Metal–Organic Frameworks

DOI: 10.1002/anie.201310211

Azobenzene-Functionalized Metal–Organic Polyhedra for the Optically Responsive Capture and Release of Guest Molecules**

*Jinhee Park, Lin-Bing Sun, Ying-Pin Chen, Zachary Perry, and Hong-Cai Zhou**

Abstract: *Stimuli-responsive metal–organic polyhedra (srMOPs) functionalized with azobenzene showed UV-irradiation-induced isomerization from the insoluble trans-srMOP to the soluble cis-srMOP, whereas irradiation with blue light reversed this process. Guest molecules were trapped and released upon cis-to-trans and trans-to-cis isomerization of the srMOPs, respectively. This study provides a new direction in the ever-diversifying field of MOPs, while laying the groundwork for a new class of optically responsive materials.*

Tremendous research effort has been devoted to the study of stimuli-responsive materials because of their potential applications in drug delivery, adaptable surface coating, and molecular machines.[1] As compared with traditional stimuli, such as a change in temperature[2] or pH value,[3] electric or magnetic fields,[4] and chemicals,[5] light has distinct advantages. Light with wavelengths near the visible region is generally nondestructive, has high spatial and periodic resolution, and generates few side products. Since optically responsive materials can function more accurately and predictably, systems for the capture and release of guest molecules upon irradiation with light have played a significant role in drug-delivery studies.[6] For example, light-induced coumarin release was demonstrated in polymeric micelles consisting of photochromic spiropyran units.[7]

Azobenzene is one of the most studied light-responsive units owing to its robustness, as well as rapid and reversible isomerization.[8] Upon irradiation with UV and visible light, azobenzene and its derivatives undergo reversible *trans–cis* isomerization, which alters the distance between the two end *para* carbon atoms from 9 to 5.5 Å and the dipole moment from 0.52 to 3.08 D.[8c] On the basis of the photochemical and photophysical properties of azobenzene, optically triggered solubility changes of polymers, morphological changes of micelles, and gas-adsorption changes in metal–organic frameworks (MOFs) have been widely investigated.[9]

Self-assembled molecular cages have attracted considerable research attention as a result of their aesthetic structures and intriguing potential for a wide range of applications, such as gas storage, separation, drug delivery, and catalysis.[10] Among these cages, metal–organic polyhedra (MOPs) consisting of metal and organic components can be structurally tuned through both inorganic and organic syntheses.[11] The judicious choice of functional groups on geometrically fixed building blocks can precisely tune the functions and properties of the MOPs, thus enabling them to respond to external stimuli.[12] A MOP built with a bulky organic linker was found by our research group to exhibit a thermally sensitive molecular-sieving effect.[13] Previously, a MOP for the controlled capture and release of guest molecules upon irradiation with light has rarely been reported.[6a] Herein we report for the first time optically responsive MOPs derived from organic linkers containing azobenzene units. Because MOPs are suitable for capturing guest molecules, such as gas, drug, and dye molecules, the capture and release of the guest molecules becomes controllable through the isomerization of the azobenzene units.

As compared with other types of MOPs, cuboctahedra contain more organic linkers.[11a] The presence of these 24 organic linkers increases the isomerization effect of the pendent azobenzene units. A ligand with a 120° bridging angle, 2,4-dimethylphenyldiazenylisophthalate ($\mathbf{L^1}$), was synthesized on the basis of the Mills reaction.[14] The *trans*-to-*cis* isomerization of $\mathbf{L^1}$ upon exposure to UV light (365 nm) was confirmed by ^{1}H NMR spectroscopy (Figure 1a; see also Figure S10 in the Supporting Information). A reaction between $Cu(OAc)_2$ and the acidic form of the ligand afforded a green precipitate, srMOP-1 (srMOP stands for stimuli-responsive MOP). The as-synthesized srMOP-1 was soluble in chloroform. Vapor diffusion of diethyl ether into a solution of srMOP-1 in chloroform yielded crystalline srMOP-1. However, owing to light-induced isomerization of $\mathbf{L^1}$, it was difficult to grow crystals large and robust enough for structure determination, even under light- and temperature-controlled conditions. Our previous report showed that coordination assemblies are generally determined by the bridging angle of the organic linker.[11b] On the basis of this knowledge, we used

