Photoswitching in Two-Component Surface-Mounted Metal–Organic Frameworks: Optically Triggered Release from a Molecular Container

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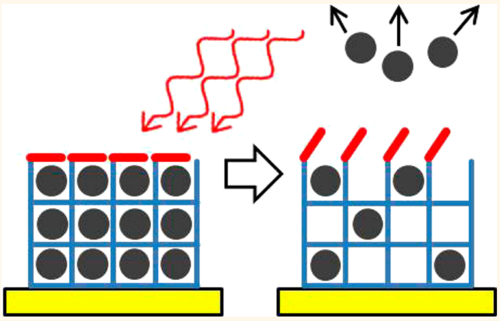
ABSTRACT The remote control of surface properties is one of the key challenges in interfacial systems chemistry. Here, we report the realization of a SURMOF (surface-mounted metal–organic framework)-based hybrid system in which a crucial component can be switched by light. The realization of this two-component system is made possible by installing vertical compositional gradients *via* liquid-phase epitaxy. After loading the porous coating with guest molecules, its release is initiated by illumination with visible light and monitored by a quartz crystal microbalance.



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A particularly interesting challenge in the fabrication of smart interfaces is the integration of remote control. While a primary goal is to use optical switching to change physicochemical properties such as wettability, the light-induced release of molecules stored inside a porous coating represents an important milestone in interfacial systems chemistry. A particular interesting realization could consist of a two-component system with a separate storage region (a reservoir containing the molecules to be released) and a switching unit (a valve that can be opened and closed with an optical signal). Here, we report on the attainment of such a system, the principal layout of which is shown in Figure 1, by using a supramolecular chemistry approach. In this system the permeability of the top layer can be reversibly switched by light. The supramolecular architecture used for the realization of this remote control release is based on metal–organic frameworks (MOFs) grown epitaxially on a solid substrate using liquid-phase epitaxy (LPE).

MOFs are crystalline solids formed by connecting metal or metal-oxo clusters *via* organic linkers.[1] The high porosity of MOFs, in combination with other unique properties such as flexibility and high variability, makes MOFs perfectly suited for many applications, including gas storage and separation,[2] catalysis,[3] and sensors.[4] Combining the high flexibility of MOFs with a recently introduced LPE process allows surface-mounted metal–organic frameworks (SURMOFs) to be synthesized.[5,6] SURMOFs permit combinations of vertical compositional gradients[7,8] and lateral patterning;[9,10] thus, complex interfacial architectures may be realized.

The basic structure of our command-release coating is shown in Figure 2. It consists of an initial layer of $Cu_2(BPDC)_2(BiPy)$[11] (BPDC: biphenyl-4,4′-dicarboxylic acid, BiPy: 4,4′-bipyridine) in its noninterpenetrated form,[12] onto which a second layer of $Cu_2(AB\text{-}BPDC)_2(BiPy)$ (AB-BPDC: 2-azobenzene 4,4′-biphenyldicarboxylic acid, see Supporting Information) is deposited.

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The basic layer was synthesized in 50 cycles on the functionalized gold surface; subsequently the covering, azobenzene-containing layer was synthesized in 45 cycles on top. The X-ray diffractograms of the sample, first only with the basic layer and then with the photoswitchable layer on top, are shown in Figure 3. The $Cu_2(BPDC)_2(BiPy)$ SURMOF grows essentially in the [001] direction, as does the $Cu_2(AB\text{-}BPDC)_2(BiPy)$ SURMOF on top. During the synthesis of the covering layer of $Cu_2(AB\text{-}BPDC)_2(BiPy)$ on the $Cu_2(BPDC)_2(BiPy)$ SURMOF, the areas of the (001) and (002) peaks increase by roughly one-third (from 0.35 to 0.53 cps·deg and from 1.66 to 2.03 cps·deg, respectively).

The first, bottom layer serves as the storage medium. It contains 1.5 nm pores, and in principle, it can store all molecules that are smaller than the channels of the pore system. Molecule storage is a general property of MOFs, and previous work has demonstrated huge storage capacities for a large number of different compounds, including small molecules such as H_2, CO_2, and CH_4, as well as dye and luminescent molecules,[13,14] chiral molecules,[15] drugs,[16] and proteins.[17] In the case of SURMOFs, loading with molecules can be recorded quantitatively using a quartz crystal microbalance (QCM).[18,19] An analysis of QCM results reveals that the butanediol (BD) uptake by the SURMOF yields 1.9 μg cm^{-2}. This corresponds to an adsorption capacity of five BD molecules inside each pore of the $Cu_2(BPDC)_2(BiPy)$ SURMOF (see Figure SI2).

