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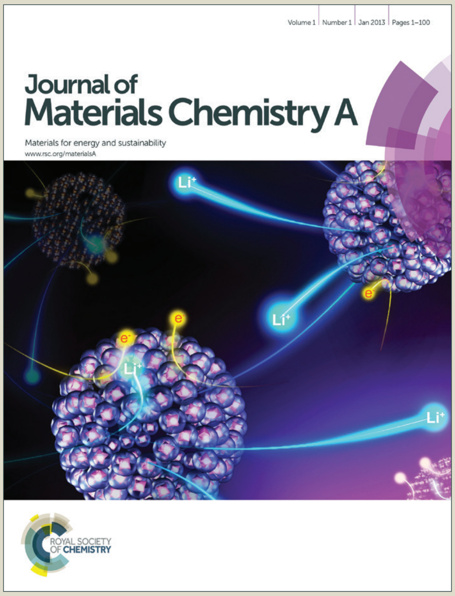

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ARTICLE TYPE

High storage capacities and separation selectivity of C2 hydrocarbons over methane in the metal-organic framework Cu-TDPAT

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We report the storage capacities and separation selectivity of an *rht*-type metal organic framework (MOF), Cu-TDPAT (TDPAT=2,4,6-tris(3,5-dicarboxylphenyl-amino)-1,3,5-triazine), for C2 hydrocarbons over CH_4. Henry's constant, isosteric heat of adsorption (Q_{st}), and IAST selectivity are calculated based on single component sorption isotherms. Theoretical calculations indicate that both open metal sites and Lewis basic sites have strong interactions with C2 molecules. The combination of these two kinds of sites leads to the highest C_2H_2/CH_4 selectivity of 127.1 as well as record high C_2H_4 adsorption enthalpies. To mimic real world conditions, breakthrough experiments are conducted on equimolar four-component mixture containing C_2H_2, C_2H_4, C_2H_6, and CH_4 at room temperature and 1 atmosphere. The findings show that Cu-TDPAT is a promising candidate for CH_4 capture and purification.

Introduction

Nowadays, energy requirements for global industrialization are still based on fossil fuel. Improving the utilization rate of fossil fuels is pressing to make rational use of resources and address the grand energy challenges. As a main form of fossil fuel, natural gas is a cleaner alternative to conventional fuels. Methane, the major component of natural gas, is not only a prevalent and inexpensive fuel for industry and residential use but also a very important raw material in chemical and petrochemical industry for the production of various C1 and C2 chemicals.[1] C2 hydrocarbons (C2s) are the major impurities in naturally occurring methane and are the main products of oxidative coupling of methane in the process of converting natural gas into a more useful chemical feedstock. Separation of C2s from methane (C1), with the aim of upgrading the quality of natural gas and providing an alternative chemical source of C2s for further chemical processing and transformation, has therefore become a feasible measure for the efficient usage of fossil fuels. The traditional separation technology of the cryogenic distillation, which is based on their different vapor pressures and thus boiling points, consumes a lot of energy. Among several new energy-efficient technologies for such important hydrocarbon separations, adsorptive separation is one of the most promising ones, so a variety of microporous adsorbents have been examined for the separation of these light hydrocarbons.[2]

Recently, great efforts have been devoted to developing versatile strategies for the storage and separation of C2s in an environmentally benign and economical fashion. Metal-organic frameworks (MOFs)[3,4] possess potential application in C2s capture and sorption, and much attention has been dedicated to improve their capture and sorption ability at room temperature.[5]

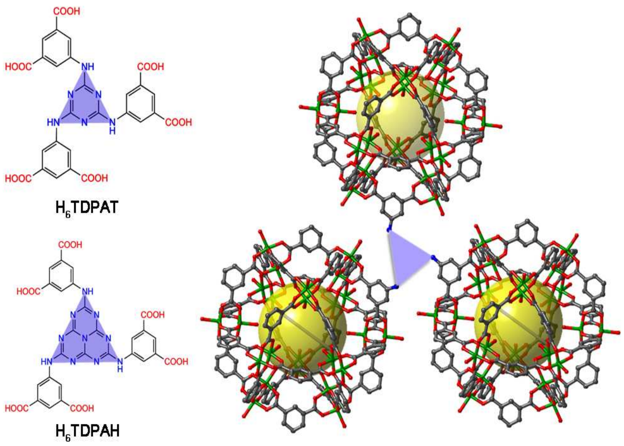

Figure 1. N-rich ligands (H_6TDPAT and H_6TDPAH) and a portion of the (3,24)-connected *rht*-net built on TDPAT and TDPAH is shown (Cu, green; C, gray; O, red; N, blue. H atoms are omitted for clarity).

