

A Metal–Organic Framework with Optimized Porosity and Functional Sites for High Gravimetric and Volumetric Methane Storage Working Capacities

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Extensive research has been devoted to developing new porous materials with high methane storage capacity. While great progress has been made in recent years, it still remains very challenging to target simultaneously high gravimetric and volumetric methane (CH₄) working capacities (deliverable amount between 5.8 and 65 bar) in a single material. Here, a novel metal–organic framework (termed as UTSA-110a) constructed by an extended linker containing a high density of functional nitrogen sites, exhibiting both very high gravimetric and volumetric working capacities of 317 cm³ (STP: 273.15 K, 1 atm) g^{−1} and 190 cm³ (STP) cm^{−3}, respectively, for robust MOFs, is reported. Both of these values are higher than those of two benchmark materials: HKUST-1 (207 cm³ (STP) g^{−1} or 183 cm³ (STP) cm^{−3}) and UTSA-76a (267 cm³ (STP) g^{−1} or 187 cm³ (STP) cm^{−3}). Computational studies reveal that it is the combination of optimized porosity and favorable binding sites that leads to the simultaneously high gravimetric and volumetric working capacities in this material.

The sharp rise in the concentration of atmospheric carbon dioxide (CO₂), from 278 ppm at the beginning of industrial revolution to >400 ppm today, has pushed the implementation of a cleaner fuel for replacing conventional petroleum fuels to a level of utmost importance.^[1] Natural gas, which is nearly 95% methane (CH₄), represents a cleaner and cheaper fuel because of its abundant reserves, high research octane number (RON = 107), and low CO₂ emission; however, it still remains the least utilized fuel. Despite having these benefits, the widespread use of natural gas as a transportation fuel in the automotive industry has been hindered by its relatively low volumetric energy storage density. One of the current technologies to improve the storage density is compressed natural gas (CNG), stored as supercritical fluid at room temperature (RT) and 200–300 bar in an

oversized fuel tank. However, the tank size, cost, and safety issues restrict the usage of CNG in light-duty vehicles with little space. In this context, adsorbed natural gas (ANG) systems, which has attracted a considerable interest in recent years, show great potential to store high densities of methane in porous materials at RT and moderate pressures. To guide the research of ANG technology, the U.S. Department of Energy (DOE) updated the research program in 2012 with the ambitious goals of 350 cm³ (STP) cm^{−3} and 700 cm³ (CH₄) g^{−1} for volumetric and gravimetric storage capacities at room temperature, respectively.^[2]

Realization of efficient adsorbent materials is of critical importance to the success of ANG technology. Metal–organic frameworks (MOFs), as an emerging type of solid crystalline materials, show great promise for methane storage due to the powerful reticular chemistry that enables us to ideally target materials with desired and appropriate structure, pore space, and functionality.^[3–6] Over the past two decades, a large number of MOFs such as HKUST-1, UTSA-76, Co(BDP), MOF-5, NU-125, Al-soc-MOF-1, MAF-38, MOF-205, and NJU-Bai43 have been exploited as outstanding storage adsorbents, exhibiting some of the highest gravimetric or volumetric methane storage capacities.^[7–12] Since the automobile industry requires that a sufficient pressure differential (generally 5.8 bar),^[13,14] set by the Advanced Research Projects Agency-Energy (ARPA-E) of the

