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**DOI**

[10.1039/c5cc08210b](https://doi.org/10.1039/c5cc08210b)

**Publication date**

2016

**Document Version**

Final published version

**Published in**

Chemical Communications

[Link to publication](#)

**Citation for published version (APA):**

Wen, H. M., Li, B., Wang, H., Krishna, R., & Chen, B. (2016). High acetylene/ethylene separation in a microporous zinc(II) metal-organic framework with low binding energy. *Chemical Communications*, 52(6), 1166-1169. <https://doi.org/10.1039/c5cc08210b>

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Cite this: *Chem. Commun.*, 2016, 52, 1166

Received 1st October 2015,  
Accepted 16th November 2015

DOI: 10.1039/c5cc08210b

www.rsc.org/chemcomm

## High acetylene/ethylene separation in a microporous zinc(II) metal–organic framework with low binding energy†

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**A novel zinc(II) metal–organic framework UTSA-67a with narrow one-dimensional (1D) pore channels and inner cages of moderate size has been developed for highly selective separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures at room temperature.**

The removal of acetylene from acetylene/ethylene mixtures (1/99) is an industrially important task given the fact that pure ethylene has been widely utilized for the production of polymers and other useful chemicals. During steam cracking of ethane to produce ethylene in industry, a small amount of acetylene (typically 1%) is unavoidably generated as one of the by-products. Because acetylene has a deleterious effect on end-products of ethylene such as polyethene, it is necessary to remove acetylene from crude ethylene to the acceptable level of no more than 40 ppm of impurity. The commercial technologies for the removal of acetylene include partial hydrogenation and solvent extraction, which are high cost and energy-intensive.<sup>1</sup> One alternative energy-efficient strategy is the adsorptive separation technology which is based on the selective adsorption of porous materials for acetylene and ethylene. The development of new porous materials is the key to implement this adsorptive technology for this important industrial separation.

The last two decades have witnessed the emergence of porous metal–organic frameworks (MOFs), which can be straightforwardly self-assembled from metal ions/clusters and organic linkers. They have become very promising candidates for gas storage and separation.<sup>2,3</sup> The richness of metal ions/clusters and organic linkers has enabled us to rationally tune and predesign their structures, pore/window sizes, and functionalities for

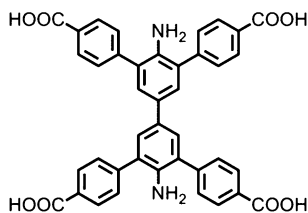
the separation of some specific gas molecules.<sup>4</sup> Recently, microporous MOFs have been of great interest as promising candidates for the separation of light hydrocarbons.<sup>5–9</sup> Among the diverse gas separations, MOFs for the separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> have been very challenging and not fully explored because of their similar sizes, volatilities, and electronic structures of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>.<sup>5c</sup> Nowadays two types of MOFs have been realized for this important separation: (a) those with small pore windows and thus sieving effects as exemplified in mixed MOFs (M<sup>2</sup>MOFs) series<sup>10,11</sup> and (b) those with specific open metal sites as indicated in MOF-74 series.<sup>12,13</sup> Despite high selectivities for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation, those M<sup>2</sup>MOFs exhibit extraordinarily low C<sub>2</sub>H<sub>2</sub> uptake capacities due to their narrow pore windows. In contrast, high densities of open metal sites within the MOF-74 series can notably enhance their C<sub>2</sub>H<sub>2</sub> uptake capacities; however, their large pores lead to quite low selectivities.<sup>12</sup> Furthermore, the high densities of open metal sites also result in a strong binding energy for C<sub>2</sub>H<sub>2</sub> molecules and thus significantly high regeneration energy costs. Therefore, an ideal MOF for this challenging separation should not only have narrow pore channels to maximize the sieving effects for achieving high separation selectivity, but also have inner cages of moderate size to improve C<sub>2</sub>H<sub>2</sub> uptake capacity. Very recently, our group has realized a very promising MOF UTSA-100, whose pore structures almost meet the above criteria, which exhibits the best performance so far for the removal of acetylene from 1% acetylene/ethylene mixtures.<sup>15</sup> This encourages us to seek new MOF materials that have similar structures for highly efficient C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation.

