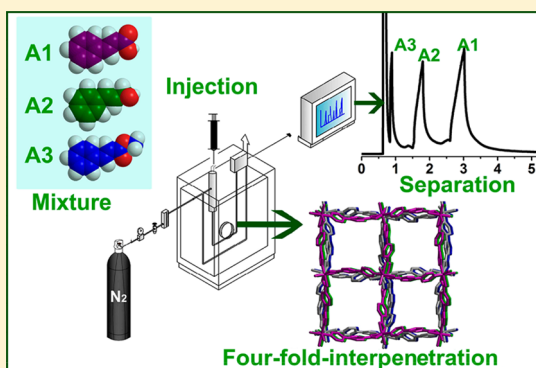


Fourfold-Interpenetrated MOF [Ni(pybz)₂] as Coating Material in Gas Chromatographic Capillary Column for SeparationYan Zhang,^{†,||} Li Wang,^{*,†,||} Ru-Xin Yao,[‡] and Xian-Ming Zhang^{*,‡,||}[†]College of Chemistry & Chemical Engineering, Xinjiang Normal University, Urumqi 830054, China[‡]School of Chemistry & Material Science, Shanxi Normal University, Linfen 041004, China

S Supporting Information

ABSTRACT: A fourfold interpenetrated diamond-like topological metal–organic framework (MOF), Ni(pybz)₂ [pybz = 4-(4-pyridyl)-benzoate] was successfully synthesized and fully characterized. This MOF can serve as coating material in gas chromatographic capillary column for the separation of some low boiling point essential oils. The prepared columns have good recognition ability and excellent selectivity toward a series of organic compounds, including alcohols, aldehydes, ketones, carboxylic acid, ethers, ester, and amines. It is found that the strained metal sites, van der Waals interactions, C–H... π attraction, and weak nonclassical hydrogen bond contribute to the recognition and selectivity of prepared columns. The grand canonical Monte Carlo technique is used to simulate the interactions of the adsorbates with MOF. The calculated van der Waals energies agree with the results of gas chromatographic separation.



■ INTRODUCTION

In the past two decades, metal–organic frameworks (MOFs) have attracted great attention for their applications in gas storage, separation, catalysis, and many other areas due to their pore-related and tunable structures.^{1,2} In a subfield of applications, high surface areas, variable structures and pore sizes, adsorption sites, etc., make MOFs appealing as good chromatographic separation materials. Recently, MOFs such as MIL-53,³ MIL-101,⁴ MOF-508,⁵ and MIL-47,⁶ have been shown to be appealing as stationary phases for liquid chromatography (LC) and gas chromatography (GC). However, most of the previous works were performed on packed columns, which often results in poor resolution due to the considerable diffusion resistance of bulky packing.^{5,6} To overcome drawback, MOF-coated capillary columns have been developed to provide improved separation efficiency in thin coatings.⁷ The first example of an MOF-coated capillary column for high-resolution gas chromatography was MIL-101 for the separation of xylene isomers and ethylbenzene.⁸ A zeolitic imidazolate framework-8 (ZIF-8) nanocrystal coated capillary was shown to have a strong ability to sieve branched alkanes from linear alkane isomers.⁹ Chiral MOF-coated open tubular columns were used in high-resolution gas chromatographic separation of chiral compounds.⁷ Table S1 in the Supporting Information summarizes some selected MOF coating materials in gas chromatographic capillary column for separation. Despite significant progress in this area, much work remains to be done on the utilization of MOFs as stationary phases for high-resolution capillary GC separation.

In this work we report the first example of fourfold-interpenetrated diamond topological MOF, [Ni(pybz)₂] (1),

with one-dimensional (1D) channels as a stationary phase in capillary gas chromatography separation. Similar fourfold-interpenetrated diamond MOF has ever been used in solvent exchange and gas sorption, which confirm the possibility of the removal of guest molecular in the pores.¹⁰ The stationary phase possesses the following characteristics:¹¹ (i) the fourfold-interpenetrated framework renders extra structural stability; (ii) the 4-(4-pyridyl)benzoate organic ligand with a large number of aromatic rings and polarized C–O/C=O groups exposed in the channels may create weak molecular interacting sites; (iii) metal center coordinated by strained chelating carboxylate groups may interact with adsorbate molecules to relieve the strain. All these characteristics in combination with well-prepared capillary gas chromatographic column contribute to separation of six series of analogues with different functional groups (R–OH, H–(R)C=O, (RR')C=O, HO–(R)C=O, RO–C(R')=O, R–O–R').

■ EXPERIMENTAL SECTION

Synthesis. All of the analytically pure chemicals were received from commercial sources and used without further purification. A mixture of Ni(NO₃)₂·6H₂O (290.8 mg, 1.0 mmol) and 4-(4-pyridyl)benzoic acid (Hpybz) (199.2 mg, 1.0 mmol) was dissolved in 7.5 mL of *N,N*-dimethylformamide (DMF), and then triethylamine (0.15 mL) was added to a 25 mL Teflon-lined stainless vessel, which was heated at 150 °C for 3 d. The autoclave was cooled to room temperature, and green block-shaped crystals were collected, washed with DMF, and dried in vacuum (Yield: 90% based on Ni).

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Apparatus and Characterization. Single-crystal X-ray diffraction (XRD) data were collected on an APEX II CCD diffractometer at 293(2) K using Cu K α radiation ($\lambda = 1.54184$ Å) and SHELX-97 crystallographic software package,¹² PLATON for missing symmetry elements.¹³ The powder XRD pattern was collected on a Bruker D8 ADVANCE X-ray diffractometer using Cu K α radiation in the 2θ angular range of 5–60°. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range of 400–4000 cm^{−1} on a Shimadzu IR Affinity-1 spectrometer. The samples embedded in dried KBr matrixes (5 mg of the sample and 500 mg of KBr). Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere using NETZSCH STA 449F3 equipment with a heating rate of 10 °C min^{−1}. The scanning electron microscope (SEM) imaging was performed using a Hitachi SU8010 cold field emission scanning electron microscope (FESEM). Capillary columns were carefully cut with a ceramic column cutter to ensure a relatively clean break and stick on the sample stage. The resulting samples were coated with 2 nm layer of gold using an Emitech K550X automated sputter coater. The sorption isotherm for CO₂ was measured using Autosorb iQ₂ (Quantachrome) adsorption analyzer at 195 K. The desolvated **1** was obtained by exchange of as-prepared 1·DMF with acetone and then vacuuming at 353 K for 7 h, then at 383 K for 1 h.

All separations were performed on an Agilent 6890N gas chromatographic system with a flame ionization detector (FID) with the ChemStation software to control the data acquisition and processing. High-purity nitrogen (99.999%) was employed as the carrier gas. The inlet and detector temperature of GC was set at 250 °C, and injection volume was 0.1 μ L.

