In Silico Tuning of the Pore Surface Functionality in Al-MOFs for Trace CH$_3$I Capture

Xiaoyu Wu, Linjiang Chen,* Eric Jean Amigues, Ruiyao Wang, Zhongfu Pang, and Lifeng Ding*

Cite This: ACS Omega 2021, 6, 18169−18177

ABSTRACT: Aluminum (Al)-based metal−organic frameworks (MOFs) have been shown to have good stability toward γ irradiation, making them promising candidates for durable adsorbents for capturing volatile radioactive nuclides. In this work, we studied a series of existing Al-MOFs to capture trace radioactive organic iodide (ROI) from a gas composition (100 ppm CH$_3$I, 400 ppm CO$_2$, 21% O$_2$, and 78% N$_2$) resembling the off-gas composition from reprocessing the used nuclear fuel using Grand canonical Monte Carlo (GCMC) simulations and density functional theory (DFT) calculations. Based on the results and understanding established from studying the existing Al-MOFs, we proceed by functionalizing the top-performing CAU-11 with different functional groups to propose better MOFs for ROI capture. Our study suggests that extraordinary ROI adsorption and separation capability could be realized by −SO$_3$H functionalization in CAU-11. It was mainly owing to the joint effect of the enhanced pore surface polarity arising from −SO$_3$H functionalization and the μ-OH group of CAU-11.

INTRODUCTION

Nuclear energy is promising to be one of the leading emission-free energy source to power the global economy.$^1$ $^2$ During reprocessing the used nuclear fuel or tackling nuclear accidents,$^3$ the removal of the harmful volatile radioactive nuclides,$^4$ $^{129}$I, $^{131}$I with their molecular forms iodine (I$_2$), and radioactive organic iodides (ROI), is essential to ensure the safe use of the nuclear energy.$^5$ Compared with iodine, CH$_3$I, which is the main kind of the ROI species, is known to be much more difficult to be separated and immobilized because of its comparatively inert chemical reactivity.$^5$ Existing methods for ROI retention and separation based on adsorption include immobilizing gaseous iodine onto AgZ,$^6$ activated charcoals,$^7$ and amine-impregnated activated carbon.$^8$ $^9$ However, high regeneration costs and poor separation efficiency have limited these adsorbents from having wide applications.$^{10}$

As a novel class of functional porous crystalline solids that are assembled using "Molecular Lego"-like organic/inorganic blocks, metal−organic frameworks (MOFs) have been receiving growing interest for ROI capture in the past few years. Unlike conventional porous adsorbents, MOFs feature their tunable pore geometry, precise surface functionality control, large surface areas, and the ease for postsynthetic functionalization, which render them as a new generation of functional materials for adsorption and separation applications.

Recently, Chebbi et al.$^{11}$ investigated a series of MOFs for CH$_3$I capture at 35 °C, in which HKUST-1(Cu) had the highest saturated CH$_3$I uptake (425 mg/g). Li et al.$^{12,13}$ suggested that a total CH$_3$I uptake of 80 wt % could be reached under 150 °C by N,N$'$-dimethyl ethylenediamine (DMEDA)-grafted MIL-101(Cr) due to the strong ionic coupling of CH$_3$I with tertiary nitrogen of an amine group forming ionic (R$_3$N$^-$CH$_3$)$^+$I$^-$.$^{14}$ Lan et al.$^{14}$ computationally screened 187 covalent organic frameworks COFs (which are MOFs' analogue but the main composition is light element linked by covalent bonds) for I$_2$ and CH$_3$I capture. They found that 3D-Py-COFs with a larger accessible surface area or a void fraction have the best I$_2$ uptake and COF-103 with a pore size of 9 Å is identified as the best-performing material for CH$_3$I capture, respectively. The durability of MOFs has always been a concern when MOFs are employed in practical applications.$^{15,16}$

