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Cryst. Growth Des., **Just Accepted Manuscript** • DOI: 10.1021/acs.cgd.7b00111 • Publication Date (Web): 03 Mar 2017

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Highly Enhanced Gas Uptake and Selectivity via Incorporating Methoxy Groups into a Microporous Metal–Organic Framework

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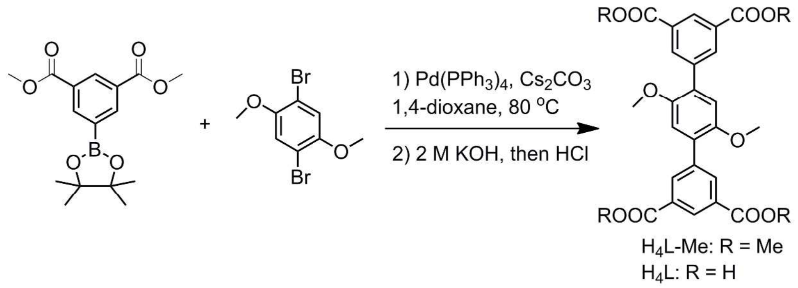
ABSTRACT: A porous metal–organic framework $[Cu_2L(H_2O)_2]\cdot 7DMF\cdot 4H_2O$ (**UTSA-90**, H_4L = 2',5'-dimethoxy-[1,1':4',1''-Terphenyl]-3,3'',5,5''-tetracarboxylic acid) functionalized with methoxy groups has been successfully constructed and structurally characterized, which is isoreticular to **NOTT-101**. A single crystal structure determination reveals that the incorporation of bulky methoxy groups can efficiently split the large pores and channels of **NOTT-101a** into smaller ones within **UTSA-90**. Compared with **NOTT-101a**, the activated **UTSA-90a** exhibits the significantly enhanced C_2H_2 (214 *vs* 184 cm^3 g^{-1}) and CO_2 (125 *vs* 83 cm^3 g^{-1}) adsorption capacities at 295 K and 1 bar. It is worth noting that the CO_2 uptake of **UTSA-90a** represents the highest reported for all the *NbO*-type MOFs. In addition, **UTSA-90a** also shows a significant enhancement in adsorptive selectivities for the separation of C_2H_2/CH_4, CO_2/CH_4 and CO_2/N_2 mixtures at ambient conditions. This work indicates that introducing bulky functional groups on the linker might be a promising approach to tune pore sizes and environments in MOFs for enhancing their gas adsorption and separation properties.

Introduction

The emergence of crystalline porous metal–organic frameworks (MOFs) has attracted much attention in the last two decades for their particularly useful applications on gas storage and separation.[1-5] The relatively simple and architectural chemistry enables us to achieve intricate design and precise control over porosity, pore size/shape, and functionality of MOF materials.[6-15] It is very important in chemistry and materials science communities to realize new materials or strategies to effectively improve gas sorption and separation capacities and thus to optimize their specific properties for the diverse purposes. Generally, the effects of functional groups with high polarity, such as Lewis basic N sites, amide, **–**OH, **–**NH_2, etc., and/or open metal sites decorating the pores of MOFs have been well documented to enhance gas uptake and separation capacities, since some gas substrates, like CO_2, C_2H_2, etc., possess a large quadrupole moment and these functional sites are able to induce polarization and thus enhance the binding affinity.[16-31] Another important way to improve gas sorption and selectivity is precise control and fine tuning of pore/channel sizes within porous MOFs at the molecular level.[32,33] In this regard, control of framework interpenetration and judicious selection of organic linkers are two general strategies.[34-37] For example, Zaworotko et al. utilized the above two strategies to finely tune pore sizes in SIFSIX series and found that **SIFSIX-3-Zn** with narrow pore windows of 3.84 Å in diameter exhibits the extremely high CO_2/CH_4 and CO_2/N_2 selectivities.[35] Chen and co-workers revealed that **UTSA-16** with small pore sizes of 3.3×5.4 $Å^2$ displays a significantly high volumetric uptake (160 cm^3 cm^{-3}) of CO_2 under ambient conditions.[38] Apparently, the realization of porous materials with relatively small pore/window sizes is very important to target high gas sorption and separation capacities.[39-41]

Recently, several new strategies have been reported and developed to effectively partition large pores into small pores within MOF materials, which certainly led to significantly enhanced gas storage and separation properties.[42-47] For example, Feng and co-workers reported a new pore space partition strategy to split large pores into smaller ones through the insertion of a secondary ligand into **MIL-88**, resulting in dramatically enhanced CO_2 uptakes to near-record values.[42,43] Wang and co-workers also partitioned the channels of **MOF-5** into confined and hydrophobic compartments by *in situ* polymerization of aromatic acetylenes for remarkably increased CO_2 adsorption and CO_2/N_2 selectivity at 273 K and 1 bar.[44] In addition, the immobilization of some bulky functional groups (e.g. methyl, *tert*-butyl) onto the frameworks have been demonstrated to be capable of finely tailoring the pore sizes and environments for gas storage and separation.[48-53] The representative example was that Chen and colleagues achieved a high C_2H_2/C_2H_4 separation in the family of mixed MOFs (**M'MOFs**) by grafting bulky *tert*-butyl groups into the linkers for finely tuning the pore spaces.[48] Inspired by their works, herein we designed and incorporated the bulky methoxy groups (–OMe) into the framework of **NOTT-101** to form a porous MOF material (termed as **UTSA-90**). Very interestingly, the incorporation of methoxy groups was able to partition the large pores and channels into smaller ones within **UTSA-90** for fine-tuning of pore spaces, which plays the most important role in trapping CO_2 and C_2H_2 molecules. As a result, the activated **UTSA-90a** exhibits not only notably improved C_2H_2 (214 $cm^3\ g^{-1}$) and CO_2 (125 $cm^3\ g^{-1}$) uptakes but also much better selectivities for separation of C_2H_2/CH_4 (60.1), CO_2/N_2 (21.7), and CO_2/CH_4 (5.3) mixtures at ambient conditions compared to those of **NOTT-101a**.

