## Materials Science

# Gated Channels and Selectivity Tuning of CO<sub>2</sub> over N<sub>2</sub> Sorption by Post-Synthetic Modification of a UiO-66-Type Metal–Organic Framework

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**Abstract:** The highly porous and stable metal–organic framework (MOF) UiO-66 was altered using post-synthetic modifications (PSMs). Prefunctionalization allowed the introduction of carbon double bonds into the framework through a four-step synthesis from 2-bromo-1,4-benzenedicarboxylic acid; the organic linker 2-allyl-1,4-benzenedicarboxylic acid was obtained. The corresponding functionalized MOF (UiO-66-allyl) served as a platform for further PSMs.

## Introduction

Metal–organic frameworks (MOFs) and their underlying concept, which involves the combination of inorganic building blocks with ubiquitous organic linking units, offer numerous possibilities for modifications.<sup>[1]</sup> In general, MOFs provide a high degree of crystallinity and high pore volumes accompanied by extraordinary internal surface areas. These unique properties make MOFs ideal candidates for gas storage and separation,<sup>[2]</sup> catalysis,<sup>[3]</sup> drug delivery,<sup>[4]</sup> and chemical sensing.<sup>[5]</sup> The host–guest interactions can be tuned by the introduction of functional groups into the framework; these groups are mainly attached to the organic-linker units. Thus, the interactions between the target molecule and the framework have been systematically tuned previously and current studies remain focused on the separation and storage of greenhouse gases.<sup>[2d,6]</sup>

The release of CO<sub>2</sub> from anthropogenic sources has led to intensified concerns about the greenhouse effect and global warming and the implications for the global society.<sup>[7]</sup> Post-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602318. From UiO-66-allyl, epoxy, dibromide, thioether, diamine, and amino alcohol functionalities were synthesized. The abilities of these compounds to adsorb CO<sub>2</sub> and N<sub>2</sub> were compared, which revealed the structure–selectivity correlations. All synthesized MOFs showed profound thermal stability together with an increased ability for selective CO<sub>2</sub> uptake and molecular gate functionalities at low temperatures.

combustion capture of CO<sub>2</sub> is hampered by its low content (~ 15%) in flue gases compared to the main component (N<sub>2</sub>) and other components present in minor quantities (H<sub>2</sub>O, O<sub>2</sub>, CO, NO<sub>x</sub>, and SO<sub>x</sub>).<sup>[8]</sup> Solid porous materials such as zeolites, functionalized silica, activated carbon, and MOFs show distinct advantages for post-combustion CO<sub>2</sub> capture compared with the very energy intensive scrubbing process that uses aqueous solutions of alkanolamines, which results in substantial efficiency losses in power plants equipped with this technology.<sup>[9]</sup> Although MOFs show lower chemical and thermal stabilities than other inorganic porous materials, the ease of modification of both the network architecture and functional groups make them promising candidates as post-combustion adsorbents. For MOFs to be an economically viable alternative in post-combustion applications, high capacities for CO<sub>2</sub> adsorption, high selectivity for CO<sub>2</sub> over N<sub>2</sub>, and robustness against the trace amounts of water present in the flue gas are prerequisite properties that research has to tackle.<sup>[10]</sup>

To match these requirements, convertible side chains, which do not interfere with the network synthesis, have recently been investigated. The use of these groups avoids the formation of additional crystal phases, decomposition, and other side reactions.<sup>[11]</sup> Mainly pioneered by Wang et al. and Cohen et al., post-synthetic modifications (PSMs) have become one of the most promising and versatile routes to obtain the desired features, for example, amines or other polarized groups, on the framework surface. Recently, the concept of molecular gates has been introduced.<sup>[12]</sup> Molecular gates enable MOFs to discriminate between different gases during adsorption and, therefore, increase the selectivity of the frameworks. Consequently, frameworks offering this feature came into focus but most lack the required stability.<sup>[12a]</sup>

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rises with the polarity of the attached groups. Herein, we report the synthesis of the highly stable MOF UiO-66-allyl and the enormous potential of PSMs for finetuning of the network-guest interactions. The unique network features allow the introduction of molecular gates at low temperatures, accompanied by a remarkable selectivity for adsorption of CO<sub>2</sub> in preference to N<sub>2</sub> at elevated temperatures.

## **Results and Discussion**

We recently reported on the conversion of olefinic side chains in a Zn-based pillared MOF.<sup>[15]</sup> As a model system, we modified a bipyridine pillar ligand connecting square paddle-wheel layers based on 9,10-triptycenedicarboxylic acid and Zn ions.<sup>[16]</sup> As this framework did not show high tolerances to basic and acidic conditions, we decided to modify the exceptionally stable UiO-66 system by attaching an olefinic side chain to benzenedicarboxylic acid H<sub>2</sub>. The stability of the network is of crucial importance for the fine tuning of CO<sub>2</sub> adsorption through PSM.

