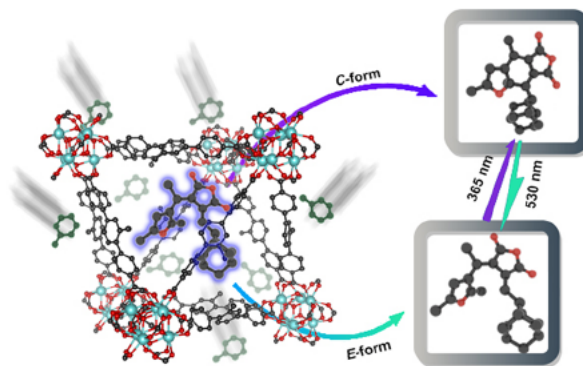


Nanoporous Metal–Organic Framework Thin Films with Embedded Fulgide for Light-Modulated Guest Adsorption and Diffusion

Chun Li, Zejun Zhang, and Lars Heinke*

ABSTRACT: Smart and photoresponsive materials and thin films allow the dynamic remote control of their central properties. By incorporation of photochromic molecules in nanoporous metal–organic frameworks (MOFs), the interaction between the MOF host and the guest molecules in the pores can be modified. Here, a MOF film of type UiO-68 is presented in which the photoswitchable feature is added by embedment of photochromic fulgide molecules of type Aberchrome 670 in the pores. The photoisomerization in the pores is explored by UV–vis and infrared spectroscopy, and the transient uptake of toluene and methanol probe molecules is explored using a quartz crystal microbalance. For the first time, a fulgide-based nanoporous material is used to remote-control the adsorption and diffusion properties. We find that the toluene uptake amount can be increased by 37% and the toluene diffusion coefficient can be increased by 40% when reversibly photoswitching the embedded fulgide from its *E*-form to *C*-form. In this way, this study aims to contribute to the field of light-responsive nanoporous materials and thus expands the range of smart coatings.



1. INTRODUCTION

Various advanced, smart applications require the dynamic remote control of the material properties.^{1–5} Such remote-controllable, also referred to as smart, materials can change their structures and properties upon exposure to external stimuli, such as heat, redox potential changes, or light irradiation. Since the control of the material properties by light is fast, easy to regulate, clean, and usually nondestructive, it is particularly attractive. An effective approach for making light-responsive materials is based on the integration of photochromic molecules.^{6,7} Upon the irradiation of light with different wavelengths, such molecules can isomerize to different (meta)stable forms.^{8,9} Popular photochromic molecules are based on azobenzene, spiropyran, diarylethene, and fulgide. So far, different materials like polymers¹⁰ and liquid crystals¹¹ were used to incorporate such molecules. While these materials already allowed the demonstration of fascinating features,^{12–14} such amorphous and dense materials suffer from two major disadvantages: The photoisomerization is often hindered or slowed down in the dense structure,¹⁵ and the amorphous structure hampers the detailed understanding of the processes on the molecular level (and also the application of detailed modeling and digital twins). Both disadvantages are avoided by using nanoporous crystalline framework materials, like metal–organic frameworks (MOFs).^{16,17} MOFs are made of metal nodes connected by organic ligands or linker molecules.¹⁸ One of the most attractive features of MOFs is their high structural variability

compared to other porous materials such as zeolites. By incorporating photochromic molecules, photoresponsive MOFs can be made. In general, the incorporation of photochromic functionality in the MOF can be realized by three approaches: (1) The photochromic molecule is part of the backbone of the MOF scaffold.^{19,20} (2) The photochromic group is a pendant side group of the linker molecule and, thus, of the MOF structure.^{21,22} (3) The photochromic molecule is embedded in the pores of the MOF without a covalent bonding to the framework.^{23–28} While approaches 1 and 2 have advantages in the structural control of the photoresponsive MOF, the advantage of approach 3 is its simplicity. It avoids the custom-made synthesis of the ligands, which is usually rather expensive. Moreover, it also allows the incorporation of photoswitchable molecules, which cannot be incorporated by approaches 1 and 2. A major focus of photoswitchable MOF materials is on light-modulated guest adsorption, in which the uptake capacity of various guest molecules has been varied, typically by a few tens of percent.^{16,17,26,29–32} While various photoswitchable MOFs

