PCCP

ROYAL SOCIETY OF CHEMISTRY

Cis-to-Trans Isomerization of Azobenzene Investigated by Using Thin Films of Metal-Organic Frameworks

SCHOLARONE™
Manuscripts

Cis-to-Trans Isomerization of Azobenzene Investigated by Using Thin Films of Metal-Organic Frameworks

Xiaojuan Yu,[a,‡] Zhengbang Wang,[a,‡] Maria Buchholz,[a] Nena Füllgrabe,[a] Sylvain Grosjean,[b] Fabian Bebensee,[a] Stefan Bräse,[c,d] Christof Wöll,[a] Lars Heinke[a]

[a] Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-mail: Lars.Heinke@KIT.edu
[b] Soft Matter Synthesis Lab, Institute of Biological Interfaces (IBG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[c] Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany
[d] Institute of Toxicology and Genetics, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[‡] These authors contributed equally to this work.

Abstract

The activation barrier for *cis*-to-*trans* isomerization is a key parameter for governing the properties of photoswitchable molecules. This quantity can be computed by using theoretical methods, but experimental determination is not straightforward. Photoswitchable molecules typically do not change their conformation in the pure crystalline state. When the molecules are in solution, the switching is affected by the viscosity and polarity of the solvent and when embedded in polymers, the conformational change is affected by the polymer matrix. Here, we describe a novel approach where the photoswitchable group is integrated in a highly crystalline, porous molecular framework. Sufficiently large pore sizes in such metal-organic frameworks, MOFs, allow unhindered switching and the strictly periodic structure of the lattice eliminates virtually all contributions from inhomogeneities. Using IR spectroscopy to probe the conformational state of azobenzene, the energy barrier separating the *cis* and the *trans* state could be determined by an Arrhenius analysis of the data accumulated in a temperature regime between 314 K and 385 K. The result, 1.09 eV +/- 0.09 eV, is in very good agreement with the activation energy reported for the thermal *cis*-to-*trans* isomerization of free azobenzene as computed by DFT calculations.

Introduction

Remote control of physical and chemical properties is a very attractive feature of materials and enables various applications. In particular, the photoswitching of azobenzene and its derivatives has attracted a lot of attention in material science[1-5] but also in the life sciences, e.g. in the field of optogenetics,[6,7] where the function of biomolecules can be turned on and off by light *in vitro* and *in vivo*. For improving the performance of photoswitchable devices, a detailed understanding of the photoisomerization processes is crucial. While pure azobenzene ($C_{12}H_{10}N_2$), which has a melting point of about 70°C, shows no photoswitching behavior in the condensed, crystalline form, it can be photoswitched in solution or when it is incorporated in e.g. polymers,[4] liquid crystals,[3] or metal-organic frameworks.[8-10]

The *trans*-conformation of azobenzene is the thermodynamically more stable state. The *trans*-to-*cis* switching is driven by absorption of light. The back-switching can either be also driven by light (of different wave length) or, alternatively, thermally induced. This thermally driven process is not only crucial for the performance of light-induced switching (since it determines the life time of the *cis* state), but can also serve as a sensitive test for the pathways describing the conformational change. As a result, the *cis*-to-*trans* isomerization of azobenzene in solution,[11,12] adsorbed on various surfaces[13,14] or in small pores,[15] as well as incorporated in polymer chains[16] was investigated in numerous studies. These studies generally revealed a significant impact of the environment around the azobenzene on the switching properties and on the thermal activation energy. The solvent effect on the activation energy for the azobenzene back-switching ranges from less than 10% for nonpolar solvents to more than 30% for polar solvents.[12] An even larger impact of the solvents was found for functionalized azobenzene molecules, where the activation energy may vary by a factor of three or larger.[17,18] To the best of our knowledge, all measurements reported previously were affected by such environmental effects. Consequently, a reliable reference value determined for the thermal *cis*-to-*trans* relaxation of azobenzene molecules under conditions where matrix effects can be excluded is not available. Such a value, however, is crucial for comparisons to calculated values from theory.