Scheme 1. The synthetic route to the organic linker H_4L.



Results and Discussion

The organic linker H_4L was readily synthesized through a Suzuki cross-coupling reaction of 1,4-dibromo-2,5-dimethoxybenzene and 2 equiv. of 5-(4,4,5,5-tetra-methyl-1,3,2-dioxaborolan-2-yl) isophthalate,[54] followed by hydrolysis and acidification (Scheme 1). Solvothermal reaction of H_4L with $Cu(NO_3)_2 \cdot 2.5H_2O$ in DMF/MeCN/H_2O (6/1/1, v/v) under acidic conditions at 80 °C for 1 day afforded blue block crystals of **UTSA-90** in about 61% yield (based on the ligand). **UTSA-90** has a formula of $[Cu_2L(H_2O)_2]\cdot 7DMF\cdot 4H_2O$, as determined by single-crystal XRD analysis, thermogravimetric (TGA) and elemental analysis. **UTSA-90** shows thermal stability up to 270 °C by TGA. The phase purity of the bulk sample was confirmed by powder X-ray diffraction (PXRD), where the measured PXRD patterns were in good agreement with the simulated ones from single-crystal diffraction data (Figure S3).

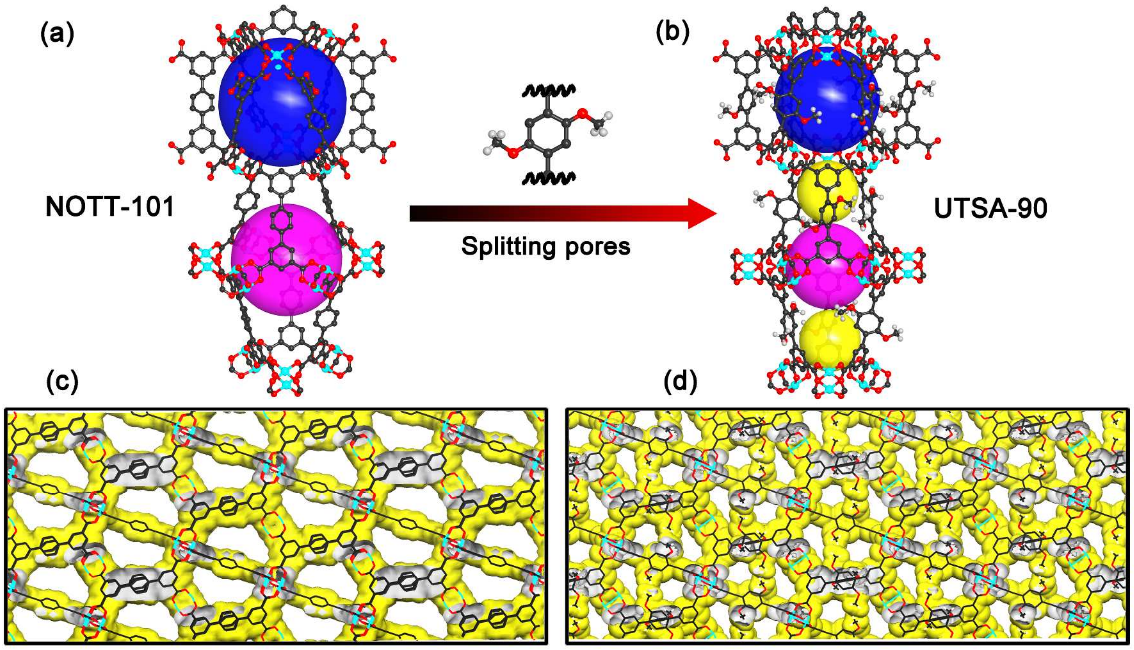


Figure 1. Comparison of crystal structures of **NOTT-101** and **UTSA-90**. (a, b) Detail of pore spaces in **NOTT-101** and **UTSA-90**, respectively, and (c, d) the channels of **NOTT-101** (c) and **UTSA-90** (d), viewed along the *a* and *b* axes, illustrating the changes of pore and channel sizes after introducing the bulky methoxy groups into the framework. Spheres denote the pores within the frameworks (Turquoise: Cu, red: O, black, C and white, H).

