Porous metal–organic frameworks with Lewis basic nitrogen sites for high-capacity methane storage†

Bin Li,a Hui-Min Wen,a Hailong Wang,a Hui Wu,b Taner Yildirim,bc Wei Zhou*b and Banglin Chen*a

The use of porous materials to store/deliver natural gas (mostly methane) in vehicles requires large amounts of methane being stored per unit volume. In this work, we report several porous metal–organic frameworks (MOFs) with NOTT-101 type structures, containing Lewis basic nitrogen sites through the incorporation of pyridine, pyridazine, and pyrimidine groups into the organic linkers. They exhibit significantly higher total volumetric methane storage capacities (~249–257 cm³ (STP) cm⁻³ at room temperature (RT) and 65 bar) than NOTT-101a (here the MOF abbreviation with “a” at the end represents the fully activated MOF). The most significant enhancement was observed on UTSA-76a with functional pyrimidine groups (237 cm³ (STP) cm⁻³ in NOTT-101a vs. 257 cm³ (STP) cm⁻³ in UTSA-76a). Several multivariate (MTV) MOFs constructed from two types of organic linkers (pyrimidine-functionalized and unfunctionalized) also show systematically improved methane storage capacities with increasing percentage of functionalized organic linkers. The immobilized functional groups have nearly no effect on the methane uptakes at 5 bar but significantly improve the methane storage capacities at 65 bar, so the reported MOFs exhibit excellent methane storage working capacities of ~188–197 cm³ (STP) cm⁻³.

Broader context
Natural gas (NG), mainly methane, has long been considered as a viable alternative energy resource to replace conventional petroleum-based fuels for vehicles because of its abundant supply and relatively low CO₂ emission. Among diverse porous materials, the emerging porous metal–organic frameworks have shown bright promise for methane storage applications. This work demonstrates that the methane storage total capacities and working capacities of porous MOFs can be significantly increased through the immobilization of Lewis basic nitrogen sites in the organic linkers. Our findings suggest that the incorporation of suitable functional groups into MOFs could be a general and effective approach to further increase the methane storage and working capacities of MOFs.

Introduction
The research and application of clean energy have become more and more important for our daily life than perhaps ever before due to concerns over global energy crisis, ground-level air quality, and climate change. Among the possible fuels, natural gas (NG), whose component is mainly methane, has long been considered as a viable alternative energy resource to replace current conventional petroleum-based fuels because of its abundant reserves and relatively low CO₂ emission. However, a current challenge for the widespread use of natural gas as an alternative vehicular fuel is the development of technologies and materials to efficiently and safely store and deliver it under ambient temperature and moderate pressure. Although compressed natural gas (CNG), stored as a supercritical fluid at room temperature and 200–300 bar in steel cylinders, is currently used in vehicles powered by natural gas, the large tank size required restricts its application to larger vehicles such as trucks. For everyday use in passenger vehicles, adsorbed natural gas is better suited in terms of both cost and safety.
The use of adsorption-based storage technology depends on the development of efficient adsorption materials. Among diverse porous adsorbents for methane storage, porous metal-organic frameworks (MOFs) are known to be promising due to their high porosities, tunable pores, and versatile chemistry.\textsuperscript{1-4} In fact, BASF has demonstrated model vehicles fuelled with natural gas stored using MOF materials,\textsuperscript{5} and recently stated that it is ready to market a methane-storage system filled with MOF materials in 2015.\textsuperscript{5} Furthermore, the Advanced Research Projects Agency-Energy (ARPA-E) of the U.S. Department of Energy (DOE) has also recently set new methane storage targets to guide the research on adsorbent based methane storage systems, with the ambitious goal of a volumetric storage capacity of 350 cm\(^3\) (STP: 273.15 K, 1 atm) cm\(^{-3}\) and a gravimetric storage capacity of 0.5 g (CH\(_4\)) g\(^{-1}\) (adsorbent) at room temperature. Even if we do not consider the adsorbent material packing loss, the new volumetric target still needs to be 263 cm\(^3\) (STP) cm\(^{-3}\), which is equivalent to that of CNG at 250 bar and 298 K.\textsuperscript{6}