[*] Dr. J. Park
Nano Hybrid Technology Research Center
Creative and Fundamental Research Division
Korea Electrotechnology Research Institute
Changwon, 641-120 (Republic of Korea)
Dr. L.-B. Sun, Y.-P. Chen, Z. Perry, Prof. Dr. H.-C. Zhou
Department of Chemistry, Texas A&M University
College Station, TX 77842 (USA)
E-mail: zhou@tamu.edu
Y.-P. Chen, Prof. Dr. H.-C. Zhou
Department of Materials Science and Engineering
Texas A&M University
College Station, TX 77843 (USA)

[**] This research was partially supported as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015. We also acknowledge the US DOE (DE-AR000073 and DE-FC36-07GO17033), the National Science Foundation (NSF CBET-0930079), and the Welch Foundation (A-1725). We thank Dr. Joseph P. Riebenspies for structure refinement and advice in crystallography.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310211.

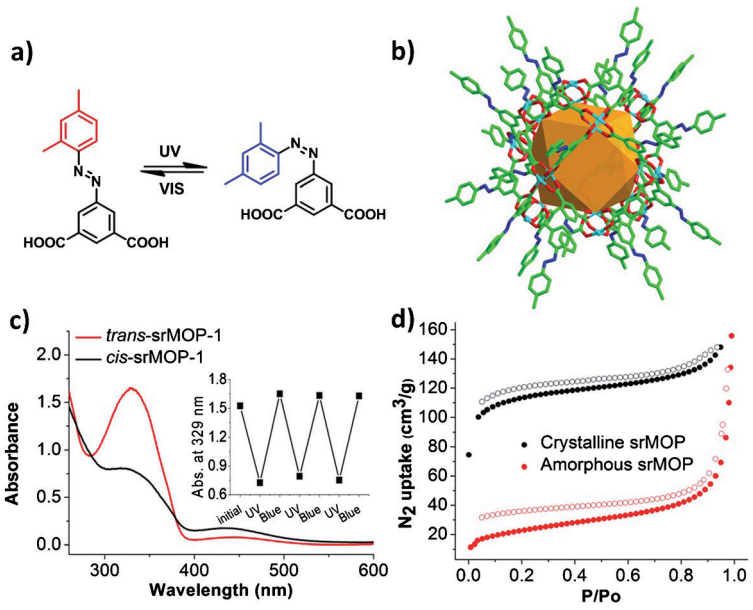


Figure 1. a) Light-induced *trans*/*cis* isomerization of 5-(2,4-dimethylphenyldiazenyl)-isophthalic acid, $H_2\mathbf{L}^1$. b) Crystal structure of srMOP-2 as an azobenzene-functionalized cuboctahedral cage, as determined by single-crystal X-ray diffraction analysis. c) Absorption spectra of srMOP-1 with pendent azobenzene groups in chloroform: in the dark after irradiation with blue light (red); after UV irradiation (black). The inset shows the changes in absorbance at 329 nm of srMOP-1 in solution on alternate irradiation with UV and blue light. d) N_2-adsorption isotherm of crystalline srMOP-1 and amorphous srMOP-1. Crystalline srMOP-1 shows enhanced microporosity.

a mixture of two ligand precursors, 5-(*p*-tolyldiazenyl)isophthalic acid ($\mathbf{H_2L^2}$) and 5-*tert*-butylisophthalic acid ($\mathbf{H_2L^3}$), both with a 120° bridging angle, to grow an analyzable crystal. Vapor diffusion of diethyl ether into the mixture of $\mathbf{H_2L^2}$, $\mathbf{H_2L^3}$, and $Cu(OAc)_2$ in *N*,*N*-dimethylacetamide afforded single crystals of srMOP-2 suitable for structure determination. Presumably, because the inclusion of $\mathbf{L^3}$ not only reduces the inclusion of the azobenzene-containing ligand $\mathbf{L^2}$ but also suppresses the isomerization of $\mathbf{L^2}$ from *trans* to *cis* owing to steric hindrance by the surrounding *tert*-butyl groups of the $\mathbf{L^3}$ ligand, it leads to the formation of stable crystals.

