

# A cationic microporous metal–organic framework for highly selective separation of small hydrocarbons at room temperature†

Cite this: *J. Mater. Chem. A*, 2013, **1**, 9916

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A new three-dimensional cationic metal–organic framework  $Zn_8O(EDDA)_4(ad)_4 \cdot (HEDDA)_2 \cdot 6DMF \cdot 27H_2O$  (**ZJU-48**;  $H_2EDDA = (E)-4,4'-(\text{ethene-1,2-diyl})\text{dibenzoic acid}$ ;  $ad = \text{adenine}$ ) was solvothermally synthesized and structurally characterized. **ZJU-48** features a three-dimensional structure with a cationic skeleton and has one-dimensional pores along the *c* axis of about  $9.1 \times 9.1 \text{ \AA}^2$ . The activated **ZJU-48a** exhibits a BET surface area of  $1450 \text{ m}^2 \text{ g}^{-1}$ . The structural features of the charged skeleton of **ZJU-48a** have enabled its stronger charge-induced interaction with  $C_2$  hydrocarbons than with  $C_1$  methane, resulting in highly selective gas sorption of  $C_2$  hydrocarbons over  $CH_4$  with the adsorption selectivity over 6 at 298 K. The separation feasibility has been further established by the simulated breakthrough and pulse chromatographic experiments, thus methane can be readily separated from their quaternary mixtures at room temperature.

Received 28th May 2013

Accepted 13th June 2013

DOI: 10.1039/c3ta12086d

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## 1 Introduction

Hydrocarbons are very important raw materials for industrial products and fine chemicals, so it is important to develop materials for efficient and safe storage of hydrocarbons.<sup>1</sup> Furthermore, their technological development for the separation of  $C_2$  hydrocarbons from  $C_1$  methane will promote their efficient practical usage. For example, methane is a clean alternative to other automobile fuels whereas ethane is an important material for the production of ethylene during industrial scale cracking processes. The traditional cryogenic distillation method for small hydrocarbon separation suffers from high energy cost, while the oil-absorption method is not efficient;<sup>2</sup> it is thus necessary to develop and explore more efficient separation technologies and materials. The implementation of adsorbent based methodologies through pressure

swing adsorption (PSA) and thermal swing adsorption (TSA) has shown promise in cost efficient separation of these small hydrocarbons. In fact, a number of microporous materials have been explored for the separation of  $C_2$  hydrocarbons from methane over the last two decades.<sup>3</sup>

Microporous metal–organic framework (MOF) materials are self-assembled from organic ligands and metal ion/cluster centres through coordination bonding and have been rapidly emerging as new types of microporous adsorbents for gas storage and separation.<sup>4–23</sup> The pore sizes of MOFs can be systematically optimized to make the small gas molecules go through the pores while the large ones are blocked outside. Also, MOF pores can be immobilized with different functional sites such as open metal sites,  $-\text{NH}_2$ ,  $-\text{OH}$ , and Lewis pyridine sites, to enhance MOF interactions with different gas molecules. Among the different strategies used, the open metal site strategy has been particularly useful for both gas storage and separation.<sup>5–12</sup> Ionic MOFs recently have attracted much attention. An ionic MOF skeleton can serve as an ionic host to accommodate different guests with balanced charge by electrostatic interactions and further cooperatively realize specific functions. Furthermore, some cations and anions can be utilized to tune the pore sizes to enhance gas selectivity, as demonstrated in a few examples of MOFs.<sup>13–19</sup>

We and others have mainly focused on immobilizing open metal sites and optimizing pore sizes to target MOF materials for the highly selective separation of small hydrocarbons.<sup>20–26</sup> Because  $C_2$  hydrocarbons have quite different polarizability properties from  $C_1$  methane, ionic frameworks might be of

