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PAPER IN FOREFRONT

Ester-functionalized pillar[6]arene as the gas chromatographic stationary phase with high-resolution performance towards the challenging isomers of xylenes, diethylbenzenes, and ethyltoluenes

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Abstract

This work presents the first example of the utilization of polar ester group functionalized pillar[6]arene (P6A-C10-OAc) as a stationary phase for capillary gas chromatographic (GC) separations. The statically coated P6A-C10-OAc column showed a high column efficiency of 5393 plates/m and moderate polar nature. Its resolving capability and retention behaviors were investigated for a mixture of 20 analytes and more than a dozen isomers from apolar to polar in nature. As evidenced, the P6A-C10-OAc column achieved high-resolution separations of all the analytes and good inertness. Importantly, it exhibited distinctly advantageous performance for high resolution of the challenging isomers of xylenes, diethylbenzenes, ethyltoluenes, and halobenzenes over the commercial HP-5 (5% phenyl dimethyl polysiloxane), HP-35 (25% phenyl dimethyl polysiloxane), and PEG-20M (polyethylene glycol) columns.

Keywords Pillar[6]arene · Xylene · Diethylbenzene · Ethyltoluene · Gas chromatography · Stationary phase

Introduction

Gas chromatography (GC) has been widely used in various fields including chemical, pharmaceutical, and petroleum industries because of its low cost, short analysis time, and high selectivity [1, 2]. The highly effective separation of analytes with a close nature in GC depends on a stationary phase with advantageous selectivity. Therefore, more and more stationary phases such as polymers [3], ionic liquids (ILs) [4–6], metal-organic frameworks (MOFs) [7, 8], macrocycles, covalent organic frameworks (COFs) [9, 10], and carbon nanomaterials [11, 12] are developed to be applied in GC. Xylene, halobenzene, and benzaldehyde are important industrial raw materials, which are widely used in the chemical industry. Besides, they are important environmental pollutants, and their efficient separation is a challenging task in the field of analysis. Due to their very similar physicochemical properties, it is difficult to effectively separate these compounds and their isomers with conventional stationary phases [13]. Therefore, it is necessary to develop new stationary phases for gas chromatography with high selectivity for these target analytes.

Pillararenes, as a new class of macrocyclic hosts after crown ethers [14–16] cyclodextrin [17–19], calixarene [20], and cucurbituril [21–23], are made up of 1,4-disubstituted hydroquinone units linked by methylene bridges at the 2,5-positions and have received much more attention since they were synthesized by Ogoshi and co-workers in 2008 [24]. The number of repeated hydroquinone subunits determines the size of the cavity and the exist of the benzene rings gives the pillararenes electron-rich cavity. For

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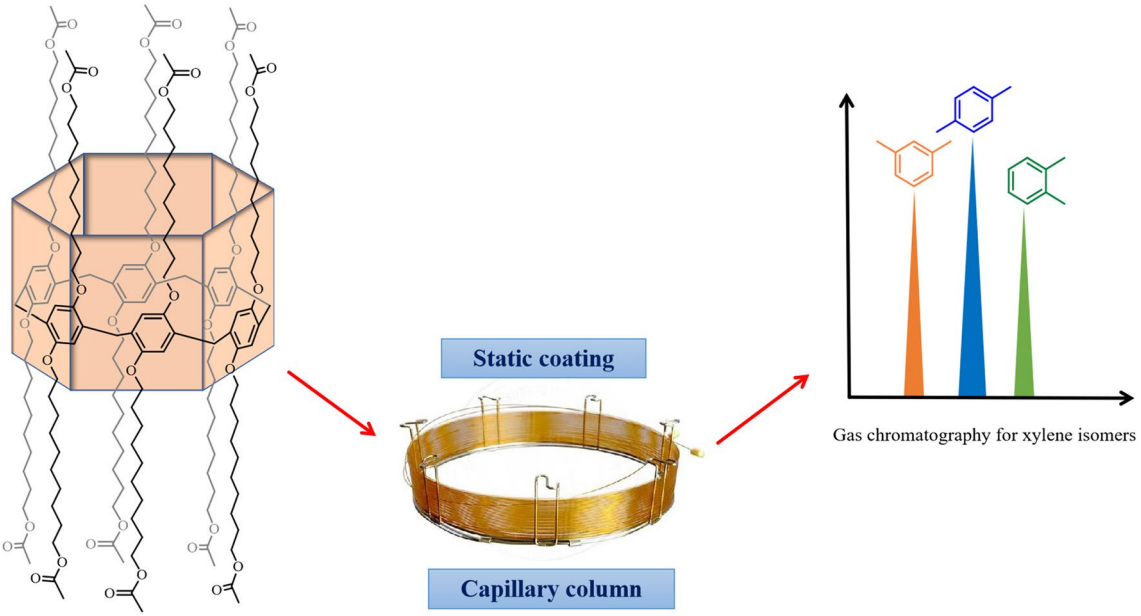