X-ray diffraction (XRD) analysis of single crystals of **UTSA-90** revealed that this framework crystallizes in the hexagonal space group $R\overline{3}m$, where the framework nodes consist of dinuclear $Cu_2(COO)_4$ secondary building units (SBUs) coordinated by the carboxylates of L^{4-} in paddlewheel fashion (Figure 1). **UTSA-90** forms a three-dimensional (3D) *NbO*-type topology, which is isoreticular to **NOTT-101**.[55] As shown in Figure 1a, the **NOTT-101** framework has two types of cages: one cage (blue) of about 11.2 $Å^2$ in diameter and the other large irregular elongated cage (pink) of about 9.6 × 22.3 $Å^2$. The incorporation of bulky methoxy groups into the linker of **NOTT-101** can remarkably alter the MOF pore structures. Firstly, the diameter of the blue cage is significantly decreased from 11.2 Å in **NOTT-101** to 8.9 Å in **UTSA-90** because of six –OMe groups pointing into the cage (Figure 1b). Secondly, the large irregular cage can be divided into three small cages by two series of three –OMe groups in close contact: one squashed cuboctahedral cage at the center (pink) and two extraordinarily small cages of ~ 3.5 Å on the top and bottom (yellow). Furthermore, the large pore channels in **NOTT-101** along *a*- and *b*-axes can be also fragmented into numerous smaller channels by the grafted –OMe groups within **UTSA-90** (Figure 1c and 1d). These observed changes in pore spaces can be further confirmed by the calculated geometric pore size distributions (PSD) of **NOTT-101** and **UTSA-90** (Figure 2).[56] As depicted in Figure 2, when the –OMe groups are incorporated into the framework, the pores with widths of about 12 Å in **NOTT-101** diminish, whereas new pores with widths of 8.7 Å (reduced/partitioned pores) emerge in **UTSA-90**. These results suggest that the immobilized methoxy groups play important roles in the diminution and partition of pore spaces, which would certainly have a significant effect on gas adsorption and separation properties.

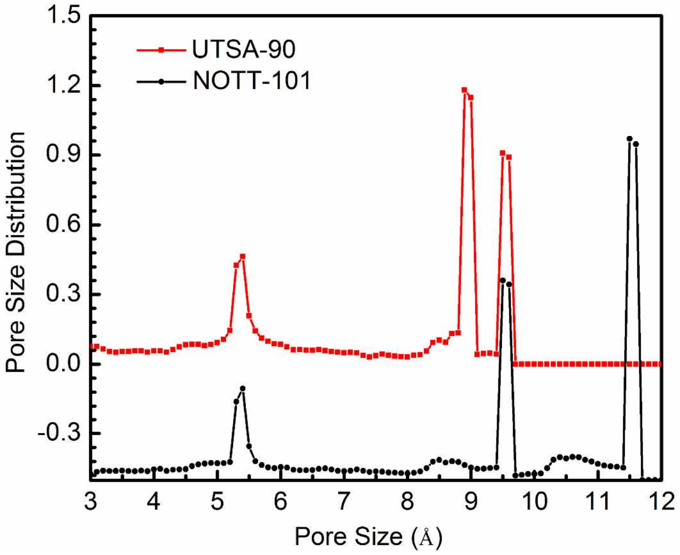


Figure 2. Pore size distributions of **UTSA-90** (black line) and **NOTT-101**(blue line), calculated using the well-known method by Gubbins et al.[56] The van der Waals diameters of the framework atoms were adopted from the Cambridge Crystallographic Centre.

The permanent porosity of activated **UTSA-90a** was determined by nitrogen adsorption isotherms at 77 K. Before adsorption measurements, the as-synthesized sample was solvent-exchanged by dry acetone at least 10 times, and then heat treated at room temperature for 24 h and at 373 K for an additional 24 h under high vacuum to yield the desolvated **UTSA-90a**. As shown in Figure 3a, **UTSA-90a** exhibits a reversible type I character with a saturated N_2 adsorption capacity of about 562 cm^3/g at 77 K and 1 bar, corresponding to a pore volume of

0.88 cm^3 g^{-1}. This value is very close to the calculated pore volume of 0.82 cm^3 g^{-1} from single-crystal structure, indicating that the sample was desolvated completely. The Brunauer–Emmett–Teller (BET) surface area of **UTSA-90a** was found to be 2273 m^2 g^{-1}. As expected, these values are much lower than those reported in the isoreticular **NOTT-101a** (1.08 cm^3 g^{-1} and 2805 m^2 g^{-1}) because of the free volume occupation by the immobilized methoxy groups.

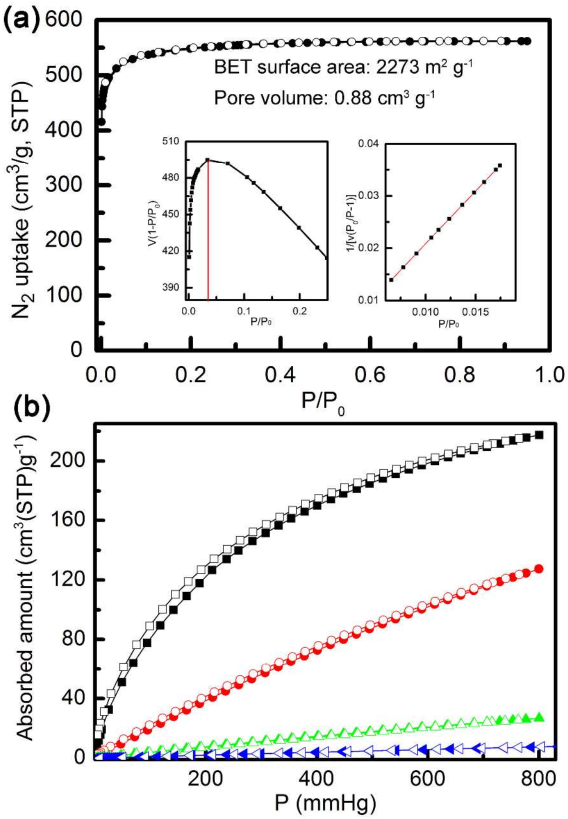


Figure 3. Gas sorption study on the activated **UTSA-90a**. (a) Nitrogen isotherm at 77 K with consistency and BET plots. (b) C_2H_2 (black), CO_2 (red), CH_4 (green), and N_2 (blue) sorption isotherms for **UTSA-90a** at 295 K.

