Gram-scale, high-yield synthesis of a robust metal–organic framework for storing methane and other gases†

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We have synthesized and characterized a new metal–organic framework (MOF) material, NU-125, that, in the single-crystal limit, achieves a methane storage density at 58 bar (840 psi) and 298 K corresponding to 86% of that obtained with compressed natural gas tanks (CNG) used in vehicles today, when the latter are pressurized to 248 bar (3600 psi). More importantly, the deliverable capacity (58 bar to 5.8 bar) for **NU-125** is 67% of the deliverable capacity of a CNG tank that starts at 248 bar. (For crystalline granules or powders, particle packing inefficiencies will yield densities and deliverable capacities lower than 86% and 67% of high-pressure CNG.) This material was synthesized in high yield on a gram-scale in a single-batch synthesis. Methane adsorption isotherms were measured over a wide pressure range (0.1–58 bar) and repeated over twelve cycles on the same sample, which showed no detectable degradation. Adsorption of CO_2 and H_2 over a broad range of pressures and temperatures are also reported and agree with our computational findings.

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Broader context

Natural gas is a promising alternative to petroleum-based fuels for vehicles. However, it is a challenge to store natural gas at sufficiently high densities to satisfy driving range requirements. One solution is to store natural gas at very high pressures (245 bar), which is the approach used by most natural gas powered vehicles in the United States today. Another potential solution is to use a porous material to adsorb natural gas, leading to higher densities at lower pressures. In this work we describe a novel adsorbent, the metal–organic framework **NU-125**, which is able to store at 58 bar 86% as much methane as an empty cylinder would store at 248 bar. We also show that **NU-125** can be synthesized at gram scales and can withstand multiple adsorption/desorption cycles, which demonstrates potential for future use in adsorbed natural gas (ANG) tanks.

There has been increasing interest in the use of natural gas as a transportation fuel for vehicles, especially in countries that import significant amounts of oil.[1–3] However, adoption of natural gas vehicles (NGVs) has been hindered by technical and economic barriers imposed by the high pressures required (typically 248 bar in the USA) to achieve energy densities ($\sim$9.3 MJ L^{-1}) for reasonable driving ranges.[4] The compressed natural gas (CNG) fuel tanks in current use need to be heavily reinforced, which increases their cost and weight, and they cannot be designed to conform to the shape of the vehicle as with traditional gasoline tanks. Additionally, the refueling-station infrastructure required to transport, store, and compress natural gas to such high pressures requires significant capital, which deters the investment required to build a natural gas vehicle economy.[4]

A possible solution is to use porous materials that can store natural gas within their pores in high concentration but at relatively low pressures.[5] However, porous materials that are available commercially, such as activated carbon, do not have sufficiently high storage capacities and, to date, no suitable material has been commercialized.[4]

In response to this important technological challenge, the scientific community has recently reported many novel porous materials specifically for use in NGVs with ever increasing

methane storage capacities.[6–12] Many of these materials belong to a versatile class of materials known as metal–organic frameworks (MOFs) that are synthesized by the self-assembly of modular molecular "building blocks" into stable, highly porous crystals.[13,14] Due to the modularity of the building blocks, an enormous number of MOF materials are possible, which has led to large-scale computational screening approaches to identify MOFs that would be optimal for methane storage.[15,16]

While these reports are helpful in understanding the design principles for high-capacity methane storage materials, identifying a practical material of potential commercial interest requires taking many technical considerations into account (*i.e.*, besides total capacity). The adsorbent material must have a high *deliverable* capacity (amount adsorbed at the highest pressure minus amount adsorbed at the lowest pressure), which in turn requires one to design a material around a relevant operating pressure range. A typical two-stage compressor can rapidly fill fuel tanks up to pressures in the ∼60 to 70 bar range, but higher pressures require additional compression stages.[17,18] Therefore, reducing the compression pressure from 248 bar to ∼60 to 70 bar would drastically reduce the capital cost of refueling stations, while further reductions in pressure may only provide marginal benefits. The lowest pressure is constrained by the fuel injection requirements of typical internal combustion engines (∼5 to 8 bar).[19] Thus, a practical porous material for NGVs should have a high deliverable capacity between ∼5 and 8 bar and ∼60 to 70 bar. Additionally, the porous material must be synthesized in high yield and be robust enough for repeated storage/release cycles.

