Metal-organic frameworks

A highly stable zirconium-based metal-organic framework material with high surface area and gas storage capacities

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We designed, synthesized and characterized a new Zr-based metal–organic framework material, **NU-1100**, which exhibits a pore volume of 1.53 cm^3/g and Brunauer-Emmett-Teller (BET) surface area of 4020 m^2/g; to our knowledge currently the highest published for Zr-based MOFs. CH_4/CO_2/H_2 adsorption isotherms were measured over a broad range of pressures and temperatures and are in excellent agreement with the computational predictions. The total hydrogen adsorption at 65 bar and 77 K is 0.092 g/g which corresponds to 43 g/L. The volumetric and gravimetric methane storage capacities at 65 bar and 298 K are ~180 v_{STP}/v and 0.27 g/g, respectively.

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Well-defined metal-organic frameworks (MOFs) featuring molecular-scale pores and high internal surface areas, constitute a growing and remarkably chemically diverse class of materials of potential utility in a wide range of applications including catalysis,[1,2] gas separation,[3,4] sensing,[5] and storage[6,7,8]. In particular, MOFs have attracted much interest for on-board hydrogen or methane storage in vehicles. Both methane and hydrogen are promising candidates as replacements for gasoline (petrol). However, their compact storage in molecular form, especially in the case of hydrogen, remains a great challenge. Sorption or cryosorption in nanoporous materials is a promising way to lower the pressure required for storage of a given deliverable quantity of gas. In addition to high porosity, chemical stability of the sorbent is important, since alternative fuels such as natural gas often contain trace contaminants (water, acids). Further practical requirements for on-board applications include thermal stability and mechanical stability (required for damage-free pelletization of the adsorbent; pelletization lowers back-pressure during tank filling, thereby facilitating more rapid filling).

Over the last decade, significant progress has been made towards building new classes of MOFs with desired material characteristics. To a significant degree, MOFs can now be considered as programmable.[9] This circumstance has been achieved by tailoring the pore geometry and volume, surface area, and density of MOFs *via* the incorporation of different linkers and metal centers. Control over these parameters is crucial for constructing materials with high-capacity gas uptake, as well as stability. However, most known MOFs are not sufficiently stable to allow their application for gas storage in the presence of water or acid.[10] To overcome this problem, we targeted Zr-based MOFs. These materials are known to possess high chemical and mechanical stability due strong ionic bonding between Zr^{4+} and carboxylate oxygen atoms.[11,12,13,14,15] However, Zr-MOFs have been much less extensively investigated for hydrogen or methane storage than have many other MOF families.

Recent studies have demonstrated the feasibility of tuning the porosity of Zr-based MOFs by selective linker removal,[16,17] control over the framework topology, or ligand modifications.[18] These studies suggest that appropriate design of Zr-MOFs can lead to materials with high surface area, a feature of exceptional importance for hydrogen storage at low temperatures.[6] Reticular synthesis, a methodology based on systematic extension of organic linkers between inorganic nodes, is the first choice approach for constructing MOFs with higher surface areas and pore volumes than the prototypical structure in a MOF series. We

sought to utilize this approach to design a new high surface area Zr-MOF based on the non-interpenetrating **ftw** topology.[19]

In the current work, we designed and synthesized a highly-porous Zr-MOF, **NU-1100**, based on $Zr_6O_4(OH)_4^{12+}$ clusters and a pyrene-based tetratopic ligand 4-[2-[3,6,8-tris[2-(4-carboxyphenyl)ethynyl]-pyren-1-yl]ethynyl]-benzoic acid (**L₄H**).
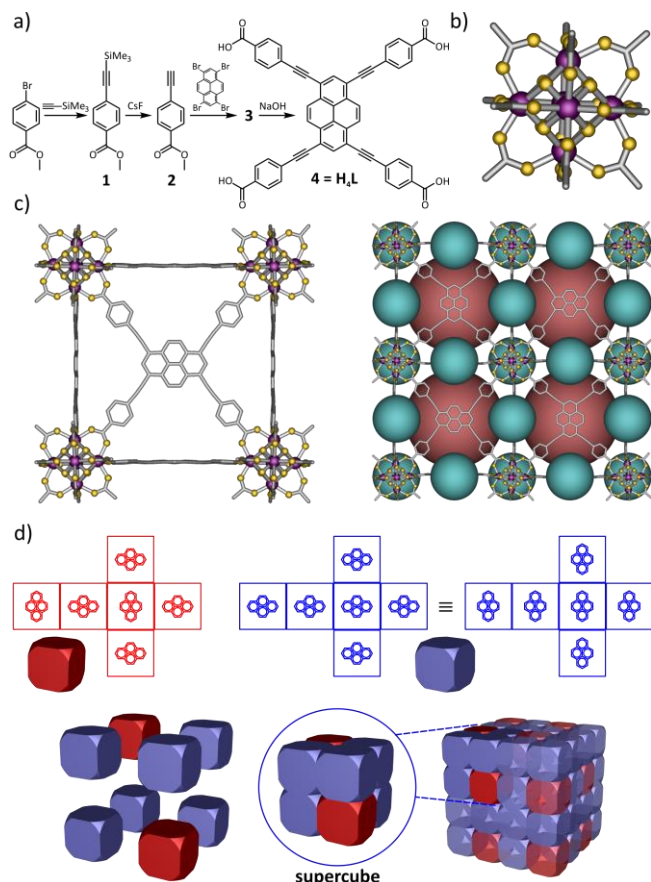

