DOI: 10.1002/cplu.201402067

Metal–Organic Framework Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) for Improved Enantioseparations on a Chiral Cyclodextrin Stationary Phase in Gas Chromatography**

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Initial efforts to combine a chiral metal–organic framework (MOF), Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) (D-Cam = D-camphoric acid, bdc = 1,4-benzenedicarboxylic acid, tmdpy = 4,4′-trimethylenedipyridine), with peramylated β-cyclodextrins to investigate whether the use of a MOF can enhance enantioseparations on a cyclodextrin stationary phase are reported. Compared with columns of peramylated β-cyclodextrin incorporated in a MOF containing sodium chloride, the column of peramylated β-cyclodextrin + MOF shows excellent selectivity for the recognition of racemates, and higher resolutions are achieved on the peramylated β-cyclodextrin + MOF stationary phase. Experimental results indicate that the use of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) can improve enantioseparations on peramylated β-cyclodextrins. This is the first report that chiral MOFs can improve enantioseparations on a chiral stationary phase for chromatography.

Introduction

Chirality is one of the major phenomena in nature and it is also an essential feature of biological systems.[1] For many chiral drugs, different enantiomers are known to have different physiological and therapeutic effects. Usually, only one of the two enantiomers is pharmaceutically active, whereas the other may be inactive or toxic.[2] The separation of chiral compounds is of great importance in many industries.

Cyclodextrins (CDs), which are cyclic oligosaccharides composed of D-(+)-glucopyranose units, can form host–guest complexes with organic compounds. They can be derivatized with different functional groups at different positions. Much progress has been made since β-CD was used to separate some optical isomers on capillary columns[3], and Koenig and co-workers introduced hydrophobic groups into CDs in 1988.[4] Owing to their high melting points, Schurig et al. dissolved peralkylated CDs in polysiloxanes, such as OV-1701, to obtain a high column efficiency.[5] Commercial columns of permethylated β-CDs have been achieved.[6] CD derivatives are widely used and show highly selective separations, especially for positional isomers and enantiomers.[7] In addition, Armstrong et al. also used different derivatized CDs to separate enantiomers in TLC, HPLC, and GC.[8]

Metal–organic frameworks (MOFs), which are a subclass of the broader family of coordination polymers, consist of an extended network of metal ions coordinated to multidentate organic molecules.[9] MOFs have been shown to hold great promise for applications in catalysis, adsorption, microreactors, anion exchange, and many other areas owing to their fascinating structures.[10] In recent years, a large number of chiral MOFs have been synthesized.[11] The selective adsorption and high thermal and chemical stability of MOFs have also made these materials useful for GC[12] and HPLC.[13] Chiral MOFs show great potential for the separation of enantiomers in GC and HPLC.[14] The marriage of the unique properties of chiral MOFs and excellent features of peralkylated β-CDs to develop novel stationary phases should be promising for enhanced GC separation of enantiomers.

For the first time, we report that MOFs can improve the enantioseparation of a chiral stationary phase in chromatography. Herein, we report our efforts to a combine chiral MOF, Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) (D-Cam = D-camphoric acid, bdc = 1,4-benzenedicarboxylic acid, tmdpy = 4,4′-trimethylenedipyridine), with peramylated β-CDs to investigate whether the use of a chiral MOF can enhance enantioseparations on a chiral CD stationary phase. The Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) compound possesses a 3D framework containing enantiopure building blocks embedded in intrinsically chiral topological nets and has excellent thermal stability, a high surface area, and unusual integrated homochirality features. Moreover, the stationary phase has three homochiral features: a 3D intrinsically homochiral net, homohelicity, and enantiopure molecular chirality (Figure S1 in the Supporting Information). The MOF Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) was synthesized by heating a mixture of

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[**] D-Cam = D-camphoric acid, bdc = 1,4-benzenedicarboxylic acid, tmdpy = 4,4′-trimethylenedipyridine.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cplu.201402067.

D-camphoric acid, 1,4-benzenedicarboxylic acid, 4,4′-trimethylenedipyridine, and $CoCO_3$ in ultrapure water at 120 °C for 5 days, according to the method reported by Zhang et al,[15] and purple crystals were obtained (see the Supporting Information). The successful synthesis of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) was confirmed by powder XRD analysis (Figure S2 in the Supporting Information). Meanwhile, the thermogravimetric analysis curve of the Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) sample showed that the MOF was thermally stable below 300 °C, and therefore, suitable for GC usage (Figure S3 in the Supporting Information).