Scheme 1 Separation of xylene isomers on the P6A-C10-OAc capillary column using gas chromatography

example, pillar[6]arenes (approximately 6.7 Å) have larger cavities than pillar[5]arenes (approximately 4.7 Å), and the difference makes pillar[6]arenes capture large aromatic guests such as toluene, styrene, and isopropylbenzene [25, 26]. Meanwhile, the upper and lower rims of pillararenes have many active sites that can be functionalized with kinds of substituents to increase their solubility, stability, and selectivity [27]. What's more, the electron-rich hydrophobic cavities could accommodate diverse guests with electron-deficient and neutral guests including imidazolium cation, *n*-hexane, and biimidazole derivatives by non-covalent interactions, such as π-π, dipole-dipole, H-bonding, and so on [28, 29]. Different from the traditional hosts, pillararenes have highly symmetrical pillar-shaped structures and it endows them binding with guests selectively [30]. Next, pillararenes are functionalized freely on the position of the benzene rings or the phenolic rims and it makes them dissolve easily in organic solvents [31]. On the basis of the above features, pillararenes have become important platforms for the study of macrocyclic chemistry and materials science. After several years of investigation, pillararenes have been introduced into a great variety of areas, such as sensors [32], separation [33], nanomaterials [34], drug delivery [35], and so on. In GC, pillararenes which have a rigid structure, easy derivatization, and special host-guest interaction become potential candidates as new stationary phases.

In our work, we report a novel pillar[6]arene-based material functionalized with polar ester groups (P6A-C10-OAc) with unique amphiphilic conformation for GC separations (Scheme 1). Introducing long alkyl chains can lower its melting point, thereby improving its film-forming ability. Meanwhile, the introduction of polar ester functional groups can improve its selectivity and make it more suitable for the separation of polar analytes. In this work, the P6A-C10-OAc column was investigated for its column efficiency, polarity, separation performance, and mechanism, especially for separating some challenging and important isomers. Meanwhile, the P5A-C10-OAc column and commercial HP-5, HP-35, and PEG-20M columns were employed for reference.

Experimental

Materials and equipment

All the reagents and solvents were of analytical grade and used without further purification. Temperature program: 40 ℃ (1 min) to 160 ℃ at 10 ℃/min, flow rate at 0.6 mL/min. Paraformaldehyde (POM) was obtained from Aladdin Industrial Corp. (Shanghai, China). $BF_3{\cdot}Et_2O$ was obtained from Alfa Aesar Co., Ltd. (Shanghai, China). Cyclohexyl chloride, 1,4-hydroquinone, 1,10-dibromodecane, and potassium carbonate were obtained from Sun Chemical Technology Co., Ltd. (Shanghai, China). Potassium acetate was obtained from Damao Chemical Reagent Co., Ltd. (Tianjin, China).