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U.S. Department of Energy,^[2] remains unused in the fuel tank, working capacity is key to evaluate the performance of methane storage materials. At present, the highest volumetric working capacity for robust MOFs was held by HKUST-1 ($183 \text{ cm}^3 \text{ (STP) cm}^{-3}$) and UTSA-76 ($187 \text{ cm}^3 \text{ (STP) cm}^{-3}$); however, the relatively low porosities have limited their total and working CH_4 gravimetric uptakes.^[10,11] We note that, in addition to volumetric uptake, the gravimetric uptake is also important. A common strategy to improve the gravimetric capacity is to increase the porosity of MOFs.^[15] However, despite having the highest gravimetric working capacities of over $400 \text{ cm}^3 \text{ (CH}_4\text{) g}^{-1}$, most of benchmark MOFs with ultralarge porosities such as Al-soc-MOF-1, MOF-205, PCN-68, and NU-111, exhibit only moderate volumetric working uptakes of $\approx 150\text{--}170 \text{ cm}^3 \text{ (STP) cm}^{-3}$.^[16] Therefore, it remains a great challenge to develop an ideal MOF with both high gravimetric and volumetric CH_4 working capacities.

To address this challenge, it is important to optimize both volumetric/gravimetric methane storage capacities in a single material. As revealed, the gravimetric uptake of robust MOFs at 65 bar is basically proportional to the porosity, while MOFs should have balanced porosities and framework densities, and high densities of functional sites/cages for high volumetric uptake.^[6,15] In order to target high volumetric and gravimetric uptakes concurrently, some attempts have been devoted to increase the porosity via systematically elongating the linkers in MOFs with high volumetric uptakes. However, they have been met with very limited success, as exemplified by the HKUST-like tbo-MOFs and the ntt-MOFs.^[16–18] This is because the direct increase in porosity typically correlates to an increase in pore diameters, which can be detrimental to the framework density and strength of methane binding affinity, thus sacrificing the total and working volumetric uptakes.^[17] To overcome this limitation, it is important to maintain or compensate the methane binding strength associated with the surface area/porosity increase in MOFs. In this regard, the UTSA-76 series with functional N sites are particularly of interest because they offer additional functional sites as secondary adsorption sites that can enhance the interactions with CH_4 molecules, thus optimizing their volumetric total and working capacities (at RT and 65 bar) to be record-high.^[11] On the basis of this fundamental framework template, if we expand the UTSA-76 framework with an extended linker containing a higher density of functional N sites, the enhanced porosity should improve the total gravimetric uptake, and notably, the incorporated functional sites may have a positive influence on CH_4 –framework interactions to optimize the volumetric uptake. Moreover, high porosity can also contribute to reduce the low-pressure methane adsorption and be beneficial for the more important working capacities.^[7a] These synergistic effects should enable

