal-induced water sorption. The film presents several contractions induced by capillary stresses during capillary condensations of water. Each contraction is associated to filling of the three mesoporous families: two cages of MIL-101(Cr) and one for interparticle voids. Here again, after desorption, the film recovers its initial thickness.



Figure S4 *Evolution of the measured temperature and optical signal as function of the time for the fastest cycles*

The Figure shown the data of refractive index as function of the temperature measured by the thermocouple for the faster cycles. No time delay is observed between the temperature and optical profiles (at least within the temporal resolution of the measurement) further confirming that the trend observed in Figure 3 can only be attributed to the adsorption kinetics of the material.



Figure S5 *a*) SEM micrograph of the cross section view of a colloidal ZIF-8 film on Si, (c) XRD pattern of the colloidal film.

The SEM micrograph in Figure S5a displays a cross section view of ZIF-8 colloidal film obtained after synthesis and deposition. The film is composed of nanoparticles having average size of 40 nm (as evaluated by SEM micrographs) and a thickness of around 300nm. The cristallinity of the materials was first confirmed by X-ray diffraction as shown in Figure (S5b).



Figure S6 (a) Schematic representation of the ZIF-8 structure and (b) Refractive index evolutions as function of the temperature in presence of $0.2 P/P_0$ of IPA

The crystal lattice of ZIF-8 consists of tetrahedral metal centers, often zinc ions, interconnected by organic imidazolate linkers. This framework imparts ZIF-8 with a precisely defined pore size, approximately 11.6 angstroms as illustrated in Figure S6a. ZIF-8's micropores are hydrophobic, repelling water molecules and enhancing its affinity for less polar species (organic molecules, alcohol). To extend the scope of the cyclic thermo-ellipsometry we thus applied the approach on a ZIF-8 colloidal film in presence of IPA vapors. Figure (S6b) illustrate isobars were carried out in presence of a constant relative vapour pressure of IPA = $0.2 \text{ P/P}_0^{(20^{\circ}\text{C})}$ and expressed as the evolution of refractive index (at 700nm) as function of the temperature. The isobars were recorder at a heating/cooling rate of 3°C min⁻¹. At T = 90°C, the colloidal film presents a low refractive index of 1.22 suggesting that the film is "empty" (E). At around 60°C the increase in refractive index, correspond to IPA filling the ZIF-8 microposity. At 30°C the porosity of the MOF is filled (state "MF"). Further cooling leads to the capillary condensation of IPA molecules in the mesopores formed by inter-particle voids of the film (F state). By heating back, the process is reversible. Interestingly, already at 3°C min⁻¹ a hysteresis loop between the state "MF" and "E" is observed, unusual since the material is microporous and should present no hysteresis.

To further probe the evolution of this hysteresis and investigate the thermo-temporal response we carried out a cycling experiment between 90 and 35°C with increasing scan rates. This temperature range was chosen to exclusively investigate the microporosity of the ZIF-8. The derivative of the refractive index with respect to time $\Delta n/\Delta t$ as a function of temperature is shown in Figure (S7a) for each scan rate. In this configuration, only one adsorption and desorption peak is observed, in agreement with the fact that ZIF-8 present a single-size porosity. By increasing the scan rate, the adsorption and desorption peaks shift toward lower and higher temperature respectively.



Figure S7 (*a*) Derivative of the refractive index with respect to time as function of the temperature for different scan rate (*a*) Evolution of the adsorption and desorption temperatures as function of the scan rate (the dashed arrows are guides for the eye)

Figure S7b displays the evolution of adsorption or desorption temperatures (position of the peak) as a function of the scan rate. The analysis indicates that both adsorption and desorption temperatures strongly vary with the scan rate. Specifically, at a low scan rate (3°C min⁻¹), the difference between adsorption and desorption temperatures is minimal, around 2°C, while an increase in the heating and cooling rate up to 20°C min⁻¹ widens the hysteresis. This trend further confirms that, in these conditions, the system is not at thermodynamic equilibrium and that the sorption response strongly depends on the rate at which the temperature is varied. Indeed, under equilibrium conditions, microporous materials such as ZIF-8 should exhibit no hysteresis. Considering the trend of the experiment reported in Figure S7b, one can suggest that a scan rate below 3°C min⁻¹ should be chosen to analyze ZIF-8 at thermodynamic equilibrium. This result further underscores the importance of this thermo-temporal analysis in probing the sorption performances of MOFs.

- 1 A. Demessence, P. Horcajada, C. Serre, C. Boissière, D. Grosso, C. Sanchez and G. Férey, *Chemical Communications*, 2009, 7149.
- 2 J. Cravillon, S. Münzer, S.-J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chemistry of Materials*, 2009, **21**, 1410.