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ta12086d

interest and important as new types of MOF materials for the separation of these hydrocarbons by the enhanced adsorbent-adsorbate interactions through charge-induced forces.<sup>17</sup> Herein, we report the first example of cationic microporous MOFs  $\text{Zn}_8\text{O}(\text{EDDA})_4(\text{ad})_4 \cdot (\text{HEDDA})_2 \cdot 6\text{DMF} \cdot 27\text{H}_2\text{O}$  (**ZJU-48**;  $\text{H}_2\text{EDDA} = (E)\text{-}4,4'$ -(ethene-1,2-diyl)dibenzoic acid; ad = adenine) with a BET surface area of  $1450 \text{ m}^2 \text{ g}^{-1}$  for highly selective separation of  $\text{C}_2$  hydrocarbons from  $\text{C}_1$  methane, which has been established exclusively by the sorption isotherms and simulated breakthrough and pulse chromatographic experiments.

## 2 Experimental

### 2.1 Materials and measurements

All the chemicals were commercially available and used without further purification. Elemental analyses of C, H, and N were performed on an EA1112 microelemental analyser. Powder X-ray diffraction (PXRD) patterns were collected in the  $2\theta = 3\text{--}60^\circ \text{C}$  range on an X'Pert PRO diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) at room temperature. Thermogravimetric analyses (TGAs) were conducted on a Netzsch TGA 209 F3 thermogravimeter with a heating rate of  $10^\circ \text{C min}^{-1}$  in an  $\text{N}_2$  atmosphere.

### 2.2 Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyser was used to measure gas adsorption. In order to remove guest solvent molecules in the framework, a fresh sample of **ZJU-48** was exchanged with chloroform 10 times and then activated at 273 K under high vacuum for 12 h until the outgas rate was  $<5 \mu\text{mHg min}^{-1}$  prior to measurements. During the sorption measurement the sample was maintained at 77 K with liquid nitrogen and 273 K with an ice-water bath (slush), respectively. As the center-controlled air condition was set at 296 K, a water bath of 296 K was used for adsorption isotherms at 296 K.

Isotherm data were analysed using the virial equation:

$$\ln(n/p) = A_0 + A_1n + A_2n^2 + \dots$$

where  $p$  is the pressure,  $n$  is the amount adsorbed, and  $A_0$ ,  $A_1$ , etc. are virial coefficients. The Henry's law constant ( $K_{\text{H}}$ ) is equal to  $\exp(A_0)$ , and the selectivity can be obtained from the constant  $K_{\text{H}}$ .

### 2.3 Synthesis of ZJU-48

$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.183 mmol, 40 mg), adenine (0.074 mmol, 10 mg),  $\text{H}_2\text{EDDA}$  (0.113 mmol, 30 mg) were dissolved in a mixed solvent of DMF (13.5 ml) and  $\text{H}_2\text{O}$  (1 ml), then 0.1 ml of  $\text{HNO}_3$  with a concentration of 62% was added, and the mixture was transferred to and sealed in a 20 ml Teflon-lined autoclave, which was heated at  $125^\circ \text{C}$  for 1 day. After slow cooling to room temperature, yellow crystals of **ZJU-48** were collected by filtration. Anal. calcd for  $\text{Zn}_8\text{C}_{134}\text{N}_{26}\text{H}_{174}\text{O}_{58}$ : C, 44.67; H, 4.83; N, 10.11. Found: C, 44.77; H, 4.41; N: 10.12%.

**Table 1** Crystallographic data collection and refinement results for **ZJU-48**

<b>ZJU-48</b>	
Chemical formula	$\text{C}_{116}\text{H}_{78}\text{Zn}_8\text{N}_{20}\text{O}_{25}$
Formula weight	2675.10
Temperature (K)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Tetragonal
Space group	$P4/n$
$a$ ( $\text{\AA}$ )	28.7876(11)
$b$ ( $\text{\AA}$ )	28.7876(11)
$c$ ( $\text{\AA}$ )	11.1348(5)
$V$ ( $\text{\AA}^3$ )	9227.7(6)
$Z$	2
Density (calculated $\text{g cm}^{-3}$ )	0.767
Adsorption coefficient ( $\text{mm}^{-1}$ )	1.058
$F(000)$	2136
Crystal size ( $\text{mm}^3$ )	$0.46 \times 0.36 \times 0.21$
Goodness of fit on $F_2$	1.074
$R_1, wR_2 [I > 2\sigma(I)]^a$	0.0816, 0.2139
$R_1, wR_2$ (all data) <sup>a</sup>	0.1324, 0.2340