To increase the gas uptake capacity and selectivity, current efforts are largely devoted to enhancing the C2s binding affinity in MOFs.[6] Strategies reported include ligand functionalization,[7] construction of size/shape specific pore,[8] particularly incorporation of open metal sites (OMSs).[9] The *rht*-type MOFs built on supramolecular building blocks (SBBs) serve as excellent platform, in which a dendritic hexacarboxylate ligand of 3-fold symmetry is linked by 24 "square paddlewheel" $M_2(COO)_4$ unit to form a robust network that possesses both high concentration of OMSs and highly porous structure with large surface area and pore volume. A number of recent studies clearly show that their gas uptake capacity is among the highest reported to date.[10] To reach higher C2s uptake and selectivity, another strategy that has been developed is modification of the pores with Lewis basic sites (typically -CONH- and pyridyl).[11] It can be foreseen that MOFs containing both OMSs and LBSs will lead to excessive C2s uptake and selectivity. Although several reports have emerged on porous MOFs with either OMSs or LBSs for C2s storge and separation, MOFs that excel in both tasks are scarce.[12]

Previously our group incorporated 1,3,5-triazine and s-heptazine functional groups in ligand structure design for MOF synthesis (see Figure 1). The resulting *rht*-type MOFs Cu-TDPAT[13] and Cu-TDPAH[14] (where TDPAT = 2,4,6-tris(3,5-dicarboxylphenyl-amino)-1,3,5-triazine and TDPAH = 2,5,8-tris(3,5-dicarboxylphenylamino)-s-heptazine) exhibited excellent storage capacities and separation selectivity. Interestingly, Cu-TDPAT has higher isosteric heat (Q_{st}) of CO_2 (42.2 kJ·mol^{-1}) than Cu-TDPAH (33.8 kJ·mol^{-1}), probably owing to the smaller size of ligand, narrower pores and higher density of OMSs (see Table S4). In addition, Cu-TDPAH displays the highest C_2H_2/CH_4 selectivity of 80.9 at the time but reveals a moderate adsorption enthalpy of 23.5 kJ·mol^{-1}. It can be expected that Cu-TDPAT, the smallest member of *rht*-type MOFs, may exhibit higher adsorption enthalpy and better separation capacity than Cu-TDPAH. Here, adsorption isotherms, isosteric heats of adsorption, ideal adsorbed solution theory (IAST) selectivities, Henry's law selectivities, breakthrough experiments and theoretical calculations are evaluated to assess the utility of Cu-TDPAT for C2s/C1 separations.

Results and discussion

Hydrocarbon adsorption isotherms

In order to evaluate the performance of Cu-TDPAT for C2s/C1 separations, single-component gas adsorption isotherms were measured for hydrocarbons at 298K and 273K. Sorption isotherms are repeatable, which means that the material can be easily regenerated and reused. The uptake capacities at 1 atm and 273 K for C_2H_2, C_2H_4, C_2H_6, and CH_4 are 248.3, 218.0, 217.7, and 51.6 cm^3·g^{-1}, respectively, while those at 1 atm and 298 K are 177.7, 164.4, 154.4, and 28.3 cm^3·g^{-1}, respectively. (see Figure 2, Figure S2, Figure S3, Figure S6, Figure S9 and Figure S13 in SI). The uptake capacity of Cu-TDPAT for C_2H_2 at 298 K is among the highest for MOF materials (e.g. HKUST (201 cm^3·g^{-1}),[9a] CoMOF-74 (197 cm^3·g^{-1})[5a], NOTT-101 (184 cm^3·g^{-1}) and PCN-16 (176 cm^3·g^{-1})[15]). This illustrates that the combined feature of open metal sites, Lewis basic sites and *rht*-type pore shape do lead to the efficient adsorption of acetylene molecules in Cu-TDPAT. The comparison of some microporous MOFs for acetylene storage is listed in Table S1.

