## Supporting Information

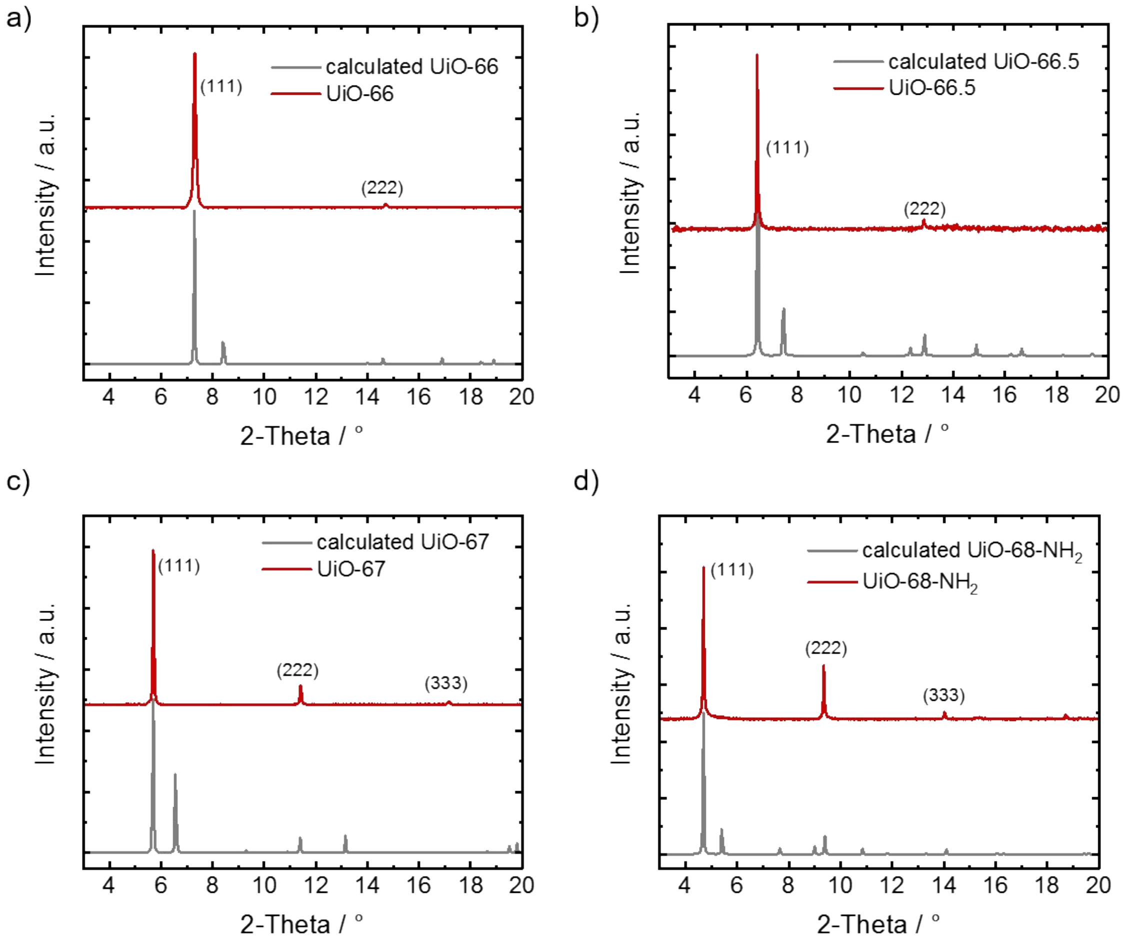


**Figure S1**. XRD data of the samples (red) compared with the XRD data calculated for the respective MOF structures (grey). The experimentally observed diffraction peaks are labeled. The MOFs are a) UiO-66, b) UiO-66.5, c) UiO-67 and d) UiO-68-$NH_2$.