Figure 1. a) Scheme for **L₄H** synthesis. b, c) Structural elements and crystal packing of **NU-1100** (Zr atoms are shown as purple spheres, O atoms – as yellow spheres, and carbon skeleton – as gray sticks. Dark pink and light blue spheres occupy two major pore types in the crystal. d) Schematic representation of **NU-1100** supramolecular structure as a superposition of two different cubes (red and blue).

Two major design considerations in selecting the linker were that: i) the ligand should exhibit planar geometry to make the connectivity motif required for the **ftw** topology possible and ii) the relative dimensions of the linker should be such that the four carboxylates define a rectangle that closely approximates a square, thereby enable the formation of cube-like boxes upon coordination to nodes. With this in mind, we designed ligand **L₄H** and computationally tested the possibility of its incorporation (as **L⁴⁻**) into the **ftw** topology. The initial model of the **NU-1100** structure was optimized by applying a procedure based on molecular energy minimizations described previously.[7] The resulting model demonstrated that **L⁴⁻** can form a MOF with the desired topology without serious distortion of bond lengths and angles (Fig. S3.1).

The ligand **L₄H** was synthesized in four steps, including Sonogashira coupling reactions, followed by saponification of the

resulting tetraester (Fig. 1a, for synthetic details see ESI). The structure of **L₄H** was confirmed by single crystal X-ray diffraction studies, which revealed the planar geometry of the molecules resulting in dense packing in the crystal structure (Fig. S4.1), which is commonly observed for conjugated systems.[20, 21] Solvothermal reaction of **L₄H**, $ZrOCl_2·8H_2O$ and benzoic acid (*used as a modulator*) in *N,N'*-dimethylformamide (DMF) at 120 ºC gave a material with a powder X-ray diffraction (PXRD) pattern similar to that simulated for our preliminary computational model (Fig. S3.2) indicating the formation of a structure with the targeted **ftw** topology. Single crystals of **NU-1100** were obtained and the structure was analyzed by means of single crystal X-ray diffraction studies. The sample was found to have *Im-3* space group with an **ftw** topology;[19] to our knowledge this represents the first example of isoreticular extension of the **ftw** topology. The structure of **NU-1100** consists of 12-connected $Zr_6O_4(OH)_4^{12+}$ nodes linked by planar tetratopic molecules of **L⁴⁻** to form two types of pores (Fig. 1b,c). Ligand orientation is different in adjacent, rectilinear and nearly cubic, boxes, with two possible combinations of the box faces that finally form a "supercube" (Fig. 1c,d). Alternating orientations of the linker molecule in the crystal structure demonstrate a way for a two-fold symmetrical ligand to be incorporated into a topology that, in principle, requires four-fold symmetrical ligands, resulting in a highly symmetric cubic space group. Such arrangement helps to compensate the small deviation of the linker periphery from a perfect square geometry (length to height ratios of the ligand carbon core are 0.96 and 0.97 in the crystal structures of **L₄H** and **NU-1100** respectively).