Calculations of selectivities based on the Henry's law selectivity

The significant differences in storage capacities suggest that highly selective C2s/C1 separations are feasible with these materials. The separation ratios of C2 hydrocarbons (C_2H_2, C_2H_4 and C_2H_6) versus C1(CH_4) are based on the Henry's Law selectivity. The Henry's Law selectivity for gas component *i* over *j* at a specific temperature is calculated based on the following equation.

$$S_{ij} = K_{Hi} / K_{Hj} \quad (1)$$

The Henry's Law constants were calculated directly from the adsorption isotherms. The calculated C_2H_2/CH_4, C_2H_4/CH_4 and C_2H_6/CH_4 adsorption selectivities at 273 K are 154.3:1, 124.7:1, and 16.4:1, respectively, while those at 298 K are 127.1:1, 85.0:1, and 12.1:1, respectively (Some virial parameters are summarized in Table S2). To the best of our knowledge, the C_2H_2/CH_4 separation selectivity of 127.1 is the highest to date (see Table 1). The highly selectivity sorption for C2s/C1 and remarkable high C2s storage capacities highlight the promise of Cu-TDPAT in the practical C2s separation.

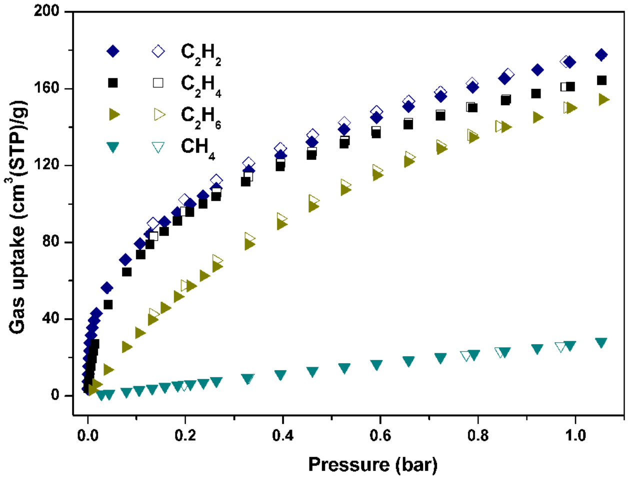

Figure 2. C_2H_2, C_2H_4, C_2H_6 and CH_4 sorption isotherms at 298 K. (adsorption: filled; desorption: open).

Prediction of the gas adsorption selectivity by IAST

Since binary gas adsorption isotherms cannot be conveniently and rapidly measured, it is necessary to use an adsorption model, such as ideal adsorbed solution theory (IAST), to predict binary mixture adsorption from the experimental pure-gas isotherms. The accuracy of the IAST for estimation of binary mixture equilibrium in different zeolites[15] and metal-organic frameworks[16] has already been established in a number of publications in the literature. In order to perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. In practice, several methods to do so are available. We found for this set of data the dual-site Langmuir-

Compounds	Uptake of C_2H_2[a]	Uptake of CH_4	$Q_{st}(CH_4)$[b]	$Q_{st}(C_2H_2)$	S_{ij}[c]	Ref.
Cu-TDPAT	178	28.3	20.7	42.5	127.1	This work
Cu-TDPAH	155	22.1	13.8	23.5	80.9	14
UTSA-50a	90.6	18.8	18.6	39.4	68	12b

UTSA-15a	34	2.5	13.6	39.5	55.6	17
UTSA-36a	57	13	24.4	29.0	13.8	18
$Zn_5(BTA)_6(TDA)_2$	44	10	26.1	37.3	15.5	19
$[Zn_4(OH)_2(1,2,4\text{-}BTC)_2]$	53	10	14.8	28.2	14.7	20
Cu(BDC–OH)	43	13	18.5	25.7	9.26	21
UTSA-38a	64	-	18.9	24.7	5.6	22

Table 1. Comparison of several porous MOFs for their C_2H_2/CH_4 separation at 298K.

[a] The unit for the gas uptake is cm^3 (STP) per gram. [b] Q_{st} (kJ mol^{-1}) is the enthalpy at zero coverage. [c] S_{ij} is the Henry Law selectivity.