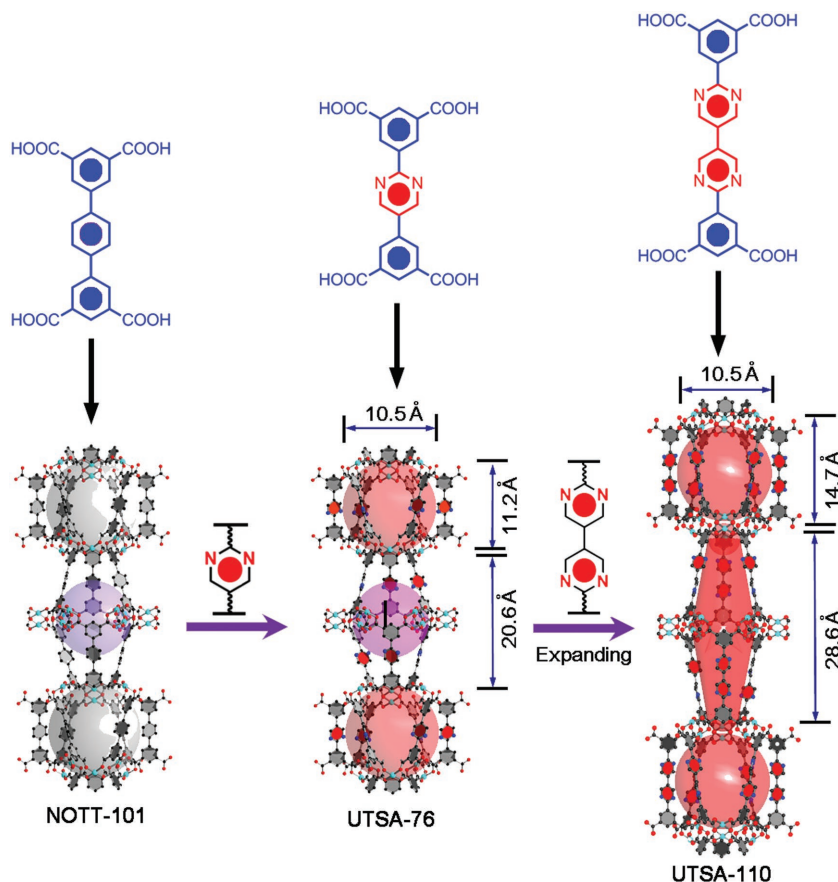


Figure 1. Comparison of crystal structures of NOTT-101, UTSA-76, and UTSA-110, revealing the tailoring of pore sizes and functionalities within UTSA-110.

us to target some new porous MOFs with higher gravimetric and volumetric working capacities simultaneously.

Taking all the above into account, we herein designed and synthesized a new ligand (H_4L) by adding one more functional pyrimidine ring into the linker of UTSA-76 (Figure 1), and utilized it to construct the expanded NbO-type MOF $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2]_n$ (termed as UTSA-110). The resulting MOF has a larger surface area ($3241 \text{ vs } 2820 \text{ m}^2 \text{ g}^{-1}$) and higher content of functional N sites ($3.94 \text{ vs } 2.64 \text{ mmol cm}^{-3}$) than UTSA-76. As expected, we found that UTSA-110a exhibits high gravimetric and volumetric total methane uptakes at RT and 65 bar, reaching $402 \text{ cm}^3 \text{ (STP) g}^{-1}$ and $241 \text{ cm}^3 \text{ (STP) cm}^{-3}$, respectively. In combination with the relatively lower unused CH_4 uptake at 5.8 bar ($51 \text{ cm}^3 \text{ (STP) cm}^{-3}$) with HKUST-1 ($83 \text{ cm}^3 \text{ (STP) cm}^{-3}$) and UTSA-76a ($69 \text{ cm}^3 \text{ (STP) cm}^{-3}$), UTSA-110a exhibits both higher gravimetric and volumetric working capacities of $317 \text{ cm}^3 \text{ (STP) g}^{-1}$ and $190 \text{ cm}^3 \text{ (STP) cm}^{-3}$ than those of HKUST-1 ($207 \text{ cm}^3 \text{ (STP) g}^{-1}$ and $183 \text{ cm}^3 \text{ (STP) cm}^{-3}$) and UTSA-76a ($267 \text{ cm}^3 \text{ (STP) g}^{-1}$ and $187 \text{ cm}^3 \text{ (STP) cm}^{-3}$), two benchmark compounds for methane storage in robust MOFs.

The organic linker of H_4L was synthesized through a multi-step reaction procedure (see the Supporting Information for details). Solvothermal reaction of H_4L with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in a mixture of N,N-diethylformamide (DEF)/1,4-dioxane/ H_2O (in the presence of hydrochloric acid) at 80°C for 3 d afforded blue block crystals of UTSA-110 with a framework

