Metal-Organic Framework-based resistive gas sensor

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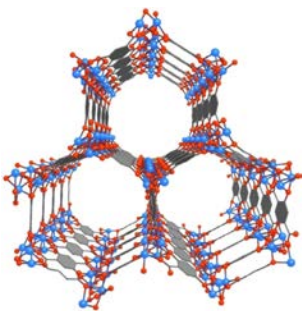
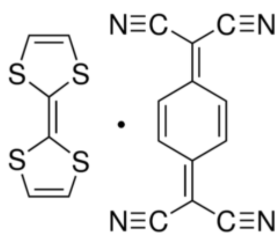
Summary:

Metal-organic frameworks (MOFs) do not conduct electric charges, i.e. they are insulators. However, when the pore volume of a MOF of the structure type Co-MOF-74 is filled with an electrically conducting guest molecules like tetrathiafulvalene (TTF) or tetracyanoquinodimethane (TCNQ), the MOF becomes conducting. In this MOF type with one-dimensional pore structure, the Co^{2+} are accessible for gas molecules. These gas molecules compete with TTF for the Co^{2+} interaction. We expected that adsorption of guest molecules from the gas phase will alter the conductivity. We have indeed found that the resistivity is altered by adsorption of guest molecules from a surrounding atmosphere like CO_2 or CH_4.

First we synthesized the MOF of the structure type Co-MOF-74 with 1D pores of 1.1 to 1.2 nm pore width as shown in Figure 1a. In this MOF, Co^{2+} ions are bridged by 2,5-dihydroxytherephthalic acid. In a second step the pores of the MOF are filled with the redox-active TTF or TCNQ guest molecules (Figure 1b). We developed a measurement setup with a home-built resistance cell as shown in Figure 1c. The pressed MOF powder is located between two electrodes. Now the current as a function of the voltage can be measured. To check the sensing capability of Co-MOF-74-TTF by measuring the electric conductivity upon gas adsorption, a measurement setup including a cell for gas sensing was built. The cell features a gas inlet and outlet for changing the gas atmosphere in the round bottom flask. The capacitor (Figure 1c) consists of two stainless steel electrodes which are held together with screws.

Pressed pellets of the MOF powders are placed between the electrodes. The capacitor is connected to the potentiostat with copper wires through the air-tight glass stopper as shown in Figure 1c.





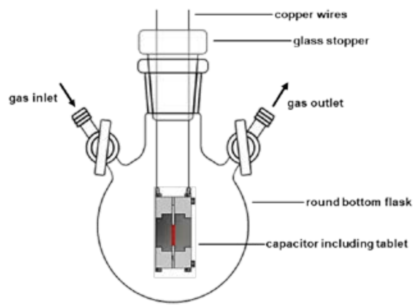


***Figure 1**: MOF, TTF and TCNQ structures and measurement setup.*

(a) The 1D channel system of MOF-74 filled with electrically conducting guest molecules.

(b) Redox-active guest molecules can be either TTF (tetrathiafulvene, left) or TCNQ (tetracyanoquinodimethane, right).

(c) Measurement setup with the home-built conductivity cell the MOF is contained as a pressed powder between the electrodes.

