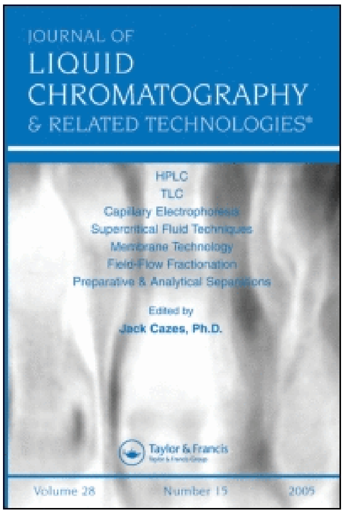

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Preparation and Characterization of *p*-tert-Butylcalix[4]arene Modified Sol-Gel Column for Open-Tubular Capillary Electrochromatography

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Abstract: Using the sol-gel method, *p*-tert-butyl-calix[4]arene sol-gel coating capillary (BCx4-SGCC) was prepared and characterized by infrared spectroscopy and electroosmotic flow. Their separation performance was investigated by using benzenediol positional isomers and axially chiral binaphthyl derivative 2-amino-2′-hydroxy-1,1′-binaphthyl (BHA) without symmetric carbon center as probes. The migration behaviors of these analytes on the BCx4-SGCC with the open tubular capillary electrochromatography separation mode were influenced by the supermolecular interaction between calixarene and analytes. The results from the quantum chemistry calculation using DFT-B3LYP/STO-3G** base set were consistent with the migration behaviors of benzenediol and BHA.

Keywords: Calixarene, Open-tubular capillary electrochromatography, Quantum chemistry calculation, Sol-gel method

INTRODUCTION

Open tubular capillary electrochromatography (OT-CEC) is an important separation mode in capillary electrophoresis (CE). Its electroosmotic

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property and the selectivity of the capillary column can be altered by the capillary inner wall modification. Usually modification is achieved with three methods such as physically coating,[1,2] chemically bonding,[3,4] and sol-gel bonding.[5–8] The sol-gel method features many advantages such as high phase ratio, high column capacity, high stability, and reproducibility. Thus, the sol-gel method has been widely used in OT-CEC.[9,10]

Calixarenes are regarded as the third generation of the host molecule after crown ethers and cyclodextrins, their applications as GC capillary coating[11] and HPLC stationary phase[12] have shown special selectivity. In CE, calixarenes were mainly used as the additives in earlier years.[13,14] Because their UV absorption is too high to permit sensitive detection of the analytes, calixarenes were used as the column modification reagents to prepare the coating of the capillary by a physically coating method,[15] chemically bonding,[16–18] and so-gel method.[19] The results indicated that the sol-gel column presents more advantages than the others. To validate the sol-gel method, *p*-tert-butyl-calix[4]arene sol-gel coating capillary (BCx4-SGCC) was prepared and characterized in this work. At the same time, the electrophoretic migration behaviors of benzenediol positional isomers and axially chiral binaphthyl derivative 2-amino-2′-hydroxy-1, 1′-binaphthyl (BHA) without a symmetric carbon center as probes were investigated through a discussion of the interaction between *p*-tert-butyl-calix[4]arene and analytes based on a quantum chemistry calculation.

EXPERIMENTAL

Reagents

Unless specified otherwise, all chemicals were of analytical reagent grade and obtained from Beijing Chemical Factory (Beijing, China). γ-Glycidoxypropyltrimethoxysolane (KH-560) and tetraethoxysilane (TEOS) were purchased from the Wuhan University Chemical Plant (Wuhan, China). R- and S-2-amino-2′-hydroxy-1,1′-binaphthyl (BHA) was purchased from Gaoke Biochemistry Limited Company of Changzhou (Jiansu, China). Trifluoroacetic acid (TFA) was obtained from Fluka Corp. Methanol (MeOH) and acetonitrile (MeCN) were of HPLC grade and purchased from the Luzhong Reagent Plant of Shanghai (Shanghai, China). Water was purified using Milli-Q purification equipment. All running solutions for CE were degassed and filtered through a 0.22 µm membrane.

