Construction of ntt-Type Metal–Organic Framework from C$_2$-Symmetry Hexacarboxylate Linker for Enhanced Methane Storage

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ABSTRACT: By using a shortened hexacarboxylate linker of C$_2$-symmetry, a ntt-type metal–organic framework (UTSA-61) was constructed. Powder X-ray diffraction (XRD) crystallographic analysis revealed that UTSA-61 features the connection of the organic linker with four Cu$_2$ paddlewheels and one large [-Cu$_2$(O$_2$CR)$_4$-H$_2$O-Cu$_2$(O$_2$CR)$_4$]$_2$ cluster. This work confirms that a dendritic hexacarboxylate linker may support two cuboctahedral cages close to each other in ntt-type frameworks. Moreover, removing two ethynyl groups from PCN-61 (the prototypical ntt-type MOF) leads to optimized T-Td/T-Oh cages in UTSA-61 and results in preferable methane uptake than those of previously reported ntt-type MOFs. The activated UTSA-61a therefore exhibits a high methane storage capacity of 244 cm$^3$ (STP) cm$^{-3}$ at 298 K and 65 bar, and a high working capacity of 176 cm$^3$ (STP) cm$^{-3}$ (between 5 and 65 bar). These results rank UTSA-61a as one of the very few MOFs with both high volumetric methane storage and working capacities, rendering UTSA-61a as a promising adsorbent for on-board methane storage application.

INTRODUCTION

Methane, as the main component (nearly 95%) of natural gas (NG), is one of the most important energy resources for clean and efficient utilization. Several advantages, such as the abundant reserves, high research octane number (RON = 107), and low CO$_2$ emission, make methane a better alternative as the driving power source for small- or midsize vehicles than conventional fossil fuels. To facilitate its application as a vehicular fuel, high-capacity methane storage media are urgently needed. According to the U.S. Department of Energy (DOE) recommendation, a valid candidate should be able to surpass the volumetric uptake of 180 cm$^3$ (STP) cm$^{-3}$ at room temperature and 35 bar. Recently, the DOE raised its ambitious target to 350 cm$^3$ (STP) cm$^{-3}$ at room temperature and 35 bar. 8a The family of ntt-MOFs features the connection of 24-edged cuboctahedra with dendritic hexacarboxylate linkers of C$_2$-symmetry. There are three types of cages in ntt-frameworks: a cuboctahedral cage (cubOh), a truncated tetrahedral cage (T-Td), and a truncated octahedral cage (T-Oh). In all ntt-type frameworks, the cuboctahedral cages are basically identical, due to the same formation from 24 isophthalate moieties and 12 [Cu$_2$(COO)$_4$] paddlewheels. So far, some efforts have been devoted to enlarge the length of C$_2$-symmetry linker to achieve larger T-Td and T-Oh cages. 6–8 However, large voids often suffer from weaker affinity toward methane molecules (particularly near the pore center), resulting in poor volumetric uptake. Further linker expansion also tends to increase the framework instability upon solvent removal. 8

