

## Experimental Section

The layer-by-layer (lbl) **SURMOF synthesis** on solid surfaces was previously discussed in detail.<sup>1,2</sup> The lbl growth process consisted of alternately immersing the substrate in the ethanolic solutions of the building units, i.e., the metal nodes (here: 15 min in 1 mM copper(II) acetate) and the organic linkers (here: 30 min in 0.1 mM AzoBiPyB and 0.1 mM Dcam). Between each immersion step, the samples were cleaned with pure ethanol. The conditions and concentrations were chosen by following publications where the syntheses of similar SURMOF structures have been optimized.<sup>3-5</sup> The SURMOF samples were prepared in 70 cycles for the QCM, 20 cycles for the UV-vis and CD, 100 cycles for the IRRAS and 75 cycles for the XRD experiments. The sample thickness, which is proportional to the number of synthesis cycles, was optimized for the respective experiment. While AzoBiPyB was custom-made and the synthesis was previously published,<sup>6</sup> all other chemicals were purchased from Sigma Aldrich and Alfa Aesar.

**X-ray diffraction** measurements in out-of-plane geometry with a wavelength of  $\lambda = 0.154$  nm (Cu  $K_{\alpha,1,2}$  radiation) were carried out using a Bruker D8-Advance diffractometer equipped with a position-sensitive detector in  $\theta$ - $\theta$  geometry. The in-plane XRD measurements were carried out with a Bruker D8 Discover.

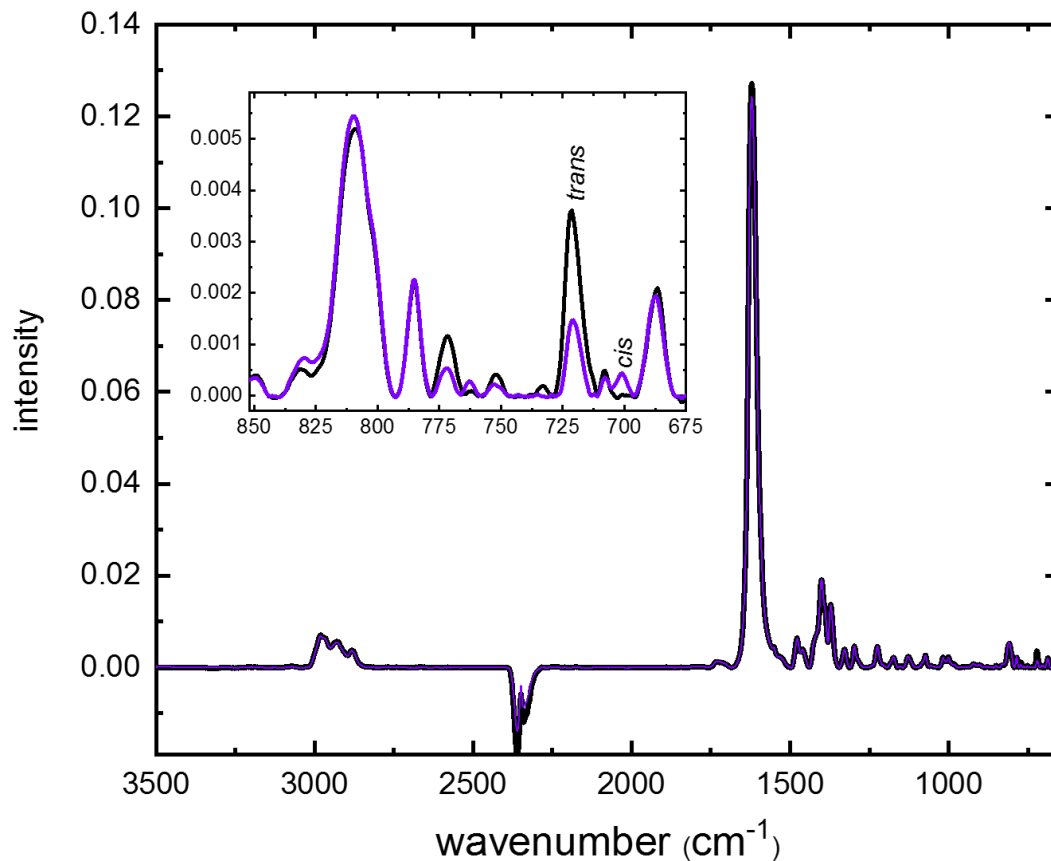
The **UV-vis spectra** were recorded with a Cary5000 spectrometer equipped with a UMA unit from Agilent. The spectra of the SURMOF sample on a quartz substrate were measured in transmission mode in a wavelength range from 190 nm to 800 nm.

