



# Article A Microporous Zn(bdc)(ted)<sub>0.5</sub> with Super High Ethane Uptake for Efficient Selective Adsorption and Separation of Light Hydrocarbons

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Abstract: Separating light hydrocarbons ( $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ ) from CH<sub>4</sub> is challenging but important for natural gas upgrading. A microporous metal-organic framework, Zn(bdc)(ted)0.5, based on terephthalic acid (bdc) and 1,4-diazabicyclo[2.2.2]octane (ted) ligands, is synthesized and characterized through various techniques, including powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and porosity analysis. The adsorption isotherms of light hydrocarbons on the material are measured and the isosteric adsorption heats of  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  are calculated. The prediction of C2–4/C1 adsorption selectivities is accomplished using ideal adsorbed solution theory (IAST). The results indicate that the material exhibits exceptional characteristics, including a Brunauer-Emmett-Teller (BET) surface area of 1904 m<sup>2</sup>/g and a pore volume of 0.73 cm<sup>3</sup>/g. Notably, the material demonstrates remarkable  $C_2H_6$ adsorption capacities (4.9 mmol/g), while CH<sub>4</sub> uptake remains minimal at 0.4 mmol/g at 298 K and 100 kPa. These findings surpass those of most reported MOFs, highlighting the material's outstanding performance. The isosteric adsorption heats of  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  on the Zn(bdc)(ted)<sub>0.5</sub> are higher than  $CH_4$ , suggesting a stronger interaction between  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  molecules and  $Zn(bdc)(ted)_{0.5}$ . The molecular simulation reveals that  $Zn(bdc)(ted)_{0.5}$  prefers to adsorb hydrocarbon molecules with richer C-H bonds and larger polarizability, which results in a stronger dispersion force generated by an adsorbent-adsorbate induced polarization effect. Therefore, the selectivity of  $C_4H_{10}/CH_4$  is up to 180 at 100 kPa,  $C_3H_8/CH_4$  selectivity is 67, and the selectivity of  $C_2H_6/CH_4$  is 13, showing a great potential for separating C2–4 over methane.

Keywords: MOFs; light hydrocarbons; adsorption and separation; Zn(bdc)(ted)<sub>0.5</sub>

# 1. Introduction

One of the most pressing environmental challenges is the ongoing rise in atmospheric carbon dioxide resulting from extensive fossil fuel consumption. In comparison to traditional fossil fuels, natural gas exhibits diminished carbon emissions, relatively lower pollutant discharges (such as NOx), and can be harnessed to mitigate fluctuations in renewable energy sources. Natural gas, primarily composed of methane (75–90%), also encompasses impurities (such as  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ , collectively ranging from 0–20%) [1,2]. Hence, the extraction of heavier hydrocarbons becomes imperative to meet the requisites of natural gas enhancement and secure storage. It is challenging to effectively separate natural gas into a single component, but it is very important in the petrochemical industry. Innovative methods for the efficient separation of methane from mixed light hydrocarbons into pure components must be investigated, as traditional approaches (such as



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). cryogenic distillation) are very energy intensive [3]. Recent advancements have highlighted the significance of adsorptive separation technology as an efficient, cost-effective, and low-energy-consumption technique. In the process of adsorption, the meticulous selection of a suitable adsorbent plays a crucial role.

In the context of porous materials, metal-organic frameworks (MOFs) are the focus of significant attention. MOFs are being considered for their potential application in numerous areas, ranging from adsorption and separation [4–6] to catalysis [7,8], luminescence [9–11], electronics [12,13], magnetism [14], drug delivery [15], and sensing [16]. To date, MOF materials have been developed into prospective resources for methane purification. Yuan et al. [17] reported a facile synthesis of MIL-100 (Fe) at room temperature, which exhibited  $CH_4$ ,  $C_2H_6$ , and  $C_3H_8$  uptake capacities of 0.36, 2.22, and 6.78 mmol/g, respectively, at 100 kPa and 298 K. The IAST-predicted selectivity was 6.0 for  $C_2H_6/CH_4$  at 298 K. Lv et al. [18] found that CTGU-15 demonstrated exceptionally high  $C_3H_8$  uptake (12.13 mmol/g) and relatively low CH<sub>4</sub> uptake (0.40 mmol/g) at 298 K and 100 kPa, but it had low  $C_2H_6$  uptake (2.13 mmol/g) and low  $C_2H_6/CH_4$  selectivity (5.2). Chen et al. [19] discovered that InOF-1 exhibited a high  $C_2H_6/CH_4$  selectivity of 17 at 100 kPa and 298 K. However, it also exhibited a relatively high  $CH_4$  uptake of 0.64 mmol/g. Shi et al. [20] reported that PCN-224 demonstrated a high  $C_2H_6/CH_4$  selectivity of 12 at 100 kPa and 298 K. Nevertheless, this material exhibited a relatively low  $C_2H_6$  uptake of 2.94 mmol/g. Therefore, the development of MOFs that exhibit low CH<sub>4</sub> uptake, high C<sub>2</sub>H<sub>6</sub> uptakes, and high  $C_2H_6/CH_4$  selectivities is of utmost importance to meet the industrial application requirements for natural gas purification.

