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An Indium-based microporous metal-organic framework with unique three-way rod-shaped secondary building units for efficient methane and hydrogen storage

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A novel microporous indium-based MOF material with unique 3-way rod-shaped secondary building units (SBUs), UTSA-22, was reported and exhibited high methane (CH₄) and hydrogen (H₂) storage. At 298 K and 65 bar, the total CH₄ volumetric uptake for UTSA-22 is 174 cm³(STP)/cm³. Moreover, UTSA-22 shows a high CH₄ working capacity of 146 cm³(STP)/cm³ in the pressure range of 5-65 bar at 298 K. In addition, UTSA-22 shows a high H₂ gravimetric storage capacity (1.2 wt%) at 298 K and 100 bar.

As a primary greenhouse gas, carbon dioxide was released globally to reach a record high as fossil fuel demand is growing tremendously. Methane (CH₄), a primary component in natural gas, is considered a potential alternative to liquid fossil fuels since it is clean, abundant, and renewable on earth.¹ However, the low energy densities have limited its practical applications. In this regard, to utilize methane as a transportation fuel, a suitable adsorbent with high CH₄ storage capacity at low pressures will be desired (When methane was used as a transportation fuel storing by an adsorbent).² Therefore, significant interest is attracted by adsorbed natural gas systems in overcoming these problems, including filling the tank with porous material for storing high-density methane at moderate pressure. According to the guideline of the department of energy (DOE) in the U.S.,³ the ambitious target of the volumetric

and gravimetric storage capacities for CH₄ storage are up to 350 cm³(STP)/cm³ and 0.5 g/g, respectively, at room temperature (R.T.) for the next generation of clean energy automobiles considering the ignored loss of the packing adsorbent. Thus, comprehensive research efforts are devoted to developing novel adsorbent materials with high CH₄ storage capacity to achieve the challenging storage goals.^{4, 5}

Featuring high Brunauer-Emmett-Teller (BET) surface areas, tunable pore functions, metal-organic frameworks (MOFs) are emerging as a new generation of crystalline materials, which outperform the conventionally used activated carbon, zeolites, and silica gels in a multitude of different physio-chemical aspects.⁶⁻¹⁵ A large number of MOFs has been demonstrated to be promising for CH₄ storage, considering both the volumetric and gravimetric CH₄ uptakes and storages.¹⁶⁻²⁴ It is worth noting that the CH₄ volumetric working capacity (also known as deliverable capacity) is considered to be a much more important parameter to assess the performance of these absorptive materials for practical applications due to the limited gas tanks in the vehicles, which reflects the actual driving range by natural gas.²⁵⁻²⁷ At present, to achieve high working capacity, maximizing the amount of methane stored at high pressure and minimizing the methane storage at low pressure (around 5 bar) is necessary.²⁸⁻³⁰ Several strategies have been proven to improve CH₄ working capacity, such as optimizing the pore structure, tuning the framework's flexibility, and incorporating strong binding sites.³¹⁻³⁵ But it is still challenged to optimize the pore structure with appropriate CH₄ binding affinity for balancing the trade-off of methane adsorption between the low and high pressure, therefore to obtain superior volumetric working capacity.³⁶⁻³⁹

Herein, a three-dimensional microporous metal-organic framework [In₅(TTETA)_{11/3}(OH)₄(H₂O)·30H₂O·19DMF] (**UTSA-22**, H₃TTETA = 4,4',4''-((2,4,6-trimethylbenzene-1,3,5-triyl)tris(ethyne-2,1-diyl)) tribenzoic acid) with unique 3-way rod-shaped SBUs was synthesized under solvothermal conditions. It was found that the activated **UTSA-22** shows a

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high methane uptake of $174 \text{ cm}^3(\text{STP})/\text{cm}^3$ at 298 K and 65 bar, which is higher than those of DUT-4 ($164 \text{ cm}^3(\text{STP})/\text{cm}^3$),³ Fe-NDC ($160 \text{ cm}^3(\text{STP})/\text{cm}^3$)⁴⁰ and VNU-22 ($155 \text{ cm}^3(\text{STP})/\text{cm}^3$).⁴⁰ Moreover, the value is comparable to some of the top performance materials considering the significant low surface

area of **UTSA-22** ($2173 \text{ m}^2/\text{g}^1$), such as MOF-205 ($183 \text{ cm}^3(\text{STP})/\text{cm}^3$),⁴¹ FJI-H23 ($179 \text{ cm}^3(\text{STP})/\text{cm}^3$),⁴² and BUT-22 ($182 \text{ cm}^3(\text{STP})/\text{cm}^3$).¹⁶ Additionally, H_2 storage capacity of **UTSA-22** can reach 1.2 wt% (8.45 g/L) at 100 bar and 298 K.

