Switching the Proton Conduction in Nanoporous, Crystalline Materials by Light

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Proton conducting nanoporous materials attract substantial attention with respect to applications in fuel cells, supercapacitors, chemical sensors, and information processing devices inspired by biological systems. Here, a crystalline, nanoporous material which offers dynamic remote-control over the proton conduction is presented. This is realized by using surface-mounted metal–organic frameworks (SURMOFs) with azobenzene side groups that can undergo light-induced reversible isomerization between the stable trans and cis states. The trans–cis photoisomerization results in the modulation of the interaction between MOF and guest molecules, 1,4-butanediol and 1,2,3-triazole; enabling the switching between the states with significantly increased (trans) and reduced (cis) conductivity. Quantum chemical calculations show that the trans-to-cis isomerization results in the formation of stronger hydrogen bridges of the guest molecules with the azo groups, causing stronger bonding of the guest molecules and, as a result, smaller proton conductivity. It is foreseen that photoswitchable proton-conducting materials may find its application in advanced, remote-controllable chemical sensors, and a variety of devices based on the conductivity of protons or other charged molecules, which can be interfaced with biological systems.

Proton-conducting solids attract substantial attention with respect to applications as electrolyte membrane in fuel cells,[1] which enable efficient and clean production of electric energy from hydrogen and oxygen. For more than 50 years, polymers like Nafion have been applied as electrolyte membranes in fuel cells despite their disadvantages, such as a limited temperature range and a broad pore size distribution due to their amorphous structure.[2] A novel class of materials which is able to further improve the performance of the proton-conducting materials in fuel cells is metal–organic frameworks (MOFs). MOFs are crystalline, nanoporous solids, self-assembled from metal clusters or ions and organic linker molecules.[3] MOFs have many unique properties like large specific surface areas, well-defined nanoporous structures and an enormous structural and chemical variety. Moreover, their structure and functionality can be altered by pre- and postsynthetic methods.[4] Water-based proton conduction in various MOFs has been investigated and conductivities in the range of $10^{-3}$ to $1$ S m$^{-1}$ have been realized at room temperature.[1c,5] In addition, MOFs may also be used as host frameworks for water-free proton conduction at temperatures exceeding 100 °C. In that context, guest molecules like triazole[6] and histamine[7] enabled conductivities in the range of $10^{-3}$ to $0.1$ S m$^{-1}$. Proton-conducting materials are also intensively investigated for uses in chemical sensors,[8] supercapacitors,[9] and information processing devices.[10] It is expected that, as a result of their exclusive properties, namely, structurally well-defined microporous environment combined with straightforward modifications with functional receptors, MOFs will enable substantial improvement of these applications.[11]

One particular aim with respect to advanced properties is the dynamic control of the material conduction. Since light may serve as a simple, practical and typically noninvasive signal for dynamic remote-control, photochromic molecules, which undergo reversible isomerization when irradiated with light of different colors, attract considerable attention.[12] An intensively investigated photoswitchable molecule is azobenzene, which can be reversibly switched from its trans to cis state by irradiation with UV light and vice versa by irradiation with visible light or thermal relaxation.[13] By incorporation of such photoswitchable molecular moieties in materials like polymers, stimuli-responsive materials were realized where key material properties can be remote-controlled. Azobenzene-based photoswitchable smart polymers, were used as light-driven motors[14] and actuators.[15] Azobenzene-containing MOFs[16] have been used for remote-control of the adsorption[17] and diffusion[18] properties of the guest molecules and remote-controllable membrane separation of gas mixtures has been

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demonstrated. While UV-light was required to induce the switching in most photoswitchable MOFs and porous aromatic frameworks, it has been recently reported that MOFs can be switched with visible light only. Moreover, azobenzene and other photoswitchable molecules like diarylethene have been used to switch the conductivity of organic transistors, functionalized carbon nanotubes or graphene and create nonvolatile optical memories. In addition, azobenzene-containing self-assembled monolayers on gold substrates were used to modify the work function and the conductivity by about 20%. Recently, photoconduction in an amorphous melt of coordination polymers was presented where UV irradiation results in an increase of the proton conductivity, which goes back to its original value when the UV light is switched off. The photoswitching of the conductivity of crystalline materials as well as the remote-controlled switching of the proton conduction between two stable states, i.e., one state with high conductivity and one with low conductivity, have not yet been reported.

