

## Supporting Information

### **Tetrazine functionalized zirconium MOF as optical sensor for oxidizing gases**

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## 1. General information

All chemicals were obtained commercially and used without further purification. Dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid, 1,2,4,5-tetrazine-3,6-dicarboxylic acid (ref. 11) and UiO-66 (ref. 9) were synthesized as described previously.

Nitrous gases were produced by slowly adding hydrochloric acid to a cooled solution of sodium nitrite in water.

Powder X-ray diffraction patterns were collected in transmission geometry with a STOE STADI P diffractometer operated at 40 kV and 30 mA with monochromatic Cu-K $\alpha_1$  ( $\lambda = 0.15405$  nm) radiation and with a scan speed of 30 s/step and a step size of 0.1°.

Nitrogen physisorption isotherms were measured on a Belsorp max apparatus at 77 K using high purity nitrogen (N<sub>2</sub> 99.999%).

The UV/vis measurements of the liquid phase were carried out using a UV-1650 PC spectrometer (Shimadzu). The absorbance of liquid samples was measured using 10 mm cuvettes.

Solid state UV/Vis measurements were carried out using a Varian Cary 4000 UV/vis spectrophotometer.

The pH value was measured using PCE-228 pH meter.

The elemental analysis for C and H were performed with CHNS 932 analyzer (LECO).

Thermal analyses were carried out under air atmosphere using a Netzsch STA 409 thermal analyzer with rate of 5 K min<sup>-1</sup>.

Scanning electron microscopy was performed using a Hitachi SU8020.

## 2. Synthetic procedures

### Synthesis of UiO-66(dhtz)

UiO-66(dhtz) was synthesized by adding of UiO-66 (54.2 mg; equivalent to 0.2 mmol of bdc) to a solution of dihydro-1,2,4,5-tetrazine-3,6-dicarboxylic acid (34.4 mg; 0.2 mmol) and potassium hydroxide (22.4 mg; 0.4 mmol) in 2 ml water. The resulting solution has a pH value of 11. The mixture was allowed to stand for five days at room temperature. After filtration the MOF was washed several times with water and ethanol and activated in vacuum at room temperature.

Elemental analysis for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>](bdc)<sub>5.1</sub>(dhtz)<sub>0.9</sub>: wt.% obs. (calc.): C: 31.95 (31.94), N: 3.05 (3.02), H: 2.13 (1.58).

### Liquid phase oxidation of UiO-66(dhtz) with nitrous gases

50 mg UiO-66(dhtz) are suspended in 10 ml chloroform. A stream of nitrous gases is bubbled through this suspension leading to an immediate color change.

### Liquid phase oxidation of UiO-66(dhtz)with bromine

50 mg UiO-66(dhtz) are suspended in 10 ml chloroform. The addition of 0.1 ml bromine leads to an immediate color change.

### Gas phase oxidation of UiO-66(dhtz) with nitrous gases

A gas stream of nitrous gases is introduced in a reaction chamber containing 50 mg UiO-66(dhtz) leading to an immediate color change. Afterwards the MOF was activated at room temperature.

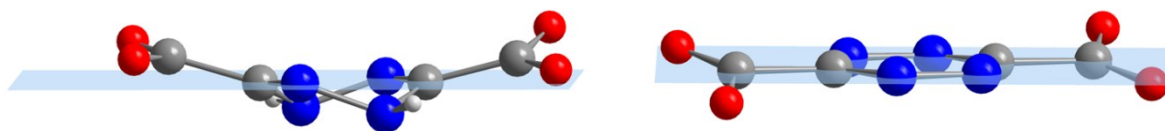
### Gas phase oxidation of UiO-66(dhtz)with bromine

A gas stream of bromine in nitrogen is introduced in a reaction chamber containing 50 mg UiO-66(dhtz) leading to an immediate color change. Afterwards the MOF was activated at room temperature.