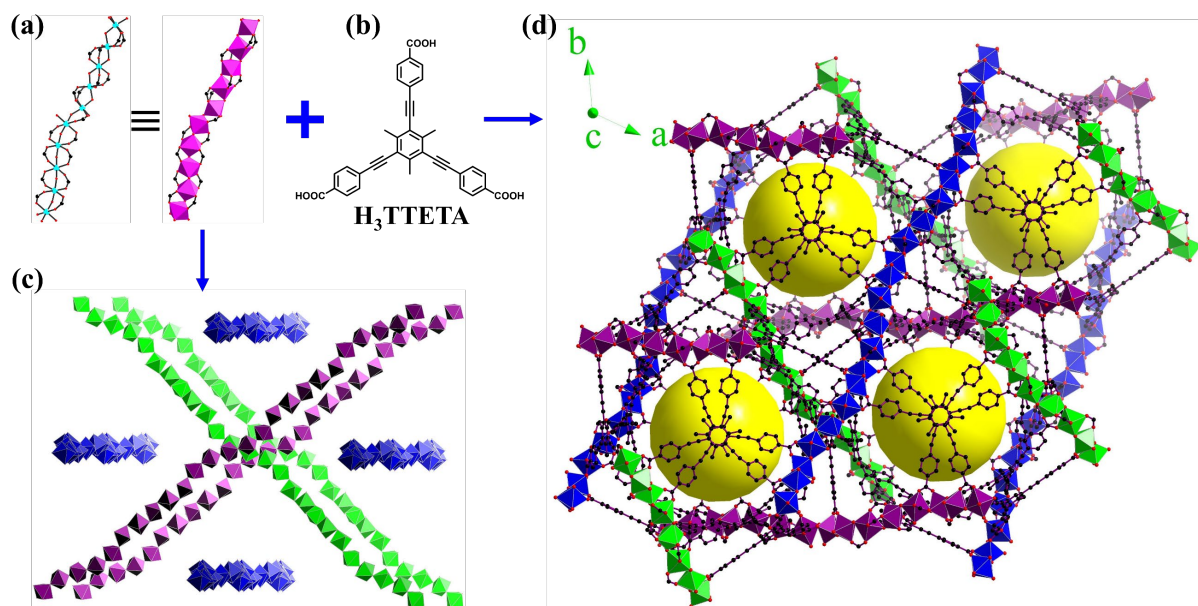


Figure 1. (a) infinite 1D rod-shaped SBU, (b) Structural formula of the ligand, H_3TTETA , (c) the packing of the SBUs, and (d) the three-dimensional framework structure of **UTSA-22** viewed along the crystallographic c -axis (color code: In, turquoise; C, black; O, red; octahedral geometry constituted by In and O; hydrogen atoms are not shown for clarity)

Solvothermal reactions of H_3TTETA with $\text{In}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and nitric acid yielded single crystals of **UTSA-22**. Single-crystal X-ray diffraction analysis displayed that **UTSA-22** crystallizes in the trigonal system, space group $R\bar{3}c$. Three independent In^{3+} atoms, 11/6 TTETA^{3-} ligands, and one $\mu_2\text{-OH}^-$ group were observed in the asymmetric unit of **UTSA-22**. Both In^{3+} atoms are coordinated with four carboxylate O atoms coming from four different TTETA^{3-} ligands in the equatorial positions and two $\mu_2\text{-OH}^-$ groups in the apical positions. The lengths of In–O and In–OH are in the range of 2.050(4)–2.209(6) and 2.026(6)–2.094(6) Å, respectively (Table S2). For the TTETA^{3-} ligand, two carboxyl groups coordinate with two adjacent In^{3+} atoms in bimonodentate coordination, and the remaining carboxyl group coordinates with the In^{3+} atom in a monodentate mode (Figure 1). The uncoordinated carboxylate O atom (O12) can form hydrogen bonding interactions with a $\mu_2\text{-OH}^-$ (O2, the distance is 2.6 Å, Figure S1). The connection of In^{3+} atoms with carboxylate and $\mu_2\text{-OH}^-$ groups in order of "In1–In2–In3–In2–In1" results in an infinite rod-shaped secondary building unit (SBUs). The SBUs are bridged by TTETA^{3-} ligands making a three-dimensional structure with one type of double-wall disordered octahedral cage (Figure S2). The diameter of the octahedral cage is about 18 Å. In addition, two types of pore walls with a thickness of 3.6 and 7.7 Å, respectively, are observed in **UTSA-22** (Figure S3). Interestingly, the 1D chains in **UTSA-22** are arranged in a three-way model, which differs from the commonly observed one-way or two-way models (Figure 1).⁴³