Each group of the analytes used as probes was dissolved in 25 mL MeCN to yield a stock solution of 500 µg/mL. The working solutions were prepared by diluting each stock solution in the mobile to form the desired concentrations of 10, 50 and 100 μg/mL, respectively. Each separation was performed in triplicate.

Preparation of *p*-tert-Butylcalix[4]arene Sol-Gel Coating Capillary Column

p-tert-Butylcalix[4]arene (BCx4) was synthesized in our laboratory according to the literature.[20] Its purity (>98%) was characterized using the HPLC[21] and CE methods.[22] The preparation of BCx4 sol-gel capillary column was schemed and shown in Figure 1. Details of the preparation procedure are as follows.

Capillary Activation

A new fused silica capillary was activated by flushing with 1 M NaOH for 30 min, H_2O for 15 min, 1 M HCl for 15 min, H_2O for 15 min, and drying at 120°C with flushing N_2 for 20 min.

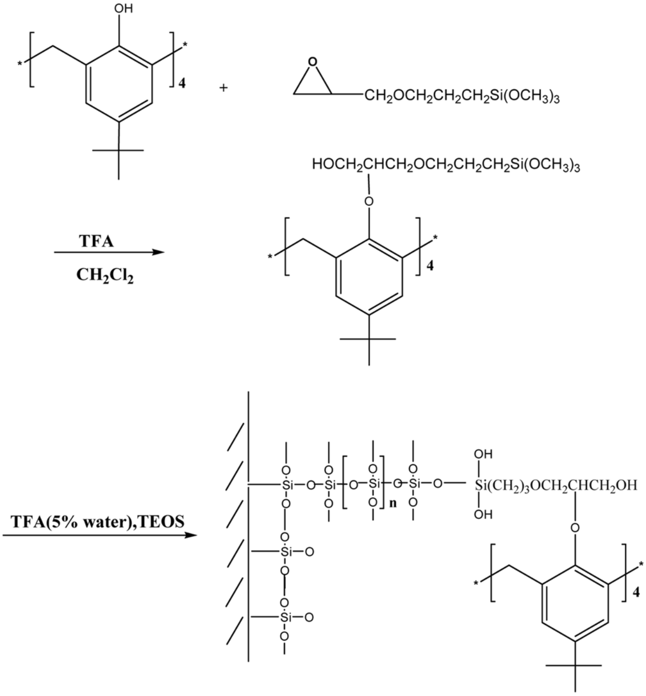


Figure 1. Preparation scheme of BCx4-SGCC.

Preparation of *p*-tert-Butylcalix[4]arene Sol-Gel Coating (BCx4-SGC)

In a plastic tube, a 4.6 mg BCx4, 150 µL CH_2Cl_2, 5 µL TFA, and 15 µL KH-560 were mixed and reacted under ultrasonic agitation for 2 h. Then a 20 µL TEOS and 3.5 mL 95% TFA were added and thoroughly mixed by ultrasonic agitation for another 5 min, and a clear sol solution produced. A 1 mL sol solution was transferred onto a glass object plate ($2 \times 10\,cm^2$) and placed at room temperature for 30 min. Then N_2 flushing was employed to produce a dry sol-gel film. This film formation process was repeated three times. The glass plate with sol-gel film was placed in the column oven of GC-2001 gas chromatograph (Tengzhou, Shandong Province of China), heated from room temperature to 150°C at 2°C min and then kept at 150°C for 4 h under N_2 protection. Finally, the glass plate with BCx4-SGC coating was washed with $CHCl_3$, MeCN, and water, respectively. For validating the presence of BCx4 in the BCx4-SGC, the dried BCx4-SGC was scraped from the glass plate, collected, and characterized by infrared (IR) spectrum.

Preparation of *p*-tert-Butylcalix[4]arene Sol-Gel Coating Capillary (BCx4-SGCC)

For the preparation of BCx4-SGCC, an aliquot of the clear sol solution produced using the procedure described previously was transferred into an activated capillary instead of a glass object plate. After the capillary with sol solution was placed at room temperature for 30 min, the sol solution was removed by flushing N_2. Similarly, this sol-gel film formation process was repeated three times. Then it was heated and conditioned in a GC oven at 150°C as above. Finally, the capillary was flushed with MeCN and water for 15 min, respectively. Consequently, the BCx4-SGCC column was completed.