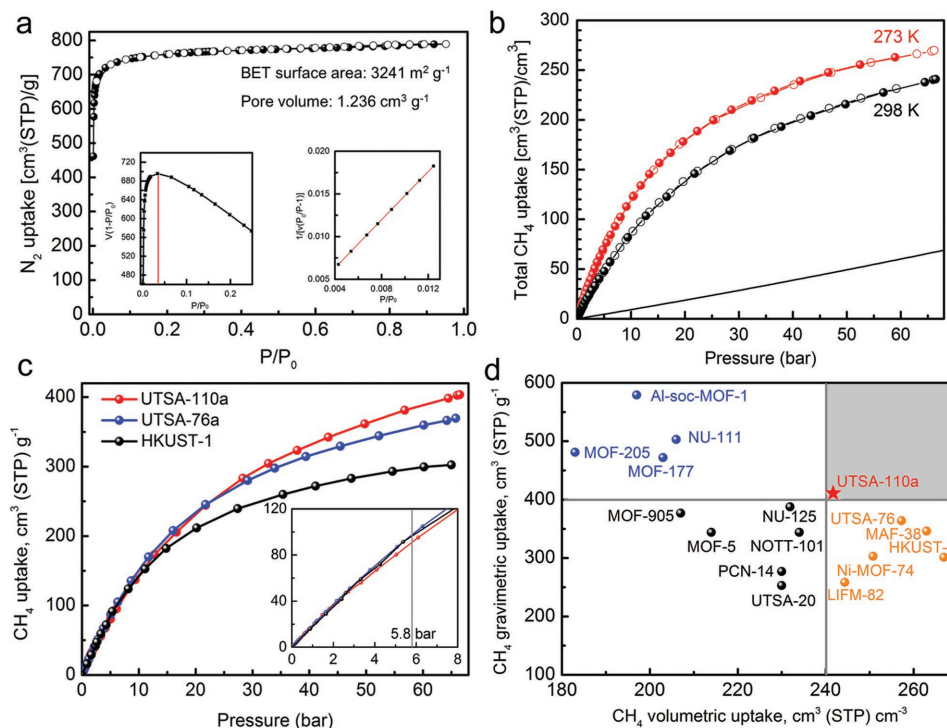


Figure 2. a) Nitrogen isotherm at 77 K with consistency and BET plots for the activated UTSA-110a sample. b) Total volumetric methane sorption isotherms of UTSA-110a at the indicated temperatures. Data of pure methane gas stored in a high-pressure gas tank is represented as dashed black curve. c) Comparison of total gravimetric CH₄ adsorption isotherms of HKUST-1, UTSA-76, and UTSA-110a at 298 K. d) Total CH₄ gravimetric/volumetric uptakes at 65 bar and RT for UTSA-110a in comparison to the best robust MOF materials reported to date.

formula of $[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2]_n$. Single-crystal X-ray diffraction analysis revealed that the framework of UTSA-110 is isorecticular to NOTT-102, which consists of paddle-wheel dinuclear $\text{Cu}_2(\text{COO})_4$ secondary building units (SBUs) linked by the carboxylates of L^{4-} organic linkers to form 3D NbO-type structures. This framework displays two types of cages: one cuboctahedral cage of about $10.5 \times 14.7 \text{ \AA}^2$, and another large irregular elongated cage of $\approx 9.6 \times 28.6 \text{ \AA}^2$. As illustrated in Figure 1, due to the longer organic linkers, the length of these two types of cages are much larger than those of UTSA-76 and NOTT-101 (11.2 and 20.6 Å) along one direction. Moreover, UTSA-110 has a higher content of uncoordinated N sites ($3.94 \text{ mmol cc}^{-1}$) exposed on the pore surfaces than that of UTSA-76 ($2.64 \text{ mmol cc}^{-1}$). These optimized features of pore spaces and functional sites may play an extra effect on methane storage capacities, particularly on working capacities.

Prior to methane adsorption measurements, we first measured the N_2 adsorption isotherms at 77 K on the activated UTSA-110a to examine its porosity. As shown in Figure 2a, the N_2 isotherms at 77 K exhibit reversible type-I behavior without any hysteresis, characteristic of microporous materials. The Brunauer–Emmett–Teller (BET) surface area and pore volume of UTSA-110a were determined to be $3241 \text{ m}^2 \text{ g}^{-1}$ and $1.263 \text{ cm}^3 \text{ g}^{-1}$, respectively, which are comparable to those of the isorecticular NOTT-102 ($3342 \text{ m}^2 \text{ g}^{-1}$ and $1.268 \text{ cm}^3 \text{ g}^{-1}$). These values are much higher than HKUST-1 ($1850 \text{ m}^2 \text{ g}^{-1}$ and $0.78 \text{ cm}^3 \text{ g}^{-1}$) and UTSA-76 ($2820 \text{ m}^2 \text{ g}^{-1}$ and $1.09 \text{ cm}^3 \text{ g}^{-1}$), indicating its significantly larger porosity.