⁴⁶ Similar SBUs have been reported in a recently published work.⁴⁷ It should be pointed out that, while preparing this manuscript, the single crystal structure of **UTSA-22** was reported by Li and co-workers, and this MOF was used for the detection of selective antibiotics in water.⁴⁸ The total potential solvent accessible void volume of the framework is 65% of the whole structure as estimated by *PLATON*.⁴⁹

The phase purity of **UTSA-22** was examined by powder X-ray diffraction (PXRD) measurement (Figure S5). The PXRD peaks of the as-synthesized sample match those simulated ones coming from the single-crystal data, proving the high phase purity of **UTSA-22**. The crystal structure remains intact after activation. In the thermogravimetric analysis (TGA) spectrum, two steps of weight loss were clearly observed: one is in the temperature range of 21–69 °C with a weight loss of 12%, and the other one is in the temperature range of 69–137 °C with a weight loss of 30% (Figure S6). Considering that in the synthesis of **UTSA-22**, only water, DMF, and HNO_3 (10 μL , 16 M) are used, and the trace HNO_3 will decompose to NO_2 under high temperature. Thus, it is believed that the two steps of weight loss belong to that of water and DMF in the pores of **UTSA-22**, respectively. The calculated amount of water and DMF molecules in the pores of **UTSA-22** are 30 and 19, respectively, which is reasonable considering the large cell parameters ($a = b = 51.504(3)$ Å, $c = 50.096(4)$; $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; $v = 115083(17)$ Å³) of the host framework. The framework of **UTSA-22** is stable to up to ~ 400 °C, followed by its decomposition (Figure S6).

Besides, in the FT-IR spectra, a slight red shift of the characteristic peaks belonging to the carbonyl group in **UTSA-22** was observed compared with those of the H₃TTETA ligand, demonstrating the coordination between the carboxylate groups and metals (Figure S7). At 77 K, **UTSA-22** was examined by N₂ adsorption to obtain the permanent porosity (Figure 2a).

Saturated N₂ uptake for **UTSA-22** is 581 cm³(STP)/g¹, corresponding to 2173 m²/g as BET surface area (Figure S8-S9). Therefore, the experimental total pore volume of **UTSA-22** is 0.90 cm³/g, which is close to the theoretical one of 0.93 cm³/g by PLATON calculation.