Finally, materials proposed as candidates for commercialization must be validated by accurately measuring the high-pressure volumetric gas storage, which has previously been shown to critically depend on the assumed equation of state, as well as other criteria.[20]

We sought to create a material that met the multitude of constraints mentioned above and now report a new porous material, the **NU-125** MOF, that is robust, can be made in high yield on the gram-scale, and importantly, can achieve storage densities nearly as high (86%) as existing CNG tanks but at less than 1/4 the pressure. **NU-125** is synthesized from Cu^{2+} salt and a new hexa-carboxylic acid linker (see **LH₆** in Scheme 1). The synthesis and characterization of **LH₆** is described in the ESI.†
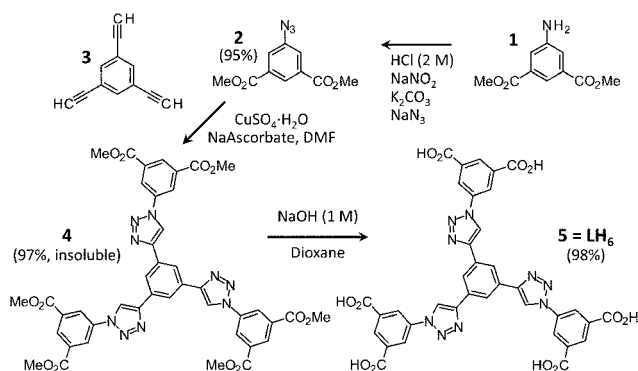
Briefly, **LH₆** was obtained *via* saponification of the corresponding hexaester precursor, which, in turn, was obtained *via* click chemistry involving **2** and **3**. (Not explored here, but clearly important for actual commercialization, are: (a) acceptable manufacturing-scale materials cost, and (b) material resilience with regard to anticipated chemical impurities.)

We investigated the scalability of this synthesis by using successively larger vessels (from a 1 dram vial up to a 1 L jar, concentrations of solvents and reagents were scaled proportionally, see Fig. 1A). In each case, we obtained **NU-125** in high yield (the smallest vial yielded 20 mg of MOF while the 1 L jar yielded 2 g of MOF). (Clearly any practical commercial use of a MOF would require upward scaling by additional orders of magnitude.) A sample from each crystalline precipitate was characterized by powder X-ray diffraction (PXRD). The measurement confirmed that the same product was obtained in each case (see Fig. 1B).

X-ray diffraction (XRD) analysis of single crystals of **NU-125** revealed a non-catenated structure with an $I4/m$ space group in which the framework nodes consist of Cu_2^{II} units coordinated by the carboxylates of L^{6-} in paddlewheel fashion (see Fig. 2). The experimental structure has unit cell dimensions of $a = b = 31.31$ Å and $c = 44.81$ Å at 225 K. The solvent-free **NU-125** structure has a density of 0.578 g cm^{-3}, which is used in converting the measured methane storage capacity to volumetric units.[21] **NU-125** has an *rht* topology, which was pioneered by Eddaoudi[22] and has since been used by us and many other groups.[23–27] **NU-125** has four distinct cages, as shown in Fig. 2. The relationship between the framework topology and the
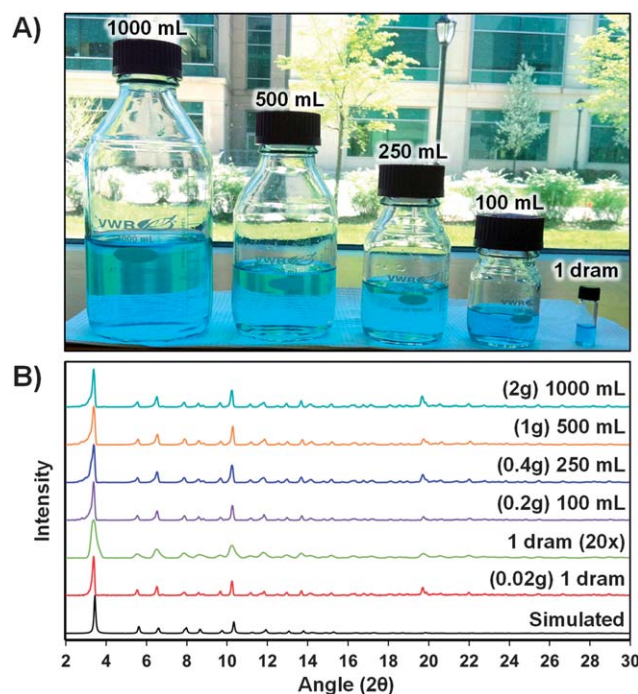