Among highly porous MOFs, ntt-type framework has attracted our particular attention because all ntt-type MOFs possess high-concentration of open metal sites (OMSs) and non-interpenetrated frameworks. 6 The large surface area and pore volume as well as high density of OMSs endow ntt-type MOFs with the record CO$_2$ uptake capacity to date. 7 The prototypical ntt-MOF, PCN-61, also exhibits a relatively high methane storage capacity (219 cm$^3$ (STP) cm$^{-3}$) at room temperature (RT) and 65 bar. 6a The family of ntt-MOFs features the connection of 24-edged cuboctahedra with dendritic hexacarboxylate linkers of C$_2$-symmetry.
Therefore, a balance between high porosity and framework density should be taken into account for the development of new ntt-type MOFs to effectively store methane. With this in mind, we aimed at shortening the hexacarboxylate linker in PCN-61 to build new ntt-type MOFs. Note, however, there is a limit on how short the hexacarboxylate linker can be before the ntt topology is no longer viable. Our previous example of UTSA-61, using the smallest hexacarboxylate linker (3,3′,3″,5,5′,5″-benzene-1,3,5-triazine-1,3,5-triylhexabenoic acid, H6BHB), exhibits a zyg topology instead of ntt topology. The zyg framework consists of one-dimensional (1D) hexagonal channels supported by non-coplanar H6BHB. So, the coplanarity of the central benzene ring with three peripheral ones cannot be achieved in H6BHB due to the obvious steric hindrance; however, this coplanarity is needed to form a ntt-type framework (Figure 1). A previously reported molecular simulation for a hypothetical ntt-type structure also revealed that the shortest distance of ~4.9 Å between two paddlewheels from adjacent cuboctahedral cages is too short to accommodate two terminal solvent molecules, and thus, 2,4,6-tris(3,5-isophthalate)-5-yl(1-ethynyl-2-isophthalate) (H6L), was synthesized by a two-step reaction procedure, where compounds 1 and 2 in Scheme 1 are the intermediate substances. 1H NMR spectra were recorded on a Varian Mercury 500/400 MHz spectrometer using tetramethylsilane (TMS) as internal standards. The coupling constants were reported in Hertz. 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.

**Experimental Section**

**General Procedures and Materials.** All reagents and solvents were commercially available and used without further purification. The C₂-symmetry hexacarboxylate linker, 5,5′-benzene-1,3-diylbis(2-isophthalate)-5-yl(1-ethynyl-2-isophthalate) (H₆L), was synthesized as described in a previous publication. The synthesis of H₆L was carried out using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 5 °C min⁻¹.

**Sorption Measurements.** A Micromeritics ASAP 2020 surface area analyzer was used to measure N₂ gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh sample of UTSA-61 was guest-exchanged with dry acetone at least 10 times, filtered, and degassed at 373 K for 24 h until the outgas rate was 5 μm Hg min⁻¹ prior to measurements. The activated sample of UTSA-61a (here the MOF abbreviation with “a” at the end represents the fully activated MOF in which all coordinated and noncoordinated solvent molecules are removed) was maintained at 77 K with liquid nitrogen. High-pressure CH₄ sorption isotherms were measured using a Sievert-type apparatus at NIST. A detailed description of the experimental setup, calibration, and the isotherm measurement can be found in a previous publication.

**Synthesis of Compound 2.** Compound 1 (2.16 g, 4.0 mmol) and 1,3-diethylcarboxylate-4-ethynylbenzene (1.23 g, 5.0 mmol) were dissolved in tetrahydrofuran/triethylamine (THF/Et₃N v/v = 1/1, 100 mL) at room temperature under N₂ atmosphere. To the solution were added Pd(PPh₃)₄ (100 mg) and CuI (5 mg). The reaction mixture was stirred for 36 h at room temperature. The reaction was monitored by thin layer chromatography (TLC). Upon completion, the solution was first filtered, and the filtrate was then concentrated under reduced pressure. The resultant solid was washed with water (30 mL) and then recrystallized in THF to obtain the pure product. Yield: 78% (2.2 g). 1H NMR (500 MHz, CDCl₃, ppm): δ 8.75 (s, 2H), 8.68 (8.1H), 8.54 (s, 4H), 8.44 (s, 2H), 7.90 (s, 2H), 7.89 (s, 1H), 4.46 (q, J = 6.5 Hz, 4H), 4.02 (s, 12H), 7.15 (t, J = 7.1 Hz, 6H).

