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Chiral Metal–Organic Frameworks for High-Resolution Gas Chromatographic Separations

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S *Supporting Information*

ABSTRACT: Chiral metal–organic framework coated open tubular columns are used in the high-resolution gas chromatographic separation of chiral compounds. The columns have excellent selectivity and also possess good recognition ability toward a wide range of organic compounds such as alkanes, alcohols, and isomers.

Metal–organic frameworks (MOFs), a subclass of the broader family of coordination polymers, consist of an extended network of metal ions (or clusters) coordinated to multidentate organic molecules.[1] In recent years, MOFs have been shown to hold great promise for applications in gas storage,[2] separation,[3] catalysis,[4] and many other areas[5] due to their fascinating structures. The selective adsorption and high thermal and chemical stability of MOFs have also made these materials useful for gas chromatography (GC)[6] and liquid chromatography.[7] A large number of chiral MOF materials have been synthesized,[8] and the application of chiral MOFs in the separation of racemic compounds[9] has been reported. In order to overcome the poor resolution on MOF packed columns, which arises from the considerable diffusion resistance of bulky packing, MOF-coated capillary columns have been reported to offer improved separation efficiency in thin coatings.[10] The first example reported of a chiral chromatographic column in high performance liquid chromatography was when the enantiopure three-dimensional porous Zn–organic framework was used as the stationary phase for the separation of a racemic mixture of chiral alkyl aryl sulfoxides.[11]. There are many GC chiral stationary phases, such as cyclodextrin and its derivatives,[12] chiral ionic liquids,[13] especially the chiral metal-complex stationary phases,[14] that have been investigated. However, to the best of our knowledge, there has been no attempt to utilize chiral MOFs as stationary phases in GC.

Herein we report a chiral MOF-coated open tubular column for high-resolution GC separation of compounds. The stationary phase possesses a three-dimensional chiral channel framework which has the formula [{Cu(sala)}$_n$] (H_2sala = *N*-(2-hydroxybenzyl)-L-alanine). Some racemates, isomers, alkanes, alcohols, and Grob's test mixture were used as the targets for separation.

The [{[Cu(sala)]$_2$(H_2O)}$_n$] was synthesized by the addition of cupric acetate to H_2sala according to the method of Ranford et al.[15] (see the Supporting Information), and the coated fused-silica open tubular column with [{Cu(sala)}$_n$] was prepared by a dynamic coating method using an ethanol suspension of the chiral framework material. [{[Cu(sala)]$_2$(H_2O)}$_n$] is a single-handed helical coordination polymer. On heating, the single-stranded helices lose water molecules and cross-link to produce a chiral open framework [{Cu(sala)}$_n$]. Rehydration experiments have been unsuccessful, suggesting that this process is irreversible.[15] We chose the chiral open framework [{Cu(sala)}$_n$] as the chiral stationary phase because of its excellent thermal stability and three-dimensional framework with chiral channels. Table S1 summarizes the chromatographic properties of four columns with different inner diameters or lengths.

Table 1. Separation of Racemates on MOF Column D

Racemates	Temp (°C)	Retention factor (k_1)	Separation factor (α)
Citronellal	90	1.13	1.26
Camphor	105	1.25	1.02
Alanine[a]	115	1.72	1.31
Leucine[a]	100	2.04	1.12
Valine[a]	90	2.07	1.33
Isoleucine[a]	115	1.49	1.30
Proline[a]	105	2.32	1.17
2-Methyl-1-butanol[b]	120	1.29	1.01
1-Phenyl-1,2-ethandiol[b]	125	1.19	1.28
Phenyl-succinic acid[c]	100	1.12	1.32
1-Phenyl-ethanol[b]	135	1.18	1.29

[a] Trifluoroacetyl isopropyl ester derivate. [b] Trifluoroacetyl derivate. [c] Isopropyl ester derivate.

Figure S3 shows scanning electron microscopy (SEM) images of the cross section of the fabricated open tubular column A and the coating on its inner wall. The fabricated column had an approximately 1 μm thick MOF coating on the inner wall. As can be seen from the thermogravimetric analysis curve (Figure S2), the column was thermally stable below 220 °C and therefore suitable for GC usage.