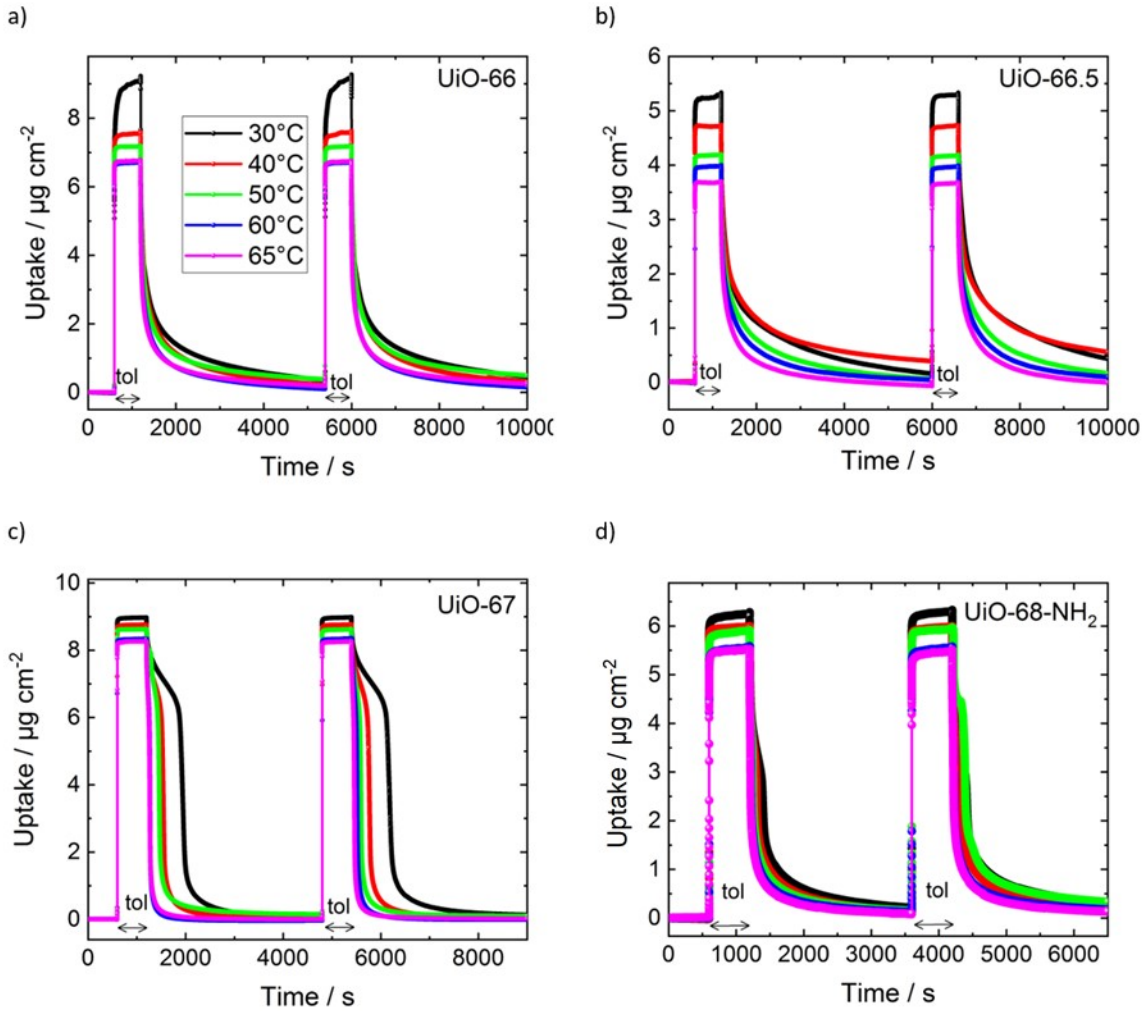


**Figure S2**. Toluene uptake *versus* time for a) UiO-66, b) UiO-66.5, c) UiO-67 and d) UiO-68-$NH_2$. The temperatures are 30°C (black), 40°C (red), 50°C (green), 60°C (blue) and 65°C (magenta). The uptake is measured by QCM. The uptake and release of the toluene vapor was performed twice, showing an essentially identical uptake and release.