To meet the new targets set by the DOE MOVE program, there has been growing interest in the investigation of MOFs with high methane storage capacities in recent years.\textsuperscript{6-12} A variety of factors such as open metal sites (OMSs), pore spaces, pore metrics (pore size distributions) and framework densities have been demonstrated to affect the performance (total volumetric and gravimetric uptake) of MOF materials for methane storage.\textsuperscript{8-12} In the past two decades, a large number of MOFs such as HKUST-1,\textsuperscript{13} UTSA-76,\textsuperscript{14} NU-125,\textsuperscript{10a} UTSA-20,\textsuperscript{9} MOF-177,\textsuperscript{15} NOTT-101,\textsuperscript{16} and PCN-14\textsuperscript{17} have been developed as potential absorbents for methane storage. Two independent groups have reported that HKUST-1 exhibits an exceptionally high volumetric methane storage capacity of 267 cm\(^3\) (STP) cm\(^{-3}\) and a working capacity of 190 cm\(^3\) (STP) cm\(^{-3}\) at room temperature and 65 bar.\textsuperscript{6c,13} This is the first MOF material whose volumetric methane storage capacity has potentially met the new DOE target when the packing loss is ignored. Although significant progress has been made on the volumetric methane storage capacities, their working capacities (defined here as a deliverable amount of methane between 65 and 5 bar) are still far away from the new DOE targets. Recently, Simon \textit{et al.} used a materials genome approach to computationally screen over 650,000 porous crystalline adsorbents, and suggested that there may exist a physical up-limit on their methane storage capacities, and it may be difficult to reach the current DOE targets for adsorption-based methane storage.\textsuperscript{18} Such a situation has motivated chemists and material scientists to develop novel approaches to target new porous materials whose methane storage capacities can be much higher than those conventional ones.

The effects of functional groups/sites within porous MOFs on their gas separations have been well documented.\textsuperscript{19,20} There has also been a lot of work carried out on the immobilization of open metal sites for their gas storage. However, porous MOFs with only open metal sites have some limitation for methane storage, because these open metal sites significantly contribute to the high methane storage capacities at a low pressure of 5 bar, so their methane storage working capacities are very difficult to be further optimized. This is particularly demonstrated by the MOF-74 series, whose maximal methane storage working capacity is only ~142 cm\(^3\) (STP) cm\(^{-3}\) for MgMOF-74.\textsuperscript{8c} The ideal porous MOFs for high methane storage and working capacities are those with suitable functional sites, which can significantly enhance methane storage capacities at higher pressure (for example, 65 bar) but have minimal effects on methane storage capacities at 5 bar. With this in mind, we herein chose NOTT-101 as the fundamental framework backbone because of its high methane storage capacity and easily adjustable functionality on the center phenyl rings.\textsuperscript{16,21} We present two approaches to functionalize the pores of the NOTT-101 framework: synthesis of new functional ligands with Lewis basic nitrogen sites, and mixing of linkers bearing different functionalities. To avoid changing the Brunauer–Emmett–Teller (BET) surface areas and/or pore volumes of the frameworks significantly (so that we can isolate the effect of functional groups), three functional linkers were specially designed and synthesized by simply using pyridine, pyridazine, and pyrimidine groups to replace the center phenyl ring of the ligand of NOTT-101 (Scheme 1). All functional linkers have been successfully used to construct isoreticular NOTT-101 structures, namely ZJU-5, UTSA-75, and UTSA-76, respectively. Furthermore, by mixing two different types of linkers (H\(_4\)L\(_1\) and H\(_4\)L\(_4\)), three multivariate (MTV) MOFs of different ratios of these two linkers were also prepared with the iso-structural NbO net. As expected, the activated MOFs reported here have comparable BET surface areas and pore volumes to those of NOTT-101a (the MOF abbreviation without “a” represents the as-synthesized material, while the one with “a” at the end represents the fully activated material). However, the functionalized MOFs with Lewis basic nitrogen sites show notably higher volumetric methane storage capacities and working capacities than those of NOTT-101a. The maximal enhancement was realized on UTSA-76a with functional pyrimidine groups, where the methane storage working capacity gets significantly improved from 181 cm\(^3\) (STP) cm\(^{-3}\) in NOTT-101a to 197 cm\(^3\) (STP) cm\(^{-3}\) in UTSA-76a. In our MTV-MOFs, as the percentage of incorporated functionalities increases, the volumetric methane storage and working capacities are also systematically improved. These results suggest that incorporation of suitable functional groups into MOFs can indeed improve both the total volumetric methane storage and working capacities, which provides a new promising route to target some new porous MOFs with higher methane storage and working capacities.