Bare fused-silica capillary columns were purchased from YongnianRuifeng Chromatogram Apparatus Co., Ltd. (Hebei, China). A commercial PEG-20M column (PEG-20M, 5 m × 0.25 mm i.d.; film thickness, 0.25 μm) was obtained from Lanzhou Atech Technologies Co., Ltd. (Gansu, China). Commercial HP-5 (5% phenyl methylpolysiloxane, 5 m × 0.25 mm i.d.; film thickness, 0.25 μm) and

HP-35 (35% phenyl methylpolysiloxane, 5 m × 0.25 mm i.d.; film thickness, 0.25 μm) were obtained from Agilent Technologies Co., Ltd. (Palo Alto, CA).

An Agilent 7890A gas chromatograph including a split/splitless injector, flame ionization detector (FID), and an autosampler was used in this work to test all the analytes. All the separations were carried out under the setting GC conditions, in which the temperature of the injection port and FID detector, the split ratio, the injection volume, and the oven temperature programs for the separations are all shown in the figure captions. Thermogravimetric analysis (TGA) was used on a DTG-60AH instrument (Shimadzu, Japan). A Tensor II Fourier transform infrared spectrometer (Bruker Platinum ART) and a Bruker Biospin 400 MHz instrument (Bruker Biospin) were used to record the IR spectrum and ^{1}HNMR spectrum, respectively.

Synthesis of the P6A-C10-OAc stationary phase

The synthetic route of P6A-C10-OAc is shown in Fig. 1. For the synthesis of C10-2Br: the compounds of 1,10-dibromodecane (10.90 g, 36.33 mmol), 1,4-hydroquinone (1.00 g, 9.08 mmol), potassium carbonate (1.26 g, 9.08 mmol), and potassium iodide (1.51 g, 9.08 mmol) were added into acetone (50 mL). The mixture was refluxed at 65 ℃ for 72 h under nitrogen, then cooled to room temperature and filtered. The filtered cake was washed with CH_2Cl_2, and the filtrate was evaporated under vacuum. Next, the brown residue was purified by silica-gel column chromatography with petroleum ether (b.p. 60-90 ℃)/dichloromethane (v:v = 5:1) as the eluent, and the obtained white solid was further purified by recrystallization. After drying under vacuum at 30 ℃, the white solid (22% yield) was gained. The ^{1}H NMR and FT-IR spectrum of C10-2Br are presented in Fig. S1 and Fig. S2.

For the synthesis of P6A-C10: the mixture of C10-2Br (2.00 g, 3.65 mmol), paraformaldehyde (0.33 g, 10.94 mmol), $BF_3{\cdot}Et_2O$ (0.52 g, 3.65 mmol), and cyclohexyl chloride (CyC_6-Cl, 30 mL) was stirred at 35 ℃ for 3 h. After the reaction is completed, deionized water (30 mL) was used to quench the reaction. Next, the organic phase was extracted by CH_2Cl_2 and then dried with anhydrous $MgSO_4$. After filtering and evaporation, the white crude was purified by silica gel column chromatography with petroleum ether (b.p. 60–90 °C)/dichloromethane (v:v = 5:1 to 1:1). Finally, the P6A-C10 (10% yield) was obtained by drying under the vacuum. The ^{1}H NMR and FT-IR spectrum of P6A-C10 are presented in Fig. S3 and Fig. S4.