The measured PXRD pattern of the **NU-1100** sample is in excellent agreement with the simulated pattern from single-crystal structure data, confirming the single-phase nature of the bulk sample (Fig. 2a). Thermal gravimetric analysis (TGA) of the "as synthesized" material shows 60% weight loss, corresponding to an equivalent accessibility by solvent molecules (Fig. S5.3). These initial results demonstrated the highly porous nature of the studied material. A TGA measurement of the **NU-1100** sample activated at 120 ºC (Fig. S5.3) reveals stability up to 500 ºC. A small weight loss is observed above ~200 ºC for both "as synthesized" and desolvated samples, corresponding to the elimination of water molecules from $Zr_6O_4(OH)_4^{12+}$ nodes.[16]

Computationally, **NU1100** was predicted to have a large surface area and pore volume with high capacities for sorption of N_2, H_2, CH_4 and CO_2. In order to validate these predictions, we have thermally activated (see ESI for activation details) a sample of **NU-1100** and studied its porosity by collecting nitrogen isotherms at 77 K, which were measured independently at Northwestern University (NU) and the National Institute of Standards and Technology (NIST) (Fig. S5.4). Temperature-dependent high-pressure adsorption measurements were performed at NIST using a computer-controlled Sieverts apparatus, the details of which have been published elsewhere.[22] The experimental isotherms and resulting BET surface areas measured at NU (Fig. S5.7) and NIST are very similar: 4020 m²/g and 4060 m²/g, respectively. These numbers are also in good agreement with the calculated value of 4333 m²/g (Fig. S5.8) and represent, to our knowledge, the highest reported to date for Zr-based MOFs. The pore volume of **NU-1100**, derived from the measured N_2 isotherm, is 1.53 cc/g, which is lower than the calculated value of 1.67 cc/g (78.1% porosity) by PLATON.[23] The pore size distributions extracted from simulated and experimental

isotherms using the density functional theory (DFT) method (Fig. S5.6) are in good agreement and show the two pore types observed in the **NU-1100** crystal structure (Fig. 1c).

Besides its high thermal stability, **NU-1100** shows excellent stability against water, retaining its crystallinity and full porosity following soaking in liquid water for 24 h (Fig. 2).
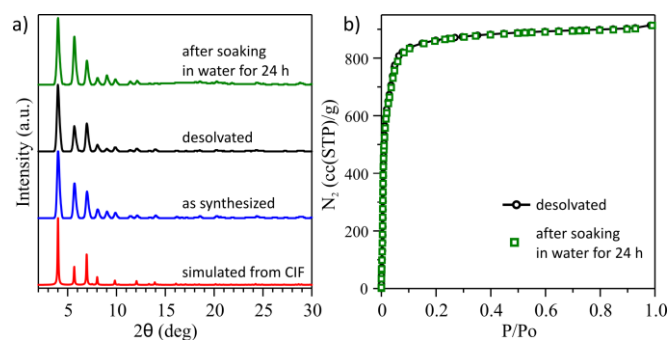

Figure 2. a) PXRD patterns of **NU-1100** after different treatments in comparison to the simulated pattern; b) N_2 adsorption isotherms of activated **NU-1100** at 77 K before and after immersion in water.

Fig. 3 shows CH_4, CO_2, and H_2 adsorption isotherms over a wide range of pressures and temperatures. Low temperature adsorption isotherm measurements are indispensable since they provide information on the maximum gas storage capacity of the material. The excess H_2 isotherm at 77 K (Fig. S6.1) shows a shallow maximum uptake of 0.062 g/g near 45 bar and a slight decrease to 0.06 g/g at 65 bar. Consistent with this nearly flat excess isotherm, the total isotherm does not saturate with increasing pressure, reaching a very high value of 0.092 g/g at 65 bar (the highest pressure examined). The corresponding volumetric uptake is 43 g/L, among the highest values reported to date for H_2 storage (i.e., 35 g/L for **PCN-68**,[24] 36 g/L for **MOF-200**,[8] 41 g/L for **MOF-210**,[8] 47 g/L for **NU-100**,[7] 49 g/L for **NU-111**[25] and **MOF-177**[26]). It is important to note that these benchmark MOFs such as **NU-100** and **MOF-177** are based on copper paddlewheels or Zn_4O clusters, which are not as stable as the Zr-based **NU-1100**. Hydrogen uptake drops rapidly with increasing temperature. Nevertheless **NU-1100** shows a non-negligible total uptake of 0.012 g/g at 298 K and 65 bar.

Additionally, **NU-1100** exhibits significant CO_2 uptake at high pressures. The maximum CO_2 uptake at 220 K is 37.3 mmol/g, which gives a pore volume of 1.42 cc/g (7% lower than that derived from nitrogen and methane). The CO_2 uptake at room temperature and 30 bar is ca. 26.2 mmol/g, corresponding to 70% of the total pore volume.