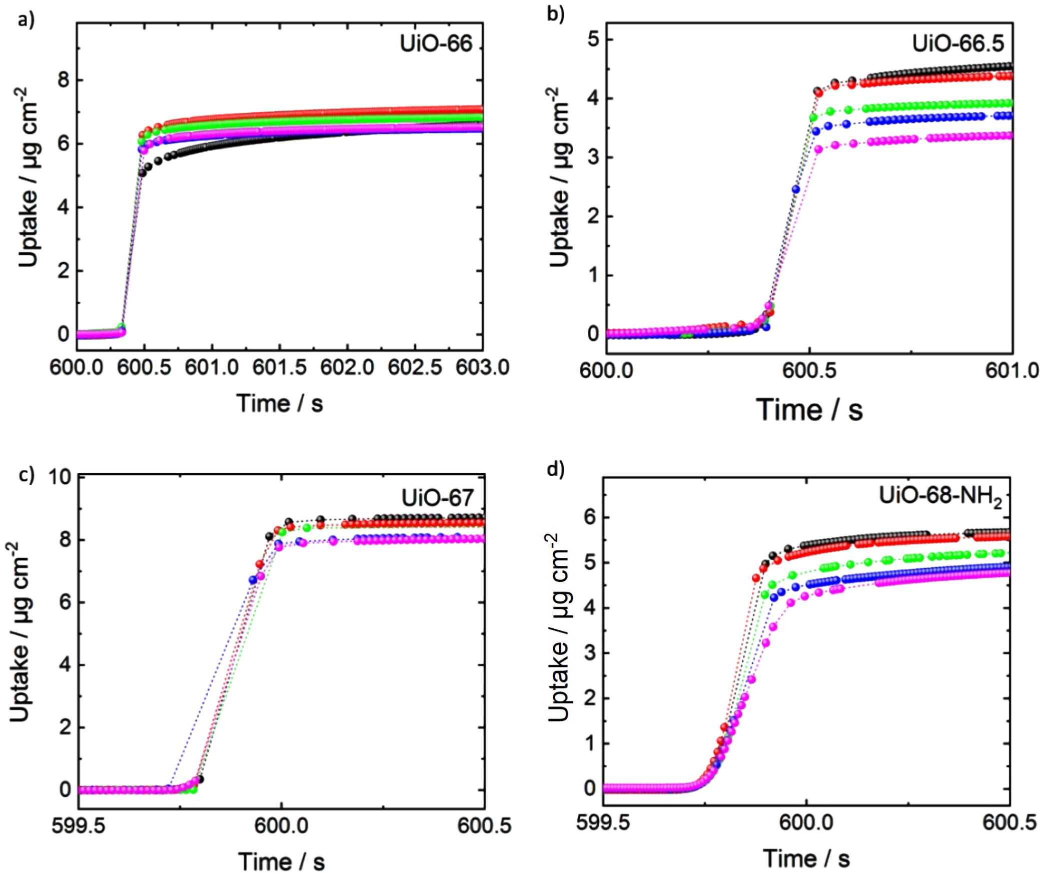


**Figure S3**. Toluene uptake *versus* time for a) UiO-66, b) UiO-66.5, c) UiO-67 and d) UiO-68-$NH_2$. The temperatures are 30°C (black), 40°C (red), 50°C (green), 60°C (blue) and 65°C (magenta). The plots are zoom-ins of the data of Figure 3.

