Selective Detection of NO_2 with a Novel Calixarene-based Metal-organic Framework

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Gas sensors with high sensitivities to an analyte often suffer from cross-sensitivities to other molecules. One consequence is that these materials only work with optimum performance in the application environment they were designed for. Small changes of these environments like a different humidity or different temperature can affect the sensor properties.

The development of sensors with highest selectivities to target molecules can reduce this problem. The complexation of NO_2 using calixarenes is an example of a highly selective organic reaction.[2] It leads to a deeply blue colored complex, which makes it possible to use the molecule as a colorimetric sensor. Usually it proceeds in volatile organic solvents that ensure the accessibility of the sensing molecules. Additionally, Lewis acids which are necessary for the sensing reaction have to be dissolved in these solutions (Figure 1).

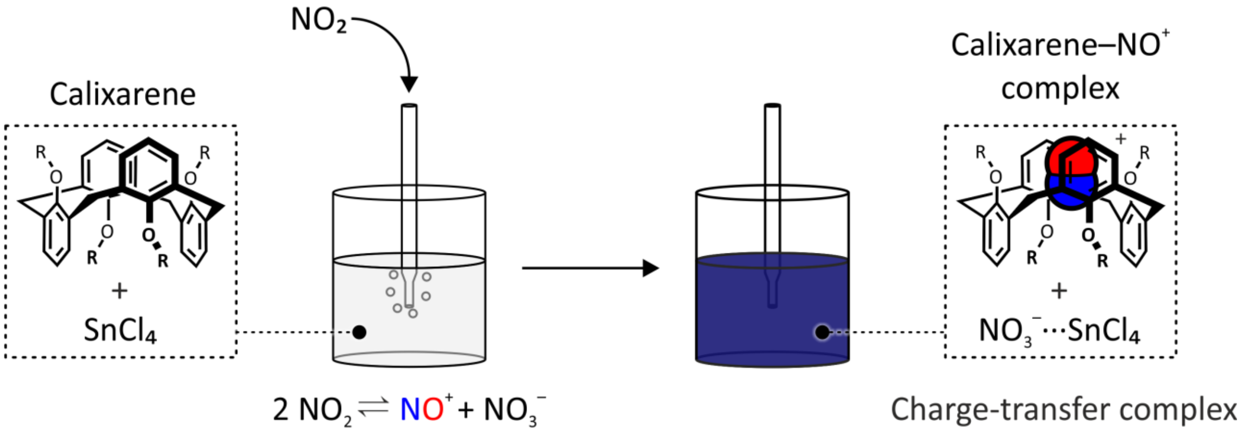

Figure 1. Illustration of the selective reaction between NO_2 and calixarenes. NO_2 dissociates to nitrosonium cations (NO^+) and Nitrate anions (NO_3^-). The NO^+ molecule forms a deeply blue colored charge-transfer complex with the calixarenes.

The aim of our work is to transfer the complexation of NO_2 by calixarenes to the solid state by creating metal-organic frameworks (MOFs) that are based on calixarenes. The reaction of tetracarboxylic acid H_4*cal* with $ZrCl_4$ leads to the formation of Zr-*cal* MOF (Figure 2a) in which the calixarenes are accessible through a complex three dimensional pore system (Figure 2b). The impressive, reversible color change of the solid from white to purple during the reaction with NO_2 proves in particular the accessibility of the calixarene cavity and the ability of the compound to serve as a colorimetric sensor in solid state (Figure 2c). The inorganic part of the framework provides the Lewis acidity that is needed for the reversibility of the sensing reaction.