The established high porosity and fine-tuning over pore metrics in **UTSA-90a** have prompted us to examine its gas sorption properties. The single-component gas adsorption isotherms for **UTSA-90a** were collected up to 1 bar at 273 K and 295 K, respectively (Figure 3b and S6). As shown in Figure 3b, **UTSA-90a** can adsorb an exceptionally high amount (214 cm^3 g^{-1}) of C_2H_2 at 295 K and 1 bar, being notably higher than that of **NOTT-101** (184 cm^3 g^{-1}). Table S1 further lists the comparison of **UTSA-90a** with some promising MOFs for C_2H_2 storage at ambient conditions. It can be seen from the table that the C_2H_2 uptake of **UTSA-90a** is among the highest reported for MOF materials to date, and even outperforms those of two benchmark MOFs: **HKUST-1** (201 cm^3 g^{-1})[57] and **CoMOF-74** (197 cm^3 g^{-1}).[58] Similarly, **UTSA-90a** also shows a significantly enhanced CO_2 uptake capacity (125 cm^3 g^{-1}, 24.6 wt%) than **NOTT-101a** (83 cm^3 g^{-1}, 16.5 wt%) at 295 K and 1 bar. It should be pointed out that this gravimetric CO_2 uptake of **UTSA-90a** represents the highest value observed to date in the entire family of *NbO*-type MOFs (Table 1),[59-67] including those functionalized with strong affinity sites, for example Lewis basic N sites,[60] amide,[64] amino,[63] methylol,[53] and so on. Compared with other types of MOFs, to the best of our knowledge, only a handful of MOFs such as **Mg-MOF-74** (178 cm^3 g^{-1}),[68] **Co-MOF-74** (155 cm^3 g^{-1}),[68] **MAF-X25ox** (159 cm^3 g^{-1}),[69] **CPM-231** (151 cm^3 g^{-1}),[70] **Cu-TDPAT** (132 cm^3 g^{-1}),[71] and **Cu(Me-4py-trz-ia)** (136 cm^3 g^{-1})[72] have much higher CO_2 gravimetric uptake at ambient conditions (Table S2). In terms of volumetric uptake, the value of **UTSA-90a** is moderately high reaching 96 cm^3 cm^{-3}, but still superior to other reported *NbO*-type MOFs excluding **NbO-Pd-1** (Table 1).

The high C_2H_2 and CO_2 uptakes for **UTSA-90a** suggest that incorporating bulky methoxy groups plays an important role in enhancing gas sorption capacities. To better understand these observations, we calculated the coverage-dependent adsorption enthalpies of **UTSA-90a** for C_2H_2 and CO_2 below 1 bar by the well-established virial method. As shown in Figure S8, the initial Q_{st} values of C_2H_2 and CO_2 for **UTSA-90a** were estimated to be 36.5 and 20.5 KJ/mmol, respectively. The Q_{st} of C_2H_2 at zero coverage is close to that of **NOTT-101a** (37.1 KJ/mmol),[37] whereas the value of CO_2 is slightly lower than **NOTT-101a** (23.3) and those *NbO*-type MOFs with functional sites, such as **NbO-Pd-1** (24.8), **HKUST-1** (31.2), and **NOTT-125** (25.4). These results indicate that the immobilized methoxy groups may not offer additional strong adsorption sites to enforce the interaction with gas molecules. Therefore, the suitable pore sizes formed by the partition effect of methoxy groups within **UTSA-90a** are presumably responsible for the dramatically enhanced C_2H_2 and CO_2 uptake capacities. Such phenomena was also clearly exemplified by **UTSA-16** and **PCN-88** with moderate Q_{st} values for high CO_2 uptakes due to the optimized pore sizes for efficiently trapping CO_2 molecules.[38,73]

Table 1. Comparison of CO_2 uptake of **UTSA-90a** with some promising Cu-based *NbO*-type MOFs.

MOFs	S_{BET} [m^2 g^{-1}]	V_p (g cm^{-3})	CO_2 uptake[a]		Q_{st}[b]	Ref.
			cm^3 g^{-1}	cm^3 cm^{-3}		
UTSA-90a	2273	0.88	125	96	20.5	This work
NbO-Pd-1	1568	0.60	124	116	24.8	59
ZJNU-44	2314	0.916	116	87	-	60
ZJNU-40	2209	0.88	108	80	18.4	61
QI-Cu	1631	0.662	102	85	23.7	53
NJU-Bai14	2384	0.924	100	75	24.5	62
ZJU-8a	2501	1.02	95	66	21.9	63
HNUST-1	1400	0.571	93	54	31.2	64
NOTT-125	2471	1.10	93	63	25.4	65
NOTT-101a	2805	1.08	83	58	23.3	61
SNU-50	2300	1.08	80	52	25.8	66
NU-135	2600	1.02	80	60	25.5	67

[a] At room temperature and 1 bar. [b]The CO_2 adsorption enthalpies at zero coverage.