Preparation of Capillary Column. The columns were prepared by a dynamic coating method in accordance with previous method.³ Briefly, 10 mL of ethanol suspension of 10 mg of **1** (1 mg mL^{−1}) was introduced into one end of the open tubular column, and the other end was connected to a vacuum system to remove the solvents under vacuum pump to leave a wet coating layer on the inner wall of the capillary column. The suspension was then conditioned from room temperature to 200 °C, increasing its temperature at a rate of 2 °C min^{−1}, and finally at 200 °C for 120 min.

Computational Details. Monte Carlo simulations of the adsorption of (2E)-3-phenylprop-2-enoic acid, (2E)-3-phenylprop-2-en-1-ol, and methyl 3-phenylprop-2-enoate inside the channel of [Ni(pybz)₂] were performed by sorption module of Accelrys Materials Studio package.¹⁴ The geometries of these three compounds were optimized by using the forcite module before sorption calculation. Fixed loading of one guest molecule was used to simulate host and guest van der Waals interactions. At least 1×10^6 equilibration steps were used in the simulations. We used atom-based summation method and cubic spline truncation method, with cutoff distance of 15.5 Å, spline width of 1 Å, and buffer width 0.5 Å during simulation of van der Waals interaction. Ewald summation was used to account for the periodicity of the lattice in the computation of electrostatic contributions. All Lenard-Jones (LJ) parameters to model the framework atoms were taken from the Universal Force Field (UFF).

RESULTS AND DISCUSSIONS

Crystal Structure. X-ray crystallography reveals that **1** crystallizes in the tetragonal chiral space group *P*4₂1. Crystal data, details of data collection, and structure refinement information are given in Table 1. The selected bond distances and angles are listed in Table S2 in the Supporting Information. The asymmetric unit is composed of one nickel center and two pybz ligands. The nickel(II) center is coordinated to two nitrogen atoms and four chelating carboxylate oxygen atoms from two different pybz ligands, which exhibits a twisty octahedral geometry (Figure 1a). The pybz adopts a tridentate mode to link two nickel centers. The Ni–O and Ni–N distances are in the scope of 2.043(3)–2.199(2) Å. The cis and trans L–Ni–L (L = O or N) angles are in the extent of 61.74(7)–101.69(8)° and 155.50(9)–158.59(9)°, respectively. When pybz

Table 1. Crystal Data and Structural Refinement for 1·DMF

empirical formula	C ₂₇ H ₂₃ N ₃ NiO ₅
formula weight	528.19
temperature (K)	293(2)
wavelength (Å)	1.54184
crystal system	tetragonal
space group, <i>Z</i>	<i>P</i> 4 ₂ 1, 8
unit-cell dimensions (Å)	<i>a</i> = 22.5091(2) <i>b</i> = 22.5091(2) <i>c</i> = 12.8050(2) $\gamma = 90^\circ$
volume (Å ³)	6487.7(2)
density (calcd) (mg/m ³)	0.932
absorption coefficient (mm ^{−1})	1.047
<i>F</i> (000)	1872.0
crystal size (mm)	0.28 × 0.24 × 0.20
<i>T</i> _{max} / <i>T</i> _{min}	0.689/1.000
limiting indices	−15 ≤ <i>h</i> ≤ 15, −27 ≤ <i>k</i> ≤ 27, −27 ≤ <i>l</i> ≤ 27
reflections collected/unique	3701/296
completeness to θ (%)	98.02
refinement method	full-matrix least-squares on <i>F</i> ²
Flack parameter	0.16(4)
goodness-of-fit on <i>F</i> ²	1.097
final <i>R</i> indices [<i>F</i> _o ² > 2 σ (<i>F</i> _o ²)] ^a	<i>R</i> ₁ = 0.0412, <i>wR</i> ₂ = 0.1229
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.1251
largest difference peak and hole (e/Å ³)	0.36/−0.33

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \text{ and } wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2} \text{ for } F_o^2 > 2\sigma(F_o^2).$$

ligands are regarded as one linker, each nickel atom is connected to its four neighbors. This feature brings about a diamond network, where Ni···Ni edges are ~ 12.9 Å, and the maximum size is ~ 22.5 Å. The overall structure is a fourfold interpenetrated three-dimensional (3D) architecture with a diamond topology (Figure 1c). Along the *c*-axis, the framework still exhibits 1D square grid channels with dimension of 7.6 Å × 7.6 Å (Figure 1d), which occupies 47.0% of the unit cell volume (6487.7 Å³) as estimated by PLATON.

The experimental powder XRD result agrees well with the simulated one from the single-crystal data, indicating the purity of the synthesized sample. XRD after 200 °C heating was in good agreement with the previous experiment, indicating permanent porosity after removal of guest. The variable-temperature XRD also validates this critical point (Figures S1 and S2 in the Supporting Information).

Thermogravimetric (TG) Analysis. The TG curve of **1** shows that the encapsulated molecule guest DMF can be removed at ~ 220 °C to give porous frameworks. The first step loss of $\sim 13.5\%$ is observed between room temperature and 220 °C, which is equivalent to the total weight of solvent DMF molecule (calcd 13.8%). The diffraction patterns of **1** from 30 to 220 °C are similar, showing that the overall framework is stable up to 220 °C after removal of uncoordinated DMF guest molecule. Thus, combined TG and XRD results indicate that **1** has excellent thermal stability at least up to 220 °C (Figure S3 in the Supporting Information).

Sorption Properties. The sorption properties of **1** were studied with CO₂ and N₂ to give Brunauer–Emmett–Teller (BET) and pore distribution. The gas-sorption isotherms of CO₂ for **1** at 195 K show a type I behavior characterized by a saturated adsorptive capacity of 66 cm³/g at relatively low pressure (Figure

