Metal–Organic Framework [Cd(LTP)_2]_n for Improved Enantioseparations on a Chiral Cyclodextrin Stationary Phase in GC

Jiang-rong Yang1,2, Sheng-ming Xie1, Jun-hui Zhang3, Ling Chen1, Rui-yu Nong1, and Li-ming Yuan1,3,*

1Department of Chemistry, Yunnan Normal University, Kunming 650500, P.R. China, 2Dehong Vocational College, Mangshi 678400, P.R. China, and 3Department of Chemistry, East China Normal University, Shanghai 200241, P.R. China

*Author to whom correspondence should be addressed. Email: yuan_limingpd@126.com

Received 12 August 2015; Revised 13 April 2016

Abstract
Metal–organic frameworks (MOFs) are a class of novel porous materials consisting of clusters or chains of metal ions and organic linkers. The chiral MOF [Cd(LTP)_2]_n (LTP = L(-)-thiazolidine-4-carboxylic acid) possesses infinite extension three-dimensional supramolecular reticular structure with right-handed helix. In this work, three capillary columns (A, B and C) containing MOF [Cd(LTP)_2]_n, permethylated β-cyclodextrin (CD) and sodium chloride, and MOF [Cd(LTP)_2]_n and permethylated β-CD, respectively, have been prepared and their respective enantioseparation abilities have been investigated. The polarities of all of the MOFs and permethylated β-CDs are moderate. The numbers of theoretical plates (plate m^-1) of the three columns have been measured using n-dodecane at 120°C, which followed an increasing order of A (3100) < B (3800) < C (4300). Some racemates were separated with different resolutions on Columns A, B and C. The results indicated that the incorporated MOF [Cd(LTP)_2]_n enhanced the separations of racemates on a permethylated β-CD stationary phase with high column efficiency and good reproducibility in gas chromatography.

Introduction
Cyclodextrins (CDs) are cyclic oligosaccharides containing 6(α-CD)-, 7(β-CD)- or 8(γ-CD)-α-1,4-linked D-glucose molecules (1–3). They can be derivatized with various functional groups at different positions (4). The study of CD as a chiral GC stationary phase commenced in 1983 (5). In 1987, permethylated β-CD was used for the first time to separate some optical isomers on glass capillary columns, and Koenig and co-workers appended hydrophobic groups onto CDs in 1988 (6–8).

Metal–organic frameworks (MOFs) with their favorable properties, such as high surface area, porosity, multifunctionality and good stability, have become attractive as a new class of stationary phases for use in chromatography (9–11). Recently, many reports about chiral MOFs as the stationary phase in gas chromatography have been reported (12–22). In addition, chiral MOFs also show potential for applications as stationary phases in HPLC and CEC (23–41).

We envisaged that combining the excellent properties of chiral MOFs with the unique properties of permethylated β-CD in a new chiral stationary phase may allow enhanced GC separations of enantiomers. In this research, we reported incorporation of the chiral MOF [Cd(LTP)_2]_n into a β-CD, which afforded a column useful for enhanced GC separation of racemates. The MOF, [Cd(LTP)_2]_n, possesses infinite extension three-dimensional supramolecular reticular structure with right-handed helix (Figure 1). To the best of our knowledge, there has been no report on the use of MOFs to improve the chiral recognition ability of permethylated β-CD.

Experimental
Reagents and materials
All chemicals and reagents used were at least of analytical grade and were used without further purification. Cd(CH₃COO)₂·2H₂O
(≥99%) was purchased from Gracia Chemical Technology (Chengdu, China). L-(-)-thiazolidine-4-carboxylic acid was obtained from Adamas (Basel, Switzerland). HPLC-grade ethanol was obtained from Tedia (OH, USA). Untreated fused-silica capillary columns with a polyimide outer coating were manufactured at Yongnian Optical Fiber Factory (Hebei, China). Ultrapure water (18.2 MΩ cm) was produced by an ELGA LabWater water purification system (High Wycombe, UK).

Instruments

All GC separations were performed on a Shimadzu GC-2014C system (Kyoto, Japan) with capillary control unit, flame ionization detector and split injection port. Nitrogen (99.999%) was used as the carrier gas with a linear velocity of 8–20 cm s⁻¹. The injector was held at 250°C and the injection split ratio was 40:1. X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-3B diffractometer (Tokyo, Japan) using CuKα radiation. Thermogravimetric analysis (TGA) was performed on a ZRY-1P Simultaneous Thermal Analyzer (Shanghai, China) from room temperature to 600°C at a ramp rate of 10°C min⁻¹. Scanning electron microscopy (SEM) images were acquired on a Philip model XL 30ESEM TMP scanning electron microscope (Eindhoven, The Netherlands) operated at 30.0 kV.