The **infrared spectra** were recorded with a Fourier-Transform Infrared Reflection Absorption (FT-IRRA) Spectrometer Bruker Vertex 80 with a liquid nitrogen-cooled mercury-cadmium-telluride mid band detector. The spectra were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal. A perdeuterated 1-hexadecanethiol self-assembled monolayer on a gold substrate was used as background reference sample.

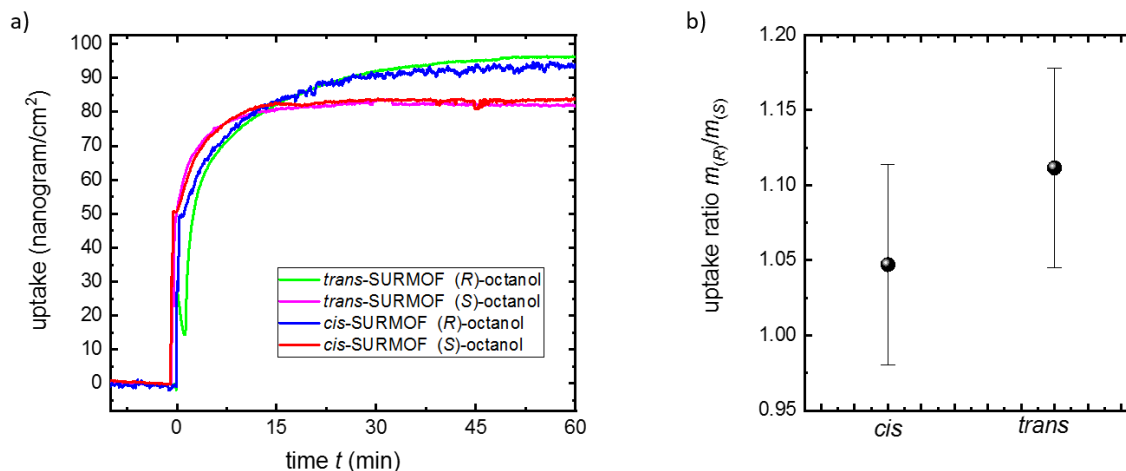
**CD spectra** of the SURMOF samples deposited on a quartz glass substrate were recorded at room temperature with a Jasco J-810 spectropolarimeter as described earlier.<sup>7</sup> The samples were fixed perpendicular to the incident light beam on a rotation stage with a computer-controlled stepping motor. To reduce artefacts due to linear dichroism or birefringence arising from imperfections in the sample (e.g. slight vertical misalignment of the substrates, strain in the quartz glass plates) spectra were recorded every 45.0° of rotation of the sample at 8 angles and averaged. Afterwards, background correction was done by subtracting the averaged spectrum of the pure quartz glass plate.

For the **QCM uptake** experiments, the QCM cell was connected to the gas flow system with argon as carrier gas.<sup>8,9</sup> The pure argon gas flow was instantly switched to the gas flow enriched with the guest molecules, here (*S*)-(-)-1-phenylethanol or (*R*)-(+)-1-phenylethanol vapor, resulting in the guest-molecule uptake by the MOF thin film. The uptake amount by the MOF was quantified by the QCM in a straightforward fashion by measuring the frequency shift and, thus, determining the mass density changes of the sample. Before each uptake experiment, the sample was activated in pure argon flow at 50°C for

16 h. In addition to emptying the pore space, the activation also results in a thermal relaxation of the sample to the *trans* state. Prior to the uptake by the *cis*-azobenzene SURMOF, the samples were irradiated with light of 365 nm wavelength from an UV LED for 20 min. From the distance between the tip of the optical fiber connected to the LED and the sample (approximately 5 cm) and the optical power of the LED (81 mW, radiant flux), we estimate a light intensity of roughly  $4 \text{ mW cm}^{-2}$ . Since the time constant for the *trans*-to-*cis* switching of the azobenzene-SURMOF-samples under irradiation with these conditions was determined as approximately 8 min,<sup>10</sup> it can be assumed that the maximum amounts of *cis* azobenzene were obtained in all samples after 20 min. All QCM experiments were performed at 50°C. During the QCM experiments, the samples remain in the closed cell under argon atmosphere, preventing exposure to (humid) air. The enantiopure uptake by the *trans* and *cis* SURMOF were alternatively performed, i.e. (*R*) in *trans* then (*S*) in *trans*, (*S*) in *cis*, (*R*) in *cis*. This set of uptake experiments was performed with 2 different SURMOF samples 3 times. By comparing the resonance frequency of the QCM sensors before and after the synthesis, the SURMOF mass densities were determined to be approximately  $3.44 \text{ } \mu\text{g cm}^{-2}$  and  $2.05 \text{ } \mu\text{g cm}^{-2}$ . This allows the quantification of the uptake by the MOF thin film in molecules per unit cell, molec per uc.