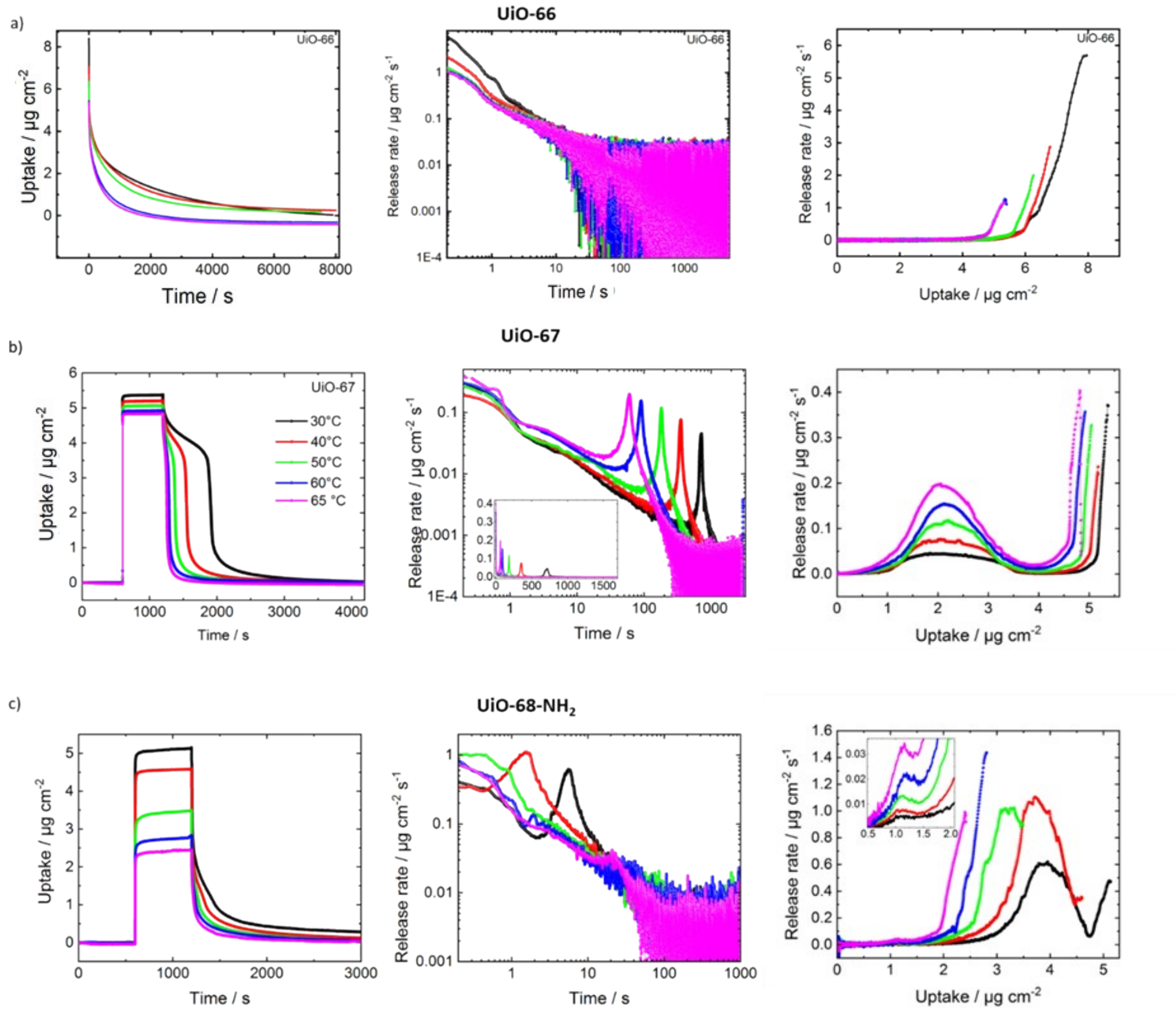


**Figure S4**. Toluene uptake and release for a **second set of samples** of a) UiO-66, b) UiO-67 and c) UiO-68-$NH_2$. The temperatures are 30°C (black), 40°C (red), 50°C (green), 60°C (blue) and 65°C (magenta), see also legend. The uptake is measured by QCM and the experiments are performed like in Figure 3. Left-hand side: The QCM uptake data *versus* time. Center: Toluene desorption rate *versus* time. Right-hand side: Toluene desorption rate *versus* toluene loading. Please note, the absolute loading in the data in Figure 3-5 is different (due to a different film thickness), but the relative features are the same.