Preparation of Sol-Gel Coating Capillary Without *p*-tert-Butylcalix[4]arene (SGCC)

The preparation procedure of the SGCC column was similar to that of BCx4-SGCC without the addition of BCx4 during the formation of the sol solution.

Apparatus and Electrophoretic Conditions

A Bruker Vector 22 instrument was used to obtain the IR spectra of the sol-gel coating. The CE and OT-CEC experiments were performed on an

Agilent $HP^{3D}CE$ system with a photodiode array detector and 3D ChemStation Software (Agilent Tech, Waldbronn, Germany). The pHS-3C pH apparatus was purchased from Weiye Factory (Shanghai, China), and used to measure the apparent pH values of the running buffer solution in CE.

The bare fused silica capillary was purchased from Yongnian Photo Fiber Factory (Hebei Province, China). Their dimensions are inner diameter of 75 µm and outer diameter of 375 µm. The bare fused silica capillary (BFSC) without sol-gel modification, sol-gel coating capillary (SGCC), and BCx4-SGC*C* column, was cut to a total length of 49.0 cm (40.5 cm to the detector window), respectively. Initially the new capillary was rinsed with 1.0 mol/L NaOH for 10 min, water for 5 min, and the running buffer solution for 20 min. Prior to each injection, the capillary column was rinsed with the running buffer solution for 2 min. All the separations were run at 20°C. Samples were injected from the anode end of the capillary using a dynamic pressure of 50 mbar for 5 s.

Quantum Chemistry Calculation Method

To optimize geometries of the guest analytes, host BCx4, and host guest complexes and to calculate their vibration frequencies, the quantum chemistry calculation (QCC) method with DFT-B3LYP/STO-3G** basis set was employed. This DFT-B3LYP/STO-3G** includes the Becke-style three-parameter density function theory, the Lee-Yang-Parr correction function, and the STO-3G** basis set. It is a small base group, and suitable for the calculation of a larger molecular system. All calculations were performed using the Gaussian 03 series of programs.

RESULTS AND DISCUSSION

Characterization of BCx4-SGC Coating and BCx4-SGCC Column

As indicated in the introduction, although a physically coating method[15] is simple, its coating is not stable. A chemically bonding method[16] could provide a stable coating, however the column capacity is not high enough to provide the selectivity and retention of the analyte. Thus, in this work, one of our aims was how to get a stable coating with a relatively higher capacity using the sol-gel method.

To validate the formation of BCx4-SGC coating, the infrared (IR) spectra of BCx4 and BCx4-SGC coating were carried out as shown in Figure 2. It can be seen from Figure 2 that the characteristic absorption band of the benzene ring appears at $1610 \pm 10\,\mathrm{cm}^{-1}$ and $1470 \pm 10\,\mathrm{cm}^{-1}$;

