

Supporting Information:

Photoswitchable Nanoporous Films by Loading Azobenzene in Metal-Organic Frameworks of Type HKUST-1

Kai Müller,^a Jasmine Wadhwa,^a Jasleen Singh Malhi,^a Ludger Schöttner,^a Alexander Welle,^{a,c} Heidi Schwartz,^b Daniela Hermann,^b Uwe Ruschewitz,^b and Lars Heinke^a

^a Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^b Department of Chemistry, University of Cologne, Greinstraße 6, 50939 Köln, Germany.

^c Karlsruhe Nano Micro Facility, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

Supporting Information 1: SURMOF Synthesis, Used Chemicals, Synthesis of *O*-Tetrafluoroazobenzene and Methods

HKUST-1 SURMOFs were prepared in a step-by-step fashion by alternatively dipping the substrates in the solutions of the MOF components, i.e. ethanolic 1 mM copper(II) acetate solution and ethanolic 0.2 mM trimesic acid (also known as benzene-1,3,5-tricarboxylic acid) solution.¹

The samples were prepared in 40 synthesis cycles. The SURMOF substrates are quartz glass functionalized by oxygen plasma treatment (for UV-vis experiments) or gold-coated QCM sensors as well as gold-coated silicon wafers, functionalized with an 11-mercapto-1-undecanol self-assembled monolayer.

The chemicals, i.e. trimesic acid (98%, Alfa Aesar), copper(II) acetate (99.9% metal, Alfa Aesar), azobenzene (98%, Sigma Aldrich), 11-mercapto-1-undecanol (99%, Sigma Aldrich), 1,4-butanediol (99%, Alfa Aesar) and ethanol (99.5%, VWR Chemicals) were used without further purification.

o-Tetrafluoroazobenzene (*tF*-AZO) was synthesized in an optimized procedure following ref.²:

350.0 mg (2.73 mmol) 2,6-difluoroaniline were dissolved in 25 ml CHCl₃ and 3.03 g (6.83 mmol) Pb(IV)-acetate were added. The red suspension was heated for 1.5 h under reflux and subsequently stirred at room temperature overnight. After filtration the solution was washed with acetic acid (50 %) and the organic phase was dried with MgSO₄, before the solvent was removed under reduced pressure. The crude residue was purified by column chromatography (dichloromethane/cyclohexane, 3:2) to give *o*-tetrafluoroazobenzene as an orange solid (131 mg, 38 %; ref.²: 24 %). The product is always a mixture of the *trans* and *cis* isomer.

Ethanolic solution of pure *trans o*-tetrafluoroazobenzene is obtained by thermal relaxation at 60°C for about 1 week.

X-ray diffraction, using a Bruker D8 Advance with a wavelength of $\lambda = 0.154$ nm and a θ - θ geometry, was employed to study the crystalline structure.

UV-vis spectroscopy in transmission mode was used for investigating the azobenzene loading and the *trans-cis* isomerization of the azobenzene.³ The spectra were recorded by means of a Cary5000 spectrometer with a UMA unit from Agilent.

Infrared reflection-absorption (IRRA) spectroscopy was used for quantifying the isomerization yield.³ A FTIR spectrometer of type Bruker VERTEX 80 was used. All results were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal. Perdeuterated hexadecanethiol-SAMs on gold-coated silicon wafers were used for reference measurements.

The quantification of the uptake amount m of the guest molecules (here: 1,4-butanediol) was realized by using a QCM.^{4, 5} An E4-QCM from Q-Sense working at a resonance frequency of approximately 5 MHz was used.

X-ray photoelectron spectroscopy (XPS) was carried out under ultra-high-vacuum chamber with a base pressure in the 10^{-10} mbar range. The spectrometer is equipped with a VG Scienta R4000 electron energy analyzer. All Spectra were recorded under normal emission angle using Al K α (nonmonochromatic, 1486.68 eV) radiation.

Stoichiometric calculations were made on the base of Gaussian line fitted peak areas normalized to the respective relative sensitivity factor after Shirley-background subtraction. [J. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129-137.]