For the synthesis of P6A-C10-OAc: P6A-C10 (1.00 g, 298.62 μmol) and potassium acetate (0.70 g, 7.17 mmol)

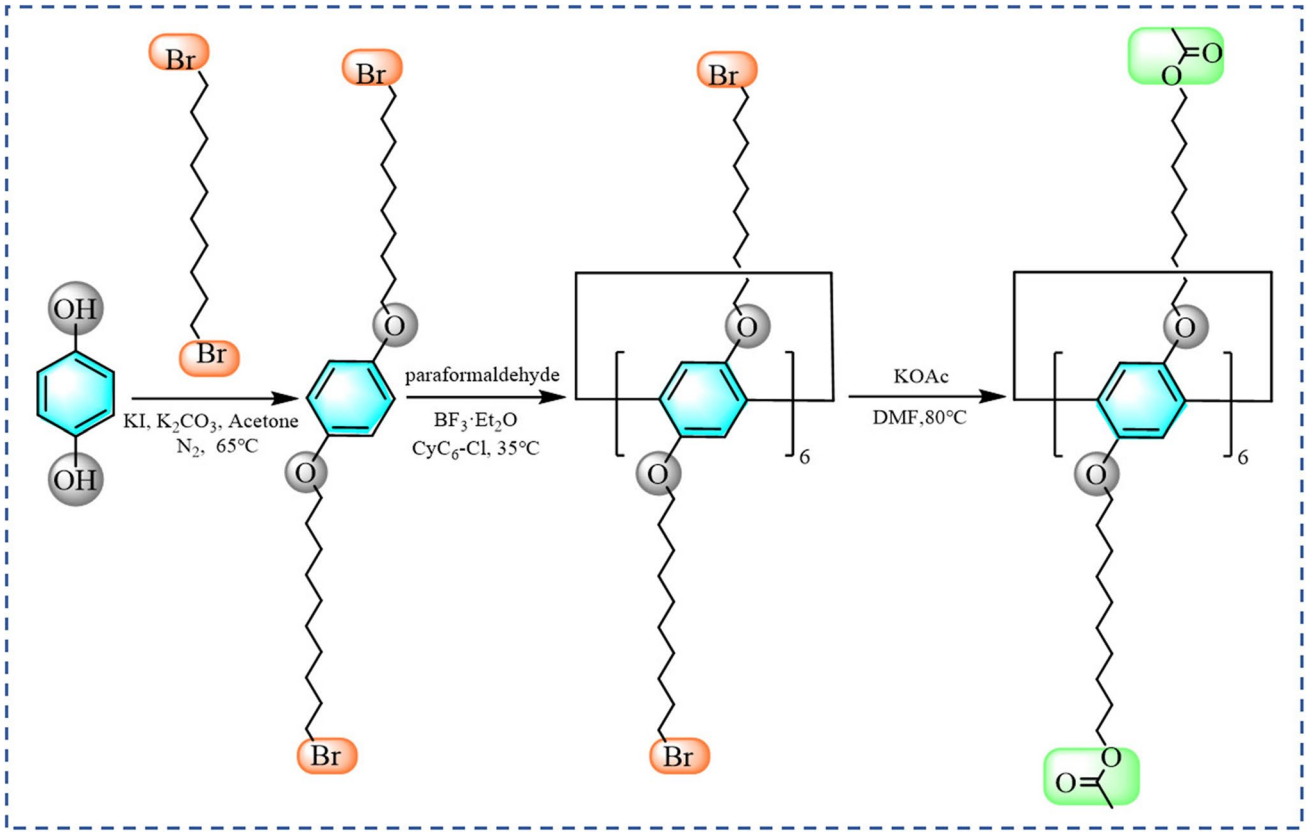

Fig. 1 Synthesis of P6A-C10-OAc

were dissolved in *N*,*N*-dimethylformamide (DMF, 30 mL). Then, the solution was refluxed at 80 ℃ under nitrogen for 48 h. After completion, the solution was cooled to 25 ℃ and put into saturated brine (30 mL). Next, the yellow crude product was obtained by filtering. Finally, it was purified by silica gel column chromatography with dichloromethane/methanol (v:v = 40:1). Finally, a yellow solid (65% yield) of the P6A-C10-OAc compound was obtained after drying under vacuum. The ^{1}H NMR and FT-IR spectrum of P6A-C10-OAc are presented in Fig. S5 and Fig. S6.