With this goal in our mind, we reported herein the synthesis of a novel porous MOF (termed as UTSA-67) by making use of a new tetracarboxylate ligand whose structural features indeed meet the above-mentioned criteria: narrow 1D pore channels with 3.3 Å diameter for their high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> sieving effects, moderate inner cages of 7 Å for high C<sub>2</sub>H<sub>2</sub> uptake capacity, and low binding energy due to the absence of open metal sites. As expected, the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation selectivity of UTSA-67a is comparable to that of UTSA-100a, and three times higher than

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† Electronic supplementary information (ESI) available: Synthesis and characterization of UTSA-67, PXRD, TGA, sorption isotherms, and breakthrough simulations. CCDC 1425153. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc08210b



**Scheme 1** Schematic structure of the new organic ligand ( $H_4L$ ) that serves as a linker in UTSA-67.

those of the MOF-74 series. The inner cages of moderate size within UTSA-67a can notably improve the  $C_2H_2$  uptake capacity.<sup>16</sup> Most importantly, the absence of open metal sites within UTSA-67a results in the very low binding energy and thus low regeneration energy costs, which are much lower than those of most of the examined MOFs. Taking these results together, UTSA-67a is indeed among the best materials for the selective removal of acetylene from ethylene/acetylene mixtures.

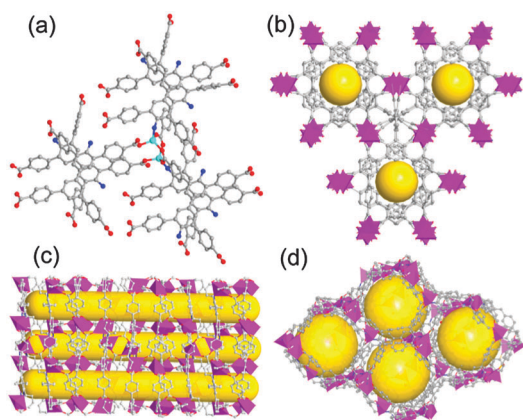
The organic linker ( $H_4L$ , Scheme 1) was simply prepared through the Suzuki cross-coupling reaction of 3,3',5,5'-tetrabromo-benzidine with 4 equiv. of 4-methoxycarbonylphenylboronic acid, followed by hydrolysis and acidification. Reactions of the organic linker and  $Zn(NO_3)_2 \cdot 6H_2O$  in DMF-EtOH at 80 °C for 24 h afforded yellow block crystals. Based on single-crystal XRD studies, TGA and elemental analysis, the as-synthesized UTSA-67 can be formulated as  $[Zn_2L] \cdot 2DMF \cdot 4H_2O$ . The phase purity of the bulk material was independently confirmed by powder X-ray diffraction (Fig. S3, ESI<sup>†</sup>).

Single-crystal X-ray diffraction analysis reveals that UTSA-67 adopts a three-dimensional network that crystallizes in a hexagonal space group  $P6_322$ . As shown in Fig. S5 (ESI<sup>†</sup>), each organic linker contains two bridging carboxylates, two monodentate carboxylates and two coordinated amino groups. The secondary building unit (SBU) is a binuclear zinc cluster in which two equivalent Zn1 atoms are coordinated by two amino groups and four carboxylate groups from six different ligands with a  $Zn1 \cdots Zn1$  distance of 3.702(1) Å (Fig. 1a). Topologically, each binuclear zinc cluster and each organic

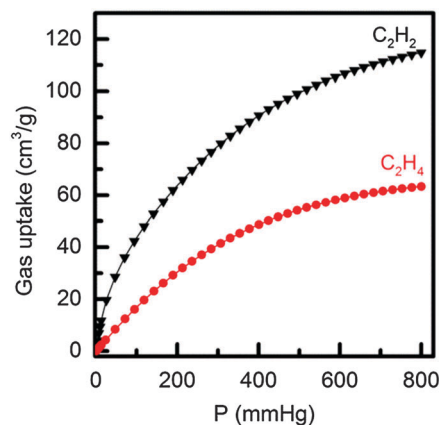
linker can be regarded as 6-connected nodes, which are linked with each other to form a (6,6)-connected network with the nia topology. There exist one-dimensional open channels of about 3.3 Å in diameter along the  $c$  axis (Fig. 1b), while no channels along the  $a$  and  $b$  axes (Fig. 1c). To our surprise, there are a lot of inner cages of moderate size around the 1D pore channels (Fig. 1d), which can be used to improve the high  $C_2H_2$  uptake. These unique pore structures of UTSA-67 suggest its great potential for selective adsorptive separation of  $C_2H_2$ - $C_2H_4$  mixtures.