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) was performed on a TOF.SIMS5 instrument (ION-TOF GmbH, Münster, Germany). This spectrometer is equipped with a Bi cluster primary ion source and a reflectron type time-of-flight analyzer. UHV base pressure was $< 5 \times 10^{-8}$ mbar. For high mass resolution the Bi source was operated in the “high current bunched” mode providing short Bi $_3^+$ primary ion pulses at 25 keV energy, a lateral resolution of approx. 4 μm , and a target current of 0.26 pA at 200 μs cycle time. The short pulse length of 0.9 ns allowed for high mass resolution. The primary ion beam was scanned across a $200 \times 200 \mu\text{m}^2$ field of view on the sample, and 64×64 data points were recorded. Spectra were calibrated on the omnipresent C $^+$, C $_2^+$, C $_3^+$, and Au $^+$; or on the C $^+$, CH $^+$, CH $_2^+$, and CH $_3^+$ peaks. Based on these datasets, the chemical assignments for characteristic fragments were determined. For depth profiling a dual beam analysis was performed in fully interlaced mode. The sputter gun operated with Ar $_{1500}^+$ ions, 10 keV, scanned over a concentric field of $350 \times 350 \mu\text{m}^2$, target current 6 nA, was applied to erode the sample.

An LED with a power of 112 mW (365 nm), 65 mW (400 nm), 135 mW (455 nm) and 55 mW (365 nm) was used. The power was determined by the factory. These values may serve as an upper limit and a rough orientation of the light power, since the LED intensity may have decreased (e.g. aging effect) and the power loss in the used light cables is not considered.

Supporting Information 2: UV-vis spectra of azobenzene and *O*-Tetrafluoroazobenzene in ethanol

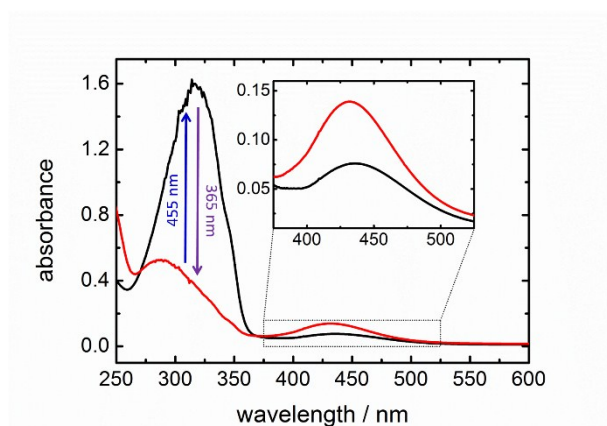


Figure S2-A: The UV-vis transmission spectra of the ethanolic azobenzene solution. Upon irradiation with 365 nm, the azobenzene photoisomerization from *trans* to *cis* is clearly visible by the decrease of the π - π^* band at about 320 nm and an increase of the n - π^* band at approximately 430 nm. By irradiating the sample with 455 nm, the *cis* azobenzene undergoes photoisomerization to the *trans* state, i.e. the π - π^* band increases and the n - π^* band decreases again (spectrum not shown).

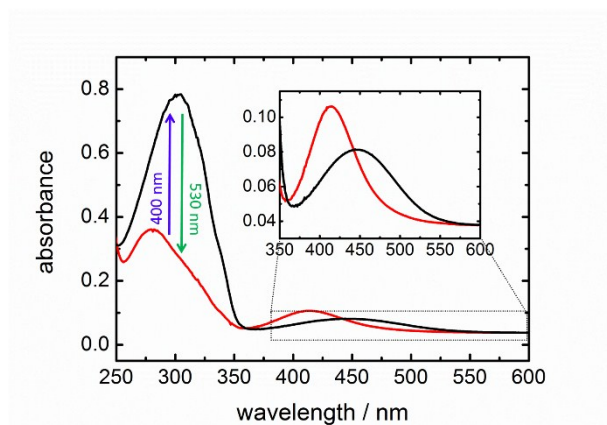


Figure S2-B: The UV-vis transmission spectra of the ethanolic *o*-tetrafluoroazobenzene solution. By irradiation with light of 530 nm wavelength, the molecule undergoes *trans*-to-*cis* photoisomerization and a decrease of the π - π^* band (at 300 nm) as well as a decrease of the n - π^* band of the *trans* isomer (at 450 nm) and an increase of the n - π^* band of the *cis* isomer (at 410 nm) were observed. By irradiation with 400 nm, the π - π^* band (at 300 nm) and the n - π^* band of the *trans* isomer (at 450 nm) increased while the n - π^* band of the *cis* isomer (at 410 nm) decreased.