**Synthesis of 5,5′-Benzene-1,3-diylbis(2-isophthalate)-5-yl(1-ethynyl-2-isophthalate) (H₆L).** Compound 2 (2.2 g, 3.1 mmol) was suspended in 50 mL THF and then a 2 M KOH aqueous solution (75 mL) was added. The mixture was stirred under reflux overnight until it became clear. The THF was then removed under reduced pressure, and dilute HCl was added to the remaining aqueous solution to acidify to pH = 2. The precipitate was collected by filtration, washed several times with water, and then dried to give a pale yellow powder. Yield: 1.76 g (95%). 1H NMR (400 MHz, d₆-DMSO, ppm): δ 8.51 (s, 6H), 8.46 (s, 1H), 8.35 (s, 2H), 8.11 (s, 1H), 8.07 (s, 2H).
Crystal Growth & Design

Synthesis of UTSA-61. A mixture of the organic linker $H_6L$ (8 mg, 0.014 mmol) and Cu(NO$_3$)$_2$·2H$_2$O (24.0 mg, 0.104 mmol) was dissolved into DMF solvent (1.5 mL) in a screw-capped vial (20 mL), to which 20 μL of HBF$_4$ was added. The vial was capped and heated in an oven at 65 °C for 36 h. Blue precipitates were collected by filtration and washed several times with N$_2$ gas. The obtained solid sample was sealed in glass capillaries, and PXRD measurements were performed on a Rigaku Ultima IV diffractometer, operated at 40 kV and 40 mA. Data were collected over 14 h at room temperature in the 2θ range of 2−50° with a step size of 0.02°. Rietveld refinement was performed using the GSAS package.$^{11}$

Powder X-ray Crystallography. Attempts to obtain single-crystals large enough for single-crystal X-ray diffraction measurement were not successful. We thus relied on powder X-ray diffraction (PXRD) to confirm the high phase purity of the crystalline powder sample and to obtain the crystallographic structure solution. The samples were sealed in glass capillaries, and PXRD measurements were performed on a Rigaku Ultima IV diffractometer, operated at 40 kV and 40 mA. Data were collected over 14 h at room temperature in the 2θ range of 2−50° with a step size of 0.02°. Rietveld refinement was performed using the GSAS package.$^{11}$

RESULTS AND DISCUSSION

Crystallographic Structural Analysis. The PXRD patterns of as-synthesized and fully activated UTSA-61 are shown in Figure S1. The diffraction peak positions remain nearly unchanged before and after sample activation, suggesting that the UTSA-61 framework structure is robust. On the basis of the PXRD data, we solved the crystal structure of UTSA-61, using direct method. Rietveld refinement of the PXRD data of the activated sample (Figure S2) exhibits excellent goodness of fit ($R_p = 0.0913$ and $R_p = 0.0723$), further confirming our crystal structure solution. UTSA-61 crystallizes in tetragonal space group $I_4/mmm$. Its framework is isoreticular to those of PCN-6x series. In contrast to PCN-6x system, the introduction of $C_2$-symmetry linker indeed reduces the crystallographical symmetry of ntt-type frameworks. As expected, the asymmetric unit of UTSA-61 framework possesses four metal sites and half a $L_6 \cdot$ anion. There is a symmetry mirror plane which goes along with ethynyl triply bond (Figure 2a). Therefore, the whole $L$ molecule can be generated by the mirror symmetry operation of half $L$ fragment. This also enables four benzene rings of $L$ linker as coplanar as possible. Four metal sites are divided into two pairs to engage in the paddlewheel conformation. One pair of $Cu_2$ entity can generate three symmetry-related counterparts and the other pair results in one counterpart. The $L_6$ linker is coordinated to six $Cu_2$ paddlewheels while each $Cu_2$ paddlewheel is connected with four linkers. Each $Cu$ center shows a square-pyramidal geometry leaving the axial position for solvent molecule. However, two of four metal sites are located on special positions which are involved in a $-[Cu_2(O_2CR)_4 \cdot H_2O \cdot Cu_2(O_2CR)_4]-$ connection with their symmetry-related counterpart. This means that a dendritic hexacarboxylate linker may support three cuboctahedral cages in which two cubOh cages are permitted to locate next to each other (Figure 2a, b). The formation of $-[Cu_2(O_2CR)_4 \cdot H_2O \cdot Cu_2(O_2CR)_4]-$ is pointed out in particular essentially the possibility for building up ntt-type framework. Finally, the 3D framework features the connection of $L_6$ linker with four $Cu_2$ paddlewheels and one large $-[Cu_2(O_2CR)_4 \cdot H_2O \cdot Cu_2(O_2CR)_4]-$ cluster.