Fig. 1 Investigating the scalability of **NU-125** synthesis by using (A) successively larger vessels and (B) validating samples from each vessel *via* PXRD measurements. Indicated volumes refer to vessel size, not the amount of solvent used. Total MOF yield from each vessel is indicated in grams.
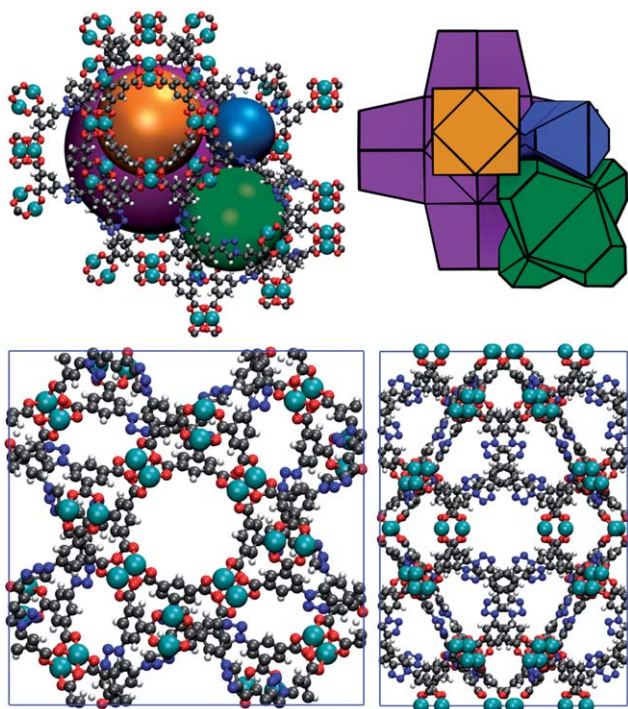

Scheme 1 Synthesis of hexa-carboxylic acid strut used to construct **NU-125** (**LH₆**).

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Fig. 2 The structure of the **NU-125** framework as revealed by X-ray analysis. Large purple, orange, green, and blue spheres indicate the largest spheres (24, 16, 15, and 11 Å, respectively) that can fit into the four distinct cages, depicted as polyhedra of the corresponding color. Small gray, white, red, blue, and cyan spheres represent carbon, hydrogen, oxygen, nitrogen, and copper atoms, respectively. Coordinated water molecules have been removed to better represent the activated structure.
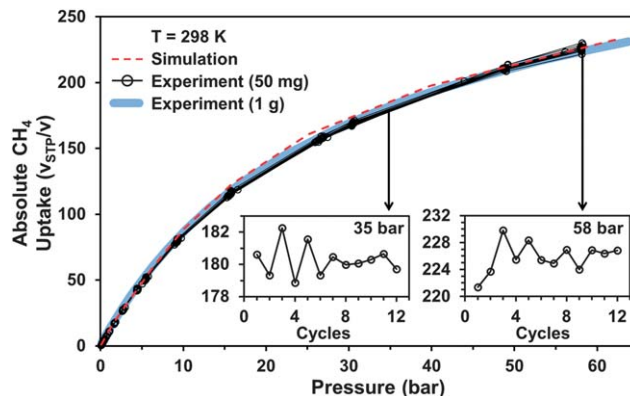