Methane adsorption isotherms of **NU-1100** are shown in Fig. 3 and 4. We obtained a maximum uptake of ca. 404 v_{STP}/v (38.6 mmol/g) at 125 K. This value effectively corresponds to the upper limit for the amount of gas that can be adsorbed under very high external pressures at ambient temperature. The observed maximum CH_4 uptake gives a pore volume of 1.54 cm^3/g (assuming liquid methane density at 125 K), which is in excellent agreement with the nitrogen pore volume. This suggests that methane is able to access most of the pores in **NU-1100** that are accessible to nitrogen at 77 K. The material has high volumetric and gravimetric methane storage capacities at 65 bar and 298 K of ca. 180 v_{STP}/v and 0.27 g/g, respectively. Ultimately, the
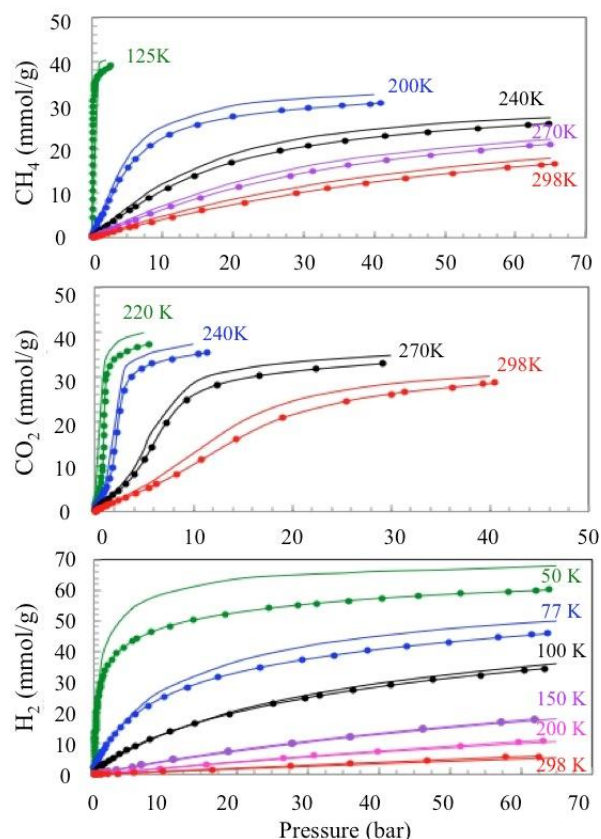

Figure 3. Total gravimetric gas uptake isotherms for **NU-1100** at various temperatures. The lines with filled circles are experimental data while the solid lines are simulated isotherms using the Dreiding force field.

deliverable methane capacity determines the driving range of a natural gas vehicle (NGV). In this case it is important for a porous material to have low capacity in the ca. 5 bar range, and high capacity in the 60–70 bar range. The adsorption isotherm of **NU-1100** has a relatively shallow gradient at low pressure; taking 5 bar as the specific lower pressure limit and 65 bar as the upper limit, the volumetric deliverable capacity of **NU-1100** is 156 v_{STP}/v at 298 K. This value is lower than that of **HKUST-1** (190 v_{STP}/v) and similar to other promising methane storage MOFs, such as **UTSA-20** (170 v_{STP}/v) and **PCN-14** (157 v_{STP}/v).[22] However, the advantages that **NU-1100** can offer are: i) high gravimetric deliverable capacity (0.24 g/g), which is higher than in the abovementioned MOFs - 56% higher than in **HKUST-1** (0.154 g/g), 75% higher than in **PCN-14** (0.136 g/g), and 78% higher than in **UTSA-20** (0.134 g/g); ii) high thermal stability; and iii) high water stability when compared to the abovementioned MOFs. Simulated isotherms for CH_4, CO_2 and H_2 are in good agreement with the experimental data (Fig. 3); however there is a systematic overprediction of adsorption at all temperatures.[27]