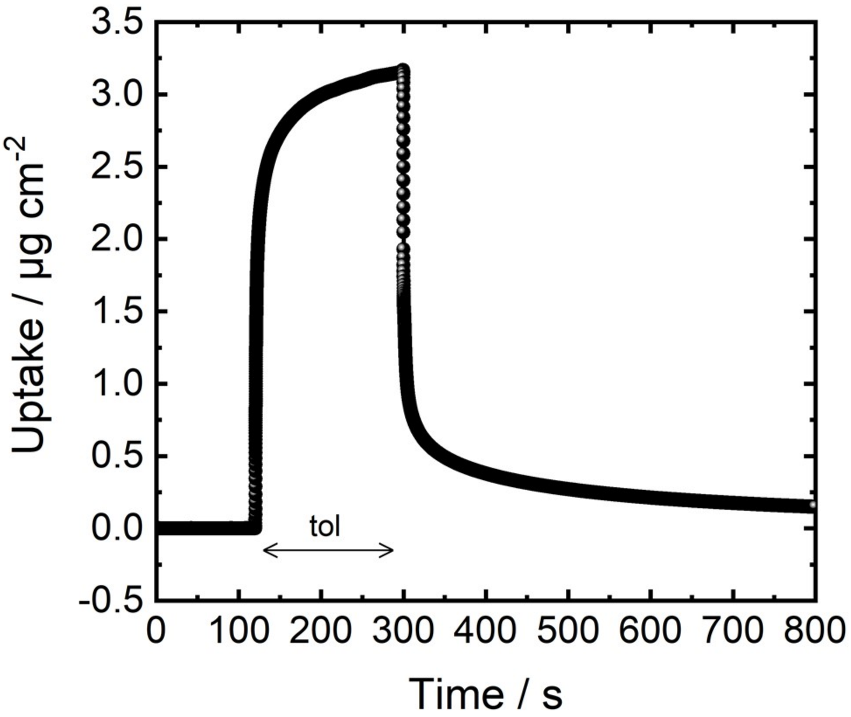


**Figure S5**. Toluene uptake and release *versus* time in ZIF-8. The uptake is measured by QCM. The time interval where the nitrogen flow is enriched with toluene (tol) is labeled. The temperature is 30°C. Fitting the data with mono-exponential fits results in a time constant of 20.9 s for the uptake process and 20.5 s for the release.