#### Linker synthesis

Methyl ester protection of the commercially available 2-bromo-1,4-benzenedicarboxylic acid, followed by a  $Pd^0$ -catalyzed Stille coupling reaction gave dimethyl 2-allylbenzene-1,4-dicarboxylate. Subsequent deprotection under basic conditions produced 2-allyl-1,4-benzenedicarboxylic acid (2-allyl-BDC) in good yield (Scheme 1 and Scheme S1 in the Supporting Information).

#### **MOF** preparation

In Zr-carboxylates, the formation of undesirable crystal phases is suppressed because of their structural homogeneity compared with other metal-linker combinations that are used in MOF synthesis. The UiO-66 analogue was prepared by the combination of  $ZrCl_4$  with 2-allyl-BDC in DMF. The addition of water to the reaction mixture was indispensable for the formation of the nanocrystalline powder, as a full hydrolysis of  $ZrCl_4$  is essential.

The crystallinity of the sample was verified using powder Xray diffraction (PXRD) and the diffraction pattern obtained was compared with literature data for the parent network. The pattern clearly confirmed the integration of the previously unknown 2-allyl-1,4-benzenedicarboxylate linker into the UiO-66 network (Scheme 2).

The reaction times for PSMs in MOFs fundamentally depend on the diffusion limitations within the microporous solids. Fast mass transport through the MOF cavities can be achieved by small uniform MOF-particles and a high degree of activation. The standard synthesis reported in the literature<sup>[13b]</sup> yielded MOF samples with low Brunauer–Emmett–Teller (BET) surface areas. Behrens et al. developed a modulated MOF synthesis for Zr-carboxylate networks using monocarboxylic acids to slow down the crystallization rate and increase the accessible pore volumes through improved crystallization.<sup>[17]</sup>

After activation, acetic acid modulation increased the accessible surface area in the unfunctionalized UiO-66 network from 711 to 1189  $m^2g^{-1}$  (see Scheme S2 in the Supporting Information) through slowing down the crystallization rate.<sup>[17]</sup> The maximum surface area was obtained by using 10 vol% of acetic acid in the reaction solution; this concentration of acetic acid was also used in the synthesis of the functionalized MOF UiO-66-allyl (736  $m^2g^{-1}$ ). The drop in the BET value for the derivative can be attributed to the increased steric demand in the pores by the attached side chains. Nevertheless, the allylic side chains could be successfully introduced while preserving both crystallinity and porosity (Figure 1).

#### Post-synthetic modifications

The permanent porosity and stability of Zr-based MOFs make the UiO-66-allyl network a perfect substrate for PSM. The integrated C=C double bond can be converted through a variety of PSMs (Scheme 2) to tune the adsorption properties for different gases like CO<sub>2</sub> and N<sub>2</sub>.

Epoxidation of the double bond was chosen as the model PSM, as it had been successfully applied in our previous work.<sup>[15]</sup> The chemical stability of the network emerged as a challenge in the characterization of the PSM results. Besides XRD and BET measurements, solution NMR was the method of choice to quantify the degree of conversion of the allylic side chains. Cohen et al. reported the acidic disintegration of UiO-



Scheme 1. Synthesis of 2-allyl-1,4-dicarboxylic-acid (L1).

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Scheme 2. Synthesis of and PSMs applied to UiO-66-allyl: bromination to yield UiO-66-dibromide, epoxidation with dimethyldioxirane to yield UiO-66-epoxide, and a thiol-ene click reaction using EtSH to yield UiO-66-ethylsulfide. Tandem PSM with nucleophilic ring opening in UiO-66-epoxide to yield UiO-66-aminoalcohol, and nucleophilic substitution in UiO-66-dibromide to yield UiO-66-diamine.

66 using hydrofluoric acid.<sup>[18]</sup> The application of this method to the UiO-66-epoxide lead to side reactions hampering further analysis. Cyclic esters and side products that were not further investigated were found (Supporting Information, Scheme S3). To avoid any further problems in product determination, we developed a new disintegration method using deuterated sodium hydroxide in D<sub>2</sub>O. Under these conditions, the newly formed epoxide was quantitatively ring opened and converted to the glycol (Figure 2). The nearly quantitative yields achieved using the oxidizing reagent dimethyldioxirane, together with the remaining crystallinity and the high nitrogen surface area (BET=617 m<sup>2</sup>g<sup>-1</sup>), emphasize the suitability of the MOF for PSMs.