Next, we collected high-pressure methane adsorption isotherms for UTSA-110a at 273 and 298 K, as presented in

Figure 2b. Owing to the high porosity, UTSA-110a exhibits one of the highest total gravimetric uptakes for MOFs, reaching $402 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$ (0.288 g g^{-1}) at 65 bar and 298 K (Figure S7, Supporting Information). This value is much higher than that of UTSA-76a ($363 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$) and HKUST-1 ($302 \text{ cm}^3 (\text{STP}) \text{ g}^{-1}$) under the same conditions (Figure 2c). Moreover, UTSA-110a performs gravimetrically better than MOFs with similar surface areas, such as MFM-115a,^[19] NOTT-102, and MOF-905 (Table 1). Using the crystal density of UTSA-110a (0.600 g cm^{-3}), the calculated total volumetric uptake is $\approx 241 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$ at RT and 65 bar, among very few MOFs with the capacity over $240 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$.^[6c] This value is slightly higher than that of the isorecticular NOTT-102 ($233 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$), indicating that the incorporated functional N sites might have a positive effect on methane storage capacities. However, this capacity is lower than the currently best-performing MOFs, such as HKUST-1 ($267 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$)^[10] and UTSA-76a ($257 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3}$).^[11]

A comprehensive comparison of total gravimetric/volumetric CH₄ uptakes at RT and 65 bar for UTSA-110a versus the best MOF materials reported is presented in Figure 2d. Interestingly, we found that MOFs with the highest gravimetric (volumetric) uptakes generally exhibit modest volumetric (gravimetric) capacities. This implies that there exists a notably mutual compromise between gravimetric and volumetric capacities for the MOFs, mainly attributed to the opposite relationship between the porosity and CH₄–framework interactions.^[10,17] However, UTSA-110a exhibits a notable balance of high volumetric and gravimetric total capacities at RT and 65 bar. On one hand, its gravimetric uptake is much higher than MOFs with very high

Table 1. Comparison of some promising robust MOFs for high-pressure methane storage.

MOFs	$S_{\text{BET}}^{\text{a)}}$ [$\text{m}^2 \text{g}^{-1}$]	$V_{\text{p}}^{\text{b)}}$ [$\text{cm}^3 \text{g}^{-1}$]	$D_{\text{c}}^{\text{c)}}$ [g cm^{-3}]	Total uptake ^{d)} at 65 bar		Working capacity ^{e)}		Initial Q_{st} [kJ mol^{-1}]	Ref.
				[$\text{cm}^3 \text{g}^{-1}$]	[$\text{cm}^3 \text{cm}^{-3}$]	[$\text{cm}^3 \text{g}^{-1}$]	[$\text{cm}^3 \text{cm}^{-3}$]		
UTSA-110a	3241	1.263	0.600	402	241	317	190	14.5	This work
UTSA-76a	2820	1.092	0.699	363	257	267	187	15.5	[11]
HKUST-1	1850	0.78	0.883	302	267	207	183	17.0	[10]
LIFM-82	1624	0.71	0.922	267	245	199	182	17.5	[9a]
NOTT-102a	3342	1.268	0.587	396	233	308	182	14.9	[14]
MFM-115a	3394	1.38	0.611	389	238	296	181	16.3	[19]
AIMOF-soc-1	5585	2.30	0.34	579	197	497	169	11.0	[16a]
MOF-905	3490	1.34	0.537	377	207	318	175	11.7	[7a]
MAF-38	2022	0.808	0.761	346	263	231	176	21.6	[7d]
NU-125	3286	1.41	0.589	395	232	297	174	15.1	[8a]
NU-111	4930	2.09	0.409	503	206	422	173	14.2	[10]
PCN-14	2170	0.85	0.829	277	230	181	154	17.6	[10]