Fig. 3 High-pressure CH_4 adsorption measurements on the **NU-125** MOF at 298 K, carried out at NIST on both 50 mg and 1 g samples. Adsorption isotherms were measured in twelve successive cycles over a period of a month (only on the 50 mg sample) with no detectable sample degradation.

geometry of the four cages has been discussed in detail recently for another MOF of *rht* topology, **NU-111**.[27] The XRD-derived crystal structure was subsequently used to simulate N_2/CH_4/CO_2/H_2 gas adsorption (see ESI† for simulation details). To simulate electrostatic interactions, the atoms of the **NU-125** structure were assigned partial charges using a recently described charge equilibration method.[28–30]

After the guest solvent molecules were removed *via* supercritical CO_2 (ref. 13, 31 and 32) (see ESI† for activation details), the porosity was examined by nitrogen adsorption at 77 K. The experimental and simulated N_2 isotherms are in excellent agreement and yield similar Brunauer–Emmett–Teller[33] (BET) surface areas (3120 m^2 g^{-1} experimental *vs.* 3380 m^2 g^{-1} simulated, see Fig. S11 and S17 in the ESI†[34]). The pore volume of **NU-125**, derived from the measured N_2 isotherm, is 1.29 cm^3 g^{-1} (74% empty space), which is in good agreement with the calculated value of 1.32 cm^3 g^{-1} (76.4% porosity) by PLATON.[35] Since both the pore volume and BET surface area of **NU-125** are very close to the optimum values for methane storage at 35 bar as predicted in our earlier work,[15] we decided to explore methane and other gas storage properties of **NU-125** in detail.

Temperature-dependent high pressure adsorption measurements were performed at the Center for Neutron Research, National Institute of Standards and Technology (NIST) using a computer-controlled Sieverts apparatus, details of which have been published elsewhere[20] and are briefly

discussed in the ESI.† As shown in Fig. 3, **NU-125** has an absolute methane storage capacity at 298 K of 228 v_{STP}/v at 58 bar, which corresponds to 86% of the methane stored in a CNG tank at 248 bar.[36]

Ultimately, the deliverable capacity determines the driving range of NGVs. Here, it is as important for a porous material to have *low* capacity in the 5–8 bar range as it is for the material to have high capacity in the 60–70 bar range. Hence, **NU-125** benefits from a careful balance of strong binding sites and weakly binding surfaces, resulting in an adsorption isotherm that is not too steep at low pressures. Taking 5.8 bar as a specific lower pressure limit and 58 bar as the upper limit, Fig. 3 shows that the deliverable capacity of **NU-125** is 174 v_{STP}/v at 298 K. When compared to a CNG tank operating on the same lower pressure limit, a tank filled with **NU-125** could, in principle, deliver 67% as much fuel (although this does not take into account the powder packing density, which would necessarily reduce capacity). However, it is clear that CH_4 adsorption does not plateau at 58 bar (see Fig. 3), so that if incrementally higher pressures were attainable without incurring significant cost (*i.e.*, still using low-cost compressors), higher deliverable capacities could be obtained.

Finally, in order to test sample stability, the methane isotherm measurements were repeated (cycled) twelve times in succession over a period of one month, during which other gas isotherms such as H_2 and CO_2 were also performed. The variations in the results were on the order of 2% at 35 bar and 4–5% at 58 bar. There was no noticeable downward or upward trend between cycles, and the fluctuations may have been due to changes in the ambient temperature. The absence of sample degradation over time from cycling indicates that **NU-125** is robust, although repeated exposure to gas mixtures containing CH_4 and impurities common to natural gas would be a more realistic test.