The P5A-C10-OAc was synthesized in the same procedure.

Fabrication of the P6A-C10-OAc capillary column

P6A-C10-OAc was statically coated on the inner surface of the capillary column (5 m long × 0.25 mm i.d.) [36, 37]. First of all, to roughen the inner surface of the capillary column, it was pretreated with a saturated solution of sodium chloride in methanol. After the solution already passed the column, the condition of the column was performed from 40 to 200 ℃ at 10 ℃/min and held for 3 h under nitrogen flow. Then, the pretreated column was coated with the solution of the P6A-C10-OAc stationary phase in dichloromethane (0.2%, w/v) at room temperature. Next, one end of the coated column was sealed and the other end was connected to the vacuum system to slowly remove the solvent under vacuum at 40 °C. Finally, the P6A-C10-OAc column was conditioned from 40 °C (held for 30 min) to 180 °C at 1 °C/min and held at 180 °C for 7 h under nitrogen.

Results and discussion

Characterization of the P6A-C10-OAc column

Thermogravimetric analysis (TGA) was used to measure the intrinsic thermal stability of the P6A-C10-OAc stationary phase. As illustrated in Fig. 2a, the P6A-C10-OAc stationary phase showed about 5% loss mass at 297 ℃, confirming its advantageous thermal stability as the stationary phase for GC separations [38]. To further investigate the column efficiency of the P6A-C10-OAc column, the Golay curve was determined by measuring the height equivalent to a theoretical plate (HETP) of *n*-dodecane at different flow rates at 120 ℃ and the results are exhibited in Fig. 2b. As shown, the minimum HETP of 0.23 mm was displayed at 0.5 mL/min corresponding to the column