In the crystal structure of srMOP-2, one dicopper (Cu_2) paddlewheel unit is assembled with four ligands. When the ligands are viewed as linear edges and the Cu_2 paddlewheel units as vertices, 24 ligands and 12 Cu_2 paddlewheel units form a cuboctahedral cage (Figure 1b; shown in brown). In srMOP-2, one third of the positions were occupied by $\mathbf{L^2}$, whereas the rest were filled with $\mathbf{L^3}$ (see Figure S5). Similarly, the assembly of $\mathbf{L^1}$ and a copper salt should lead to another cuboctahedral cage, srMOP-1. The mass spectrum of srMOP-1, which revealed a prominent peak for $Cu_{24}\mathbf{L^1}_{24}$, strongly supports such an assumption (see Figure S33). Furthermore, images of srMOP-1 and srMOP-2 from transmission electron microscopy also displayed well-defined cages with diameters of 3.9–4.3 nm, in good agreement with the formation of the cuboctahedral cages (see Figures S7 and S8).

The reversible isomerization of srMOP-1 was monitored by UV/Vis spectroscopy (Figure 1c). When srMOP-1 in chloroform was irradiated with UV light (365 nm), the absorption band at 329 nm, the characteristic feature of the *trans* form, disappeared, and a new band appeared at 440 nm, thus indicating the formation of the *cis* form. When the photostationary state was reached, the solution was irradiated with blue light, and the band intensity at 329 nm was restored. This result demonstrates the reversibility of the *trans*/*cis* isomerization of srMOP-1 through alternating irradiation with UV and blue light.

As-synthesized srMOP-1 was soluble in chloroform but gradually precipitated under dark conditions. Complete precipitation took more than 2 weeks. As confirmed by powder X-ray diffraction, whereas as-synthesized srMOP-1 was amorphous, the srMOP-1 precipitate was crystalline. We examined the porosity difference between amorphous and crystalline srMOP-1 through N_2 adsorption at 77 K. We activated a sample by treatment with methanol to exchange the encapsulated and coordinated solvents. The methanol-exchanged sample was subsequently degassed under reduced pressure at 100 °C for 5 h. In the low-pressure region, the N_2-adsorption isotherm of amorphous srMOP-1 showed a low and slow increase in uptake, whereas crystalline srMOP-1 demonstrated a steep increase in uptake (Figure 1d). The pore-size distributions calculated from the N_2-adsorption isotherms at 77 K indicated that crystalline srMOP-1 had enhanced microporosity as compared with amorphous srMOP-1 (see Figures S22 and S23). Like srMOP-2, srMOP-1 contained a 14–16 Å pore, which is further evidence for the formation of the cuboctahedral cage of srMOP-1 (see Figures S22, S23, and S24). Previously reported MOFs containing a cuboctahedral cage as a building unit, such as the PCN-6X series, showed a similar pore size attributed to the presence of the cuboctahedral cage in the structures.[15] Presumably, the larger microporosity content in crystalline srMOP-1 originates from the long-range order, whereas amorphous srMOP-1 is made from randomly oriented cages, and as a result, adjacent cages can block pore windows. Our recent study shows that a 1D polyhedral-cage chain has a greatly increased gas uptake as compared with discrete cages because interdigitation of the bulky groups between adjacent cages hampers the rearrangement of the cages during the activation process and gives a final structure with a continuous open channel.[9e]

Interestingly, crystalline srMOP-1 in chloroform became soluble upon UV irradiation. This increased solubility could have two possible reasons. First, *trans*-to-*cis* isomerization of the pendent azobenzene units on srMOP-1 weakens the intercage interaction. In *trans*-srMOP-1, the dangling phenyl groups of the azobenzene units point away from the cage and increase interactions (e.g. π–π interactions) between the MOPs. In contrast, *cis*-srMOP-1 has the dangling phenyl groups bent toward its cage, thus decreasing interaction with other MOPs. Second, owing to the larger dipole moment of *cis*-azobenzene, *cis*-srMOP-1 has higher solubility in the polar solvent as compared with *trans*-srMOP-l. Because the MOP derived from $\mathbf{L^2}$ showed very low solubility in most conven-

tional solvents, we excluded this MOP from further investigation.

Such isomerization can be utilized for light-induced guest release. Because isomerization of the pendent azobenzene units cannot change the inner cavity of the cuboctahedral cage of srMOP-1, small guest molecules captured within the inner cavity cannot be influenced by *trans*-to-*cis* isomerization of srMOP-1. The decreased H_2 uptake and increased hysteresis on the desorption branch upon UV irradiation for 1 h (see Figure S25) indicates the limited diffusion of the gas molecules in and out of the cavity. A lower pressure was required to release adsorbed H_2 molecules from the MOPs because the pore windows were partially blocked by the dimethylphenyl groups of the *cis*-isomer ligands in srMOP-1.

