Surface Chemistry

Water-Stable Zirconium-Based Metal–Organic Framework Material with High-Surface Area and Gas-Storage Capacities


Abstract: We designed, synthesized, and characterized a new Zr-based metal–organic framework material, NU-1100, with a pore volume of 1.53 cc g<sup>-1</sup> and Brunauer–Emmett–Teller (BET) surface area of 4020 m<sup>2</sup> g<sup>-1</sup>; to our knowledge, currently the highest published for Zr-based MOFs. CH<sub>4</sub>/CO<sub>2</sub>/H<sub>2</sub> adsorption isotherms were obtained 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<sup>-1</sup>, which corresponds to 43 g L<sup>-1</sup>. The volumetric and gravimetric methane-storage capacities at 65 bar and 298 K are approximately 180 v<sub>STP</sub>/v and 0.27 g g<sup>-1</sup>, respectively.

Well-defined metal–organic frameworks (MOFs) featuring molecular-scale pores and high internal-surface areas constitute a growing and remarkable 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. Further practical requirements for on-board applications include thermal, chemical, 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 by 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.[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<sup>4+</sup> and carboxylate oxygen atoms.[11–15] 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.[20] Reticular synthesis, a methodology based on systematic extension of organic linkers between inorganic nodes, is the first choice approach for constructing MOFs with higher sur-

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face 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 ftw (4,12-connected net) topology.\textsuperscript{(16)}

Herein, we designed and synthesized a highly porous Zr MOF, NU-1100, based on Zr\(_6\)O\(_4\)(OH)\(_4\)\textsuperscript{12-} clusters and a pyrene-based tetrapotic ligand \(4-[2-[3,6,8\text{-}tris[2\text{-(4-carboxyphenyl)]ethynyl\text{-}pyren-1\text{-}y]ethynyl\text{-}benzoic acid (L}_4\text{H}.\)

Two major design considerations in selecting the linker were: 1) the ligand should exhibit planar geometry to make the connectivity motif required for the ftw topology possible; and 2) the relative dimensions of the linker should be such that the four carboxylates define a rectangle that closely approximates a square, thereby enabling the formation of cube-like boxes upon coordination to nodes. With this in mind, we designed ligand L\(_4\)H 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.\textsuperscript{(20, 21)} The resulting model demonstrated that L\(_4\) can form a MOF with the desired topology without serious distortion of bond lengths and angles (Figure S3.1 in the Supporting Information).

The ligand L\(_4\)H was synthesized in four steps, including Sonogashira coupling reactions, followed by saponification of the resulting tetraester (Figure 1a, for synthetic details, see the Supporting Information). The structure of L\(_4\)H 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 (Figure S4.1 in the Supporting Information), which is commonly observed for conjugated systems.\textsuperscript{(20, 21)} Solvothermal reaction of L\(_4\)H, ZrOCl\(_2\)·8H\(_2\)O and benzoic acid (used as a modulator) in N,N\text{-}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 (Figure S3.2 in the Supporting Information), 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.\textsuperscript{(20, 21)} 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\(_6\)O\(_4\)(OH)\(_4\)\textsuperscript{12-} nodes linked by planar tetrapotic molecules of L\(_4\) to form two types of pores (Figure 1b and 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” (Figure 1c and d). Alternating orientations of the linker molecule in the crystal structure demonstrated a way for a twofold symmetrical ligand to be incorporated into a topology that, in principle, requires fourfold symmetrical ligands, resulting in a highly symmetric cubic space group.

Such an 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 L\(_4\)H 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 (Figure 2a). Thermal gravimetric analysis (TGA) of the “as synthesized” material showed 60% weight loss, corresponding to an equivalent accessibility by solvent molecules (Figure S5.3 in the Supporting Information). These initial results demonstrated the highly porous nature of the studied material. A TGA measurement of the NU-1100 sample activated at 120 °C revealed stability up to 500 °C (Figure S5.3 in the Supporting Information). A small weight loss was observed above approximately 200 °C for both “as synthesized” and desolvated samples, corresponding to the elimination of water molecules from Zr\(_6\)O\(_4\)(OH)\(_4\)\textsuperscript{12-} nodes.\textsuperscript{(16)}

Computationally, NU-1100 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\(_2\). To validate these predictions, we have...
thermally activated a sample of NU-1100 and studied its porosity by collecting nitrogen isotherms at 77 K, which were obtained independently at Northwestern University (NU) and the National Institute of Standards and Technology (NIST; for details, see the in the Supporting Information and Figure S5.4). Temperature-dependent high-pressure adsorption measurements were performed at NIST by using a computer-controlled Sievert apparatus, the details of which have been published elsewhere[22]. The experimental isotherms and resulting BET surface areas obtained at NU (Figure S5.7 in the Supporting Information) 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 (Figure S5.8 in the Supporting Information) and represent, to our knowledge, the highest reported to date for Zr-based MOFs. The pore volume of NU-1100, derived from the obtained 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 by using the DFT method (Figure S5.6 in the Supporting Information) are in good agreement and showed the two pore types observed in the NU-1100 crystal structure (Figure 1c).