Apart from establishing a supercluster connection, the sizes of the T-Td/T-Oh cages also attracted our attention. Despite the lower symmetry, the overall 3D framework of UTSA-61 is similar to other reported ntt-type networks, and there are three types of cages, namely, cuboctahedral cage (cubOh), truncated tetrahedral cage (T-Td), and truncated octahedral cage (T-Oh). The cubOh cage is derived from 24 isophthalate moieties riding on all cuboctahedral edges so that no variation is observed for its inner void (Figure 2d). As shown in Figure 2e, f, the T-Td cage has four $L_6$ linkers on its four hexagonal faces, and eight $L$ linkers lie on the hexagonal surfaces of T-Oh cage. Comparing to other ntt-type framework, the inner cavity of cubOh cage is similar in size, while T-Td/T-Oh cages afford significantly diversified dimensions. In UTSA-61, the $C_2$-symmetry linker defines the deformed hexagons of T-Td/T-Oh polyhedra and in turn affects the cage interior. Using the well-developed method by Gubbinset al.$^{12}$, pore size distributions (PSD) were calculated for PCN-61, the smallest ntt-type MOFs (Here, termed as TDPAT), and UTSA-61 (Figure 3b). Three color spheres are used to denote the different cages with different dimensions ($\sim$13 Å for blue cuboctahedron, $\sim$9 Å for red T-Td, and $\sim$17 Å for rose T-Oh) in UTSA-61 (Figure 3a). It is quite evident that UTSA-61 has a smaller inner sphere for T-Td/T-Oh cages than that of PCN-61. However, the cage sizes are somewhat larger than that of TDPAT. A suitable T-Td/T-Oh cage sizes may play an important role in optimizing methane storage capacity. The calculated total accessible pore fraction of the activated UTSA-61 framework is $\sim$70.70%, and the crystal density is 0.724 g·cm$^{-3}$.

Permanent Porosity. Thermogravimetric analysis (TGA) indicates that, under a N$_2$ atmosphere, UTSA-61 exhibits good thermal stability and remains stable up to 250 °C (Figure. S2).

![Figure 2.](image-url)
The permanent porosity of UTSA-61a was confirmed by the N\textsubscript{2} adsorption isotherm at 77 K, which exhibits a fully reversible type-I behavior with a maximum N\textsubscript{2} uptake of 625 cm\textsuperscript{3} g\textsuperscript{-1} at 1 atm (Figure 4a). The adsorption curve shows steep N\textsubscript{2} uptake below P/P\textsubscript{0} = 0.04, and a plateau from P/P\textsubscript{0} = 0.1 to near saturation. On the basis of the N\textsubscript{2} data, UTSA-61a has an experimental BET surface area of 2171 m\textsuperscript{2} g\textsuperscript{-1} (Langmuir surface area of 2739 m\textsuperscript{2} g\textsuperscript{-1}). The total experimental pore volume of UTSA-61a is 0.968 cm\textsuperscript{3} g\textsuperscript{-1}, consistent with the geometric pore volume derived from the crystal structure. Pore size distribution derived from the N\textsubscript{2} adsorption data at 77 K falls in the range of ~8–18 Å, which agrees well with theoretical PSD calculation for three cages (Figures 3b and S4).