Received: April 19, 2021
Accepted: June 24, 2021
Published: July 12, 2021
Volkringer et al. performed a study of the structural stability of a series of MOFs under γ irradiation, where Al-based MOFs were demonstrated to be able to remain intact under a γ irradiation with doses up to 1.75 mGy, whereas the other tested transition-metal-based MOF materials, such as HKUST-1(Cu) and UiO-66(Zr), were destructed under such irradiation. The radiation stability of the Al-based MOFs was attributed to the smaller γ-ray absorption cross section of aluminum (2.5 barns per atom), compared to those of the transition metals, copper, zinc, and zirconium (>5.3 barns per atom); a smaller cross section implies a lower γ ray absorption and hence higher robustness of the MOF under γ irradiation.17

Inspired by Volkringer et al.’s study, we envisage that other Al-based MOFs might also exhibit a high resistance to γ irradiation, which is a desirable property of the adsorbent materials for capturing volatile ROIs in an irradiation environment. However, we did not attempt any MOF synthesis or stability test under γ irradiation in this study, but we offer our predictions as experimental targets for the future.

Herein, we investigated a series of Al-based MOFs: BasoliteA520,18 CAU-3-BDC,19 CAU-3-NDC,19 CAU-11,20 DUT-5-bpdc,21 DUT-5-ndc,21 NOTT-300,22 and CAU-8-ODB23 for capturing trace CH₃I resembling the used nuclear fuel reprocessing conditions (Figure 1). All of the selected Al-MOFs were previously reported to have good thermal and chemical stability. Six out of the total nine Al-MOFs structures feature 1D metal-oxide chain except for 2D MOF CAU-8-ODB and 3D MOF CAU-3-NDC and CAU-3-BDC, which possess a similar rhombohedral system while differing in secondary building edges (BDC₂⁻ and NDC₂⁻, respectively).

Unlike other Al-MOFs, which contain a μ-OH group, O-CH₃I in CAU-3 series bridges the Al³⁺ vertices. GCMC simulations and DFT calculations were employed to study the adsorption and separation performance of CH₃I in the MOFs. Our modeling results suggested that CAU-11 possessed both the top-performing CH₃I adsorption capacity and selectivity. Based on the experimental fact that CAU-11 has been successfully functionalized through a postsynthetic approach without harming the parent framework,25 we propose a series of hypothetic CAU-11 derivatives (namely, CAU-11-X) by grafting a series of functional groups on to the SDBA linker of CAU-11 to further promote the separation performance of trace CH₃I under a realistic condition. This study of fine-tuning the surface functionalities and pore geometry will aid in the novel design of low-cost and stable materials for effective ROI capture for industrial applications. To our best knowledge, this is the first systematic investigation of trace CH₃I capture using Al-based radiation-resistant MOFs.

Figure 1. Space-filling model of the selected Al-MOFs in this work (color scheme: Al, pink; C, brown; O, red; and H, white. The model of CAU-8-ODB can be found in the Supporting Information (Figure S1)).

Table 1. Selected Al-MOF Properties and Separation Performance under Simulated Conditions

| MOF          | ligand molecules | uptake (cm³/g) | selectivity | LCD' (Å)  | SA_{sim} (m²/g) | SA_{exp} (m²/g) | V_p-sim (cm³/g) | V_p-exp (cm³/g) |
|--------------|------------------|----------------|-------------|-----------|----------------|----------------|----------------|----------------|
| BasoliteA520 | FA<sup>d</sup>   | 2.24           | 8.18 × 10³  | 5.82      | 1174.66       | 1025           | 0.56           | 0.47           |
| CAU-3-BDC    | H₂BDC<sup>e</sup>| 0.07           | 4.06 × 10²  | 11.07     | 2389.16       | 1920           | 0.88           | 0.64           |
| MIL-5<sup>24</sup> | H₂BDC       | 0.52           | 2.19 × 10³  | 6.97      | 1410.96       | 1140           | 0.61           | 0.68           |
| CAU-3-NDC    | H₂NDC<sup>f</sup>| 0.04           | 2.02 × 10²  | 13.81     | 3129.4        | 2750           | 1.17           | 0.95           |
| CAU-11<sup>20</sup> | H₂SDBA<sup>g</sup> | 11.18         | 6.64 × 10⁴  | 5.89      | 469.78        | 350            | 0.31           | 0.17           |
| DUT-5-bpdc   | H₂bpdc<sup>h</sup> | 0.04          | 1.93 × 10³  | 11.33     | 2376.25       | 2335           | 1.08           | 0.81           |
| DUT-5-ndc    | H₂NDC         | 0.09           | 4.41 × 10²  | 8.90      | 2067.21       | 1996           | 0.83           | 0.68           |
| NOTT-300<sup>22</sup> | H₄L<sup>i</sup> | 1.19           | 3.75 × 10³  | 5.72      | 1326.7        | 1370           | 0.54           | 0.38           |
| CAU-8-ODB    | H₂ODB<sup>j</sup> | 0.36           | 1.91 × 10³  | 6.74      | 1401.78       | 1004           | 0.67           | 0.47           |