In this context, methylene blue (MB), which is too large to be trapped in the core of the cage but may be captured in among the *trans*-srMOP-1 cages, was selected as the guest molecule. Since the UV/Vis spectra of MB and srMOP-1 do not overlap, the amount of MB captured and released by srMOP-1 can be directly monitored by UV/Vis spectroscopy. We chose a solvent system in which both *trans*- and *cis*-srMOP-1 are insoluble and MB is soluble. In this case, the solubility difference between *trans*- and *cis*-srMOP-1 will not account for guest release, which can mainly be attributed to the weaker interaction between *cis*-srMOP-1 structures. To meet this prerequisite, we used a mixed solvent: 10% methanol in acetone (v/v). To load MB into *trans*-srMOP-1, we mixed MB in methanol and srMOP-1 in acetone, and the resulting solution was stirred for 5 h in the dark. Owing to disorder of the srMOP-1 packing in this mixed solvent system, we were unable to locate MB in this srMOP-1 precipitate. The concentration of MB in the solution decreased, with 0.039 mg of MB adsorbed per 1 mg of srMOP-1 (as calculated on the basis of the UV/Vis spectrum of MB in solution). MB@*trans*-srMOP-1 was separated from uncaptured MB by centrifugal separation, and 10% methanol/acetone was added to MB@*trans*-srMOP-1. As expected, in the dark there was no noticeable change in the UV/Vis spectrum of the solution even after 90 min. However, upon UV irradiation, a considerable increase in the MB-band absorption was observed (Figure 2b). This increase implies that MB enclosed in the space between *trans*-srMOP-1 structures was released when the UV light was turned on (Figure 2a). The release of MB stopped when UV irradiation was stopped (see Figure S27). This result indicates that the interaction between *cis*-srMOP-1 structures is not strong enough to generate pockets to retain guest molecules, and therefore the captured guest molecules are released upon the formation of *cis*-srMOP-1.

The UV-light-induced release of MB prompted us to develop a system for the reversible capture and release of guests by srMOP-1. We tried to harness the solubility difference between *trans*- and *cis*-srMOP-1. As previously mentioned, the aggregation of *trans*-srMOP-1 in chloroform required at least 2 weeks owing to its relatively high solubility in chloroform. To accelerate this aggregation process, we adopted a mixed solvent system: 5% acetone in chloroform. In this solvent system, *trans*-srMOP-1 showed much lower solubility, whereas *cis*-srMOP-1 remained highly soluble. At higher acetone/chloroform ratios, the solubility of both *trans*- and *cis*-srMOP-1 decreased. The photoinduced solubility change of srMOP-1 in 5% acetone/chloroform was also confirmed by UV/Vis spectroscopy (see Figure S28). The turbid suspension of insoluble *trans*-srMOP-1 was prepared by irradiation with blue light for 1 h. The suspension was centrifuged at 15000 rpm, and then only the clear supernatant obtained was used to record a UV/Vis absorption spectrum. The spectrum showed that there was only a very small amount of srMOP-1 in the supernatant. The turbid suspension was then exposed to UV light for 30 min and became a transparent green solution. The spectrum showed strong absorption peaks of *cis*-srMOP-1. It indicated that *trans*-to-*cis* isomerization enhanced the solubility of srMOP-1.

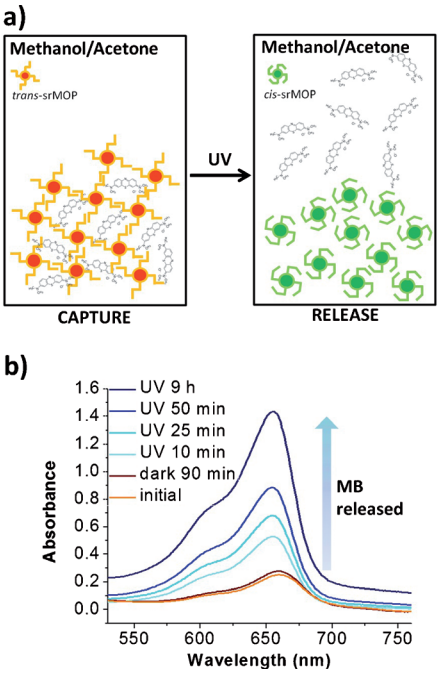


Figure 2. a) Schematic illustration of the capture of MB by *trans*-srMOP-1 and its release from *cis*-srMOP-1. The two isomers *trans*- and *cis*-srMOP-1 are insoluble. b) UV/Vis spectra of MB in solution in 10% methanol/acetone. As MB was released from *cis*-srMOP-1, the absorbance of MB in the solution increased.