**High-Pressure Methane Storage.** The suitable pore size of UTSA-61a prompted us to measure the methane storage capacities, using a volumetric Sievert apparatus.\textsuperscript{10} The adsorption data were recorded from 0 to 65 bar at 273 and 298 K, respectively (Figures 4b and S5). The total volumetric methane uptake of UTSA-61a shows a high storage capacity of 194 cm\textsuperscript{3} (STP) cm\textsuperscript{-3} at 298 K and 35 bar. When further increasing the pressure to 65 bar, the total volumetric uptake can reach 244 cm\textsuperscript{3} (STP) cm\textsuperscript{-3}. It is worth emphasizing that the values at 35 and 65 bar are the highest reported among all ntt-type MOFs (Table 1), making UTSA-61a one of a few MOFs with very high volumetric methane capacities. It is obvious that removing two ethynyl groups from PCN-61 to UTSA-61 optimizes the T-Td/T-Oh cages (particularly, by reducing the large pore size of the T-Oh cage), and then enhances methane uptake (Figure 5). In addition, UTSA-61a has a moderately high gravimetric storage capacity of 0.241 g g\textsuperscript{-1}, larger than some benchmark MOFs, such as HKUST-1 (0.216 g g\textsuperscript{-1}), UTSA-20 (0.181 g g\textsuperscript{-1}), Ni-MOF-74 (0.148 g g\textsuperscript{-1}), and PCN-14 (0.204 g g\textsuperscript{-1}).\textsuperscript{13} To better compare the methane storage performance among ntt-type frameworks, all data for high-pressure methane storage from this work and other related references\textsuperscript{6e,h,14} are summarized in Table 1.

<table>
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<th>MOFs</th>
<th>S\textsubscript{BET} m\textsuperscript{2} g\textsuperscript{-1}</th>
<th>g cm\textsuperscript{-3}</th>
<th>Working capacity cm\textsuperscript{3} cm\textsuperscript{-3}</th>
<th>working capacity cm\textsuperscript{3} cm\textsuperscript{-3}</th>
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<td>UTSA-61</td>
<td>2171</td>
<td>0.241</td>
<td>244 (194)</td>
<td>176</td>
<td>this work</td>
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<td>Cu-TDPAT</td>
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<td>0.203</td>
<td>222 (181)</td>
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<tr>
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<td>166</td>
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<tr>
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<td>0.279</td>
<td>219 (171)</td>
<td>174</td>
<td>8a</td>
</tr>
<tr>
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<td>187 (136)</td>
<td>152</td>
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<td>0.287</td>
<td>232 (182)</td>
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\textsuperscript{a}At 298 K. \textsuperscript{b}The working capacity is defined as the difference of methane uptake between 65 and 5 bar.
temperature-dependent isotherms (Figures S6 and S7). As shown in Figure S6, the initial \( Q_v \) of UTSA-61a for methane adsorption is \( \sim 16.1 \text{ kJ mol}^{-1} \), which is slightly higher than that of NU-111 (14.2 kJ mol\(^{-1}\)) and NU-125 (15.1 kJ mol\(^{-1}\)). This is mainly attributed to the relatively higher concentration of open metal sites in UTSA-61a (2.79 mmol mL\(^{-1}\)) than in NU-111 (1.36 mmol mL\(^{-1}\)) and NU-125 (1.82 mmol mL\(^{-1}\)). Thus, UTSA-61a shows a higher volumetric methane uptake at 5 bar \( [68 \text{ cm}^3 \text{ (STP)} \text{ cm}^{-3}] \) compared to that of NU-111 \( [27 \text{ cm}^3 \text{ (STP)} \text{ cm}^{-3}] \) and NU-125 \( [50 \text{ cm}^3 \text{ (STP)} \text{ cm}^{-3}] \). However, with increasing \( \text{CH}_4 \) loading, the open metal sites and the inside surface of the cages are almost occupied by \( \text{CH}_4 \) molecules. At this time, the \( \text{CH}_4 \)-\( \text{CH}_4 \) interactions start to kick in and play an important role on the increase in \( Q_v \) at high loading.\(^{15,16}\) As a result, the \( Q_v \) value of UTSA-61a slowly climbs up and reaches a maximum of \( \sim 17.5 \text{ kJ mol}^{-1} \) at high loading. This \( Q_v \) variation in UTSA-61a is commonly observed in most of reported MOFs for methane storage.\(^{15,16}\) The maximum value of \( Q_v \) for UTSA-61a is significantly larger than that observed in NU-111 and NU-125,\(^15\) leading to significantly higher volumetric methane storage at 65 bar and thus comparable working capacity.