Supporting Information 3: TOF-SIMS Depth Profiles

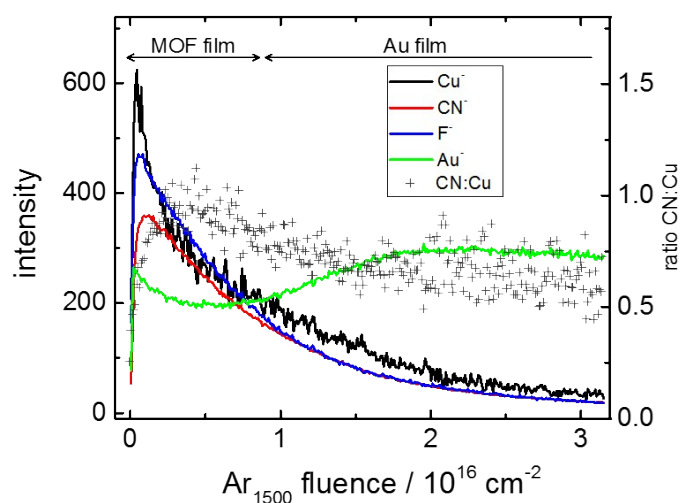


Figure SI3: TOF-SIMS depth profiles of the *o*-tetrafluoroazobenzene-loaded HKUST-1 SURMOF. Left axis: Signal intensities of Cu⁺ (both isotopes, black line), CN⁺ (red line), F⁻ (blue line) and gold clusters (green line) plotted against erosion beam (argon cluster) fluence as a measure of depth. Right axis: Normalized ratio of CN:Cu signals (black crosses).

In the sample, nitrogen is only contained in the azobenzene guest molecules and not in the MOF. Thus, CN⁺ ions serve as unambiguous indicator (or marker) for azobenzene. (Since fluorine is only contained in the *o*-tetrafluoroazobenzene guest molecules, F⁻ is an unambiguous indicator for *o*-tetrafluoroazobenzene too.)

On the other hand, Cu is only contained in the MOF and not in the guest molecules. Thus, it serves as indicator for the MOF.

It should be stated that ToF-SIMS cannot determine the absolute concentrations of the molecules or molecular components. Thus, only a normalized ratio can be determined from the ToF-SIMS. Absolute ratios follow from the XPS experiments, Fig. 2e and Fig. SI6a.

Due to the roughness of the film and due to film inhomogeneities (e.g. possibly pinholes), the transition from the azobenzene-loaded MOF (Cu, CN and F signal) to the gold substrate (Au signal) does not appear as a sharp line. (Ideally, at the beginning (fluence of 0), no Au can be detected. After a certain fluence, when the homogenous film is homogeneously sputtered away, the Au signal instantly increases and the azobenzene@MOF signals instantly decrease.) Nevertheless, the almost identical concentration course of the azobenzene and the MOF signals clearly shows that the azobenzene is pretty homogeneously distributed in the MOF film, that means in the MOF pores.

Supporting Information 4: UV-vis spectra of long-term study

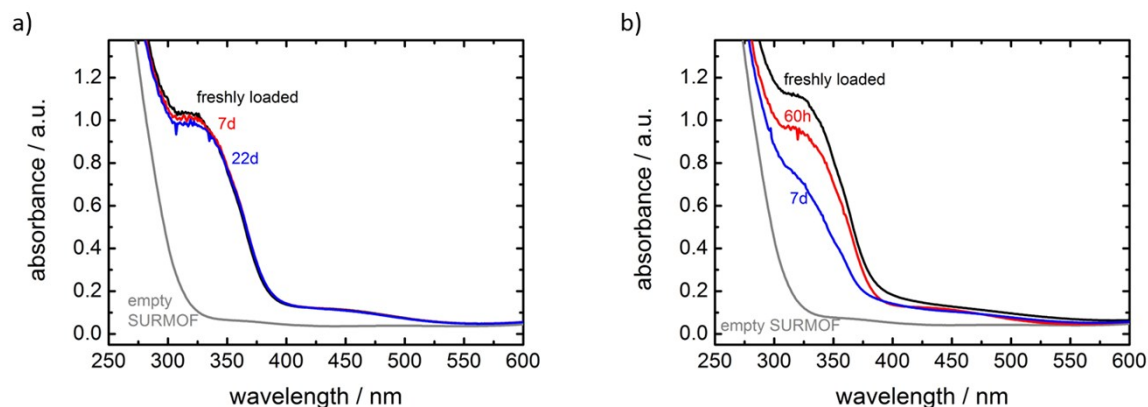


Figure S14: UV-vis spectra of azobenzene-loaded HKUST-1 SURMOF. The samples were stored at (a) room temperature ($\sim 25^\circ\text{C}$) and (b) 60°C . The spectra of the empty SURMOF is grey, the freshly azobenzene-loaded SURMOF is black. The red spectra are measured after 7 days in a) and 60 h in b); the blue spectra are measured after 22 days in a) and 7 days in b).