<sup>a</sup>Largest cavity diameter. <sup>b</sup>Geometric surface area. <sup>c</sup>Pore volume. <sup>d</sup>Fumaric acid. <sup>e</sup>Terephthalic acid. <sup>f</sup>1,4-Naphthalenedicarboxylic acid. <sup>g</sup>4,4′-Sulfonyldibenzoic acid. <sup>h</sup>4,4′-Biphenyldicarboxylic acid. <sup>i</sup>Biphenyl-3,3′,5,5′-tetracarboxylic acid. <sup>j</sup>4,4′-Oxydibenzoic acid.
RESULTS AND DISCUSSION

Table 1 presents the geometric properties together with separation performance of the selected Al-MOFs. We noted that the theoretically calculated surface area and porosity of Al-MOFs are slightly higher than those reported from experiments. This could be attributed to imperfect crystalline or incomplete activation during MOF synthesis. With the abundant presence of CO₂, O₂, and N₂, the adsorption of dilute 100 ppm CH₃I in most of the selected MOFs has been difficult due to the competing nature of the other gas molecules against CH₃I. Nevertheless, there are a few well-performing MOFs with high CH₃I uptake, which possess relatively narrow pore channels. CAU-11, BasoliteA520, and NOTT-300, which possess relatively small largest cavity diameters (LCD) (5.89, 5.82, and 5.72 Å, respectively) enjoy high selective capture toward CH₃I (11.18, 2.24, and 1.19 cm³/g, respectively). Such adsorption behavior that the separation performance could be enhanced by tuned pore size was also observed in studies of acid gas removal and purification of natural gas using MOFs.

To further reveal the correlation between MOF characteristics and the CH₃I separation capability, structure−property relationships were mapped for the selected nine Al-MOFs; as shown in Figure 2a, the CH₃I gravimetric uptake increases as density increases. However, a nonlinear correlation could be observed. Figure 2b–d shows that there is a sharp drop of CH₃I uptake when LCD, the surface area, and the pore volume of the MOFs are increased to around 6.5 Å, 1000 m²/g, and 0.5 cm³/g, respectively. Above all, extraordinary CH₃I capture performance (11.18 cm³/g uptake and 6.64 × 10⁴ selectivity) could be found in CAU-11 owing to compact interaction with CH₃I provided by a constricted porosity (surface area: 469.78 m²/g and pore volume: 0.31 cm³/g), followed by BasoliteA520 (surface area: 469.78 m²/g and pore volume: 0.31 cm³/g) and NOTT-300 (surface area: 469.78 m²/g and pore volume: 0.31 cm³/g).
Figure 3a presents the asymmetric edge unit of CAU-11, which forms the lozenge-shaped narrow channel geometry. Interconnected by an SDBA linker, Al\(^{13}\) vertices were bridged through \(\mu\)-OH groups.\(^{25}\) Compared with NOTT-300 (Figure 3b) where only the \(\mu\)-OH group contributes to an electrostatic field, the \(\mu\)-SO\(_2\) vertex of the SDBA ligand bridging two phenyl rings along with the \(\mu\)-OH group also provides a polarized channel surface enhancing the electrostatic potential field. As indicated from the DDEC calculated atomic charges on the asymmetric unit of CAU-11 (Figure 3a), the sulfur atom indicated from the DDEC calculated atomic charges on the \(\mu\)-SO\(_2\) group possess point charges of 0.465 and \(-1.122\), respectively. With the aid of 1-D narrow pore channels, the polarized pore surface provides the overlapped electrostatic interaction with CH\(_3\)I to enhance its uptake in CAU-11. As shown in Figure 3c, the isosteric heat of CH\(_3\)I in CAU-11 outperforms all other selected MOFs. Such tuned polarity of the channel surface in MOFs was studied to play vital roles in CO\(_2\) storage and capture.\(^{28,29}\)