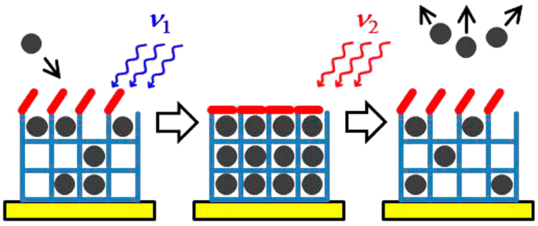

Figure 1. Optically triggered release from two-component SURMOFs. Porous films composed of two different layers are synthesized on solid surfaces. The bottom layer serves as a reservoir and can be loaded with different molecules, whereas the top layer serves as a valve that can be opened and closed.

The interesting and active part of the hetero-SURMOF responsible for the optically induced release is the top MOF layer, which contains an azobenzene-based strut (Figure 2). Azobenzene is a prototype photoactive molecule that undergoes a transition between two geometries, the *trans* state and *cis* state (see Figure 2b). Isolated azobenzene, as well as many of its derivatives, including azobenzene-containing polymers, have been studied extensively during the past decades.[20,21] The ground state of azobenzene is the planar *trans* conformation. Absorption of ultraviolet (UV) light induces a transition to the *cis* state, in which the molecule exhibits a pronounced aplanar structure. A transition back to the *trans* conformation can be induced in two

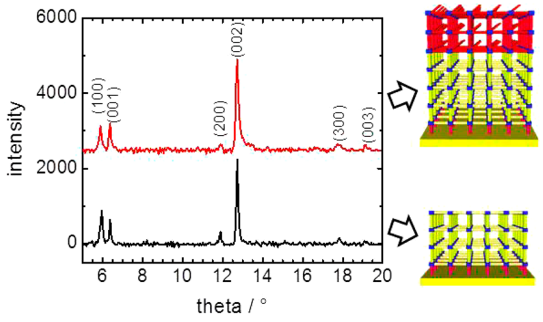

Figure 3. Out-of-plane X-ray diffractogram of the Cu_2-$(BPDC)_2(BiPy)$ SURMOF (black, lower graph) and with the $Cu_2(AB\text{-}BPDC)_2(BiPy)$ layer on top (red, upper graph).