\begin{scheme}
\begin{center}
\includegraphics[width=\textwidth]{Scheme1.png}
\end{center}
\end{scheme}

\textbf{Scheme 1} Schematic structure of the organic ligands H\(_4\)L\(_1\)–H\(_4\)L\(_4\) that serve as linkers in NOTT-101 (a), ZJU-5 (b), UTSA-75 (c), and UTSA-76 (d), respectively.
Experimental section

General procedures and materials

All reagents and solvents were commercially available and used without further purification. Organic linkers of H4L1,33 H4L2,34 and H4L431 were prepared according to the literature procedure. The organic linker H4L3 was prepared through Suzuki cross-coupling reactions as detailed in the ESL.1 1H NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The coupling constants were reported in Hertz. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. The elemental analyses were performed using Perkin-Elmer 240 CHN analyzers from Galbraith Laboratories, Knoxville. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku Ultima IV diffractometer operated at 40 kV and 40 mA with a scan rate of 1.0 deg min⁻¹.

Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh samples were guest-exchanged with dry acetone at least 10 times, filtered and degassed at room temperature. All reagents and solvents were commercially available and used without further purification. Organic linkers of H4L1,33 H4L2,34 and H4L431 were prepared according to the literature procedure. The organic linker H4L3 was prepared through Suzuki cross-coupling reactions as detailed in the ESL.1 1H NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The coupling constants were reported in Hertz. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. The elemental analyses were performed using Perkin-Elmer 240 CHN analyzers from Galbraith Laboratories, Knoxville. Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) patterns were measured using a Rigaku Ultima IV diffractometer operated at 40 kV and 40 mA with a scan rate of 1.0 deg min⁻¹.

Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh samples were guest-exchanged with dry acetone at least 10 times, filtered and degassed at room temperature (296 K) for one day, and then at 373 K for another 24 hours. Gas sorption measurements

General preparation of MOF materials

The samples of UTSA-76 and ZJU-5 were synthesized using methods reported in the corresponding literature.14,20b All other MOFs were prepared based on the methods as follows. The phase purity of the bulk materials was confirmed by PXRD (Fig. S3–S7, ESI†).

Synthesis of UTSA-75. A mixture of the organic linker H4L3 (15.0 mg, 0.037 mmol) and Cu(NO3)2·2.5H2O (30.0 mg, 0.129 mmol) was dissolved into a 8 mL mixed solvent (DMF/MeCN/H2O, 6/1/1, v/v) in a screw-capped vial (20 mL). 50 μL of 37% HCl was added. The vial was capped and heated in an oven at 80 °C for 24 h. Blue block crystals were obtained by filtration and washed with DMF several times to afford UTSA-75 in 70% yield. UTSA-75 has a best formula as [Cu4L3(H2O)2]·3DMF·5H2O, which was obtained based on the single-crystal X-ray structure determination, elemental analysis and TGA. Anal. calcd for C27H49N5O5Cu4: C, 43.89; H, 5.38; N, 7.61; found: C, 43.79; H, 5.37; N, 7.69. TGA data for loss of 3DMF and 7H2O: calcd: 42.14%, found: 42.11%. IR (neat, cm⁻¹): 1629, 1589, 1450, 1354, 1248, 1082, 772, 726, 660.

Synthesis of UTSA-77. The organic linker H4L1 (12.0 mg, 0.03 mmol), H4L4 (3.0 mg, 0.0075 mmol) and Cu(NO3)2·2.5H2O (30.0 mg, 0.129 mmol) were dispersed into a 8 mL mixed solvent (DMF/MeCN/H2O, 6/1/1, v/v) in a screw-capped vial (20 mL), and then 50 μL of 37% HCl was added. The vial was capped and heated in an oven at 80 °C for 24 h. Blue block crystals were obtained by filtration and washed with DMF several times to afford UTSA-77. Yield: 67%. UTSA-77 has a best formula as [Cu(L1)0.6(L4)0.4(H2O)2]·4DMF·4H2O, which was obtained based on the 1H NMR, elemental analysis and TGA. Anal. calcd for C33H56N8O18Cu2: C, 43.89; H, 5.38; N, 6.62; found: C, 43.79; H, 5.37; N, 6.66. TGA data for loss of 4DMF and 6H2O: calcd 43.10%, found: 43.14%. IR (neat, cm⁻¹): 1621, 1589, 1450, 1395, 1252, 1090, 1038, 772, 717, 660.