In sharp contrast to the high C_2H_2 and CO_2 uptake capacities, as depicted in Figure 3b, **UTSA-90a** shows little CH_4 (26 cm^3 g^{-1}) and N_2 (6.9 cm^3 g^{-1}) uptake at 1 bar and 295 K. The marked difference between CO_2/C_2H_2 and CH_4/N_2 adsorption isotherms indicates that **UTSA-90a** has a great potential on the separation of C_2H_2/CH_4, CO_2/CH_4 and CO_2/N_2 mixtures. The well-known Ideal Adsorbed Solution Theory (IAST) was used to calculate the adsorption selectivity of **UTSA-90a** for the following three binary mixtures: C_2H_2–CH_4 (50/50, v/v), CO_2–CH_4 (50/50, v/v), and CO_2–N_2 (15/85, v/v), which are mostly related to acetylene purification, natural gas upgrading, and post-combustion CO_2 capture applications, respectively. Figure 4a–4c present the IAST selectivities of C_2H_2–CH_4, CO_2–N_2 and CO_2–CH_4 separation for **UTSA-90a** and **NOTT-101a** at room temperature. The adsorption selectivity of **UTSA-90a** for C_2H_2/CH_4, CO_2/N_2, and CO_2/CH_4 separation was found to be 60.1, 21.7, and 5.3, respectively (at 295 K and 1 bar), all of which show a significant improvement compared with those of **NOTT-101a** (40.8, 13.8, and 4.7). We note that the C_2H_2/CH_4 selectivity of 60.1 is much higher than most of other promising MOFs reported to date,[74] such as **FJI-C4** (51),[75] **UTSA-35a** (19),[76] and **ZJU-199** (27).[77] In addition, the IAST selectivity of CO_2/N_2 (19 to 22) for **UTSA-90a** is also very respectable, which outperforms any other reported *NbO*-type MOF (except **NbO-Pd-1**), even including those functionalized with Lewis basic N sites (**ZJUN-44**: 16.3),[60] oxamide (**NOTT-125a**: 16),[65] benzothiadiazole (**ZJNU-40**: 17),[61] and amino (**ZJU-8a**, 12.3).[63] Most importantly, this value is also comparable to that of some famous MOFs, for example **Cu-BTTri** (21),[78] **Cu-TPBTM** (22),[19] **PCN-88** (18),[73] and **HKUST-1** (20),[79] suggesting its great potential on capturing CO_2 from flue gas. All the observed results indicate that the incorporation of bulky methoxy groups for splitting pore spaces within MOFs shows a great benefit not only for improving gas uptakes, but also for the selectivity of CO_2 and C_2H_2 over CH_4 and N_2 in the low pressure region.

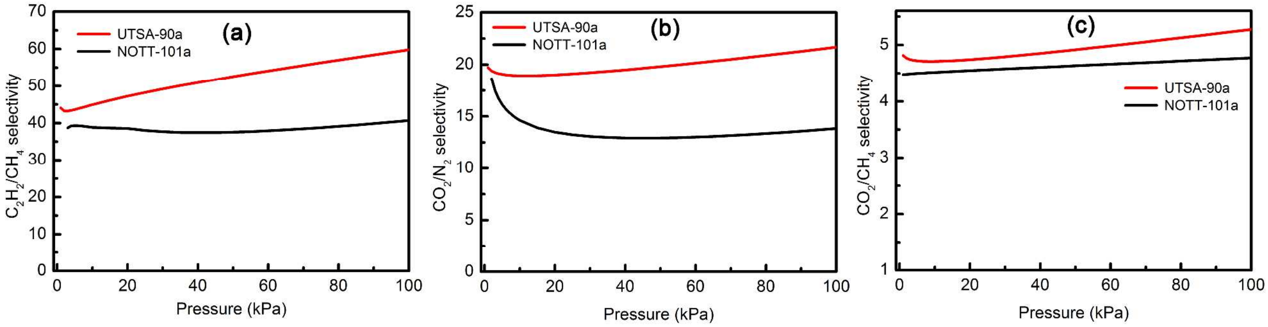


Figure 4. Comparison of IAST selectivities of (a) C_2H_2–CH_4 (50/50, v/v), (b) CO_2–N_2 (15/85, v/v), and (c) CO_2–CH_4 (50/50, v/v) mixtures between **UTSA-90a** and **NOTT-101a** at room temperature.

Conclusions

In summary, we have designed and synthesized an organic linker with functional methoxy groups, and successfully constructed its copper (II) metal–organic framework (**UTSA-90**). By introducing the bulky –OMe groups into the framework, fine tailoring of pore spaces can be achieved within **UTSA-90**, where the large pores and channels can be split into smaller ones. These partitioned pores played the most important role in enhancing gas adsorption and separation capacities. As a result, **UTSA-90a** exhibited not only significantly improved C_2H_2 and CO_2 uptakes, but also much better selectivities for separation of C_2H_2/CH_4, CO_2/CH_4 and CO_2/N_2 mixtures than the isoreticular **NOTT-101a** at ambient conditions. Our work here demonstrated a promising strategy that the incorporation of bulky functional groups into MOF materials has the potential to finely tune the MOF pore sizes and metrics, and thus optimize their gas sorption and separation properties.

ASSOCIATED CONTENT

Supporting Information.

This Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021//x0xx00000x.

Crystallographic data, NMR, TGA, PXRD, Heats of adsorption, adsorption isotherms, and additional figures and tables.