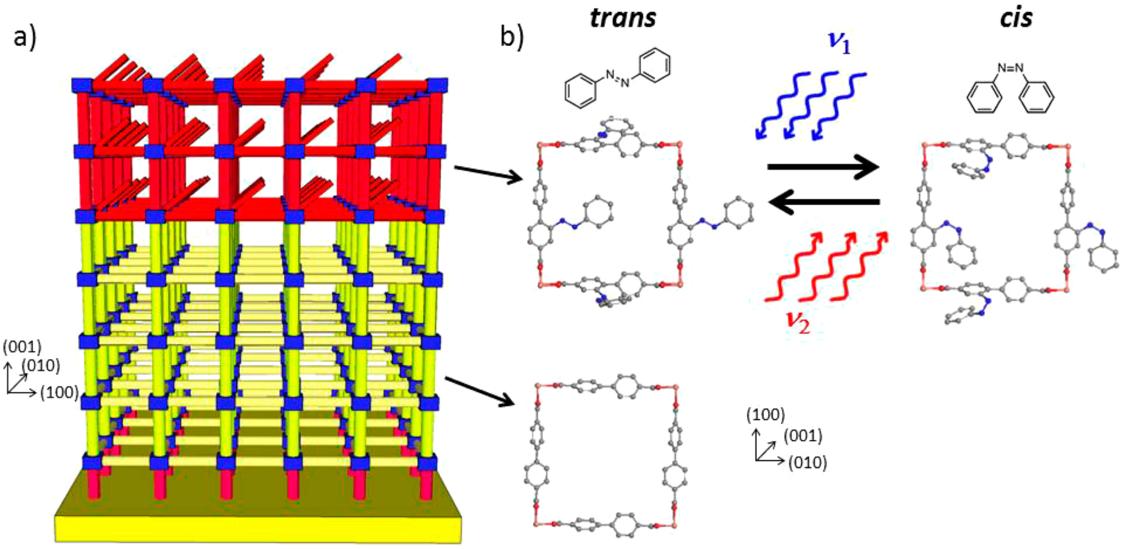

Figure 2. Sketch of the layered photoswitchable SURMOF. (a) The bottom, passive SURMOF is grown on the gold substrate, and an active SURMOF containing photoswitchable azobenzene is grown on top. (b) View of the pore window in the [001] direction. The azobenzene embedded in the MOF structure as well as molecular azobenzene can be switched from the *trans* to the *cis* state by UV light (ν_1) and *vice versa* by visible light (ν_2).

ways, by illumination with visible (vis) light or by thermal relaxation. In addition to the conformation change from *trans* to *cis*, the charge distribution in the azobenzene molecule also changes. While azobenzene in the *trans* state has no dipole moment, the dipole moment in the *cis* state amounts to 3 D, a fairly large value.[21] The two different azobenzene conformations can be distinguished by their UV–vis absorption spectra. While the *trans* azobenzene exhibits a strong $\pi \rightarrow \pi^*$ absorption band at about 340 nm, in *cis* azobenzene a pronounced $n \rightarrow \pi^*$ band at roughly 450 nm is observed.[22] The synthesis of azobenzene-based MOFs in a powder form has been reported previously,[23–25] as has the release from the MOF powder material.[26–28] However, a modular, two-component system that integrates the container and the valve-like switch in a homogeneous coating has not been reported to date.

RESULTS AND DISCUSSION

The uptake of butanediol in the two-layered SURMOF is shown in Figure 4. It is clearly visible from the QCM data that the photoswitchable top layer influences the overall uptake significantly. In *trans* state, the uptake is approximately 15 times faster than in *cis* state.

Since the uptake by the two-layered SURMOF is significantly slower than by a simple $Cu_2(BPDC)_2(BiPy)$ SURMOF (see Figure 4), it can be concluded that the overall mass transfer is dominated by the mass transport resistance in the photoswitchable top layer. The transport resistance of this layer can be described by their permeability k, which correlates with the diffusivity D by $k = D/\delta$ (where δ denotes the thickness of this layer).[29] This permeability can also be calculated by $k = d/\tau$, where τ denotes the time constant of the uptake and d denotes the thickness of the molecular container. By assuming ideal layer-by-layer growth, the thickness d of the $Cu_2(BPDC)_2(BiPY)$ container is 70 nm.[30] The permeability of the photoswitchable top layer in the *trans* state is therewith determined to be 8.5×10^{-11} m s^{-1}, whereas the permeability in the *cis* state is only 5.4×10^{-12} m s^{-1}.

In the present case, the azobenzene unit has not been optimized to yield a strong change in the channel width, *e.g.*, by attaching appropriate end groups or side groups. An analysis of the channel widths in the *trans* and *cis* states reveals only small differences. We attribute the permeability change in the top layer to the larger dipole moment of the azobenzene unit in the *cis* state. In the *cis* state, the BD molecules adsorb quite strongly and effectively decrease the channel width, thus blocking the diffusion. This hypothesis is supported by the higher total overall adsorption capacity for the SURMOF in the *cis* state compared to the *trans* state (see Figure 4).

After the top SURMOF layer switches to the *cis* state, the BD molecules are stored in the container. The leakage rate is rather small, as evidenced by the QCM data shown in Figure 5. As revealed by the data in Figure 5, the release of BD is initiated when the azobenzene linkers are switched to the *trans* state. This demonstrates that the release from the molecular container is remotely controlled directly by light. The switching of the top layer, which serves as a valve, is completely contactless, unlike conventional remote control devices, where (usually electrical) contacts are required. A quantitative analysis of the QCM data reveals that all BD molecules stored in the SURMOF are released during the light-initiated desorption.

