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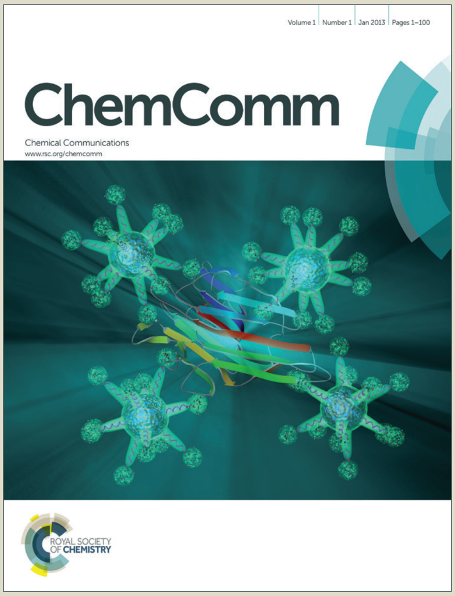

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ARTICLE TYPE

High Performance Gas Adsorption and Separation of Natural Gas in Two Microporous Metal-Organic Frameworks with Ternary Building Units

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Two novel MMOFs, JLU-Liu5 and JLU-Liu6, are based on ternary building units and exhibit high adsorption selectivity for CO_2, C_2H_6 and C_3H_8 over CH_4 that is attributed to steric effects and host-guest interactions. These MMOFs are promising materials for gas adsorption and natural gas purification.

Currently, growing attention has been drawn to environmental and energy issues, which is closely related to the survival of mankind. Natural gas (NG) consists predominantly of CH_4, small amounts of CO_2 and hydrocarbon impurities, which reduce the conversion rate and energy content. Therefore, separation and purification CH_4 from the raw gases mixture is necessary before utilization.

In the past decades, microporous metal-organic frameworks (MMOFs) have been proven as promising materials for revolutionizing industrial applications, such as storage and separation of gases and purification of NG.[1,2] With respect to designing and synthesizing optimal metal-organic frameworks (MOFs) with excellent gas separation capabilities, different strategies including those based on interpenetration (size-selectivity),[3] Lewis basic sites (LBSs),[4] open metal sites (OMSs) (interaction),[5] and ionic skeleton (charge-induce force)[6] have been frequently employed. The synthetic strategy based on secondary building units (SBUs) is an effective method for the design and construction of MOF materials with OMSs. In general, MOFs based on the binary SBUs (with one kind of inorganic SBU and one kind of organic SBU) are common, such as HKUST-1 (4-c "square" $[Zn_2(RCO_2)_4]$); MOF-5 (6-c "octahedra" $[Zn_4(u_4\text{-}O)(RCO_2)_6]$); MIL-101 (6-c " trigonal prisms" $[Cr_3(u_3\text{-}O)\text{-}(RCO_2)]_6)$; and UiO-66 (12-c $[Zr_6O_4(OH)_4(RCO_2)_{12}]$ clusters).[7] However, MOFs based on ternary SBUs are unique and extremely difficult to form. In this paper, an approach referred to as the ternary SBUs approach is used for the synthesis of MOFs that are assembled using one kind of organic SBU and two kinds of inorganic SBUs that are based on a single metal. Our approach is quite different to that most reported MOFs constructed by mixed metals or mixed ligands. Until now, there are only a few MOFs built from ternary SBUs: USF-3, USF-4, UMCM-150, CPM-5, $[Cu_6O(TZI)_3(H_2O)_9(NO_3)]_n\cdot(H_2O)_{15}$, asc-1, asc-2, asc-3, and MCF-39.[8] Therefore, design and synthesis of novel MOFs based on the ternary SBUs approach have great significance and grand challenges. Herein, we utilized the unsymmetrical pentacarboxylate ligand with multiple coordination sites, and the metal (In/Zn) which can form two kinds of SBUs in one structure,[8b,d,h] successfully synthesized two anionic MMOFs, $[CH_3NH_3][In_3L_2(H_2O)_{2.5}]\cdot 8NMF$ (**JLU-Liu5**) and $[(CH_3)_2NH_2][Zn_5L_2(OH)(H_2O)(DMF)_2]$ (**JLU-Liu6**) (H_5L = 3,5-di(3'5'-dicarboxylphenyl) benzoic acid).