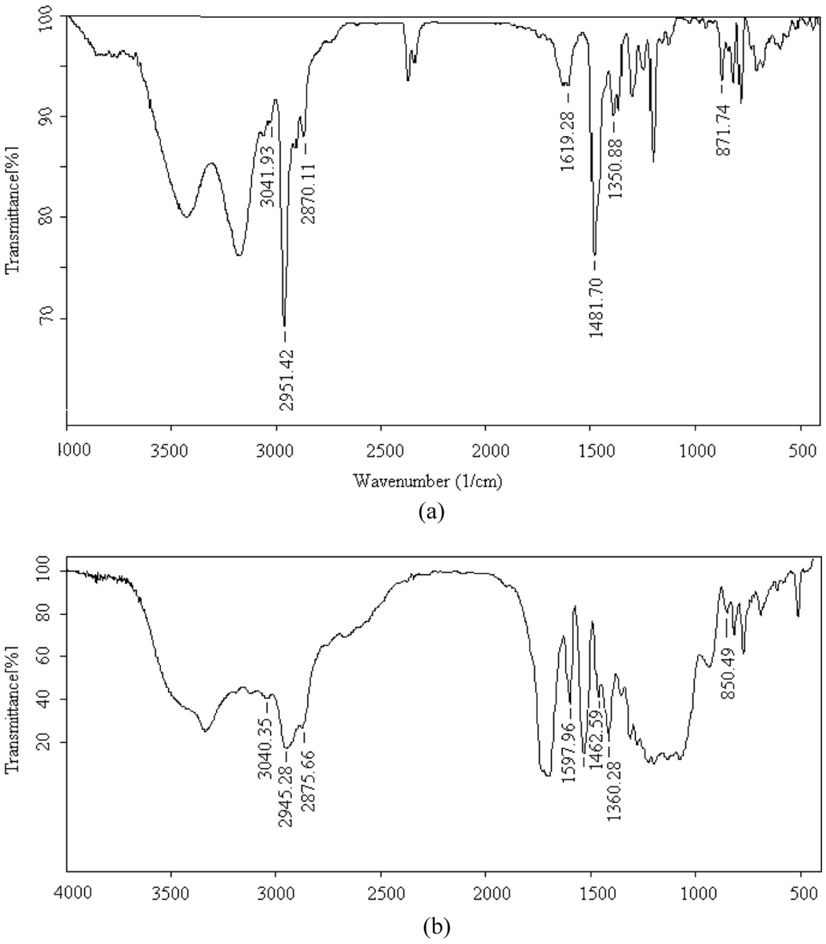


Figure 2. IR spetra of BCx4 (a) and BCx4-SGC (b).

the peak at $3040 \pm 10\,\text{cm}^{-1}$ id assigned to the C–H stretching frequency of the benzene ring of BCx4. Peaks at $2945 \pm 10\,\text{cm}^{-1}$ and $2875 \pm 10\,\text{cm}^{-1}$ are assigned to the C-H stretching frequency, and peaks at $1360 \pm 10\,\text{cm}^{-1}$ and $860 \pm 10\,\text{cm}^{-1}$ are attributed to the C–H bending frequency of the *tert*-butyl group. These spectra indicate that BCx4 is included in the BCx4-SGC coating.

To obtain a stable coating with a relatively higher capacity using the sol-gel method, the repetition times of the sol-gel film formation were optimized in the preparation procedures of the BCx4-SGC and BCx4-SGCC. As expected, with an increase of the repeat times of the sol-gel film formation, the coating thickness increased and the electroosmotic

Table 1. μ_{eof} of BCx4-SGCC with the different repeat times of sol-gel film formation

Repeat times	1	2	3	4	5	6
$\mu_{eof}\,(10^{-4}\,\text{cm}^2/\text{V·s})^a$	3.02	2.12	1.75	1.72	1.78	1.81

[a]The conditions for obtaining μ_{eof} capillary, 49.0 × 40.5 cm × 75 μm; running buffer, 40 mM phosphate sodium (pH 6.0); applied voltage, +18 kV, detection wavelength, 200 nm; test solution, 0.1% DMSO.

flow (EOF) mobility (μ_{eof}) reached a steady value (Table 1). It can be seen from Table 1 that the μ_{eof} values remained at *ca.* $1.75 \times 10^{-4}\,\text{cm}^2/\text{V}\cdot\text{s}$ over three repetitions. Thus, three repetitions were optimized to obtain the desired BCx4-SGCC column. Unless specified otherwise, all BCx4-SGCC columns used in the following sections were obtained using the optimized preparation conditions.

To compare the difference between the bare fused silica capillary (BFSC), sol-gel coating capillary (SGCC), and BCx4-SGC*C* columns, the μ_{eof} values for the three columns were determined and are shown in Figure 3. As can be seen from Figure 3, the BCx4-SGC*C* column possessed much lower and more stable EOF values than both BFSC and SGCC columns over the pH values from 5 to 9. Such low and stable EOF values within a wide pH range were helpful to obtain the reproducible separation of the analytes.