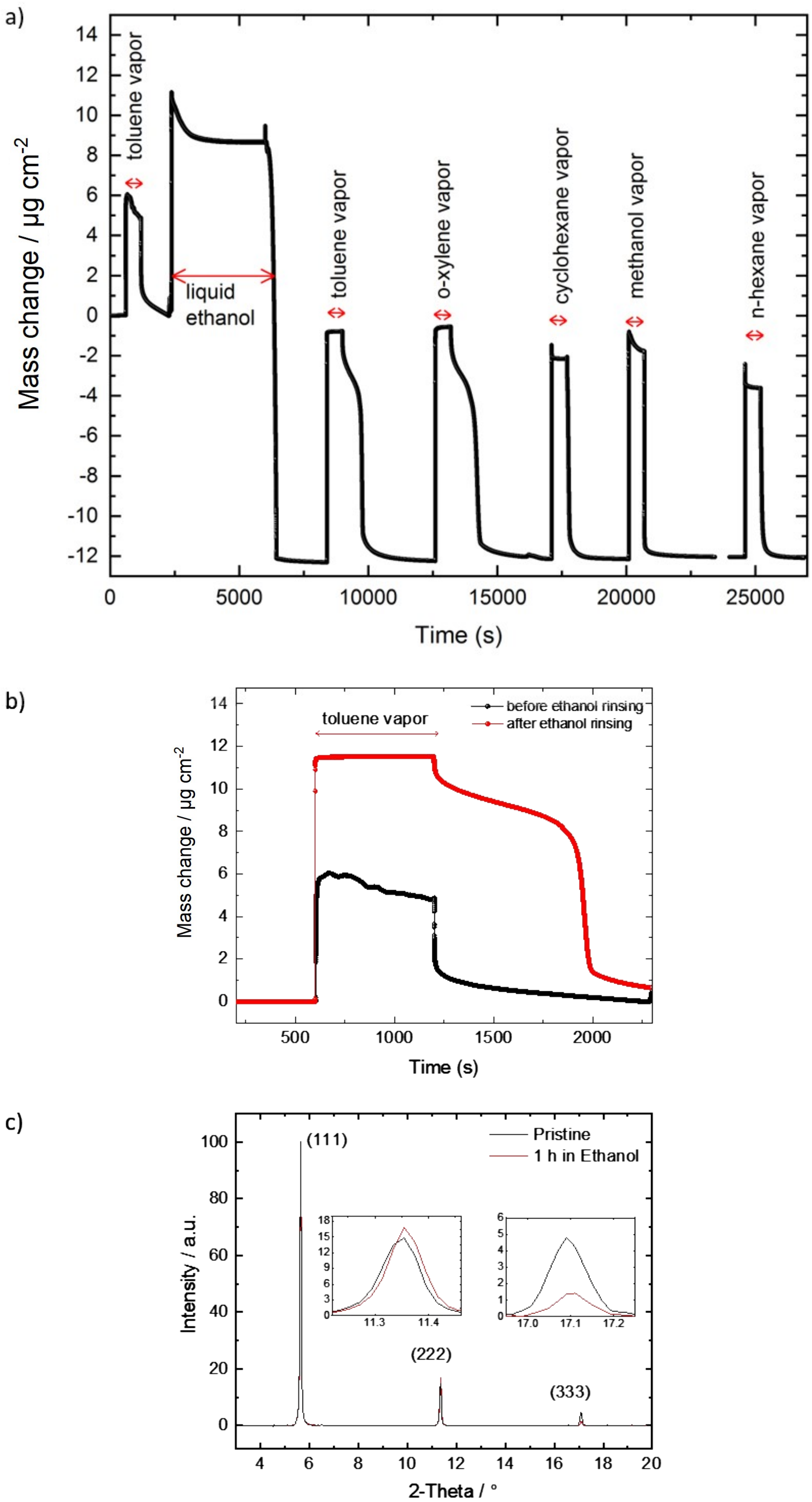


**Figure S6**. **a)** Uptake and release of toluene vapor, liquid ethanol (i.e. rinsing the QCM cell with ethanol), toluene, o-xylene, cyclohexane, methanol and n-hexane vapor *versus* time for UiO-67 MOF film. The mass of the MOF film decreases by about 12.3 µg $cm^{-2}$, upon rinsing the sample with liquid ethanol. **b)** Toluene uptake and release of the sample before and after ethanol rinsing for 1 h. The slow, step-like release kinetics, indicating the molecular clustering, can only be observed after emptying the MOF pores. **c)** The XRD of the sample before and after rinsing the sample with ethanol. The intensity is normalized to the (111) peak. The change of the intensities of the (222) and (333) reflexes (see insets) indicate the change of the XRD form factor, most likely due to the emptying of the MOF pores from remains from the synthesis.

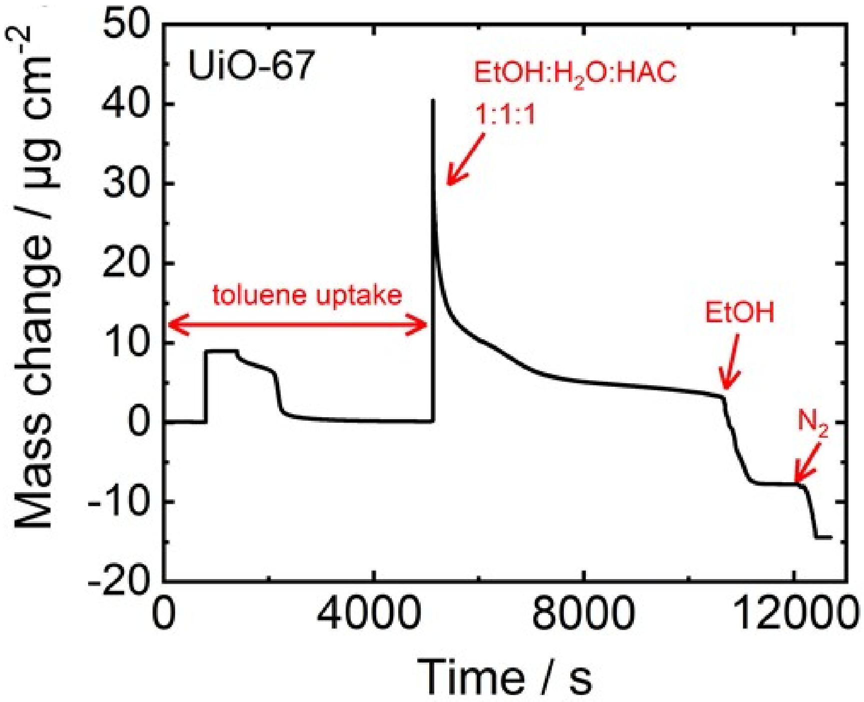


**Figure S7**. Dissolving the UiO-67 film sample (Figure 3-5) for the estimation of the MOF mass. After the toluene uptake and release experiments, an ethanol/water/acidic-acid solution (1:1:1) was pumped through the QCM cell, dissolving the MOF film. Then, ethanol is pumped through the cell and later it is switched back to the nitrogen flow drying the sample, see labels. The mass of the sample decreases by 14.4 µg cm$^{-2}$.