have been presented employing azobenzene, spiropyran, or diarylethene as a functional component,^{16,17,19–22,24–28} to date, there has been only one study using photochromic fulgide molecules in MOFs.²³ There, fulgide of type Aberchrome 670 was embedded in the pores of MOFs of type MOF-5 or MIL-68(In) and the photoisomerization of the fulgide molecule between the *E* and *C* isomers in the pores was explored. Any functionality of fulgide-based nanoporous crystalline materials, especially with respect to light-modulated guest adsorption and diffusion, has not yet been presented.

Here, a new light-responsive system (which may also be referred to as a new light-responsive guest-MOF material) is presented based on fulgide-type photochromic molecules, referred to as Aberchrome 670 (Aber670), embedded in MOF films of type UiO-68-CH₃. (UiO stands for Universitetet I Oslo.) The MOF material is referred to as Fulg@UiO-68. The host MOF was chosen because of its suitable pore size (large enough to incorporate Aber670) and the relatively nonpolar pore environment. The fulgide *E*-*C* photoisomerization in the MOF pores is explored by UV-vis and infrared spectroscopy. By using a quartz crystal microbalance (QCM), we explore the transient uptake of probe molecules like toluene and methanol by the sample with the fulgide molecules in the *E* and *C* states (Figure 1). We show for the first time that fulgide molecules can be employed for controlling the adsorption capacity and the diffusion properties of the guest molecules in nanoporous materials. In this way, this study aims to contribute to the field of light-responsive MOFs and thus expands the range of smart materials.

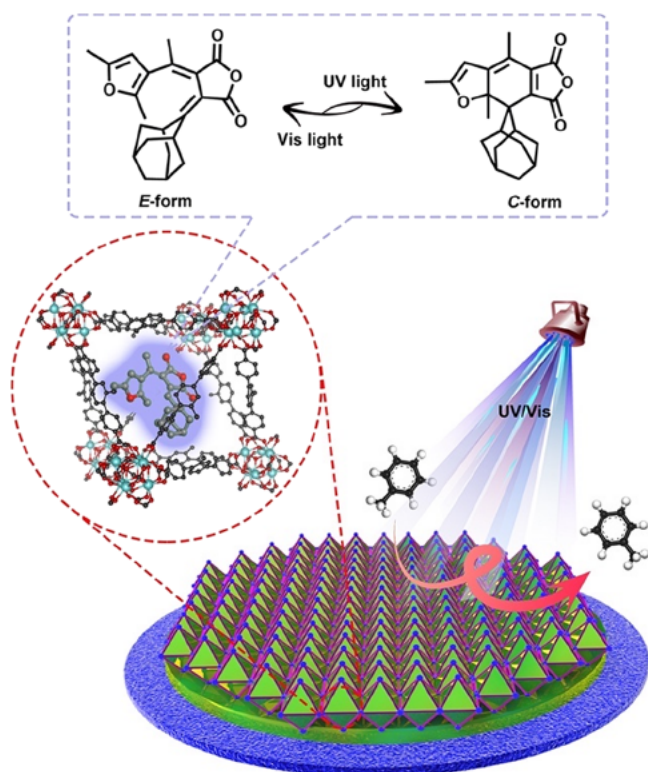


Figure 1. Schematic presentation of the reversible isomerization between the *E*-form and *C*-form of fulgide of type Aber670 (top). The octahedral pore of MOF UiO-68-CH₃ (with the film oriented in the (111) orientation) with one Aber670 molecule in the center as well as the toluene adsorption measured by QCM are sketched below.