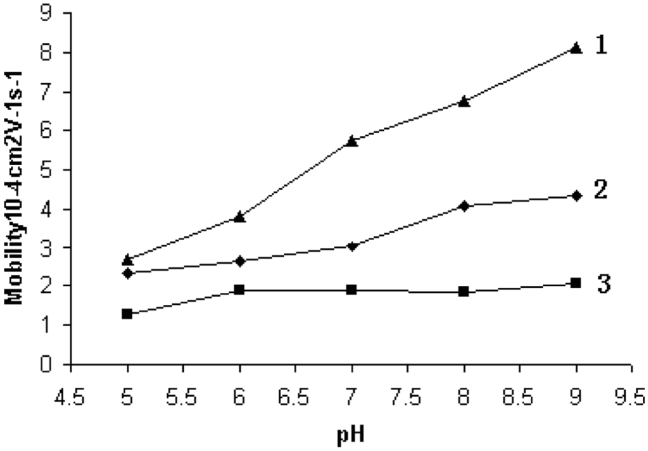


Figure 3. Effect of pH values on the μ_{eof} of three columns. Conditions as those in Table 1. Column: 1, BFSC column; 2, SGCC column; 3, BCx4-SGCC column.

Table 2. μ_{eof} values (n = 3) of six batches of the BCx4-SGC**C** column

	μ_{eof}^{a} (10^{-4} cm^2/V·s)	RSD (%)
Batch		
1	1.75	3.90
2	1.86	
3	1.76	
4	1.68	
5	1.83	
6	1.71	
Week (batch 3)		
1	1.76	3.82
2	1.77	
3	1.80	
4	1.84	
5	1.87	
6	1.92	

[a]The conditions as Table 1.

Stability and Reproducibility of the BCx4-SGCC Column

To evaluate the stability and reproducibility of the BCx4-SGC*C* column, the μ_{eof} values of six batches of BCx4-SGC*C* columns prepared over a period of 3 months were determined and are shown in Table 2. It can

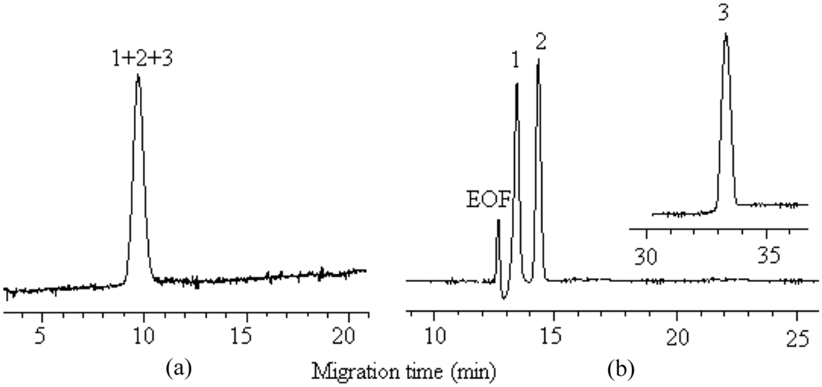


Figure 4. Typical electrophoretic separations of *o*, *m*, and *p*-benzenediols. Conditions: capillary, 49.0 × 40.5 cm × 75 μm; running buffer, 40 mM broax (pH 6.3); applied voltage, +12 kV, detection wavelength, 200 nm; sample injection: 50 mbar × 5 s. Columns: (a), SGCC column; (b), BCx4-SGCC column. Peaks: 1, *p*-benzenediol (10 μg/mL); 2, *m*-benzenediol (10 μg/mL); 3, *o*-benzenediol (10 μg/mL).