As shown in Figure 4a, the phenol rings of SDBA ligands in CAU-11 have good coverage of the pore surface in CAU-11, which are the least polarized part of the ligands. We further drafted eight different types of functional groups in silico varying between polarities and size onto a phenol ring of the SDBA ligand to study to effect of pore size and tuned functionality onto the selective adsorption nature toward trace CH\(_3\)I. Potential synthetic routes for the grafted ligands (Figure 4b) are proposed in Section S10 of the Supporting Information. The \(-\mu\)-SO\(_2\)H-functionalized ligand, diphenylsulfone-3,3′-disulfo-4,4′-dicarboxylic acid, has been synthesized and used to construct MOFs before.\(^{30}\) More generally, diarylsulfones show good versatility in incorporating chemical functionalities.\(^{31}\) However, we envisage that some syntheses might be elaborate and challenging.

The hypothetical structures with grafting modification were optimized using DFT calculations as presented in the methodology section. To ensure the accessibility of CH\(_3\)I into the hypothetical functionalized CAU-11-X series, MOFs whose pore limiting diameter (PLD) are smaller than 4.23 Å (the smallest Van der Waals diameter of CH\(_3\)I) are treated as inaccessible MOFs and excluded; a resulting eight CAU-11-X MOFs were obtained for further investigation (Figure 4b). Theoretical characterized porosity of the hypothetically designed MOFs and models of CH\(_3\)I-inaccessible CAU-11-X series are provided in the Section S7 of the Supporting Information. The adsorption isotherms of the four gases (CH\(_3\)I, CO\(_2\), O\(_2\), and N\(_2\)) up to 1 bar in the CAU-11-X MOFs were simulated by GCMC simulations and are given in Figure S22. Compared with CO\(_2\), O\(_2\), and N\(_2\), CH\(_3\)I features a relatively larger molecular size, as shown in Figure S19, which contributes to an enhanced overlapped interaction between the gas molecules and the pore surface. As shown in Figure S22a, CH\(_3\)I adsorption isotherms of functionalized CAU-11-X series feature type I micropore filling adsorption mechanism, where the uptake can be saturated at relatively low pressure.

To elucidate the trace CH\(_3\)I separation performance of CAU-11-X series MOFs, we further studied the trace CH\(_3\)I separation performance under resembled nuclear industrial off-gas composition as the same conditions in the investigations of preliminary Al-MOFs. It appears that merely judging the CH\(_3\)I separation performance from adsorption isotherms up to 1 bar has provided false impression that postsynthetic modification is not working. As illustrated in Table 2, CAU-11-SO\(_2\)H gives the best performance in selectively capturing CH\(_3\)I by GCMC simulations (19.7 cm\(^3\)/g and 5.14 × 10\(^{-5}\)), which is much higher than that of pristine CAU-11. The functionalization of CAU-11 has provided higher isosteric heat of adsorption (\(Q_s\)) of CH\(_3\)I with the MOFs with the exception of \(-\mu\)-SO\(_2\)H functionalization, which enabled higher CH\(_3\)I uptake, as shown in Figure 5a. The overall \(Q_s\) ranking is \(\mu\)-SO\(_2\)H > \(-\mu\)-CN > \(-\mu\)-NH\(_2\) > \(-\mu\)-NO\(_2\) > \(-\mu\)-SO\(_2\) > \(-\mu\)-Br > -F > -H > -\(\mu\)-CH\(_3\)I, which fits well the CH\(_3\)I uptake ranking. The \(Q_s\) ranking from the GCMC simulations agrees well with the binding affinities obtained from DFT calculations, which confirms the validity of the GCMC simulation results. Moreover, as shown in Figure 5b, CH\(_3\)I selectivity ranking in the MOFs is positively correlated with the binding affinity differences between CH\(_3\)I and CO\(_2\), N\(_2\), and O\(_2\). In general, CO\(_2\) poses stronger