2. EXPERIMENTAL SECTION

2.1. Materials. The components for the synthesis of the MOF films are the metal nodes, which are 98% zirconium tetrachloride octahydrate (ZrOCl₂·8H₂O), and the linker molecules, which are methyl-triphenyldicarboxylic acid (TPDC-CH₃). The solvents are 99.8% acetic acid (HAC), 99.8% toluene (Tol), 99.8% *N,N*-dimethylformamide (DMF), and 99.8% ethanol (EtOH). The fulgide-type photochromic molecules are Aberchrome 670, purchased from Tokyo Chemical Industry. All chemicals were purchased from Alfa Aesar and VWR and used without further purification. The substrates for the MOF films are gold-coated QCM sensors with a resonance frequency of 5 MHz from Q Sense, purchased from Biolin Scientific, and quartz glass from GVB Solutions in Glass.

2.2. MOF Film Synthesis and Photoswitch Embedment. The UiO-68 MOF films were synthesized via vapor-assisted conversion (VAC).³³ Details of the VAC synthesis and mechanism can be found in reference 33. The bottom part of a 200 mL Teflon-lined stainless-steel autoclave was filled with Raschig rings (1 cm × 1 cm) to obtain an elevated flat platform for the substrates (i.e., the gold-coated QCM sensors or the quartz glass). DMF (4.2 mL) and acetic acid (0.8 mL) were filled in the autoclave. A substrate was placed on top of the Raschig rings, fully coated with 40 μL of freshly prepared MOF precursor solution (17.4 mM ZrOCl₂, 17.4 mM linker, and 1.7 M acetic acid in DMF), and then heated to 100 °C for 3 h. After cooling down to room temperature, the obtained MOF films were dried in vacuum.

The embedment of the fulgide-type photochromic molecules in the pores of the UiO-MOF-film was performed by soaking the MOF sample in the ethanolic solution of Aber670 (3 mg mL⁻¹) at room temperature for 24 h. Afterward, the sample surface was briefly rinsed with ethanol and the sample was dried in a flow of pure nitrogen.

2.3. Characterizations. The X-ray diffraction (XRD) data of the MOF films were recorded with a Bruker D8 ADVANCE X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.154$ nm).

The scanning electron microscopy (SEM) measurements were performed on a TESCAN VEGA3. To avoid charging effects, all samples were coated with a 3–4 nm-thick platinum film before recording the SEM images.

UV-vis spectroscopy in transmission mode was used for investigating the Aber670 loading and the isomerization of Aber670. All measurements were performed using a Cary5000 spectrometer with a UMA unit from Agilent. The step size was set to 1 nm, and the accumulation time was 0.1 s.

Infrared reflection-absorption (IRRA) spectroscopy was performed with a Bruker Vertex 80 spectrometer with a resolution of 2 cm⁻¹. All results were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal.

The transient uptake amount of the guest molecules (here, toluene and methanol) was quantified by using a QSense E4 QCM-D working at a resonance frequency of approximately 5 MHz. The QCM cell was connected to the gas flow system with nitrogen as a carrier gas. Before each uptake experiment, the sample was activated in pure nitrogen flow at 65 °C until a stable baseline was reached (typically after a few hours) and the MOF pores were empty. Then, the uptake experiments were performed at 50 °C with the sample alternately illuminated with UV and green light.

3. RESULTS AND DISCUSSION

The UiO-type MOF films were prepared on the substrate via vapor-assisted conversion.³³ The loading of the photoswitches in the MOF pores was performed by immersing the sample in ethanolic Aber670 solution.

The crystallinity of the sample was explored by X-ray diffraction (XRD) (Figure 2 a). The XRD data of the empty sample show that the film is highly crystalline and the diffractogram is in agreement with the targeted UiO-68 structure. Moreover, it shows that the film is grown in the (111) orientation perpendicular to the substrate. Upon the