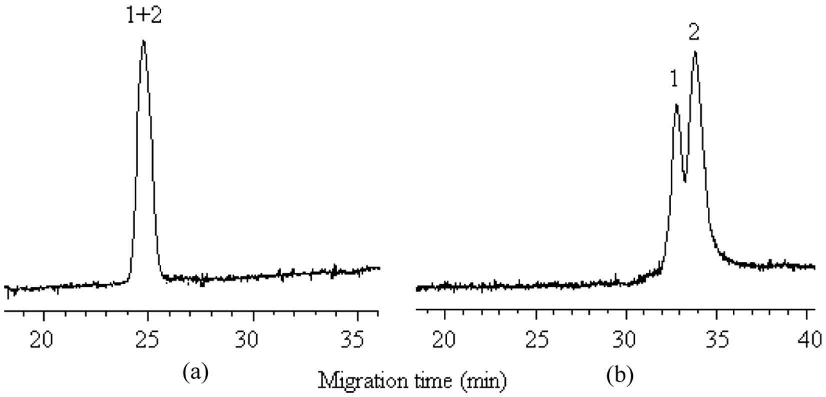


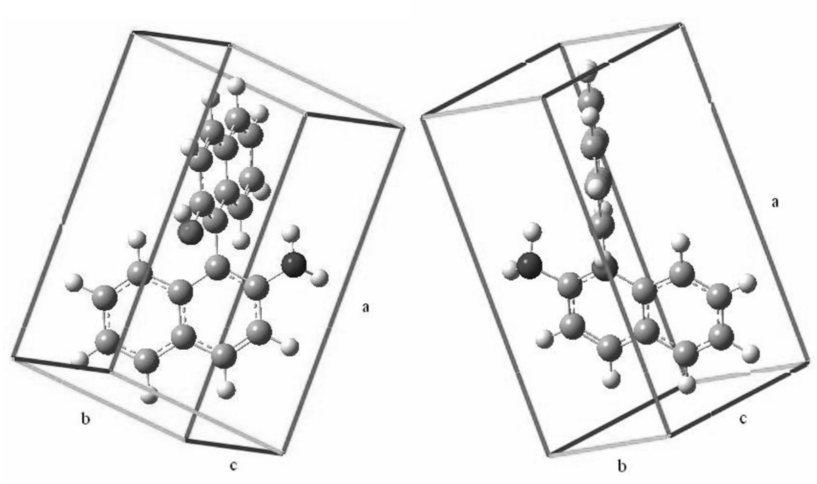
Figure 5. Typical electrophoretic separations of R and S-BHA. Conditions: capillary, 49.0 × 40.5 cm × 75 μm; running buffer, 40 mM phosphate sodium (pH7.25); applied voltage, +20 kV, detection wavelength, 220 nm; sample injection: 50 mbar × 5 s. Columns: (a), SGCC column; (b), BCx4-SGCC column. Peaks: 1, R-BHA (40 μg/mL); 2, S-BHA (50 μg/mL).

be seen from Table 2 that the preparation method of BCx4-SGC*C* column provided good reproducibility with relative standard deviation (RSD) of μ_{eof} values less than 3.90%. For Batch 3, the EOF increase over 6 weeks was less than 9% with RSD of 3.82%. These results imply that the preparation method featured good repetition and the BCx4-SGCC column had high stability.

Applications of the BCx4-SGCC Column

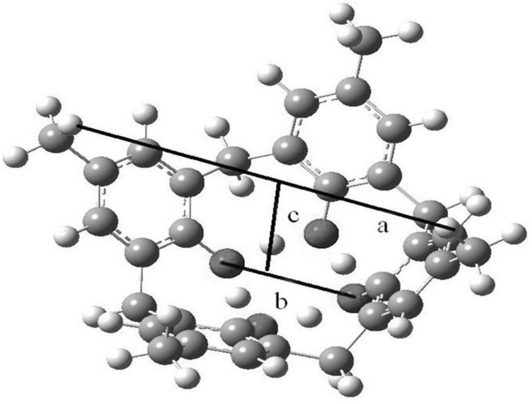
As known, calixarenes possess good selectivity for the positional isomers because of their special configurations such as cavity shape, cavity size, conformation, and substituent. In this work, benzenediols were selected as the analytical probes, the electrophoretic separation of *o*-, *m*-, and *p*-benzenediol was investigated on the BCx4-SGCC column. Through optimizing the conditions, the optimal separation of benzenediols were obtained and are indicated in Figure 4. As it can be seen from Figure 4, three benzenediol isomers can not be resolved from each other on the SGCC column without BCx4, and can reach the baseline separation on BCx4-SGCC column with BCx4. This implies that BCx4 played an important role in their separation. It is noteworthy that *o*-benzenediol migrated for more than 30 min.