### Liquid phase reduction of UiO-66(tz) with sodium dithionite

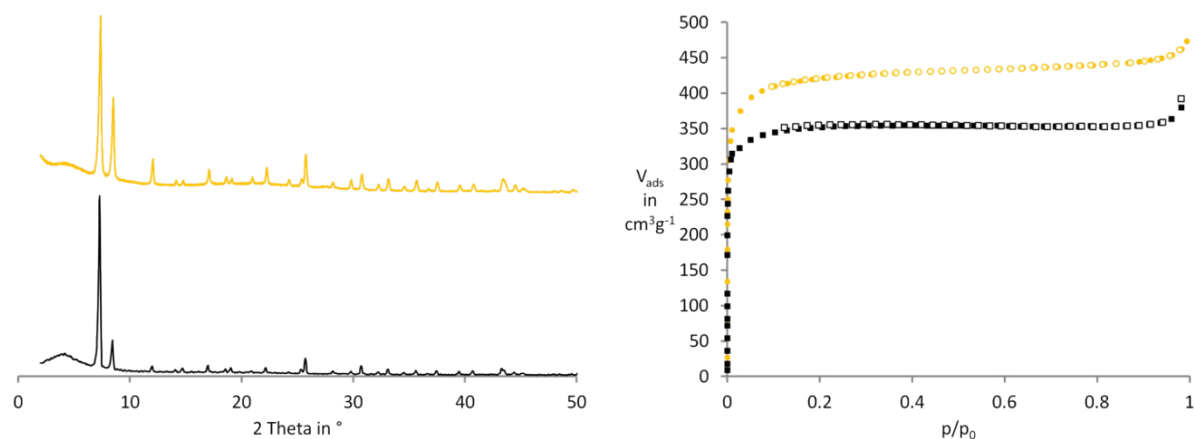
50 mg UiO-66(tz) are added to 3 ml of a 0.01 M sodium dithionite solution. After the color of the powder has changed from pink to yellow (15 min) the MOF is washed for several times with water and ethanol. Finally UiO-66(dhtz)\_i is activated at room temperature.

### 3. Conformation of the linkers



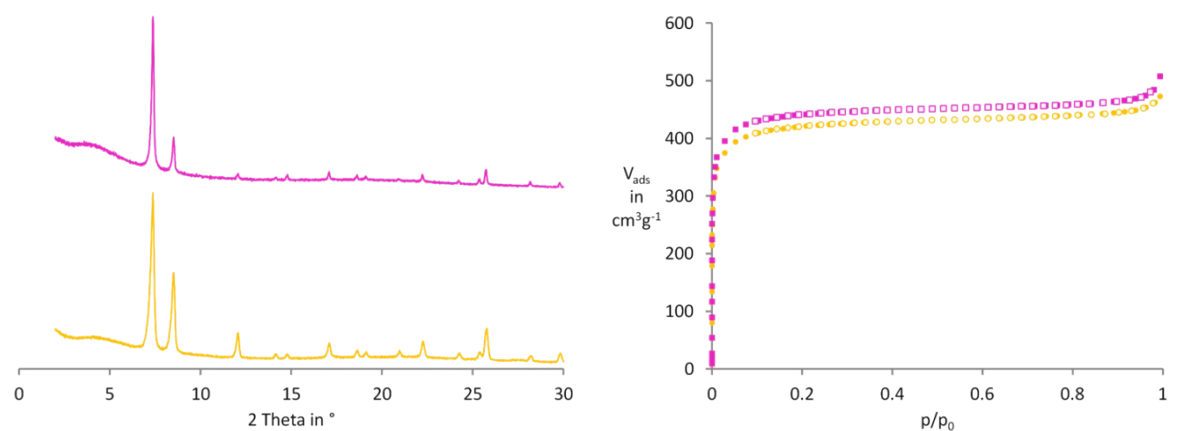
**Figure S1:** Conformation of the boat like dihydro-1,2,4,5-tetrazine unit (left) and the planar 1,2,4,5-tetrazine unit (right).

### 4. PXRD patterns and adsorption isotherms of UiO-66 and UiO-66(dhtz)



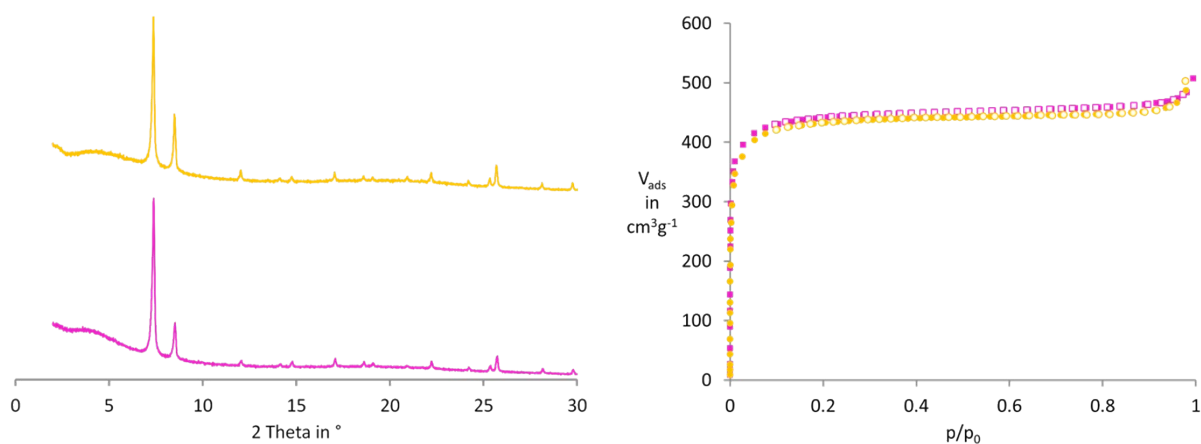
**Figure S2:** Left: XRD patterns of UiO-66 (black) and UiO-66(dhtz) (yellow); Right: nitrogen physisorption isotherms at 77 K of UiO-66 (black squares) and UiO-66(dhtz) (yellow circles). Solid symbols illustrate the adsorption branches and open symbols the desorption branches.