This study presents a comprehensive analysis of a highly microporous Zn-based MOF,  $Zn(bdc)(ted)_{0.5}$ . The main focus is investigating the adsorption behavior of light hydrocarbons, including CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>. The material is thoroughly characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA), and N<sub>2</sub> adsorption techniques. To examine the adsorption isotherms of light hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>) at various temperatures, a volumetric approach is employed. The determination of the isosteric adsorption heats of these hydrocarbons is based on single-component isotherms collected at three distinct temperatures. Additionally, the C2–4/C1 adsorption selectivities of the MOF are predicted utilizing the Ideal Adsorbed Solution Theory (IAST). To gain insights into the adsorption and separation mechanism of C2–4 hydrocarbons from CH<sub>4</sub> within the Zn(bdc)(ted)<sub>0.5</sub> framework, Metropolis Monte Carlo simulations are employed.

# 2. Results and Discussion

# 2.1. XRD Analysis

Figure 1 displays the X-ray diffraction pattern of the synthesized Zn(bdc)(ted)<sub>0.5</sub>·2DMF·0.2H<sub>2</sub>O sample, along with the simulated pattern for comparison. The major peaks observed in the synthesized sample closely correspond to the simulated XRD pattern, which was obtained using the Reflex module in the Materials Studio program, based on its single-crystal data [21]. Additionally, the positions of these characteristic peaks were consistent with the results reported in the literature [22]. The well-defined and resolved peaks shown in Figure 1 signify the excellent purity and crystalline nature of the sample synthesized in this study.



**Figure 1.** XRD patterns of the  $Zn(bdc)(ted)_{0.5} \cdot 2DMF \cdot 0.2H_2O$  (**top**) compared with the simulated pattern (**bottom**).

# 2.2. Structure Analysis

Figure 2 displays the secondary building unit (SBU) of  $Zn(bdc)(ted)_{0.5}$ , which is a paddle-wheel  $Zn_2(COO)_4(ted)_2$  unit. Each paddle-wheel SBU is interconnected by bdc in the two-dimensional network (xy plane), with Zn ions serving as the metal center. The apexes of Zn ions in the building units are bonded by ted molecules, forming a three-dimensional porous framework. This framework ultimately results in the formation of two interlacing channels of different sizes (7.5 × 7.5 Å and 4.8 × 3.2 Å) [23]. Zn(bdc)(ted)\_{0.5} adopts the tetragonal crystal system with the space group P4/ncc [23].



**Figure 2.** SBU unit of Zn(bdc)(ted)<sub>0.5</sub>, where green represents Zn, gray represents C, red represents O, and blue represents N.

# 2.3. SEM Analysis

Figure 3 illustrates the morphology of the synthesized  $Zn(bdc)(ted)_{0.5} \cdot 2DMF \cdot 0.2H_2O$  as observed through scanning electron microscopy. The images demonstrate that  $Zn(bdc)(ted)_{0.5} \cdot 2DMF \cdot 0.2H_2O$  exhibits well-defined crystallinity and a lump morphology [22].



Figure 3. SEM image of the Zn(bdc)(ted)<sub>0.5</sub>·2DMF·0.2H<sub>2</sub>O.

# 2.4. Thermogravimetric Analysis

Figure 4 reveals the TG profile for Zn(bdc)(ted)<sub>0.5</sub>·2DMF·0.2H<sub>2</sub>O, indicating the compound's excellent thermal stability to 260 °C. The curve reveals three well-defined weightloss steps. The initial step, observed in the temperature range from ambient to 170 °C, corresponds to a significant weight loss of 34.3%. This weight loss is primarily attributed to the evaporation of solvent molecules (DMF and H<sub>2</sub>O) that are coordinated within the framework of Zn(bdc)(ted)<sub>0.5</sub>. The second and third steps are observed in the temperature ranges of 260–330 °C and 330–510 °C, resulting in losses of 11.6% and 17.6%, respectively, owing to the successive structural decomposition of the ted and bdc ligands.



Figure 4. Thermogravimetric analysis of the Zn(bdc)(ted)<sub>0.5</sub>·2DMF·0.2H<sub>2</sub>O.

## 2.5. Porosity Analysis

A nitrogen adsorption-desorption experiment was conducted to determine the compound's surface area and porosity. Figure 5 presents the N<sub>2</sub> sorption isotherm of Zn(bdc)(ted)<sub>0.5</sub> at 77 K. The N<sub>2</sub> isotherm on this compound exhibits a distinctive type-I sorption behavior, characterized by a prominent rise at low relative pressures of nitrogen, followed by a plateau. This behavior signifies the presence of abundant micropores within the adsorbent. The Langmuir and BET surface areas are determined to be 2025 and 1904 m<sup>2</sup> g<sup>-1</sup>, respectively. The pore volume and median pore width, estimated using the Horvath-Kawazoe method, are 0.73 cm<sup>3</sup> g<sup>-1</sup> and 8 Å. The establishment of the permanent porosity of Zn(bdc)(ted)<sub>0.5</sub> provides motivation for considering its potential application for the adsorption of light hydrocarbons.



**Figure 5.** Nitrogen sorption isotherms at 77 K of the  $Zn(bdc)(ted)_{0.5}$ , where the hollow square represents adsorption, and solid square represents desorption. The inset displays the pore size distribution curve that corresponds to it.