Synthesis of [Cd(LTP)₂]ₙ

[Cd(LTP)₂]ₙ was synthesized according to the method of Dong et al. (42). Briefly, a solution of Cd(CH₃COO)₂·2H₂O (0.067 g, 0.23 mmol) in H₂O (4 mL) was added a solution of LTP (0.075 g, 0.56 mmol) in H₂O (4 mL) to give a mixed solution. After several days, colorless cubic block crystals were obtained. The products were washed with H₂O and dried in air.

Derivatization of isomers

Because of the low volatility of amino acids and some alcohol compounds, it is generally difficult to directly analyze them by gas chromatography. The aim of derivatization is to make an analyte more volatile, less reactive, and thereby improve its chromatographic behavior. In this study, amino acids were derivatized as follows (43): (i) a solution was obtained by dissolving amino acid (<10 mg) in 1 mL of isopropyl alcohol/acetyl chloride (3:1, v/v), which was heated at 110°C for 30 min. The volatiles were then removed under a stream of nitrogen; (ii) the residue was taken up in tetrahydrofuran (1 mL) containing a small amount of trifluoroacetic anhydride. The mixture was heated at 80–100°C for 30 min. Finally, the volatiles were removed under a stream of nitrogen and the product was stored in dichloromethane or diethyl ether. Therefore, alcohol compounds were derivatized following Step (ii).

Preparation of chiral columns

Preparation of solutions of the crystalline phases for coating: a saturated methanolic solution of sodium chloride (or a suspension of the MOF) (6 mL) and methanol (0.6 mL) were added to chloroform (8 mL) in a 100 mL beaker. After rapid stirring for 5 min, further chloroform (4–8 mL) was added and the mixture was stirred for a further 2 min. The solution was then transferred to a container.

The inner surface of the untreated fused-silica capillary column was corroded with 1 M NaOH for 3 h. Thereafter, it was washed successively with ultrapure water for 1 h, 0.1 M HCl for 1 h and ultrapure water once more until the outflow was neutral. The capillary column was dried with a nitrogen purge for 6 h at 120°C.

To investigate whether the incorporation of [Cd(LTP)₂]ₙ could enhance enantioseparations on a permethylated β-CD stationary phase, we prepared three capillary columns for GC, each of 20 m long × 0.25 mm i.d. Column A contained the chiral MOF [Cd(LTP)₂]ₙ, Column B contained sodium chloride and permethylated β-CD and Column C contained the chiral MOF [Cd(LTP)₂]ₙ and permethylated β-CD. Columns A and B were prepared for comparison. Column A was prepared by a dynamic coating method, whereas Column B was first coated with sodium chloride crystals by a dynamic method and then further coated by a static method, employing a solution containing 4.5 mg mL⁻¹ (w/v) of permethylated β-CD (30%) and OV-17 (70%) in dichloromethane at 36°C. Column C was prepared in the same manner as Column B.

Figure 1. (a) A 2D homochiral layer structure in the bc plane; (b) Cd-carboxyl right-handed helical chain with a pitch of 8.964 Å.

Yang et al.
MOF column (Column A)

A pretreated capillary column was coated by a dynamic coating method. A solution of \([\text{Cd(LTP)}_2]_n\) was forced through the column under gas pressure at a rate of 1–2 cm s\(^{-1}\) to leave behind a wet coating layer on the inner wall. The coated column was purged with nitrogen, and then the coating process was repeated in the opposite direction by exchanging the inlet and the outlet. Finally, the column was purged thoroughly with nitrogen for 3 h at 200°C.

Permethylated \(\beta\)-CD column (Column B)

The capillary column was prepared by first coating sodium chloride on its inner surface. The method was the same as that described for the coating of the MOF crystals. The column was heated at 300°C for 1–2 h and then coated by a static method, employing a solution containing 4.5 mg mL\(^{-1}\) (w/v) of permethylated \(\beta\)-CD (30%) and OV-17 (70%) in dichloromethane at 36°C. After coating, the column was set aside for 1 h prior to conditioning under nitrogen. Further conditioning of the capillary column was carried out using a temperature program of 30°C for 5 min, ramping from 30°C to 200°C at a rate of 2°C min\(^{-1}\) and 200°C for 5 h.