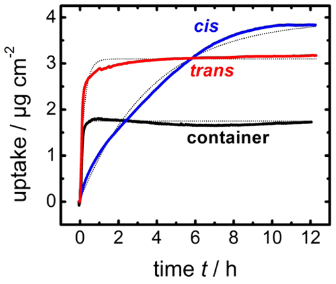

Figure 4. BD uptake by the two-layered SURMOF in the *trans* state (red) and in the *cis* state (blue). The time constants of the monoexponential fits (thin dotted lines) are 0.23 h in the *trans* and 3.6 h in the *cis* state. The uptake by a $Cu_2(BPDC)_2(BiPy)$ SURMOF is plotted in black (with a time constant of 0.06 h).

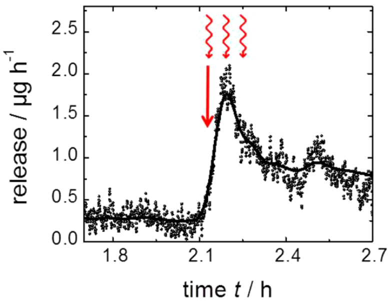

Figure 5. Release of the prototype molecule (butanediol, BD) from a two-layered, photoswitchable SURMOF determined by a quartz crystal microbalance. Beginning at the time indicated by the red arrow, the sample is irradiated with light at 560 nm wavelength.

CONCLUSIONS

A two-component thin MOF film synthesized by liquid-phase epitaxy was employed to realize optically triggered release of guest molecules. The bottom layer of this SURMOF can store guest molecules and serves as a reservoir. The top SURMOF layer, which controls the uptake and release of guest molecules, contains photoswitchable linkers and can be photoswitched between *trans* and *cis* state. It could be shown by QCM that the uptake rate by the SURMOF varies dramatically between the top layer in *trans* or *cis* state and the release of guest molecules can be optically triggered. We conclude that SURMOFs equipped with photoswitchable linkers allow a straightforward realization of functional coatings with optical remote control. This approach has a potential that goes substantially beyond the results presented here. Improving the tailoring of the azobenzene units to the pore and channel geometry within the MOF lattice will enable the channels to be directly closed. The implementation of two photoswitches that are sensitive to different photon energies will further enhance the flexibility of this approach. In addition to allowing for the release of two different molecules, two switches operated at different photon energies may be used to realize photon-driven pumps.

METHODS

SURMOFs are oriented, highly crystalline thin MOF films that are grown by liquid-phase epitaxy in a well-defined layer-by-layer mode on a functionalized solid substrate.[5,6] Unlike the solvothermal approach used in conventional MOF syntheses, the layer-by-layer growth is realized by the sequential immersion of the substrate in each of the two reactant solutions. These two solutions are the metal complexes and the organic ligand molecules (here, 0.5 mM copper acetate as well as 0.1 mM BiPy and BPDC [or AB-BPDC, see Supporting Information] in ethanol). After each immersion step, the substrate is rinsed with ethanol to remove any unreacted, weakly adsorbed reactants. To nucleate the growth on the surface and to control the SURMOF's crystal orientation, the substrate surface is functionalized with an 11-mercapto-1-undecanol self-assembled monolayer (MUD SAM). The SURMOF growth is very uniform, and a film roughness as low as the height of a unit cell can be reached under optimized conditions.[9] Here, the basic $Cu_2(BPDC)_2(BiPy)$ SURMOF is synthesized in 50 cycles, and the covering SURMOF $Cu_2(AB\text{-}BPDC)_2(BiPy)$ is synthesized in 45 cycles.

A QCM from Q-Sense is used to record the uptake and release by the thin MOF film.[18,19,31] The basic principle of QCM is that stimulation causes vibrations in a piezoelectric quartz crystal so that the resonance frequencies can be recorded. An increase in the mass leads to a decrease in the resonance frequency of the QCM sensor, and the change in the mass density can be calculated from the resonance frequency shift using the Sauerbrey equation.[32] Standard gold-coated QCM sensors have been functionalized with an MUD SAM; subsequently, the SURMOF was epitaxially grown in a straightforward fashion. The QCM cell is connected to a gas flow system with argon as the carrier gas. With this gas flow system, it is possible to switch instantly between a pure argon flow and a argon flow enriched with the guest molecule, here 1,4-butanediol at room temperature (25 °C). This results in a BD partial pressure of roughly 1 Pa. All QCM experiments are performed at a constant temperature of 60 °C, which is precisely controlled by the Q-Sense setup.