Both bromination with elemental bromine and a UV-initiated thiol-ene click reaction using ethyl mercaptane proceeded in nearly quantitative yields and good conversions of the double bond, which were comparable to the results of our previous work.<sup>[15a]</sup> Although crystallinity was retained in both cases according to PXRD, the accessible BET surface area of the activated samples dropped to 5 and 52 m<sup>2</sup>g<sup>-1</sup>, respectively. This result will be discussed in detail below in the section describ-

ing gas adsorption behavior. The basic workup of the dibromide compound led to a substitution reaction resulting in the formation of a glycol-containing product identical to the epoxidation product.

Polar functional groups, especially amine functionalities, are well known to increase the interaction and selectivity with guest molecules, such as CO2, in porous networks.[13a] Nevertheless, the introduction of primary amines through PSM has not been widely investigated, with the exception of the post-synthetic deprotection of N-Boc-tagged networks. Bocprotecting groups hamper the framework interpenetrations that occur during MOF assembly, and subsequent removal of these groups can both increase the pore volume and unmask an unprotected amine functional group. Following this route, Telfer and co-workers were able to unmask an amine functionality in IRMOF-12 as well as the secondary amine of proline in IRMOF-Pro.<sup>[19]</sup> Although there are some examples of aminetagged MOFs in the literature, there are, to our knowledge, no vicinal diamino- or amino alcohol-tagged frameworks known until now.[13a, 19b, 20] Through the integration of these functionalities, a variety of possible applications arise, especially as chelat-



Figure 1. PXRD and BET surfaces obtained by modulated MOF synthesis using acetic acid as a modulator for UiO-66 and UiO-66-allyl.



**Figure 2.** <sup>1</sup>H NMR spectra of the tandem functionalized linkers after disintegration using NaOD in  $D_2O$ : a) UiO-66-epoxide (for comparison), b) UiO-66-aminoalcohol and unreacted UiO-66-epoxide, c) UiO-66-diamine.

ing ligands for catalytic active metal ions and  $\text{CO}_2$ -sorption substrates.

As there are different literature examples for both the nucleophilic ring-opening of epoxides and the substitution of halides using ammonia, we developed tandem PSMs for the conversion of our epoxy- and dibromide-tagged networks. On account of the fragility of the network under strongly basic conditions, it was necessary to avoid any traces of water by both activating the network before modification and working under CHEMISTRY A European Journal Full Paper

dry and inert atmosphere conditions. After drying the MOF powder under vacuum at 120 °C for 16 h in a steel autoclave, the autoclave was pressurized with dry ammonia at room temperature and heated to 80 °C overnight. After removing the gas in vacuo, the samples were characterized using standard methods (see the Supporting Information). The conversion of the dibromo-functionalized UiO-66 was quantitative, forming the diamine as proven by NMR spectroscopy.

Nevertheless, the PXRD of the functionalized network showed a decrease in reflex intensity. This can be attributed to a decrease in the crystal size, congestion of the pores by the ammonium bromide byproduct (reflexes at 22.30 and 31.70  $2\Theta$ , Figure 3), or an overall loss in crystallinity. BET measure-



**Figure 3.** PXRD analysis of the different UiO-66 derivatives before (UiO-66allyl) and after PSM (see the Supporting Information for enlarged versions of the diffractograms).

ments were conducted and revealed only a low active surface for nitrogen adsorption (6 m<sup>2</sup>g<sup>-1</sup>). Although the combination of these analytics indicated framework destruction,  $CO_2$  adsorption measurements were inconsistent with these results (Figure 5) and showed a higher  $CO_2$  uptake than the unfunctionalized UiO-allyl-network.

As aqueous monoethanolamine is the current commercially used  $CO_2$ -scrubbing reagent, this functional group promises a high interaction potential with  $CO_2$  as a guest molecule. We therefore carried out the nucleophilic ring-opening of UiO-66-epoxide with the goal of preparing an amino alcohol-functionalized UiO-66 network. The nucleophilic attack of ammonia leads to the corresponding amino alcohol without the formation of any side products. The reaction product showed remaining crystallinity and a conversion of the epoxide of 45%, determined by NMR spectroscopy, which could not be accelerated by varying the reaction conditions. However, BET surfacearea measurements revealed an accessible surface of only  $3 \text{ m}^2\text{g}^{-1}$ , which will be discussed below.

The introduction of diamino and amino alcohol functionalities offers not only a high potential for host–guest interactions but also the potential to introduce catalytically active metal ions by inclusion of donor atoms during PSM.<sup>[11]</sup>

The wide range of PSMs that were available for the UiO-66 system is demonstrated by the multitude of different reaction

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conditions applied, and the exceptional chemical stability of the system was proven by the crystallinity remaining after treatment with ammonia.