## CONCLUSION

In summary, UTSA-61a exhibits one of the best performances for methane storage among all reported ntt-type MOFs. We believe that a good balance among porosity, density, and pore size is in favor of the high volumetric methane uptake capacity. Success in constructing ntt-type MOFs from a shortened \( C_2 \)-symmetry linker is very encouraging and provides an important route to optimize the cage size for methane storage. It is expected that the shortened \( C_2 \)-symmetry linker can be further functionalized to target higher methane storage and working capacity in ntt-type MOFs. Work along this line is underway in our laboratory.

## ASSOCIATED CONTENT

Supporting Information The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00737.

Rietveld refinement of the experimental PXRD data. Pore size distribution (PSD) derived from \( N_2 \) adsorption isotherm, TG curve, powder X-ray diffraction patterns, excess high-pressure \( \text{CH}_4 \) adsorption isotherms and \( \text{CH}_4 \) adsorption \( Q_v \). Virial fitting method and derivation of \( Q_v \) for \( \text{CH}_4 \) adsorption (PDF).

Accession Codes

CCDC 1528518 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES


2. See DOE MOVE program at https://arpa-e-foa.energy.gov/


On the Use of Coordination Polymer to Improve Methane Storage Performance.


Supporting Information for:
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Figure S1. Powder X-ray diffraction patterns for as-synthesized and activated UTSA-61 samples.
**Figure S2.** Rietveld refinement of the experimental powder x-ray diffraction pattern of UTSA-61a. The calculated pattern (line) is in good agreement with the experimental data (circles) as evidenced by the difference pattern (line below observed and calculated patterns). Vertical bars indicate the calculated positions of Bragg peaks. Goodness of fit data: $R_{wp}=0.0913$, $R_p=0.0723$.

**Figure S3.** Thermogravimetric analysis of as-synthesized UTSA-61 sample.
Figure S4. Pore size distribution (PSD) in UTSA-61, derived from the 77K-N₂ adsorption isotherm, based on the NLDFT model.

Figure S5. Excess high-pressure CH₄ adsorption isotherms of UTSA-61a at 273 and 298 K.
Derivation of the isosteric heat of adsorption ($Q_{st}$)

A virial type expression of the following form was used to fit the CH$_4$ total adsorption isotherm data at 273 K and 298 K.

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i$$

Here, $P$ is the pressure expressed in bar, $N$ is the amount adsorbed in cc(STP)/cc, $T$ is the temperature in K, $a_i$ and $b_i$ are virial coefficients, and $m$, $n$ represents the number of coefficients required to adequately describe the isotherms. $m$ and $n$ were gradually increased until the contribution of extra added $a$ and $b$ coefficients was deemed to be statistically insignificant towards the overall fit, as determined using the average value of the squared deviations from the experimental values was minimized. The values of the virial coefficients $a_0$ through $a_m$ were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

Here, $Q_{st}$ is the coverage-dependent isosteric heat of adsorption and $R$ is the universal gas constant of 8.3147 J K$^{-1}$mol$^{-1}$. 

Figure S6. Isosteric heat of adsorption ($Q_{st}$) of CH$_4$ in UTSA-61a, derived using the virial method.
Figure S7. Derivation of $Q_m$ for CH$_4$ adsorption in UTSA-61a from virial fitting of the absolute adsorption isotherm data. The virial coefficients are shown on the right.

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