Freundlich equation was successful in fitting the data. As can be seen in Table S3, the model fits the isotherms very well (R^2>0.9999).

$$N = N_1^{\max} \times \frac{b_1 p^{1/n_1}}{1+b_1 p^{1/n_1}} + N_2^{\max} \times \frac{b_2 p^{1/n_2}}{1+b_2 p^{1/n_2}} \quad (2)$$

Here, P is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), N is the adsorbed amount per mass of adsorbent (mmol/g), $N_1^{\max}$ and $N_2^{\max}$ are the saturation capacities of sites 1 and 2 (mmol/g), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), and n_1 and n_2 represent the deviations from an ideal homogeneous surface. The fitted parameters were then used to predict multi-component adsorption with IAST.

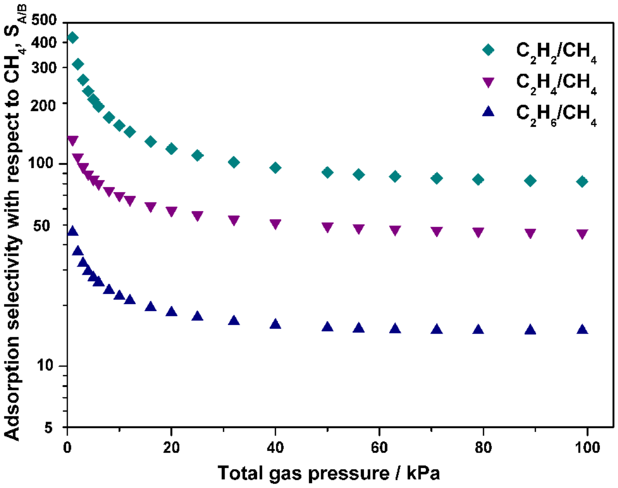

Figure 3. Calculations of the adsorption selectivity, $S_{A/B}$, for equimolar C_2H_2/CH_4, C_2H_4/CH_4 and C_2H_6/CH_4 mixtures at 298 K in Cu-TDPAT using IAST.

The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as $(x_A/y_A)/(x_B/y_B)$, where x_i and y_i are the mole fractions of component i (i = A, B) in the adsorbed and bulk phases, respectively. Figure 3 shows the IAST calculations of the adsorption selectivity for equimolar C_2H_2/CH_4, C_2H_4/CH_4, and C_2H_6/CH_4 mixtures at 298 K in Cu-TDPAT.

The resulting selectivities sort in the order as follows, C_2H_2/CH_4>C_2H_4/CH_4>C_2H_6/CH_4, in accordance with what is calculated from Henry's law. As shown in the figure, the C_2H_2/CH_4 selectivity has its highest value (~422) at very low pressure and decreases drastically as the pressure increases. It reaches a plateau at about 40 kpa and remains relatively constant at higher pressures. The selectivity at 100 kpa is estimated to be ~82 for C_2H_2/CH_4, the highest value reported to date. Fractionation of these gas mixtures is expected to be practically feasible.

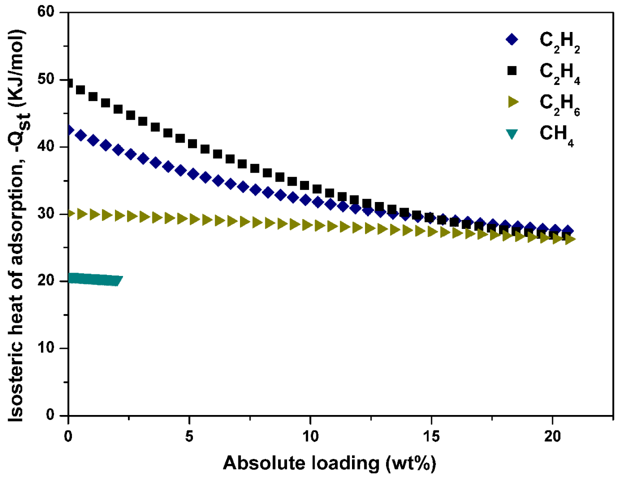

Figure 4. The isosteric heats of adsorption for C_2H_2, C_2H_4, C_2H_6 and CH_4 in Cu-TDPAT.