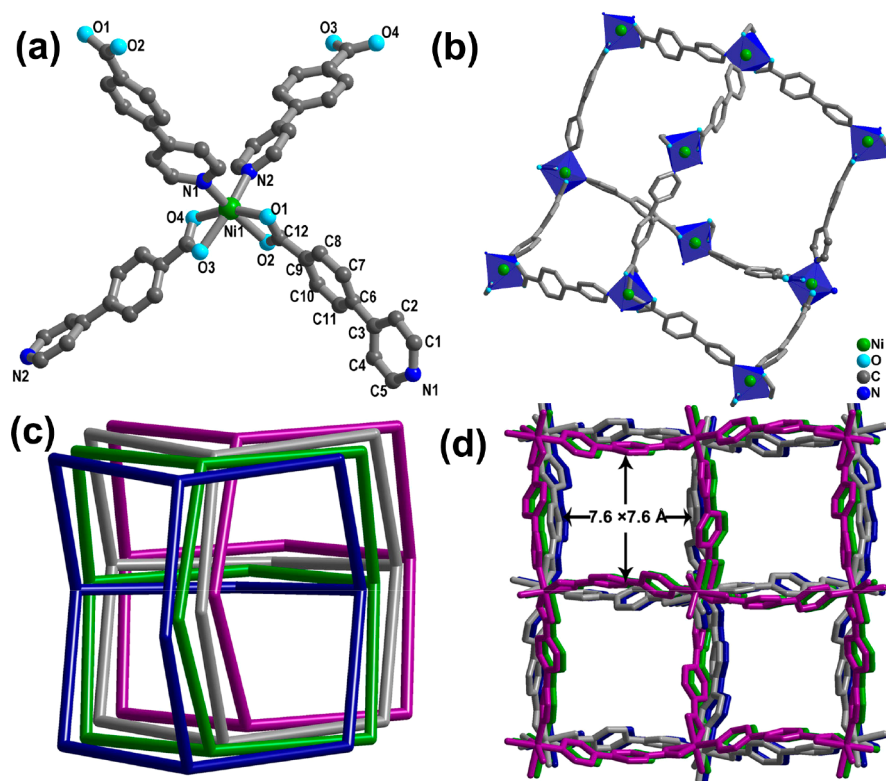


Figure 1. (a) The coordinated environment of Ni(II); (b) perspective view of single set of diamond network; (c) the fourfold interpenetrated net; (d) 3D framework with 1D square channels in **1**.

2). The data with a pressure range of $P/P_0 = 0.07$ to 0.13 was used to fit BET¹⁵ model; the apparent surface area of **1** is $228 \text{ m}^2/\text{g}$.

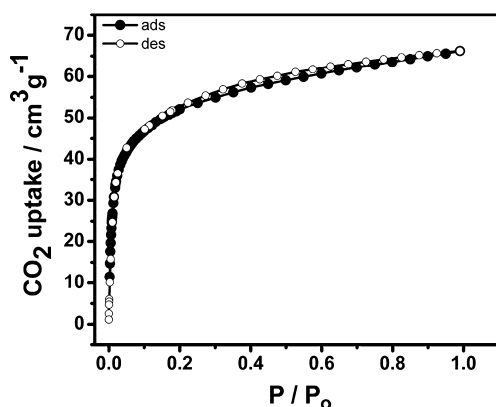


Figure 2. CO_2 gas sorption isotherms for **1** measured at 195 K.

(Figure S4a in the Supporting Information), and a Langmuir surface area of $341 \text{ m}^2/\text{g}$ was obtained (Figure S4b in the Supporting Information). As shown in Figure 3, the pore-size distribution of $\sim 0.78 \text{ nm}$ is obtained from nonlocal density functional theory (NLDFT), consistent with the theoretically calculated pore size by single-crystal structure. Moreover, disordered connection among the phenyl rings in the actual framework might be responsible for the pore behavior. However, being different from CO_2 gas-sorption isotherms, the desolvated sample has nearly no N_2 sorption at all, similar to its Co analogue and some MOFs with large pores.^{16,17}

Polarity of the $[\text{Ni}(\text{pybz})_2]$ stationary phase was evaluated by calculating the McReynolds constants¹⁸ (ΔI) at 120°C . The

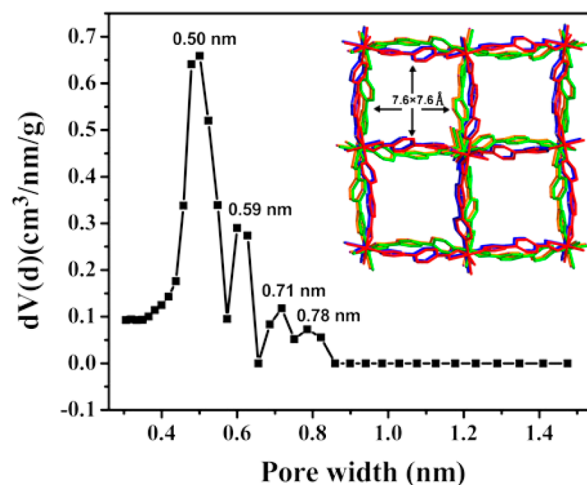


Figure 3. Pore-size distribution of **1**. (inset) Pore size of **1** in the proposed structure.

McReynolds constants for the **1**-coated column are summarized in Table 2, which indicate that **1** stationary phase was weakly polar.

Gas Chromatographic Separation. The images of single crystals of **1**-DMF and **1**-coated capillary column were shown in Figure 4a,b. Figure 5a–d shows the SEM images of the cross section of the fabricated capillary column and the **1**-coated films on the inner wall of the capillary column. The fabricated capillary column approximately had $1.5 \mu\text{m}$ thick of **1** coating on the inner wall.

During chromatography separation procedure, the selective adsorption capacities of microporous materials are mainly determined by (1) size-exclusive effects and (2) differential

Table 2. McReynolds Constants for 1-Coated Column

probe	benzene (X)	1- butanol (Y)	2- pentanone (Z)	1- nitropropane (U)	pyridine (S)
<i>I</i> for [Ni(pybz) ₂]	700	740	700	740	840
<i>I</i> for squalene ^a	653	590	627	652	699
ΔI	47	150	73	88	141

^a*I* for squalene data from ref 18.

interactions with the substrates. Sometimes size-exclusion chromatography (SEC)¹⁹ is used to separate molecules in solution by their size, where molecular size can be calculated by molecular shape, bond length, bond angle, and van der Waals radii.²⁰ However, some observed facts show that the calculated molecular size is not completely applicable to the molecular sieve system, that is, the molecules with much larger molecular sieve diameter can still be adsorbed and react in the zeolite molecular sieve channels.²¹ King et al. introduced molecular dynamic diameters, which are in good agreement with experimental results.²² The so-called dynamic diameter means the minimum distance that can be reached when two molecules collide is zero kinetic energy. The kinetic minimum cross-sectional diameters for analysts are given in Table S3 in the Supporting Information. Structurally, fourfold interpenetrated framework **1** exhibits 1D square-sectioned channels with a window size of 7.6 Å × 7.6 Å, which is larger or close to the size of kinetic minimum cross-sectional diameter of the analysts, facilitating passing through the pores.