In this article, we present the dynamic remote-control over proton conduction properties in a nanoporous, crystalline material. The proton-conduction of the guest molecules is controlled by trans-cis photoisomerization of the azobenzene side groups of the host MOF structure, so that the material can be switched between a state with (relatively) high and a state with (relatively) low conductivity. The microporosity of the MOFs is essential to provide enough free volume for the azobenzene for isomerizing effectively, in order to achieve high photoswitching yields and hence, large photomodulation of conductivity. UV light, which is required for the isomerization of plain azobenzene, may have an influence on the conductivity due to potential UV excitation of organic molecules in MOFs, in addition to being potentially damaging for the materials. Thus, we use o-fluoroazobenzene moieties, which can be switched by green light (530 nm) from trans to cis and by violet light (400 nm) from cis to trans. The thermodynamically stable ground state is trans. The cis state can also be considered as stable in the dark for the course of the experiments, since the thermal cis-to-trans relaxation occurs with a time constant of ~2 years at room temperature. High isomerization yields can be achieved, i.e., the ratio of trans azobenzene can be tuned between 14% (cis state) and 87% (trans state) by irradiation with green and violet light, respectively. Here, the protonic conduction of 1,4-butanediol and 1,2,3-triazole molecules in the MOF pores is investigated. Butanediol is chosen for its suitable size, its functionality as well as its polar character, in order to take advantage of the polarity difference between trans and cis azobenzenes. Triazole, but also butanediol, have boiling points, which enables their application in high-temperature proton conduction. By using thin, well-defined films prepared in a layer-by-layer fashion, referred to as surface-mounted MOFs, SURMOFs and using interdigitated gold electrode substrates, the conductivity was measured in a reliable and straightforward fashion. Moreover, the setup with the small film thickness guarantees the in situ irradiation of the entire sample.

The SURMOF films with a pillared-layered Cu$_2$(F$_2$AzoBDC)$_2$·(dabco) structure are synthesized on the quartz substrate with interdigitated gold electrodes on top (F$_2$AzoBDC = (E)-2-((2,6-difluorophenyl)diazenyl)terephthalic acid) and dabco = 1,4-Diazabicyclo[2.2.2]octane; see Figure 1 and Figure S1, Supporting Information). The crystalline structure and the oriented growth can be seen from the X-ray diffractograms (Figure 1b). Irradiation of the SURMOF with green light (530 nm) causes trans-to-cis photoisomerization of the azobenzene side group, resulting in the cis state of the SURMOF (Figure 1c). The amount of cis azobenzene was determined to be ~86%. Violet light (400 nm) causes cis-to-trans photoisomerization, resulting in the trans state of the SURMOF with about 13% cis (and 87% trans) azobenzene, see also infrared and UV-vis spectra in Figure S2 (Supporting Information).

The conduction properties of the SURMOF were investigated by measuring the impedance spectra in a frequency range from 0.5 Hz to 5 MHz as well as by measuring the current when an alternative voltage of 1 V and 1 Hz is applied. The SURMOF samples were located in a chamber with a controlled argon gas flow. In pure argon, the amount of argon molecules in the MOF pores is very small and the pores are virtually empty. For the unloaded SURMOF, i.e., when the MOF pores are empty, the impedance spectra show only a capacitive resistance, see Figure S4 (Supporting Information). It can be estimated that the ohmic resistance of the MOF film is significantly larger than 100 GΩ. From the SURMOF thickness of 150 nm (see scanning electron microscopy (SEM) image in Figure S3 of the Supporting Information) and the geometry of the interdigitated electrode, a conductivity of less than 10$^{-8}$ S m$^{-1}$ follows. When a voltage of 1 V at a frequency of 1 Hz is applied, a current of ~0.09 nA is measured, see Figure S4c (Supporting Information). trans-cis photoisomerization of the azobenzene side groups induced by exposure to green or violet light does not affect the measured current and does not change the conduction properties.