Here, we report a novel approach for studying the switching of azobenzene units within the strictly crystalline, highly porous environment of MOFs. MOFs, metal-organic frameworks, are nanoporous solids composed of metal ions and organic linker molecules.[19] Their high porosity, combined with other outstanding properties like their high variability and flexibility, makes MOFs suitable for a large variety of applications like gas storage and separation, catalysis and in sensor applications. By means of liquid-phase epitaxy, surface-mounted MOFs (SURMOFs) can be directly prepared on the solid substrate surface.[20-22] SURMOFs can be patterned laterally,[23,24] and also the introduction of vertical compositional gradients is possible.[25] Furthermore, SURMOFs can be studied in a straightforward fashion by surface-sensitive spectroscopic techniques like X-ray photoelectron spectroscopy (XPS)[26] and infrared reflection-

absorption spectroscopy (IRRAS).[26] Mass changes in SURMOFs can be precisely determined by means of a quartz crystal microbalance.[27,28]

Two pillared-layer MOF structures based on organic linker molecules with azobenzene side groups are investigated: $Cu_2(BDC)_2(AzoBiPyB)$ and $Cu_2(DMTPDC)_2(AzoBiPyB)$ (AzoBiPyB: 4,4'-(2-(phenyldiazenyl)-1,4-phenylene)dipyridine;[29] BDC: benzene-1,4-dicarboxylic acid, DMTPDC: 2,2"-dimethyl-[1,1':4',1"-terphenyl]-4,4"-dicarboxylic acid, see supporting information (SI) 1). In both cases, the pore size is sufficiently large to allow photoisomerization, see figure 1. The azobenzene is connected by one phenyl ring to the framework, while the other phenyl ring points into the pore. When the MOF structure is brought into ultrahigh vacuum (UHV), the outer phenyl unit can switch freely, i.e. no solvent or gas molecules hinder its motion. While in principle UHV-studies allow for a much wider range of temperatures than the corresponding studies in solution, in the present case the range of 314-385 K was found to be sufficient to determine the activation barrier for the thermally induced *cis*-to-*trans* isomerization. We employ IR spectroscopy to study the conformational changes. Although this method has substantial advantages over UV-Vis spectroscopy, which is used in most other works to monitor the back-switching,[11,12,17,18] it is seldom employed, since the vibrational modes sensitive to the conformational change often have low excitation probabilities and since the background of the solvent or matrix often obscures the *cis*-to-*trans* induced changes in the IR-spectra of the photoswitchable molecule. In contrast to UV-Vis spectroscopy, any influence of the spectroscopic investigation on the conformation of the molecule can be certainly excluded for IR spectroscopy.
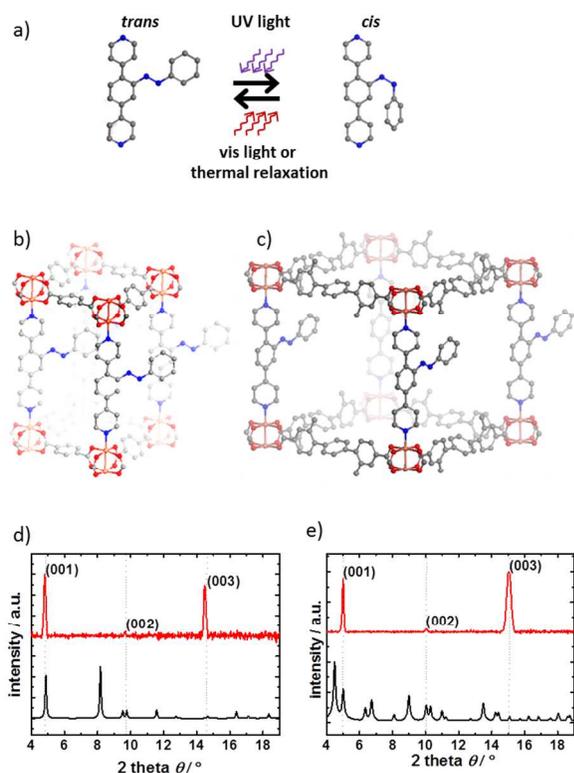
Figure 1: Structure of the azobenzene-containing linker and MOFs. a) The AzoBiPyB linker has an azobenzene side group, which can undergo photoisomerization from *trans* to *cis* when irradiated with UV light and which isomerizes to the basic *trans* state due to irradiation with visible light or thermal relaxation. The pillared-layer MOF structures of $Cu_2(BDC)_2(AzoBiPyB)$ (b) and $Cu_2(DMTPDC)_2(AzoBiPyB)$ (c) with the azobenzene groups in the *trans* state are shown. The X-ray diffractograms of $Cu_2(BDC)_2(AzoBiPyB)$ (d) and $Cu_2(DMTPDC)_2(AzoBiPyB)$ (e) demonstrate a high degree of crystallinity. Due to the oriented growth in (001) direction, only the XRD reflexes belonging to the (001) crystallographic direction can be observed in the out-of-plane XRD data. The experimental out-of-plane XRD data (red) is compared with the respective computed powder data (black). The in-plane-XRD of $Cu_2(BDC)_2(AzoBiPyB)$ is shown in SI2.