Column with \([\text{Cd(LTP)}_2]_n\) and permethylated \(\beta\)-CD (Column C):

The column was first coated with \([\text{Cd(LTP)}_2]_n\) by the aforementioned dynamic coating method. It was then further coated by the static method, employing a solution containing 4.5 mg mL\(^{-1}\) (w/v) of permethylated \(\beta\)-CD (30%) and OV-17 (70%) in dichloromethane at 36°C.

Results

Characterization of MOF \([\text{Cd(LTP)}_2]_n\)

The successful synthesis of MOF \([\text{Cd(LTP)}_2]_n\) was confirmed by PXRD analysis (Figure 2). As can be seen from the TGA curve in Figure 3, the host framework of the MOF was thermally stable below 220°C, making it suitable for GC usage.

Chromatographic properties of the chiral columns

Table I summarizes the chromatographic properties of Columns A, B and C. Numbers of theoretical plates (plate m\(^{-1}\)) of Columns A, B and C were measured using \(n\)-dodecane at 120°C, which followed an increasing order of A (3100) < B (3800) < C (4300). The results indicated that the MOF \([\text{Cd(LTP)}_2]_n\) layer enhanced the coating properties of the permethylated \(\beta\)-CD. The coating thickness of the stationary phase employing a static method is controlled according to the formula \(d = 1/4DC\), where D and C denote the inner diameter of capillary and the concentration of stationary liquid (mg mL\(^{-1}\)), respectively. A coating thickness (~0.28 \(\mu\)m) was obtained using a concentration of 4.5 mg mL\(^{-1}\) (w/v) via the static method. For a dynamic coating method, the coating thickness is controlled by the linear velocity and the concentration of the MOF solution (44). The dynamic coating thickness was ~1 \(\mu\)m. Therefore, the coating thicknesses of Columns A, B and C were ~1.00, 1.28 and 1.28 \(\mu\)m, respectively.

![Figure 2. XRD pattern of \([\text{Cd(LTP)}_2]_n\); (a) simulated MOF; (b) synthesized MOF.](https://academic.oup.com/chromsci/article-abstract/54/9/1467/2235958/1469)

![Figure 3. TGA curve of \([\text{Cd(LTP)}_2]_n\).](https://academic.oup.com/chromsci/article-abstract/54/9/1467/2235958/1469)

![Figure 4. (a) 2-hexanol at 100°C under an N\(_2\) linear velocity of 9.65 cm s\(^{-1}\) on Column A; (b) 2-hexanol at 150°C under an N\(_2\) linear velocity of 8.13 cm s\(^{-1}\) on Column B; (c) 2-hexanol at 150°C under an N\(_2\) linear velocity of 12.06 cm s\(^{-1}\) on Column C.](https://academic.oup.com/chromsci/article-abstract/54/9/1467/2235958/1469)
Polarity evaluation of the chiral stationary phases

McReynolds constants were determined using benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine as test solutes to describe the polarities of the stationary phases. Table II shows the McReynolds constants of the five reference analytes on the three columns at 120°C. The polarities of all of the MOF and permethylated β-CD are moderate.

Separation performances of the chiral columns

The most important advantage of the novel stationary phase is its enantioselectivity and resolving ability in GC. Consequently, we compared the abilities of the three chiral stationary phases to separate racemates. The following 14 racemates were separated on Columns A, B and C: (±)-limonene, (±)-dihydrocarvyl acetate, (±)-citronellal, (±)-2-hexanol, (±)-menthol, (±)-1-phenylethyl amine, (±)-1-cyclohexyl amine, (±)-rose oxide, (±)-limonene, (±)-citronella, (±)-dihydrocarvyl acetate, (±)-1-phenylethanol, (±)-2-amino-1-butanol, (±)-2-methyl-1-butanol, (±)-2-phenyl-1-propanol, DL-alanine, and DL-arginine.

