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Tetrazine functionalized zirconium MOF as an optical sensor for oxidizing gases†

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Dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate was introduced into the chemically stable UiO-66 structure by a postsynthetic linker exchange reaction to create an optical sensor material for the detection of oxidative agents such as nitrous gases. The incorporated tetrazine unit can be reversibly oxidized and reduced, which is accompanied by a drastic colour change from yellow to pink and vice versa. The high stability of the framework during redox reaction was proven by powder X-ray diffraction and nitrogen physisorption measurements.

Gas sensors are widely used for monitoring the concentration of different gases such as methane in coal mines or carbon monoxide for personal protection using portable devices. An ideal sensor should be sensitive and stable enough to operate under ambient conditions and additionally produce a signal with a short response time that is easy to sense without the need for further equipment, the so-called wireless gas sensor.¹ One of the simplest, and arguably most powerful, means of transducing a sensing signal is *via* a visible change in the color of the material.² Furthermore, a sensor needing no power to work is independent of the availability of power sources being operational anytime and anywhere.

NO_x (nitrous gases) is a generic term for nitric oxide (NO) and nitrogen dioxide (NO₂), which are poisonous gases often released into the atmosphere by motor vehicles and industrial and domestic combustion processes. Therefore detection and monitoring of nitrous gases is of great interest and many NO_x gas sensors have been investigated, for example, metal oxide semiconductors, solid electrolytes, and conducting polymers such as polypyrrole and polyaniline.

The modular design of metal-organic frameworks (MOFs) along with a high porosity (allowing a rapid accessibility for guest molecules)

opens the way for the targeted synthesis of desired sensor materials.³ It has already been demonstrated that depending on the introduced functionalities, MOFs can be specifically designed for the sensing of various analytes including chiral substrates,⁴ toxic methyl-mercury,⁵ chlorine,⁶ solvent molecules,⁷ and other small organic molecules.⁸

For the sensing of NO_x we chose the dihydro-1,2,4,5-tetrazine unit since it can be easily oxidized to 1,2,4,5-tetrazine. The remarkable feature of this redox reaction is the drastic colour change, as the 1,2,4,5-tetrazine unit is pink whereas the dihydro-1,2,4,5-tetrazine unit has a yellow colour. To achieve the high chemical as well as thermal stability of the active material for application under ambient or even harsh conditions, [Zr₆O₄(OH)₄](COO)₁₂ was aimed at as the secondary building unit (SBU).⁹ It is known that MOFs based on this SBU (especially UiO-66, in which the [Zr₆O₄(OH)₄] clusters are connected by twelve benzene-1,4-dicarboxylate (bdc)) show an exceptionally high thermal and chemical stability.¹⁰ As a linker, containing a 1,2,4,5-tetrazine moiety, dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate (dhtz) was used (Fig. 1).¹¹ Unfortunately, the direct synthesis of a UiO-66 analogue starting from ZrCl₄ and H₂dhtz was not successful, probably due to thermal stress and instability of the tetrazine unit against low pH values. In 2012, Cohen *et al.* demonstrated a much milder route to incorporate functionalized bdc-ligands into the UiO-66 structure.¹² They have shown that UiO-66 is in equilibrium with a supernatant solution containing substituted bdc-ligands leading to a postsynthetic exchange (PSE). This finding paves the way to implement sensitive functionalities by suspending UiO-66 in a solution of the correspondingly functionalised linker. Since the distance between the carbon atoms of carboxylic groups is similar in bdc (5.55 Å)¹³ and dhtz (5.43 Å)¹⁴ a replacement of bdc by dhtz seems feasible. However, the major difference is hidden in the conformation of the ring: in contrast to the planar aromatic ring in bdc, the central six-membered ring of dhtz has boat conformation (Fig. S1, ESI†). After oxidation of dhtz to 1,2,4,5-tetrazine a conformational change occurs, as the ring becomes planar and the distance between the carbon atoms of the carboxylic groups is 5.56 Å.¹⁵

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† Electronic supplementary information (ESI) available: General procedure, synthetic details, physisorption data, PXRD pattern, UV/vis spectra. See DOI: 10.1039/c4cc08136f

Fig. 1 Top: introduction of dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate (dhtz) into the UiO-66 framework by post-synthetic exchange giving UiO-66(dhtz); bottom: scanning electron microscope images of UiO-66 (left) and UiO-66(dhtz) (right).