Synthesis of UTSA-78. Synthesis of UTSA-78 is similar to that of UTSA-77 except using 5.0 mg H4L1 and 10.0 mg H4L4. Yield: 71%. UTSA-78 has a best formula as [Cu3(L1)0.6(L4)0.4(H2O)2]·4DMF·5H2O, which was obtained based on the 1H NMR, elemental analysis and TGA. Anal. calcd for C33.6H49.6N4.4O18Cu2: C, 41.83; H, 5.35; N, 7.68. TGA data for loss of 4DMF and 6H2O: calcd: 43.04%, found: 44.12%. IR (neat, cm⁻¹): 1629, 1589, 1450, 1395, 1252, 1090, 1038, 772, 717, 660.

Synthesis of UTSA-79. Synthesis of UTSA-79 is similar to that of UTSA-77 except using 3.0 mg H4L1 and 12.0 mg H4L4. Yield: 69%. UTSA-79 has a best formula as [Cu4(L1)0.6(L4)0.4(H2O)2]·4DMF·4H2O, which was obtained based on the 1H NMR, elemental analysis and TGA. Anal. calcd for C32.7H48.7N5.0O18Cu2: C, 41.78; H, 5.24; N, 8.42; found: C, 41.76; H, 5.23; N, 8.48. TGA data for loss of 4DMF and 6H2O: calcd: 43.05%, found: 42.92%. IR (neat, cm⁻¹): 1653, 1625, 1589, 1442, 1359, 1248, 1098, 1046, 769, 752, 725, 653.

Results and discussion

MOF structures and permanent porosities investigated for methane storage

The crystal structures of the MOFs investigated in this work are schematically shown in Fig. 1. Single-crystal X-ray diffraction analysis reveals that all these MOFs are isoreticular to NOTT-101. As described in previous published studies, the frameworks
consist of paddle-wheel dinuclear Cu$_2$(COO)$_4$ secondary building units (SBUs) and organic linkers, which are bridged together to form 3D NbO-type structures.$^{19}$

The frameworks contain two types of cages: one cuboctahedral cage of about 10.2 Å in diameter, and another large irregular elongated cage of about 9.6 $\times$ 22.3 Å$^2$ (Fig. 1). Because of the incorporation of functional organic groups, the pore surfaces within these isoreticular MOFs are slightly different.

To estimate the surface area and pore volume, nitrogen adsorption isotherms at 77 K were examined on the activated MOFs. As shown in Fig. S9–S14 (see ESI†), all N$_2$ isotherms exhibit reversible type-I behavior without any hysteresis, characteristic of microporous materials. The BET surface areas, pore volumes, densities of the activated structures, and the volumetric metal and nitrogen atom concentrations are summarized in Table 1. As expected, the BET surface areas and pore volumes of the new MOFs are comparable to those of NOTT-101a, and are in good agreement with the theoretical pore volumes (−1.02−1.05 cm$^3$ g$^{-1}$) calculated based on their X-ray single-crystal structures. These MOFs also have similar volumetric metal concentrations. However, they contain different concentrations of Lewis basic nitrogen sites due to the introduction of different functional groups. As shown in Table 1, UTSA-75a and UTSA-76a show the highest nitrogen concentrations (~2.64 mmol cc$^{-1}$). Despite the nearly identical structures, BET surface areas and pore volumes, the different concentrations of Lewis basic nitrogen sites in the pores of functionalized MOFs may result in different methane storage performances, particularly methane storage working capacities.