Table 2. CH\(_3\)I Separation Performance of the Functionalized CAU-11-X and Adsorption Affinity of the Adsorbates

| CAU-11-X   | CH\(_3\)I uptake (cm\(^3\)/g) | selectivity | \(E_{CH_3I}^{\text{st}}\) (kJ/mol) | \(E_{CO_2}\) (kJ/mol) | \(E_{N_2}\) (kJ/mol) | \(E_{O_2}\) (kJ/mol) |
|------------|-------------------------------|-------------|---------------------------------|----------------------|----------------------|----------------------|
| \(-\mu\)-SO\(_2\)H | 19.7                          | 5.14 × 10\(^{-5}\) | 91.29                           | 47.09                | 28.35                | 26.91                |
| \(-\mu\)-Br  | 9.84                          | 9.37 × 10\(^{-5}\) | 77.1                            | 35.91                | 24.3                 | 23.5                 |
| \(-\mu\)-CH\(_3\)I | 7.75                          | 7.18 × 10\(^{-5}\) | 72.44                           | 33.45                | 21.92                | 21.82                |
| \(-\mu\)-CN   | 14.6                          | 1.35 × 10\(^{-5}\) | 79.75                           | 40.61                | 25.61                | 24.3                 |
| \(-\mu\)-NO\(_2\) | 12.11                         | 9.23 × 10\(^{-5}\) | 78.44                           | 37.59                | 24.8                 | 24.04                |
| \(-\mu\)-NH\(_2\) | 12.7                          | 1.03 × 10\(^{-5}\) | 79.27                           | 36.87                | 24.72                | 23.89                |
| \(-\mu\)-Cl    | 11.95                         | 9.58 × 10\(^{-5}\) | 77.34                           | 36.03                | 24.12                | 23.38                |
| \(-\mu\)-F     | 8.54                          | 5.81 × 10\(^{-5}\) | 75.32                           | 38.31                | 24.86                | 24.32                |
| \(-\mu\)-H      | 11.18                         | 6.64 × 10\(^{-5}\) | 71.9                            | 32.85                | 21.87                | 21.04                |

\(^{\text{a}}\)DFT-derived binding enthalpy.
adsorption competitiveness than \( \text{N}_2 \) and \( \text{O}_2 \) during the separation of CH\(_3\)I.

The adsorption enthalpy of CH\(_3\)I in CAU-11-SO\(_3\)H, at a close-to-saturation loading of 23.38 cc/g, was 85 kJ/mol, which is high for physisorption and could indicate difficulty in desorption. To evaluate the possibility of releasing CH\(_3\)I from CAU-11-SO\(_3\)H, we compared the zero-coverage isosteric heats of adsorption \( (Q_a) \) of CH\(_3\)I in CAU-11-SO\(_3\)H and HKUST-1(Cu), using the Widom particle insertion method. The zero-coverage \( Q_a \) is a direct measure of the adsorbent–adsorbate interaction strengths, which was calculated to be 77 and 67 kJ/mol for CH\(_3\)I in CAU-11-SO\(_3\)H and HKUST-1(Cu), respectively. In our calculations, any strong adsorbate interaction with the open metal sites of HKUST-1(Cu) was not captured beyond what was described by the used force field model for HKUST-1(Cu), which was a combination of UFF and DDEC charges. Therefore, the more accurate \( Q_a \) for HKUST-1(Cu) would be much higher than 67 kJ/mol should the strong adsorbate interactions with the open metal sites be included. Indeed, an appreciable percentage (5%) of adsorbed CH\(_3\)I in HKUST-1(Cu) was found to be from chemisorption; nonetheless, it was also shown that HKUST-1(Cu) exhibited a good adsorption/desorption cyclability.\(^{11}\) Based on the relative adsorption strengths of CH\(_3\)I in CAU-11-SO\(_3\)H and HKUST-1(Cu), we envisage that the release of CH\(_3\)I from CAU-11-SO\(_3\)H might be possible.