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The modified MOF systems were analyzed by the common methods used for PSM experiments, including PXRD, thermogravimetric analysis, solution <sup>1</sup>H NMR spectroscopy, and nitrogen adsorption measurements using the BET method (see the Supporting Information). Because UiO-66-allyl was prepared as a microcrystalline powder, no single-crystal analysis was possible. To clarify the structure of this material, the crystal phase was compared to that of the original UiO-66 using PXRD.

The disintegration using NaOD offered direct access to linker solutions in deuterated water following removal of the Zr-containing salts using centrifugation. This method also revealed that the allylic side chain was preserved during the MOF synthesis, as shown in the Supporting Information. The <sup>1</sup>H NMR spectra of the corresponding PSM products can be attributed to either the direct reaction products or tandem products obtained as a result of the basic workup. The conversion of the C=C double bond can also be evaluated using this method.

#### Gas adsorption

Nitrogen adsorption isotherms revealed the influence of the newly introduced functional groups on the accessible surface area in the network. In comparison with the parent compound (723 m<sup>2</sup>g<sup>-1</sup>), all PSM products showed a remarkable decrease in BET values. The smallest decrease was determined for UiO-66-epoxide, which had a pore surface area of 498 m<sup>2</sup>g<sup>-1</sup>. UiO-66-thioether exposes accessible pores, with the surface area reduced to 52 m<sup>2</sup>g<sup>-1</sup>. UiO-66-dibromide, UiO-66-diamine, and UiO-66-ethanolamine show only low or no accessible pore surface areas at 77 K in nitrogen adsorption experiments (Figure 4).

Different groups have previously reported that  $CO_2$  adsorption depends on the interaction of the integrated side chains in UiO-66 with the corresponding gas. Polar groups were found to be more attractive for  $CO_2$  sorption than nonpolar functionalizations.<sup>[9,13a,14,21]</sup> However, until now, there have



Figure 4.  $\mathsf{N}_2$  adsorption isotherms recorded for UiO-66-allyl and PSM derivatives at 77 K.

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been no studies looking at the influence of allyl, epoxide, dibromide, ethylsulfide, diamine, or ethanolamine groups in UiO-66 MOFs on the capacity for  $N_2$  and  $CO_2$  sorption.

The  $N_2$  adsorption isotherms recorded at 35 °C show a strong dependence on the attached side chains in the framework cavities (Figure 5). While diamine and ethanolamine dis-



Figure 5.  $N_2$  and  $CO_2$  high-pressure adsorption isotherms recorded for UiO-66-allyl and PSM derivatives at 308 K.

play uptakes are comparable to the parent framework, dibromide, thioether, and epoxide show remarkably increased uptakes (up to 200% higher). As the selectivity of the substrate plays an essential role in any possible gas separation applications, the CO<sub>2</sub> adsorption isotherms of the PSM products and UiO-66-allyl were also recorded, and are shown in Figure 5. The isotherms clearly illustrate the influence of polar groups on the adsorption properties. Although it shows the highest BET surface value, UiO-66-allyl shows the lowest CO<sub>2</sub> loading of all the substrates investigated. The amino alcohol-tagged MOF (UiO-66-aminoalcohol) exhibited the highest adsorption of CO<sub>2</sub> combined with one of the lowest values for N<sub>2</sub>, followed by UiO-66-epoxide and UiO-66-thioether. The total CO<sub>2</sub> loading of UiO-66-aminoalcohol was about 51 wt% at 35 °C and 20 bars. The comparatively low loading of UiO-66-diamine may be caused by congestion of the pore system resulting from the large amino groups, as well as the NH<sub>4</sub>Br byproduct of the tandem PSM. As expected, the dibromo-functionalized MOF, without polar groups, displayed the lowest CO<sub>2</sub> loading of the PSM derivatives. Nevertheless, the CO<sub>2</sub> loading was still higher than that observed for the parent system. Compared to litera-



ture data, UiO-66-aminoalcohol hosts up to ten percent more CO\_2 than the amino tagged UiO-66-NH\_2 at 25  $^\circ\text{C}$  and 20 bars.  $^{[13a]}$ 

To the best of our knowledge, this is the highest  $CO_2$  adsorption loading of a functionalized UiO-66 MOF in the literature, and points out the importance of adjustable host-guest interactions in MOFs that are available through PSMs. Chemisorption of  $CO_2$  was excluded for all substrates using ATR-IR measurements (see the Supporting Information, Scheme S7). Thus, UiO-66-aminoalcohol represents a promising candidate for possible  $CO_2$ -N<sub>2</sub> gas separation.