**Functionalization of NOTT-101 for high-capacity methane storage**

We examined the methane storage capacities of three functionalized MOFs: ZJU-5a, UTSA-75a, and UTSA-76a, and compared with NOTT-101a. Detailed methane adsorption isotherm data are shown in Fig. S15–S17 (see ESI†). Let us first consider the volumetric methane storage capacity. As shown in Fig. 2, NOTT-101a exhibits the lowest total volumetric methane storage capacity of 237 cm$^3$ (STP) cm$^{-3}$ at 65 bar and RT among the investigated MOFs. When pyridine groups were incorporated into the framework, the methane storage capacity of ZJU-5a was increased to 249 cm$^3$ (STP) cm$^{-3}$. The volumetric methane storage capacities can be further improved in UTSA-75a and UTSA-76a by incorporation of pyridazine and pyrimidine groups into NOTT-101a, respectively. The most significant enhancement was realized on UTSA-76a with functional pyrimidine groups. Fig. S21 (see ESI) shows the comparison of the total volumetric methane storage capacities at 298 K between UTSA-76a and NOTT-101a. It is notable that the volumetric uptake at 65 bar and 298 K can be remarkably improved from 237 cm$^3$ (STP) cm$^{-3}$ in NOTT-101a to 257 cm$^3$ (STP) cm$^{-3}$ in UTSA-76a. The gravimetric methane storage capacities of the reported MOFs of 0.257–0.263 g (CH$_4$) g$^{-1}$ are also systematically higher than NOTT-101a of 0.247 g (CH$_4$) g$^{-1}$ (see Fig. S21, ESI†).

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**Table 1** Structural parameters of the MOFs studied in this work

<table>
<thead>
<tr>
<th>MOFs</th>
<th>$S_{BET}^a$ (m$^2$ g$^{-1}$)</th>
<th>$V_p^b$ (cm$^3$ g$^{-1}$)</th>
<th>$D_e^c$ (g cm$^{-3}$)</th>
<th>N$^d$ (mmol cc$^{-1}$)</th>
<th>Metal$^e$ (mmol cc$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTSA-75a</td>
<td>2838</td>
<td>1.06</td>
<td>0.698</td>
<td>2.63</td>
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<tr>
<td>UTSA-76a</td>
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<td>1.09</td>
<td>0.699</td>
<td>2.64</td>
<td>2.64</td>
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<tr>
<td>ZJU-5a</td>
<td>2829</td>
<td>1.08</td>
<td>0.679</td>
<td>2.58</td>
<td>2.56</td>
</tr>
<tr>
<td>UTSA-77a</td>
<td>2807</td>
<td>1.08</td>
<td>0.690</td>
<td>0.52</td>
<td>2.61</td>
</tr>
<tr>
<td>UTSA-78a</td>
<td>2840</td>
<td>1.09</td>
<td>0.694</td>
<td>1.75</td>
<td>2.62</td>
</tr>
<tr>
<td>UTSA-79a</td>
<td>2877</td>
<td>1.08</td>
<td>0.697</td>
<td>1.97</td>
<td>2.63</td>
</tr>
<tr>
<td>NOTT-101a</td>
<td>2805</td>
<td>1.08</td>
<td>0.688</td>
<td>0</td>
<td>2.61</td>
</tr>
</tbody>
</table>

$a$ BET surface areas calculated from N$_2$ isotherms at 77 K. $b$ Pore volumes calculated from the maximum amounts of N$_2$ adsorbed. $c$ Framework densities of fully activated MOFs without guest molecules and terminal waters. $d$ The volumetric concentrations of nitrogen sites in the frameworks. $e$ The volumetric concentrations of open copper sites in the frameworks.

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**Fig. 1** Crystal structures of NOTT-101 (grey), ZJU-5 (green), UTSA-75 (yellow), and UTSA-76 (red). Spheres denote pores within the frameworks.

**Fig. 2** The experimental total volumetric methane storage capacities at 65 bar and room temperature of NOTT-101a (grey), ZJU-5a (green), UTSA-75a (yellow), and UTSA-76a (red), indicating that the methane uptake can be gradually improved by incorporating varied functional groups into NOTT-101a.
MTV-MOFs for methane storage: mixing of functionalities within the NOTT-101 framework

In order to further validate the fact that the introduction of functional groups within the pores of NOTT-101a can indeed improve the methane storage capacities, we synthesized three MTV-MOFs (termed as UTSA-77, UTSA-78 and UTSA-79, respectively) in which two types of linkers (H₄L4 and H₂L1) with the ratio of 1:4, 2:1, and 4:1, respectively, were assembled into the frameworks. The MTV-MOFs with the general formula of \[[\text{Cu}_2(L1)_{x}(L4)_y(H_2O)_z]·nDMF·mH_2O\] \(x = 0.20, 0.33, \) and \(0.80\) can be readily synthesized by varying the original molar ratios of these two ligands through the same synthetic procedures. The molar ratios of the two ligands in the resulting MOFs match well with the original molar ratios of two ligands in the starting reaction mixture, which were confirmed by ¹H NMR spectra of their acid-digested samples. As shown in Fig. 3, the proton signals of UTSA-78 from each linker can be assigned based on their chemical shifts. The corresponding linker ratio for L1:L4 was calculated to be 1:2. Similarly, the linker ratios in UTSA-77 and UTSA-79 were estimated to be 4:1 and 1:4, respectively (Fig. S22 and S23, ESI†). In addition, the formation of highly crystalline and phase-pure MTV-MOFs was confirmed by PXRD analyses of the as-synthesized samples (Fig. S5–S7, ESI†). No extra diffraction peaks were observed from the experimental PXRD patterns in these MTV-MOFs, revealing that these MTV-MOFs are isoreticular to NOTT-101 and UTSA-76.