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|; wR_2 = \left[ \frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2}$$

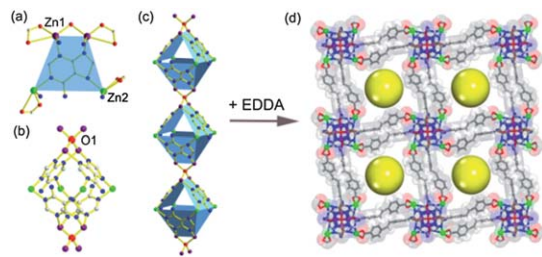
### 2.4 X-Ray collection and structure determination

Single crystal diffraction data were collected on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite monochromatic Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The structure of **ZJU-48** was solved by direct methods and refined with full-matrix least-squares on  $F_2$  with the SHELXL-97 program package. The H atoms on the ligand were placed in idealized positions and refined using a riding model. The H atoms on the coordinated solvent O atoms could not be located. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules, thereby producing a set of solvent-free diffraction intensities. CCDC 931058. Crystallographic data are summarized in Table 1.

## 3 Results and discussion

**ZJU-48** was synthesized by the solvothermal reaction of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , adenine and  $\text{H}_2\text{EDDA}$  in a mixture solvent of DMF- $\text{H}_2\text{O}$  with the addition of a small amount of  $\text{HNO}_3$  at  $125^\circ \text{C}$  for 1 day as yellow prismatic single crystals. The structure was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) (Fig. S3†) and thermogravimetric analysis (TGA) (Fig. S2†). The crystalline product is insoluble in most of the common organic solvents.

The X-ray single crystal structure of **ZJU-48** showed that it crystallized in the tetragonal space group  $P4/n$ . As shown in Fig. 1, **ZJU-48** is a three-dimensional (3D) framework comprising Zn-adenine rod chains, which were further linked to EDDA ligands *via* their carboxylate groups. Within the Zn-adenine rod chains, four Zn1 atoms adopt tetrahedral



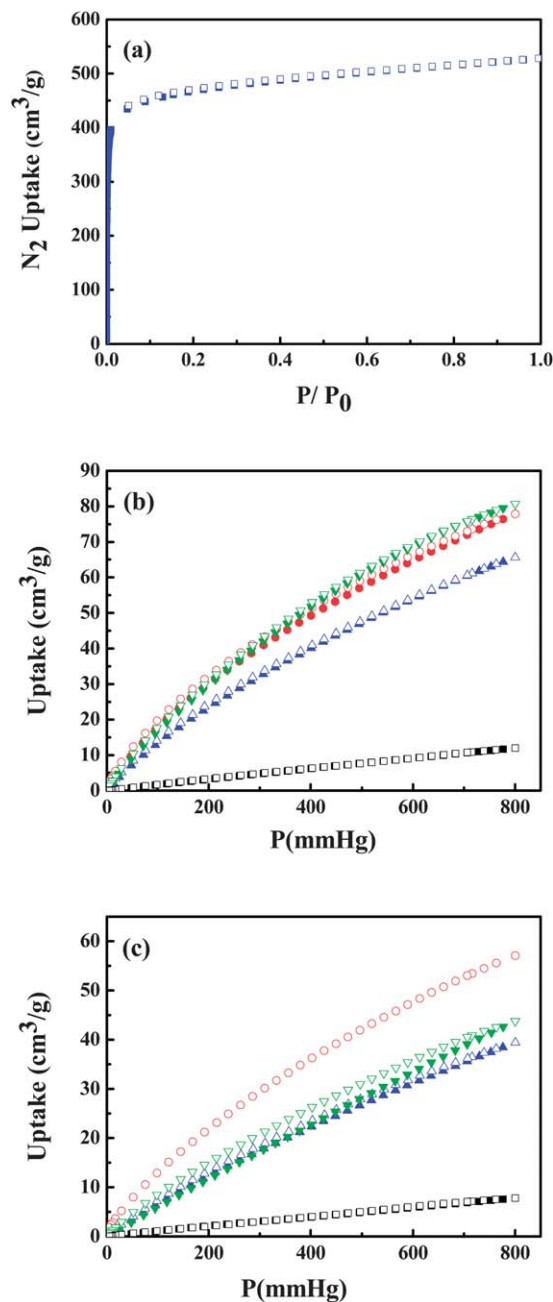
**Fig. 1** View of 3D **ZJU-48**. (a) Each adenine ligand coordinated to two Zn1 and two Zn2 atoms to form walls of octahedral cages; (b) four Zn1 atoms adopt tetrahedral geometry through coordination to a  $\mu_4$ -oxygen atom O1 to form the  $Zn_4O$  SBU structure; (c) Zn2-adenine octahedron is linked with  $Zn_4O$  to form Zn-adenine rod chains; (d) EDDAs link Zn-adenine rod chains to give the 1D channels of  $9.1 \times 9.1 \text{ \AA}^2$  extending along the  $c$  direction.