^{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)}At 298 K; ^{e)}Defined as the difference of the amount of methane adsorbed between 65 and 5.8 bar.

volumetric uptake (e.g., HKUST-1, UTSA-76a, and MAF-38). On the other hand, UTSA-110a outperforms those larger-pore MOFs volumetrically, such as Al-soc-MOF-1, MOF-205, and NU-111 (Figure 2d). To the best of our knowledge, this is the first MOF whose gravimetric and volumetric uptake can reach $400 \text{ cm}^3 (\text{STP}) \text{g}^{-1}$ and $240 \text{ cm}^3 (\text{STP}) \text{cm}^{-3}$ simultaneously. This unique balance of total capacities enables us to target both high gravimetric and volumetric CH_4 working capacities.

In practical applications, the driving range of an ANG vehicle is primarily determined by the working capacity of the adsorbent (also called deliverable capacity), defined as the different amount of methane adsorbed between 5.8 and 65 bar, which is more important than the total volumetric/gravimetric uptakes. As shown in Figure 2c, relative to UTSA-76a and HKUST-1, UTSA-110a exhibits a much higher gravimetric uptake at 65 bar but slightly lower adsorption at 5.8 bar owing to the larger porosity. UTSA-110a therefore shows a notably higher gravimetric working capacity of $317 \text{ cm}^3 (\text{STP}) \text{g}^{-1}$, which is 20 and 54% larger than UTSA-76 ($267 \text{ cm}^3 (\text{STP}) \text{g}^{-1}$) and HKUST-1 ($207 \text{ cm}^3 (\text{STP}) \text{g}^{-1}$), respectively. In terms of the more important volumetric working capacity, we found that the incorporation of functional N sites can improve the methane uptake at 65 bar while has a negligible effect on the adsorption at 5.8 bar (Figure S8, Supporting Information), leading to the enhanced working capacity of $190 \text{ cm}^3 (\text{STP}) \text{cm}^{-3}$ compared to the isorecticular NOTT-102 ($182 \text{ cm}^3 (\text{STP}) \text{cm}^{-3}$). Notably, this value is even higher than the best-performing HKUST-1 ($183 \text{ cm}^3 (\text{STP}) \text{cm}^{-3}$) and UTSA-76a ($187 \text{ cm}^3 (\text{STP}) \text{cm}^{-3}$) (Table 1). Some detailed comparisons of UTSA-110a with UTSA-76a and HKUST-1 are given in Figure 3a. The ability of UTSA-110a to outperform working capacities of HKUST-1 and UTSA-76a both gravimetrically and volumetrically enables it to establish a new benchmark for methane storage in robust MOFs.

We further compared the gravimetric/volumetric working capacities of UTSA-110a with other benchmark robust MOFs.

