

Photoswitchable Films of Metal-Organic Frameworks for Continuously Tunable Molecular Membrane Separation

**Lars Heinke,¹ Kai Müller,¹ Zhengbang Wang,¹ Christof Wöll,¹ Alexander Knebel,²
Jürgen Caro,² Sylvain Grosjean,³ Stefan Bräse,³ and David Bléger⁴**

¹ *Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT),
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

² *Institute for Physical Chemistry and Electrochemistry, Leibniz University Hanover,
Callinstraße 3a, 30167 Hannover, Germany*

³ *Institute of Organic Chemistry (IOC), KIT, Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany*

⁴ *Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Strasse 2, 12489
Berlin, Germany*

E-mail: Lars.Heine@KIT.edu

Metal-organic frameworks (MOFs) are nanoporous, crystalline materials, assembled from metal nodes and organic linker molecules. In addition to many potential applications of the (conventional) powder MOF material, well-defined thin films seem perfectly suited for challenging uses and as unique model systems. These thin films are prepared in a layer-by-layer fashion on a solid substrate by using liquid-phase epitaxy, referred to as surface-mounted MOFs, SURMOFs. Incorporating photochromic molecules like azobenzene in the crystalline structure enables the switching of physical and chemical MOF properties by light. The *trans*-to-*cis* switching or vice versa of the azobenzene side groups by UV or visible light, respectively, can be used for various uses, such as realizing the remote-controlled release of guest molecules from a nanoporous container.

In addition, thin films of MOFs with azobenzene side groups can be used as membranes for the separation of molecular mixtures, see Figure 1. The photoswitchable MOF films enable a dynamic control of the selectivity by *trans*-*cis* photoisomerization, thus enabling remote-controlled, continuous adjustment of the permeate flux. For H₂:CO₂, the separation factor can be tuned between 3 and 8 by switching the photochromic moieties.^[2]

Using fluorinated azobenzene moieties enables the remote-control of the membrane permeation with violet and green light, avoiding UV light. There, the separation of various binary molecular mixture can be remote-controlled.^[3]

Further applications of azobenzene-containing MOF films will also be discussed in the presentation.

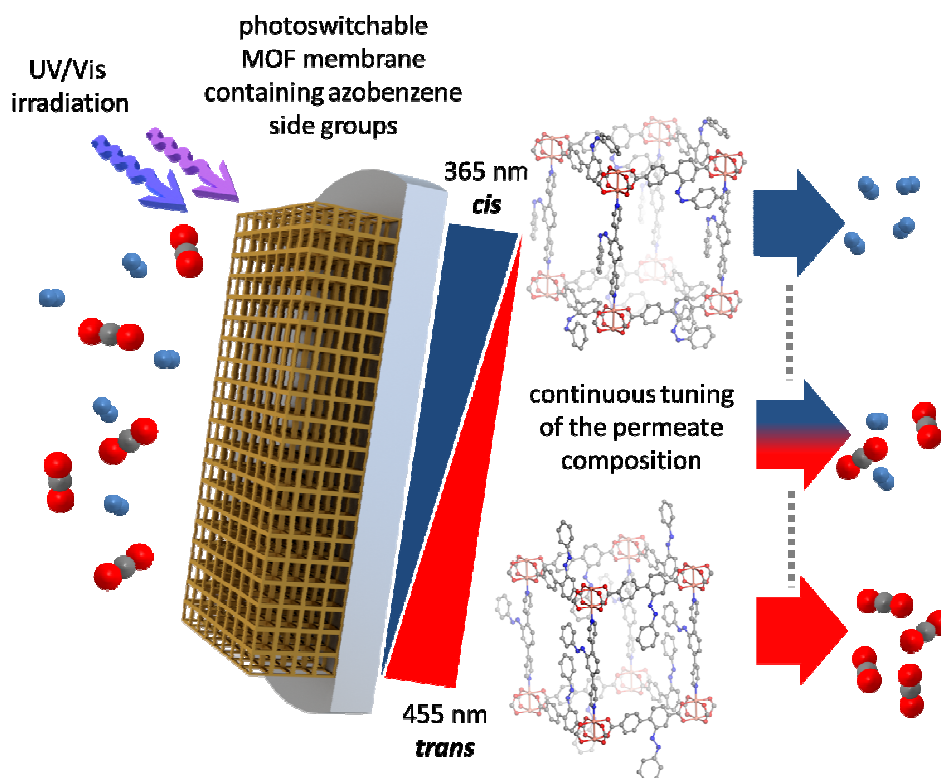


Figure 1. Schematic illustration of tunable, remote-controllable molecular selectivity by a photoswitchable MOF membrane. The MOF membrane contains azobenzene side groups which can undergo light-induced *trans-cis* isomerization. This enables that the molecular separation factor, giving the composition of the permeation flux, can be continuously tuned.^[2]

Funding: Funding by the Volkswagen Foundation, the Fonds der Chemischen Industrie (Lecturer-Award) and the Baden-Württemberg-Foundation is gratefully acknowledged.

References:

- [1] L. Heinke, M. Cakici, M. Dommaschk, S. Grosjean, R. Herges, S. Bräse, C. Wöll *Photoswitching in Two-Component Surface-Mounted Metal–Organic Frameworks: Optically Triggered Release from a Molecular Container*, ACS Nano 8, **2014**, 1463-1467.
- [2] Z. Wang, A. Knebel, S. Grosjean, D. Wagner, S. Bräse, C. Wöll, J. Caro, L. Heinke *Tunable Molecular Separation by Nanoporous Membranes* Nat. Commun. 7, **2016**, 13872.
- [3] K. Müller, A. Knebel, F. Zhao, D. Bléger, J. Caro, L. Heinke *Switching Thin Films of Azobenzene-Containing Metal–Organic Frameworks with Visible Light* Chem.Eur.J. **2017**, in press.