To examine the reversibility of the light-induced solubility change, we exposed this green solution to blue light, and within 30 min the solution became turbid, thus indicating the formation of insoluble *trans*-srMOP-1. Upon irradiation with blue light for 1 h, full conversion of the *cis*-to-*trans* isomerization process occurred. Because of the less-efficient isomerization of solid-state azobenzene, this insoluble *trans*-/soluble *cis*-srMOP isomerization took longer than the isomerization of the soluble srMOP.[16] Irradiation for longer than 1 h caused no further formation of precipitates. When the solution was in the dark, irradiation for at least 3 h was required before noticeable precipitation was observed, thus indicating that irradiation with blue light accelerated the formation of *trans*-srMOP-1. The reversible formation of a turbid suspension and a clear solution was observable even with the naked eye (Figure 3). Such a phenomenon can be used to adjust light

transmittance by irradiation with light, for example, in a stimuli-responsive filter.[5c,17]

This reversible solubility change of srMOP-1 can be utilized in the photoinduced reversible release and capture of guest molecules. The strategy employed is illustrated schematically in Figure 4a. To incorporate MB into *trans*-srMOP-1, we added a solution of MB in methanol to a suspension of *trans*-srMOP-1 in chloroform. An aliquot of acetone was subsequently added, and the solution was irradiated with blue light to generate MB@*trans*-srMOP-1 as a solid. Excess uncaptured MB was removed by centrifugal separation. The solid MB@*trans*-srMOP-1 was washed with fresh acetone and placed in 5% acetone/chloroform for a guest-release experiment. The absorption spectrum of the supernatant of the solution showed a small peak at 650 nm, thus indicating that almost all MB molecules were adsorbed on *trans*-srMOP-1.

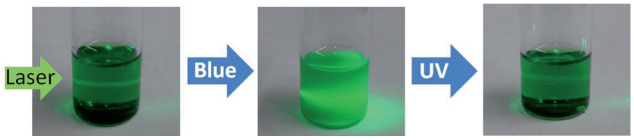


Figure 3. Photographs showing that transparent *cis*-srMOP-1 in 5% acetone/chloroform (left) becomes a turbid suspension of *trans*-srMOP-1 (middle) upon irradiation with blue light. UV-light-induced *trans*-to-*cis* isomerization gives soluble *cis*-srMOP-1 again and thus a clear solution (right).