geometry through coordination to a  $\mu_4$ -oxygen atom O1 to form the  $Zn_4O$  SBU structure, which were further linked with two adenine–Zn2 octahedrons. **ZJU-48** has one-dimensional pores along the  $c$  axis of about  $9.1 \times 9.1 \text{ \AA}^2$ , which were filled with guest molecules. The void space accounts for approximately 62.3% of the whole crystal volume ( $4247.5 \text{ \AA}^3$  out of the  $9227.7 \text{ \AA}^3$  per unit cell volume) by PLATON analysis. The most interesting thing is that **ZJU-48** is an ionic MOF with the cationic skeleton. The  $N_2$  sorption isotherm at 77 K showed that **ZJU-48** displayed Type-I sorption behaviour with a BET surface area of  $1450 \text{ m}^2 \text{ g}^{-1}$  (Fig. 2(a)).

Thermogravimetric analysis (TGA) of **ZJU-48** showed that approximately 25.1% weight loss occurred before  $220 \text{ }^\circ\text{C}$  due to the release of  $H_2O$  and DMF solvent molecules, and the framework is stable up to  $400 \text{ }^\circ\text{C}$ . PXRD studies indicate that the activated **ZJU-48a** generated at  $0 \text{ }^\circ\text{C}$  under high vacuum for 1 day keeps the highly-crystalline feature whose pattern matches with that of the as-synthesized one, indicating that **ZJU-48** is robust. The robust properties and the permanent porosity of **ZJU-48** encouraged us to examine its potential application for storage and selective separation of small hydrocarbons. Sorption isotherms are repeatable, which means that **ZJU-48** can be easily re-utilized. As shown in Fig. 3, **ZJU-48a** can take up moderate amounts of  $C_2H_2$  of  $77.83$  and  $57.07 \text{ cm}^3 \text{ g}^{-1}$  at  $273$  and  $296 \text{ K}$ , respectively, under 1 atm. Although the amount of adsorbed  $C_2H_2$  in **ZJU-48a** at  $296 \text{ K}$  is lower than those with high density of open metal sites such as Zn-MOF-74 ( $122 \text{ cm}^3 \text{ g}^{-1}$ ), the  $C_2H_2$  uptake of **ZJU-48a** at  $296 \text{ K}$  is comparable with our previously reported **UTSA-36** ( $57 \text{ cm}^3 \text{ g}^{-1}$ ) with smaller pore sizes, and is higher than **MOF-5** ( $26 \text{ cm}^3 \text{ g}^{-1}$ ) with larger pore sizes.