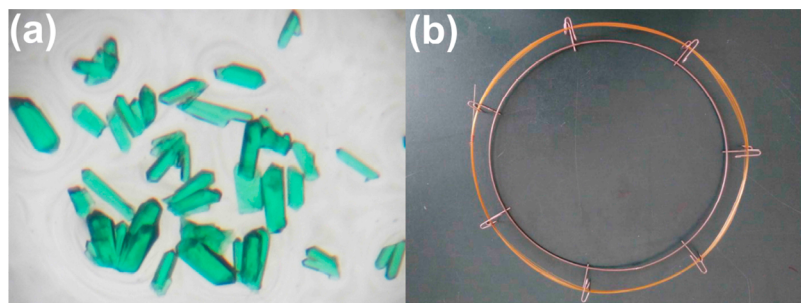
In this work we choose [Ni(pybz)₂] as the stationary phase because of its attractive structural characteristics as a candidate for gas chromatography separation. These features include: (i) Strained metal sites. As described, nickel is imposed on high strain by the chelating carboxylate. During the separation process, strained metal sites may interact with adsorbate molecules with functional groups like R–OH or HO–(R)C=O to relieve the strain (Figure 6a). (ii) van der Waals interactions, that is, dipole–dipole contribution between C=O from adsorbate and the O–C of pybz carboxylate groups of the adsorbent MOFs (Figure 6b). (iii) C–H... π attraction due to existence of abundant aromatic rings of pybz for possible interaction with adsorbate molecules. The attractive interaction between the positively charged hydrogen atoms (or σ bond) of one aromatic ring and another conjugated π electron is shown in Figure 6c. (iv) Weak nonclassical hydrogen bond (Figure 6d).

To further corroborate the aforementioned speculation, six series of linear alkanes, aromatic hydrocarbons, and cyclic hydrocarbons with a variety of functional groups (R–OH, H–

(R)C=O, (RR')C=O, HO–(R)C=O, RO–C(R')=O, R–O–R') were used as test solutes (Figure 7). The whole separation design of six series of spices is illustrated in Scheme 1. First, the aromatic hydrocarbons with different functional groups (HO–(R)C=O, R–OH, RO–C(R')=O), with **A1** ((*2E*)-3-phenylprop-2-enoic acid), **A2** ((*2E*)-3-phenylprop-2-en-1-ol), and **A3** (methyl 3-phenylprop-2-enoate) were chosen as test solutes. The mixtures were eluted in the order of **A3**, **A2**, and **A1**. Here, three adsorbates have the same aromatic and C=C structure (Ar–C=C–R) but different functional groups of R–OH, RO–C(R')=O, and HO–(R)C=O. It is expected for the last eluted compound **A1**, there are four possible interactions with adsorbent **1**: dipole–dipole interactions between $\delta^+C=O^{\delta-}$ from adsorbate and $\delta^-O-C^{\delta+}$ of pybz carboxylate groups, C–H... π attractive interaction between the positively charged hydrogen atoms and the π electrons of aromatic ring both from adsorbates and MOF, weak hydrogen bond interaction between weak hydrogen bond donors of R–OH groups of adsorbates and polarized C–O/C=O groups of MOF, and stained metal sites and carboxyl groups of HO–(R)C=O from adsorbates. As for the second eluted compound **A2**, there are three possible interactions: dipole–dipole interaction, C–H... π attractive interaction, and weak hydrogen bond interaction between adsorbates and MOF. For the first eluted compound **A3**, there are two possible interactions: dipole–dipole interactions and C–H... π attractive interaction between adsorbates and MOF. As can be seen, number of interacting types corresponds to flow sequence of **A3**, **A2**, and **A1**.

The molecular interaction is further supported by FT-IR measurement of **A1** (*trans*-cinnamic acid) adsorbed MOF sample (Figure S5). In pure **A1**, the bands at 3068, 3024, and 1628 cm^{−1} are assigned to the C–H and C=C stretching vibration modes of the benzene ring, respectively, while the bands at 1678 cm^{−1} are assigned to the C=O stretching vibration mode of the carboxyl group.^{23,24} In addition, carboxylic acids also show C–O stretching band at ~1220 cm^{−1} and in-plane bending band of O–H at 1420 and 1448 cm^{−1},^{24,25} respectively. Compared with the pure **A1**, several significant changes are observed in the mixture of **A1** and **1**. When mixed, the relative intensity of C=O of the carboxyl stretching vibration band at 1678 cm^{−1} is weakened, whereas the band of the O–H of stretching vibration at 1448 cm^{−1} almost disappeared. These changes demonstrate that there are significant interactions between the **A1** and **1**, involving mainly the polarized carboxyl C=O and O–H of **A1** and MOF.

To elucidate the nature of the aforementioned interactions, the sequence of interaction of HO–(R)C=O, R–OH, RO–C(R')=O, and MOF has been further verified by Metropolis Monte Carlo simulations. To clarify van der Waals interactions

Figure 4. (a) The green block single crystal of 1·DMF. (b) Capillary column coated with **1**.

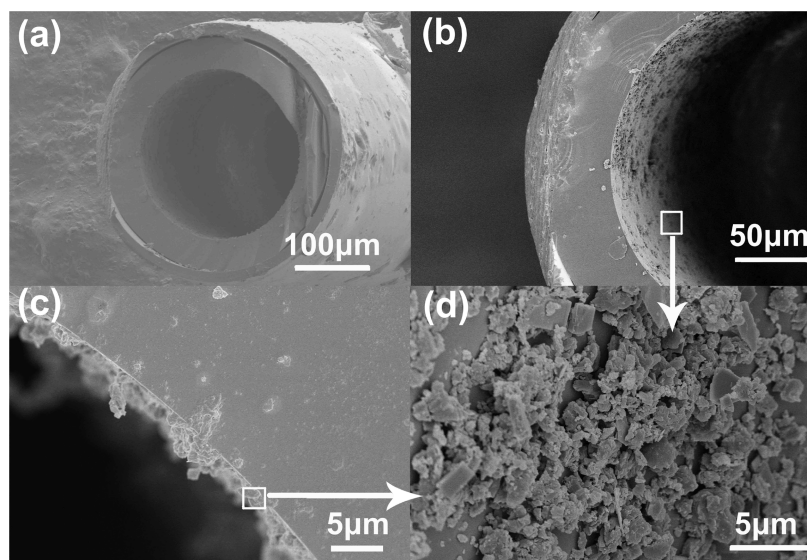


Figure 5. SEM images of the capillary column. (a) The cross section of 1-coated open tubular column; (b) the part of the cross section of open tubular column coated with 1; (c) an $\sim 1.5\ \mu\text{m}$ thickness of 1 coating on the inner wall; (d) the inner wall of coated open tubular column.