Accession Codes

CCDC 1529733 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

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ACKNOWLEDGMENT

This work was supported by Grant AX-1730 from the Welch Foundation (BC).

REFERENCES

(1) Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. *Science* **2013**, *341*, 974–987.

(2) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724–781.

(3) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869–932.

(4) He, Y.; Zhou, W.; Qian, G.; Chen, B. *Chem. Soc. Rev.* **2014**, *43*, 5657–5678.

(5) Li, B.; Wen, H.-M.; Cui, Y.; Zhou, W.; Qian, G.; Chen, B. *Adv. Mater.* **2016**, *28*, 8819–8860.

(6) Férey, G.; Serre, C. *Chem. Soc. Rev*. **2009**, *38*, 1380–1399.

(7) Zhang, J.-P.; Liao P.-Q.; Zhou H.-L.; Lin R.-B.; Chen, X.-M. *Chem. Soc. Rev.* **2014**, *43*, 5789-5814.

(8) Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G. *Acc. Chem. Res.* **2016**, *49*, 483–493.

(9) Farha, O. K.; Eryazici, I.; Jeong, N. C.; Hauser, B. G.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Nguyen, S. T.; Yazaydın, A. Ö.; Hupp, J. T. *J. Am. Chem. Soc*. **2012**, *134*, 15016–15021.

(10) Yuan, D.; Zhao, D.; Sun D.; Zhou, H.-C. *Angew. Chem. Int. Ed*. **2010***, 49*, 5357–5361.

(11) Cui, X.; Chen, K.; Xing, H.; Yang, Q.; Krishna, R.; Bao, Z.; Wu, H.; Zhou, W.; Dong, X.; Han, Y.; Li, B.; Ren, Q.; Zaworotko, M. J.; Chen. B. *Science* **2016**, *353,* 141-144.

(12) Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel S.; Fischer, R. A. *Chem. Soc. Rev*. **2014**, *43*, 6062–6096.

(13) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. *Science* **2010**, *330*, 650–653.

(14) Wang, C.; Liu, D.; Lin, W. *J. Am. Chem. Soc.* **2013**, *135*, 13222–13234.

(15) Li, B.; Chrzanowski, M.; Zhang, Y.; Ma, S. *Coord. Chem. Rev.* **2016**, *307*, 106-129.

(16) Zhang, Z.; Yao, Z.-Z.; Xiang, S.; Chen, B. *Energy Environ. Sci*. **2014**, *7*, 2868–2899.

(17) Fracaroli, A. M.; Furukawa, H.; Suzuki, M.; Dodd, M.; Okajima, S.; Gándara, F.; Reimer, J. A.; Yaghi, O. M. *J. Am. Chem. Soc*. **2014**, *136*, 8863-8866.

(18) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc*. **2010**, *132*, 38–39.

(19) Zheng, B.; Bai, J.; Duan, J.; Wojtas, L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 748–751.

(20) Luo, F.; Yan, C.; Dang, L.; Krishna, R.; Zhou, W.; Wu, H.; Dong, X.; Han, Y.; Hu, T.-L.; O'Keeffe, M.; Wang, L.; Luo, M.; Lin, R.-B.; Chen, B. *J. Am. Chem. Soc.* **2016**, *138*, 5678–5684.

(21) Zhang, H.-X.; Liu, M.; Wen, T.; Zhang, *J. Coord. Chem. Rev*. **2016**, *307*, 255–266.

(22) Zhang, J.-P.; Zhu, A.-X.; Lin, R.-B.; Qi, X.-L.; Chen, X.-M. *Adv. Mater*. **2011**, *23*, 1268–1271.

(23) Li, B.; Wen, H.-M.; Zhou, W.; Xu, J. Q.; Chen, B. *Chem* **2016**, *49*, 557–580.

(24) Bao, S.-J.; Krishna, R.; He, Y.-B.; Qin, J.-S.; Su, Z.-M.; Li, S.-L.; Xie, W.; Du, D.-Y.; He, W.-W.; Zhang, S.-R.; Lan, Y.-Q. *J. Mater. Chem. A* **2015**, *3*, 7361−7367.

(25) Du, L.; Lu, Z.; Zheng, K.; Wang, J.; Zheng, X.; Pan, Y.; You, X.; Bai, J. *J. Am. Chem. Soc.* **2013**, *135*, 562–565.

(26) Xiong, Y.; Fan, Y.-Z.; Yang, R.; Chen, S.; Pan, M.; Jiang J.-J.; Su C.-Y. *Chem. Commun.* **2014**, *50*, 14631−14634.

(27) Jia, J.; Wang, L.; Zhu, G. *Chem. Eur. J*. **2014**, *20*, 9073– 9080.

(28) Yoon, J. W.; Chang, H.; Lee, S.-J.; Hwang, Y. K.; Hong, D.-Y.; Lee, S.-K.; Lee, J. S.; Jang, S.; Yoon, T.-U.; Kwac, K.; Jung, Y.; Pillai, R. S.; Faucher, F.; Vimont, A.; Daturi, M.; Ferey, G.; Serre, C.; Maurin, G.; Bae, Y.-S.; Chang, J.-S. *Nat. Mater*. **2016**, DOI: 10.1038/NMAT4825.

(29) Bloch, Eric D.; Queen, W, L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. *Science* **2012**, *335*, 1606−1610.

(30) Sato, H.; Kosaka, W.; Matsuda, R.; Hori, A.; Hijikata, Y.; Belosludov, R. V.; Sakaki, S.; Takata, M.; Kitagawa, S. *Science.* **2014***, 343,* 167−170.