To investigate whether the use of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) could improve enantioseparations on a peramylated β-CD stationary phase, three capillary columns were prepared for GC: column A (20 m long × 0.25 mm i.d.) contained the chiral MOF, column B (20 m long × 0.25 mm i.d.) contained sodium chloride and peramylated β-CD, and column C (20 m long × 0.25 mm i.d.) contained chiral MOF and peramylated β-CD. Columns A and B were prepared for comparison. Column A was coated through a dynamic coating method. Column B was coated with sodium chloride crystals by a dynamic method and was then coated by a static method employing a solution of peramylated β-CD and OV-17 (4.5 mg mL^{-1}; 3:7 w/v) in dichloromethane at 36 °C. The method for the preparation of column C was the same as that for column B. The thickness of the static coating method can be calculated[16] and is about 0.28 μm on the column. The dynamic method was used for the coating of crystals and the thickness was controlled through the coating velocity and concentration. It can be seen from the SEM image that this is approximately 1 μm. Thus, the thickness of the coatings on columns A, B, and C is approximately 1.28 μm.

Results and Discussion

Table 1 summarizes the chromatographic properties of columns A, B, and C. The plate numbers ("n") for the three columns followed an increasing order of A (2767) < B (3563) < C (4268); this indicated that the MOF layer enhanced the coating properties of the β-CDs.

Table 2 gives the McReynolds constants of the five reference analytes on columns A, B, and C. 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.[17] The McReynolds constants show that the polarity of the MOF is moderate and the peramylated β-CD is a low-polar stationary phase.

Table 1. Characteristics of the columns (A, B, C) upon using *n*-dodecane as the tested compound at 120 °C.

Column	Column dimensions [m×μm.i.d.]	*T* [°C]	Capacity factor [k]	Linear velocity [cm s^{-1}]	Column efficiency [n m^{-1}]
A	20×250	120	1.33	13.67	2767
B	20×250	120	2.97	11.91	3563
C	20×250	120	2.98	12.02	4268

Table 2. McReynolds constants of columns A, B, and C at 120 °C.

Column	Benzene	1-Butanol	2-Pentanone	1-Nitropropane	Pyridine	Av.
A	78	393	249	225	208	230.6
B	25	113	62	101	92	78.6
C	34	105	62	100	149	90

The most important advantage of the novel stationary phase is its enantioselective and resolving abilities in GC. The following 10 racemates were separated on columns A, B, and C: (±)-2-hexanol, (±)-linalool, (±)-citronellal, (±)-methyl L-β-hydroxyisobutyrate, (±)-limonene, (±)-rose oxide, (±)-dihydrocarvyl acetate, (±)-menthol, DL-valine, and DL-leucine; details are provided in Table 3. The enantiomeric resolutions on three different stationary phases are exhibited in Figure S4 in the Supporting Information. Table 3 shows the temperatures, retention factors (α_1') for the first eluted enantiomers, and separation factors (α). The retention factor k_1' is $(t_1-t_0)/t_0$ and the

Table 3. Separations of racemates on three capillary columns.

Column	Compound	*T* [°C]	k_1	α
A	2-hexanol	110	1.93	1.00
	(±)-linalool	140	2.65	1.00
	(±)-citronellal	140	2.45	1.11
	(±)-methyl L-β-hydroxyisobutyrate	120	2.05	1.00
	(±)-limonene	140	2.68	1.02
	(±)-*cis*-rose oxide	120	3.72	1.00
	(±)-*trans*-rose oxide		3.97	1.00
	(±)-dihydrocarvyl acetate	130	4.74	1.06
	(±)-menthol	130	3.09	1.13
	DL-valine[a]	150	2.61	1.00
	DL-leucine[a]	140	3.99	1.00
B	2-hexanol	65	2.07	1.01
	(±)-linalool	100	4.26	1.00
	(±)-citronellal	120	2.13	1.00
	(±)-methyl L-β-hydroxyisobutyrate	85	3.72	1.03
	(±)-limonene	140	2.35	1.05
	(±)-*cis*-rose oxide	90	5.79	1.00
	(±)-*trans*-rose oxide		6.45	1.00
	(±)-dihydrocarvyl acetate	85	16.35	1.02
	(±)-menthol	150	0.44	1.07
	DL-valine[a]	130	1.38	1.00
	DL-leucine[a]	110	6.81	1.02
C	2-hexanol	70	1.93	1.00
	(±)-linalool	70	5.77	1.02
	(±)-citronellal	115	4.11	1.08
	(±)-methyl L-β-hydroxyisobutyrate	93	4.05	1.05
	(±)-limonene	130	3.06	1.07
	(±)-*cis*-rose oxide	100	4.17	1.05
	(±)-*trans*-rose oxide		5.39	1.02
	(±)-dihydrocarvyl acetate	85	30.7	1.03
	(±)-menthol	140	0.55	1.08
	DL-valine[a]	130	1.08	1.10
	DL-leucine[a]	90	8.22	1.04