Prior to gas adsorption measurements, the as-synthesized UTSA-67 was solvent-exchanged with dry acetone, and then evacuated at 273 K for 36 h and at room temperature for an additional 24 h under high vacuum to yield the activated UTSA-67a. As shown in Fig. S6 (ESI<sup>†</sup>), the permanent porosity of UTSA-67a was unambiguously established by nitrogen sorption at 77 K. The  $N_2$  sorption isotherm at 77 K exhibits a typical Type-I sorption behaviour, characteristic of a microporous material, with an  $N_2$  uptake of  $302.68 \text{ cm}^3 \text{ g}^{-1}$ . The Brunauer-Emmett-Teller (BET) surface area and pore volume were estimated to be  $1137 \text{ m}^2 \text{ g}^{-1}$  and  $0.47 \text{ cm}^3 \text{ g}^{-1}$ , respectively.

The unique pore structure and permanent microporosity in UTSA-67a motivated us to examine its potential applications for the industrially important  $C_2H_2/C_2H_4$  separation. We first collected the single-component adsorption isotherms for acetylene and ethylene up to 1 atm at 296 K, respectively. Due to the large cages around the 1D pore channels, UTSA-67a can take up a high amount of  $C_2H_2$  ( $116 \text{ cm}^3 \text{ g}^{-1}$ ) at 1 atm and 296 K (Fig. 2), which is much higher than that of some of the promising MOFs, such as M'MOF-3a, UTSA-100a, and UTSA-60a<sup>7a</sup> (Table 1). However, a much lower  $C_2H_4$  uptake ( $63 \text{ cm}^3 \text{ g}^{-1}$ , at 296 K and 1 bar) was observed for UTSA-67a, attributable to the extremely small 1D pore channels of 3.3 Å.<sup>10</sup> The  $C_2H_2/C_2H_4$  uptake ratio of UTSA-67a was estimated to be 1.84 (Table 1), which is notably higher than the MOF-74 series (1.11–1.16) and NOTT-300 (1.48). Both the relatively high  $C_2H_2$  uptake and  $C_2H_2/C_2H_4$  uptake ratio of UTSA-67a further prompted us to investigate its feasibility to selectively separate  $C_2H_2$  from binary  $C_2H_2/C_2H_4$  mixtures.



**Fig. 1** X-ray single crystal structure of UTSA-67 indicating (a) the binuclear zinc-carboxylate unit linked by six organic ligands; (b) the pore channels viewed along the  $c$  axes; (c) viewed along the  $a$  and  $b$  axes; (d) the inner cages of about 7 Å in diameter along the  $c$  axes. All hydrogen atoms have been omitted for clarity. Cyan, blue, red, and gray spheres represent Zn, N, O, and C atoms, respectively.



**Fig. 2** Single-component adsorption isotherms for  $C_2H_2$  (black) and  $C_2H_4$  (red) of UTSA-67a at 296 K.

Table 1 Comparison of some microporous MOFs for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation at room temperature

	UTSA-67a	M'MOF-3a	FeMOF-74	NOTT-300	UTSA-100a
Surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	1137	110	1350	1370	970
Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.47	0.165	0.626	0.433	0.399
Size of pore window (Å)	3.3 × 3.3	3.4 × 4.8	11 × 11	6.5 × 6.5	4.3 × 4.3
C <sub>2</sub> H <sub>2</sub> uptake (mmol g <sup>-1</sup> )	5.13	1.90	6.80	6.34 <sup>b</sup>	4.27
C <sub>2</sub> H <sub>4</sub> uptake (mmol g <sup>-1</sup> )	2.81	0.40	6.10	4.28 <sup>b</sup>	1.66
C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> uptake ratio	1.84	4.75	1.11	1.48	2.57
Selectivity <sup>c</sup>	5–6	24.03	2.08	2.17	5–10.7
Ref.	This work	13	13	14	14

<sup>a</sup> BET. <sup>b</sup> At a temperature of 293 K. <sup>c</sup> IAST analysis for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures containing 1% acetylene at 100 kPa.