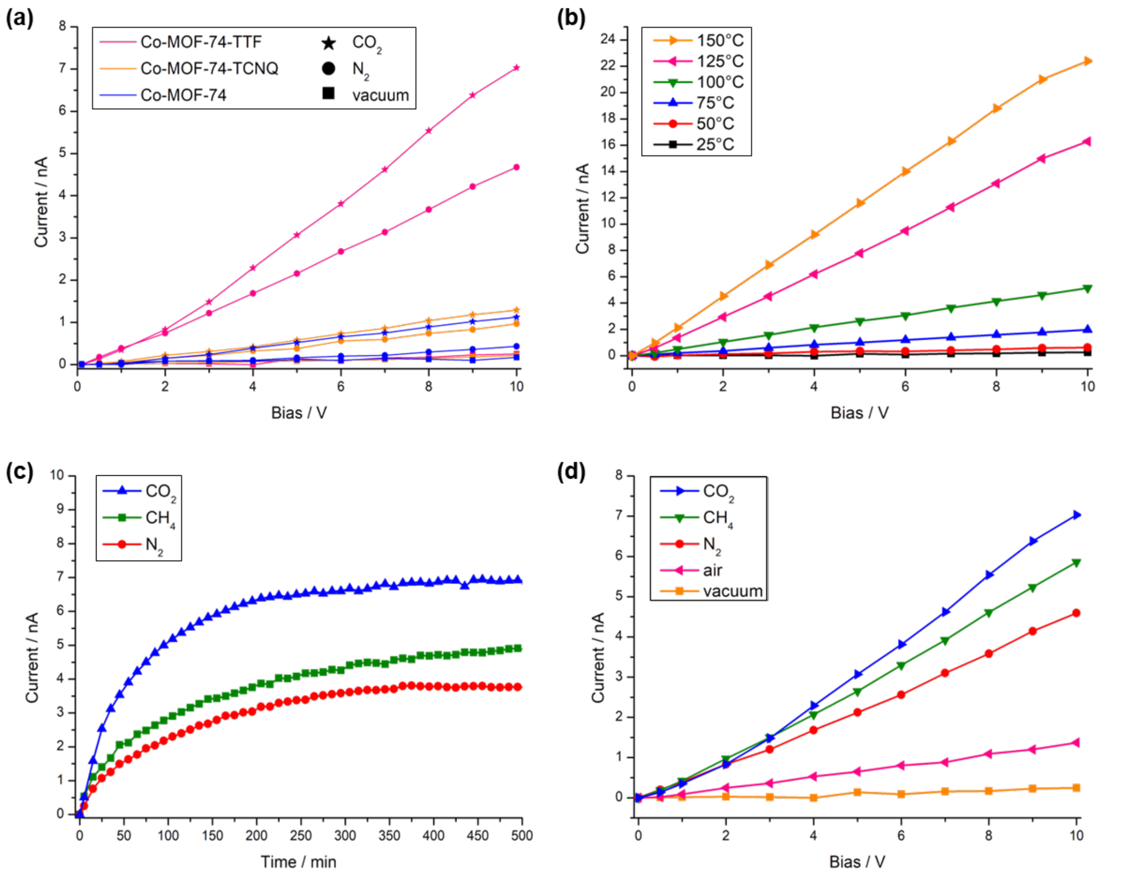


Figure 2: *Results of resistive gas sensing. (a) I-V-curves of Co-MOF-74-TTF compared to Co-MOF-74 and Co-MOF-74-TCNQ under vacuum, N_2 and CO_2 atmosphere. (b) I-V-curves of Co-MOF-74-TTF under vacuum at different temperatures. (c) Long-time conductivity measurements of Co-MOF-74-TTF under N_2, CH_4 and CO_2 atmospheres with a bias of 10 V. The atmosphere was changed from vacuum to N_2/CH_4/CO_2 at 0 min. (d) I-V-curves of Co-MOF-74-TTF measured after 24 h under vacuum, air, N_2, CH_4 and CO_2 atmosphere.*

Figure 2a) shows that Co-MOF-74-TTF has a significantly higher conductivity in comparison to the non-infiltrated MOF and the TCNQ-doped one. From Figure 2b) we can learn that the conductivity of the Co-MOF-74/TTF composite increases with increasing temperature without any gas molecules (under vacuum). Due to the presence of gas molecules the conductivity in general increases (Figure 2c) and this increase is characteristic of the gas species. However, due to the transport limitation inside the pressed pellet, no equilibrium of the gas uptake was observed within the first 500 min. Therefore, the following I-V curves were measured 24 h after the initial gas dosing. Due to the different strengths of the interactions between a gas and the MOF, conductivity changes could be observed. The highest conductivity was obtained for CO_2, due to the strong interaction between CO_2 and the Co^{2+}-centers of the MOF. For weaker gas-MOF interactions (CO_2>CH_4>N_2), a smaller decrease of the conductivity is observed (Figure 2c and d). These I-V experiments under different gas atmospheres were performed, recommending Co-MOF-74-TTF as an excellent material for gas sensing devices based on a modification of resistivity. In future work the response time of the sensor must be shortened, which could be achieved by preparing thin films of the Co-MOF-74-TTF composite.

For further information see: I. Strauss, A. Mundstock, M. Treger, K. Lange, S. Whang, C. Chmelik, P. Rusch, N.C. Bigall, T. Pichler, H. Shiozawa, J. Caro, *Metal-organic framework Co-MOF-74-based host-guest composites for resistive gas sensing*, ACS Appl. Mater. Interfaces 11 (2019) 14175-14181.