Supporting Information 5: IRRAS of Azobenzene@HKUST-1 SURMOF

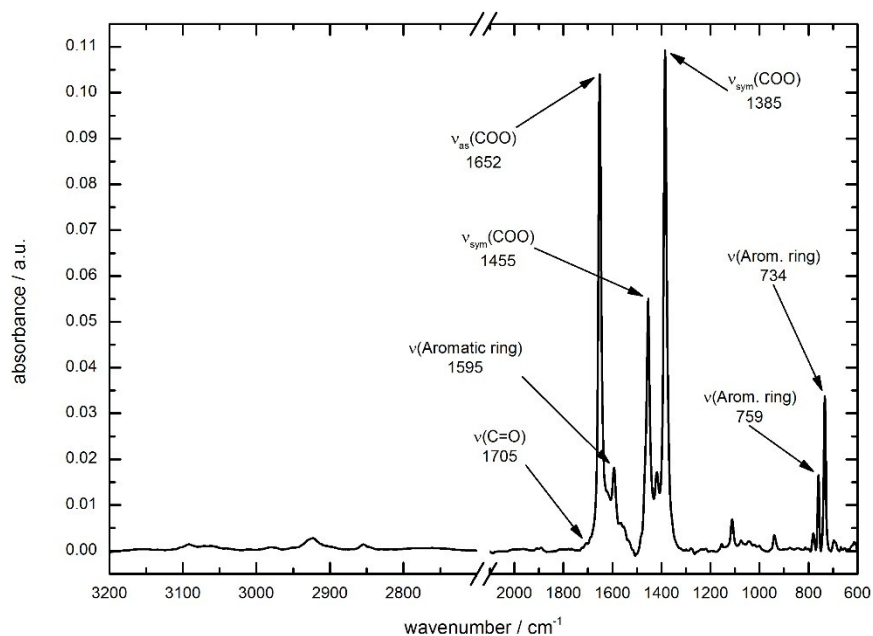


Figure S15: IRRAS spectrum of the *trans*-azobenzene-loaded HKUST-1 SURMOF. The largest vibration bands of the HKUST-1 SURMOF are labelled.

Supporting Information 6: XPS of *o*-tetrafluoroazobenzene-loaded HKUST-1 SURMOF

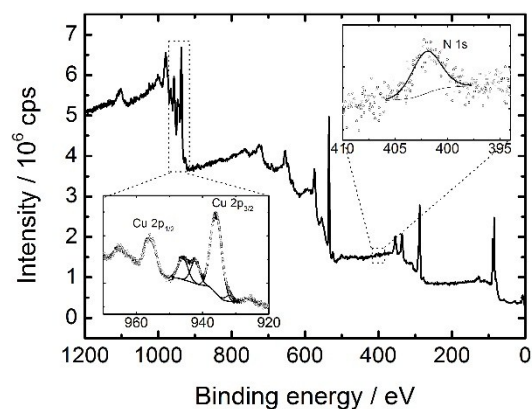


Figure SI6-A: X-ray photoelectron spectrum of the *o*-tetrafluoroazobenzene-loaded HKUST-1 SURMOF. A Cu:N ratio of 8.5 was determined, which corresponds to an average *o*-tetrafluoroazobenzene loading of 3.8 molecules per HKUST-1 unit cell (or 0.95 molecules per large pore).