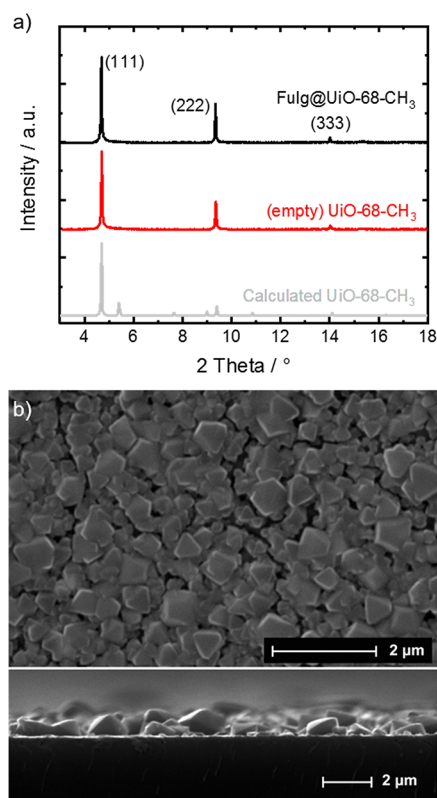


Figure 2. (a) X-ray diffractograms of the MOF film before (red) and after (black) loading of fulgide of type Aber670. The data are compared with the calculated structure of MOF UiO-68 (gray). The experimentally observed diffraction peaks are labeled. (b) SEM images of the MOF film sample. Top view (above) and side view of a broken sample (below).

immersion of the sample in the Aber670 solution, the intensity ratio of the XRD reflexes changes. The ratio of the peak intensities of the (222) reflex compared to the (111) reflex increases from 0.35 to 0.45. This indicates that the XRD form factor changed, which is a solid indication that the loading of the guest molecules (Aber670) was successful.

The film morphology was explored by scanning electron microscopy (SEM) (Figure 2b). The images show that the film covers the substrate surface homogeneously. The MOF film is composed of individual crystallites with a size of about 0.5 μm .

Ultraviolet–visible (UV–vis) spectroscopy was used to explore the photoisomerization properties of the fulgide of type Aber670 embedded in the MOF film (Figure 3a) compared with the photoswitch in ethanolic solution (Figure S1a). Initially, the fulgide molecule is in the *E*-form and absorbs light essentially only in the UV range. For the photoswitch in solution (Figure S1a), irradiation with UV light at 365 nm for 5 min results in a ring closing reaction to the *C*-form. The spectrum upon UV light irradiation (i.e., of the *C* isomer) shows a broad absorption band in the visible region at approximately 500 to 600 nm.^{34,35} Irradiation of the solution with green light at 530 nm results in an absorption spectrum very similar to the initial spectrum. For the fulgide molecule embedded in the MOF film, very similar shifts of the UV–vis spectra upon irradiation with UV and green light were observed (Figure 3a), indicating the *E*-*C* photoswitching of the fulgide molecule in the MOF pores. Repeating the UV and green light irradiation for four cycles results in the essentially

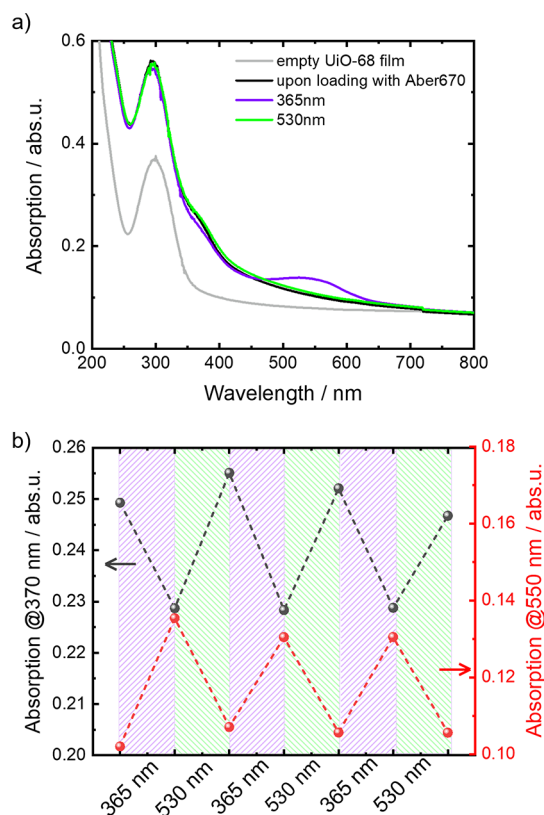


Figure 3. (a) UV–vis spectra of the sample before Aber670 loading (gray) and after loading (black). The irradiation of the Fulg@UiO-68 sample with UV light resulted in the violet spectrum and that with subsequent green light resulted in the green spectrum. (b) Absorbance of the Fulg@UiO-68 sample at 370 nm (black) and at 550 nm (red) after the repeated irradiation at 365 or 530 nm for 5 min each.