R- and S-BHA are a pair of axially chiral binaphthyl derivatives without a symmetric carbon center. Due to the special configuration



R-BHA S-BHA

a=11.298311 Å, b=7.229961 Å, c=5.886727 Å. a=11.294153 Å, b=7.210424 Å, c=5.910320 Å

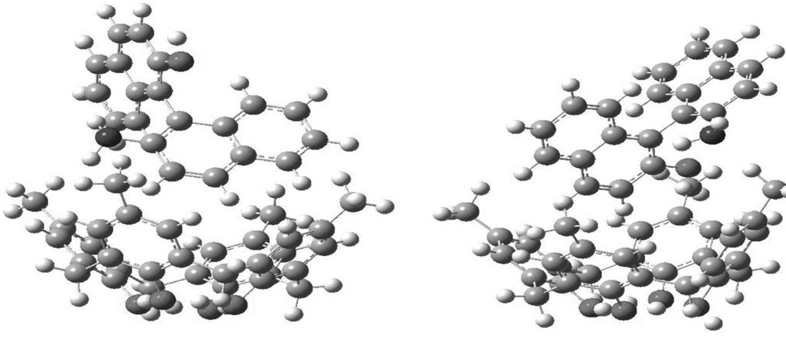


BCx4

a=9.90869 Å , b=3.35310 Å , depth c = 5.33501 Å

Figure 6. Optimized structures of R-BHA, S-BHA and BCx4.

of BCx4, it is expected that R- and S-BHA can be resolved from each other by the CEC method with the BCx4-SGCC column. In fact, a partial separation of both R- and S-BHA was observed and is displayed in Figure 5. This implies that there are different interactions between BCx4 and R-BHA, and between BCx4 and S-BHA.



S-BHA-BCx4 supramolecular R-BHA-BCx4 supramolecular

Figure 7. Optimized structure of supramolecular S-BHA-BCx4 and R-BHA-BCx4.

Discussion on the Migration Behaviors of BHA and Benzenediols

We found that the quantum chemistry calculation (QCC) is a useful method to describe the interaction between calix[4]arene and analyte.[12,23] Thus, in the present work, using the same DFT-B3LYP/STO-3G** base set, the QCC was carried out on the Gaussian 03 series of programs to obtain the optimized structure (Figure 6) of R-BHA, S-BHA, and BCx4 and their volume parameters at the lowest energy in vacuum.

From Figure 6, the upper rim diameter, lower rim diameter, and cavity depth of BCx4 cavity are about 10, 3, and 5 Å, respectively, and dimensions of R- and S-BHA is *ca.* 11 Å × 7 Å × 5 Å. Thus, it is possible that R- and S- BHA can partly enter into the BCx4 cavity in its maximal length direction because of the two naphthyl planes being vertical.

Table 3. Calculated entropy change ΔS, enthalpy change ΔH, Gibbs free energy change ΔG and stabilization energy ΔE of supramolecular BHA-BCx4

Parameters	R-BHA-BCx4	S-BHA-BCx4
Migration time (min)	32.75	34.90
ΔS_{vac} (J/mol·k)	−182.3990	−176.0002
ΔS_{solv} (J/mol·k)	−156.3849	−176.5524
ΔH_{vac} (kJ/mol)	159.6005	−5.0972
ΔH_{solv} (kJ/mol)	214.7786	50.0150
ΔG_{vac} (kJ/mol)	213.9815	55.4341
ΔG_{solv} (kJ/mol)	261.4030	102.6534
ΔE_{vac} (kJ/mol)	155.8977	−0.2390
ΔE_{solv} (kJ/mol)	186.9524	47.7571

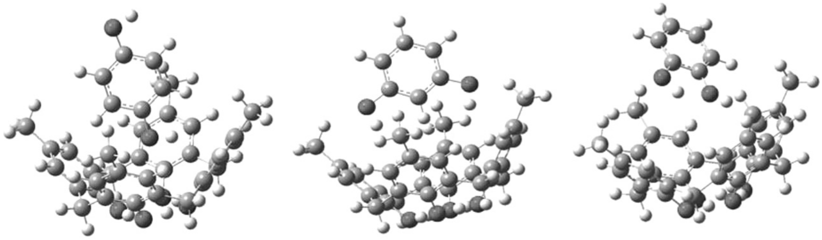

p-benzenediol-BCx4 *m*-benzenediol-BCx4 *o*-benzenediol-BCx4

Figure 8. Optimized structure of supramolecular *o*-, *m*-, and *p*-benzenediol-BCx4.