Experimental

The investigated SURMOFs were prepared on a smooth gold surface, which was functionalized with an 11-mercapto-1-undecanol self-assembled monolayer (MUD SAM). The synthesis was performed in a layer-by-layer fashion by alternatingly and repetitively exposing the functionalized substrate surface to the solution of the metal complexes (1mM ethanolic copper(II) acetate solution) and to the solution of the organic linker molecules (0.1 mM ethanolic AzoBiPyB and BDC solution or 0.1 mM ethanolic AzoBiPyB and DMTPDC solution). The samples were prepared in 50 synthesis cycles. The crystallinity of the samples were checked by X-ray diffraction (XRD), see figure 1d and e. More details about the

layer-by-layer synthesis can be found in ref. [20-22] The syntheses of the AzoBiPyB- and DMTPDC-linkers are described in the supporting information (SI1), all other chemicals are purchased from Sigma Aldrich.

The photoisomerization was investigated in UHV to enable precise and reproducible measurements. Before the experiments, the samples were activated at 120°C *in vacuo* for 4h to ensure that the MOF pores are empty. The isomerization state of the activated azobenzene-SURMOF samples was monitored by means of time-resolved infrared reflection absorption spectroscopy (IRRAS). The IR spectrometer (Bruker Vertex 80v, Bruker Optics, Ettlingen, Germany) is installed at a dedicated UHV apparatus (Prevac, Rogów, Poland) comprising various surface science techniques with a base pressure of less than $2 \cdot 10^{-10}$ mbar.[30] The UHV apparatus is equipped for precisely regulating the sample temperature in a wide range between room temperature and 393 K. All IRRAS data were acquired at grazing incidence (80°) without polarization of the incident IR light and each spectrum contains 128 scans, which allows to follow the isomerization process with a sufficiently high temporal resolution (15 s) employing a liquid nitrogen cooled MCT midband detector. Spectra are displayed as difference spectra of the measured sample with respect to a clean gold reference. The photoisomerization from the *trans* to the *cis* state was performed by irradiation with UV light from an LED with a wavelength of 365 nm.