identical absorption spectra (Figure 3b). The reproducibility of the absorption spectra demonstrates the excellent reversibility and the robustness of the Fulg@UiO-68 material. The UV–vis spectrum 7 days later (Figure S1b) was very similar to the initial spectrum of the Fulg@UiO-68 film, demonstrating the stability of the material. It also shows that the photoswitch molecules do not desorb from the MOF pores. Thus, Fulg@UiO-68 is stable and suitable to investigate the sorption properties as well as its response to the photoisomerization.

A molecular sketch of one fulgide molecule in the large (octahedral) pore of UiO-68 is shown in Figure S6 in the Supporting Information. It should be stated that the exact position and distribution of fulgide in the pores are not known. Most likely, the fulgide molecules are mobile and change their position in the pores.

The absorbance of the sample at a wavelength of 365 nm is approximately 0.25 (see Figure 3a). This means that 55% of UV light penetrates the film (with a thickness of approximately 0.5 μm ; see Figure 2b) and the entire sample is essentially irradiated (and can be photoswitched). Based on this and on Lambert–Beer’s law, for a 2 μm -thick film, only 10% of UV light could penetrate the sample, whereas only 1% of UV light could penetrate a 4 μm -thick film of Fulg@UiO-68 and the (fast) photoswitching of the entire film would not be realized.

To get further insights into the photoisomerization of Aber670 in the UiO-68 pores, the vibrational infrared reflection-absorption (IRRA) spectra were recorded before

and after irradiation by UV and green light (Figure 4). The IRRA spectra show characteristic peaks of $-C-O$, $O-C-O$, and $-C=O$ stretching vibrations at 924 cm^{-1} , 1226 cm^{-1} , and $1755-1818\text{ cm}^{-1}$, respectively (Figure 4b), indicating the presence of Aber670 inside the MOF.^{23,36} The reference IR spectra of pure Aber670 are shown in the Supporting Information, Figure S2. Upon UV irradiation, significant changes of the intensities of the peaks in correlation with fulgide in the MOF pores were observed; in particular, the intensities of the peaks at 924 cm^{-1} , 1226 cm^{-1} , and $1755-1818\text{ cm}^{-1}$ decrease (see Figure 4b). The MOF vibration bands did not change upon UV light irradiation. Thus, both the UV-vis and IRRA spectra clearly indicate the E - C isomerization of fulgide. Moreover, the intensity changes of the IR vibration bands allow the quantification of the switching yield (Figure 4b). The pristine sample is composed of 100% E isomers. Upon UV light irradiation, the intensities of the bands at 924 and 1226 cm^{-1} (which are assigned to E -fulgide) decrease to 40% of its original areas. Thus, upon UV irradiation, only 40% of the E isomers are left and 60% are converted to the C isomer. Upon green light irradiation, the original isomer ratio (100% E) is obtained.

By vapor uptake experiments using toluene and methanol as probe molecules, the photoresponsive properties of the Fulg@UiO-68 material were explored, especially with respect to the guest mass transfer and host-guest interaction. The amount of the guest uptake was quantified with a quartz crystal microbalance (QCM).³⁷ The uptake experiments were performed for the sample upon UV light irradiation, resulting in the C -form (i.e., 60% C and 40% E), and upon green light irradiation, resulting in the E -form (100% E). Each uptake

experiment was performed six times (see Figure S3), and representative toluene uptake curves are shown in Figure 5a. The data show that, compared to the E -form (upon green light irradiation), there is a significant increase in toluene uptake amount by the C -form (upon UV light irradiation). Based on the data (Figure 5b), the E -to- C uptake increase is approximately 37%. In detail, the value is $0.48 \pm 0.03\text{ }\mu\text{g cm}^{-2}$ for E versus $0.66 \pm 0.03\text{ }\mu\text{g cm}^{-2}$ for C (with the standard deviation as an error).