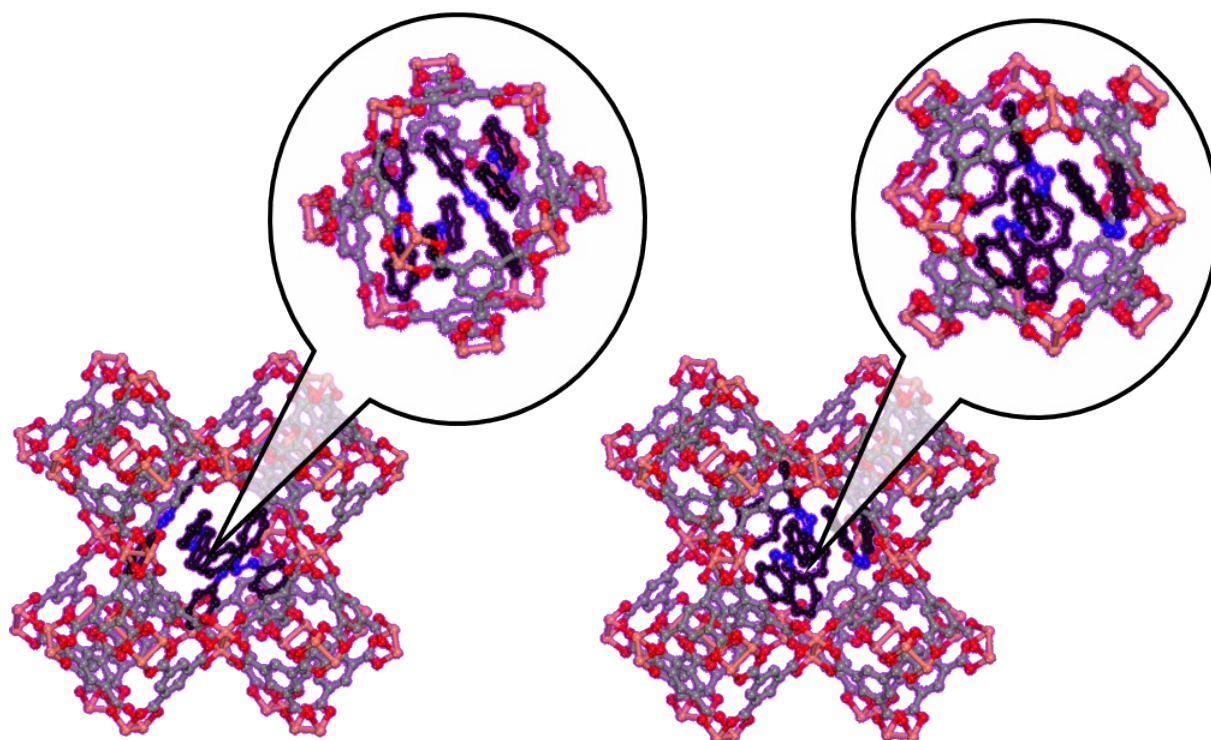


Figure SI6-B: Sketch of 4 azobenzene molecules in 1 large pore of HKUST-1. All molecules are in the *trans* state on the left-hand side and in the *cis* state on the right-hand side. The figures are modelled and optimized using MaterialsStudio®. In the pores, there is space for at least 15 further ethanol solvent molecules.

Supporting Information 7: QCM Uptake Experiments – Influence of Light Intensity

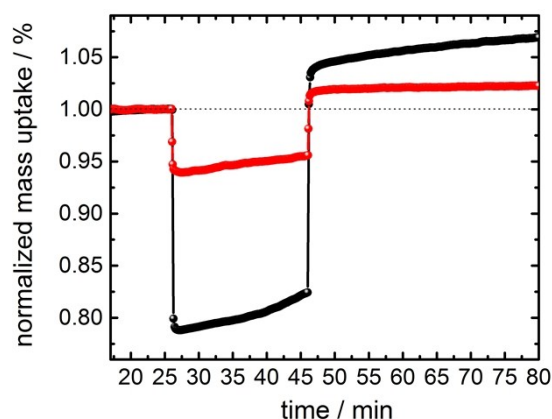


Figure S17: Comparison of Butanediol-Uptake-Switching with LED Distance of 1cm and 2cm. The black curve is measured with a light-fiber – sample distance of 1 cm, the red curve with a distance of 2 cm. This means the illumination intensity of the red curve is approximately 25 % of the intensity of the black curve. Then the LED is switched on at 26 min, the apparent mass change as a result of the change of the resonance frequency is 22 % (black) and 6 % (red). This means that one quarter of the irradiation intensity results in a frequency change (and apparent mass change) of approximately one quarter. Thus, we conclude that the jump of the apparent mass change as a result of the jump of the resonance frequency (Sauerbrey equation: $\Delta m \sim C \cdot \Delta f$, here $C = 17.7 \text{ ng cm}^{-2} \text{ Hz}^{-1}$)⁶ is caused by the irradiating power, i.e. by small local temperature changes of the SURMOF@QCM-sensor.