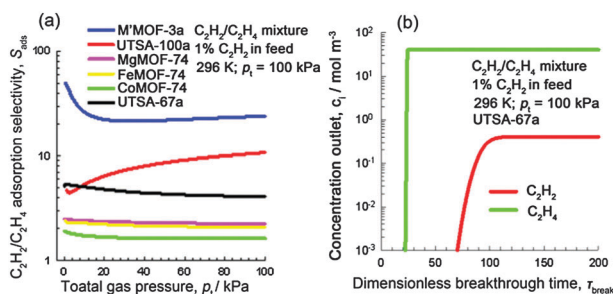


Fig. 3 (a) IAST calculations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> adsorption selectivities for UTSA-67a and other examined MOFs at 296 K. (b) Transient breakthrough of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture containing 1% C<sub>2</sub>H<sub>2</sub> mixture in an adsorber bed packed with UTSA-67a. The total bulk gas phase is at 296 K and 100 kPa. The partial pressures of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the inlet feed gas mixture are, respectively,  $p_1 = 1$  kPa and  $p_2 = 99$  kPa. For the breakthrough simulations, the following parameter values were used, as before,  $L = 0.12$  m;  $\varepsilon = 0.75$ ; and  $u = 0.00225$  m s<sup>-1</sup>.

We utilized Ideal Adsorbed Solution Theory (IAST) to calculate the adsorption selectivity of UTSA-67a for the binary C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture containing 1% C<sub>2</sub>H<sub>2</sub>. Fig. 3a makes a comparison of the adsorption selectivity of the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixture (1:99, v/v) as a function of total bulk gas phase pressure between UTSA-67a and other well-known porous MOFs at 296 K. It can be seen that the initial adsorption selectivity of UTSA-67a lies in the range of 5–6 at room temperature. This value is comparable to that of UTSA-100a (the best reported MOF so far for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation through a breakthrough and/or fixed bed) and almost three times higher than those obtained for the MOF-74 series and NOTT-300. This is really remarkable, making UTSA-67a one of the promising MOFs with high adsorption selectivities for C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation. Fig. S9 (ESI<sup>†</sup>) compares the gravimetric uptake capacities of C<sub>2</sub>H<sub>2</sub> for adsorption from mixtures containing 1% C<sub>2</sub>H<sub>2</sub>. At a total gas phase pressure of 100 kPa, UTSA-67a shows a comparatively high uptake capacity, which is comparable to FeMOF-74 and CoMOF-74, but higher than NOTT-300 and M'MOF-3a.<sup>14</sup> As a result, the combined features of high adsorption selectivity and C<sub>2</sub>H<sub>2</sub> uptake capacity for UTSA-67a once again highlight its promising potential for highly selective adsorptive separation of C<sub>2</sub>H<sub>2</sub>–C<sub>2</sub>H<sub>4</sub> mixtures.

In order to further prove the feasibility, we performed transient breakthrough simulations using the methodology described in previous literature (ESI<sup>†</sup>).<sup>15</sup> Fig. 3b shows the

concentrations of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> exiting the adsorber packed with UTSA-67a as a function of the dimensionless time,  $\tau$ , at a total pressure of 1 bar and a temperature of 296 K. We found that the ethylene gas broke through first due to its lower adsorptivity relative to acetylene. There was a significant time interval between the breakthrough of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, indicating that UTSA-67a can efficiently separate C<sub>2</sub>H<sub>2</sub> from the C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> (1/99) mixture at room temperature. The breakthrough time,  $\tau_{\text{break}}$  of UTSA-67a, corresponding to the exit gas containing 40 ppm C<sub>2</sub>H<sub>2</sub>, can be determined from Fig. S10 (ESI<sup>†</sup>). During the time interval  $0 - \tau_{\text{break}}$ , pure C<sub>2</sub>H<sub>4</sub> can be collected, which can satisfy the feedstock requirements of polymerization reactors in the polymer industry. Table S4 (ESI<sup>†</sup>) presents a comparison of the amount of C<sub>2</sub>H<sub>2</sub> captured plotted as a function of the time interval break, where the C<sub>2</sub>H<sub>2</sub> capture capacity of UTSA-67a is comparable to the MOF-74 series, but higher than M'MOF-3, NOTT-300, and UTSA-60a.