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

Figure 3 shows CH$_4$, CO$_2$, and H$_2$ adsorption isotherms over a wide range of pressures and temperatures. Low-temperature adsorption-isotherm data are indispensable, because they provide information on the maximum gas-storage capacity of the material. The excess H$_2$ isotherm at 77 K (Figure S6.1 in the Supporting Information) showed 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,[24] 41 g/L for MOF-210,[24] 47 g/L for NU-100,[7] and 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$_2$O clusters, which are not as stable as the Zr-based NU-1100. Hydrogen uptake drops rapidly with increasing temperature. Nevertheless, NU-1100 showed a non-negligible total uptake of 0.012 g/g at 298 K and 65 bar.

Additionally, NU-1100 exhibited 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 approximately 26.2 mmol/g, corresponding to 70% of the total pore volume.

Methane-adsorption isotherms of NU-1100 are shown in Figure 3. We obtained a maximum uptake of approximately 404 v/g (38.6 mmol/L) 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 gave a pore volume of 1.54 cc/g (assuming liquid methane density at 125 K), which is in excellent agreement

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 soaking in water.

Figure 3. Total gravimetric gas-uptake isotherms for NU-1100 at various temperatures. The lines with filled circles are experimental data, whereas the solid lines are simulated isotherms by using the Dreiding force field.
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 approximately 180 v_{TP}/v and 0.27 g g^{-1}, 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 approximately 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_{TP}/v at 298 K. This value is lower than that of HKUST-1 (190 v_{TP}/v) and similar to other promising methane storage MOFs, such as UTSA-20 (170 v_{TP}/v) and PCN-14 (157 v_{TP}/v). However, the advantages that NU-1100 can offer are: 1) high gravimetric deliverable capacity (0.24 g g^{-1}), which is higher than in the abovementioned MOFs: 56% higher than in HKUST-1 (0.154 g g^{-1}), 75% higher than in PCN-14 (0.136 g g^{-1}), and 78% higher than in UTSA-20 (0.134 g g^{-1}); 2) high thermal stability; and 3) high water stability compared to the abovementioned MOFs. Simulated isotherms for CH₄, CO₂, and H₂ are in good agreement with the experimental data (Figure 3); however, there is a systematic overprediction of adsorption at all temperatures.[21]

Importantly, we have tested the cycling stability of NU-1100. Upon multiple cycles of methane adsorption/desorption, which are shown in Figure S6.7 in the Supporting Information, showing good agreement with simulated values. The magnitudes of the Q_{st} values for CH₄ and CO₂ are significantly smaller than in UiO-66, the prototypical Zr based MOF.[11, 14] In the case of UiO-66, the Q_{st} for CO₂ varies from 28 to 24 kJ mol^{-1}, whereas in NU-1100, there is a sharp decrease from 25 to 16 kJ mol^{-1} at low loading. We attribute this initial Q_{st} value to the presence of OH groups from Zr clusters as the primary adsorption sites.[14] In the case of methane, UiO-66 has a Q_{st} around 18–19 kJ mol^{-1}, whereas NU-1100 showed a Q_{st} near 11 kJ mol^{-1}. However, for smaller gas molecules, such as H₂, Q_{st} is almost the same as in UiO-66. The initial Q_{st} of 5 kJ mol^{-1} is roughly constant over the whole H₂ loading range.

In conclusion, we have synthesized and characterized a highly porous and stable Zr-based MOF material NU-1100, which exhibited very promising gas uptake for hydrogen and natural-gas-storage applications. According to PXRD and sorption measurements, NU-1100 demonstrated high stability against water. The total volumetric hydrogen adsorption at 65 bar and 77 K is 43 g L^{-1} (0.092 g g^{-1}), which places it among the best performing MOFs for hydrogen storage at low temperatures. The volumetric deliverable capacity of NU-1100 between 65 and 5 bar is approximately 160 v_{TP}/v, which is comparable to those of the most promising methane-storage materials, but its gravimetric deliverable capacity (0.24 g g^{-1}) 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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[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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