(31) Yang, S.; Ramirez-Cuesta, A. J.; Newby, R.; Garcia-Sakai, V.; Manuel, P.; Callear, S. K.; Campbell, S. I.; Tang, C. C.; Schröder, M. *Nat. Chem*. **2015**, *7*, 121−129.

(32) Li, B.; Wen, H.-M.; Zhou, W.; Chen, B. *J. Phys. Chem. Lett*., **2014**, *5*, 3468–3479.

(33) Chen, K.-J.; Madden, D. G.; Pham, T.; Forrest, K. A.; Kumar, A.; Yang, Q.-Y.; Xue, W.; Space, B.; Perry, J. J.; Zhang, J.-P.; Chen, X.-M.; Zaworotko, M. J. *Angew. Chem. Int. Ed*. **2016**, *55*, 10268 –10272.

(34) Jiang, H.-L.; Makal, T. A.; Zhou, H.-C. *Coord. Chem. Rev*. **2013**, *257*, 2232–2249.

(35) Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80–84.

(36) Assen, A. H.; Belmabkhout, Y.; Adil, K.; Bhatt, P. M.; Xue, D.-X.; Jiang, H.; Eddaoudi, M. *Angew. Chem. Int. Ed*. **2015**, *54*, 14353–14358.

(37) He, Y.; Li, B.; O'Keeffe, M.; Chen, B. *Chem. Soc. Rev*. **2014** , *43*, 5618–5656.

(38) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. *Nat. Commun*. **2012**, *3*, 954–963.

(39) Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M. *Nat. Commun*. **2014**, *5*, 4228.

(40) Cadiau, A.; Adil, K.; Bhatt, P. M.; Belmabkhout, Y.; Eddaoudi, M. *Science* **2016**, *353*, 137–140.

(41) Hu, T.-L.; Wang , H.; Li, B.; Krishna, R.; Wu, H.; Zhou, W.; Zhao, Y.; Han, Y.; Wang, X.; Zhu, W.; Yao, Z.; Xiang, S.; Chen, B. *Nat. Commun*. **2015**, *6*, 7328 .

(42) Zhao, X.; Bu, X.; Zhai, Q.-G.; Tran, H.; Feng, P. *J. Am. Chem. Soc*. **2015**, *137*, 1396−1399.

(43) Zhao, X.; Bu, X.; Nguyen, E. T.; Zhai, Q.-G.; Mao, C.; Feng, P. *J. Am. Chem. Soc*. **2016**, *138*, 15102−15105.

(44) Ding, N.; Li, H.; Feng, X.; Wang, Q.; Wang, S.; Ma, L.; Zhou, J.; Wang, B. *J. Am. Chem. Soc*. **2016**, *138*, 10100−10103.

(45) Gamage, N.-D. H.; McDonald K. A.; Matzger, A. J. *Angew. Chem. Int. Ed*. **2016**, *55*, 12099 –12103.

(46) Zhang, Z. J.; Nguyen, H. T. H.; Miller, S. A.; Ploskonka, A. M.; DeCoste, J. B.; Cohen, S. M. *J. Am. Chem. Soc*. **2016**, *138*, 920−925.

(47) Chen, D.-M.; Tian, J.-Y.; Liu, C.-S.; Du, M. *Chem. Commun.* **2016**, *52*, 8413−8416.

(48) Das, M. C.; Guo, Q.; He, Y.; Kim, J.; Zhao, C.-G.; Hong, K.; Xiang, S.; Zhang, Z.; Thomas, K. M.; Krishna, R.; Chen, B. *J. Am. Chem. Soc*., **2012**, *134*, 8703–8710.

(49) Wang, C.; Li, L.; Tang, S.; Zhao. X. *ACS Appl. Mater. Inter.* **2014**, *6*, 16932−16940.

(50) Burtch, N. C.; Jasuja, H.; Dubbeldam, D.; Walton, K. S. *J. Am. Chem. Soc.* **2013**, *135*, 7172−7180.

(51) Li, L.; Bell, J. G.; Tang, S.; Lv, X.; Wang, C.; Xing, Y.; Zhao, X.; Thomas, K. M. *Chem. Mater.* **2014**, *26*, 4679−4695.

(52) Hu, Z.; Nalaparaju, A.; Peng, Y.; Jiang, J.; Zhao, D. *Inorg. Chem.* **2016**, *55*, 1134–1141.

(53) Hu, Z.; Zhang, K.; Zhang, M.; Guo, Z.; Jiang, J.; Zhao, D. *ChemSusChem* **2014**, *7*, 2791–2795.

(54) Chen, Z.; Xiang, S.; Liao, T.; Yang, Y.; Chen, Y.-S.; Zhou, Y.; Zhao, D.; Chen. B. *Cryst. Growth Des.* **2010**, *10*, 2775–2779.

(55) Li, B.; Wen, H.-M.; Wang, H.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou, W.; Chen, B. *J. Am. Chem. Soc*. **2014**, *136*, 6207−6210.

(56) Bhattacharya, S.; Gubbins K. E. *Langmuir* **2006**, *22*, 7726−7731.

(57) Xiang, S.; Zhou, W.; Gallegos, J. M.; Liu, Y.; Chen, B. *J. Am. Chem. Soc*. **2009**, *131*, 12415−12419.