Table S2 gives the McReynolds constants of the five reference analytes on column A. The average of the five McReynolds constants is sometimes used as an approximate polarity scale. The respective constants are thought to measure various interactions between the stationary phase and the analytes.[16] The

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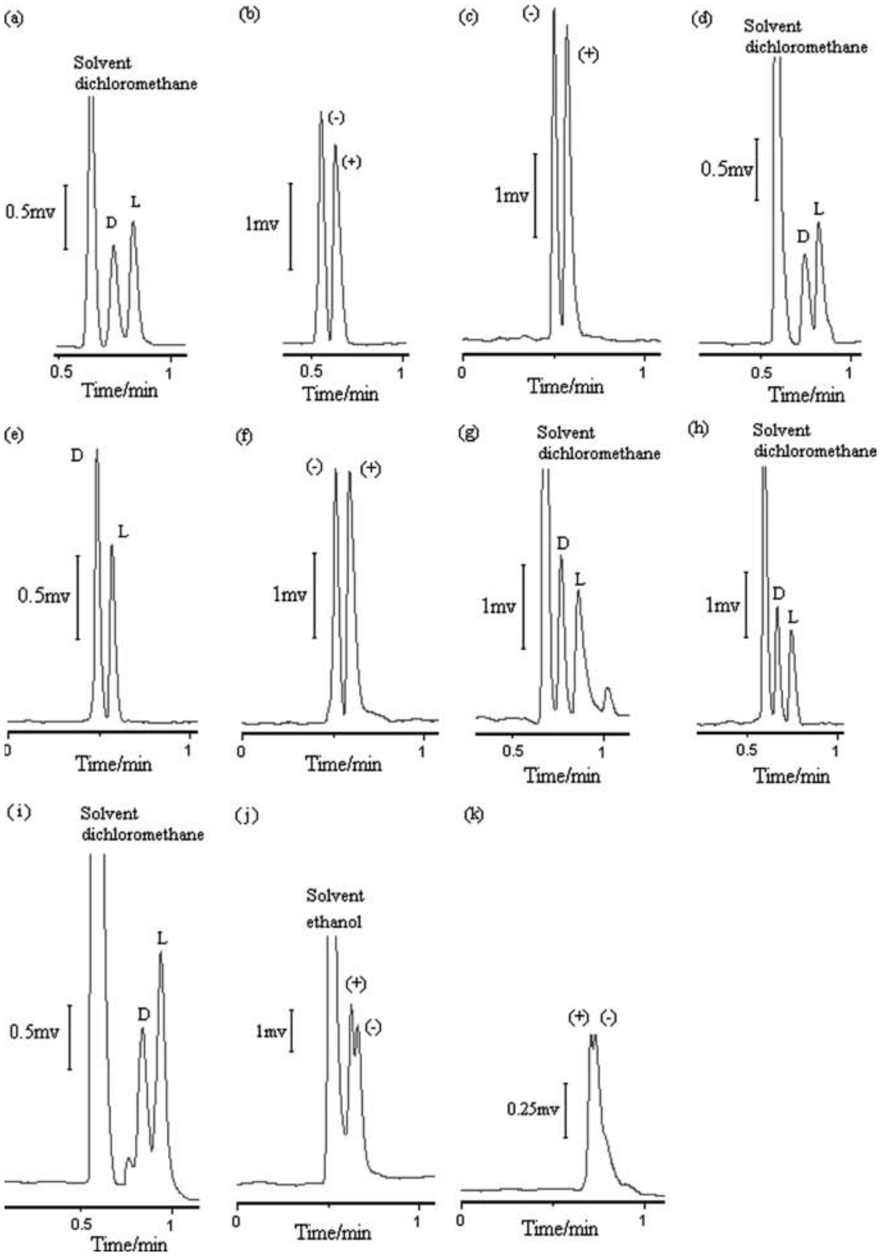

Figure 1. GC chromatograms on the MOF-coated open tubular column D (2 m long × 75 μm i.d.) for the separation of racemates. (a) Isoleucine derivative at 115 °C under a N_2 linear velocity of 12.5 cm s^{-1}; (b) citronellal at 90 °C under a N_2 linear velocity of 13.6 cm s^{-1}; (c) 1-phenyl-1,2-ethandiol at 125 °C under a N_2 linear velocity of 13.5 cm s^{-1}; (d) leucine derivative at 100 °C under a N_2 linear velocity of 13.7 cm s^{-1}; (e) phenyl-succinic acid at 100 °C under a N_2 linear velocity of 14.0 cm s^{-1}; (f) 1-phenyl-ethanol at 135 °C under a N_2 linear velocity of 13.8 cm s^{-1}; (g) valine derivative at 90 °C under a N_2 linear velocity of 13.5 cm s^{-1}; (h) alanine derivative at 115 °C under a N_2 linear velocity of 13.1 cm s^{-1}; (i) proline derivative at 105 °C under a N_2 linear velocity of 13.0 cm s^{-1}; (j) camphor at 105 °C under a N_2 linear velocity of 12.5 cm s^{-1}; (k) 2-methyl-1-butanol derivative at 120 °C under a N_2 linear velocity of 11.0 cm s^{-1}.

elution sequence of the probes was benzene, nitropropane, 2-pentanone, pyridine, and 1-butanol. The McReynolds constants show that the polarity of the MOFs is moderate.