[a] Trifluoroacetyl isopropyl ester derivate. Because there are *cis* and *trans* forms for (±)-rose oxide. The values of k_1' for *cis*-rose oxide and *trans*-rose oxide have been displayed in Table 3, respectively.

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separation factor, α, is k_2'/k_1', in which t_0 is the column void time, which was tested by using methane. As seen from Table 3 and Figure S4 in the Supporting Information, the separation of all of the tested enantiomers was weak on column A, except for the separation of citronellal (column A (1.11) > column C (1.08) > column B (1.00)). Column A was only able to separate four racemates. Column B, in which contained peramylated β-CDs, was able to separate six chiral compounds. Column C, in which Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) had been incorporated with peramylated β-CDs, was able to separate nine chiral compounds.

It is clear that (±)-linalool (Figure 1), (±)-rose oxide (Figure 2), and DL-valine (Figure 3) could not be separated on columns A and B, whereas they were well separated on column C. Furthermore, column C gave a higher resolution for the enantioseparations of DL-leucine (Figure 4) than column B. The chromatograms of column C show good peaks and baseline or at least 60% valley separation. The repeatability of the chiral MOF-incorporated peramylated β-CD column was determined from five repeated injections of racemates. The relative standard deviations for the five replicate separations of linalool were 0.31 and 2.2% for retention time and peak area, respectively. Furthermore, three similar columns of MOF-incorporated peramylated β-CD stationary phase (20 m × 250 μm i.d.) were prepared to investigate the column–column reproducibility, the relative standard deviations for the first-eluted enantiomer retention factor of leucine was 6.2%. The results showed that the technique was reliable and reproducible. The above results demonstrate that incorporated Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) indeed plays a significant role in the enhanced separation of racemates.

To study the reason for this resolution enhancement, some segments were cut from five capillary columns, then analyzed by means of a scanning electron microscope. SEM results reveal the presences of different stationary phases on these columns (Figure 5). Figure 5a shows a SEM image of the cross section of the pretreated open tubular column; there is nothing on it. Figure 5b shows an image of the cross section of the peramylated β-CD column coating, which was uniformly coated on the inner wall. Fabricated column A had a MOF coating approximately 1 μm thick on the inner wall (Figure 5c). SEM results of columns B and C revealed that sphere-shaped sodium chloride particles and MOF were incorporated with the β-CDs on the inner surface of the columns, respectively (Figure 5d and e).

The intrinsic characteristics of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy), such as a high surface area, unusual integration of molecular chirality, absolute helicity, and a 3D intrinsic chiral net, enabled the marriage of chiral MOF with β-CDs to form a greater chiral microenvironment, in which the steric fit between the chiral channel framework and conformation of the racemates, which is one possible reason for the enhanced racemate resolving ability of the MOFs + CDs capillary column. Besides this factor, the combination of the interactions of two different stationary phases with racemates may also play some role. However, the influence of the chiral microenvironment on the chiral properties of the chromatographic systems is very complicated and far from being understood, although some information and suggestions have already been published. Further studies on these aspects will be carried out.