By enriching the gas flow with the vapor of the guest molecules, here 1,4-butanediol or 1,2,3-triazole, the nanoporous SURMOF in the gas flow is loaded with the guest molecules from the vapor phase. The X-ray diffractograms (Figure 1b and Figure S1, Supporting Information) show that the ratio of the area of the (001) diffraction peak to the area of the (001) peak changes from 2.8 (empty trans-SURMOF) to 1.9 upon loading with butanediol and to 3.4 upon loading with triazole. When switching the SURMOF from trans to cis, the (001):(002) ratio changes from 2.8 to 4.8 for the empty SURMOF (see Figure S1c in the Supporting Information), from 1.9 to 6.0 for the butanediol-loaded SURMOF (see Figure 1b) and from 3.4 to 4.3 for the triazole-loaded SURMOF (see Figure S1d in the Supporting Information). The XRD peaks remain at the same positions upon loading or trans-cis switching. Thus, the change of the XRD peak intensities, i.e., of the XRD form factor, is a clear indication for the SURMOF loading with the guest molecules. Uptake experiments using a quartz crystal microbalance (Figure S8, Supporting Information) show that the butanediol (equilibrium) loading is ~1/3 molecule per pore in average and the triazole (equilibrium) loading is ~1 molecule per pore in average. The mass transfer is very slow and loading takes several hours. The increase of the uptake amount as a result of the trans-cis isomerization, as observed in ref. [21b], also takes several hours to equilibrate. Upon loading the SURMOF pores with 1,4-butanediol, the current increases to ~2 nA when a voltage of 1 V at a frequency of 1 Hz is applied, see
trans $\times 10^{-10}$ respectively (see Figure S5 in the Supporting Information). This fluorinated azobenzene side groups can be switched with green light (530 nm) from trans to cis and with violet (400 nm) from cis to trans. The black lines show the connection to the electric circuit and the impedance spectrometer. b) X-ray diffractograms of the pristine, empty trans-Cu$_2$(F$_2$AzoBDC)$_2$(dabco)-SURMOF (black), the sample upon butanediol loading (violet) and the butanediol-loaded sample switched to the cis state (green). The gray line shows the calculated powder diffractogram of the structure. The diffraction peaks are labeled. c) UV–vis absorption spectra of the Cu$_2$(F$_2$AzoBDC)$_2$(dabco)-SURMOF on quartz. The black lines show the spectra of the sample in the pristine trans state. The green and violet lines show the spectra of the sample after irradiation with green light (cis state) and violet light (trans state), respectively. The black and violet spectra are virtually identical. The intensity changes of the $\pi \rightarrow \pi^*$ (at 320 nm) clearly indicate the photoswitching of the azobenzene side groups by irradiation with green and violet light.

Figure 1. Photoswitchable MOF films on interdigitated electrode substrate. a) Sketch of the SURMOF film (green) on the interdigitated gold electrodes (yellow) on quartz (light blue) substrate. The Cu$_2$(F$_2$AzoBDC)$_2$(dabco) MOF structure with a view along the [001] direction is shown. The fluorinated azobenzene side groups in the MOF structure are in the trans state. When the sample is irradiated with green light, the sample is switched to the cis state and the current decreases by $\approx$35%. By irradiation with violet light, the sample is switched back to the trans state and the initial current is recovered. The trans–cis switching of the azobenzene-containing SURMOF host structure and the reversible current and conductivity switching of the guest molecules can be repeated for many cycles without a significant decrease of the switching effect (photobleaching). The slight increase of the current in the cis state in the dark, i.e., after 530 nm irradiation, is explained by the slow increase of the butanediol loading from the gas phase as a result of the trans–to–cis isomerization.$^{[21b]}$