(58) Xiang, S.; Zhou, W.; Zhang, Z.; Green, M. A.; Liu, Y.; Chen, B. *Angew. Chem. Int. Ed.* **2010**, *49*, 4615−4618.

(59) Spanopoulos, I.; Bratsos, I.; Tampaxis, C.; Vourloumis, D.; Klontzas, E.; Froudakis, G. E.; Charalambopoulou, G.; Steriotis, T. A; Trikalitis P. N. *Chem. Commun*., **2016**, *52*, 10559–10562.

(60) Song, C.; Hu, J.; Ling, Y.; Feng, Y.; Krishna, R.; Chen D.-l.; He. Y. *J. Mater. Chem. A* **2015**, *3*, 19417–19426.

(61) Song, C.; He, Y.; Li, B.; Ling, Y; Wang, H.; Feng, Y.; Krishna, R.; Chen, B. *Chem. Commun.* **2014**, *50*, 12105–12108.

(62) Zhang, M.; Wang, Q.; Lu, Z.; Liu, H.; Liu, W.; Bai, J. *Cryst. Eng. Comm*. **2014**, *16*, 6287–6290.

(63) Cai, J.; Wang, H.; Wang, H.; Duan, X.; Wang, Z.; Cui, Y.; Yang, Y.; Chen, B.; Qian. G. *RSC Adv*. **2015**, *5*, 77417–77422.

(64) Zheng, B.; Liu, H.; Wang, Z.; Yu, X.; Yia, P.; Bai, J. *Cryst. Eng. Comm.* **2013**, *15*, 3517–3520.

(65) Alsmail, N. H.; Suyetin, M.; Yan, Y.; Cabot, R.; Krap, C. P.; Jian L.; Easun, T. L.; Bichoutskaia, E.; Lewis, W.; Blake, A. J.; Schröder, M. *Chem. Eur. J.* **2014**, *20*, 7317–7324.

(66) Thazhe, K. P.; Dae, H. H.; Suh, M. P. S. *Chem. Eur. J*. **2010**, *16*, 14043–14050.

(67) Kennedy, R. D.; Krungleviciute, V.; Clingerman, D. J.; Mondloch, J. E.; Peng, Y.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Hupp, J. T.; Yildirim, T.; Farha, O. K.; Mirkin, C. A. *Chem. Mater.* **2013**, *25*, 3539−3543.

(68) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870–10871.

(69) Liao, P.-Q.; Chen, H.; Zhou, D.-D.; Liu, S.-Y.; He, C.-T.; Rui, Z.; Ji, H.; Zhang J.-P.; Chen, X.-M. *Energy Environ. Sci*. **2015**, *8*, 1011–1016.

(70) Zhai, Q.-G.; Bu, X.; Mao, C.; Zhao, X.; Daemen, L.; Cheng, Y., Ramirez-Cuesta, A. J.; Feng, P. *Nat. Commun.***2016**, *7*, 13645.

(71) Li, Y.; Yao, K.; Zhu, Y.; Deng, Z.; Yang, F.; Zhou, X.; Li, G.; Wu, H.; Nijem, N.; Chabal, Y. J.; Lai, Z.; Han, Y.; Shi, Z.; Feng, S.; Li, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 1412–1415.

(72) Lassig, D.; Lincke, J.; Moellmer, J.; Reichenbach, C.; Moeller, A.; Glaser, R.; Kalies, G.; Cychosz, K. A.; Thommes, M.; Staudt, R.; Krautscheid, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 10344–10348.

(73) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nat. Commun.* **2013**, *4*, 204.

(74) Bao, Z.; Chang, G.; Xing, H.; Krishna, R.; Ren, Q.; Chen, B. *Energy Environ. Sci.* **2016**, *9*, 3612−3641.

(75) Li, L.; Wang, X.; Liang, J.; Huang, Y.; Li, H.; Lin, Z.; Cao, R. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9777−9781.

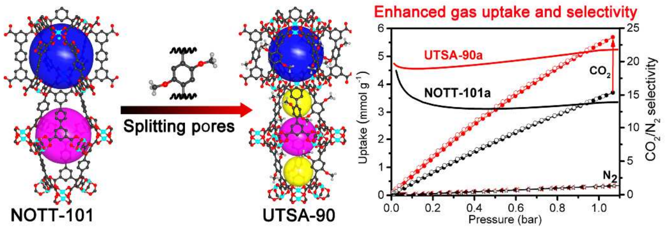
(76) He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem. Commun.* **2012**, *48*, 6493−6495.

(77) Zhang, L.; Zou, C.; Zhao, M.; Jiang, K.; Lin, R.; He, Y.; Wu, C.-D.; Cui, Y.; Chen, B.; Qian, G. *Cryst. Growth Des.* **2016**, *16*, 7194−7197.

(78) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784–8786.

(79) Zhang, Z.; Li, Z.; Li, J. *Langmuir* **2012**, *28*, 12122−12133.

Table of Contents Graphic:



By incorporating the bulky methoxy groups into the framework of **NOTT-101a** for splitting large pores/channels into smaller ones, a microporous metal–organic framework (**UTSA-90**) has been realized to display not only significantly improved C_2H_2 and CO_2 uptakes but also better selectivities for separation of C_2H_2/CH_4 (60.1 vs 40.8), CO_2/CH_4 (21.7 vs 13.8), and CO_2/N_2 (5.3 vs 4.7) mixtures than **NOTT-101a** at ambient conditions.