Table III. Separations of Racemates on Three Capillary Columns

<table>
<thead>
<tr>
<th>Compound</th>
<th>Column A</th>
<th></th>
<th></th>
<th>Column B</th>
<th></th>
<th></th>
<th>Column C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>k_1</td>
<td>α</td>
<td>T (°C)</td>
<td>k_1</td>
<td>α</td>
<td>T (°C)</td>
<td>k_1</td>
</tr>
<tr>
<td>(±)-2-hexanol</td>
<td>100</td>
<td>0.03</td>
<td>1.00</td>
<td>150</td>
<td>1.17</td>
<td>1.00</td>
<td>150</td>
<td>13.93</td>
</tr>
<tr>
<td>(±)-menthol</td>
<td>140</td>
<td>0.34</td>
<td>1.00</td>
<td>150</td>
<td>2.85</td>
<td>1.00</td>
<td>140</td>
<td>8.49</td>
</tr>
<tr>
<td>(±)-1-phenylethanol</td>
<td>150</td>
<td>0.39</td>
<td>1.00</td>
<td>140</td>
<td>2.78</td>
<td>1.00</td>
<td>120</td>
<td>3.57</td>
</tr>
<tr>
<td>(±)-1-cyclohexyl amine</td>
<td>140</td>
<td>0.24</td>
<td>1.00</td>
<td>135</td>
<td>0.76</td>
<td>1.00</td>
<td>150</td>
<td>0.88</td>
</tr>
<tr>
<td>(±)-rose oxide</td>
<td>120</td>
<td>0.32</td>
<td>1.00</td>
<td>140</td>
<td>2.10</td>
<td>1.00</td>
<td>140</td>
<td>2.77</td>
</tr>
<tr>
<td>(±)-limonene</td>
<td>90</td>
<td>0.54</td>
<td>1.10</td>
<td>120</td>
<td>3.37</td>
<td>1.04</td>
<td>115</td>
<td>4.68</td>
</tr>
<tr>
<td>(±)-citronella</td>
<td>90</td>
<td>0.13</td>
<td>1.07</td>
<td>120</td>
<td>1.57</td>
<td>1.06</td>
<td>115</td>
<td>2.07</td>
</tr>
<tr>
<td>(±)-dihydrocarvyl acetate</td>
<td>130</td>
<td>0.73</td>
<td>1.02</td>
<td>120</td>
<td>5.19</td>
<td>1.03</td>
<td>140</td>
<td>12.07</td>
</tr>
<tr>
<td>(±)-1-phenylethanol</td>
<td>140</td>
<td>1.05</td>
<td>1.00</td>
<td>150</td>
<td>8.11</td>
<td>1.05</td>
<td>140</td>
<td>5.56</td>
</tr>
<tr>
<td>(±)-2-amino-1-butanol</td>
<td>120</td>
<td>0.05</td>
<td>1.00</td>
<td>150</td>
<td>2.68</td>
<td>1.00</td>
<td>150</td>
<td>10.09</td>
</tr>
<tr>
<td>(±)-2-methyl-1-butanol</td>
<td>150</td>
<td>0.08</td>
<td>1.00</td>
<td>115</td>
<td>3.69</td>
<td>1.00</td>
<td>130</td>
<td>10.74</td>
</tr>
<tr>
<td>(±)-2-phenyl-1-propanol</td>
<td>150</td>
<td>0.11</td>
<td>1.00</td>
<td>140</td>
<td>4.56</td>
<td>1.02</td>
<td>120</td>
<td>9.81</td>
</tr>
<tr>
<td>DL-lysine</td>
<td>95</td>
<td>0.11</td>
<td>1.00</td>
<td>150</td>
<td>3.71</td>
<td>1.03</td>
<td>140</td>
<td>4.01</td>
</tr>
<tr>
<td>DL-arginine</td>
<td>95</td>
<td>0.23</td>
<td>1.00</td>
<td>130</td>
<td>1.78</td>
<td>1.00</td>
<td>120</td>
<td>2.51</td>
</tr>
</tbody>
</table>

Note: Tri: Trifluoroacetyl derivate.

Figure 5. (a) Menthol at 140°C under an N_2 linear velocity of 8.58 cm s^{-1} on Column A; (b) menthol at 150°C under an N_2 linear velocity of 8.13 cm s^{-1} on Column B; (c) menthol at 140°C under an N_2 linear velocity of 12.06 cm s^{-1} on Column C.

Figure 6. (a) 1-phenylethylamine at 150°C under an N_2 linear velocity of 8.58 cm s^{-1} on Column A; (b) 1-phenylethylamine at 140°C under an N_2 linear velocity of 8.13 cm s^{-1} on Column B; (c) 1-phenylethylamine at 120°C under an N_2 linear velocity of 12.06 cm s^{-1} on Column C.

Figure 7. (a) 1-cyclohexyl amine at 140°C under an N_2 linear velocity of 8.58 cm s^{-1} on Column A; (b) 1-cyclohexyl amine at 135°C under an N_2 linear velocity of 8.87 cm s^{-1} on Column B; (c) 1-cyclohexyl amine at 150°C under an N_2 linear velocity of 12.06 cm s^{-1} on Column C.