The IRRA spectra of both SURMOFs before and after UV irradiation as well as after waiting overnight (i.e., when the initial *trans* state is reobtained) are shown in figure 2. Although there are some differences due to the different structure of the BDC and DMTPDC linker molecules, the IRRA spectra of both samples can be used to investigate the switching of the azobenzene side groups. Intensity shifts which are caused by UV irradiation are clearly visible. For both MOF structures, the intensity of the IR absorption band at about 720 cm^{-1} decreases upon irradiation with UV light and increases again by thermal relaxation. Accordingly, the corresponding vibration must be specific to the *trans* azobenzene conformation. The IR bands at about 730 cm^{-1} and 705 cm^{-1} observed in the spectra measured in Cu$_2$(BDC)$_2$(AzoBiPyB), on the other hand, increase after UV irradiation and are thus related to a vibration of *cis* azobenzene.[31] Based on work by Duarte *et al.*, the band at 720 cm^{-1} can be assigned to the γ(CH) and τ(ring) vibrations of *trans* azobenzene and the band at 705 cm^{-1} to the corresponding vibration of *cis* azobenzene.[32] (The red shift relative to the frequencies reported by Duarte et al. results from the differences in the molecular structure, i.e. from attaching the azobenzene to the biphenyl and terphenyl organic linkers.)
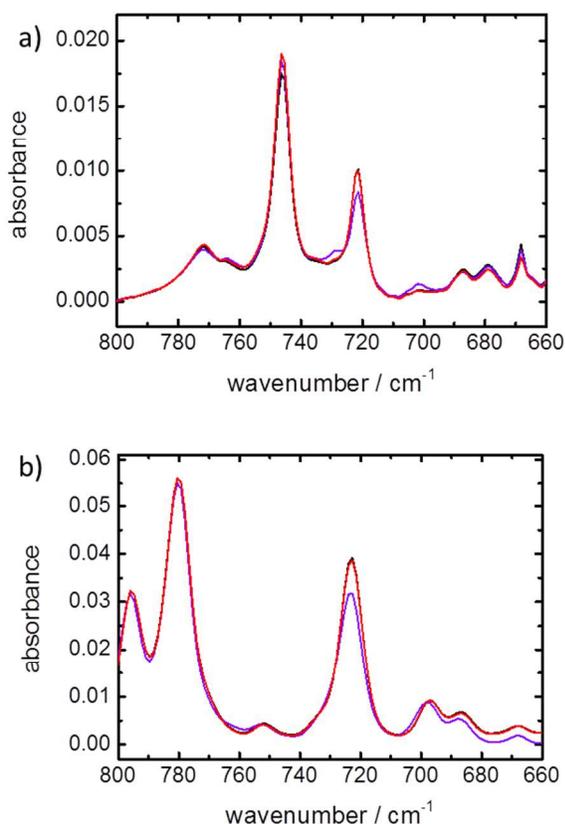
Figure 2: IRRA spectra of Cu$_2$(BDC)$_2$(AzoBiPyB) (a) and Cu$_2$(DMTPDC)$_2$(AzoBiPyB) (b) SURMOFs. The IR spectra of the pristine SURMOFs (black), i.e. with the azobenzene groups in the *trans* state, of the SURMOF irradiated with UV light for about 20 min (violet), i.e. some azobenzene groups photoisomerized to the *cis* state, and after waiting overnight (red), i.e. all azobenzene groups relaxed to the *trans* state, are shown. The spectra of the pristine sample and upon waiting overnight are virtually identical. The difference of the *cis* and *trans* spectra is shown in SI3.

Results and Discussion

By using the intensity of the IR band at about 720 cm^{-1} as a measure for the relative amount of *trans* azobenzene, we are able to monitor the change of the isomerization state of azobenzene by IRRAS with a time resolution of up to 15 s. For Cu$_2$(BDC)$_2$(AzoBiPyB), the intensity of the IR band at about 705 cm^{-1} can be additionally used as a measure for the relative amount of *cis* azobenzene. This approach enables us to study the *cis*-to-*trans* isomerization of azobenzene in the dark at different temperatures, here in a range of 314 K to 385 K. Figure 3 displays the temporal progress of the *cis*-to-*trans* isomerization for each of the MOFs for two different temperatures, namely 353 K and 373 K. Note, in a previous study, it was demonstrated that the path along which the phenyl-ring moves in the course of the isomerization may be blocked by parts of the MOF-lattice, and cases have been identified where switching is not possible.[29] For