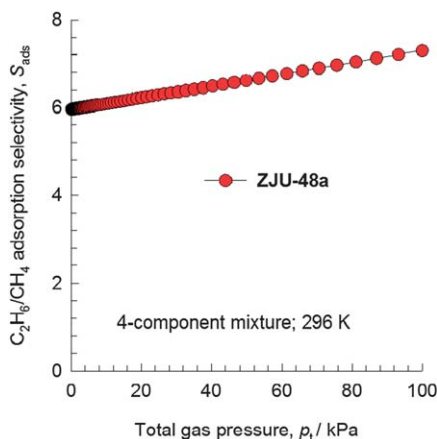
**ZJU-48a** systematically exhibits different adsorption capacities to  $CH_4$  than those of  $C_2H_6$ ,  $C_2H_4$  and  $C_2H_2$  at both  $273$  and  $298 \text{ K}$ . **ZJU-48a** can take up  $C_2H_2$  ( $77.83 \text{ cm}^3 \text{ g}^{-1}$ ),  $C_2H_4$  ( $65.65 \text{ cm}^3 \text{ g}^{-1}$ ),  $C_2H_6$  ( $80.66 \text{ cm}^3 \text{ g}^{-1}$ ) but a much lower amount of  $CH_4$  ( $11.96 \text{ cm}^3 \text{ g}^{-1}$ ) at 1 atm and  $273 \text{ K}$ ; and  $C_2H_2$  ( $57.07 \text{ cm}^3 \text{ g}^{-1}$ ),  $C_2H_4$  ( $39.43 \text{ cm}^3 \text{ g}^{-1}$ ),  $C_2H_6$  ( $43.78 \text{ cm}^3 \text{ g}^{-1}$ ) and also a lower amount of  $CH_4$  ( $7.82 \text{ cm}^3 \text{ g}^{-1}$ ) at 1 atm and  $296 \text{ K}$ . This indicated that **ZJU-48a** is a promising material for highly selective adsorptive separation of  $C_2$  hydrocarbons from  $CH_4$ .

In order to establish the feasibility of this separation, we performed calculations using the Ideal Adsorbed Solution



**Fig. 2** (a)  $N_2$  sorption isotherm at  $77 \text{ K}$  and  $CH_4$  (black),  $C_2H_6$  (green) and  $C_2H_4$  (blue),  $C_2H_2$  (red) sorption isotherms of **ZJU-48a** at (b)  $273 \text{ K}$  and (c)  $296 \text{ K}$ . Solid symbols: adsorption, open symbols: desorption.

Theory (IAST) of Myers and Prausnitz.<sup>27</sup> Fig. S4† shows IAST calculations of the component molar loadings in equilibrium with an equimolar  $CH_4$ – $C_2H_2$ – $C_2H_4$ – $C_2H_6$  mixture as a function of the total bulk gas phase pressure at  $296 \text{ K}$ . The IAST calculations indicated that the hierarchy of adsorption capacity is commonly  $CH_4 < C_2H_6 \approx C_2H_4 < C_2H_2$ , making the  $CH_4/C_2H_6$  separation the crucial one. As shown in Fig. 3, the adsorption selectivities of  $C_2H_6$  with respect to  $CH_4$  are in excess of 6 for a range of pressure to  $100 \text{ kPa}$ , indicating the feasibility of this MOF for the practical application in  $C_2/C_1$  separation, although this selectivity value is lower than those best MOFs with high



**Fig. 3** IAST calculations of the  $C_2H_6/CH_4$  adsorption selectivity for adsorption from an equimolar  $CH_4-C_2H_2-C_2H_4-C_2H_6$  mixture at the total bulk gas phase at 296 K.

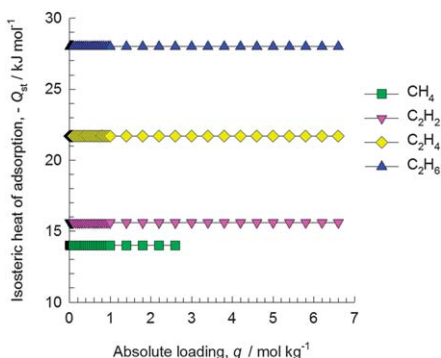
density open metal sites such as Cu(BTC) (HKUST-1), Mg-MOF-74 and Co-MOF-74 for  $C_2/C_1$  separation, with the selectivity values of about 11, 14 and 18, respectively (Fig. S5†).