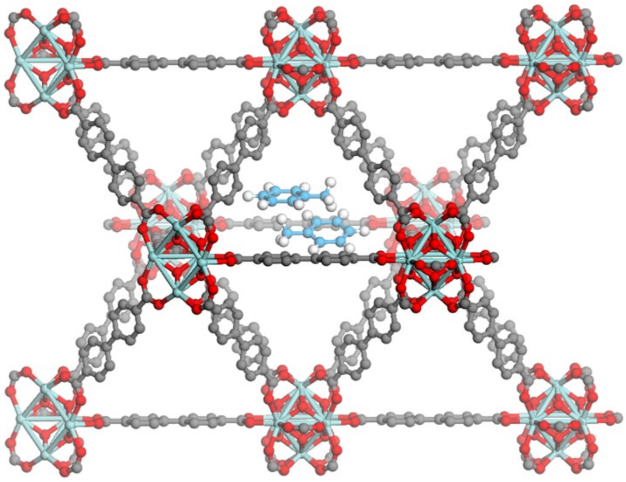

**Figure S8**. A toluene dimer sketched inside the large octahedral UiO-67 pore. The geometry of the dimer is taken from in refs.[1, 2], where it was calculated for 2 isolated molecules. Interactions with the MOF host are not considered here.

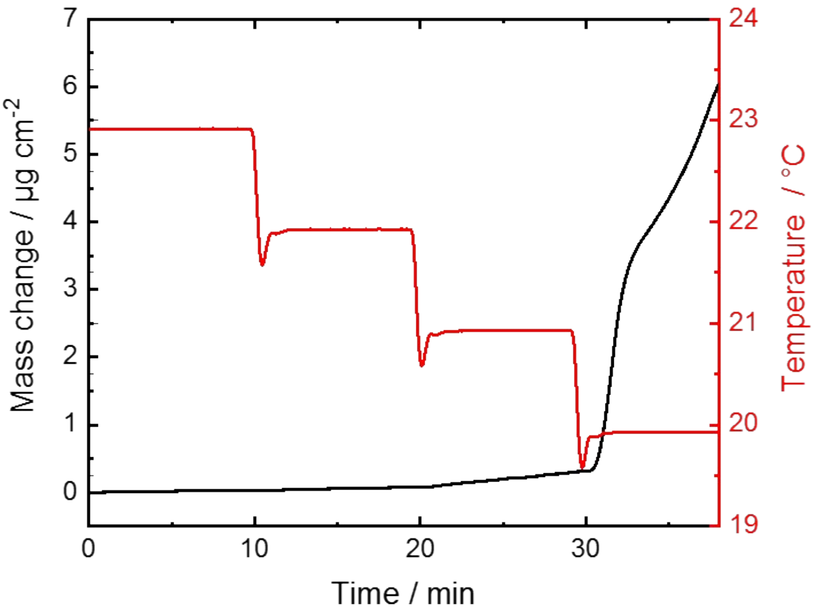


**Figure S9:** Dew points of the toluene vapor. The gas flow enriched with the toluene vapor was flowing over a blank QCM sensor. The temperature of the QCM sensor was decreased step-by-step, starting from 23°C with a step size of 1°C. The vapor was made by bubbling the nitrogen gas flow through the wash bottles at room temperature, 21.5°C. When the temperature of the QCM sensors was below the dew point of the vapor, the vapor condensed and the determined mass on the QCM sensor increased.

The determined dew point is 20°C, which corresponds to toluene vapor with a partial pressure of approximately 30 mbar, see ref.[3].

## References:


1. T. M. D. Palma, A. Bende and A. Borghese, *Chemical Physics Letters*, 2010, **495**, 17-23.
2. S. Chakrabarty, J. J. Ferreiro, M. Lippe and R. Signorell, *J Phys Chem A*, 2017, **121**, 3991-4001.
3. L. M. Besley and G. A. Bottomley, *Journal of Chemical Thermodynamics*, 1974, **6**, 577-580.