In addition to performing multiple cycles at the same conditions, we also measured high pressure CH_4 adsorption over a wide range of temperatures *on the same sample* (see Fig. 4A). Such temperature-dependent adsorption isotherm measurements, in particular those at low temperatures, are

indispensable because they provide information on the maximal gas storage capacity of the material. For **NU-125**, we obtained about 400 v_{STP}/v methane uptake at 125 K, which effectively corresponds to the upper limit for the amount of gas that can be adsorbed under very large external pressures at ambient temperature. The observed maximum CH_4 uptake is very close to the upper limit of 440 v_{STP}/v as obtained from taking the nitrogen-based pore volume and assuming liquid methane density at 125 K. This suggests that methane is able to access most of the pores available in **NU-125** that are accessible to nitrogen at 77 K.

We also measured CO_2, and H_2 adsorption over similarly wide pressure and temperature ranges (see Fig. 4B and C). The maximum excess H_2 uptake at 77 K is about 6 wt% (Fig. S21†), which is in close agreement to what we expect from "Chahine's rule"[37] (*i.e.*, 1 wt% for every 500 m^2 g^{-1}). This empirical rule is observed for most carbon (or carbon-rich) nanoporous materials in which van der Waals interactions are the dominant mechanism for adsorption. At room temperature, we observe 1 wt% (absolute) hydrogen uptake at 65 bar. **NU-125** also exhibits significant CO_2 uptake at high pressures. The maximum CO_2 uptake at 220 K is about 32 mmol g^{-1}, which is in good agreement with the upper limit of 34.4 mmol g^{-1} as estimated from the nitrogen pore volume and liquid density of CO_2 at this temperature. The CO_2 uptake at room temperature and 30 bar is about 25 mmol g^{-1}, corresponding to filling 80% of the total pore volume. At 0.15 bar and 298 K (*i.e.*, a condition that is close to flue gas from coal power plants), the CO_2 uptake is about 3 wt%, which is lower than open-metal MOF-74 but higher than many MOFs reported in a recent CO_2 screening survey.[38]

Fig. 4 also shows our simulated isotherms, which are in excellent agreement with experiments and give further confidence to the results reported here. The agreement between theory and measurement is particularly good near room temperature, at which the interactions with open-metal sites are likely less important. For all gases, there is a small but systematic over-prediction of adsorption at lower temperatures.

In order to get better insight into the nature of the adsorption sites and interactions in **NU-125**, we extracted isosteric heats of adsorption (Q_{st}) from the temperature-dependent isotherms shown in Fig. 4 using the Clausius–Clapeyron equation.[20] (All isotherms were used; see ESI† for further details.) The results are summarized in Fig. 5. The magnitudes of the Q_{st} values are consistent with other Cu-based paddlewheel MOFs. For both CH_4 and H_2, the Q_{st} value is high initially and then drops after ~4 mmol g^{-1} are adsorbed.[39] Interestingly, this corresponds closely with the amount of gas required to populate the open Cu sites: 3.1 mmol g^{-1}. However, the density of C_2N_3 rings in **NU-125** is the same as open Cu sites; hence, it is not clear from Q_{st} data which of these two sites binds guest molecules first. The behavior of Q_{st} with CO_2 loading is quite different. CO_2 shows an initial slight decrease, as in the case of H_2 and CH_4, but then begins to increase. We attribute this
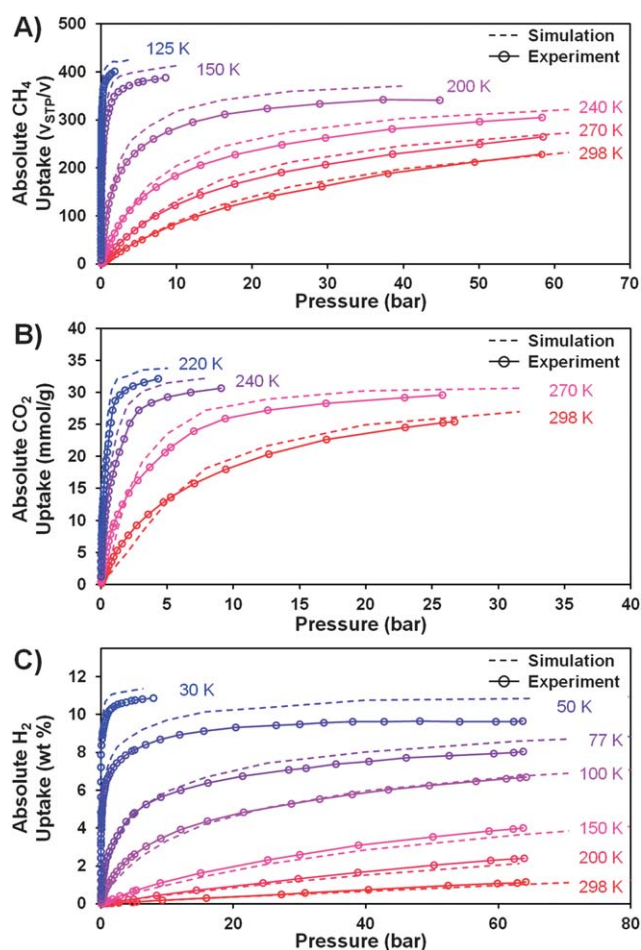