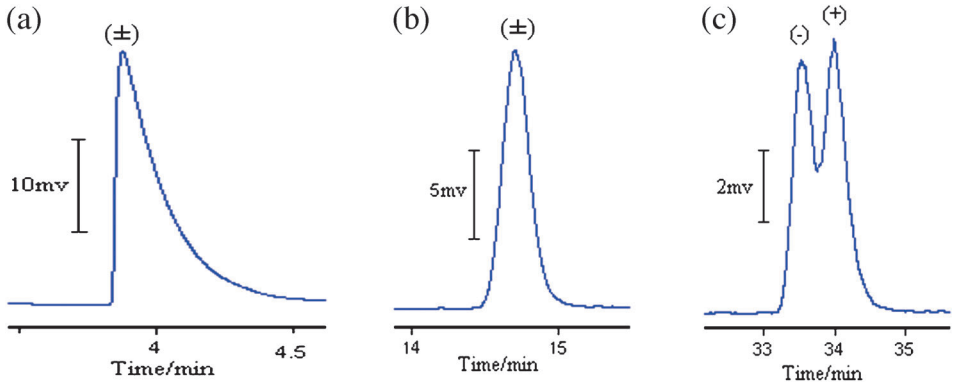

Figure 1. a) Linalool at 140 °C under a N_2 linear velocity of 17.14 cm s^{-1} on column A. b) Linalool at 100 °C under a N_2 linear velocity of 11.91 cm s^{-1} on column B. c) Linalool at 70 °C under a N_2 linear velocity of 8.83 cm s^{-1} on column C.

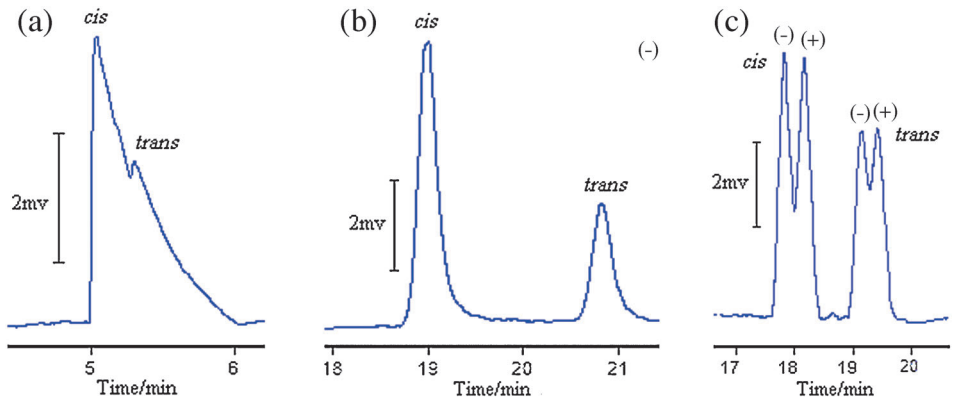

Figure 2. a) Rose oxide at 120 °C under a N_2 linear velocity of 16.14 cm s^{-1} on column A. b) Rose oxide at 90 °C under a N_2 linear velocity of 11.91 cm s^{-1} on column B. c) Rose oxide at 100 °C under a N_2 linear velocity of 12.37 cm s^{-1} on column C.

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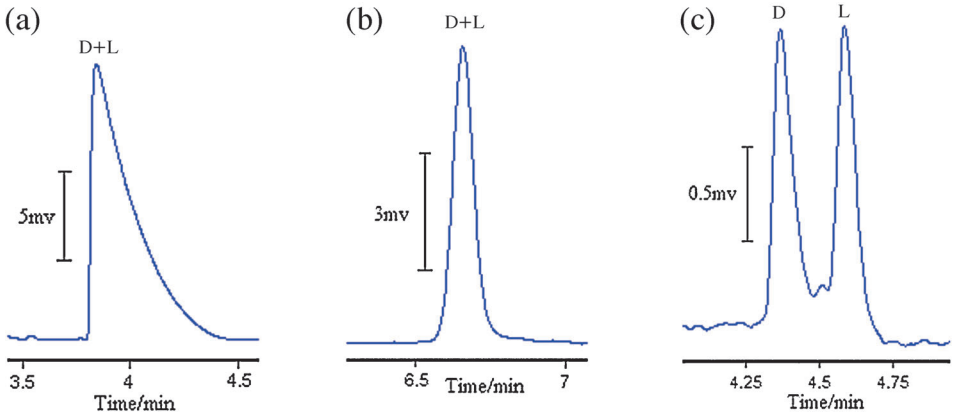

Figure 3. a) Derivatized valine at 150 °C under a N_2 linear velocity of 18.03 cm s^{-1} on column A. b) Derivatized valine at 130 °C under a N_2 linear velocity of 14.32 cm s^{-1} on column B. c) Derivatized valine at 130 °C under a N_2 linear velocity of 15.89 cm s^{-1} on column C.