the cases studied here, the *trans*-to-*cis* switching can be readily achived as demonstrated by corresponding changes in the UV-Vis[29] and IR spectra (see fig. 2).
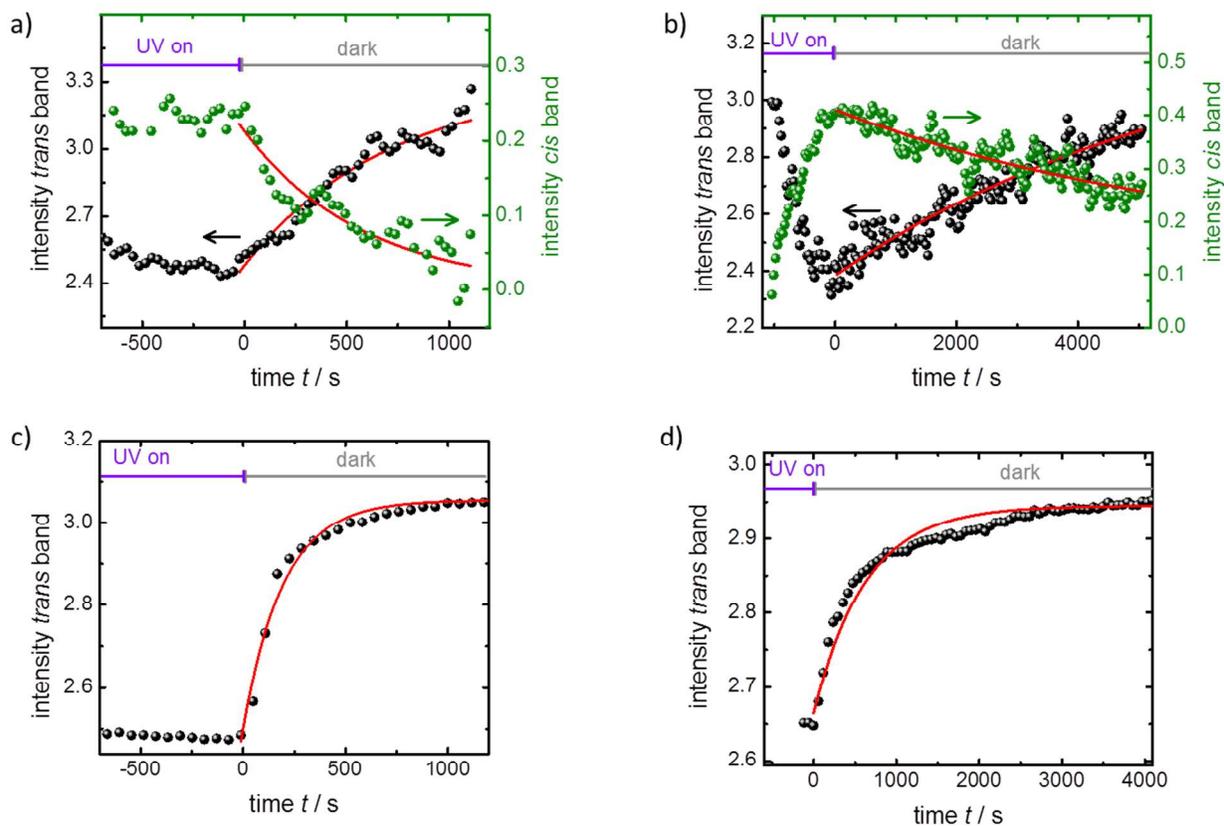
Figure 3: Variation of the *trans* and *cis* bands after switching off the UV light. Initially the samples are irradiated with UV light, resulting in *trans*-to-*cis* photoisomerization. Then, at $t = 0$ s, the UV light is switched off and the azobenzene groups relaxe to the *trans* state. For $Cu_2(BDC)_2(AzoBiPyB)$ (a and b) and for $Cu_2(DMTPDC)_2(AzoBiPyB)$ (c and d), the isomerization is investigated by observing the *trans*-azobenzene band at about 720 cm^{-1} (black). In addition to this band, the *cis*-azobenzene band at about 705 cm^{-1} (green) is analyzed for $Cu_2(BDC)_2(AzoBiPyB)$. The rate constants are determined by fitting the kinetic data with mono-exponential fits (red lines). The temperatures are 373 K in a) and c) as well as 353 K in b) and d).