Figure 8. (a) Rose oxide at 120°C under an N_2 linear velocity of 8.58 cm s^{-1} on Column A; (b) rose oxide at 140°C under an N_2 linear velocity of 8.13 cm s^{-1} on Column B; (c) rose oxide at 140°C under an N_2 linear velocity of 12.06 cm s^{-1} on Column C.

Polarity evaluation of the chiral stationary phases

McReynolds constants were determined using benzene, 1-butanol, 2-pentanone, 1-nitropropane and pyridine as test solutes to describe the polarities of the stationary phases. Table II shows the McReynolds constants of the five reference analytes on the three columns at 120°C. The polarities of all of the MOF and permethylated β-CD are moderate.

Separation performances of the chiral columns

The most important advantage of the novel stationary phase is its enantioselectivity and resolving ability in GC. Consequently, we compared the abilities of the three chiral stationary phases to separate racemates. The following 14 racemates were separated on Columns A, B and C: (±)-limonene, (±)-dihydrocarvyl acetate, (±)-citronellal,
Figure 9. (a) 2-amino-1-butanol at 120°C under an N₂ linear velocity of 11.32 cm s⁻¹ on Column A; (b) 2-amino-1-butanol at 150°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) 2-amino-1-butanol at 150°C under an N₂ linear velocity of 12.06 cm s⁻¹ on Column C.

Figure 10. (a) 2-methyl-1-butanol at 150°C under an N₂ linear velocity of 8.58 cm s⁻¹ on Column A; (b) 2-methyl-1-butanol at 115°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) 2-methyl-1-butanol at 130°C under an N₂ linear velocity of 12.06 cm s⁻¹ on Column C.

Figure 11. (a) Arginine at 95°C under an N₂ linear velocity of 9.74 cm s⁻¹ on Column A; (b) arginine at 130°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) arginine at 120°C under an N₂ linear velocity of 12.06 cm s⁻¹ on Column C.

Figure 12. (a) Dihydrocarvyl acetate at 130°C under an N₂ linear velocity of 9.14 cm s⁻¹ on Column A; (b) dihydrocarvyl acetate at 150°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) dihydrocarvyl acetate at 140°C under an N₂ linear velocity of 11.06 cm s⁻¹ on Column C.

Figure 13. (a) Citronellal at 90°C under an N₂ linear velocity of 8.58 cm s⁻¹ on Column A; (b) citronellal at 120°C under an N₂ linear velocity of 11.91 cm s⁻¹ on Column B; (c) citronellal at 115°C under an N₂ linear velocity of 12.98 cm s⁻¹ on Column C.

Figure 14. (a) 1-phenylethanol at 140°C under an N₂ linear velocity of 15.14 cm s⁻¹ on Column A; (b) 1-phenylethanol at 140°C under an N₂ linear velocity of 11.91 cm s⁻¹ on Column B; (c) 1-phenylethanol at 150°C under an N₂ linear velocity of 8.83 cm s⁻¹ on Column C.

Figure 15. (a) 2-phenyl-1-propanol at 150°C under an N₂ linear velocity of 8.58 cm s⁻¹ on Column A; (b) 2-phenyl-1-propanol at 140°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) 2-phenyl-1-propanol at 125°C under an N₂ linear velocity of 12.06 cm s⁻¹ on Column C.

Figure 16. (a) Alanine at 95°C under an N₂ linear velocity of 9.74 cm s⁻¹ on Column A; (b) alanine at 130°C under an N₂ linear velocity of 8.13 cm s⁻¹ on Column B; (c) alanine at 120°C under an N₂ linear velocity of 12.06 cm s⁻¹ on Column C.
(±)-rose oxide, (±)-1-phenylethylamine, (±)-1-cyclohexyl amine, (±)-1-phenylethanol, (±)-menthol, (±)-2-hexanol, (±)-2-amino-1-butanol, (±)-2-methyl-1-butanol, (±)-2-phenyl-1-propanol, DL-alanine and DL-arginine (Figures 4–17). The capacity factors ($k_1$) for the first eluted enantiomers and the separation factors ($\alpha$) are summarized in Table III. The retention factor $k_1'$ is given by $(t_1-t_0)/t_0$, where $t_0$ is the column void time, and the separation factor $\alpha$ is $k_2'/k_1'$.