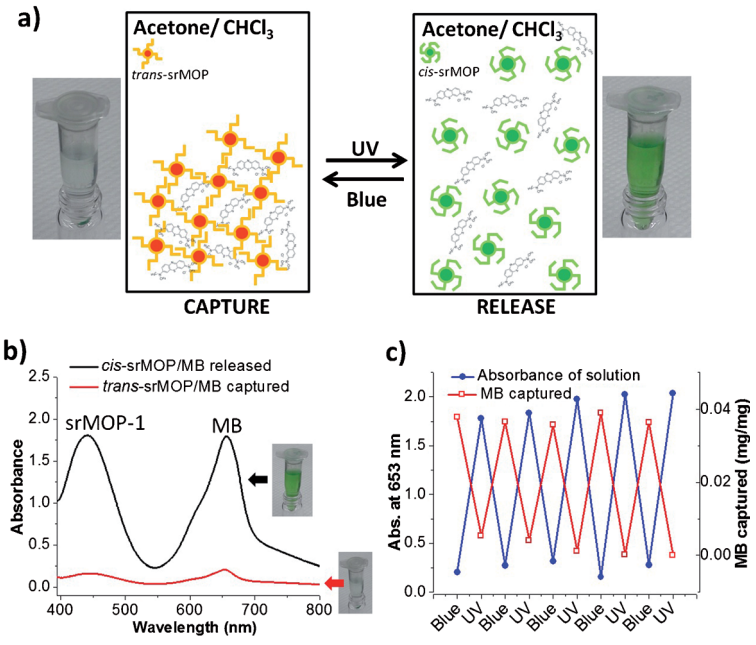


Figure 4. a) Schematic illustration of the reversible formation of insoluble *trans*- and soluble *cis*-srMOP-1, which enable the photoinduced capture and release of MB, respectively. The left photograph shows the clear supernatant with insoluble MB@*trans*-srMOP-1 at the bottom after centrifugation at 15000 rpm. The right photograph shows a homogeneous solution of *cis*-srMOP-1 and MB. b) UV/Vis spectra of a solution of srMOP-1 and MB after UV irradiation (black) as well as after irradiation with blue light (red). c) Absorbance of the solution at 653 nm (blue) and the corresponding concentration of MB captured in srMOP-1 (red).

Upon UV irradiation for 30 min, the absorption peak of MB increased drastically, accompanied by the generation of soluble *cis*-srMOP-1 in solution (Figure 4b). This result implies that insoluble *trans*-srMOP-1 was converted into soluble *cis*-srMOP-1, which could no longer retain the adsorbed MB. Therefore, the MB concentration in solution increased. Irradiation of the solution with blue light caused formation of the insoluble *trans* isomer, the recapture of MB, and thus a decrease in the concentration of MB in solution. Remarkably, more than 96% of the released MB was recaptured through *cis*-to-*trans* isomerization of srMOP-1 within 1 h, and almost complete recapture of MB was observed after irradiation with blue light for 4 h. In our system, the temperature increased by 1 and 3.5 °C during irradiation with blue light for 4 h and irradiation with UV light for 1 h, respectively. This temperature change would have a negligible effect on the isomerization of azobenzene and the capture/release rate of MB. Therefore, this rapid capture/release of MB is a consequence of the high-yielding rapid isomerization of the pendent azobenzene units on srMOP-1 upon irradiation with light. Figure 4c shows the reversibility of the capture and release of MB for five cycles of alternating irradiation with UV (30 min) and blue light (1 h). The amounts of MB captured/released for the five cycles of irradiation with blue/UV light were similar, thus suggesting the high reproducibility of *trans*/*cis* isomerization of the azobenzene units.

The integrity of $\mathbf{L^1}$ after the guest-capture/release experiments was confirmed by a ^{1}H NMR spectroscopic study of digested srMOP-1 in DCl/[D_6]dimethyl sulfoxide. The spectrum was identical to that of the as-synthesized ligand, thus indicating the robustness of $\mathbf{L^1}$ (see Figure S7). The mass spectrum of srMOP-1 after the fifth cycle of the capture/release experiment was recorded, and a peak at *m*/*z* 8702 due to intact srMOP-1 was observed ($Cu_{24}L_{24}{\cdot}n\,H_2O$; see Figure S33). The mass spectrum revealed that the isomerization did not decrease the stability of srMOP-1.

In summary, we have shown that srMOP-1 functionalized with azobenzene groups can undergo reversible *trans*/*cis* isomerization. The isomer *trans*-srMOP-1 showed low solubility and strong interaction between cages. Guest MB molecules were captured in the pockets in among *trans*-srMOP-1 units. Upon UV irradiation, *trans*-srMOP-1 isomerized to *cis*-srMOP-1, whereupon a decrease in the interaction between srMOP-1 cages was observed, along with an increase in solubility. Therefore, *trans*-to-*cis* isomerization of srMOP-1 facilitated the release of MB. Remarkably, highly reversible capture and release of MB was possible by alternate irradiation with blue and UV light. Before any practical applications of such optically responsive MOPs may be considered, there are still many aspects that must be explored, such as biocompatibility,[10c] optimization of the isomerization conditions to enhance energy efficiency, and modification of the srMOPs to enable

isomerization induced by visible or near-IR light in versatile solvent systems.[18] Nonetheless, the reversible capture/release of guest molecules as presented herein will provide a new direction in the ever-diversifying field of MOPs, while laying the groundwork for new optically responsive materials.