To figure out why **ZJU-48a** exhibits selective separation for small hydrocarbons, the isosteric heat of adsorption,  $Q_{st}$ , defined as

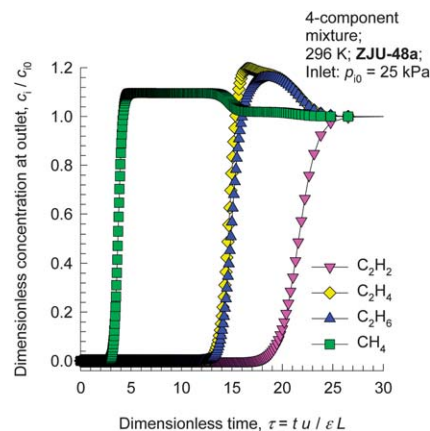
$$Q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q$$

was determined using the pure component isotherm fits. Fig. 4 shows data on the loading dependence of  $Q_{st}$  for adsorption of  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  on **ZJU-48a**. The isosteric heat of adsorption of  $CH_4$  on **ZJU-48a** is  $14.0 \text{ kJ mol}^{-1}$ , whereas the isosteric heats of adsorption of  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  are 15.6, 21.7 and  $28.0 \text{ kJ mol}^{-1}$ , respectively. The isosteric heat for  $C_2H_6$  is very high, which is even comparable to that of Mg-MOF-74 (Fig. S6†). The higher adsorption heats of  $C_2$  hydrocarbons can be attributed to the larger van der Waals interactions between the framework and  $C_2$  hydrocarbons. The charged framework skeleton of **ZJU-48a** results in even stronger interactions with those easily polarized  $C_2$  hydrocarbons.<sup>17</sup>

To further demonstrate the feasibility for the practical separation, the breakthrough experiments were simulated



**Fig. 4** The isosteric heats of adsorption of  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$  and  $CH_4$  on **ZJU-48a**.



**Fig. 5** Breakthrough simulation results for **ZJU-48a** for separation of an equimolar  $CH_4-C_2H_2-C_2H_4-C_2H_6$  mixture in a fixed bed adsorbent at the total bulk gas phase at 296 K and 100 kPa. The x-axis represents the dimensionless time,  $\tau$ .

based on the established methodology described in the work of Krishna and Long which has been exclusively confirmed by the experimental breakthrough experiments.<sup>25</sup> Fig. 5 shows the data on the concentrations at the exit of the adsorber for **ZJU-48a**. The x-axis in Fig. 5 represents a dimensionless time,  $\tau$ , defined by dividing the actual time,  $t$ , by the characteristic time,  $L\epsilon/u$ . We note that **ZJU-48a** has the capability of separating  $CH_4$  in pure form from this quaternary mixture. The breakthrough of  $C_2H_4$  and  $C_2H_6$  occurs at approximately the same time, indicating that **ZJU-48a** is not suitable for separation of  $C_2H_4-C_2H_6$  mixtures. The separation capability of **ZJU-48a** is also underscored in pulse chromatographic simulations (Fig. S7†). The breakthrough and pulse chromatographic simulations confirm the potency of **ZJU-48** in separation of  $CH_4$  from mixtures containing  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  species.

## 4 Conclusions

In summary, we have synthesized a novel porous metal-organic framework **ZJU-48** with the cationic skeleton for the highly selective separation of  $C_2$  hydrocarbons over methane. The cationic skeleton in **ZJU-48** enhanced the interactions by electrostatic interaction between MOF and more polarized gas molecules, leading to highly selective separation of  $C_2$  hydrocarbons over  $C_1$  methane. The realization of this first example of cationic microporous MOF **ZJU-48** for the highly selective separation of  $C_2/C_1$  hydrocarbons might facilitate the extensive research endeavour to explore this ionic MOF approach, so some novel ionic MOF materials will be emerging for the separation of these industrially important hydrocarbons.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 51229201, 51272231 and 51010002), and Grant AX-1730 from the Welch Foundation (B.C.). We also appreciate the support from NSFC (21273033, 21203024) and the Award 'Minjiang Scholar Program' in Fujian Province, China.



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