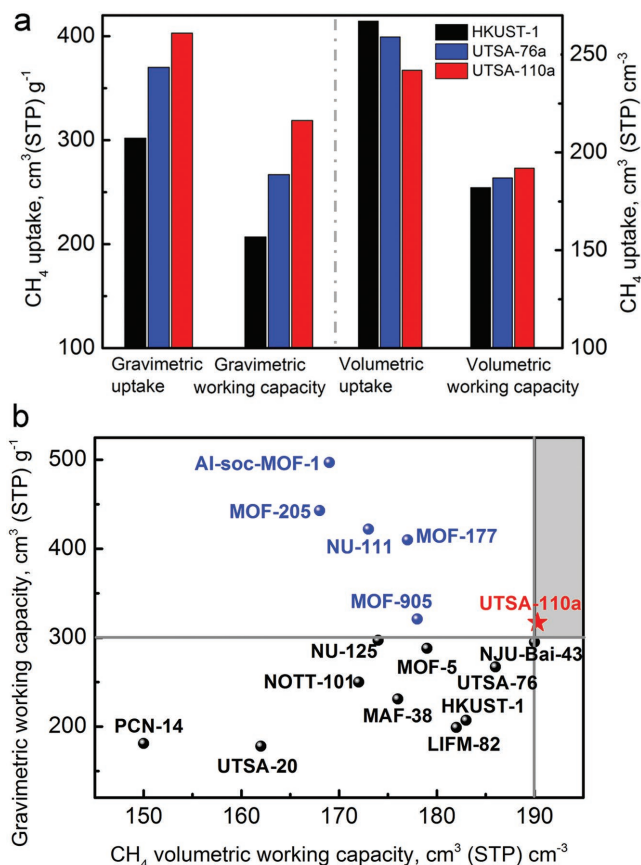


Figure 3. a) A detail comparison of the methane storage capacities of UTSA-110a with two best-performing MOFs (UTSA-76a and HKUST-1). b) The CH_4 gravimetric/volumetric working capacities (between 5.8 and 65 bar) for UTSA-110a in comparison to the best robust MOFs reported to date.

Figure 3b illustrated that UTSA-110a exhibits the highest volumetric working capacity among the indicated MOFs. Most importantly, the gravimetric working capacity of UTSA-110a is also exceptionally high. This capacity is only lower than very few MOFs with ultrahigh surface areas (e.g., Al-soc-MOF-1, MOF-205, and NU-111), but much higher than those MOFs with high volumetric capacity over $180 \text{ cm}^3 \text{ (STP) cm}^{-3}$ (Table 1). Although the volumetric working capacity is slightly lower than the flexible material Co(bdp) ($197 \text{ cm}^3 \text{ (STP) g}^{-1}$), UTSA-110a shows a 25% gravimetrically higher than that of Co(bdp) ($254 \text{ cm}^3 \text{ (STP) g}^{-1}$).^[14] These results reported here thus indicate that UTSA-110a exhibits an uncommon balance of very high gravimetric and volumetric working capacities.

The exceptionally high gravimetric and volumetric working capacities simultaneously in UTSA-110a are very encouraging. It indicates that the optimized porosity and immobilization of some functional groups into MOFs might have played some important roles to enhance both gravimetric and volumetric working capacities. The very high gravimetric working capacity could directly originate from the large porosity of UTSA-110a. To better understand the origin of the ultrahigh volumetric working capacity in UTSA-110a, we first calculated the isosteric heats of adsorption (Q_{st}) from the temperature-dependent isotherms using the virial method (Figures S9 and S10, Supporting Information). The initial Q_{st} of UTSA-110a is around 14.5 kJ mol^{-1} , which is comparable to NOTT-102a, but much lower than UTSA-76a (15.5 kJ mol^{-1}) and HKUST-1 (17.0 kJ mol^{-1}). This is because UTSA-110a has a higher surface area and lower density of open metal sites ($1.95 \text{ mmol cc}^{-1}$) than UTSA-76a ($2.64 \text{ mmol cc}^{-1}$) and HKUST-1 ($4.38 \text{ mmol cc}^{-1}$, Table S2, Supporting Information), which determines the lower initial Q_{st} value and the low-pressure methane adsorption amount.^[10,11] Therefore, UTSA-110a exhibits much lower methane uptake at 5.8 bar ($51 \text{ cm}^3 \text{ (STP) cm}^{-3}$) than that of UTSA-76a ($69 \text{ cm}^3 \text{ (STP) cm}^{-3}$) and HKUST-1 ($83 \text{ cm}^3 \text{ (STP) cm}^{-3}$). To further understand the role of functional N sites in the methane adsorption of UTSA-110a, we carried out first-principles dispersion-corrected density-functional theory (DFT-D) calculations. It was found that the methane adsorption next to the N sites of pyrimidine rings on the UTSA-110a ligand is $\approx 11\%$ stronger than on the NOTT-102 ligand (the calculated static CH_4 binding energies: 18.1 kJ mol^{-1} for pyrimidine in UTSA-110a vs 16.3 kJ mol^{-1} for benzene in NOTT-102). These calculated CH_4 binding energies are not equivalent to the values of Q_{st} , which can only be used for the qualitative (not quantitative) comparison with Q_{st} (see the Supporting Information for the detailed explanation). Mulliken population analysis further indicated that the N sites in pyrimidine have a more negative charge than the C atoms in benzene (Figure S12, Supporting Information), suggesting that the linkers of UTSA-110a indeed have stronger CH_4 -ligand electrostatic interactions. Since functional N sites are not really strong adsorption sites relative to open metal sites,^[11] the dipyrimidine sites in UTSA-110a can serve as secondary adsorption sites to do benefit the CH_4 adsorption on the linkers and thus enhance the uptake at high pressure, although modestly.