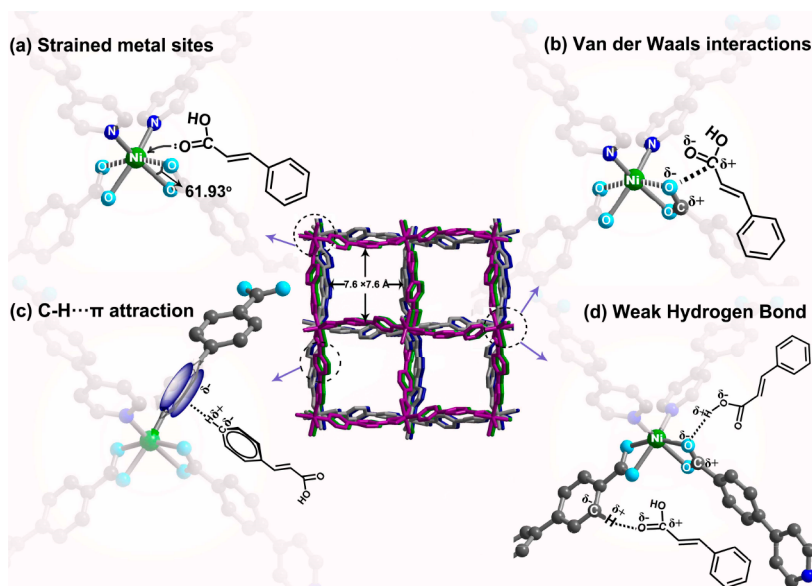


Figure 6. Four possible kinds of interaction between adsorbates and adsorbents: (a) Strained metal sites; (b) van der Waals interactions; (c) C–H $\cdots\pi$ attraction; (d) weak hydrogen bond.

between adsorbate and MOF, adsorption positions of **A1**, **A2**, and **A3** in **1** were located (Figure 8). The van der Waals interactions are -15.2 , -16.6 , $-17.0\ \text{kcal mol}^{-1}$ for **A3**, **A2**, and **A1**, respectively, which is in good agreement with the results of gas chromatographic separation.

Local van der Waals interactions between adsorbates and pybz of MOF were shown in Figure 9. For all three adsorbates, there exist $\pi\cdots\pi$ stacking interactions between the benzene ring of pybz and phenylethylene of adsorbates with C $\cdots$ C distance of 3.4 – $3.7\ \text{\AA}$. Besides, weak C–H $\cdots$ O hydrogen bonds are also found in **A1** and **A2** with C $\cdots$ O distance of 3.4 – $3.7\ \text{\AA}$ and H $\cdots$ O distance of 2.9 – $3.1\ \text{\AA}$. For **A3**, there is weak C–H $\cdots\pi$ interaction between methyl and benzene ring of pybz with H $\cdots$ C_{centroid} distance of $2.8\ \text{\AA}$. These local interactions from the simulation confirm our analyses earlier.

Among the systems from aromatic hydrocarbons to oxygen-containing linear adsorbates, **B1** (decyl aldehyde), **B2** (decanoic

acid), and **B3** ((*Z*)-3,7-dimethylocta-2,6-dien-1-ol) were chosen as test solutes, with the mixtures eluted in the order of **B1**, **B3**, and **B2**. The three adsorbates show similar linear structure but different polarization and functional groups of H–(R)C=O, HO–(R)C=O, and R–OH. There are different interactions between adsorbates and **1**. There are dipole–dipole interaction, weak hydrogen bond interaction, and strained metal sites between the carboxyl groups of **B2** and MOF in the last eluted **B2**. As for the second eluted **B3**, there are dipole–dipole interactions and weak hydrogen bond interaction between the –C–OH groups of **B3** and MOF. For the first eluted **B1**, there are only dipole–dipole interactions between the H–C=O groups of **B1** and MOF.

Then **C1** (decyl aldehyde), **C2** (decanoic acid), and **C3** (1-butoxy-1-oxopropan-2-yl butyrate) were chosen as test solutes, with the mixtures eluted in the order of **C1**, **C3**, and **C2**. Similar to the aforementioned **B** series, the three adsorbates have similar

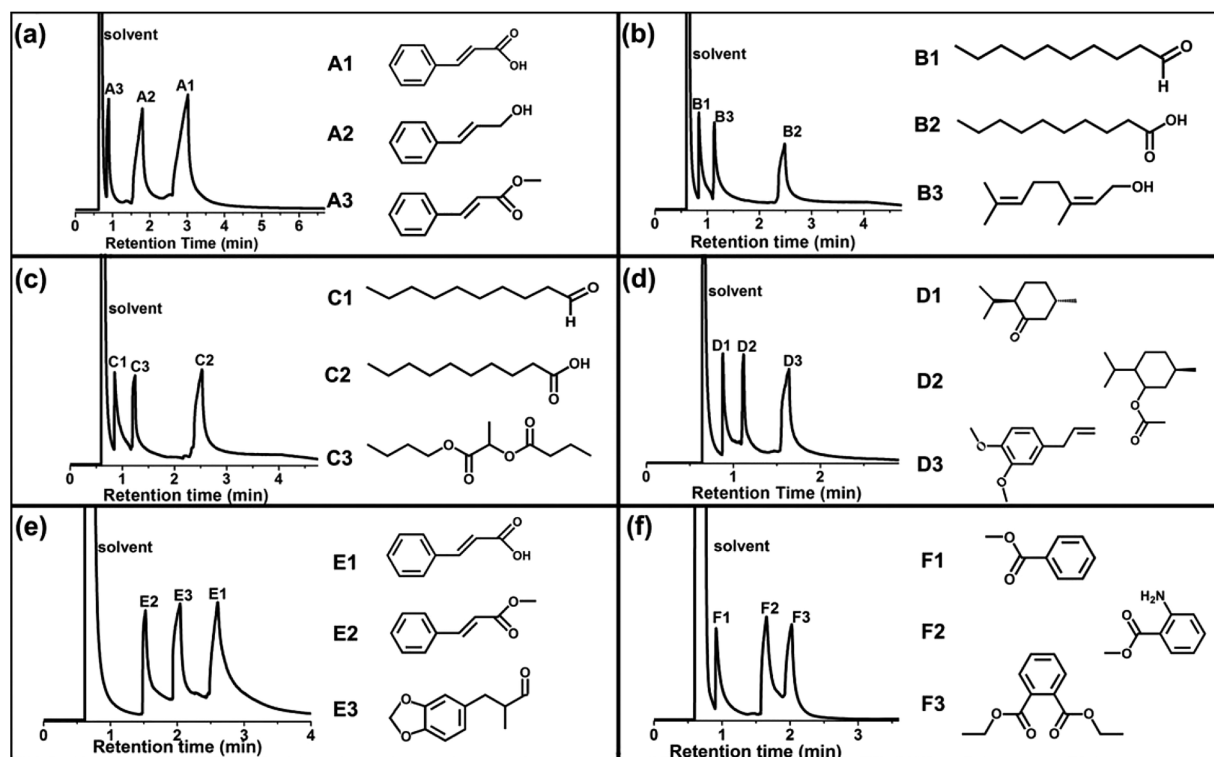
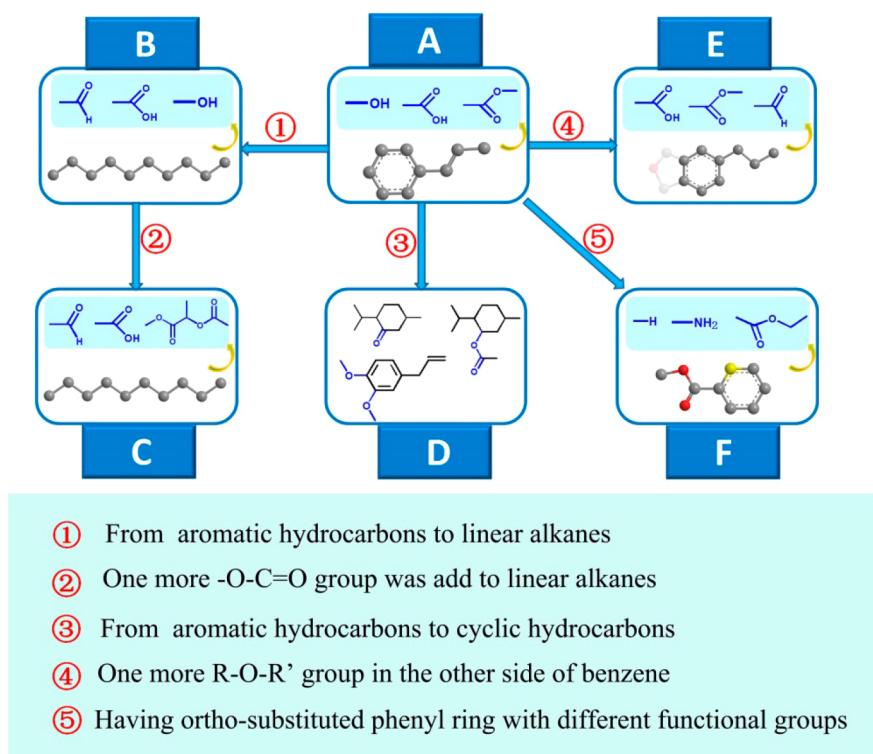


