# Chiral 3D Open-Framework Material Ni(D-cam)(H<sub>2</sub>O)<sub>2</sub> Used as GC **Stationary Phase**

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Metal-organic frameworks (MOFs) have been explored for analytical applications ABSTRACT because of their outstanding properties such as high surface areas, flexibility and specific structure features, especially for chromatography application in recent years. In this work, a chiral MOF Ni (D-cam) (H<sub>2</sub>O)<sub>2</sub> with unusual integration of molecular chirality, absolute helicity, and 3-D intrinsic chiral net was chosen as stationary phase to prepare Ni(D-cam)(H<sub>2</sub>O)<sub>2</sub>-coated open tubular columns for high-resolution gas chromatographic (GC) separation. Two fused-silica open tubular columns with different inner diameters and lengths, including column A (30 m  $\times$  250  $\mu$ m i.d.) and column B (2 m×75 µm i.d.), were prepared via a dynamic coating method. The chromatographic properties of the two columns were investigated using n-dodecane as the analyte at 120 °C. The number of theoretical plates (plates/m) of the two metal-organic framework (MOF) columns was 1300 and 2750, respectively. The racemates, isomer and linear alkanes mixture were used as analytes for evaluating the separation properties of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated open tubular columns. The results showed that the columns offered good separations of isomer and linear alkanes mixture, especially racemates. Chirality 26:27-32, 2013. © 2013 Wiley Periodicals, Inc.

KEY WORDS: metal-organic frameworks; open tubular columns; stationary phase; gas chromatography; separation

## **INTRODUCTION**

Recently, metal-organic frameworks (MOFs) represent a relatively novel class of hybrid inorganic-organic porous crystalline materials, which have received increasing attention because of their fascinating coordination structures and unusual properties, such as uniform structured nanoscale cavities, high surface area, chemical tunability, as well as excellent chemical and thermal stability. The crystal lattice of the MOFs is constructed by coordination bonds between metal ions or clusters and organic building blocks (multidentate organic ligands). Up to now, a large number of MOFs have been synthesized and obtained diverse applications in many fields including gas storage, catalysis, drug delivery, sensing and separation, which have been covered in some significant reviews.<sup>1-9</sup> Particularly, a series of MOFs have been explored for analytical applications because of their diverse structures and unusual properties.<sup>10</sup> For instance, MOFs have been used as novel multi-functional materials for direct application to in-field sampling,<sup>11,12</sup> solid-phase extraction (SPE),<sup>13–17</sup> solid-phase microextraction (SPME),<sup>18–21</sup> high-resolution gas chromatography (GC),<sup>19,22–26</sup> high performance liquid chromatography (HPLC)<sup>27–32</sup> and capillary electrophoresis (CE).<sup>33</sup>

Chirality plays important roles in chemistry and biology, and biological evolution is absolutely dependent on the occurrence of chiral recognition and catalysis. Considering the importance of chiral recognition, tremendous research efforts have been invested into the development of chiral recognition materials. Therefore, the design and synthesis of chiral MOFs have attracted great attention because of their potential applications in chiral separation and asymmetric catalysis. The main advantages for chiral MOFs are that their framework structures, chiral pore environment and functionality can be finely controlled by the choice of metal ions or clusters and chiral ligands. In recent years, a large number of chiral MOFs have been synthesized.<sup>34-40</sup> and used as seaparation materials and catalysis. To date, there are only a few studies on Chiral MOFs that are used as chiral stationary phases (CSPs) for separation of racemic compounds in liquid chromatography  $(LC)^{41-44}$  and high-resolution gas chromatography (GC).<sup>45</sup>

MOFs with an intrinsically chiral topology such as quartz, srs, and zeolite beta have attracted interest for decades due to their potential applications in chiral recognition. Chiral Nickel(II) complex containing (+)-camphor has been used as the chiral stationary phase in GC, which exhibited excellent chiral recognition ability for racemic alkyl-substituted cyclic ethers.<sup>48</sup> Here we report a chiral MOF Ni(D-cam)  $(H_2O)_2$  with unusual integration of molecular chirality, absolute helicity, and 3-D intrinsic chiral net (Figure 1) as chiral stationary phase for high-resolution gas chromatographic (GC), which was synthesized by using D-(+)-camphoric acid as ligand according to the method of Zhang et al.<sup>49</sup> In this work, we fabricated a Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated open tubular column for separation of organic compounds, including racemates, aromatic isomers and linear alkanes. The chiral column has excellent selectivity and also possesses good recognition ability toward these organic compounds, especially chiral compounds.