Fig. 4 High-pressure (A) CH_4, (B) CO_2, and (C) H_2 absolute adsorption isotherms measured and simulated over a broad range of temperatures. Excess isotherms are provided in the ESI (see Fig. S21†).
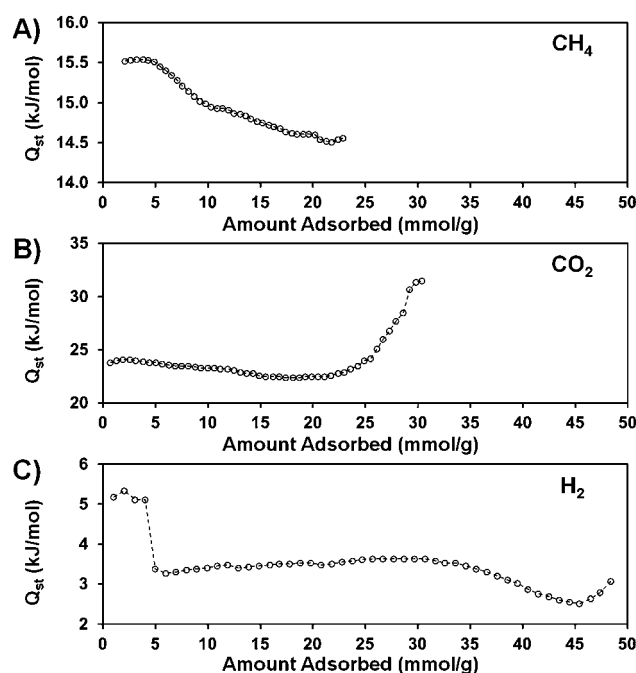

Fig. 5 Isosteric heats of adsorption (Q_{st}) for (A) CH_4, (B) CO_2, and (C) H_2 as a function of gas loading in mmol(gas) g^{-1}(MOF). In each case, absolute adsorption data were used to obtain Q_{st} values.

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increase to attractive CO_2–CO_2 interactions, which become important at higher loading. We are planning to carry out detailed neutron scattering studies to determine the binding sites in **NU-125** and will publish those results in due course.

In conclusion, we have synthesized and characterized a stable, robust, and promising material for potential use in natural-gas powered vehicles. We have demonstrated that the synthesis is scalable to the gram level and that the deliverable CH_4 capacity, under reasonable operating pressure range assumptions (but neglecting particle packing inefficiencies), is 67% of what can be delivered by CNG tanks in use today but at only 23% of the pressure. Our computational simulations agree very well with measurements over a wide pressure and temperature range. We have also shown that this material may be useful in high-pressure CO_2 and H_2 related applications.

Acknowledgements

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