From the temporal evolution of the *trans*- and *cis*-azobenzene bands, the rate constants for the *cis*-to-*trans* isomerization in the dark, i.e. for the thermal relaxation, were determined. The activation energies for the thermal *cis*-to-*trans* isomerization was determined by using an Arrhenius plot of the rate constants (figure 4). This analysis yields an activation energy of 1.18 eV $\pm$ 0.12 eV in $Cu_2(BDC)_2(AzoBiPyB)$ and 1.09 eV $\pm$ 0.09 eV in $Cu_2(DMTPBDC)_2(AzoBiPyB)$.

The smaller rate constants in $Cu_2(BDC)_2(AzoBiPyB)$ compared to $Cu_2(DMTPDC)_2(AzoBiPyB)$ (roughly by a factor of 4) might be caused by the fact that the distance between the azobenzene side groups in $Cu_2(BDC)_2(AzoBiPyB)$ is shorter than in $Cu_2(DMTPDC)_2(AzoBiPyB)$. While the azobenzene-side groups cannot have contact with each other in $Cu_2(DMTPDC)_2(AzoBiPyB)$, a mutual steric hindrance of the azobenzene side groups cannot be excluded in $Cu_2(BDC)_2(AzoBiPyB)$ and thus may explain the smaller rate constants. It can be concluded that the azobenzene side groups in $Cu_2(DMTPDC)_2(AzoBiPyB)$, where any contact of the azobenzene moieties with each other or with other parts of the framework is excluded, represents the better model system for the isolated azobenzene molecule.

The activation energy of the *cis*-to-*trans* isomerization of the azobenzene side groups in the better model system, $Cu_2(DMTPDC)_2(AzoBiPyB)$, amounts to 1.09 eV ± 0.09 eV. This finding is in excellent agreement with the activation energy obtained in theoretical calculations. For instance, activation energies of 1.17 eV and of 25 kcal mol^{-1} (i.e. 1.1 eV) were calculated by Dokić *et al.*[12] and Wang *et al.*,[33] respectively. Cembran *et al.* calculated 20 kcal mol^{-1} (i.e. 0.9 eV) for the rotation and 25 kcal mol^{-1} (i.e. 1.1 eV) for the inversion mechanism.[34] This shows that the isolated azobenzene side groups in the MOF structures present good model systems to investigate the isomerization processes of azobenzene. Therefore, these model systems can be used to further investigate features of the photoswitching in even greater detail.
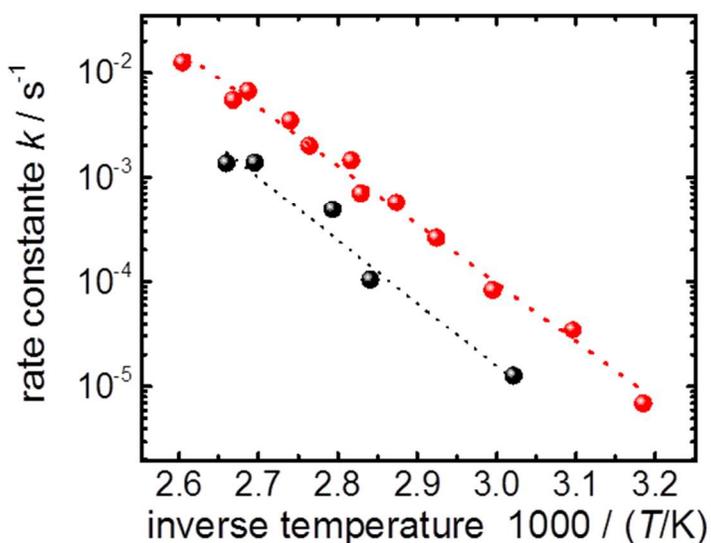
Figure 4: Arrhenius plot of the *cis*-to-*trans* isomerization. The rate constants of the *cis*-to-*trans* isomerization of the azobenzene-side groups in the $Cu_2(BDC)_2(AzoBiPyB)$ (black) and $Cu_2(DMTPDC)_2(AzoBiPyB)$ (red) are plotted