The astonishing differences in the adsorption properties of the frameworks at different temperatures point to a gatedpore effect in the MOFs similar to that found by Fischer et al.<sup>[12a]</sup> This group described a honeycomb-like zinc-dicarboxylate-bipyridine network with flexible ether side chains. The effect was attributed to the low thermal energy of the ether substituents and subsequent congestion of the pore windows, which prevented N<sub>2</sub> diffusion at low temperatures. Nevertheless, these examples did not employ covalent PSM for the introduction of the molecular gates.

The tandem PSMs performed by epoxidation and nucleophilic ring-opening impressively demonstrate the versatility and viability of PSM to precisely adjust adsorption properties in MOFs. UiO-66-allyl showed only a low capacity for CO<sub>2</sub> adsorption, at about 13 wt% at 35 °C and 20 bars. The oxidized UiO-66-epoxide exhibited an increased CO<sub>2</sub> adsorption of 48 wt% with a preserved BET surface of 498 m<sup>2</sup>g<sup>-1</sup>. The final product, UiO-66-aminoalcohol, displayed the highest CO<sub>2</sub> loading of 51 wt% in combination with a closed-gate effect for nitrogen diffusion at 77 K and the lowest N<sub>2</sub> loading at 35 °C.

## Conclusion

We have successfully used PSMs to introduce molecular gates into the MOF UiO-66-allyl. The obtained functionalities enable a powerful tuning for the adsorption of  $CO_2$  over  $N_2$ .

The functionalization of the linking 1,4-benzenedicarboxylate ligand, as well as the optimization of the MOF synthesis using acetic acid as a modulator, was intensively investigated to optimize both crystallinity and pore accessibility. The known bromination (UiO-66-dibromide), epoxidation (UiO-66-epoxide), and thiol-ene click reaction (UiO-66-ethylsulfide) PSMs were applied UiO-66-allyl and resulted in the formation of the desired products in good to quantitative yields. Furthermore, we have, for the first time, introduced a vicinal 1,2-diamino functionality into UiO-66 using a tandem PSM by the reaction of the dibromide with dry ammonia at elevated temperatures (UiO-66-diamine). In another tandem PSM, we successfully ring-opened the epoxide with ammonia to give the corresponding vicinal amino alcohol functionalized compound (UiO-66-aminoalcohol). These tandem PSM steps illustrate the exceptional stability of the UiO-66 system.

All the products resulting from PSM displayed increased  $CO_2$  adsorptions, and, with the exception of UiO-66-epoxide, displayed gated pores with a major decreased in the uptake of nitrogen gas at 77 K in comparison with the mother compound

UiO-66-allyl. The  $CO_2$  adsorption of UiO-66-aminoalcohol was nearly four times higher than that of the mother compound, and was exceptionally high when compared with other compounds reported in the literature.

The PSMs developed herein illustrate the importance of reactive side groups, introduced in pre-synthetic modifications, which do not hinder the MOF crystallization process, but may be converted in high yields to functionalities that are not accessible through pre-synthetic functionalization. Moreover, our work highlights the possibilities of tailoring host-guest interactions through PSMs and, therefore, enabling applications in gas sorption and separation.

## **Experimental Section**

#### General

All reactions containing air- and/or moisture-sensitive compounds were performed under dry argon using standard Schlenk or glovebox techniques. All chemicals were purchased from Aldrich, ABCR or Acros. Solvents were obtained from an MBraun MB-SPS solvent purification system.

UV irradiation for the photoinduced thiol-ene click reaction was executed with a MAX-302 ASAHI SECTRA. NMR spectra were recorded on a Bruker Avance 500 UltraShield (500 MHz) and a Bruker Avance 300 (300 MHz). They were recorded in ppm and the solvents residual proton signal and carbon signal were used as the internal standard. X-ray powder diffraction was measured on a STOE STADI P system with a DECTRIS MYTHEN 1 K detector. TGA was carried out on a Texas Instruments TGA-Q500 with a heating rate of 10 Kmin<sup>-1</sup>. Brunauer-Emmett-Teller (BET) adsorption measurements were obtained by using a Quantachrome Nova 4000e sorption apparatus and a PMI automatic Sorptometer. The samples were activated in vacuum at 135 °C for 2 h before measurement. Apparent surface area was calculated by applying the BET theory. CO2 and N2 isotherms were obtained at 35  $^\circ\text{C}$  in a range of 0.5–20 bar using a Rubotherm magnetic suspension balance. Approximately 300 mg of the sorbent was placed in a steel crucible and dried at 135°C for 8 h under vacuum prior to adsorption. To correct for buoyancy, reference adsorption isotherms of nonadsorbing glass spheres (300 mg, particle size: 425–600  $\mu$ m) were determined and subtracted from the isotherms. Elemental analyses were measured at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at the Technische Universität München. ESI-MS analytical measurements were performed with acetonitrile, THF, isopropanol, or toluene solutions on a Varian 500-MS spectrometer. IR spectra were recorded with a liquid nitrogen cooled Bruker Vertex 70 FTIRspectrometer with a attenuated total reflectance unit Platinum ATR of Bruker using 32 scans in a region of 4500 to 600  $\text{cm}^{-1}$ .