### 5. PXRD patterns and adsorption isotherms of UiO-66(dhtz) and UiO-66(tz)



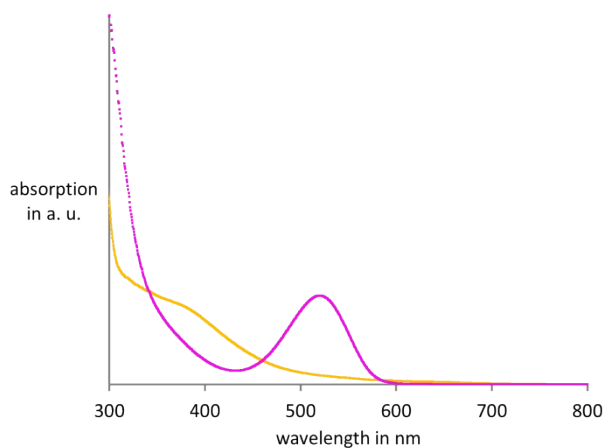
**Figure S3:** Left: XRD patterns of UiO-66(dhtz) (yellow) and UiO-66(tz) (pink); Right: nitrogen physisorption isotherms at 77 K of UiO-66(dhtz) (yellow circles) and UiO-66(tz) (pink squares). Solid symbols illustrate the adsorption branches and open symbols the desorption branches.

## 6. PXRD patterns and adsorption isotherms of UiO-66(tz) and UiO-66(dhtz)\_i



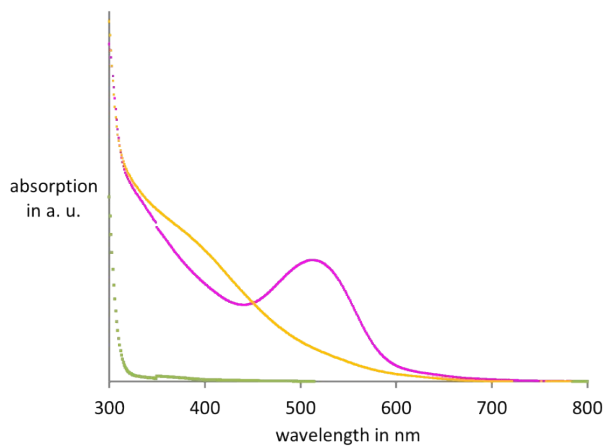
**Figure S4:** Left: XRD patterns of UiO-66(tz) (pink) and UiO-66(dhtz)\_i (yellow); Right: nitrogen physisorption isotherms at 77 K of UiO-66(tz) (pink squares) and UiO-66(dhtz)\_i (yellow circles). Solid symbols illustrate the adsorption branches and open symbols the desorption branches.

## 7. Liquid phase UV/vis measurements



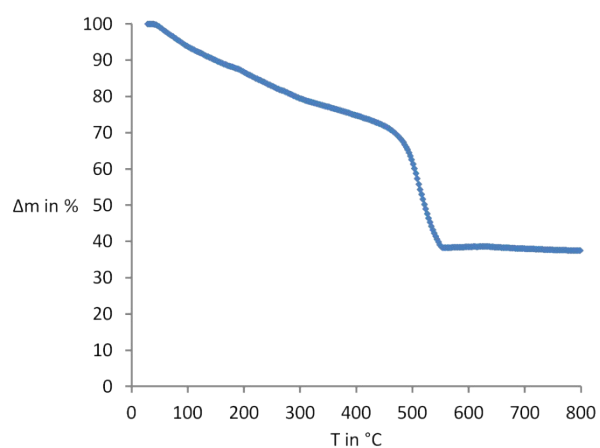
**Figure S5:** Liquid phase UV/vis spectra of H<sub>2</sub>dhtz (yellow) and H<sub>2</sub>tz (pink).

## 8. Solid state UV/vis measurements



**Figure S6:** Solid state UV/vis spectra of UiO-66 (green), UiO-66(dhtz) (yellow) and UiO-66(tz) (pink).

## 9. Thermogravimetric data



**Figure S7:** Thermogravimetric data of UiO-66(dhtz).

The mass loss for UiO-66(dhtz) starts already at around 60 °C. The loss at this rather low temperature is probably due to water, as UiO-66(dhtz) was activated only at room temperature which is further supported by the high observed hydrogen content. In addition, because of the low thermal stability of the tetrazin ligand, the framework decomposition starts already at low temperatures. The decomposition of the bdc ligand takes place at temperatures above 500 °C.