To perform the PSE, UiO-66 was dispersed in an aqueous solution of potassium dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate. Despite small geometrical differences of bdc and dhtz, the PSE took place yielding $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{5.1}(\text{dhtz})_{0.9}$ (further named as UiO-66(dhtz)). The composition was derived from elemental analysis; see ESI†.

Powder X-ray diffraction measurements confirmed the isomorphism of UiO-66(dhtz) and UiO-66. Nitrogen physisorption measurements at 77 K revealed a typical type I isotherm with an increased uptake of UiO-66(dhtz) compared to the parent UiO-66 compound (Fig. S2, ESI†). UiO-66(dhtz) has an apparent BET surface area of $1632 \text{ m}^2 \text{ g}^{-1}$ and a total pore volume of $0.73 \text{ cm}^3 \text{ g}^{-1}$.

In contrast to the purely white UiO-66, UiO-66(dhtz) has yellow colour, proving also the successful linker exchange. According to the solid state UV/vis measurements (Fig. S6, ESI†), UiO-66 shows absorption only in the UV region, whereas UiO-66(dhtz) shows a shift of the absorption edge to higher wavelengths. Exposure of UiO-66(dhtz) suspended in chloroform to nitrous gases results in oxidation of the dihydro-1,2,4,5-tetrazine to 1,2,4,5-tetrazine (to give UiO-66(tz), Fig. 2), as judged by UV/vis measurements and by a color change from yellow to pink (Fig. S5 and S6, ESI†).¹¹ UiO-66(dhtz) could also be oxidized by suspending it in a solution of bromine in chloroform. Addition of hydrogen peroxide to UiO-66(dhtz) also results in a colour change. However, in contrast to the oxidation using nitrous gases or bromine where the colour change is immediate, the oxidation by hydrogen peroxide is much slower and thus the change of colour takes place gradually over a period of several minutes. In contrast, aqueous solutions of potassium dichromate or iron(III) nitrate, respectively, were not able to oxidize UiO-66(dhtz). If the material was stored under a nitrogen or argon atmosphere, no colour change took place even after half a year.

More importantly, UiO-66(dhtz) is also able to act as a sensor for oxidizing agents in the gas phase. By adding nitrous gases

Fig. 2 Reversible oxidation and reduction of the tetrazine unit in UiO-66 and the corresponding change in colour.

or gaseous bromine directly to the activated MOF, an immediate and strong colour change is visible. Crystallinity and porosity of the MOF remain unaltered during the oxidation process, which was confirmed by XRD and physisorption measurements (Fig. S3, ESI†).

As a regeneration agent, sodium dithionite¹⁶ was used to reduce UiO-66(tz) to UiO-66(dhtz). After suspending UiO-66(tz) in an aqueous solution of sodium dithionite, the colour of the MOF changes to yellow indicating the formation of UiO-66(dhtz). Also, the reduction process does not influence the crystallinity and porosity of the MOF, as revealed by XRD (Fig. S4, ESI†), emphasising the high stability of the material towards the reduction/oxidation process. Moreover, the material can be utilised again after regeneration as reapplication of nitrous gases to UiO-66(dhtz) leads again to a colour change to pink. The compound showed such reversible redox behaviour at least over 2 cycles.

Summarising, using a postsynthetic linker exchange route, the oxidation sensitive dihydro-1,2,4,5-tetrazine-3,6-dicarboxylate was integrated into the UiO-66 framework to give UiO-66(dhtz). UiO-66(dhtz) is found to be a colorimetric chemosensor for oxidizing gases. Upon contact with oxidizing agents, such as nitrous gases, an immediate drastic colour change from yellow to pink is observed.

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