Figure 7. Representative GC chromatograms on the 1-coated open tubular column (10 m long $\times$ 0.25 mm i.d.) for the separation of: (a) **A1**: *trans*-cinnamic acid ((2*E*)-3-phenylprop-2-enoic acid); **A2**: cinnamyl alcohol ((2*E*)-3-phenylprop-2-en-1-ol); **A3**: methyl cinnamate (methyl 3-phenylprop-2-enoate); (b) **B1**: decyl aldehyde; **B2**: decanoic acid; **B3**: nerol ((*Z*)-3,7-dimethylocta-2,6-dien-1-ol); (c) **C1**: decyl aldehyde; **C2**: decanoic acid; **C3**: butyl butyryllactate (1-butoxy-1-oxopropan-2-yl butyrate); (d) **D1**: menthone ((2*S*,5*R*)-2-isopropyl-5-methylcyclohexanone); **D2**: menthyl acetate ((2*S*,1*R*,5*R*)-2-isopropyl-5-methylcyclohexyl acetate); **D3**: methyl eugenol (4-allyl-1,2-dimethoxybenzene); (e) **E1**: *trans*-cinnamic acid ((2*E*)-3-phenylprop-2-enoic acid); **E2**: methyl cinnamate (methyl 3-phenylprop-2-enoate); **E3**: helional (2-methyl-3-(3,4-methylenedioxy-phenyl)propanal); (f) **F1**: methyl benzoate (benzoic acid methyl ester); **F2**: methyl anthranilate (methyl 2-aminobenzoate); **F3**: diethyl phthalate (benzene-1,2-dicarboxylic acid diethyl ester). Injection volume is 0.1 μ L, and flow rate is 1 mL min⁻¹. Hydrogen atoms connected to carbon are omitted for clarity.

Scheme 1. Illustration for Separation Design of the Six Series of Spices



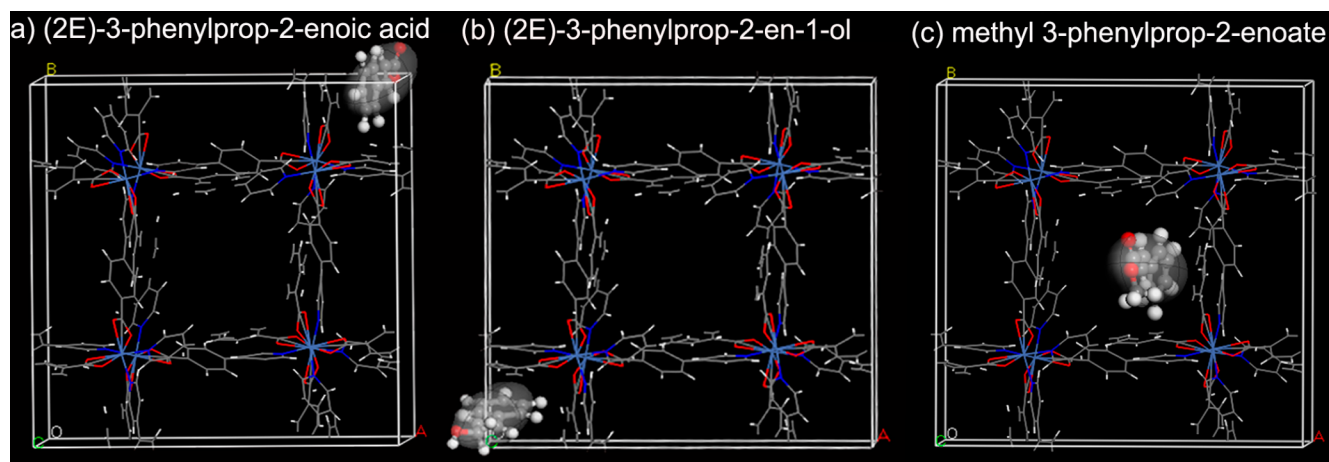


Figure 8. Simulated interaction of A1, A2, A3, and 1 viewed along the *c*-axis direction.