### Linker synthesis

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**2-Bromoterephthalic acid dimethylester**: To a stirred suspension of 2-bromoterephthalic acid (6.2 g, 25.3 mmol, 1.0 equiv) in dry methanol (100 mL), thionylchloride (7.3 mL, 101 mmol, 4.0 equiv) was added dropwise at room temperature. The reaction mixture was heated to reflux for 16 h and excess of thionylchloride and the solvent were evaporated in vacuo. To the residue, 50 mL of a saturated sodiumbicarbonate solution was added and extracted with ethyl acetate (50 mL) three times. The organic extracts were combined, dried over sodium sulfate, and evaporated in vacuo to give 6.26 g 2-bromoterepthalic acid (22.9 mmol; 92%) as a colorless



solid. <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta = 3.94$  (s, 3 H,  $-CH_3$ ), 3.95 (s, 3 H,  $-CH_3$ ), 7.80 (m, 1 H,  $H_{arom}$ ), 8.01 (dd, 1 H,  $^3J = 8.1$  Hz, 1.7 Hz,  $H_{arom}$ ), 8.31 ppm (d, 1 H,  $^3J = 1.7$  Hz,  $H_{arom}$ ); <sup>13</sup>C NMR (75.5 MHz; CDCl<sub>3</sub>):  $\delta =$  52.81, 52.91, 121.57, 128.22, 131.14, 133.83, 135.32, 136.25, 165.12, 166.26 ppm.

2-Allylterephthalic acid dimethylester: 2-Bromoterephthalic acid dimethylester (12.0 g, 43.9 mmol, 1.0 equiv) and 1.0 g tetrakis-(triphenylphosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.88 mmol; 0.02 equiv) were dissolved in 200 mL of degassed toluene under an argon atmosphere. 15.0 mL allyltri(n-butyl)tin were added and the reaction solution was heated to reflux for 5 days. The reaction mixture was guenched using 100 mL of a 4% cesium fluoride solution and extracted with ethyl acetate. After drying over sodium sulfate, the raw product was purified using flash chromatography (silica gel, hexane/ethyl acetate 95:5) to give 9.07 g 2-allylterephthalic acid dimethylester (38.7 mmol, 88%) as a colorless oil. TLC:  $R_f = 0,16$ (hexane/ethyl acetate = 95:5) [UV]; <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>):  $\delta$  = 3.77 (d, 1 H,  ${}^{3}J = 6.4$  Hz,  $-CH_{2}$ -), 3.90 (s, 3 H,  $-OCH_{3}$ ), 3.93 (s, 3 H, -OCH<sub>3</sub>'), 5.01-5.05 (m, 2H, -CH=CH<sub>2</sub>), 5.99 (ddt, 1H, <sup>3</sup>J=16.7, 10.1, 6.4 Hz, -CH=CH<sub>2</sub>), 7.90-7.94 ppm (m, 3 H, H<sub>arom</sub>); <sup>13</sup>C NMR: (75.5 MHz; CDCl<sub>3</sub>):  $\delta = 38.33$ , 52.39, 52.51, 116.35, 127.32, 130.64, 132.05, 133.05, 133.88, 136.77, 141.69, 166.44, 167.57 ppm; elemental analysis calcd (%) for  $C_{13}H_{14}O_4$ : C 66.66, H 6.02, O 27.32; found: C 66.57, H 6.09; IR (ATR): v = 3080-2840 (w, multiple weak maxima, Ar-H, C-H), 1718 (vs, C=O), 1638 (w, C=C str), 1571 (w), 1492 (w), 1434 (m), 1405 (w), 1257 (s, C-O), 1194 (m), 1111 (s), 1072 (m), 992 (m, CH=CH<sub>2</sub> twist), 963 (w), 915 (s, CH=CH<sub>2</sub> wag), 883 (w), 857 (w), 815 (m), 750 (s), 717 (m), 654 cm<sup>-1</sup> (w).