We further examined the high-pressure methane sorption isotherms of these MTV-MOFs, and compared with NOTT-101a. Detailed methane adsorption isotherm data are shown in Fig. S18–S20 (see ESI†). As mentioned earlier, all three MTV-MOFs have comparable BET surface areas and pore volumes with NOTT-101a and UTSA-76a. As shown in Fig. 4, NOTT-101a exhibits the lowest volumetric uptake of 237 cm³ (STP) cm⁻³. When the input ratio of pyrimidine groups reaches 20%, a notable increase in the volumetric methane storage capacity was observed in UTSA-77a (249 cm³ (STP) cm⁻³, Fig. 4). After that, a relatively slow increase was found in UTSA-78a and UTSA-79a when the ratio was further increased to 66.7% and 80%, respectively. Finally, UTSA-76a with a 100% ratio of pyrimidine groups exhibits the highest methane storage capacity of 257 cm³ (STP) cm⁻³. Similarly, this increasing trend was also observed for the gravimetric methane storage capacities (Table 2). These findings once again demonstrate that pyrimidine groups have significant effects on enhancing the methane storage capacities.

Methane storage working capacity

We note that the methane storage working capacity (also called “deliverable capacity”), defined here as the difference of the amount of methane adsorbed between 65 and 5 bar, is more important than the total methane storage capacities, because it determines the driving range of vehicles powered by natural gas. Based on room temperature adsorption isotherms, we can estimate the methane storage deliverable amount under isothermal conditions. This is illustrated in Fig. 5, using UTSA-75a as an example.

The methane storage working capacities are summarized in Table 2. Among the seven MOFs studied here, NOTT-101a without functional groups has the lowest methane storage working capacity. When the varied functional groups were incorporated into the pores of NOTT-101a, the functionalized MOFs show similar methane storage capacities with NOTT-101a at (or below) 5 bar (Table 2). This is because these MOFs have similar concentrations of open Cu sites (Table 1), which determines the methane adsorption amount at low pressure.²⁵ However, their methane storage capacities at 65 bar have been significantly improved compared with NOTT-101a. As a result, the methane storage working capacity can be greatly improved...
from 181 cm$^3$ (STP) cm$^{-3}$ in NOTT-101a to 188 cm$^3$ (STP) cm$^{-3}$ in ZJU-5a, 192 cm$^3$ (STP) cm$^{-3}$ in UTSA-75a, and then 197 cm$^3$ (STP) cm$^{-3}$ in UTSA-76a. Most importantly, the methane storage working capacities of UTSA-75a (192 cm$^3$ (STP) cm$^{-3}$) and UTSA-76a (197 cm$^3$ (STP) cm$^{-3}$) are higher than that of HKUST-1 (190 cm$^3$ (STP) cm$^{-3}$), setting a new record for methane storage among all the reported MOFs so far. The effect of the immobilized functional sites on improving the methane storage working capacities was also confirmed by the MTV-MOFs. It is clear that the methane storage working capacities can be enhanced by the increased ratios of pyrimidine groups (Table 2).

As discussed earlier, the incorporation of high densities of OMSs into MOFs can effectively enhance the total methane storage capacities. The representative examples are NiMOF-74 (7.74 mmol cm$^{-3}$) and CoMOF-74 (7.25 mmol cm$^{-3}$) with exceptionally high densities of OMSs. They show high methane storage capacities of 251 cm$^3$ (STP) cm$^{-3}$ and 249 cm$^3$ (STP) cm$^{-3}$ at 65 bar and RT, respectively. However, the high densities of OMSs also led to high methane adsorption at 5 bar, 122 and 113 cm$^3$ (STP) cm$^{-3}$ for NiMOF-74 and CoMOF-74, respectively. Accordingly, MOF-74 series have quite low methane storage working capacities, in the range of ~120–140 cm$^3$ (STP) cm$^{-3}$.