Overall, we believe that it is the synergistic effect of the increased porosity and functional N sites in UTSA-110a that leads to both enhanced volumetric and gravimetric working

capacities. At a low pressure of 5.8 bar, UTSA-110a shows a relatively lower CH_4 adsorption amount than UTSA-76a and HKUST-1 due to the larger porosity and lower concentration of open metal sites. However, at higher loadings of methane, the combination of the increased porosity and functionalization in UTSA-110a can optimize methane storage capacities both volumetrically and gravimetrically, thus leading to simultaneously higher volumetric and gravimetric working capacities.

In summary, we have designed and synthesized a new porous material (UTSA-110a) with optimized porosity and functional sites, exhibiting a rare combination of very high gravimetric and volumetric methane storage working capacities. Compared with the benchmark HKUST-1 and UTSA-76a, this material shows not only notably improved total gravimetric uptake but also both higher gravimetric and volumetric working capacities. We attribute these improvements in both gravimetric/volumetric capacities to the synergistic effects between the optimized porosity and functional N sites. Remarkably, the volumetric working capacity of $190 \text{ cm}^3 \text{ (STP) cm}^{-3}$ is the highest yet reported for robust MOFs. These results revealed in this work may provide some guidance to develop new MOFs with more balanced and higher gravimetric/volumetric working capacities simultaneously.

Experimental Section

Synthesis of UTSA-110: A mixture of the organic linker $\text{H}_4\text{L1}$ (10.0 mg, 0.02 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (30.0 mg, 0.129 mmol) was dissolved into a 3.4 mL mixed solvent (DEF/dioxane/ H_2O , 3/0.2/0.2 mL) in a screw-capped vial (20 mL). 40 μL of 37% HCl was added. The vial was capped and heated in an oven at 80°C for 3 d. Blue block crystals were obtained by filtration and washed with DMF several times to afford UTSA-110 in 42% yield (based on the ligand).

Single-crystal X-ray diffraction data of UTSA-110 were collected on an Agilent Supernova CCD diffractometer equipped with a graphite-monochromatic enhanced Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 293 K. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full matrix least-squares methods with the SHELX-97 program package.^[20] The solvent molecules in the compound are highly disordered. The SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.^[21] The resulting new files were used to further refine the structures. The H atoms on C atoms were generated geometrically. The crystal data are summarized in Table S1 (Supporting Information).

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 of UTSA-110 were guest-exchanged with dry acetone at least ten times, filtered and degassed at room temperature (298 K) for 1 d, and then at 373 K for another 16 h until the outgas rate was 5 mmHg min^{-1} prior to measurements. The activated sample was maintained at 77 K with liquid nitrogen. High-pressure methane sorption isotherms were measured using a Sieverts-type apparatus under computer control at NIST (National Institute of Standards and Technology, USA) lab. A detailed description of the experimental setup, calibration, and the isotherm can be found in a previous publication.^[22]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

functional sites, host–guest interactions, methane storage, porous materials, working capacity

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