The *trans*–*cis* isomerization is performed by irradiating the sample with a 365 nm mercury lamp for several hours. The relaxation to the *trans* ground state is achieved by irradiation with visible light from a tungsten filament bulb or a 560 nm LED.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Synthesis and characterization of the photoswitchable linker molecule, X-ray diffraction and UV–vis spectra of SURMOF, as well as QCM data of optically triggered release. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to Metal-Organic Frameworks. *Chem. Rev.* **2012**, *112*, 673–674.
2. Li, J. R.; Kuppler, R. J.; Zhou, H. C. Selective Gas Adsorption and Separation in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
3. Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
4. Achmann, S.; Hagen, G.; Kita, J.; Malkowsky, I. M.; Kiener, C.; Moos, R. Metal-Organic Frameworks for Sensing Applications in the Gas Phase. *Sensors* **2009**, *9*, 1574–1589.
5. Shekhah, O.; Liu, J.; Fischer, R. A.; Wöll, C. MOF Thin Films: Existing and Future Applications. *Chem. Soc. Rev.* **2011**, *40*, 1081–1106.
6. Shekhah, O.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; *et al*. Step-by-Step Route for the Synthesis of Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2007**, *129*, 15118–15119.
7. Shekhah, O.; Hirai, K.; Wang, H.; Uehara, H.; Kondo, M.; Diring, S.; Zacher, D.; Fischer, R. A.; Sakata, O.; Kitagawa, S.; *et al*. MOF-on-MOF Heteroepitaxy: Perfectly Oriented $[Zn_2(ndc)_2(dabco)]_n$ Grown on $[Cu_2(ndc)_2(dabco)]_n$ Thin Films. *Dalton Trans.* **2011**, *40*, 4954–4958.
8. Meilikhov, M.; Furukawa, S.; Hirai, K.; Fischer, R. A.; Kitagawa, S. Binary Janus Porous Coordination Polymer Coating for Sensor Devices with Tunable Analyte Affinity. *Angew. Chem., Int. Ed.* **2013**, *52*, 341–345.
9. Munuera, C.; Shekhah, O.; Wang, H.; Wöll, C.; Ocal, C. The Controlled Growth of Oriented Metal-Organic Frameworks on Functionalized Surfaces as Followed by Scanning Force Microscopy. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7257–7261.
10. Zhuang, J. L.; Friedel, J.; Terfort, A. The Oriented and Patterned Growth of Fluorescent Metal-Organic Frameworks onto Functionalized Surfaces. *Beilstein J. Nanotechnol.* **2012**, *3*, 570–578.
11. Pichon, A.; Fierro, C. M.; Nieuwenhuyzen, M.; James, S. L. A Pillared-Grid MOF with Large Pores Based on the $Cu_2(O_2CR)_4$ Paddle-Wheel. *CrystEngComm* **2007**, *9*, 449–451.
12. Shekhah, O.; Wang, H.; Paradinas, M.; Ocal, C.; Schüpbach, B.; Terfort, A.; Zacher, D.; Fischer, R. A.; Wöll, C. Controlling Interpenetration in Metal-Organic Frameworks by Liquid-Phase Epitaxy. *Nat. Mater.* **2009**, *8*, 481–484.
13. Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. Luminescent Metal-Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.
14. Streit, H. C.; Adlung, M.; Shekhah, O.; Stammer, X.; Arslan, H. K.; Zybaylo, O.; Ladnorg, T.; Gliemann, H.; Franzreb, M.; Wöll, C.; *et al*. Surface-Anchored MOF-Based Photonic Antennae. *ChemPhysChem* **2012**, *13*, 2699–2702.
15. Liu, B.; Shekhah, O.; Arslan, H. K.; Liu, J.; Wöll, C.; Fischer, R. A. Enantiopure Metal–Organic Framework Thin Films: Oriented SURMOF Growth and Enantioselective Adsorption. *Angew. Chem., Int. Ed.* **2012**, *51*, 807–810.
16. Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Ferey, G.; Morris, R. E.; Serre, C. Metal-Organic Frameworks in Biomedicine. *Chem. Rev.* **2012**, *112*, 1232–1268.
17. Deng, H. X.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gandara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; *et al*. Large-Pore Apertures in a Series of Metal-Organic Frameworks. *Science* **2012**, *336*, 1018–1023.
18. Zybaylo, O.; Shekhah, O.; Wang, H.; Tafipolsky, M.; Schmid, R.; Johannsmann, D.; Wöll, C. A Novel Method to Measure Diffusion Coefficients in Porous Metal-Organic Frameworks. *Phys. Chem. Chem. Phys.* **2010**, *12*, 8092–8097.
19. Heinke, L.; Wöll, C. Adsorption and Diffusion in Thin Films of Nanoporous Metal-Organic Frameworks: Ferrocene in SURMOF $Cu_2(ndc)_2(dabco)$. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9295–9299.
20. Bandara, H. M. D.; Burdette, S. C. Photoisomerization in Different Classes of Azobenzene. *Chem. Soc. Rev.* **2012**, *41*, 1809–1825.