# 2.6. Adsorption Isotherms of Hydrocarbons on the $Zn(bdc)(ted)_{0.5}$

Figure 6 represents the adsorption isotherms of light hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>) on the Zn(bdc)(ted)<sub>0.5</sub> at temperatures of 288 K and 298 K. The figure clearly illustrates the distinct adsorption capacities of Zn(bdc)(ted)<sub>0.5</sub> for CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> at both 288 K and 298 K. Significantly, Zn(bdc)(ted)<sub>0.5</sub> systematically adsorbs many more C2–4 hydrocarbons than C1 methane. Zn(bdc)(ted)<sub>0.5</sub> demonstrates substantial adsorption capacities for C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub>, reaching 5.72, 7.03, and 7.11 mmol/g at 288 K and 100 Kpa, respectively. In contrast, the uptake of CH<sub>4</sub> on Zn(bdc)(ted)<sub>0.5</sub> similarly, at 298 K and 100 Kpa, Zn(bdc)(ted)<sub>0.5</sub> exhibits remarkable adsorption capacities for C<sub>2</sub>H<sub>6</sub> (4.9 mmol/g), C<sub>3</sub>H<sub>8</sub> (6.6 mmol/g), and C<sub>4</sub>H<sub>10</sub> (6.9 mmol/g). These uptake values significantly surpass the CH<sub>4</sub> uptake (0.4 mmol/g), underscoring the exceptional suitability of Zn(bdc)(ted)<sub>0.5</sub> as a highly selective material for the separation of C2–4 hydrocarbons from CH<sub>4</sub> at ambient temperature.



**Figure 6.** CH<sub>4</sub> (purple olive),  $C_2H_6$  (blue triangle),  $C_3H_8$  (red circle), and  $C_4H_{10}$  (black square) sorption isotherms of Zn(bdc)(ted)<sub>0.5</sub> at (**a**) 288 K, and (**b**) 298 K.

## 2.7. Isosteric Adsorption Heats ( $Q_{st}$ ) of Hydrocarbons on the Zn(bdc)(ted)<sub>0.5</sub>

To assess the interaction strength between the framework and gas molecules, we utilized single-component isotherms obtained at three distinct temperatures (Figure 7) to determine the isosteric adsorption heat ( $Q_{st}$ ) of hydrocarbons on the Zn(bdc)(ted)<sub>0.5</sub>.

Isosteric adsorption heat ( $Q_{st}$ ) can be estimated by fitting the adsorption isotherm by using the virial equation [24]:

$$ln(p) = ln(v) + (1/T) \sum_{i=0}^{m} a_i v^i + \sum_{j=0}^{n} b_j v^j$$
(1)

where p (in the unit of Pa) is pressure, v (in the unit of mmol/g) is amount adsorbed, T (in the unit of K) is temperature and,  $a_i$ ,  $b_j$  are empirical parameters which are independent of temperature.

Adsorption isotherms obtained from different temperatures are fitted to Equation (1). Consequently, the  $Q_{st}$  can be calculated from the following equation:

$$Q_{st} = -R \sum_{i=0}^{m} a_i v^i \tag{2}$$

where *R* is the universal gas constant (8.314 J/(K·mol)), and  $Q_{st}$  (in the unit of J/mol) is the isosteric adsorption heat.



**Figure 7.** Adsorption isotherms of  $CH_4$  (**a**),  $C_2H_6$  (**b**),  $C_3H_8$  (**c**), and  $C_4H_{10}$  (**d**) on the Zn(bdc)(ted)<sub>0.5</sub> at 288–308 K.

Figure 8 displays the  $Q_{st}$  of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> on Zn(bdc)(ted)<sub>0.5</sub>. The  $Q_{st}$  values of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> on the Zn(bdc)(ted)<sub>0.5</sub> are higher than the  $Q_{st}$  of CH<sub>4</sub>, indicating a stronger interaction between the C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub>, and the Zn(bdc)(ted)<sub>0.5</sub> surfaces. Specifically, the  $Q_{st}$  values of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> are around 19.8, 21.3, 24.2, and 29.6 kJ mol<sup>-1</sup>, causing the preferential adsorption of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> over CH<sub>4</sub>.



**Figure 8.** The isosteric adsorption heats of  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  on  $Zn(bdc)(ted)_{0.5}$  (black square for  $C_4H_{10}$ , red circle for  $C_3H_8$ , blue triangle for  $C_2H_6$ , and purple olive for  $CH_4$ ).

# 2.8. Ideal Adsorbed Solution Theory Selectivity

Materials with the potential for  $CH_4$  purification require not only high C2–4 uptake and low  $CH_4$  uptake but also remarkable selectivity for C2–4/ $CH_4$ . The above results reveal that  $Zn(bdc)(ted)_{0.5}$  possesses a high C2–4 uptake and a low  $CH_4$  uptake, which prompts further investigation into the gas selectivity for C2–4/ $CH_4$ . The IAST model is commonly employed for predicting the adsorption selectivity of binary gas mixtures using experimental data from pure gas isotherms. In this study, to characterize the adsorption behavior of hydrocarbons on  $Zn(bdc)(ted)_{0.5}$  and perform the IAST calculation, the dualsite Langmuir–Freundlich (DSLF) equation is applied to correlate with the experimental isotherm data of the hydrocarbons. The DSLF model can be mathematically expressed as:

$$q = q_1^{max} \times \frac{b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + q_2^{max} \times \frac{b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}}$$
(3)

where *q* (in the unit of mmol/g) represents the adsorbed uptakes per mass of adsorbent, *p* (in the unit of kPa) represents the pressure of the bulk gas in equilibrium with the adsorbed phase, and  $q_1^{\text{max}}$  and  $q_2^{\text{max}}$  (in the unit of mmol/g) denote the saturated adsorption capacities of sites 1 and 2, respectively. The parameters  $b_1$  and  $b_2$  (in the unit of kPa<sup>-1</sup>) indicate the affinity coefficients of sites 1 and 2, and  $n_1$  and  $n_2$  represent the deviations from an ideal homogeneous surface.