Structural analysis of the two compounds show that they consist of ternary SBUs: a square pyramid organic SBU and two types of inorganic SBUs. The structures possess both an ionic skeleton with OMSs and multiple pores system merits, which contribute to strong interactions and steric effects toward small gases that effectively enhance the capability for gas adsorption and separation. Gas adsorption studies indicate that the two compounds exhibit permanent microporosity with high gas adsorption and CO_2/CH_4, C_3H_8/CH_4, and C_2H_6/CH_4 separation selectivity. Thus, they are promising materials for gas storage and NG purification.

Structural analysis of **JLU-Liu5** reveals that it is a MMOF with a new topology that is linked by ternary SBUs: the $[In(O_2CR)_4]$ and $[In_2(H_2O)(O_2CR)_4]$ SBUs with distorted tetrahedral geometries, and organic SBUs with a square pyramidal geometry (Fig. 1a-c). It is noteworthy to mention that the occurrence of other indium MOFs are known to form mononuclear (e.g., $[In(O_2CR)_4]$), $[In(OH)]_\infty$ chain or trinuclear (e.g., $[In_3O(O_2CR)_6(H_2O)_3]$) SBUs,[9] while the dinuclear $[In_2(H_2O)(O_2CR)_4]$ SBUs are rarely reported.[9c] Compared with other indium MOFs, the structure of **JLU-Liu5** is unique due to the rare co-existance of $[In(O_2CR)_4]$ SBUs and $[In_2(H_2O)(O_2CR)_4]$ SBUs. Until now, to the best of our knowledge, one unique example of an indium-based MOF with $[In(O_2CR)_4]$ and $[In_3O(O_2CR)_6(H_2O)_3]$ SBUs has been assembled using the method of ternary SBUs.[8d] In the structure, the L^{5-} ligand adopts two types of coordination modes and possesses different dihedral angles between the central and terminal benzene rings (Fig. S1a, b ESI†). Two ligands linked with two mononuclear indium centers compose a distorted metal-organic square (MOS), which interconnects to form 1D chains. These 1D chains that propagate in different directions are alternately connected by the ligands and the dinuclear indium centers to generate a 3D framework (Fig. S2,

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ESI†).

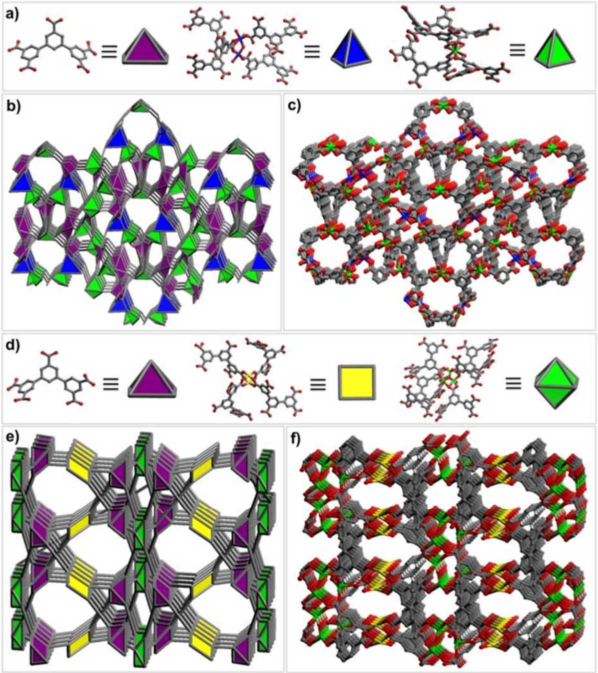

Fig. 1. Description of the structure of **JLU-Liu5**: a) ternary SBUs; b) polyhedral view of the net; c) ball and stick model of the 3D framework; d-f) for **JLU-Liu6**.