Compared to HKUST-1, the higher methane storage working capacities of UTSA-75a and UTSA-76a are attributed to their lower methane uptakes at 5 bar of 260 cm$^3$ (STP) cm$^{-3}$. Because the MOFs reported here have higher pore volumes and lower densities of OMSs, their methane storage capacities at 5 bar (~60 cm$^3$ (STP) cm$^{-3}$) are systematically lower than that of HKUST-1 (77 cm$^3$ (STP) cm$^{-3}$). The incorporation of Lewis basic nitrogen sites significantly enhances their methane storage capacities at 65 bar, leading to the MOF materials of UTSA-75a and UTSA-76a with the record methane storage working capacities. As a result, compared to those containing high densities of OMSs, the functionalized MOFs with suitable functional sites and lower densities of OMSs might be the better choice for achieving high working capacity.

Mechanistic analysis of the role of the functional groups

The high methane storage and working capacities of the functionalized MOFs are very encouraging. To investigate the origin of the enhanced methane uptakes within these MOFs, we need to first carefully compare them with NOTT-101a structurally. According to the experimental X-ray diffraction data, all the functionalized MOFs and NOTT-101a are isoreticular. Lattice parameters of the fully activated samples are very close. Clearly, the difference in methane storage of these MOFs at room temperature is not due to a change in pore geometry. Diffraction data and experimental pore volumes also demonstrated that all the MOF samples are highly crystalline, consisting of pure single phases, and fully activated, so it is not likely that the methane adsorption capacity difference between these MOFs and NOTT-101a is because of variations in sample quality. Therefore, the difference of methane storage performance between these functionalized MOFs and NOTT-101a must have an intrinsic origin related to the functional groups themselves.

Naturally, one would ask whether the Lewis basic N sites on the functionalized linkers would provide specific binding to methane molecules. Our DFT-D (dispersion-corrected density-functional theory) calculations on UTSA-76a did not seem to indicate an apparent CH$_4$ binding enhancement on the pyrimidine ring. However, for UTSA-75a, our calculations clearly show that there indeed exists an increased CH$_4$ affinity for the Lewis basic N sites. DFT calculations without vdW (van der Waals) correction show that the methane adsorption on the pyridazine ring of UTSA-75a and the central phenyl ring of NOTT-101a exhibits roughly the same binding energies, both being ~40% lower than that of methane adsorbed on the open

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Table 2

<table>
<thead>
<tr>
<th>MOFs</th>
<th>Total storage capacity$^a$ at 65 bar (35 bar)</th>
<th>Working capacity$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g g$^{-1}$ cm$^3$ cm$^{-3}$ Density (g cm$^{-3}$)</td>
<td>g g$^{-1}$ cm$^3$ cm$^{-3}$</td>
</tr>
<tr>
<td>ZJU-5a</td>
<td>0.262 (0.212) 249 (201) 0.179</td>
<td>0.198 (0.148) 188 (140) 14.15</td>
</tr>
<tr>
<td>UTSA-75a</td>
<td>0.257 (0.210) 251 (205) 0.180</td>
<td>0.197 (0.150) 192 (146) 14.93</td>
</tr>
<tr>
<td>UTSA-76a</td>
<td>0.263 (0.216) 257 (211) 0.185</td>
<td>0.201 (0.154) 197 (151) 15.44</td>
</tr>
<tr>
<td>UTSA-77a</td>
<td>0.258 (0.210) 249 (202) 0.179</td>
<td>0.195 (0.146) 188 (141) 15.04</td>
</tr>
<tr>
<td>UTSA-78a</td>
<td>0.260 (0.213) 252 (207) 0.180</td>
<td>0.197 (0.150) 191 (146) 15.09</td>
</tr>
<tr>
<td>UTSA-79a</td>
<td>0.262 (0.213) 255 (207) 0.183</td>
<td>0.198 (0.149) 193 (145) 14.65</td>
</tr>
<tr>
<td>NOTT-101a</td>
<td>0.247 (0.202) 237 (194) 0.169</td>
<td>0.189 (0.144) 181 (138) 15.49</td>
</tr>
</tbody>
</table>

$^a$ At 298 K. $^b$ Defined as the difference of the amount of methane adsorbed between 65 (35) bar and 5 bar.
Cu site. This means that there is likely no specific strong interaction (other than the vdW-type interaction) between the methane molecule and the Lewis basic N sites. With dispersive interactions explicitly included, DFT-D calculations show that the methane adsorption next to the Lewis basic N site of the pyridazine ring is ~10% stronger than on the phenyl ring. Therefore, this binding strength improvement is largely vdW-type in nature.