Figure 9 presents a comparison between the DSLF model fittings and the experimental isotherm data. The corresponding fitting parameters and the regression coefficients are listed in Table 1. The high regression coefficient  $R^2$  (up to 0.9999) indicates a good fit between the DSLF model and the single-component experimental isotherms. Therefore, the IAST model is implemented using pure gas adsorption fitted parameters.



**Figure 9.** Experimental and fitted isotherms for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  at 298 K (black square for  $C_4H_{10}$ , red circle for  $C_3H_8$ , blue triangle for  $C_2H_6$ , and purple olive for  $CH_4$ ).

Adsorbates	q_1 <sup>max</sup> (mmol/g)	b <sub>1</sub> (kPa <sup>-1</sup> )	$n_1$	q <sub>2</sub> <sup>max</sup> (mmol/g)	b <sub>2</sub> (kPa <sup>-1</sup> )	<i>n</i> <sub>2</sub>	<i>R</i> <sup>2</sup>
CH <sub>4</sub>	16.5729	$1.359  imes 10^{-4}$	0.9918	16.573	$1.0359\times 10^{-4}$	0.9918	0.9999
$C_2H_6$	7.07662	0.0022	0.8282	7.0766	0.0022	0.8282	0.9999
$C_3H_8$	1.50532	0.0016	0.2973	5.5847	0.0588	0.8818	0.9999
$C_{4}H_{10}$	3.50191	3.031	0.3748	3.8683	0.3413	1.4425	0.9999

Table 1. Equation coefficients for the DSLF isotherm model.

The IAST approach, originally developed by Myers and Praunitz [25], has been extensively employed to predict adsorption selectivity based on the isotherms of the pure components. Figure 10 presents the IAST calculations of  $C_4H_{10}/CH_4$ ,  $C_3H_8/CH_4$ , and  $C_2H_6/CH_4$  selectivities for an equimolar binary mixture maintained at isothermal conditions at 298 K. In general, the adsorption selectivities follow the order  $C_4H_{10}/CH_4 > C_3H_8/CH_4 > C_2H_6/CH_4$ . This observation can be attributed to the enhanced interaction between the material and C2–4 in comparison to CH<sub>4</sub>, suggesting a stronger affinity of the material towards C2–4. At 100 kPa, the  $C_4H_{10}/CH_4$  selectivity is up to 180, the  $C_3H_8/CH_4$  selectivity is 67, and the  $C_2H_6/CH_4$  selectivity is 13. In conclusion, Zn(bdc)(ted)<sub>0.5</sub> exhibits a significant adsorption capacity for C2–4 hydrocarbons and demonstrates a high C2–4/CH<sub>4</sub> adsorption selectivity. These findings underscore the potential of this material as a highly promising candidate for effectively separating C2–4/CH<sub>4</sub> mixtures.



**Figure 10.** IAST-predicted equimolar gas mixture adsorption selectivities for  $Zn(bdc)(ted)_{0.5}$  at 298 K (black square for  $C_4H_{10}/CH_4$ , red circle for  $C_3H_8/CH_4$ , and blue triangle for  $C_2H_6/CH_4$ ).

Table 2 lists the adsorption separation performance of light hydrocarbons for several benchmark MOFs at 298 K and 100 kPa. Notably,  $Zn(bdc)(ted)_{0.5}$  demonstrates a high ethane adsorption capacity, ranking third among the listed adsorbents and reaching an excellent level. Conversely, the methane adsorption capacity is extremely low, resulting in a remarkably high selectivity for  $C_2H_6/CH_4$  separation. To the best of our knowledge, the ethane storage capacity of  $Zn(bdc)(ted)_{0.5}$  surpasses that of CTGU-15 (2.13 mmol/g) [18], PCN-224 (2.93 mmol/g) [20], MIL-100 (Fe) (2.22 mmol/g) [17], MIL-142A (3.82 mmol/g) [26], UIO-67 (4.26 mmol/g) [27], Iso-MOF-1 (3.19 mmol/g) [28], InOF-1 (4.14 mmol/g) [19], JIU-Liu22 (3.30 mmol/g) [29], JIU-Liu37 (4.42 mmol/g) [30], and FJI-C1 (3.93 mmol/g) [31]. It is inferior to the corresponding values of JIU-Liu38 (4.96 mmol/g) [30] and and FJI-H23 (6.28 mmol/g) [32]. Overall, based on the data in Table 2,  $Zn(bdc)(ted)_{0.5}$  exhibits competitive ethane uptake and exceptional  $C_2H_6/CH_4$  adsorption selectivity, positioning it as a promising candidate for  $C_2H_6/CH_4$  separation.

**Table 2.** Comparison of adsorption separation performance of light hydrocarbons among several benchmark MOFs at 298 K and 100 kPa.