2-Allylterephhalic acid (L1): 2-Allylterephthalic acid dimethyl ester (6.28 g, 26.8 mmol, 1.0 equiv) were dissolved in 100 mL of a 1:1 mixture of THF and methanol. After the addition of sodium hydroxide solution (65 mL, 1 M, 65.0 mmol, 2.4 equiv) the mixture was stirred for 24 h at room temperature. The organic solvents were removed in vacuo and the residue was dissolved in 50 mL of water. The aqueous solution was neutralized using concentrated hydrochloric acid and the formed precipitate was isolated by filtration. The white powder was repeatedly washed with water and dried in vacuo to obtain 5.30 g 2-allylterephthalic acid (25.7 mmol, 96%) as a colorless solid. <sup>1</sup>H NMR (300 MHz; [D<sub>6</sub>]DMSO):  $\delta = 3.74$  (d, 1 H, <sup>3</sup>J = 6.6 Hz, -CH<sub>2</sub>--), 5.03 (m, 2H, -CH=CH<sub>2</sub>), 5.95 (m, 1H, -CH=CH<sub>2</sub>), 7.82–7.86 (m, 3 H, H<sub>arom</sub>), 13.26 ppm (s, 2 H, –COOH); <sup>13</sup>C NMR (75.5 MHz;  $[D_{6}]$ DMSO):  $\delta = 37.39$ , 116.19, 127.10, 130.27, 131.35, 134.70, 137.18, 140.58, 166.67, 168.31 ppm; elemental analysis calcd (%) for C<sub>11</sub>H<sub>10</sub>O<sub>4</sub>: C 64.07, H 4.89, O 31.04; found: C 63.93, H 4.79; IR (ATR): v = 3200-2500 (s, broad signal with multiple maxima, O-H, Ar-H, C-H), 1681 (s, C=O), 1634 (w, C=C str), 1568 (w), 1495 (w), 1414 (m), 1284 (s, C-O), 1206 (w), 1193 (w), 1134 (w), 1105 (w), 1070 (w), 993 (m, CH=CH2 twist), 914 (s, CH=CH2 wag), 860 (w), 784 (m), 748 (m), 706 (w), 678 (w), 654 cm<sup>-1</sup> (w).

#### **MOF-synthesis**

**UiO-66-allyl**: A solution of 1.50 g 2-allyl benzene-1,4-dicarboxylylic acid (7.27 mmol, 1.00 equiv) in 160 mL DMF was added in one portion to a solution of 1.61 g ZrCl<sub>4</sub> (6.91 mmol, 0.95 equiv) in a mixture of 164 mL DMF, 36 mL acetic acid, and 393  $\mu$ L water. The mixture was placed in a glass autoclave and heated under static conditions to 130 °C for 20 h. After cooling down the microcrystalline powder was isolated using centrifugation and repeatedly washed with DMF, methanol, and DCM. Every washing step included the treatment in an ultrasonic bath for 5 min prior to drying in vacuo at 120 °C. Elemental analysis: calcd (%) for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>)<sub>6</sub>]: C 41.62, H 2.75, O 26.88, Zr 27.74; found: C 40.92, H 2.28.

#### Postsynthetic modifications

**UiO-66-epoxide**: Activated UiO-66-allyl (300 mg, 0.95 mmol) was treated with a solution of dimethyl-dioxirane (DMDO) (0.05 M, 40 mL, 2.0 mmol) in acetone for 72 h at 4 °C. At the end of the reaction time, the solution was removed using centrifugation and the MOF powder was washed three times with 10 mL of fresh acetone. Afterwards, the product was dried in vacuo. Conversion (<sup>1</sup>H NMR): 95 %.

Proton NMR shows signals for the corresponding glycol through nucleophilic ring-opening of the epoxide.

<sup>1</sup>H NMR (500 MHz, Deuterium Oxide):  $\delta$  = 2.56–2.82 (m, 2H), 3.15–3.35 (m, 2H), 3.60 (td, <sup>3</sup>*J*=9.4, 7.8, 4.5, 1H), 7.16 (d, <sup>3</sup>*J*=7.8, 1H), 7.41–7.51 (m, 2H); elemental analysis calcd (%) for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>O<sub>5</sub>)<sub>6</sub>]<sub>0.95</sub>[Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>)<sub>6</sub>]<sub>0.05</sub>: C 39.72, H 2.63, O 30.22, Zr 27.43; found: C 41.02, H 2.89.

**UiO-66-dibromide**: Activated UiO-66-allyl (300 mg, 0.95 mmol) was placed in a Schlenk flask, suspended in 5 mL of fresh trichloromethane and cooled to 0 °C. 0.2 mL bromine (4.12 mmol) was added dropwise to the MOF and the reaction mixture was stirred at room temperature for 16 h. The solvent was removed using centrifugation and decantation. The MOF powder was washed several times using trichloromethane and dichloromethane and dried under vacuo. Conversion (<sup>1</sup>H NMR): 100%.

Proton NMR shows signals for the corresponding glycol through nucleophilic substitution of bromide by hydroxide.