Letting BCx4 and S-BHA (or R-BHA) approach as near as possible, the optimized structures (Figure 7) of BCx4-S-BHA and BCx4-R-BHA were obtained based on the quantum chemistry calculation using DFT-B3LYP/STO-3G** base set. It can be seen from Figure 7 that both the S-BHA and R-BHA approach the BCx4 cavity in different ways.

For S-BHA the naphthyl rings with the NH_2 group largely enter into the cavity of BCx4, and for R-BHA the naphthyl rings with OH group enter into the cavity of BCx4. The BHA-BCx4 supramolecular interaction was dominated with different π–π interactions and space steric hindrance for both S-BHA-BCx4 and R-BHA-BCx4.

At the same time, we also calculated their entropy change ΔS, enthalpy change ΔH, Gibbs free energy change ΔG, and stabilization energy ΔE (Table 3) of the BHA-BCx4 supramolecule. Under the conditions of both vacuum and solvent (water), as shown in Table 3 more negative values of ΔE and ΔG for S-BHA-BCx4 were obtained. These negative values imply that S-BHA-BCx4 is more stable than R-BHA-BCx4, which results in R-BHA migrating faster than S-BHA during CE running.

Table 4. Calculated entropy change ΔS, enthalpy change ΔH, Gibbs free energy change ΔG and stabilization energy ΔE of supramolecular benzenediol-BCx4

Parameters	*p*-benzenediol-BCx4	*m*-benzenediol-BCx4	*o*-benzenediol-BCx4
Migration time (min)	13.45	14.45	33.49
ΔS_{vac} (J/mol·k)	−179.6411	−191.3466	−146.4248
ΔS_{solv} (J/mol·k)	−145.4832	−191.4428	−146.4415
ΔH_{vac} (kJ/mol)	−4.5247	−10.8352	−5.8956
ΔH_{solv} (kJ/mol)	38.9869	34.2521	28.3722
ΔG_{vac} (kJ/mol)	49.0264	46.2139	37.7579
ΔG_{solv} (kJ/mol)	92.5459	91.3327	72.0310
ΔE_{vac} (kJ/mol)	−3.6791	−8.3562	−10.5437
ΔE_{solv} (kJ/mol)	336.0505	330.9314	322.3114

For *o*-, *m*-, and *p*-benzenediol, their optimized supramolecular structures (Figure 8) and thermal parameters (Table 4) of BCx4-benzenediol were also obtained using the same quantum chemistry calculation method. It can be seen from Figure 8 that three *o*-, *m*-, and *p*-benzenediol-BCx4 structures were different, which resulted from the different π–π, space steric hindrance and hydrogen bonding interactions between BCx4 and *o*-, *m*-, *p*-benzenediol. Such differences can be reflected on the thermal parameters in Table 4. From Table 4, the more negative values of ΔE and ΔG for *o*-benzenediol-BCx4 than those for m-benzenediol-BCx4 and for *p*-benzenediol-BCx4 were obtained. This order was consistent with their retention behaviors on the bonded BCx4 stationary phase[12] and migration behaviors (times) of them on BCx4-SGCC column of OT-CEC.

CONCLUSIONS

Using the sol-gel method, *p*-tert-butyl-calix[4]arene sol-gel coating capillary (BCx4-SGCC) was prepared and characterized. The BCx4-SGCC column possessed the lower and stable EOF values, and provided the desired separations of *o*-, *m*-, and *p*-benzenediol positional isomers, and partial separation of axially chiral binaphthyl derivative BHA using OT-CEC separation mode. The results indicated that it is possible that the axially chiral binaphthyl derivatives without a symmetric carbon center can be resolved on the BCx4-SGCC column with the modification of calixarene derivatives. At the same time, the electrophoretic migration behaviors of the analytes were investigated through the discussion of the interaction between calixarene and analytes based on a quantum chemistry calculation. The quantum chemistry calculation results were consistent with the migration behaviors of BHA and benzenediol on the BCx4-SGCC column with OT-CEC separation.

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