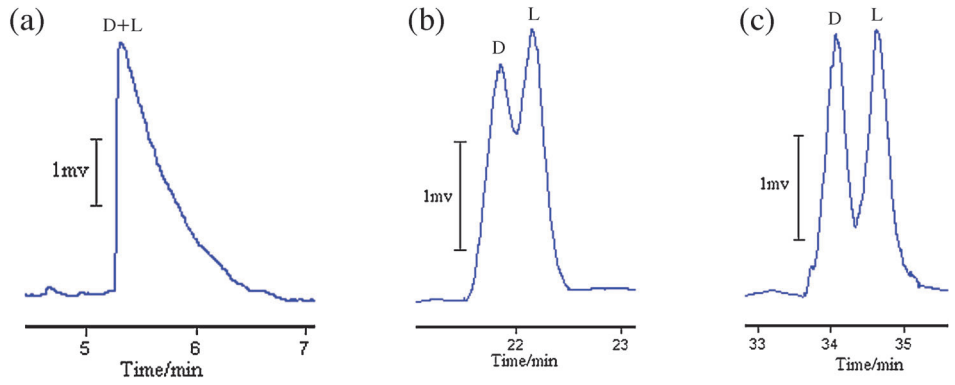

Figure 4. a) Derivatized leucine at 140 °C under a N_2 linear velocity of 17.14 cm s^{-1} on column A. b) Derivatized leucine at 100 °C under a N_2 linear velocity of 11.91 cm s^{-1} on column B. c) Derivatized leucine at 90 °C under a N_2 linear velocity of 12.02 cm s^{-1} on column C.

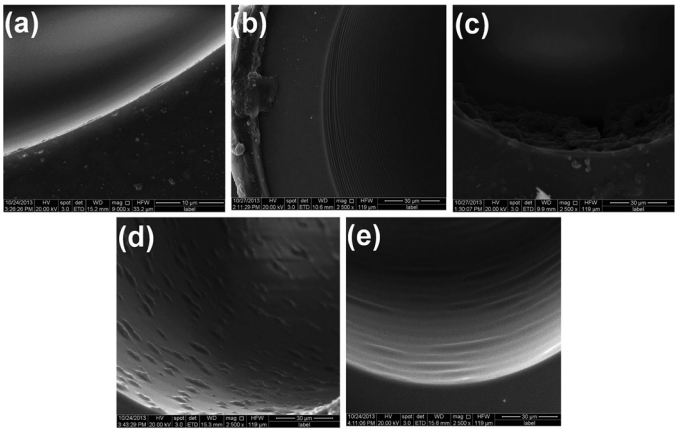

Figure 5. a) SEM image of the pretreated open tubular column. b) SEM image of the peramylated β-CD column coating. c) SEM image of the Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) column coating. d) SEM image of sodium chloride incorporated peramylated β-CDs. e) SEM image of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy)-incorporated peramylated β-CDs.

Conclusion

We have fabricated Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy)-incorporated peramylated β-CD columns for GC separation of racemates with enhanced resolution and high column efficiency. The intrinsic characteristics of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy), such as large surface area, unusual integration of molecular chirality, absolute helicity, and 3D intrinsic chiral network, make the Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy)-incorporated peramylated β-CD column attractive for enhanced GC separation of racemates. This research should lead to the development of a wide range of chromatographic columns with improved enantioselectivity on GC.

Experimental Section

The MOF crystal was synthesized according to the method reported by Zhang et al.[15] Briefly, a solution was obtained by mixing D-camphoric acid (0.1030 g), 1,4-benzenedicarboxylic acid (0.0801 g), 4,4′-trimethylenedipyridine (0.0956), and $CoCO_3$ (0.1307 g) in ultrapure water (5 mL) in a 50 mL Teflon cup; this was stirred for 20 min at room temperature. The Teflon-lined bomb was sealed and placed in an oven at 120 °C for 5 days under static conditions, and then cooled to room temperature. The product was washed with ultrapure water and chromatographically pure ethanol and dried in vacuo at 120 °C to eliminate the remaining water. Purple crystals were obtained (yield, 65 %).