Importantly, we have tested the cycling stability of **NU-1100**. Upon multiple cycles of methane adsorption/desorption, which are shown in Fig. 4, **NU-1100** shows no evidence for sample degradation [*as evident from the straight line fit with zero slope (green-dashed line)*]. The variation of the total adsorption at 65 bar is less than ±2%, which is within the experimental error of our measurements.
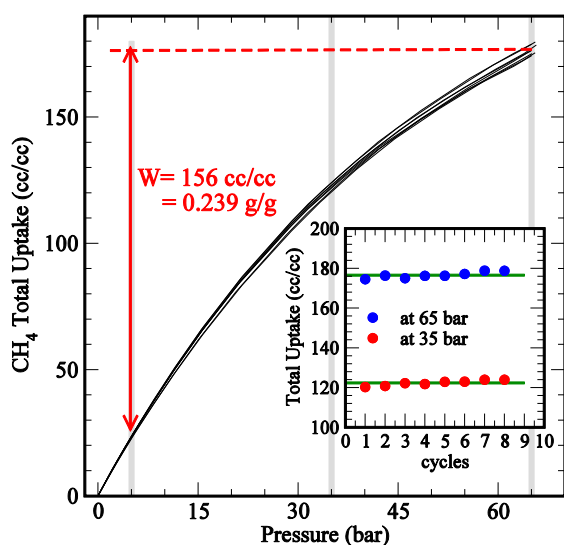
Figure 4. Total methane uptake isotherms for **NU-1100** over nine cycles, indicating no sample degradation with adsorption cycles. The inset shows the variation of the total uptake at 35 bar and 65 bar versus cycle number.

In order to get better insight into the nature of the adsorption sites and gas–framework interactions in **NU-1100**, we extracted isosteric heats of adsorption (Q_{st}) from the absolute isotherms measured at different temperatures using the Clausius-Clapeyron equation (details are given in the ESI).

The results are summarized in Fig. 5, showing good agreement with simulated values. The magnitudes of the Q_{st} values for CH_4 and CO_2 are significantly smaller than in **UiO-66** – the prototypical Zr-based MOF.[13,16] In the case of **UiO-66**, the Q_{st} for CO_2 varies from 28 kJ/mol to 24 kJ/mol, while in **NU-1100** there is a sharp decrease from 25 kJ/mol to 16 kJ/mol at low
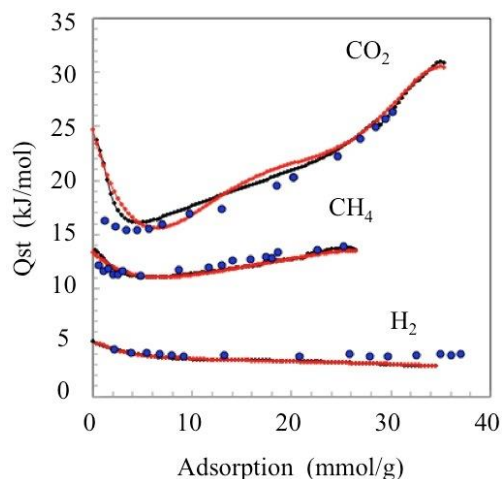

Figure 5. Isosteric heats of adsorption (Q_{st}) for **NU-1100** as a function of gas loading in mmol(gas)/g(MOF): red lines represent virial fitting, black lines represent experimental isotherm data points connected using a spline function (without curve fitting), and blue points represent data obtained from GCMC simulations (CH_4 and CO_2 at 298 K and H_2 at 100 K) using the Dreiding force field.

loading. We attribute this initial Q_{st} value to the presence of OH-groups from Zr-clusters as the primary adsorption sites.[16] In the case of methane, **UiO-66** has a Q_{st} around 18-19 kJ/mol while **NU-1100** shows a Q_{st} near 11 kJ/mol. However, for smaller gas molecules such as H_2, Q_{st} is almost the same as in **UiO-66**. The initial Q_{st} of 5 kJ/mol is roughly constant over the whole H_2 loading range.

In conclusion, we have synthesized and characterized a highly porous and stable Zr-based MOF material **NU-1100**, which exhibits very promising gas uptake for hydrogen and natural gas storage applications. According to PXRD and sorption measurements, **NU-1100** demonstrates high stability against water. The total volumetric hydrogen adsorption at 65 bar and 77 K is 43 g/L (0.092 g/g), which places it among the best performing MOFs for hydrogen storage at low temperatures. The methane volumetric deliverable capacity of **NU-1100** between 65 bar and 5 bar is ~160 v_{STP}/v which is comparable to those of the most promising methane storage materials, but its gravimetric deliverable capacity (0.24 g/g) is significantly higher. These results, together with the possibilities to tune the porosity by ligand extension, establish **NU-1100** as a promising platform to further improve gas sorption capacities in a highly-stable MOF structure.

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