Adsorbents	BET (m <sup>2</sup> g <sup>-1</sup> )	C <sub>2</sub> H <sub>6</sub> (mmol/g)	CH <sub>4</sub> (mmol/g)	C <sub>2</sub> H <sub>6</sub> /CH <sub>4</sub> Selectivity	References
CTGU-15	3163.7	2.13	0.4	5.2	[18]
PCN-224	2704	2.93	0.48	12	[20]
MIL-100(Fe)	2482	2.22	0.36	6	[17]
MIL-142A	1424.7	3.82	0.54	14.5	[26]
UIO-67	2590.6	4.26	0.56	8.1	[27]
Iso-MOF-1	3211	3.19	0.38	-	[28]
InOF-1	982	4.14	0.64	17	[19]
JLU-Liu22	1487	3.3	0.71	14.4	[29]
JLU-Liu37	1795	4.42	0.45	11	[30]
JLU-Liu38	1784	4.96	0.48	15	[30]
FJI-C1	1726.3	3.93	0.45	24	[31]
FJI-H23	3740.4	6.28	0.67	14.7	[32]
Zn(bdc)(ted) <sub>0.5</sub>	1904	4.9	0.4	13	This work

#### 2.9. Simulation Results

Figure 11 shows the calculated preferential adsorption sites in the adsorbent for a single adsorbate molecule, with the distance between the H atoms of the adsorbate and the H atoms of bdc indicated. The calculation results indicate that both C1 and C2 molecules tend to be adsorbed in the region sandwiched by two adjacent bdc ligands. Unlike C1 and C2 molecules, the ted ligand also exhibits a certain attraction towards C3 and C4 molecules, which tend to be adsorbed at the vertex of the rectangular cage. Therefore, it can be concluded that the interaction between C1/C2 molecules and the adsorbent is mainly attributed to the dispersion force between bdc and the hydrogen atoms from the adsorbate



molecules. For C3 and C4 molecules, in addition to the interaction with bdc ligands, the methylene group on the ted ligand also provides a certain amount of dispersion force.

**Figure 11.** The calculated preferential adsorption site for a single (**a**)  $CH_4$ , (**b**)  $C_2H_6$ , (**c**)  $C_3H_8$  and (**d**)  $C_4H_{10}$  in  $Zn(bdc)(ted)_{0.5}$ .

As the carbon chain length increases, the shortest distance between the adsorbate and the adsorbent gradually decreases from 3.285 Å for CH<sub>4</sub> to 3.171 Å for C<sub>2</sub>H<sub>6</sub>, 2.877 Å for C<sub>3</sub>H<sub>8</sub>, and 2.623 Å for C<sub>4</sub>H<sub>10</sub>, suggesting an increasing dispersion force. This is because the growing carbon chain makes the polarity of the adsorbate molecules gradually larger, resulting in a larger instantaneous dipole moment during adsorption. Compared with the bdc ligand, the ted ligand is less polar, so the interaction between the ted ligand and C1/C2 molecules is weaker. As the polarity of the adsorbate molecules increases, the ted ligand also participates in the interaction with the adsorbate molecules (the distances for C3 of 2.953 Å and C4 of 2.645 Å are both smaller than the shortest distance between the C3 or C4 molecule and the framework), so the selectivity of C3/C1 and C4/C1 is greater than that of C2/C1.

Additionally, it is worth noting that the closest H atom in  $C_3H_8$  to the bdc ligand comes from the methyl group, while in  $C_4H_{10}$ , the closest H atom to the ligand comes from the methylene group. With the synergistic effect of adjacent bdc ligands and ted ligands, more abundant H atoms and a longer carbon chain from  $C_4H_{10}$  prompt the C4 molecule to fully interact with the skeleton.

Figure 12 shows the interaction energy histograms for different adsorbate molecules and the adsorbent. From Figure 10, it can be seen that the order of adsorption energies between C1–C4 molecules and the adsorbent is  $C_4H_{10}$  (-37.5 kJ/mol) >  $C_3H_8$  (-28.7 kJ/mol) >  $C_2H_6$  (-22.1 kJ/mol) >  $CH_4$  (-13.0 kJ/mol). As the length of the carbon chain increases, the height of the peaks in the energy curve gradually decreases, and the width of the peaks gradually increases. On the one hand, the number of primary adsorption sites between the adsorbate and the adsorbent was changed from a single ligand to two types of ligands. On the other hand, the peak of the C4 molecule is wider and higher than that of the other molecules due to the participation of rich methylene groups in the adsorbate-adsorbent interaction, which agrees with the result from Figure 9.



**Figure 12.** Interaction energy histogram for C1–C4 with Zn(bdc)(ted)<sub>0.5</sub>.

#### 3. Materials and Methods

# 3.1. Synthesis

The chemicals utilized in this study were purchased from reputable commercial sources and used as received without undergoing any additional purification steps. The starting materials utilized include zinc nitrate hexahydrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Alfa, 98%], terephthalic acid (Alfa, 98%), 1,4-diazabicyclo[2.2.2]octane (TCI, 98%), N,N-dimethylformamide (DMF, Guanghua Chemical Co., Ltd., Guangzhou, China, 99.8%), N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>4</sub>H<sub>10</sub> (99.999%, Guangdong Huate Gas Co., Ltd., Foshan, China).