## **EXPERIMENTAL** Materials and Chemicals

All chemicals were of at least analytical grade and used without further treatment. D-(+)-camphoric acid (99%) was purchased from Adamas. Ni

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**Fig. 1.** (a) A view of 1-D left-handed *M*-helix (dashed blue line) in MOF Ni (D-cam) ( $H_2O$ )<sub>2</sub>; (b)3-D framework in MOF Ni(D-cam) ( $H_2O$ )<sub>2</sub>.

(NO<sub>3</sub>)6H<sub>2</sub>O (98%) was purchased from Alfa Aesar. Na<sub>2</sub>CO<sub>3</sub> was from Tianjin Fengchuan Chemical Reagent Science and Technology Co. Ltd. (Tianjin, China). Racemates of citronellal, alanine, methionine, leucine, proline, 1-phenyl-1,2-ethandiol, 2-amino-1-butanol, glutamic acid and phenyl-succinic acid were obtained from Sigma, their injection mass of each

#### Instrumention

The scanning electron microscopy (SEM) micrographs were recorded on a Philip model XL30ESEMTMP scanning electron microscope at 30.0 kV. The X-ray diffraction (XRD) patterns were recorded with a D/max-3B diffractometer (Rigaku, Japan) using Cu K $\alpha$  radiation. The thermogravimetric analysis (TGA) experiment was performed on a ZRY-1P simultaneous thermal analyzer (Shanghai, P. R. China) from room temperature to 800 °C at a ramp rate of 10 °C min<sup>-1</sup>.

All GC separations were performed on a Shimadzu GC-2014C (Kyoto, Japan) system with a flame ionization detector (FID), a split injection port, and a capillary control unit. The instrument control and data acquisition were carried out by the N-2000 software (Zhida Information Engineering Co., Ltd., Zhejiang University, P. R. China). Nitrogen (99.999%) was used as the carrier gas. The inlet temperature of gas chromatograph was set to 200 °C, and the temperature of FID was set to 250 °C.

#### Synthesis of $Ni(D-cam)(H_2O)_2$

Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> crystals were synthesized according to Zhang et al.<sup>41</sup> Typically, D-camphoric acid (0.1021 g), Na<sub>2</sub>CO<sub>3</sub>(0.0503 g), and Ni(NO<sub>3</sub>) 6H<sub>2</sub>O (0.3098 g) were dissolved in 7 mL ultrapure water in a 25 mL Teflon cup under stirring for 20 min at room temperature. The vessel was then sealed and heated at 120 °C for 5 days. The autoclave was subsequently allowed to cool to room temperature. The green crystals were obtained. Samples for XRD and TGA were dried at 120 °C.

# Fabrication of the Ni(D-cam)(H<sub>2</sub>O)<sub>2</sub>-coated Open Tubular Column

Untreated fused silica capillary columns with a polyimide outer coating were manufactured by Yongnian Optical Fiber Factory (Hebei province, P. R. China). The fused silica open tubular column was treated according to the following method before dynamic coating: the open tubular column



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Fig. 2. (a) Simulated and Synthesized XRD patterns of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>; (b) TGA curve of the prepared Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>; (c) SEM images of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> deposited on the inner wall of the open tubular column A; (d) SEM images of the cross section of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> coating in part of the open tubular column A. *Chirality* DOI 10.1002/chir

was filled with 1 M NaOH, sealed at both ends, and maintained for 2 h. Thereafter, the open tubular column was washed successively with ultrapure water for 1 h, 0.1 M HCl for 2 h, and ultrapure water again until the outflow reached neutrality. The column was then purged with nitrogen for 6 h at 120  $^\circ\text{C}.$ 

The Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated open tubular column was fabricated by a dynamic coating method. Briefly, a 2 mL ethanol suspension of the Ni (D-cam) (H<sub>2</sub>O)<sub>2</sub> (1 mg mL<sup>-1</sup>) was introduced into the open tubular column under gas pressure, and then pushed through the column at a rate of 50 cm min<sup>-1</sup> to leave a wet coating layer on the inner wall of the open tubular column. A 2 m long buffer tube was attached to the end of the open tubular column as a restrictor to avoid acceleration of the solution plug near the end of the column. Finally, the coated open tubular column was flushed for 6 h with nitrogen and then conditioned from 30 to 250 °C, increasing its temperature at a rate of 1 °C min<sup>-1</sup> and was held at 250 °C for 6 h.

