Metal-organic frameworks

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


We designed, synthesized and characterized a new Zr-based metal–organic framework material, NU-1100, which exhibits a pore volume of 1.53 cm³/g and Brunauer-Emmett-Teller (BET) surface area of 4020 m²/g; to our knowledge currently the highest published for Zr-based MOFs. CH₄/CO₂/H₂ 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 Vₜₚₑₜ and 0.27 g/g, respectively.

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sought to utilize this approach to design a new high surface area Zr-MOF based on the non-interpenetrating ftw topology. In the current work, we designed and synthesized a highly porous Zr-MOF, NU-1100, based on ZrO$_2$(OH)$_2$ clusters and a pyrene-based tetratopic ligand 4-[2-[3,6,8-tris(2-(4-carboxyphenyl)ethynyl)-pyren-1-yl]ethynyl]-benzoic acid (LH).

The ligand LH 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. Solvothermal reaction of LH, ZrOCl$_2$·8H$_2$O and benzoic acid (used as a modulator) in N,N-dimethylformamide (DMF) at 120 °C 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, to our knowledge this represents the first example of isoreticular extension of the ftw topology. The structure of NU-1100 consists of 12-connected ZrO$_2$(OH)$_2$ nodes linked by planar tetratopic molecules of L$^4$ 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 LH 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 °C (Fig. S5.3) reveals stability up to 500 °C. A small weight loss is observed above ~200 °C for both “as synthesized” and desolvated samples, corresponding to the elimination of water molecules from ZrO$_2$(OH)$_2$ nodes.

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. The experimental isotherms and resulting BET surface areas measured at NU (Fig. S5.7) and NIST are very similar: 4020 m$^2$/g and 4060 m$^2$/g, respectively. These numbers are also in good agreement with the calculated value of 4333 m$^2$/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. The pore size distributions extracted from simulated and experimental

Figure 1. a) Scheme for LH 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 LH and computationally tested the possibility of its incorporation (as L$^4$) 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. The resulting model demonstrated that L$^4$ can form a MOF with the desired topology without serious distortion of bond lengths and angles (Fig. S3.1).

The ligand LH was synthesized in four steps, including Sonogashira coupling reactions, followed by saponification of the resulting tetraester (Fig. 1a, for synthetic details see ESI). 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 °C (Fig. S5.3) reveals stability up to 500 °C. A small weight loss is observed above ~200 °C for both “as synthesized” and desolvated samples, corresponding to the elimination of water molecules from ZrO$_2$(OH)$_2$ nodes. These experimental isotherms and resulting BET surface areas measured at NU (Fig. S5.7) and NIST are very similar: 4020 m$^2$/g and 4060 m$^2$/g, respectively. These numbers are also in good agreement with the calculated value of 4333 m$^2$/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. 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](image1.png)

**Figure 2.** a) PXRD patterns of NU-1100 after different treatments in comparison to the as-synthesized pattern; b) N₂ adsorption isotherms of activated NU-1100 at 77 K before and after immersion in water.

Fig. 3 shows CH₄, CO₂, and H₂ 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 H₂ isotherm at 77 K (Fig. S4.1) 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 H₂ storage (i.e., 35 g/L for PCN-68, 25 36 g/L for MOF-200, 26 41 g/L for MOF-210, 27 47 g/L for NU-100, 28 49 g/L for NU-111, 29 and MOF-177 30). It is important to note that these benchmark MOFs such as NU-100 and MOF-177 are based on copper paddlewheels or Zn₂O 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 CO₂ uptake at high pressures. The maximum CO₂ 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 CO₂ 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 vSTP/g (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 CH₄ uptake gives a pore volume of 1.54 cm³/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 vSTP/g and 0.27 g/g, respectively. Ultimately, the 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 vSTP/g at 298 K. This value is lower than that of HKUST-1 (190 vSTP/g) and similar to other promising methane storage MOFs, such as UTSA-20 (170 vSTP/g) and PCN-14 (157 vSTP/g). 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 CH₄, CO₂, and H₂ are in good agreement with the experimental data (Fig. 3); however there is a systematic overprediction of adsorption at all temperatures.

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 3](image2.png)

**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.
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 ($Q_{\text{st}}$) 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 $Q_{\text{st}}$ values for CH$_4$ and CO$_2$ are significantly smaller than in Uio-66 – the prototypical Zr-based MOF. In the case of Uio-66, the $Q_{\text{st}}$ 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 loading. We attribute this initial $Q_{\text{st}}$ value to the presence of OH-groups from Zr-clusters as the primary adsorption sites. In the case of methane, Uio-66 has a $Q_{\text{st}}$ around 18-19 kJ/mol while NU-1100 shows a $Q_{\text{st}}$ near 11 kJ/mol. However, for smaller gas molecules such as H$_2$, $Q_{\text{st}}$ is almost the same as in Uio-66. The initial $Q_{\text{st}}$ 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/g, 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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**Keywords:** gas storage • hydrogen • methane • metal-organic frameworks • zirconium

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There are only a few known examples of MOFs stable in bulk water and in acidic solutions. These include: UiO-66-type, MIL-type MOFs, and Fe₂(BDP)₃(BDP= 1,4-benzenedipyrazolate) – Z. R. Herm, B. M. Wiers, J. A. Mason, J. M. van Baten, M. R. Hudson, P. Zajdel, C. M. Brown, N. Masciocchi, R. Krishna, J. R. Long, *Science* 2013, 340, 990–996.


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[27] The origin of the overprediction may be related to inactivated regions as suggested by differences between measured and calculated pore volumes.
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A highly stable zirconium-based metal-organic framework material with high surface area and gas storage capacities

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