Impedance spectroscopy in a range from 0.5 Hz to 5 MHz is used to investigate the ionic or proton conduction properties of the butanediol@Cu$_2$(F$_2$AzoBDC)$_2$(dabco)-SURMOF. The photoswitchable conduction is verified by the complex plane impedance plots, also referred to as Nyquist plots (Figure 2b). The reversible increase of the impedance, i.e., the decrease of the conductivity, is clearly visible upon trans-to-cis isomerization. From the impedance spectra, resistances of $\approx$370 and 550 M$\Omega$ are determined for the sample in trans and cis state, respectively (see Figure S5 in the Supporting Information). This corresponds to a butanediol conductivity of $9.0 \times 10^{-6}$ S m$^{-1}$ in trans and $6.1 \times 10^{-6}$ S m$^{-1}$ in cis Cu$_2$(F$_2$AzoBDC)$_2$(dabco).

Following the proof of concept for photoswitchable conduction of butanediol in azobenzene-containing MOF films, we investigate the extension of the concept to other proton-conducting molecules, such as triazole. The impedance spectra of the 1,2,3-triazole-loaded sample are shown in Figure 3. By switching the SURMOF from the initial trans state to the cis state by irradiation with green light, the ohmic resistance increases from 27 to 42 M$\Omega$, i.e., by $\approx$50%. Irradiation with violet light, causing the cis-to-trans isomerization, results in a restoration of the initial value. This means the conductivity of the 1,2,3-triazole@Cu$_2$(F$_2$AzoBDC)$_2$(dabco) can be switched between $1.2 \times 10^{-4}$ S m$^{-1}$ (trans) and $7.9 \times 10^{-5}$ S m$^{-1}$ (cis). The current versus time during the photoswitching of the 1,2,3-triazole@Cu$_2$(F$_2$AzoBDC)$_2$(dabco) is shown in Figure S7 (Supporting Information).

Since the butanediol and triazole loadings of the SURMOF result in an increase of the sample’s conductivity by more than three orders of magnitude, it can be concluded that the conductivity of the guest@Cu$_2$(F$_2$AzoBDC)$_2$(dabco)-SURMOF sample originates from the butanediol or triazole guest molecules in the pores, i.e., from the proton conduction of the guest molecules. This means the proton conductivity of the guest molecules is dynamically remote-controlled by trans–cis switching the host framework.

To gain a better understanding of the molecular mechanism of the photoswitchable conduction, quantum chemical calculations using MOPAC2016$^{[35]}$ with the semiempirical PM6-D3H4 method$^{[46]}$ were performed. A model of a single Cu$_2$(F$_2$AzoBDC)$_2$(dabco) pore with two azo side groups either in trans or in cis configuration and loaded with a butanediol or a triazole molecule was used. The calculations show that the OH group of the guest molecule forms a substantially stronger

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The stronger interaction of the guest molecule to the MOF in the cis state results in a decreased mobility since the difference in the binding energy between the trans-cis conformation directly affects the ratio of the on-off rates of the transport process. Neglecting the effects from conceivable differences of the transition state and using the energy difference in hydrogen bonding, we can estimate the relative rates for a molecule to pass to another pore and contribute to the charge transfer. Assuming a simple Arrhenius rate, the decrease of the rates upon trans-to-cis isomerization is $k_{\text{cis}}/k_{\text{trans}} = \exp(-\Delta E/k_B T) \approx 0.25$ at room temperature. In both cases, the stronger binding of the guest molecule to the host system in the cis conformation slows down the dynamic motion of the guest molecule and the transport of the protons. Moreover, strongly H-bonded protons are “trapped” and, hence, not available to participate in the transport. Calculations show that the surface at the azo moiety which is accessible to the guest molecules is ample (Figure S10, Supporting Information), indicating that steric effects can be excluded.