The transient uptake curves (Figure 5a and Figure S3a) also show that the uptake by Fulg@UiO-68 is slightly faster for the sample upon UV light irradiation (C state) compared to the sample upon green light irradiation (E state). This can also be seen in the plot of the normalized uptake versus square root of time (Figure S3b). A detailed analysis of the mass transfer kinetics was performed by fitting the experimental data with the solution of Fick's second law for a thin homogeneous film (without defects like surface barriers) and an instant change of the surface concentration (i.e., ambient pressure).^{38,39} The analysis (Figure S3) results in the diffusion coefficients, which are shown in Figure 5b. It shows that the diffusion coefficient of toluene in Fulg@UiO-68 in the E -form (upon green light

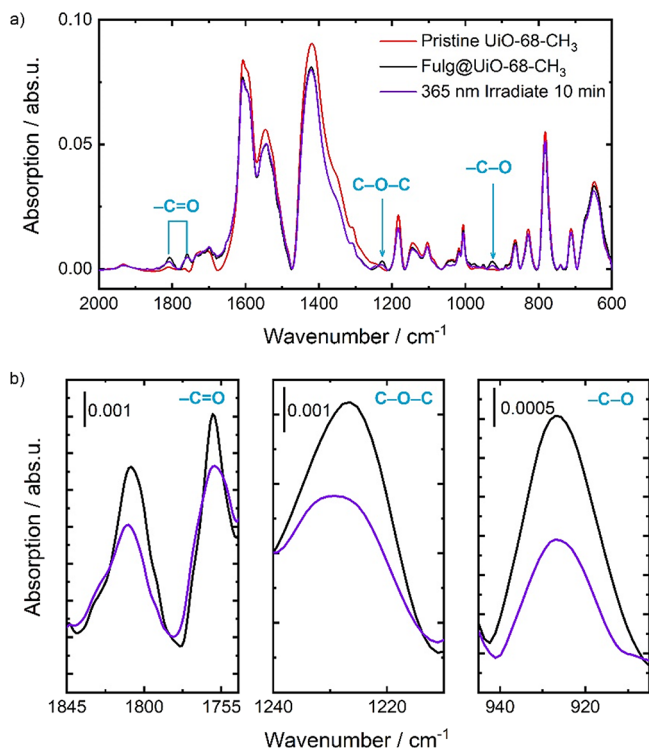


Figure 4. (a) IRRA spectra of the sample before (red), after Aber670 embedment (black), and after UV irradiation (violet). (b) IRRA spectral magnification of specific fulgide bands. Upon UV irradiation, the intensities of both bands at 924 and 1226 cm^{-1} decrease to approximately 40% of original areas.