21. Hartley, G. S.; Le Fevre, R. J. W. The Dipole Moments of Cis- and Trans-Azobenzenes and of Some Related Compounds. *J. Chem. Soc. (Resumed)* **1939**, *0*, 531–535.
22. Uchida, E.; Kawatsuki, N. Influence of Wavelength of Light on Photoinduced Orientation of Azobenzene-Containing Polymethacrylate Film. *Polym. J. (Tokyo, Jpn.)* **2006**, *38*, 724–731.
23. Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. The First Porous MOF with Photoswitchable Linker Molecules. *Dalton Trans.* **2011**, *40*, 4217–4222.
24. Bernt, S.; Feyand, M.; Modrow, A.; Wack, J.; Senker, J.; Stock, N. $Zn(C_3H_3N_2)(C_3H_2N_2\text{-}N{=}N\text{-}C_6H_5)$, a Mixed-Linker ZIF Containing a Photo-Switchable Phenylazo Group. *Eur. J. Inorg. Chem.* **2011**, 5378–5383.
25. Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. Introducing a Photo-Switchable Azo-Functionality Inside Cr-MIL-101-NH_2 by Covalent Post-Synthetic Modification. *Dalton Trans.* **2012**, *41*, 8690–8696.
26. Lyndon, R.; Konstas, K.; Ladewig, B. P.; Southon, P. D.; Kepert, P. C. J.; Hill, M. R. Dynamic Photo-Switching in Metal−Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release. *Angew. Chem., Int. Ed.* **2013**, *52*, 3695–3698.
27. Park, J.; Yuan, D. Q.; Pham, K. T.; Li, J. R.; Yakovenko, A.; Zhou, H. C. Reversible Alteration of CO_2 Adsorption upon Photochemical or Thermal Treatment in a Metal-Organic Framework. *J. Am. Chem. Soc.* **2012**, *134*, 99–102.
28. Brown, J. W.; Henderson, B. L.; Kiesz, M. D.; Whalley, A. C.; Morris, W.; Grunder, S.; Deng, H.; Furukawa, H.; Zink, J. I.; Stoddart, J. F.; *et al*. Photophysical Pore Control in an Azobenzene-Containing Metal-Organic Framework. *Chem. Sci.* **2013**, *4*, 2858–2864.
29. Kärger, J.; Ruthven, D. M.; Theodorou, D. N. *Diffusion in Nanoporous Materials*; Wiley-VCH: New York, 2012; p 902.
30. The thickness of the $Cu_2(BPDC)_2(BiPy)$ SURMOF was verified by XRD. The (001) and (002) peaks have a FWHM of 0.082° and 0.1075° corresponding to a crystalline thickness of 107 nm and 81 nm, respectively.
31. Biemmi, E.; Darga, A.; Stock, N.; Bein, T. Direct Growth of $Cu_3(BTC)_2(H2O)_3$ x H_2O Thin Films on Modified QCM-Gold Electrodes - Water Sorption Isotherms. *Microporous Mesoporous Mater.* **2008**, *114*, 380–386.
32. Reviakine, I.; Johannsmann, D.; Richter, R. P. Hearing What You Cannot See and Visualizing What You Hear: Interpreting Quartz Crystal Microbalance Data from Solvated Interfaces. *Anal. Chem.* **2011**, *83*, 8838–8848.