The synthesis of Zn(bdc)(ted)<sub>0.5</sub>·2DMF·0.2H<sub>2</sub>O was carried out using the following procedure: a mixture of zinc(II) nitrate hexahydrate [Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.597 mmol, 156 mg], terephthalic acid (H<sub>2</sub>bdc, 0.614 mmol, 102 mg), and 1,4-diazabicyclo[2.2.2]octane (ted, 0.321 mmol, 36 mg) was dissolved in 15 mL of dimethylformamide in a 20 mL glass vial. The solution was then subjected to sonication for a duration of 10 min and subsequently heated at 120 °C for 48 h. After the completion of the reaction, the resulting crystals were obtained with a yield of 78%. The crystals were then filtered and subjected to three consecutive washes using 10 mL of DMF each time. The final product weighed 200 mg.

#### 3.2. Characterization

X-ray diffraction patterns were obtained using a Rigaku D/M-2200T automated diffraction system (Ultima IV) equipped with Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The measurements were carried out at room temperature, employing a 2 $\theta$  range of 3–50°, a scan speed of 2°/min, and an operating voltage of 40 kV and current of 40 mA. Scanning electron microscopy (SEM) analysis was performed using a Hitachi S-4800 instrument after the deposition of a thin layer of gold. Thermogravimetric analyses were performed using a TA Q5000 analyzer, which ramped the temperature from ambient to 600 °C at a heating rate of 10 °C/min under a continuous nitrogen gas atmosphere. Nitrogen adsorption isotherms at 77 K were collected using a Micromeritics ASAP 2020 instrument. Prior to the measurements, the sample underwent an initial outgassing process overnight under vacuum at 393 K.

#### 3.3. Adsorption of Light Hydrocarbons

Gas sorption experiments for  $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  at various temperatures (288 K, 298 K, and 308 K) were conducted using high-resolution Micromeritics 3-Flex adsorption equipment. The gases employed in the experiments were of ultra-high purity (99.999%). Prior to the measurements, the samples underwent an initial outgassing process at 393 K under vacuum overnight. Outgassing samples of approximately 100 mg were used for gas sorption measurements.

# 3.4. Simulation

In order to investigate the adsorption and separation mechanism of C2–4 hydrocarbons over CH<sub>4</sub> in Zn(bdc)(ted)<sub>0.5</sub>, the Metropolis Monte Carlo simulation by Materials Studio 7.0 [33] was employed to mimic the adsorption behavior of the adsorbate in the MOF structure. The initial structure of Zn(bdc)(ted)<sub>0.5</sub> obtained from the Cambridge Crystallographic Data Centre [21] was optimized using the CASTEP module with convergence criteria set at  $2 \times 10^{-5}$  ev for energy, 0.1 ev/Å for force, 0.1 GPa for stress, and  $2 \times 10^{-3}$  Å for displacement. The optimization employed the GGA/PBE basis was set with the Grimme method for dispersion correction, a commonly used approach for crystal structure optimization. The energy cutoff was set at 300.0 ev and the ultrasoft pseudopotential was applied. After optimization, the sorption module was utilized to explore the gas adsorption behavior within a  $2 \times 2 \times 2$  supercell of the optimized Zn(bdc)(ted)<sub>0.5</sub> structure. During the Metropolis Monte Carlo simulation, various moves, such as insertion, transformation, deletion, rotation, and regrowth, were employed to mimic the adsorption behavior of hydrocarbons. The simulation cutoff distance was set at 12.0 Å. The interactions between adsorbate-adsorbent and adsorbate-adsorbate were described using the Lennard-Jones 12-6 potential [34]. Force field parameters for each atom were obtained from the universal force field [35]. To determine the preferred adsorption site of the  $Zn(bdc)(ted)_{0.5}$  structure for hydrocarbon molecules, a single adsorbate molecule was randomly inserted into the MOF structure using the location task in the Sorption module.

# 4. Conclusions

This study synthesized a microporous metal-organic framework  $Zn(bdc)(ted)_{0.5}$  for adsorbing and separating light hydrocarbons ( $CH_4$ ,  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$ ). The material exhibits a BET surface area of 1904  $m^2/g$  and a pore volume of 0.73 cm<sup>3</sup>/g. The resulting  $Zn(bdc)(ted)_{0.5}$  exhibits good separation performance for the recovery of  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  from CH<sub>4</sub>. Notably, the material shows a significantly high  $C_2H_6$  adsorption capacity of 4.9 mmol/g (ranking among the top reported MOFs) and a relatively low CH<sub>4</sub> adsorption capacity of 0.4 mmol/g at 298 K and 100 kPa. The isosteric adsorption heats of  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  on the Zn(bdc)(ted)<sub>0.5</sub> are higher than that of CH<sub>4</sub>, indicating a stronger interaction between  $C_2H_6$ ,  $C_3H_8$ , and  $C_4H_{10}$  molecules and Zn(bdc)(ted)<sub>0.5</sub> and demonstrating the results of single-component isotherms and selectivities. At 100 kPa, the  $C_4H_{10}/CH_4$  selectivity is up to 180, the  $C_3H_8/CH_4$  selectivity is 67, and the  $C_2H_6/CH_4$ selectivity is 13. The molecular simulation results demonstrate that Zn(bdc)(ted)<sub>0.5</sub> exhibits a preference for adsorbing hydrocarbon molecules with a higher abundance of C-H bonds and larger polarizability. This preference leads to the generation of stronger dispersion forces through the induced polarization effect between the adsorbent and the adsorbate. In conclusion,  $Zn(bdc)(ted)_{0.5}$  has significant potential for application in the recovery of  $C_{2-4}$ from natural gas.