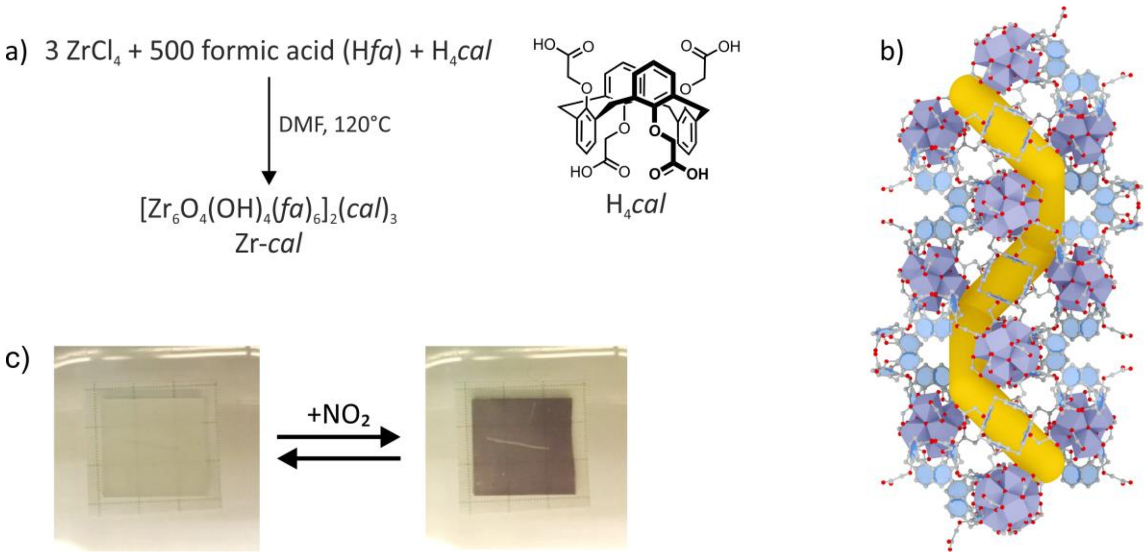

Figure 2. a) Reaction conditions for the synthesis of the novel calixarene-based MOF; b) part of the crystal structure showing a channel (diameter of 5 Å) through the MOF; c) photograph of a glass slide spray coated with the MOF and the sensing reaction with NO_2.

For the application as a NO_2 sensor material, coatings of the MOF on glass slides were prepared and investigated by SEM. We used these coated glass slides for first measurements of NO_2 in air to evaluate the potential of the novel calixarene-based MOF as a sensor material. The coated glass slides were placed inside a home-made sensor cell (Figure 3a) equipped with an LED (λ = 525 nm). The LED irradiates the coated glass slide, and a photodiode used as detector is placed behind it. When NO_2 passes the chamber, the coating turns blue and the increasing absorption of light leads to a reduced photocurrent of the photodiode. We observed a reversible change in the photocurrent depending on the concentration of NO_2 (Figure 3b). No color change was observed when we exposed the coatings to NO gas, highlighting the selectivity of the calixarene-based MOF.

This work introduces a novel principle to the application of MOFs as sensors, namely the transfer of highly specific reactions into MOFs where one of the reaction partners is exposed by being part of the porous framework, leading to sensor materials of highest selectivity.

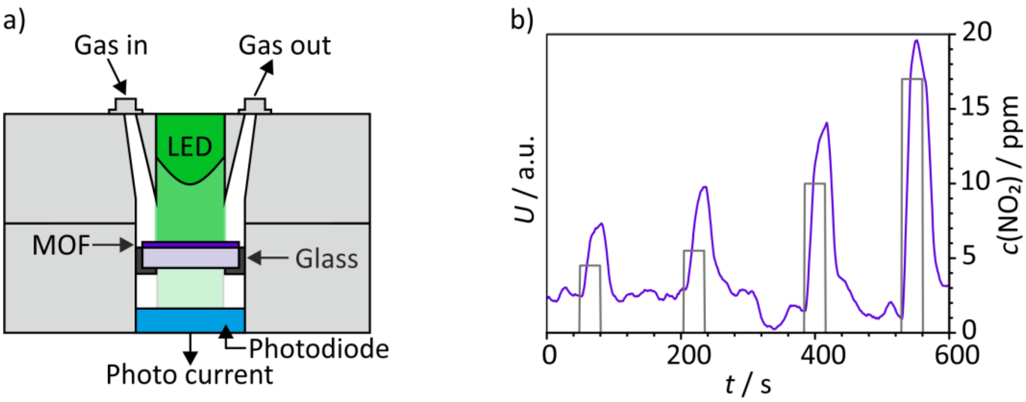

Figure 3. a) Schematic diagram of the sensor setup; b) response to different NO_2 concentrations in purified air.