Based on this analysis, it is clear that the Lewis basic N sites are not really new strong adsorption sites (with CH$_4$ binding strength comparable to the open Cu sites) in these functionalized MOFs. Then, how does the slightly enhanced adsorption affinity for these sites result in an improved methane storage performance? At RT and low pressure of 5 bar, strong CH$_4$ binding sites such as open metal sites dominate the methane adsorption amount, and according to the previous studies,$^{25}$ ~60% of these sites are populated. At RT and increased pressure, the contribution of weaker adsorption sites/non-specific pore surface starts to kick in. Indeed, at a high pressure of 65 bar, the strong adsorption sites would have been largely occupied. So the difference would be mainly on the secondary adsorption sites and general pore surface. For the functionalized MOFs with overall better secondary adsorption surfaces, the uptake at high pressure would be higher because of the enhanced vdW interactions between Lewis basic N and methane molecules.

There is one additional factor that also contributes positively to the methane uptakes at high pressure in these functionalized MOFs. The N sites in the functionalized linkers substitute the corresponding –CH$_2$ groups in NOTT-101a, and can lead to relatively large rotational freedom of the center rings of the linkers. For example, we reported recently that the UTSA-76a linker central ring (pyrimidine) has a much shallower rotational barrier (~8.2 kJ mol$^{-1}$ for pyrimidine in UTSA-76a vs. ~20.2 kJ mol$^{-1}$ for phenyl in NOTT-101a), and thus is significantly more “dynamic” than the NOTT-101a linker central ring (phenyl).$^{14}$ The center “dynamic” pyrimidine rings within UTSA-76a can more readily adjust their orientations than the central phenyl rings within NOTT-101a, thus optimizing the methane packing at high pressure. The same is likely true for other functionalized MOFs reported in this work as well.

Overall, we believe that it is the synergistic effect of these two factors that leads to an improved methane storage performance. At a low pressure of 5 bar, the functionalized MOFs and NOTT-101a show the similar uptakes due to the similar concentrations of open metal sites. However, at higher loadings of methane, the functionalized MOFs can adsorb more methane because of the enhanced vdW interaction with methane molecules and the “dynamic” functional groups, thus leading to the higher methane storage total and working capacities.

Conclusions

In this work, we have demonstrated that the incorporation of functional groups with Lewis basic nitrogen sites, including pyridine, pyridazine and pyrimidine groups, into the pores of NOTT-101 can significantly improve the total volumetric methane storage capacities, whose values at 65 bar and RT can be enhanced from 237 cm$^3$ (STP) cm$^{-3}$ in NOTT-101a to ~249–257 cm$^3$ (STP) cm$^{-3}$ in the functionalized MOFs. This is because these immobilized functional groups have a negligible effect on the methane storage capacities at 5 bar but a significant enhancement in the methane storage capacities at a high pressure of 65 bar. As a result, these functionalized MOFs exhibit impressively high methane storage working capacities of ~188–197 cm$^3$ (STP) cm$^{-3}$, setting a new record methane storage working capacity for their potential transport applications. Computational analyses indicated that the Lewis basic nitrogen sites and dynamic freedom of the functionalized linkers are the two main reasons that result in the remarkably enhanced volumetric methane storage and working capacities in the functionalized MOFs. Given the fact that it is a daunting challenge to maximize the methane storage and working capacities of porous materials (both materials genome studies$^{18}$ and our rough empirical formula (see Fig. S26–S29, ESI) show that there might exist an up-limit on the methane storage capacities of MOF materials at 65 bar and room temperature), our work provides some promise to further increase the methane storage and working capacities of MOF materials through the incorporation of suitable functional groups into MOFs. We hope that our findings can motivate more extensive research endeavors to develop new porous MOFs with even higher methane storage and working capacities in the near future.

Acknowledgements

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Notes and references