versus the inverse temperature. The activation energies are determined from the slopes of linear fits to the data points (dotted lines). The average of the rate constants for the *trans* and *cis* bands was used for $Cu_2(BDC)_2(AzoBiPyB)$, as they did not exhibit a significant difference.

Conclusion

The thermal *cis*-to-*trans* isomerization of azobenzene was investigated using a novel approach. The azobenzene molecules were integrated as linker side groups in metal-organic framework, a strictly periodic, porous material. By recording IR data for thin films of crystalline, nanoporous surface-mounted MOFs, SURMOFs, the time-constant governing the thermally-induced *cis*-to-*trans* isomerization could be investigated for a rather wide range of temperatures. The experimentally determined activation energy of 1.09 eV (+/- 0.09 eV) is in excellent agreement with theoretical results reported for free azobenzene.[12,33] The new method described here to study activation barriers for thermally induced conformational changes is generally applicable and also well suited for other photoswitchable molecules. For lower or higher activation energies the investigations can be easily extended to lower or higher temperatures, an option which is virtually non-accessible for studies in organic solvents.

Acknowledgment

References

(1)   Browne, W. R.; Feringa, B. L. *Nature Nanotechnology* **2006**, *1*, 25.
(2)   Ichimura, K.; Oh, S. K.; Nakagawa, M. *Science* **2000**, *288*, 1624.
(3)   Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873.
(4)   Jiang, H. Y.; Kelch, S.; Lendlein, A. *Adv. Mater.* **2006**, *18*, 1471.
(5)   Natansohn, A.; Rochon, P. *Chemical Reviews* **2002**, *102*, 4139.
(6)   Mayer, G.; Heckel, A. *Angew. Chem.-Int. Edit.* **2006**, *45*, 4900.
(7)   Fehrentz, T.; Schoenberger, M.; Trauner, D. *Angew. Chem.-Int. Edit.* **2011**, *50*, 12156.
(8)   Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. *Dalton Transactions* **2012**, *41*, 8690.
(9)   Heinke, L.; Cakici, M.; Dommaschk, M.; Grosjean, S.; Herges, R.; Bräse, S.; Wöll, C. *Acs Nano* **2014**, *8*, 1463.
(10)   Park, J.; Sun, L. B.; Chen, Y. P.; Perry, Z.; Zhou, H. C. *Angew. Chem.-Int. Edit.* **2014**, *53*, 5842.

(11)   Kojima, M.; Nebashi, S.; Ogawa, K.; Kurita, N. *Journal of Physical Organic Chemistry* **2005**, *18*, 994.

(12)   Dokic, J.; Gothe, M.; Wirth, J.; Peters, M. V.; Schwarz, J.; Hecht, S.; Saalfrank, P. *Journal of Physical Chemistry A* **2009**, *113*, 6763.

(13)   Henzl, J.; Mehlhorn, M.; Gawronski, H.; Rieder, K. H.; Morgenstern, K. *Angew. Chem.-Int. Edit.* **2006**, *45*, 603.