**Discussion**

**Evaluation of separation performances of the chiral columns**

As can be seen from Table III and Figures 4–11, the separations of all of the enantiomers on Column A were poor. Column A was able to separate only three enantiomers. Column B, containing NaCl and permethylated β-CD, was able to separate six chiral compounds. Column C, in which [Cd(LTP)$_2$]$_n$ was incorporated with permethylated β-CD, could separate all the 14 chiral compounds. (±)-2-Hexanol, (±)-menthol, (±)-1-phenylethylamine, (±)-1-cyclohexyl amine, (±)-rose oxide, (±)-2-amino-1-butanol, (±)-2-methyl-1-butanol and DL-arginine could be separated on Column C (Figures 4–11), but were not separated on Column A or B. Moreover, Column C gave higher resolution for separation of (±)-dihydrocarvyl acetate, (±)-citronellal, (±)-1-phenylethanol, (±)-2-phenyl-1-propanol and DL-alanine (Figures 12–16) than Column B did. Thus, the use of MOF [Cd(LTP)$_2$]$_n$ promoted enantioseparation on the permethylated β-CD stationary phase. The chromatograms obtained on Column C showed good peaks and at least 60% valley separation, indicating that MOF [Cd(LTP)$_2$]$_n$ can enhance the chiral recognition ability and enantioselectivity of permethylated β-CD.

![Figure 17](https://example.com/figure17.png)

**Figure 17.** (a) Limonene at 90°C under an N$_2$ linear velocity of 8.58 cm s$^{-1}$ on Column A; (b) limonene at 120°C under an N$_2$ linear velocity of 13.62 cm s$^{-1}$ on Column B; (c) limonene at 115°C under an N$_2$ linear velocity of 12.98 cm s$^{-1}$ on Column C.

![Figure 18](https://example.com/figure18.png)

**Figure 18.** (a) SEM image of pretreated open tubular column (scale bar = 10 μm); (b) SEM image of the column coating [Cd(LTP)$_2$]$_n$ (scale bar = 50 μm); (c) SEM image of sodium chloride incorporated permethylated β-CD (scale bar = 50 μm); (d) SEM image of [Cd(LTP)$_2$]$_n$ incorporated permethylated β-CD (scale bar = 50 μm).
Possible mechanisms for the resolution enhancement
To investigate the coating efficiencies of the stationary phase on the capillary columns, some segments were cut from the respective columns and then analyzed under a scanning electron microscopy. Figure 18a shows a pristine uncoated column. Column A was coated with a thickness of ∼1 μm of the MOF (Figure 18b). SEM images of columns B and C revealed that spherical sodium chloride particles and the MOF were incorporated with permethylated β-CD on their inner surfaces (Figure 18c and d).

In chiral recognition mechanisms, the influence of the chiral microenvironment on the chiral properties of chromatographic systems is complicated. The inherent characteristics of [Cd(LTP)2]n, such as right-handed helical channels, and infinite extension three-dimensional supramolecular reticular structure, when combined with the β-CD, formed a superior chiral microenvironment, in which the steric fit between the chiral channel framework and conformational forms of the racemates is one possible reason for the enhanced racemate resolving ability. In addition, the combination of the interactions of two different stationary phases with racemates may also play some role.

Conclusion
We have incorporated [Cd(LTP)2]n into a permethylated β-CD column for GC separation of racemates with enhanced resolution and high column efficiency. These improvements may be ascribed to the inherent characteristics of [Cd(LTP)2]n, such as its right-handed helical channels, and infinite extension three-dimensional supramolecular reticular structure. The new stationary phase consisting of a chiral MOF combined with CD shows good potential application for gas chromatography. This research may lead to the development of a wide range of chromatographic columns showing improved enantioselectivity in GC.

Acknowledgments
This work was supported by the National Natural Science Foundation (no. 21275126, 21127012) of China.

References
metal–organic framework MIL-53(Al) as the stationary phase; Analyst, (2012); 137: 133–139.


29. Fu, Y.Y., Yang, C.X., Yan, X.P.; Metal-organic framework MIL-100(Fe) as the stationary phase for both normal-phase and reverse-phase high performance liquid chromatography; Journal of Chromatography A, (2013); 1274: 137–144.

30. Fu, Y.Y., Yang, C.X., Yan, X.P.; Incorporation of metal-organic framework UiO-66 into porous polymermonoliths to enhance the liquid chromatographic separation of small molecules; Chemical Communications, (2013); 49: 7162–7164.