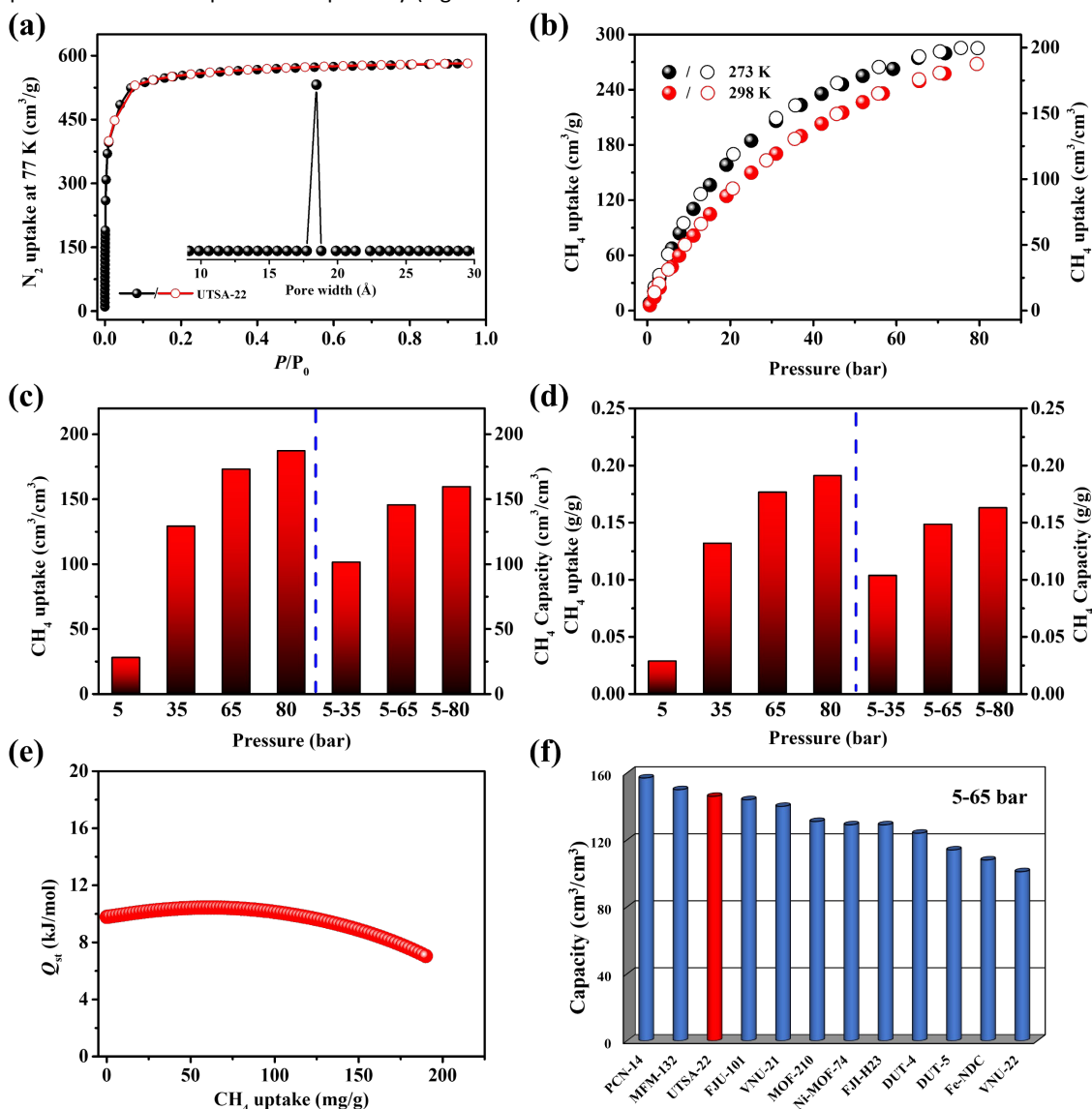


Figure 2. (a) N₂ adsorption/desorption isotherms of **UTSA-22** at 77K; (b) CH₄ isotherms at 273 and 298 K for **UTSA-22** up to 80 bar . Solid symbols: adsorption; open symbols: desorption; (c) volumetric and (d) gravimetric CH₄ uptake (at 5, 35, 65, and 80 bar, respectively)/working capacities (in the pressure range of 35-5, 65-5, and 80-5 bar, respectively) of **UTSA-22** at 298 K; (e) Q_{st} of CH₄ for **UTSA-22** by using the virial method; and (f) Comparison of the volumetric CH₄ working capacities (5-65 bar) of **UTSA-22** with some benchmark MOF materials.

The CH₄ storage capacity of **UTSA-22** was explored in the beginning accordingly. At 273 and 298 K, CH₄ adsorption isotherms were measured from 0 to 80 bar, respectively. As shown in Figure 2b, at 35 bar and 298 K, the total gravimetric CH₄ uptake of **UTSA-22** is 183 cm³(STP)/g, exceeding the DOE's previous goal (180 cm³(STP)/g), without regard to the packing density loss. At 65 and 80 bar, the total gravimetric CH₄ uptake of **UTSA-22** is 249 and 268 cm³(STP)/g at 298 K, which corresponds to 0.179 and 0.192 g/g, respectively, which is much

higher than some benchmark MOFs such as Ni-MOF-74 (210 (223) cm³(STP)/g),⁵⁰ VNU-22 (132 (140) cm³(STP)/g),⁴⁰ and Cu-tbo-MOF-5 (208 (225) cm³(STP)/g)⁵⁰ under identical conditions (Table S3). In addition, at 80 bar and 298 K, the volumetric CH₄ uptake is 188 cm³(STP)/cm³, comparable to the ones of VNU-21 (194 cm³(STP)/cm³),⁴⁰ BUT-22 (202 cm³(STP)/cm³),¹⁶ and MFM-132 (213 cm³(STP)/cm³).³⁴