(14)   Kumar, A. S.; Ye, T.; Takami, T.; Yu, B.-C.; Flatt, A. K.; Tour, J. M.; Weiss, P. S. *Nano Letters* **2008**, *8*, 1644.

(15)   Kuriyama, Y.; Oishi, S. *Chemistry Letters* **1999**, 1045.

(16)   Eisenbach, C. D. *Makromolekulare Chemie-Macromolecular Chemistry and Physics* **1978**, *179*, 2489.

(17)   Baba, K.; Ono, H.; Itoh, E.; Itoh, S.; Noda, K.; Usui, T.; Ishihara, K.; Inamo, M.; Takagi, H. D.; Asano, T. *Chemistry-a European Journal* **2006**, *12*, 5328.

(18)   Lee, Y. J.; Yang, S. I.; Kang, D. S.; Joo, S.-W. *Chemical Physics* **2009**, *361*, 176.

(19)   Zhou, H. C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673.

(20)   Shekhah, O.; Wang, H.; Kowarik, S.; Schreiber, F.; Paulus, M.; Tolan, M.; Sternemann, C.; Evers, F.; Zacher, D.; Fischer, R. A.; Wöll, C. *J. Am. Chem. Soc.* **2007**, *129*, 15118.

(21)   Heinke, L.; Tu, M.; Wannapaiboon, S.; Fischer, R. A.; Wöll, C. *Microporous Mesoporous Mat.* **2015**, DOI: 10.1016/j.micromeso.2015.03.018.

(22)   Heinke, L.; Gu, Z.; Wöll, C. *Nat Commun* **2014**, *5*, 4562.

(23)   Munuera, C.; Shekhah, O.; Wang, H.; Wöll, C.; Ocal, C. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7257.

(24)   Zhuang, J. L.; Friedel, J.; Terfort, A. *Beilstein Journal of Nanotechnology* **2012**, *3*, 570.

(25)   Shekhah, O.; Hirai, K.; Wang, H.; Uehara, H.; Kondo, M.; Diring, S.; Zacher, D.; Fischer, R. A.; Sakata, O.; Kitagawa, S.; Furukawa, S.; Wöll, C. *Dalton Trans.* **2011**, *40*, 4954.

(26)   St Petkov, P.; Vayssilov, G. N.; Liu, J. X.; Shekhah, O.; Wang, Y. M.; Wöll, C.; Heine, T. *ChemPhysChem* **2012**, *13*, 2025.

(27)   Zhou, W.; Wöll, C.; Heinke, L. *Materials* **2015**, *8*, 3767.

(28)   Heinke, L.; Wöll, C. *Physical Chemistry Chemical Physics* **2013**, *15*, 9295.

(29)   Wang, Z.; Heinke, L.; Jelic, J.; Cakici, M.; Dommaschk, M.; Maurer, R. J.; Oberhofer, H.; Grosjean, S.; Herges, R.; Bräse, S.; Reuter, K.; Wöll, C. *Phys. Chem. Chem. Phys.* **2015**, *17*, 14582

(30)   Buchholz, M.; Weidler, P. G.; Bebensee, F.; Nefedov, A.; Wöll, C. *Physical Chemistry Chemical Physics* **2014**, *16*, 1672.

(31)   Hermann, D.; Emerich, H.; Lepski, R.; Schaniel, D.; Ruschewitz, U. *Inorganic Chemistry* **2013**, *52*, 2744.

(32)   Duarte, L.; Fausto, R.; Reva, I. *Physical chemistry chemical physics : PCCP* **2014**, *16*, 16919.

(33)   Wang, L.; Wang, X. *Journal of Molecular Structure-Theochem* **2007**, *806*, 179.

(34)   Cembran, A.; Bernardi, F.; Garavelli, M.; Gagliardi, L.; Orlandi, G. *J. Am. Chem. Soc.* **2004**, *126*, 3234.