The OH···N and the NH···N bonding as well as the variation of the bonding strength between the guest molecules and the trans or cis host framework was experimentally identified by infrared spectroscopy of the loaded SURMOF. The infrared vibration spectra of butanediol- and of triazole-loaded trans and cis SURMOF samples are shown in Figure 5 and Figure S9 (Supporting Information). The broad vibration bands of OH and the NH bands are a clear indication for the formation of OH···N and NH···N bonds. Furthermore, the OH vibration of butanediol (Figure 5a) is redshifted by $\approx 40$ cm$^{-1}$ when switching the SURMOF from its trans to its cis state. When switching the host framework from trans to cis, the NH vibration of triazole (Figure 5b) also shifts to smaller wavenumbers, by $\approx 10$ cm$^{-1}$. The decreases of the vibration wavenumbers of the OH and the NH bands are a clear indication for an increase of the hydrogen bond strength, see Ch. 2.7 of ref. [37] or ref. [38]. Thus, the theoretically predicted stronger bonding of guest molecules to the cis-SURMOF than to the trans-SURMOF was experimentally verified by infrared spectroscopy.

The hydrogen bond with the nitrogen atoms of the azo group in cis conformation than with the nitrogen atoms in trans conformation, see Figure 4. A careful analysis reveals that the guest molecule forms a hydrogen bond with the azo linker in both configurations. However, in cis configuration, the molecule also interacts favorably with the second nitrogen atom, while for the azo linker in trans configuration, this interaction is significantly attenuated. In total, for both guest molecules, triazole and butanediol, the hydrogen bonding to the cis framework is 35 meV stronger than to the trans framework (for details see the Supporting Information).
In our conduction-measurement setup, the trans-to-cis switching results in a slow increase of the uptake amount from the vapor phase until the increased equilibrium loading is reached.\cite{21b} As a result of the higher loading and higher charge-carrier density, the trans-to-cis SURMOF isomerization would result in an increase of the conductivity, if the mobility of the molecules had not been affected by the switching. However, the experimental data show a decreased conductivity upon

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**Figure 4.** A single pore of Cu$_2$(F$_2$AzoBDC)$_2$(dabco) in trans a,c) and cis b,d) conformation loaded with one butanediol molecule a,b) and with triazole c,d). Both guest molecules have a stronger binding to the azo linker in cis configuration than in trans configuration, as schematically indicated by the thickness of the dotted lines. The atoms are colored in gray (C), blue (N), red (O), pink (Cu), green (F), or white (H).

**Figure 5.** An infrared spectrum of butanediol a) and triazole b) in the trans (violet) and cis (green) Cu$_2$(F$_2$AzoBDC)$_2$(dabco) SURMOF. Panel (a) shows the OH valence vibration of butanediol; panel (b) shows the NH valence vibration of triazole. The dotted lines are the fits to the data with Lorentz peaks. The spectra with the entire IR wavelength range are shown in Figure S9 (Supporting Information).
trans-to-cis isomerization. This indicates that the decreased mobility of the guest molecules in the cis SURMOF dominates over the increase of the charge carrier density. Due to the fact that the switching effect for butanediol and triazole is very similar, we believe that the photoswitching of the proton-conduction can also be generalized to various proton-conducting molecules.

In conclusion, dynamic control of proton conduction in nanoporous materials is presented by using metal-organic frameworks with azobenzene side groups loaded with proton-conducting guests. The conductivity of the guest molecules, 1,4-butanediol or 1,2,3-triazole, is reversibly switched by light-induced trans–cis isomerization of the host framework resulting in a switching between a high conductivity (trans) and low conductivity (cis) state. Quantum chemical calculations supported by infrared spectroscopy show that the switching effect is based on hydrogen bridges which are significantly stronger with the cis than with the trans azobenzene moieties. The stronger bonding with the cis state results in a decreased mobility of the guest molecules and the protons and, thus, in a decreased conductivity.