# RESULTS AND DISCUSSION Characterization of the Synthesized $Ni(D-cam)(H_2O)_2$ and $Ni(D-cam)(H_2O)_2$ -coated Open Tubular Columns

In this study, two Ni(D-cam)  $(H_2O)_2$ -coated open tubular columns with different inner diameters and lengths, including column A (30 m × 250 µm i.d.) and column B (2 m × 75 µm i.d.), were prepared by a dynamic coating method using Ni (D-cam)  $(H_2O)_2$  as the stationary phase. The column efficiency of the two Ni(D-cam)  $(H_2O)_2$ -coated open tubular columns was measured by using n-dodecane as the test compound at 120 °C. The number of theoretical plates (plates/m) of column A and column B were 1300 and 2750, respectively.

The prepared Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> crystals were dried at 120 °C under reduced pressure for XRD characterization. The successful synthesis of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> crystals was confirmed by XRD analysis (Figure 2a). Figure 2b shows that the TGA curve of the Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> crystals, which is stable up to 250 °C and therefore suitable for GC usage. SEM analysis was used to investigate the coating properties of the MOF crystals on the inner wall of the column. The SEM images showed that the column A had an approximately 2 µm thick Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> coating on the inner wall (Figure 2c and d).

To evaluate the classification of novel chromatographic stationary phases, the McReynolds constants were used to describe the polarity of Ni(D-cam)(H<sub>2</sub>O)<sub>2</sub>-coated open tubular column by choosing benzene, 1-butanol, 2-pentanone,



Fig. 3. Van Deemter plot for n-dodecane on capillary column B(2 m long  $\times\,75\,\mu m$  i.d.)under 120 °C.

1-nitropropane, and pyridine as test solutes. The respective constants of the five selected test solutes are thought to measure various interactions between the stationary phase and the analytes, including weak dispersion forces, polarizability, hydrogen-bonding ability, dipolar and acidic characters of the stationary phase. Squalane is used as a standard nonpolar stationary phase, then the McReynolds constants of the chiral MOF column were compared to that of squalane. The obtained McReynolds constants of five reference analytes were 153, 254, 192, 166, 391 for benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine on column B at 140 °C, respectively. The average of the five McReynolds constants was 231, which indicates that the polarity of the Ni (D-cam) (H<sub>2</sub>O)<sub>2</sub> is moderate. The elution sequence of the probes was benzene, nitropropane, 2-pentanone, 1-butanoland pyridine.

Figure 3 gives the Van Deemter plot of column B for n-dodecane under 120 °C. The optimal linear velocity value of this open tubular column was 11.5 cm s<sup>-1</sup>

## Gas Chromatographic Separation Properties of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated Open Tubular Column (column B)

In this work, we chose linear alkanes mixture and position isomer as analytes to investigate the separation ability and



Fig. 4. GC chromatograms on the open tubular column B (a) for the separation of alkanes using a temperature program: 50 °C for 0.5min, 40 °C/min to 180 °C, and 3 µg of injection mass of each alkane; (b) for the separation of ionone isomer at 110 °C, and 500 ng of injection mass of  $\alpha$ , $\beta$ -ionone isomer.

TABLE 1. Separation of racemates on column B

Racemates	Temperature (°C)	Retention factor $(k_1)$	Separation factor ( $\alpha$ )
citronellal	100	1.21	1.14
alanine <sup>®</sup>	100	0.96	1.56
methionine <sup>®</sup>	97	1.15	1.32
leucine <sup>®</sup>	105	0.46	2.42
proline <sup>®</sup>	100	0.49	1.99
glutamic acid <sup>®</sup>	120	1.64	1.26
2-amino-1-butanol <sup>b</sup>	120	1.13	1.15
1-phenyl-1,2-ethandiol <sup>b</sup>	135	1.67	1.22
phenyl-succinic acid <sup>°</sup>	95	1.13	1.13

<sup>a</sup>Trifluoroacetyl isopropyl ester derivate; <sup>b</sup>trifluoroacetyl derivate; <sup>c</sup>isopropyl ester derivate.