Structural analysis of **JLU-Liu6** indicates that the square pyramidal L^{5-} ligand coordinates with three octahedral $[Zn_3(O_2CR)_6]$ SBUs and two paddlewheel $[Zn_2(O_2CR)_4]$ SBUs (Fig. 1d-f), leading to a novel (4,5,6)-connected topology that has been accessed for the first time using the ternary SBUs synthetic strategy (Fig. S5a, Table S2 ESI†). In the structure, four L^{5-} ligands connect with two trinuclear SBUs and two paddlewheel SBUs to form a MOS with the edge distances of 9.9 and 14.1 Å and vertex angles of 75.8° and 104.4°, respectively. Each MOS interconnects via the paddlewheel SBUs to generate a 1D chain along the *c* axis. These chains are linked by the trinuclear SBUs to compose 2D layers along the *ac* plane, which assemble the 3D framework via the L^{5-} ligand (Fig. S3, ESI†).

The N_2 sorption isotherm of **JLU-Liu5** and **JLU-Liu6** reveals typical reversible type-I sorption behavior that is characteristic of microporous materials with Brunauer-Emmett-Teller (BET) surface areas of 707 and 544 $m^2\ g^{-1}$, respectively (Fig. S9, ESI†). Their pore volumes are 0.35 and 0.26 $cm^3\ g^{-1}$, respectively. The H_2 uptake for **JLU-Liu5** and **JLU-Liu6** are 1.46 and 1.35 wt% at 77 K and 1 bar (Fig. S10, ESI†), which is slight lower than Mn-BTT with high density of OMSs and LBSs (2.1%).[10]

The pure component gas sorption of the compounds were measured. At 273 K and 1 bar, the amount of CO_2 uptake for **JLU-Liu5** reaches to 102 $cm^3\ g^{-1}$ (Fig. 2a), which is comparable to the value of NTU-111 (124.6 $cm^3\ g^{-1}$) with nitrogen-rich triazole units.[11] Moreover, **JLU-Liu5** also exhibits notable adsorption capacities to C_2H_6 and C_3H_8 (90 and 78 $cm^3\ g^{-1}$) (Fig. 3a, d), which reach the values of BIF-24 (84.9 and 88.5 $cm^3\ g^{-1}$) under the same conditions.[12] The most remarkable feature is that the two compounds systematically adsorb more C2 and C3 hydrocarbons than CH_4 (Table S3, ESI†). To evaluate the affinity of the MMOFs for gas molecules, the isosteric heats (Q_{st}) of compounds for the small gases were calculated (Fig. S11-18, ESI†). At zero-coverage, the Q_{st} of CO_2 for **JLU-Liu5** and **JLU-Liu6** are 34.6 and 35.8 kJ mol^{-1}, which are higher than dia-7i-1-Co (30 kJ mol^{-1}).[13] It is worthwhile to note that **JLU-Liu6** shows the highest Q_{st} of C_2H_6 (46.5 kJ mol^{-1}) among MOF materials.

The CO_2/CH_4 adsorption selectivity was calculated by ideal adsorption solution theory (IAST) at general feed composition of landfill gas (50% and 50%) and a typical feed composition for natural gas purification (5% and 95%) (Fig. 2, Fig. S19 ESI†). At 298 K and 1 bar, the CO_2/CH_4 selectivity of **JLU-Liu5** are 4.6 and 4.3, and **JLU-Liu6** are 7.3 and 6.8, respectively, which outperforms many reported MOFs and carbon materials under the same conditions (Table S4). The higher selectivity of CO_2/CH_4 may be attributed to the effect of OMSs and LBSs (counterions), which provide additional electric field, and effectively improve the interaction between highly quadrupolar CO_2 molecules and the host framework.[14] Furthermore, the calculated CO_2/N_2 adsorption selectivity of **JLU-Liu5** and **JLU-Liu6** are 22.6 and 15.6 at 298 K and 1 bar, respectively (Fig. S20 ESI†). These outstanding results suggest that both compounds are promising candidates for NG purification.