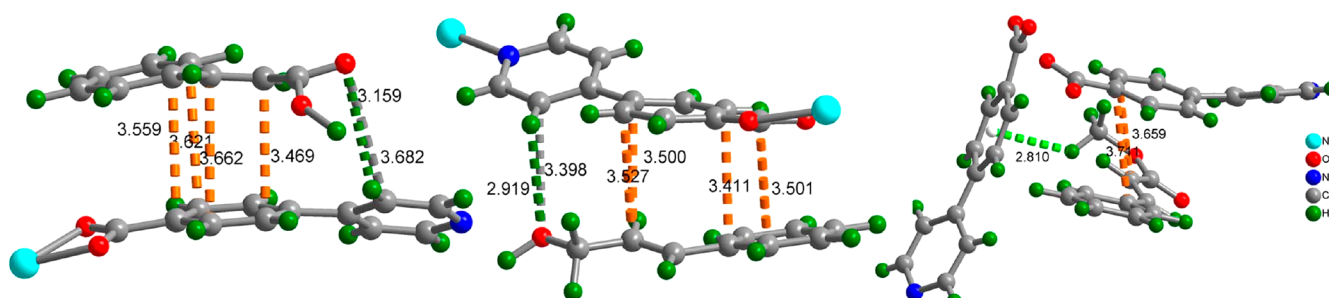


Figure 9. Perspective view of the illustrated van der Waals interactions between adsorbates and pybz of 1.

linear structure with different functional groups of $\text{H}-(\text{R})\text{C}=\text{O}$, $\text{HO}-(\text{R})\text{C}=\text{O}$, and $\text{RO}-\text{C}(\text{R}')=\text{O}$, but one more $\text{O}-\text{C}=\text{O}$ group was added to C3. It seems that more polarized groups in this group of analytes led to strong interactions between analytes and MOF.

From aromatic hydrocarbons to cycloalkanes, D1 ((2*S*,5*R*)-2-isopropyl-5-methylcyclohexanone), D2 ((5*R*)-2-isopropyl-5-methylcyclohexyl acetate), and D3 (4-allyl-1,2-dimethoxybenzene) were chosen as test solutes to check the relative contribution of $\text{C}-\text{H}\cdots\pi$ interaction, with the mixtures eluted in the order of D1, D2, and D3. Among them, D1 and D2 have similar naphthenic hydrocarbon structures but different functional group: $(\text{RR}')\text{C}=\text{O}$ and $\text{RO}-\text{C}(\text{R}')=\text{O}$, and D3 has aromatic ring skeleton and two $\text{R}-\text{O}-\text{R}'$ groups. D2 is eluted later than D1, because the dipole–dipole interaction between adsorbate and adsorbent in $\text{RO}-\text{C}(\text{R}')=\text{O}$ is larger than in $(\text{RR}')\text{C}=\text{O}$. D3 is eluted latest due to combined $\text{C}-\text{H}\cdots\pi$ attraction and dipole–dipole interaction.

With one more $\text{C}-\text{O}-\text{C}$ groups was added to E3, E1 ((2*E*)-3-phenylprop-2-enoic acid), E2 (methyl 3-phenylprop-2-enoate), and E3 (2-methyl-3-(3,4-methylenedioxyphenyl) propanal) were chosen as test solutes, with the mixtures eluted in the order of E2, E3, and E1. For this group, similar aromatic ring among the three adsorbates implies comparable $\text{C}-\text{H}\cdots\pi$ attraction. However, their functional groups are different with E1, E2, and E3 having $\text{HO}-(\text{R})\text{C}=\text{O}$, $\text{RO}-\text{C}(\text{R}')=\text{O}$, and $\text{H}-(\text{R})\text{C}=\text{O}/\text{R}-\text{O}-\text{R}'$ group, respectively. Obviously stronger coordination interaction of E1 with $\text{HO}-(\text{R})\text{C}=\text{O}$ groups is dominant, which results in E1 eluting last. In addition, larger dipole–dipole interaction gives E2 eluting later than E3, due to different arrangement of $\text{RO}-\text{C}(\text{R}')=\text{O}$ and $\text{H}-(\text{R})\text{C}=\text{O}$ group.

Lastly, for system having ortho-substituted phenyl ring with $\text{O}-\text{C}(\text{R}')=\text{O}$, $-\text{NH}_2$, and $-\text{H}$, we chose F1 (benzoic acid methyl ester), F2 (methyl 2-aminobenzoate), and F3 (benzene-1,2-dicarboxylic acid diethyl ester) as test solutes, and the mixtures were eluted in the order of F1, F2, and F3. The three compounds have the same structures $\text{Ar}-(\text{OR})\text{C}=\text{O}$ but different functional groups of $\text{R}-\text{H}$, $\text{R}-\text{NH}_2$, and $\text{RO}-\text{C}(\text{R}')=\text{O}$ connected in the ortho-position of $\text{Ar}-(\text{OR})\text{C}=\text{O}$. The dominant polarized interaction from ester groups $\text{RO}-\text{C}(\text{R}')=\text{O}$ is stronger than $-\text{NH}_2$, giving F3 eluting last. F2 with one more $-\text{NH}_2$ connected in the ortho-position of $\text{Ar}-(\text{OR})\text{C}=\text{O}$ than F1, possible weak hydrogen bond interaction between the NH_2 and MOF resulted in F2 eluting later than F1. To make the gas chromatographic separation easier to understand, we list the interactions and chromatographic elution sequence in Table S3 in the Supporting Information.

Our experiment shows that the resolution and selectivity for the separation on 1-coated capillary column were affected by injection volume and splitting ratio of the adsorbates (Figures S6 and S7). Increasing the injection volume of cinnamon analogues results in a linear increase of chromatographic peak area, but no change in the retention time except for the column overload, and thereby a stable capacity factor. This feature of the present 1-coated capillary column is favorable for applications in both qualitative and quantitative analysis. Increase of splitting ratio can improve the selectivity and column efficiency. As a result, the resolution of cinnamon analogues on the 1-coated capillary column is stable over a broad splitting ratio range, thus facilitating the choice of splitting ratio for effective separation.

We also made the comparison of 1-coated column with widely used commercial column (DB-1; Figure S8). The commercial column (DB-1) is good at separating analytes with nonpolar/

weak-polar functional groups. 1-Coated column shows better performance in separating compounds with strong polar functional groups, such as $-\text{COOH}$.

CONCLUSIONS

In summary, we have synthesized a fourfold-interpenetrated diamond MOF-coated capillary column using $\text{Ni}(\text{pybz})_2$ as the stationary phase for gas chromatography separation of low-boiling-point organic compounds. This column recognized well toward a series of organic compounds, including alcohols, aldehydes, ketones, carboxylic acid, ethers, ester, and amines. The results show that it is promising for the application of MOFs in high-resolution capillary gas chromatography. Further study focusing on structure-recognition relationship of other MOFs for high-resolution separation in gas chromatography would be interesting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00863.