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# References

- 1. Cui, W.G.; Hu, T.L.; Bu, X.H. Metal–organic framework materials for the separation and purification of light hydrocarbons. *Adv. Mater.* **2020**, *32*, 1806445. [CrossRef] [PubMed]
- Zhang, Y.; Yang, L.; Wang, L.; Cui, X.; Xing, H. Pillar iodination in functional boron cage hybrid supramolecular frameworks for high performance separation of light hydrocarbons. J. Mater. Chem. A 2019, 7, 27560–27566.
- Maqsood, K.; Pal, J.; Turunawarasu, D.; Pal, A.J.; Ganguly, S. Performance enhancement and energy reduction using hybrid cryogenic distillation networks for purification of natural gas with high CO<sub>2</sub> content. *Korean J. Chem. Eng.* 2014, *31*, 1120–1135. [CrossRef]
- 4. Dybtsev, D.N.; Chun, H.; Kim, K. Rigid and Flexible: A highly porous metal–organic framework with unusual guest-dependent dynamic behavior. *Angew. Chem. Int. Ed.* 2004, *43*, 5033–5036.
- Weyrich, J.N.; Mson, J.R.; Bazilevskaya, E.A.; Yang, H. Understanding the mechanism for adsorption of Pb(II) ions by Cu-BTC metal–organic frameworks. *Molecules* 2023, 28, 5443.
- 6. Xu, F.; Xian, S.; Xia, Q.; Li, Y.; Li, Z. Effect of textural properties on the adsorption and desorption of toluene on the metal-organic frameworks HKUST-1 and MIL-101. *Adsorpt. Sci. Technol.* **2013**, *31*, 325–339.
- 7. Wang, B.; Zhang, J.; Xue, Y.; Chong, Y.; Zhao, D.; Cheng, H.; Tian, L.; Zhang, J. Enhanced catalytic activity of TEMPO-mediated aerobic oxidation of alcohols via redox-active metal-organic framework nodes. *Molecules* **2023**, *28*, 593. [PubMed]
- 8. Jing, H.; Zhao, L.; Song, G.; Li, J.; Wang, Z.; Han, Y.; Wang, Z. Application of a mixed-ligand metal-organic framework in photocatalytic CO<sub>2</sub> reduction, antibacterial activity and dye adsorption. *Molecules* **2023**, *28*, 5204. [CrossRef]
- 9. Wang, J.; Yu, M.; Chen, L.; Li, Z.; Li, S.; Jiang, F.; Hong, M. Construction of a stable lanthanide metal-organic framework as a luminescent probe for rapid naked-eye recognition of Fe<sup>3+</sup> and acetone. *Molecules* **2021**, *26*, 1695.
- 10. Xu, F.; Wang, H.; Teat, S.J.; Liu, W.; Xia, Q.; Li, Z.; Li, J. Synthesis, structure and enhanced photoluminescence properties of two robust, water stable calcium and magnesium coordination networks. *Dalton Trans.* **2015**, *44*, 20459–20463. [CrossRef]
- 11. Zhang, L.; Li, H.; He, H.; Yang, Y.; Cui, Y.; Qian, G. Structural variation and switchable nonlinear optical behavior of metal–organic frameworks. *Small* **2021**, *17*, 2006649.
- 12. Wu, N.; Xu, D.; Wang, Z.; Wang, F.; Liu, J.; Liu, W.; Shao, Q.; Liu, H.; Gao, Q.; Guo, Z. Achieving superior electromagnetic wave absorbers through the novel metal-organic frameworks derived magnetic porous carbon nanorods. *Carbon* **2019**, *145*, 433–444.
- 13. Qi, X.; Wang, Y.; Li, K.; Wang, J.; Zhang, H.L.; Yu, C.; Wang, H. Enhanced electrical properties and restrained thermal transport in p- and n-type thermoelectric metal–organic framework hybrids. *J. Mater. Chem. A* **2021**, *9*, 310–319.
- 14. Dong, X.; Zhang, X.; Li, Y.; Xiong, D.; Fu, P.; Afzal, M.; Alarifi, A.; Sakiyama, H. Impact of N-donor auxiliary ligands on two new Co(II)-based MOFs with N-heterocyclic ligands and a magnetism study. *New J. Chem.* **2022**, *46*, 11623–11631.
- 15. Rajamohan, R.; Raorane, C.J.; Kim, S.C.; Krishnan, M.M.; Lee, Y.R. Supramolecular β-cyclodextrin-quercetin based metal-organic frameworks as an efficient antibiofilm and antifungal agent. *Molecules* **2023**, *28*, 3667. [PubMed]
- Li, Z.; Zeng, W.; Li, Y. Recent progress in MOF-based electrochemical sensors for non-enzymatic glucose detection. *Molecules* 2023, 286, 4891.
- 17. Yuan, B.; Wang, X.; Zhou, X.; Xiao, J.; Li, Z. Novel room-temperature synthesis of MIL-100(Fe) and its excellent adsorption performances for separation of light hydrocarbons. *Chem. Eng. J.* **2019**, *355*, 679–686.
- 18. Lv, D.; Liu, Z.; Xu, F.; Wu, H.; Yuan, W.; Yan, J.; Xi, H.; Chen, X.; Xia, Q. A Ni-based metal-organic framework with super-high C<sub>3</sub>H<sub>8</sub> uptake for adsorptive separation of light alkanes. *Sep. Purif. Technol.* **2021**, *266*, 118198.
- 19. Chen, Y.; Qiao, Z.; Lv, D.; Wu, H.; Shi, R.; Xia, Q.; Wang, H.; Zhou, J.; Li, Z. Selective adsorption of light alkanes on a highly robust indium based metal-organic framework. *Ind. Eng. Chem. Res.* **2017**, *56*, 4488–4495.
- 20. Shi, R.; Lv, D.; Chen, Y.; Wu, H.; Liu, B.; Xia, Q.; Li, Z. Highly selective adsorption separation of light hydrocarbons with a porphyrinic zirconium metal-organic framework PCN-224. *Sep. Purif. Technol.* **2018**, 207, 262–268.
- Allen, F.H.; Bellard, S.; Brice, M.D.; Cartwright, B.A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B.G.; Kennard, O.; Motherwell, W.D.S.; et al. The cambridge crystallographic data centre: Computer-based search, retrieval, analysis and display of information. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* 1979, B35, 2331–2339.
- 22. Xiang, H.; Ameen, A.; Gorgojo, P.; Siperstein, F.R.; Holmes, S.M.; Fan, X. Selective adsorption of ethane over ethylene on M(bdc)(ted)<sub>0.5</sub> (M = Co, Cu, Ni, Zn) metal-organic frameworks (MOFs). *Microporous Mesoporous Mater.* **2020**, *292*, 109724.
- 23. Lee, J.Y.; Olson, D.H.; Pan, L.; Emge, T.J.; Li, J. Microporous metal–organic frameworks with high gas sorption and separation capacity. *Adv. Funct. Mater.* 2007, *17*, 1255–1262.
- 24. Wang, H.; Yao, K.X.; Zhang, Z.J.; Jagiello, J.; Gong, Q.H.; Han, Y.; Li, J. The first example of commensurate adsorption of atomic gas in a MOF and effective separation of xenon from other noble gases. *Chem. Sci.* **2014**, *5*, 620–624.
- 25. Myers, A.L.; Prausnitz, J.M. Thermodynamics of mixed-gas adsorption. AIChE J. 1965, 11, 121–127.
- 26. Yuan, Y.; Wu, H.; Xu, Y.; Lv, D.; Tu, S.; Wu, Y.; Li, Z.; Xia, Q. Selective extraction of methane from C1/C2/C3 on moisture-resistant MIL-142A with interpenetrated networks. *Chem. Eng. J.* **2020**, *395*, 125057.
- 27. Zhang, Y.; Xiao, H.; Zhou, X.; Wang, X.; Li, Z. Selective adsorption performances of UiO-67 for separation of light hydrocarbons C1, C2, and C3. *Ind. Eng. Chem. Res.* 2017, *56*, 8689–8696.