<sup>1</sup>H NMR (500 MHz, Deuterium Oxide):  $\delta$  = 2.79–2.53 (m, 2H), 3.34–3.14 (m, 3H), 3.63–3.52 (m, 1H), 7.15 (d, <sup>3</sup>*J*=7.9, 1H), 7.48–7.40 (m, 3H); elemental analysis calcd (%) [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>Br<sub>2</sub>O<sub>4</sub>)<sub>6</sub>]: C 27.69, H 1.83, Br 33.49, O 17.88, Zr 19.12; found: C 26.25, H 2.15.

**UiO-66-ethylsulfide**: Activated UiO-66-allyl (250 mg, 0.79 mmol) was placed in a quartz Schlenk tube to ensure UV light transparency. Degassed ethylmercaptane (3.5 mL, 47 mmol) was added at room temperature and the mixture was allowed to stay in the dark for 2 h impregnating the pores with the reactant. Subsequently, the reaction mixture was irradiated with UV light for 8 h under moderate stirring. After the reaction, the MOF powder was washed three times using THF (5 mL) and dried in vacuo. Conversion (<sup>1</sup>H NMR): 80%. <sup>1</sup>H NMR (500 MHz, Deuterium Oxide):  $\delta$  = 0.81–0.93 (m, 3 H), 1.48–1.68 (m, 2 H), 2.19–2.33 (m, 4 H), 2.56 (t, <sup>3</sup>*J* = 7.6, 2 H), 7.07 (dd, <sup>3</sup>*J* = 12.8, 7.8, 1 H), 7.36–7.44 ppm (m, 2 H); elemental analysis calcd for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>S)<sub>6</sub>]<sub>0.80</sub>[Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>O<sub>4</sub>)<sub>6</sub>]<sub>0.20</sub>: C 41.22, H 3.70, O 23.24; S 6.99, Zr 24.85; found: C 39.13, H 3.68, S 5.65.

**UiO-66-aminoalcohol**: Activated UiO-66-epoxide (300 mg, 0.90 mmol) was placed in a 25 mL steal autoclave and pressurized with ammonia (8 bar). The autoclave was heated to 80 °C for 72 h and the ammonia was released followed by sequential washing with methanol (3×5 mL) and drying in vacuo. Conversion (<sup>1</sup>H NMR): 45%. <sup>1</sup>H NMR (500 MHz, Deuterium Oxide):  $\delta$  = 2.21–2.42 (m, 2H), 2.62–2.76 (m, 2H), 3.49–3.53 (m, 1H), 7.14 (d, <sup>3</sup>*J*=3.3, 1H), 7.44–7.47 ppm (m, 2H); elemental analysis calcd (%) for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>11</sub>NO<sub>5</sub>)<sub>6</sub>]<sub>0.43</sub>[Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>8</sub>O<sub>5</sub>)<sub>6</sub>]<sub>0.52</sub>

 $[Zr_6O_4(OH)_4(C_{11}H_8O_4)_6]_{0.05}\colon$  C 38.87, H 2.95, N 1.77, O 29.57, Zr 26.84; found: C 36.12, H 3.13, N 1.97.

**UiO-66-diamine**: Activated UiO-66-dibromide (300 mg, 0.63 mmol) was placed in a 25 mL steal autoclave and pressurized with ammonia (8 bar). The autoclave was heated to 80 °C for 16 h and the ammonia was released followed by sequential washing with methanol (3×5 mL) and drying in vacuo. Conversion (<sup>1</sup>H NMR): 100%. <sup>1</sup>H NMR (500 MHz, Deuterium Oxide):  $\delta$  = 2.15–2.39 (m, 2H), 2.54–2.76 (m, 2H), 3.43–3.55 (m, 1H), 7.12 (d, <sup>3</sup>*J*=7.9, 1H), 7.38–7.43 (m,

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2 H); elemental analysis calcd (%) for [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>)<sub>6</sub>(HBr)<sub>3</sub>]: C 33.88, H 3.40, Br 10.25, N 7.18, O 21.88, Zr: 23.40; found: C 31.23, H 3.15, N 6.88; EDX: Zr: 24.53; Br: 12.14.

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## **FULL PAPER**

The highly porous and stable metalorganic framework (MOF) UiO-66 was altered using post-synthetic modifications (PSMs). The abilities of the compounds to adsorb  $CO_2$  and  $N_2$  were compared (see scheme), which revealed the structure-selectivity correlations. All synthesized MOFs showed profound thermal stability together with an increased ability for selective  $CO_2$  uptake and molecular gate functionalities at low temperatures.



## Materials Science

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Gated Channels and Selectivity Tuning of CO<sub>2</sub> over N<sub>2</sub> Sorption by Post-Synthetic Modification of a UiO-66-Type Metal–Organic Framework