In order to evaluate the column, the performance of the column was tested by using Grob's test mixture, which contains six compounds with a variety of functional groups, imparting a wide range of polarity properties. Unexpectedly, the complicated mixture was separated efficiently with sharp peaks and in a short time (Figure S4).

Figure S5a shows a temperature-programmed chromatogram of an n-C_{10} to n-C_{15} normal alkane mixture at high resolution. Figure S5b represents a chromatogram illustrating the GC separation of a mixture of alcohols including n-C_2 to n-C_6; on column C excellent resolutions were obtained for these adsorptive analytes.

The MOF column also showed good selectivity for positional isomers of organic compounds. The results of the separation are expressed as separation factors (α) in Table S3. The separation factor is the ratio of adjusted retention time ($\alpha = t_2'/t_1'$). One typical chromatogram is shown in Figure S6. From the chromatogram, it is evident that the isomer was well resolved.

The most important advantage of this stationary phase in GC is its enantioselective and resolving abilities. The following 11 racemates were separated on column D: citronellal, camphor, alanine, leucine, valine, isoleucine, 1-phenyl-1,2-ethandiol, phenyl-succinic acid, and 1-phenyl-ethanol; the details are provided in Table 1. Their enantiomeric resolutions on the new stationary phase are exhibited in Figure 1.

Those racemates include aldehyde, ketone, organic acid, amino acid, and alcohol. The chromatograms show baseline or at least 85% valley separation for all enantiomer pairs except for camphor and 2-methyl-1-butanol. There are the same elution orders for four amino acid derivates, in which L enantiomers are eluted after D. All enantioseparations have short retention times, and it is suitable to perform a quick analysis of the enantiomers.

Van Deemter plots of capillary column D (2 m long × 75 μm i.d.) for n-dodecane under 120 °C (Figure S7) and for (−)- and (+)-citronellal under 90 °C (Figure S8) were drawn, respectively. Nonpolar n-dodecane gave the lower optimal linear velocity. The influence of flow rate was small for enantioseparation of citronellal.

In chiral recognition mechanisms, the influence of the chiral microenvironment on the chiral properties of chromatographic systems is complicated. The crystal structure of MOF $[Cu(sala)]_n$ was provided in Figure S9. It possesses the left-handed helical channel with a 2.5 nm screw pitch (Figure S10), 10.967 m^2/g BET surface area, and 0.04633 cm^3/g hole. Therefore, chiral recognition mostly depends on the surface of the crystal in which the steric fit between the chiral channel framework and conformation of the solute molecule is the main interactive force.[17] Besides these interactions, the dispersion, dipole−dipole, and hydrogen bond forces may also play some role.

To demonstrate that the single-handed helical channel is appropriate for the enantioseparation, we use metal-complex $[Cu(sala)]_2 \cdot 2H_2O$ for comparison. $[Cu(sala)]_2 \cdot 2H_2O$ was prepared to give a green powder according to Ranford et al. (Supporting Information; Figure S11). The metal-complex coated capillary does not offer a baseline separation of citronellal, phenyl-succinic acid, 1-phenyl-1,2-ethandiol, and 1-phenyl-ethanol and cannot recognize racemates of four amino acids, camphor and 2-methyl-1-butanol (Table S4, Figure S12). The chiral discrimination mechanism of the $[Cu(sala)]_2 \cdot 2H_2O$ stationary phase comes from the chiral carbon of the sala. It is interesting to see that enantioseparation is improved from $[Cu(sala)]_2 \cdot 2H_2O$ to $[Cu(sala)]_n$. This result indicates that the helical channels of the MOF make a significant contribution to the chiral separation in GC.

The above studies established that a wide range of organic compounds could be separated on the column. These MOFs could be used as a new chiral stationary phase in gas chromatography due to the excellent recognition ability of the MOFs toward alkanes, alcohols, and isomers, especially for chiral compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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