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Azobenzene Guest Molecules as Light-Switchable CO_2 Valves in an Ultrathin UiO-67 Membrane

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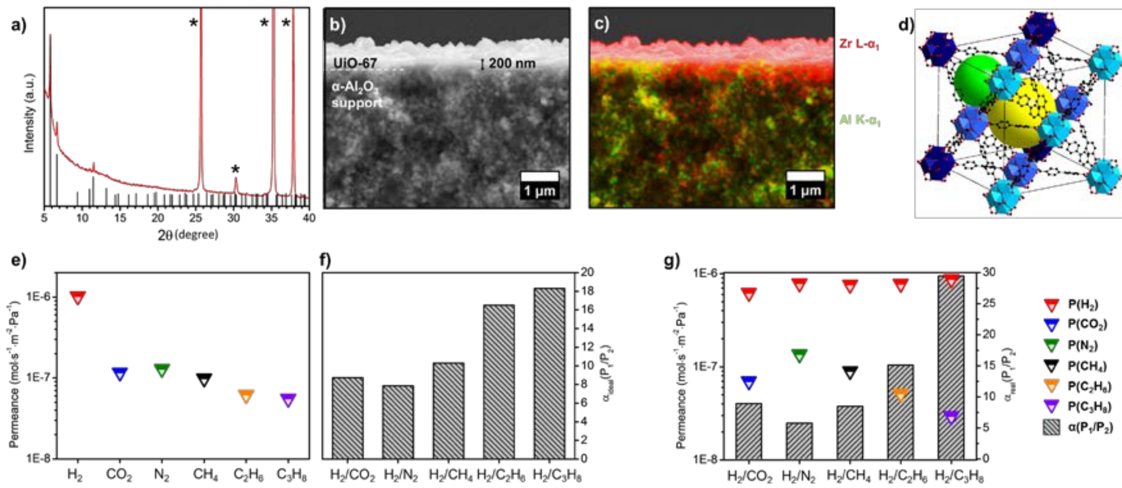
Metal-Organic Frameworks, consisting of inorganic metal- or metaloxide nodes interconnected by organic linker molecules, are an emerging class of porous materials. Thus, interesting potential applications are for example solvent purification, water desalination, catalysis, and in our case gas separation and purification.[1] We further focus on gas separation membranes with intelligent properties, towards an universal membrane which can be switched for different purification purposes. To achieve this, the metal-organic framework (MOF) UiO-67 with pore apertures of around 8 Å[2] was prepared as a 200 nm supported thin layer by solvothermal growth. This is the first report of UiO-67 as a membrane layer, and we further functionalized the membrane with switchable guests.

First of all, the pore aperture is rather big and does not show molecular-sieving for small molecules, but the MOFs separation properties rely on competitive adsorption mechanisms. The membrane was characterized in terms of its gas permeation properties and showed in experimental testing excellent selectivity for H_2 purification (Figure 1).



Afterwards the UiO-67 was loaded with azobenzene (AZB) as guest molecule, which introduces light-switchability to the membrane. The first light switchable membrane was also reported by us, being a specialized tailored MOF with switchable side-chains containing AZB moieties[3]. In the pore system, the AZB forms π-stacking complexes with the benzene rings of the MOF linker and stands in some cases into the pore aperture, thus enables switching of the channel diameter for the gases to pass through (Figure 2). AZB changes from *cis* to its *trans* isomer and by that the size from 9 Å (*trans*) to 4.5 Å (*cis*), thus open and close the entrance as shown in Figure 2c. The switching occurs form *trans* to *cis* at 365 nm, from *trans*

Figure 1 *a) The XRD of the 200 nm layer on α-Al_2O_3 support, b) SEM image and c) corresponding EDX mapping of the layer. The crystal structure is given in d). Gas permeation data for single gases and the ideal separation factor in e) and f), mixed gas permeation and real separation factor in g). Reprinted with permission from Chemistry of Materials 2017, 29, 3111–3117. Copyright 2017 American Chemical Society.*

to *cis* at 455 nm using an fibre coupled high power LED.
This makes the *in-situ* switching of the CO_2 permeance by irradiation with light possible, given in Figure 2 b). The H_2 permeance is not influences this much. The separation factor of H_2/CO_2 is switched from 14.5 in *trans* to 10 in *cis*.

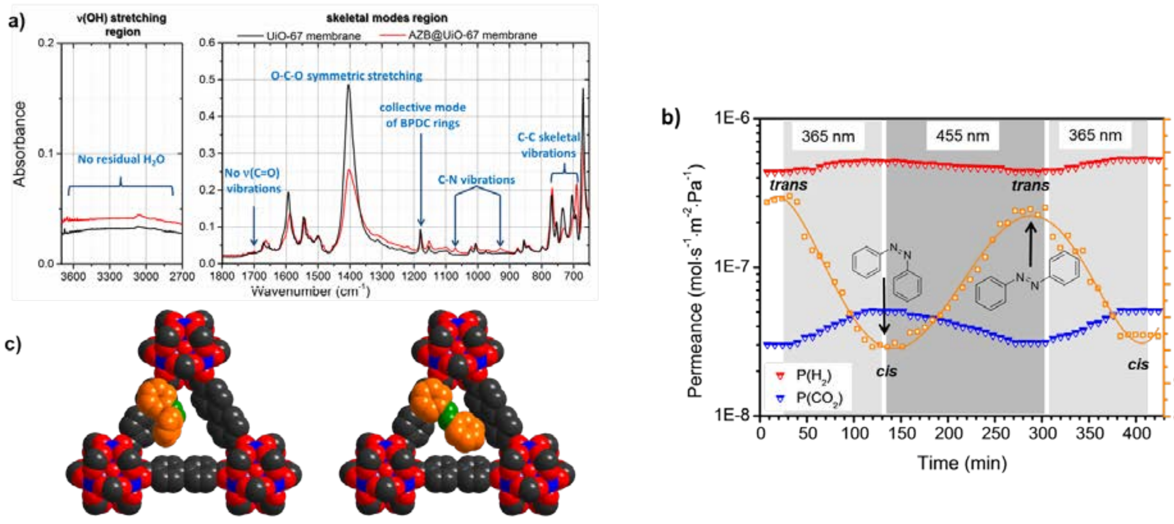


Figure 2 a) Attenuated total reflection IR-spectroscopic data of a UiO-67 membrane with and without AZB inside the pore system. The π-stacking of AZB was observed through changes in the skeletal modes region. b) Gives the gas permeation switching under constant irradiation of the AZB containing UiO-67 membrane. c) A shematic representation of the proposed mechanism for switching of the gas transport through the membrane.

The advantage of a conventional MOF (UiO-67 in this case) compared to a tailored MOF is especially the commercial availability. The linker molecules can be purchased in high quantities and the synthesis is a lot easier. Also the loading with guest molecules is quite easy to achieve by simply soaking the MOF into the AZB containing solution and temperature treatment afterwards. The ability to switch is also quite good. 12.5 % of the AZB is switchable, by a 50 % loading of the MOF, corresponding to 9 AZB molecules per unit cell. The tailored MOF had (normalized to unit cell volume of UiO-67) 20 moieties that switched.[3]

To conclude the work, an UiO-67 membrane was prepared and characterized for the first time in terms of its H_2 purification properties. Further, a light switchable guest molecule was introduced into the MOF network, which could be used to switch the gas transport of CO_2 by light over the permeance of H_2, resulting in selectivity changes. Thereby, an easy and cheap way of making a switchable membrane was achieved and functionally tested. The complete paper can be found under the following source.[4]

References:

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