This is a remarkable demonstration of dynamic remote-control over the proton conduction in nanoporous crystalline materials such as MOFs. Contrary to the case of photoconductivity,[39] which arises from the generation of mobile charge carriers with light, here the level of conductivity is related to the state of the photoswitchable moieties, which can be kept constant after the light is switched off. The fact that the switching of proton conductivity is relatively fast in these thin films is promising for the preparation of photoswitchable devices such as proton-conducting field-effect transistors incorporating the present SURMOF as active material. It is expected that the conductivity and the switching effect, i.e., conductivity on–off ratios, can be further increased by optimizing and chemically functionalizing the pore structure, e.g., by increasing the interaction with and the amount of azobenzene “proton traps” per pore, as well as by optimizing the proton carriers. Furthermore, by using water-stable MOFs[41,42] or covalent organic frameworks (COFs),[10,41] the dynamic control of proton conduction could be extended to other proton-conducting molecules like water and even applicable to biomolecule transport.

**Experimental Section**

**SURMOF Synthesis:** The layer-by-layer (lbl) SURMOF synthesis on functional surfaces was previously discussed in detail.[32a,b] 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 × 10⁻³ M copper acetate) and the organic linkers (here: 30 min in 0.1 × 10⁻³ M F₂AzoBDC and 0.1 × 10⁻³ M dabco). Between each immersion step, the samples were cleaned with pure ethanol for 2 min. The SURMOF samples were prepared in 300 lbl-synthesis cycles by using a dipping robot.[42] All solutions were kept at room temperature. The quartz glass and interdigitated gold substrates were treated by oxygen plasma (Diener Plasma; 50 sccm, pure O₂) for 10 min to remove impurities as well as to increase the number of OH functional groups and the hydrophilicity. The plain gold substrate surfaces (for quartz crystal microbalance (QCM), infrared (IR), and X-ray diffraction (XRD)) were functionalized by an 11-mercapto-1-undecanol self-assembled monolayer. The interdigitated gold electrodes on quartz substrates were measured using a Zurich Instruments MFIA Impedance Analyzer for a frequency range of 5 MHz to 0.5 Hz. The samples were contacted using a 2-probe station from CascadeMicrotech, where the samples were placed in a custom-made cell connected with a gas flow system. The gas flow system, where the carrier gas (argon or nitrogen) can be enriched with the vapor of the guest molecules (here: 1,4-butanediol or 1,2,3-triazole), is described in ref. [34a]. It allows the control of the gas atmosphere and, thus, the pore loading in the SURMOF. A Keithley 2635B Source Meter where the voltage of +1−1 V alternates with a frequency of 1 Hz was used to measure the current as a function of time. All experiments were performed at room temperature (298 K).

**XRD, QCM, and IR:** X-ray diffraction measurements in out-of-plane geometry were carried out using a Bruker D8-Advance diffractometer equipped with a position-sensitive detector in θ-2θ geometry. A Cu-anode with a wavelength of λ = 0.154 nm was used.

The uptakes of butanediol and triazole from the vapor phase by the SURMOF samples were investigated using a Q-Sense E4 QCM from Biolin Scientific. The experimental setup is explained in ref. [34].

Fourier-transform infrared reflection absorption spectrometer (IRRAS) Bruker Vertex 80 was used for the vibrational spectroscopy of the samples. The spectra were recorded in grazing incidence reflection mode at an angle of incidence of 80° relative to the surface normal using a liquid nitrogen-cooled mercury–cadmium–telluride mid band detector. Quantum Chemical Calculations: Due to the large size of a SURMOF pore, semiempirical quantum chemistry calculations were performed using the modified neglect of diatomic overlap method[43] with the PM6-D3H4 parametrization.[14] Starting from a 2Cu-Phenyl(dabco) structure, we constructed a single pore consisting of 2 × 2 × 2 Cu₂(F₂AzoBDC)₂(dabco) unit cells and saturated the ends with additional phenyl groups (replacing a phenyl linker) or methyl groups (replacing a dabco linker). Two azo side groups pointing into the pore, both in either trans or cis configuration, were added to two phenyl linkers. Side groups that would reach into neighboring pores were neglected. Structural optimization was performed on the linkers using the low memory version of the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimization routine.[44] After optimization, one butanediol or one triazole molecule was added to the pore in proximity to the nitrogen atoms of one of the azo linkers and another optimization was performed.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

azobenzene, metal–organic frameworks, photoswitching, proton conduction, remote control