Derivatization of amino acids

Owing to poor volatility, amino acids are generally difficult to analyze by GC directly. They need to be derivatized. The goal of derivatization is to make an analyte more volatile, less reactive, and thus, improve its chromatographic behavior. For this study, a solution containing a mixture of amino acid (< 10 mg) in isopropanol/acetyl chloride (1 mL, 3:1, v/v) was heated at 110 °C for 30 min, and dried with nitrogen. Tetrahydrofuran (1 mL) and a small amount of trifluoroacetic anhydride were then added. The mixture was heated at 80–100 °C for 30 min. The sample was then dried with nitrogen and remained in dichloromethane or diethyl ether.[18, 19]

The untreated fused-silica column was filled with 1 M NaOH and left for 3 h. Thereafter, the column was washed successively with ultrapure water for 1 h, 0.1 M HCl for 1 h, and ultrapure water again until the outflow reached neutrality. The column was then purged with nitrogen for 6 h at 120 °C.

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Preparation of crystal suspension[18]

Chloroform (8 mL) was placed in a 100 mL beaker, then a saturated solution of sodium chloride (6 mL) in methanol (or suspension of MOF) and methanol solvent (0.6 mL) were poured into the beaker quickly under stirring. After stirring for 5 min, chloroform (4–8 mL) was added. After stirring for another 2 min, the solution was transferred into a reservoir.

Capillary column with Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) (column A)

A pretreated capillary column was coated by a dynamic coating method. Briefly, a suspension of Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) was introduced into the column under gas pressure and then pushed through the column at a rate of 1–2 cm s^{-1} to leave a wet coating layer on the inner wall of the column. The coated column was purged with nitrogen and then the coating process was repeated by exchanging the inlet and outlet of the capillary column. Finally, the column was purged thoroughly with nitrogen for 1–2 h at 250 °C.

Peramylated β-CD column (column B)

The column was prepared by coating sodium chloride on the inner surface of the capillary. The method was the same as that used for coating the MOF crystal. The column was heated at 300 °C for 1–2 h. Then, the column was coated by a static method by employing a solution of peramylated β-CD and OV-17 (4.5 mg mL^{-1}; 3:7 w/v) in dichloromethane at 36 °C. After coating, the column was settled for 1 h for conditioning under nitrogen. Further conditioning of the capillary column was carried out by using a temperature program: 30 °C for 5 min, ramp from 30 to 250 °C at a ramp rate of 2 °C min^{-1} and 250 °C for 5 h.

Column with Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) and peramylated β-CD (column C)

First, the column was coated with Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) by a dynamic coating method. Then, the capillary column containing Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) was coated by the static method by employing a solution of peramylated β-CD and OV-17 (4.5 mg mL^{-1}; 3:7 w/v) in dichloromethane at 36 °C. The subsequent steps used were the same as those for the preparation of column B.

Acknowledgements

The study was supported by the National Natural Science Foundation (nos. 21275126, 21127012) of China.

Keywords: hiral resolution · cyclodextrins · gas chromatography · metal–organic frameworks · stationary phases

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Received: March 15, 2014
Published online on ■■ ■■, 0000

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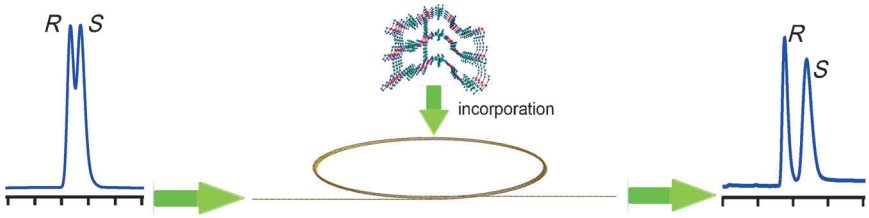

Increase the gap! The incorporation of peramylated β-cyclodextrins into the metal–organic framework Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) (D-Cam = D-camphoric acid, bdc = 1,4-benzenedicarboxylic acid, tmdpy = 4,4′-trimethylenedipyridine) enhances the gas chromatographic separation of small molecules with high column efficiency and good reproducibility (see picture).

*H. Liu, S.-M. Xie, P. Ai, J.-H. Zhang, M. Zhang, L.-M. Yuan**

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Metal–Organic Framework Co(D-Cam)$_{1/2}$(bdc)$_{1/2}$(tmdpy) for Improved Enantioseparations on a Chiral Cyclodextrin Stationary Phase in Gas Chromatography

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