The working capacity is another important factor that needs to be considered while assessing porous materials for practical

methane storage. The working capacity is the difference in total adsorption from 5 to 80 (or 65) bar. As shown in Table S3, at 298 K, the CH₄ volumetric working capacity (65-5 bar) for **UTSA-22** is 146 cm³(STP)/cm³, which is comparable or higher than those widely explored MOFs like Ni-MOF-74 (129 cm³(STP)/cm³),⁵⁰ FJU-101 (144 cm³(STP)/cm³),¹⁷ DUT-4 (124 cm³(STP)/cm³),³ and VNU-22 (101 cm³(STP)/cm³).⁴⁰ When the temperature is down to 273 K, the CH₄ volumetric working capacity (65-5 bar) increases to 157 cm³(STP)/cm³, higher than some well-known microporous MOFs such as NiMOF-74 (106 cm³(STP)/cm³),⁵¹ ZJU-70 (134 cm³(STP)/cm³),⁵² MOF-505 (112 cm³(STP)/cm³),⁵³ and PCN-14 (153 cm³(STP)/cm³).⁵¹ Additionally, the adsorption enthalpy (Q_{st}) of **UTSA-22** is 9.8 kJ/mol (figure 2e), which is lower than most reported MOFs (Table S3). Such low adsorption enthalpy involving the host-guest interactions is significantly important when the CH₄ gas is released from the gas tank.

The H₂ isotherms of **UTSA-22** were collected up to 100 bar at 273 and 298 K. As shown in Figure 3, the gravimetric H₂ of **UTSA-22** at 298 K and 100 bar is 1.2 wt%, which is higher than most reported MOFs such as Co₂(BDC)₂(dabco) (0.32 wt%),⁵⁴ Cu₂(BDC)₂(dabco) (0.42 wt%),⁵⁴ JUC-48 (1.1 wt%),⁵⁵ Mg₂(dobdc) (0.8 wt%),⁵⁶ and Cu(peip) (0.46 wt%)⁵⁷ under identical conditions. Besides, **UTSA-22** shows a remarkable high H₂ volumetric uptake of 8.45 g/L at 298 K and 100 bar, which is higher than some famous MOFs such as NU-1501-Al (8.40 g/L)⁵⁸ and Mg₂(dobdc) (7.50 g/L).⁵⁶ Q_{st} of H₂ for **UTSA-22** is 12.3 kJ/mol at zero based on the isotherms obtained at 298 and 273 K (Figure S12).

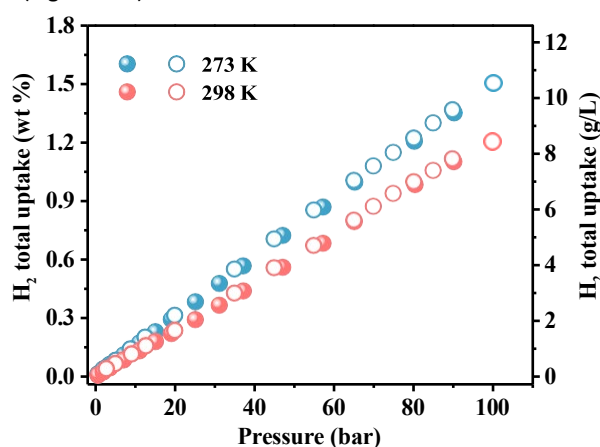


Figure 3. High-pressure hydrogen adsorption isotherm for **UTSA-22** at 273 and 298 K.

Conclusions

A novel microporous In-based MOF with unique three-way rod-shaped SBUs, named **UTSA-22**, has been designed and synthesized for efficient CH₄ and H₂ storage. Featuring cage-type structures, **UTSA-22** has a moderate BET surface area of 2173 m²/g¹ and is stable up to 400 °C. **UTSA-22** shows a high CH₄ gravimetric storage capacity of 268 cm³(STP)/g (0.192 g/g) at 80 bar and 298 K. The CH₄ volumetric delivery capacity (65-5 bar) for **UTSA-22** is 146 cm³(STP)/cm³ at 298 K, comparable to or higher than some benchmark MOF materials. Furthermore, the H₂ gravimetric uptake is 1.2 wt% for **UTSA-22** at 273 K and

100 bar. Therefore **UTSA-22** can be potentially used in the CH₄ and H₂ storage applications.

Conflicts of interest

There are no conflicts to declare.

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