Isosteric heats of gas adsorption (Q_{st})

To understand such high separation selectivity, the coverage-dependent isosteric heat of adsorption, Q_{st}, was determined by using the pure component isotherm fit the by the virial method

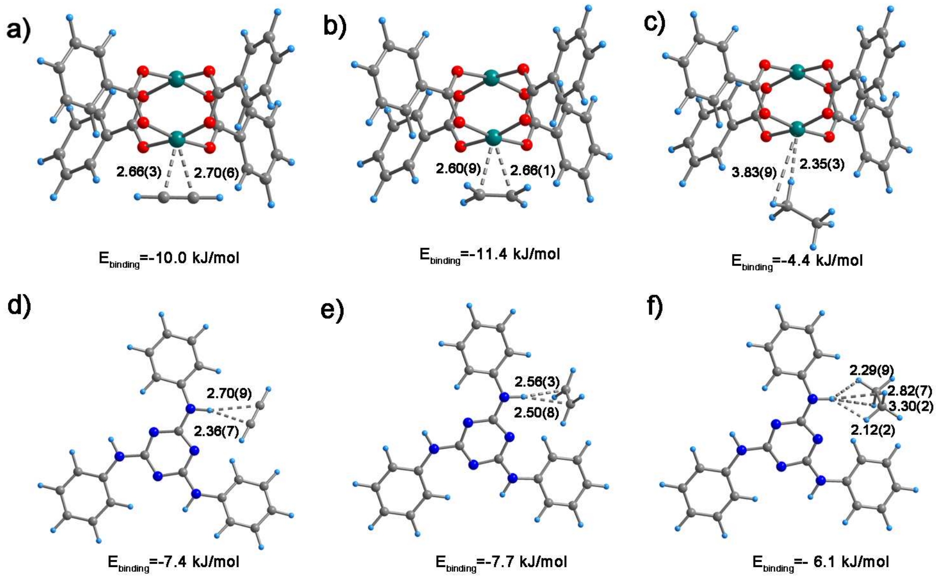

Figure 5. DFT optimized geometry for C2s. Close contact distances, in Å, are marked. Green, red, gray, blue and light blue represent Cu, O, C, N and H atoms, respectively.

(Figures S3-S14 in Supporting Information).[23] Figure 4 presents the data on the isosteric heats of adsorption for C_2H_2, C_2H_4, C_2H_6, and CH_4 in Cu-TDPAT. The Q_{st} of CH_4 in Cu-TDPAT is significantly lower, and has a value of 20.7 $kJmol^{-1}$, whereas the Q_{st} of C_2H_2, C_2H_4 and C_2H_6 are 42.5, 49.5, 30.2 $kJmol^{-1}$, respectively. It is worthwhile to note that Cu-TDPAT shows the highest Q_{st} of C_2H_4 (49.5 $kJmol^{-1}$) at zero loading for MOFs under the same conditions.[24] In fact, the Q_{st} for C_2H_2 and C_2H_6 in Cu-TDPAT are significantly higher than those found for some well-known MOFs. The Q_{st} for C_2H_2 is higher than HKUST-1 (30.4 $kJmol^{-1}$) and USTA-20 (30.8 $kJmol^{-1}$) with high density open metal sites[25,9a] and UTSA (39.4 $kJmol^{-1}$) with both open metal sites and Lewis basic sites[12b]. The low coverage Q_{st} value of C_2H_6 adsorption in Cu-TDPAT (30.2 $kJ \cdot mol^{-1}$) is the second highest one among the reported *rht*-MOFs, while Cu-TDPAH presents the highest value (33.0 $kJ \cdot mol^{-1}$) so far. The Q_{st} for C_2H_2, C_2H_4 and C_2H_6 are all greater than that for CH_4, presumably because of the combined effects of the van der Waals host-guest interactions and the electrostatic host-guest interactions in this system, thus leading to high selectivity for C2 hydrocarbons over CH_4.