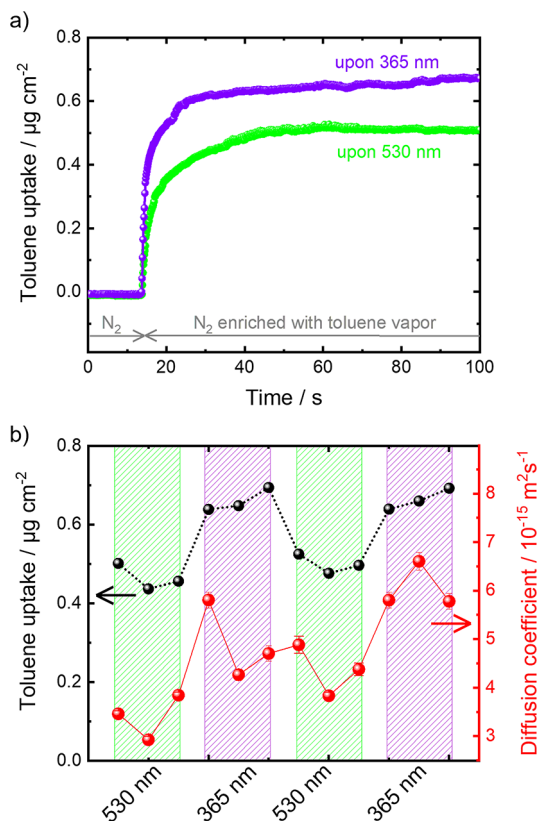


Figure 5. Uptake of toluene by the Fulg@UiO-68 sample upon UV or green light irradiation (see labels). (a) Uptake as a function of time measured by QCM. These two representative uptake curves and more uptake curves are shown in Figure S3. (b) (Final) Equilibrium loading (black) and diffusion coefficients (red) for six toluene uptake experiments with the sample upon green light and UV light irradiation. The order of the uptake experiments was as follows: First, the sample was irradiated with green light (530 nm) and three uptake experiments were performed. Then, the sample was irradiated with UV light (365 nm) and three uptake experiments were performed. Then, again, three uptake experiments upon green light and UV light irradiation were performed.

irradiation) is approximately $(3.9 \pm 0.7) \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, while the diffusion coefficient in the sample in the C-form (upon UV light irradiation) is $(5.5 \pm 0.8) \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$. The error is the standard deviation of the data. This means that the toluene diffusion coefficient increases by approximately 40% when switching the fulgide in the MOF pores from E to C.

The light-modulated uptake data with methanol as a probe molecule are shown in Figure S4. The methanol uptake by the sample in the C-form (upon UV light irradiation) is approximately 9% higher than the uptake by the sample in the E-form (upon green light irradiation).

Generally, the fulgide molecules embedded in the pores decrease the MOF pore volume, which is accessible for the guest molecules (toluene or methanol). Since the E-to-C switching of the fulgide molecules has a larger impact on the toluene uptake than on the methanol uptake, we conclude that the electrostatic interaction and the dipole moment changes of the photoswitch^{21,30} can be ruled out as a reason for the observed adsorption capacity changes. Based on the molecular properties, we suppose that the increase in adsorption amount is caused by steric effects (meaning an accessible pore volume and pore surface) in which the fulgide C isomer is more compact than the E isomer and occupies less space in the MOF pores. This means that the light-induced change of the fulgide size seems to dominate over polarity changes when modulating the toluene guest uptake. Reference experiments with an empty UiO-68-MOF film (without fulgide embedding) show that the toluene uptake by the empty MOF is not affected by light irradiation (see Figure S5, Supporting Information).

We like to stress that the observed photoinduced uptake increase for Fulg@UiO-68 (here, 37% for toluene) is significantly larger than for other systems of photoswitchable molecules embedded in MOFs (e.g., 20% photoinduced uptake increase was observed for azobenzene in HKUST-1²⁶).

4. CONCLUSIONS

A new photoswitchable nanoporous material is presented based on a MOF film of type UiO-68 with embedded photochromic fulgide molecules of type Abschrome 670 in the pores. The loading and reversible photoisomerization properties are explored by XRD, UV-vis, and IR spectroscopy. By uptake experiments with toluene and methanol probe molecules, we show that the adsorption and diffusion properties can be reversibly modulated by light irradiation, i.e., by light-induced E-C photoisomerization of fulgide in the pores.

Apart from extending the range of photoswitchable nanoporous materials, we believe that fulgide photoswitches embedded in MOF pores present many new opportunities. Based on the strong changes of the adsorption and diffusion properties, photoswitchable membrane permeation^{22,25} in MOFs with such fulgide molecules seems promising. Moreover, fulgide possesses three stable isomers,²³ which could be addressed by light (while most other photoswitches have only two stable isomers). We foresee that this may result in more advanced and more complex functionalities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.2c01810>.

Additional UV-vis spectra, infrared spectra, and QCM data (PDF)

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Notes

The authors declare no competing financial interest.

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