Received: November 25, 2013
Published online: ■■ ■■, ■■■■

Keywords: azo compounds · host–guest systems · metal–organic polyhedra · optically responsive materials · stimuli-responsive solubility

[1] a) M. A. Cohen Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V. Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, S. Minko, *Nat. Mater.* **2010**, *9*, 101 – 113; b) J. Croissant, J. I. Zink, *J. Am. Chem. Soc.* **2012**, *134*, 7628 – 7631; c) M. Natali, S. Giordani, *Chem. Soc. Rev.* **2012**, *41*, 4010 – 4029; d) X. Yan, F. Wang, B. Zheng, F. Huang, *Chem. Soc. Rev.* **2012**, *41*, 6042 – 6065.

[2] a) J. Liu, A. Li, J. Tang, R. Wang, N. Kong, T. P. Davis, *Chem. Commun.* **2012**, *48*, 4680 – 4682; b) B. Li, X. Jiang, J. Yin, *J. Mater. Chem.* **2012**, *22*, 17976 – 17983.

[3] W. Wang, D. Cheng, F. Gong, X. Miao, X. Shuai, *Adv. Mater.* **2012**, *24*, 115 – 120.

[4] S. Das, P. Ranjan, P. S. Maiti, G. Singh, G. Leitus, R. Klajn, *Adv. Mater.* **2013**, *25*, 422 – 426.

[5] a) I. Bassanetti, F. Mezzadri, A. Comotti, P. Sozzani, M. Gennari, G. Calestani, L. Marchiò, *J. Am. Chem. Soc.* **2012**, *134*, 9142 – 9145; b) M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet, B. Escuder, *Chem. Soc. Rev.* **2013**, *42*, 7086; c) T. Ogoshi, K. Kida, T.-A. Yamagishi, *J. Am. Chem. Soc.* **2012**, *134*, 20146 – 20150.

[6] a) M. Han, R. Michel, B. He, Y.-S. Chen, D. Stalke, M. John, G. H. Clever, *Angew. Chem.* **2013**, *125*, 1358 – 1362; *Angew. Chem. Int. Ed.* **2013**, *52*, 1319 – 1323; b) R. Tong, H. D. Hemmati, R. Langer, D. S. Kohane, *J. Am. Chem. Soc.* **2012**, *134*, 8848 – 8855; c) X. Mei, S. Yang, D. Chen, N. Li, H. Li, Q. Xu, J. Ge, J. Lu, *Chem. Commun.* **2012**, *48*, 10010 – 10012; d) Q. Yuan, Y. Zhang, T. Chen, D. Lu, Z. Zhao, X. Zhang, Z. Li, C.-H. Yan, W. Tan, *ACS Nano* **2012**, *6*, 6337 – 6344.

[7] H.-i. Lee, W. Wu, J. K. Oh, L. Mueller, G. Sherwood, L. Peteanu, T. Kowalewski, K. Matyjaszewski, *Angew. Chem.* **2007**, *119*, 2505 – 2509; *Angew. Chem. Int. Ed.* **2007**, *46*, 2453 – 2457.

[8] a) S. Yagai, A. Kitamura, *Chem. Soc. Rev.* **2008**, *37*, 1520 – 1529; b) J. Garcia-Amorós, S. Nonell, D. Velasco, *Chem. Commun.* **2012**, *48*, 3421 – 3423; c) G. S. Kumar, D. C. Neckers, *Chem. Rev.* **1989**, *89*, 1915 – 1925.

[9] a) M. Irie, H. Tanaka, *Macromolecules* **1983**, *16*, 210 – 214; b) "Photoresponsive Polymers": M. Irie, *Advances in Polymer Science*, *Vol. 94*, Springer, Berlin, **1990**, pp. 27 – 67; c) G. Wang, X. Tong, Y. Zhao, *Macromolecules* **2004**, *37*, 8911 – 8917; d) M. Yamamura, Y. Okazaki, T. Nabeshima, *Chem. Commun.* **2012**, *48*, 5724 – 5726; e) J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2012**, *134*, 99 – 102; f) A. Modrow, D. Zargarani, R. Herges, N. Stock, *Dalton Trans.* **2011**, *40*, 4217 – 4222; g) N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501 – 4504; h) J. W. Brown, B. L. Henderson, M. D. Kiesz, A. C. Whalley, W. Morris, S. Grunder, H. Deng, H. Furukawa, J. I. Zink, J. F. Stoddart, O. M. Yaghi, *Chem. Sci.* **2013**, *4*, 2858 – 2864.