Overall, we would like to propose CAU-11-SO\(_3\)H to be the best-performing trace CH\(_3\)I separation material, compared to other functionalization modifications, as it possesses the best CH\(_3\)I uptake and selectivity against (\( \text{N}_2 \), \( \text{O}_2 \), and \( \text{CO}_2 \)) (19.7 cm\(^3\)/g and \( 5.14 \times 10^5 \)). However, the predicted adsorption capacity is not as high as the capacity measured for HKUST-1(Cu) by Chebbi et al.,\(^{11}\) where breakthrough experiments were employed to investigate the dynamic adsorption properties of CH\(_3\)I in MOFs; see Table S19 for a comparison between CAU-11-SO\(_3\)H and selected MOFs from the literature. Different from breakthrough experiments, our GCMC simulations predict adsorption uptakes for a perfect crystalline structure, at a certain temperature and pressure, under thermodynamic equilibrium. By contrast, the dynamic adsorption in breakthrough experiments is additionally influenced by mesoscale factors, such as the height to the diameter ratio of the adsorbent bed and the flow conditions of the feed. It is also worth noting that the breakthrough experiments for HKUST-1(Cu) were conducted for 1333 ppm CH\(_3\)I with argon as a carrier gas, whereas we simulated for trace (100 ppm) CH\(_3\)I capture from a gas mixture also containing \( \text{CO}_2 \), \( \text{N}_2 \), and \( \text{O}_2 \).
To gain a molecular level of understanding of the competitive CH₃I adsorption behaviors in CAU-11-SO₃H, which proved to be the best adsorbent candidate in this study, a detailed investigation of adsorption sites and geometric positions of the adsorbates were carried out. Figure 6a presents the GCMC-simulated adsorption density plots of CH₃I molecules in CAU-11-SO₃H. CH₃I molecules are mainly located at the center of the pore channel. Due to the uniformly packed 1-D channel chain build up by SDBA-SO₃H and the induced joint effect by two polar centers provided by μ-OH groups and −SO₂, the density contour was lozenge shaped and seated parallel against the backbones of the framework. The DFT-optimized CH₃I binding position agrees well with the GCMC simulations results. It further reveals the sitting orientation of CH₃I in the channel. As shown in Figure 7b, the DFT-optimized CH₃I molecule is located in the center of the channel, where close distances of I···O and I···S are found to be 4.62 and 4.91 Å, respectively, indicating the favorable electrostatic interaction between the atom pairs. As with a less electron-dense site of the C center, the distances of C···O and C···S are found to be 5.11 and 6.35 Å, respectively. The radial distribution analysis reveals that these atom pairs (I···O, I···S, C···S, and C···O) show clear regular peaks, indicating the regular sitting of CH₃I molecules along the pore channel of CAU-11-SO₃H. Such clear well-defined peaks are missing for Nₓ, Oₓ, and CO₂ adsorption in CAU-11-SO₃H, indicating their random sitting in the MOF.

### CONCLUSIONS

To sum up, we have identified a promising Al-based MOF, CAU-11, for trace CH₃I capture, based on the combined GCMC- and DFT-calculated results. We demonstrated that the trace CH₃I separation performance could be enhanced by tuning the functionalization of the pore surface of CAU-11. The best-performing hypothetical CAU-11-SO₃H was proposed to possess both high selectivity and high adsorption capacity (19.7 cm³/g and 5.14 × 10⁻³) in trace CH₃I capture, owing to the synergistic effect of the highly polarized functional group and good pore confinement. Since Al-based MOFs have been demonstrated to be highly radiation-resistant compared with MOF structures based on other metal types, our work will provide good guidance on the design of materials that could be well applied in nuclear waste management.