**Figure S1.** Fourier-transform infrared reflection absorption spectra (IRRAS) of the  $\text{Cu}_2(\text{DCam})_2(\text{AzoBiPyB})$  SURMOF in pristine *trans* state (black) and after UV-irradiation for 20 min, *cis* state (violet). The inset shows a magnification of the *trans* azobenzene band at  $720\text{ cm}^{-1}$  and of the *cis* azobenzene band at  $700\text{ cm}^{-1}$ ; see refs.<sup>11-13</sup> The analysis of the spectra shows that the area of the *trans*-azobenzene band (integrated from  $712\text{ cm}^{-1}$  to  $728\text{ cm}^{-1}$ ) decreases from 0.026 in the pristine *trans* state to 0.0099 upon UV irradiation. That means approximately 60% of *trans* azobenzene isomerized to the *cis* form. The band of *cis* azobenzene (at  $700\text{ cm}^{-1}$ ) is not visible for the pristine sample and occurs upon UV irradiation. The large (unaffected) vibration bands, e.g., at approximately  $1400$ ,  $1600$ ,  $2800\text{ cm}^{-1}$ , result from the MOF scaffold.<sup>7, 12</sup>



**Figure S2.** a) Enantiopure uptakes of (*R*)- and (*S*)- 2-octanol by the  $\text{Cu}_2(\text{DCam})_2(\text{AzoBiPyB})$  film in *trans* state and *cis* state, see inset. The uptake is determined with a QCM in combination with a gas flow system. b) Uptake ratio of (*R*)- versus (*S*)-2-octanol in the *cis* and *trans* state of the SURMOF. The average value from 2 uptake runs with the standard deviation are shown. In contrast to the uptake of phenylethanol (with an uptake ratio of (*S*) vs. (*R*) of  $2.92 \pm 1.15$ ), there is only a small difference between the uptake of the (*R*)- and (*S*)-isomer by the *trans*-SURMOF with a ratio of  $1.11 \pm 0.06$ . The uptakes by the *cis*-SURMOF are similar, with a slightly smaller (*R*)-versus-(*S*)-uptake ratio.

## References

1. O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher, R. A. Fischer and C. Wöll, *J. Am. Chem. Soc.*, 2007, **129**, 15118-15119.
2. L. Heinke and C. Wöll, *Adv. Mater.*, 2019, DOI: doi:10.1002/adma.201806324, doi:10.1002/adma.201806324.
3. J.-L. Zhuang, M. Kind, C. M. Grytz, F. Farr, M. Diefenbach, S. Tussupbayev, M. C. Holthausen and A. Terfort, *J. Am. Chem. Soc.*, 2015, **137**, 8237-8243.
4. B. Liu, O. Shekhah, H. K. Arslan, J. Liu, C. Wöll and R. A. Fischer, *Angewandte Chemie International Edition*, 2012, **51**, 807-810.
5. Z. Gu, S. Grosjean, S. Bräse, C. Wöll and L. Heinke, *Chem. Comm.*, 2015, **51**, 8998-9001.
6. Z. Wang, L. Heinke, J. Jelic, M. Cakici, M. Dommaschk, R. J. Maurer, H. Oberhofer, S. Grosjean, R. Herges, S. Bräse, K. Reuter and C. Wöll, *Phys. Chem. Chem. Phys.*, 2015, **17**, 14582 – 14587.
7. Z.-G. Gu, J. Bürck, A. Bihlmeier, J. Liu, O. Shekhah, P. G. Weidler, C. Azucena, Z. Wang, S. Heissler, H. Gliemann, W. Klopper, A. S. Ulrich and C. Wöll, *Chem. Eur. J.*, 2014, **20**, 9879-9882.
8. D. Johannsmann, *The Quartz Crystal Microbalance in Soft Matter Research*, Springer, 2015.
9. L. Heinke, *Journal of Physics D: Applied Physics*, 2017, **50**, 193004.
10. Z. Wang, A. Knebel, S. Grosjean, D. Wagner, S. Bräse, C. Wöll, J. Caro and L. Heinke, *Nat. Comm.*, 2016, **7**, 13872.
11. L. Duarte, R. Fausto and I. Reva, *Phys. Chem. Chem. Phys.*, 2014, **16**, 16919-16930.
12. Z. B. Wang, K. Müller, M. Valasek, S. Grosjean, S. Bräse, C. Wöll, M. Mayor and L. Heinke, *J. Phys. Chem. C*, 2018, **122**, 19044-19050.
13. X. Yu, Z. Wang, M. Buchholz, N. Fullgrabe, S. Grosjean, F. Bebensee, S. Bräse, C. Wöll and L. Heinke, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22721 – 22725.