Selected bond distances and bond angles, spices details separated in gas chromatography, XRD, IR, TG, and gas chromatographic separation. CCDC number of $\text{Ni}(\text{pybz})_2$ is 1541063 (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: wangliresearch@163.com. (L.W.)

*E-mail: zhangxm@dns.sxnu.edu.cn. (X.M.Z.)

ORCID

Li Wang: 0000-0002-7425-6872

Xian-Ming Zhang: 0000-0002-8809-3402

Author Contributions

[†]These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Li, J. R.; Sculley, J.; Zhou, H. C. Metal-organic frameworks for separations. *Chem. Rev.* **2012**, *112*, 869–932.
- (2) Zeng, M. H.; Wang, Q. X.; Tan, Y. X.; Hu, S.; Zhao, H. X.; Long, L. S.; Kurmoo, M. Rigid pillars and double walls in a porous metal-organic framework: single-crystal to single-crystal, controlled uptake and release of iodine and electrical conductivity. *J. Am. Chem. Soc.* **2010**, *132*, 2561–2563.
- (3) Yang, C. X.; Liu, S. S.; Wang, H. F.; Wang, S. W.; Yan, X. P. High-performance liquid chromatographic separation of position isomers using metal-organic framework MIL-53 (Al) as the stationary phase. *Analyst* **2012**, *137*, 133–139.
- (4) Yang, C. X.; Yan, X. P. Metal-organic framework MIL-101 (Cr) for high-performance liquid chromatographic separation of substituted aromatics. *Anal. Chem.* **2011**, *83*, 7144–7150.
- (5) Chen, B. L.; Liang, C. D.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A Microporous Metal-Organic

Framework for Gas-Chromatographic Separation of Alkanes. *Angew. Chem.* **2006**, *118*, 1418–1421.

(6) Alaerts, L.; Kirschhock, C. E.; Maes, M.; van der Veen, M. A.; Finsy, V.; Depla, A.; Martens, J. A.; Baron, G. V.; Jacobs, P. A.; Denayer, J. F.; De Vos, D. E. Selective Adsorption and Separation of Xylene Isomers and Ethylbenzene with the Microporous Vanadium (IV) Terephthalate MIL-47. *Angew. Chem., Int. Ed.* **2007**, *46*, 4293–4297.

(7) Xie, S. M.; Zhang, Z. J.; Wang, Z. Y.; Yuan, L. M. Chiral metal-organic frameworks for high-resolution gas chromatographic separations. *J. Am. Chem. Soc.* **2011**, *133*, 11892–11895.

(8) Gu, Z. Y.; Yan, X. P. Metal-Organic Framework MIL-101 for High Resolution Gas-Chromatographic Separation of Xylene Isomers and Ethylbenzene. *Angew. Chem., Int. Ed.* **2010**, *49*, 1477–1480.

(9) Chang, N.; Gu, Z. Y.; Yan, X. P. Zeolitic imidazolate framework-8 nanocrystal coated capillary for molecular sieving of branched alkanes from linear alkanes along with high-resolution chromatographic separation of linear alkanes. *J. Am. Chem. Soc.* **2010**, *132*, 13645–13647.

(10) Zeng, M. H.; Tan, Y. X.; He, Y. P.; Yin, Z.; Chen, Q.; Kurmoo, M. A porous fourfold interpenetrated chiral framework exhibiting vapochromism, single-crystal-to-single-crystal solvent exchange, gas sorption, and a poisoning effect. *Inorg. Chem.* **2013**, *52*, 2353–2360.

(11) SAINT, version 7.60A; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2008.

(12) Sheldrick, G. M. SHELXTL, version 6.14; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2003.

(13) Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

(14) Getman, R. B.; Bae, Y. S.; Wilmer, C. E.; Snurr, R. Q. Review and analysis of molecular simulations of methane, hydrogen, and acetylene storage in metal-organic frameworks. *Chem. Rev.* **2012**, *112*, 703–723.

(15) Walton, K. S.; Snurr, R. Q. Applicability of the BET method for determining surface areas of microporous metal-organic frameworks. *J. Am. Chem. Soc.* **2007**, *129*, 8552–8556.

(16) Vaidhyanathan, R.; Bradshaw, D.; Rebilly, J. N.; Barrio, J. P.; Gould, J. A.; Berry, N. G.; Rosseinsky, M. J. A family of nanoporous materials based on an amino acid backbone. *Angew. Chem., Int. Ed.* **2006**, *45*, 6495–6499.

(17) Fletcher, A. J.; Cussen, E. J.; Prior, T. J.; Rosseinsky, M. J.; Kepert, C. J.; Thomas, K. M. Adsorption Dynamics of Gases and Vapors on the Nanoporous Metal-Organic Framework Material $\text{Ni}_2(4,4'\text{-Bipyridine})_3(\text{NO}_3)_4$: Guest Modification of Host Sorption Behavior. *J. Am. Chem. Soc.* **2001**, *123*, 10001–10011.

(18) McReynolds, W. O. Characterization of some liquid phases. *J. Chromatogr. Sci.* **1970**, *8*, 685–691.

(19) Garrett, R. H.; Grisham, C. M. *Biochemistry*; Brooks/Cole, Cengage Learning: Belmont, CA, 2013.

(20) Pauling, L. *Nature of the Chemical Bond*; Cornell University Press: New York, 1960.

(21) Breck, D. W. *Zeolites Molecular Sieves, Structure, Chemistry and Use*; John Wiley & Sons: New York, 1974.

(22) Kington, G. L.; Macleod, A. C. Heats of sorption of gases in chabazite, energetic heterogeneity and the role of quadrupoles in sorption. *Trans. Faraday Soc.* **1959**, *55*, 1799–1814.

(23) Nolasco, M. M.; Amado, A. M.; Ribeiro-Claro, P. J. A. Effect of hydrogen bonding in the vibrational spectra of *trans*-cinnamic acid. *J. Raman Spectrosc.* **2009**, *40*, 394–400.

(24) Hanai, K.; Kuwae, A.; Takai, T.; Senda, H.; Kunimoto, K. K. A comparative vibrational and NMR study of *cis*-cinnamic acid polymorphs and *trans*-cinnamic acid. *Spectrochim. Acta, Part A* **2001**, *57*, 513–519.

(25) Sert, Y.; Doğan, H.; Navarrete, A.; Somanathan, R.; Aguirre, G.; Cırak, C. Experimental FT-IR, Laser-Raman and DFT spectroscopic analysis of 2, 3, 4, 5, 6-Pentafluoro-*trans*-cinnamic acid. *Spectrochim. Acta, Part A* **2014**, *128*, 119–126.