Theoretical calculations

The nature of the interactions between C2 molecules and the framework of Cu-TDPAT was studied by DFT calculations (see Figure 5).[26] Optimized geometries verify that C2s binding is stabilized by multipoint interactions from OMSs and LBSs. The unsaturated hydrocarbons ethyne and ethylene bind the Cu^{2+} ions in Cu-TDPAT with Cu-C distances of 2.66(3)/2.70(6) Å and 2.60(9)/2.66(1) Å, respectively. The bond distances observed here are comparable with those observed in Co_2(dobdc), a MOF with high-spin nature of the cobalt(II) centers.[27] Despite the existence of several well-known MOFs with LBSs, to the best of our knowledge, these represent the first structures determined for C2s bound to LBSs. The binding energy of Cu-C2s and ligand-C2s are calculated. An order could be obtained by sorting the magnitudes of binding energy as $E(C_2H_4)>E(C_2H_2)>E(C_2H_6)$. These results are consistent with corresponding Q_{st} for each gas. Due to the unique structure of Cu-TDPAT, the electrostatic host-guest interactions dominate C_2H_2 and C_2H_4 adsorption in the framework (see Figure 5a, Figure 5b, Figure 5d and Figure 5e) and the van der Waals (dispersion) interactions may be the major part of the binding energy for C_2H_6 adsorption (see Figure 5c and Figure 5f). This further proved that the combined effects of the electrostatic host-guest interactions and the van der Waals host-guest interactions in this system lead to the high selectivity for C2s over CH_4.

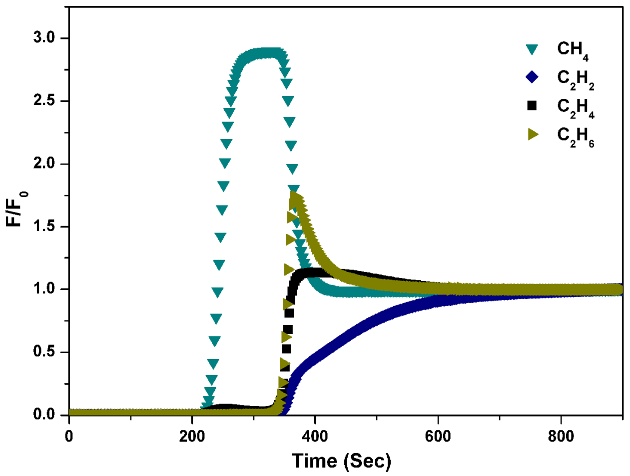

Figure 6. Column breakthrough experiment for equimolar four-component mixture containing C_2H_2, C_2H_4, C_2H_6, and CH_4 at 298 K and 1 bar in Cu-TDPAT.

Breakthrough separation experiments

To evaluate the feasibility of using Cu-TDPAT as a candidate for C2s/C1 separation under conditions that mimic a real-world situation, we conducted breakthrough experiments at room temperature on an equimolar four-component mixture containing C_2H_2, C_2H_4, C_2H_6, and CH_4 (see Figure 6).[28] CH_4 was detected in the downstream shortly after the gas mixture was introduced into the column (214 s), then C_2H_4 and C_2H_6 were both detected at 333 s, while C_2H_2 was not detected until a breakthrough time of 352 s was reached. Breakthrough times are linked to adsorption capacity. As shown in the figure, Cu-TDPAT has both high storage capacities and adsorption rate for C2s. Then we run the breakthrough experiment at the same condition for 6 times to testify the stability of Cu-TDPAT (see Figure S30 to Figure S35). The results indicate that Cu-TDPAT exhibits high C2s/C1 selectivity not only at equilibrium, but also under kinetic flow conditions, suggesting that it is a promising candidate for C2s capture and separation from gas mixtures.

Conclusions

In this work, we combined experimental and theoretical methods to investigate adsorption and separation capacity of a metal-organic framework Cu-TDPAT for C2s over methane. Theoretical calculations indicate that both open metal sites and Lewis basic sites have strong interactions with C2 molecules. For the first time we study the interaction between C2s and LBSs at the molecular level. Owing to collaborative enforcement from OMSs and LBSs, Cu-TDPAT exhibits high adsorption capability for C_2 hydrocarbons and excellent selectivity for C_2 hydrocarbons over CH_4 as well as the highest Henry's law selectivity of 127.1 for C_2H_2/CH_4, at 298K. Isosteric heats of adsorption, IAST calculations, and breakthrough experiments show that this MOF has significantly higher adsorption capacity of C2s compared to CH_4 and the record high isosteric heat of adsorption for C_2H_4 is achieved. The selective adsorption properties of Cu-TDPAT make it a promising candidate for methane purification and recycling.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details and characterization data. See DOI: 10.1039/b000000x/

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