- Fan, W.; Wang, X.; Zhang, X.; Liu, X.; Wang, Y.; Kang, Z.; Dai, F.; Xu, B.; Wang, R.; Sun, D. Fine-tuning the pore environment of the microporous Cu-MOF for high propylene storage and efficient separation of light hydrocarbons. ACS Cent. Sci. 2019, 5, 1261–1268.
- Wang, D.; Liu, B.; Yao, S.; Wang, T.; Li, G.; Huo, Q.; Liu, Y. A polyhedral metal-organic framework based on the supermolecular building block strategy exhibiting high performance for carbon dioxide capture and separation of light hydrocarbons. *Chem. Commun.* 2015, *51*, 15287–15289.
- Li, J.; Luo, X.; Zhao, N.; Zhang, L.; Huo, Y.; Liu, Y. Two finite binuclear [M<sub>2</sub>(μ2-OH)(COO)<sub>2</sub>] (M = Co, Ni) based highly porous Metal–Organic Frameworks with high performance for gas sorption and separation. *Inorg. Chem.* 2017, 56, 4141–4147.
- Huang, Y.; Lin, Z.; Fu, H.; Wang, F.; Shen, M.; Wang, X.; Cao, R. Porous anionic indium–organic framework with enhanced gas and vapor adsorption and separation ability. *ChemSusChem* 2014, 7, 2647–2653. [PubMed]
- 32. Huang, P.; Chen, C.; Hong, Z.; Pang, J.; Wu, M.; Jiang, F.; Hong, M. Azobenzene decorated NbO-type metal–organic framework for high-capacity storage of energy gases. *Inorg. Chem.* **2019**, *58*, 11983–11987. [PubMed]
- 33. Materials Studio; v7.0; Biovia Software Inc.: San Diego, CA, USA, 2014.
- 34. Barker, J.A.; Henderson, D. What is "liquid"? Understanding the states of matter. Rev. Mod. Phys. 1976, 48, 587–671.
- Rappé, A.K.; Casewit, C.J.; Colwell, K.S.; Goddard III, W.A.; Skif, W.M. UFF, A full periodic table force field for molecular mechanics and molecular dynamics simulations. J. Am. Chem. Soc. 1992, 114, 10024–10035.

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