During industrial practice, when the impurity level exceeds the desired purity level of no more than 40 ppm (indicated by the dashed line in Fig. S10, ESI<sup>†</sup>) after a certain time,  $\tau_{\text{break}}$ , the adsorption cycle needs to be terminated, so the regeneration process can be initiated. As a result, the regeneration energy cost of a fixed bed is another very important factor that needs to be considered. Fig. 4 presents a comparison of the heats of adsorption ( $Q_{\text{st}}$ ) of C<sub>2</sub>H<sub>2</sub> in UTSA-67a with other examined MOFs. Based on the Clausius–Clapeyron equation, the initial  $Q_{\text{st}}$  of UTSA-67a was calculated to be 32 KJ mol<sup>-1</sup>, which was rapidly decreased to 20 KJ mol<sup>-1</sup> with the increasing C<sub>2</sub>H<sub>2</sub> loading. We found that the values of  $Q_{\text{st}}$  in MOFs without open

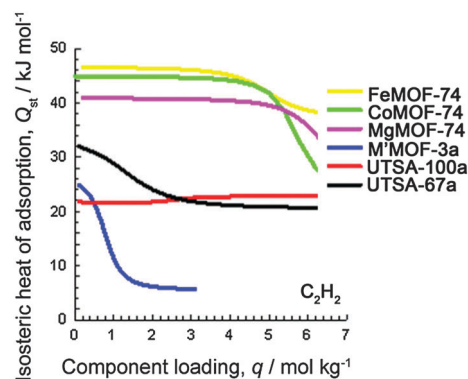


Fig. 4 Comparison of the heats of adsorption ( $Q_{\text{st}}$ ) of C<sub>2</sub>H<sub>2</sub> in various MOFs.



metal sites, like UTSA-67a, UTSA-100a and M'MOF-3a, are significantly lower than that for MOF-74 series and UTSA-60a<sup>7a</sup> with high densities of open metal sites. It is worth noting that the value of  $Q_{st}$  for UTSA-67a is also lower than the best MOF UTSA-100a after the C<sub>2</sub>H<sub>2</sub> loading exceeded 2.6 mol kg<sup>-1</sup>. These results indicate that the energy required for the regeneration of UTSA-67a will be lower than that of MOF-74 series and UTSA-100a, resulting in a significant energy saving. Such exceptionally low binding energy for UTSA-67a was mainly attributed to the absence of both open metal sites and free -NH<sub>2</sub> groups within this framework. Thus, only the large aromatic sites of UTSA-67a afford the binding energy to guest molecules. Although M'MOF-3 shows the lowest  $Q_{st}$  for C<sub>2</sub>H<sub>2</sub>, the extremely low C<sub>2</sub>H<sub>2</sub> uptake capacity limits its overall performance in C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation.

In conclusion, we have realized a new porous zinc(II) MOF UTSA-67a with narrow 1D pore channels and inner cages of moderate size for highly selective separation of C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> mixtures at room temperature. This material exhibits not only high C<sub>2</sub>H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> separation selectivity but also significantly high C<sub>2</sub>H<sub>2</sub> uptake capacity. Such a high separation capacity of UTSA-67a was mainly attributed to extremely narrow pore channels for an extensive sieving effect and inner cages of moderate size to take up the high C<sub>2</sub>H<sub>2</sub> amount. The breakthrough simulations further demonstrate the feasibility of UTSA-67a in the removal of acetylene from acetylene/ethylene mixtures containing 1% acetylene. Most importantly, the absence of both open metal sites and free -NH<sub>2</sub> groups within UTSA-67a results in its exceptionally low binding energy for C<sub>2</sub>H<sub>2</sub> adsorption, thus leading to a significant energy saving.

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

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