**Fig. 5.** GC chromatograms on the MOF-coated open tubular column B(2 m long × 75  $\mu$ m i.d.) for the separation of racemates. **a**) citronellal at 100 °C under a N<sub>2</sub> linear velocity of 11.9 cm s<sup>-1</sup>; **b**) alanine derivative at 100 °C under a N<sub>2</sub> linear velocity of 12.5 cm s<sup>-1</sup>; **c**) methionine derivative at 97 °C under a N<sub>2</sub> linear velocity of 12.3 cm s<sup>-1</sup>; **d**) leucine derivative at 105 °C under a N<sub>2</sub> linear velocity of 13.0 cm s<sup>-1</sup>; **e**) proline derivative at 100 °C under a N<sub>2</sub> linear velocity of 13.0 cm s<sup>-1</sup>; **e**) proline derivative at 100 °C under a N<sub>2</sub> linear velocity of 11.0 cm s<sup>-1</sup>; **f**) glutamic acid derivative at 120 °C under a N<sub>2</sub> linear velocity of 11.0 cm s<sup>-1</sup>; **g**) 1-phenyl-1,2-ethandiol derivative at 120 °C under a N<sub>2</sub> linear velocity of 10.0 cm s<sup>-1</sup>; **g**) 1-phenyl-1,2-ethandiol derivative at 95 °C under a N<sub>2</sub> linear velocity of 12.1 cm s<sup>-1</sup>. 1  $\mu$ g of injection mass of each racemate. <sup>a</sup> Trifluoroacetyl isopropyl ester derivate; <sup>b</sup> trifluoroacetyl derivate; <sup>c</sup> isopropyl ester derivate.

selectivity of Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated column. Figure 4a shows that all the seven *n*-alkanes (n-C<sub>10</sub> to n-C<sub>16</sub>) were baseline separated on the column B with sharp peaks and in a short time by temperature-programmed control. The elution sequence of the seven *n*-alkanes on the column B follows the order of boiling points because longer linear alkane has stronger Van der Waal's force with MOF.<sup>24</sup> Except for the normal alkanes mixture, the column can separate isomer, and the separation chromatogram of  $\alpha,\beta$ -ionone is shown in Figure 4b. As can be seen from Figure 4b, the  $\alpha,\beta$ -ionone obtained baseline separation on column B. The experimental results show that the Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> possesses high selectivity and excellent separation performance for alkanes mixture and isomers.

In Ni(D-cam)  $(H_2O)_2$ , the enantiopure ligand D-cam coexist with the 3-D intrinsically chiral topology net. In addition, the MOF Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub> has three homochiral features: a 3-D intrinsically homochiral net, homohelicity, and enantiopure molecular chirality. 3-D framework materials with integrated homochiral features have the potential for enhanced chiral recognition and enantioselectivity. Therefore, the chiral 3-D framework Ni(D-cam)( $H_2O$ )<sub>2</sub> was mainly used for the separation of racemates. Nine racemates were separated on column B, including citronellal, alanine, methionine, leucine, proline, glutamic acid, 2-amino-1-butanol, 1-phenyl-1,2-ethandiol and phenyl-succinic acid. Table 1 showed the retention factors  $(k_1)$  for the first eluted enantiomer and separation factors  $(\alpha)$ . Their enantiomeric resolutions on column B are exhibited in Figure 5. As can be seen from the separation chromatograms, the column B gave high resolution with short retention times for the enantioseparation of nine racemates, which show baseline separation for all enantiomer pairs except for proline, 1-phenyl-1,2-ethandiol and 2-amino-1-butanol. There are the same elution orders for five amino acid derivates, in which L enantiomers are eluted after D. Chirality DOI 10.1002/chir

Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated column has excellent chiral recognition ability and selectivity toward racemates due to the influence of the chiral microenviroment of Ni(D-cam)(H<sub>2</sub>O)<sub>2</sub> with its unusual integration of molecular chirality, left-handed *M*-helix, and 3-D intrinsic chiral net. Consequently, the chiral recognition ability of the Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated column for the separation of racemates primarily arises from the surface of the crystals in which the steric fit between the homochiral framework and conformation of the solute molecule is the main interactive force.<sup>50</sup> Except for these interactions, many other interactions between racemates and chiral MOF  $Ni(D-cam)(H_2O)_2$  have also enhanced the chiral recognition and enantioselectivity in GC, including hydrogen bonding, dipole-dipole, dispersion, and van der Waals forces. In addition, Ni(D-cam) (H<sub>2</sub>O)<sub>2</sub>-coated column (column B) possesses good stability, which can withstand over 500 injections without significant decline of selectivity and separation ability under 250 °C.

#### CONCLUSIONS

In conclusion, we have demonstrated a homochiral MOF  $Ni(D-cam)(H_2O)_2$  as a promising chiral stationary phase for GC separation. The  $Ni(D-cam)(H_2O)_2$ -coated open tubular column showed excellent selectivity. The results presented that chiral MOF  $Ni(D-cam)(H_2O)_2$  has excellent recognition ability toward alkanes and isomer, especially for racemates.

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