[10] a) J. E. M. Lewis, E. L. Gavey, S. A. Cameron, J. D. Crowley, *Chem. Sci.* **2012**, *3*, 778 – 784; b) T. Murase, Y. Nishijima, M. Fujita, *J. Am. Chem. Soc.* **2012**, *134*, 162 – 164; c) D. Zhao, S. Tan, D. Yuan, W. Lu, Y. H. Rezenom, H. Jiang, L.-Q. Wang, H.-C. Zhou, *Adv. Mater.* **2011**, *23*, 90 – 93.

[11] a) D. J. Tranchemontagne, Z. Ni, M. O'Keeffe, O. M. Yaghi, *Angew. Chem.* **2008**, *120*, 5214 – 5225; *Angew. Chem. Int. Ed.* **2008**, *47*, 5136 – 5147; b) J.-R. Li, A. A. Yakovenko, W. Lu, D. J. Timmons, W. Zhuang, D. Yuan, H.-C. Zhou, *J. Am. Chem. Soc.* **2010**, *132*, 17599 – 17610; c) J.-R. Li, H.-C. Zhou, *Nat. Chem.* **2010**, *2*, 893 – 898; d) K. Suzuki, K. Takao, S. Sato, M. Fujita, *J. Am. Chem. Soc.* **2010**, *132*, 2544 – 2545; e) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi, M. Fujita, *Angew. Chem.* **2004**, *116*, 5739 – 5743; *Angew. Chem. Int. Ed.* **2004**, *43*, 5621 – 5625; f) T. D. Hamilton, G. S. Papaefstathiou, T. Friščić, D.-K. i. Bučar, L. R. MacGillivray, *J. Am. Chem. Soc.* **2008**, *130*, 14366 – 14367.

[12] a) B. Kilbas, S. Mirtschin, R. Scopelliti, K. Severin, *Chem. Sci.* **2012**, *3*, 701 – 704; b) H. Furukawa, J. Kim, K. E. Plass, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 8398 – 8399.

[13] D. Zhao, D. Yuan, R. Krishna, J. M. van Baten, H.-C. Zhou, *Chem. Commun.* **2010**, *46*, 7352 – 7354.

[14] H. D. Anspon, *Org. Synth.* **1945**, *25*, 1.

[15] a) D. Yuan, D. Zhao, D. Sun, H.-C. Zhou, *Angew. Chem.* **2010**, *122*, 5485 – 5489; *Angew. Chem. Int. Ed.* **2010**, *49*, 5357 – 5361; b) D. Zhao, D. Yuan, D. Sun, H.-C. Zhou, *J. Am. Chem. Soc.* **2009**, *131*, 9186 – 9188.

[16] K. G. Yager, C. J. Barrett, *J. Photochem. Photobiol. A* **2006**, *182*, 250 – 261.

[17] J. Heo, Y. J. Kim, M. Seo, S. Shin, S. Y. Kim, *Chem. Commun.* **2012**, *48*, 3351 – 3353.

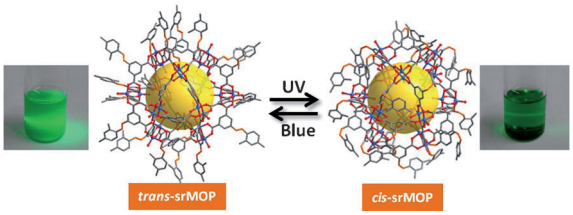
[18] H. A. Wegner, *Angew. Chem.* **2012**, *124*, 4869 – 4871; *Angew. Chem. Int. Ed.* **2012**, *51*, 4787 – 4788.

Communications

Metal–Organic Frameworks

J. Park, L.-B. Sun, Y.-P. Chen, Z. Perry, H.-C. Zhou* ——— ■■■■–■■■■

Azobenzene-Functionalized Metal–Organic Polyhedra for the Optically Responsive Capture and Release of Guest Molecules



Lock in the guests, later set them free: Stimuli-responsive metal–organic polyhedra (srMOPs) functionalized with azobenzene showed UV-light-induced isomerization from insoluble srMOPs substituted with *trans*-azobenzene to soluble srMOPs with *cis*-azobenzene units; irradiation with blue light reversed this process (see picture). Guest molecules were trapped upon *cis*-to-*trans* and released upon *trans*-to-*cis* isomerization of the azobenzene units.