After the UV light is switched off at 46 min, the increases of the uptake amounts are $\sim 7\%$ (black) and $\sim 2\%$ red, respectively. This is related to the *trans*-to-*cis* azobenzene switching. The smaller irradiation intensity (and total irradiation amount) results in a significantly decreased effect of the UV irradiation on the uptake amount switching. This indicated that only a small ratio of the azobenzene molecules were photoisomerized from *trans* to *cis*.

Supporting Information 8: Additional QCM Uptake Experiments with AB@HKUST-1-SURMOFs

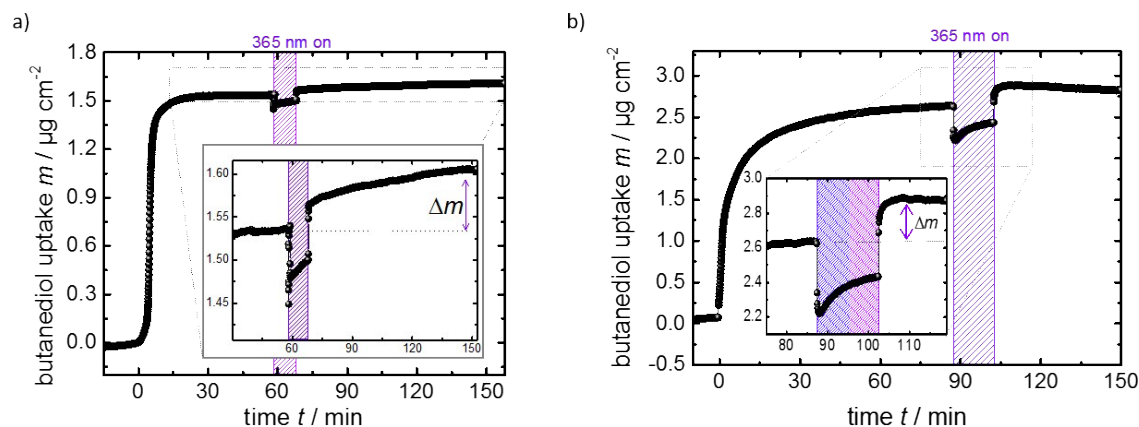


Figure S18: Uptake of butanediol by the azobenzene-loaded HKUST-1 SURMOF measured by QCM. After about 1.5 hours, when the equilibrium uptake of butanediol by the thin film in the *trans* state is reached, the sample is irradiated by UV light. The *trans*-to-*cis* isomerization results in an increase of the 1,4-butanediol uptake by Δm . The instantaneous decrease and increase of the determined mass when switching the light on and off, respectively, is most likely caused by a small (local) temperature increase during light irradiation resulting in a shift of the resonance frequency, see S17. The different uptake rates and the different uptake amounts in a) and b) are presumably a results of different densities of surface defects, due to the exposure to humid air.⁴

Supporting Information 9: QCM Uptake Experiments

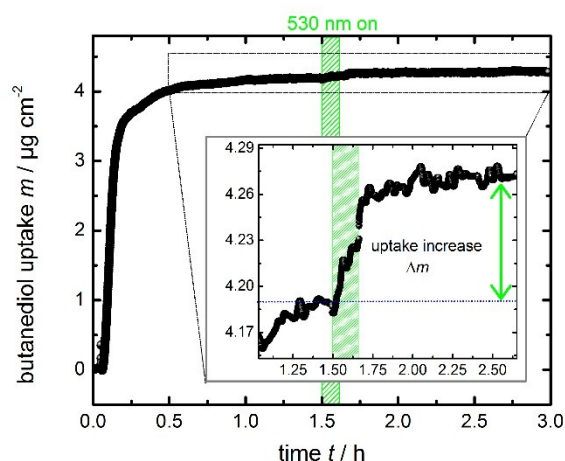


Figure S19: Uptake of 1,4-butanediol by the *o*-tetrafluoroazobenzene-loaded HKUST-1 SURMOF measured by QCM. After about 1.5 hours, when the equilibrium uptake of butanediol by the thin film in the *trans* state is reached, the sample is irradiated with green light. The *trans*-to-*cis* isomerization results in an increase of the butanediol by about 2%.

References:

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