### COMPUTATIONAL DETAILS

**Grand Canonical Monte Carlo Simulations.** The RASPA package was used to carry out the GCMC simulations of gas molecules’ adsorption and separation in the MOFs. A typical GCMC simulation consists of an equilibrium run of 2 × 10⁶ Monte Carlo (MC) cycles and a production run of 8 × 10⁶ MC cycles. All of the MOF structures were kept rigid with periodic boundary conditions applied where the unit cell numbers were adjusted to ensure the perpendicular cell width to be longer than 24.0 Å (twice as the cutoff distance of 12.0 Å). The simulated gas composition was set to 100 ppm CH₃I, 400 ppm CO₂, 78% N₂, and 21% O₂ under 423 K, 1 bar. Such a system is intended to simulate a gaseous mixture released from the reprocessing of the spent nuclear fuel. The selectivity of CH₃I in the simulated system is calculated by the following equation, where Xₐ and Xₐ are the mole fractions of targeted gas CH₃I and other gas components in the adsorbed phase, and Yₐ and Yₐ are the mole fractions of targeted gas CH₃I and other gas components in the bulk phase.

\[
\text{selectivity}_{ab} = \frac{X_a}{Y_a} / \frac{X_b}{Y_b}
\]

The structural properties, such as surface areas and porosity of the MOFs were characterized using the Zeo++ package. To accurately address the electrostatic interaction, atomic charges of the structures were computed using the high-quality density-derived electrostatic charges (DDECs) method. Lennard-Jones parameters of the adsorbents were taken from the universal force field. Lorentz–Berthelot mixing rules were implemented to address the nonbonded interaction (Table 3).

**Density Function Theory Calculations.** DFT calculations were carried out using VASP with the plane-wave pseudopotential formalism. Geometric optimization of the MOFs and their binding complexes with the gas molecules were performed with the Perdew–Burke–Ernzerhof exchange–correlation functional. DFT-D₃(BJ) dispersion correction was implemented to address the noncovalent bond interaction and the plane-wave cutoff energy was set to 500 eV.

The gas–MOF binding energies were calculated by the following equation

\[
\Delta E = E_{\text{bind}} - E_{\text{host}} - E_{\text{guest}}
\]
where $E_{\text{bind}}$ is the zero-point energy of the optimized binding complex, $E_{\text{MOF}}$ is the zero-point energy of the MOF cell, and $E_{\text{guest}}$ is the zero-point energy of the guest gas molecules. During the DFT calculations, multiple initial positions of gas molecules were attempted to search for the global minimum interaction position of the gas molecules in the MOFs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acsomega.1c02072.

The space-filling model of CAU-8-ODB$_3$ schematics of the asymmetric units of the Al-MOF$_5$; schematics of the asymmetric units of CAU-11-X; models of the simulated gases; single-component adsorption isotherms of Al-MOF$_5$; single-component adsorption isotherms of hypothetical CAU-11-X; calculated porosity properties of the CAU-11-X series; comparison between CAU-11-SO$_3$H and literature MOFs for capturing CH$_3$I; simulated adsorption and desorption of CH$_3$I in CAU-11-SO$_3$H; and potential synthetic routes for the grafted ligands (PDF)

Al-MOFs DDEC (ZIP)
CAU-11-X DDEC (ZIP)

## AUTHOR INFORMATION

### Corresponding Authors

Linjiang Chen — Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool L7 3NY, United Kingdom; Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory and Department of Chemistry, University of Liverpool, Liverpool L7 3NY, United Kingdom; Email: lchen@liverpool.ac.uk

Lifeng Ding — Department of Chemistry, Xi’an Jiaotong-Liverpool University, Suzhou Dushu Lake Higher Education Town, Jiangsu 215123, China; orcid.org/0000-0001-8761-191X; Email: Lifeng.Ding@xjtlu.edu.cn

### Authors

Xiaoyu Wu — Department of Chemistry, Xi’an Jiaotong-Liverpool University, Suzhou Dushu Lake Higher Education Town, Jiangsu 215123, China; Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool L7 3NY, United Kingdom

Eric Jean Amigues — Department of Chemistry, Xi’an Jiaotong-Liverpool University, Suzhou Dushu Lake Higher Education Town, Jiangsu 215123, China

Ruiyao Wang — Department of Chemistry, Xi’an Jiaotong- Liverpool University, Suzhou Dushu Lake Higher Education Town, Jiangsu 215123, China

Zhongfu Pang — Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool L7 3NY, United Kingdom; Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory and Department of Chemistry, University of Liverpool, Liverpool L7 3NY, United Kingdom

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02072

### Notes

The authors declare no competing financial interest.

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