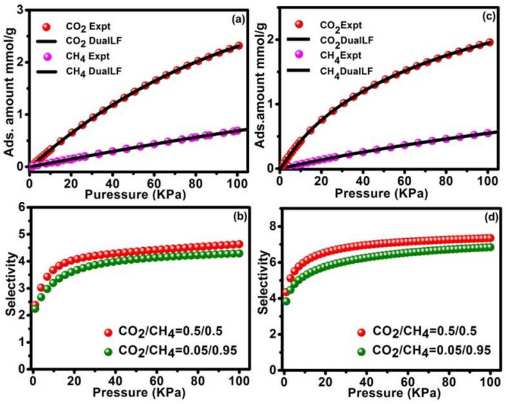

Fig. 2. CO_2 and CH_4 isotherms at 298 K along with the dual-site Langmuir-Freundlich (DSLF) fits; IAST predicted gas mixture adsorption selectivities at 298 K and 100 KPa. **JLU-Liu5** (a, b) and **JLU-Liu6** (c, d).

The permanent porosity of these compounds warrants further examination of their potential application for the industrially important small hydrocarbons separation. As shown in Fig. 3, we applied the IAST to predict the adsorption amount of each component of the mixture (Fig. S21, ESI†). The selectivity of **JLU-Liu5** and **JLU-Liu6** for equimolar C_3H_8/CH_4 binary mixtures are 107.8 and 274.6 at 298 K and 1 bar, respectively. It is highlighted that the selectivity of C_3H_8/CH_4 is much higher than the very high value (>80) for UTSA-35a.[15] The C_2H_6/CH_4 selectivity of **JLU-Liu5** and **JLU-Liu6** are 17.6 and 20.4, respectively, which are higher than that of FIR-7a-ht (14.6) with high BET surface area.[16] The high C_2H_6/CH_4 and C_3H_8/CH_4 selectivities of the two compounds may be arise from both the steric effects and host-guest interactions.

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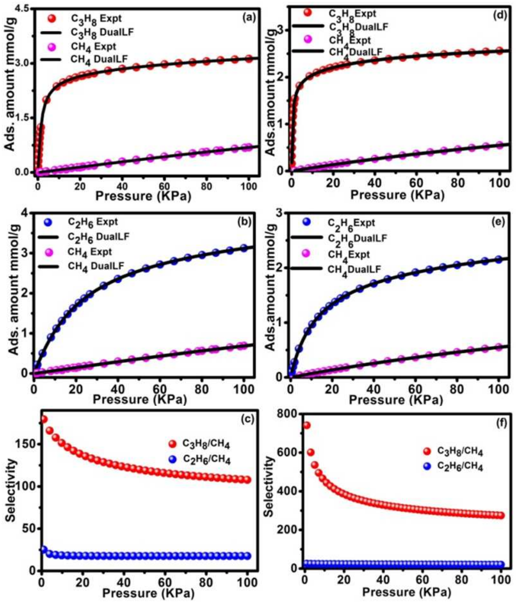

Fig. 3. C_2H_6 and C_3H_8 adsorption isotherms are fit using the DSLF model (lines); IAST predicted equimolar gas mixtures adsorption selectivities at 298 K and 100 KPa. (a, b, c for **JLU-Liu5**; d, e, f for **JLU-Liu6**).

In summary, by utilizing the unsymmetrical pentacarboxylate ligand and diverse SBUs, two novel MMOFs with permanent porosity were successfully assembled based on the powerful synthesis strategy of ternary SBUs. Such a ternary approach to construct MOFs is unique and rarely reported, and we anticipate that it will be an effective strategy to generate MOFs with high performance. It is highlighted that these two compounds exhibit high-capacity adsorption and high-efficient separation of small gases. Subsequently, application to the field of industrially important gas storage and separation of these emerging and promising porous materials is expected in the near future.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [materials and methods, crystal data and structure refinement, structure information, IR spectrum, XRD, TGA, gases adsorption and adsorptive selectivity, photoluminescent properties of **JLU-Liu5** and **JLU-Liu6**. CCDC 1000072-1000073]. See DOI: 10.1039/b000000x/

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