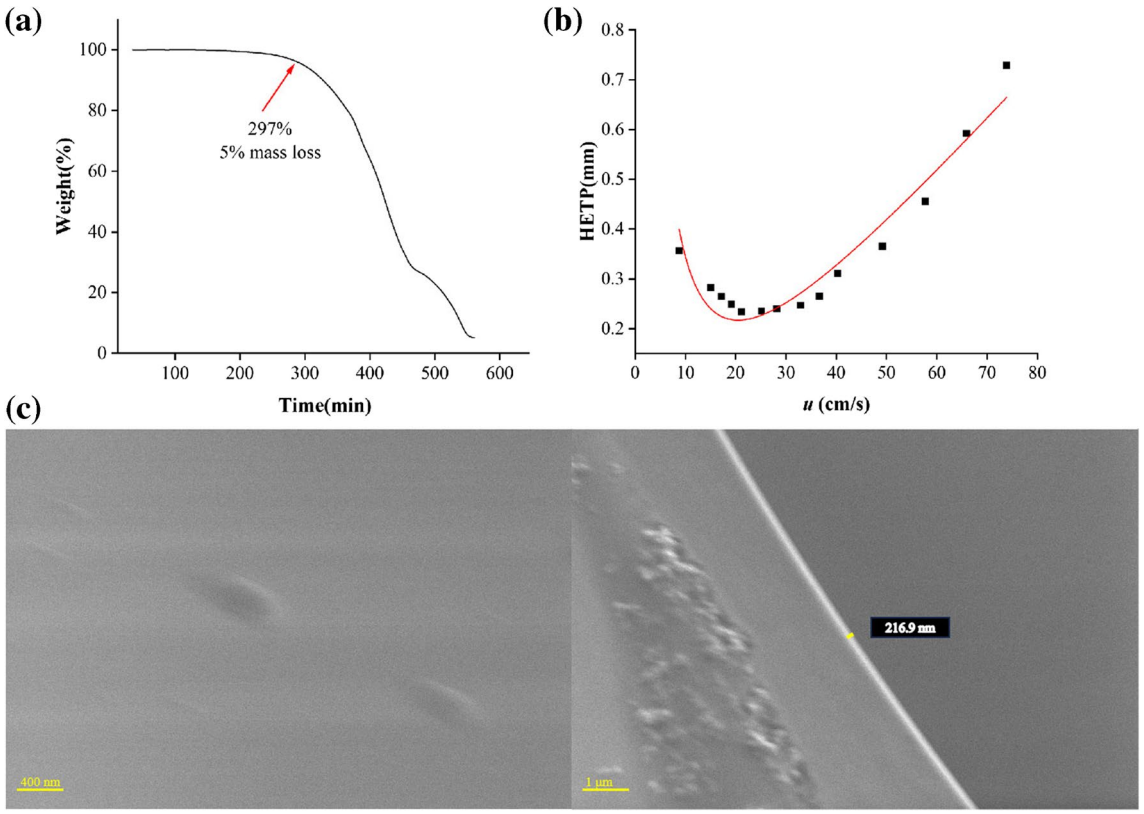

Fig. 2 TGA curve for the P6A-C10-OAc stationary phase from 50 to 600 ℃ at 10 ℃/min. **b** Golay curve of the P6A-C10-OAc column determined by *n*-dodecane at 120 ℃. **c** The cross-section SEM images on the inner wall surface and the coating of the P6A-C10-OAc column

efficiency of 5393 plates/m. Moreover, the polarity of the P6A-C10-OAc stationary phase was characterized by McReynolds constants, which were measured by the five probe compounds containing benzene (*X′*), 1-butanol (*Y′*), 2-pentanone (*Z′*), 1-nitropropane (*U′*), and pyridine (*S′*) at 120 ℃ [39]. The McReynolds constants and average value of the P6A-C10-OAc columns are listed in Table 1. The average of 134 indicates its medium polarity between HP-5 and HP-35. Figure 2c presents the SEM cross-section images of the P6A-C10-OAc column, confirming its good coating with the thickness of approximately 216 nm on the capillary column.

The separation performance of the P6A-C10-OAc column

Then, to explore the selectivity and retention behaviors of the P6A-C10-OAc stationary phase, a mixture of 20 analytes with diverse polarity was utilized and three commercial columns, namely, HP-5, HP-35, and PEG-20M, were used for comparison. Figure 3 exhibits the separation of a mixture of 20 analytes containing alkanes, alcohols, esters, aldehydes, ketones, chlorobenzenes, anilines, phenols, and naphthalenes on the P6A-C10-OAc column and three commercial columns. As shown in Fig. 3, all the analytes were baseline-separated (R>1.5) and showed advantageous separation performance on the P6A-C10-OAc column, but they were co-eluted or overlapped on three commercial columns, such as 1,2,4-trimethylbenzene/octanone (peaks 2/5), dodecane/2,3-dimethylaniline (peaks 8/15), octanol/4-methylbenzaldehyde (peaks 9/10), 1,3-dibromobenzene/2,3-dimethyl phenol (peaks 12/18), and methyl decanoate/2-bromonitrobenzene (peaks 14/20) on the HP-5 column; 1,3-dibromobenzene/2,3-dimethyl phenol (peaks 12/18) on the HP-35 column; and 1,2,4-trimethylbenzene/octanone (peaks 2/5), 4-diethylbenzene/tridecane (peaks 4/11), 3-chlorobenzaldehyde/2-methylnaphthalene (peaks 13/16), and 2,3-dimethyl phenol/2-bromonitrobenzene (peaks 18/20) on the PEG-20M column. The above results proved the advantageous performance of the P6A-C10-OAc column over the commercial columns. Moreover, the elution sequences of 1,3-dibromobenzene/*m*-chlorobenzaldehyde (peaks 12/13, b.p. 230 ℃/213 ℃) and hexadecane/*o*-bromonitrobenzene (peaks 19/20, b.p. 286.79 ℃/261 ℃) were contrast to the boiling point orders on the P6A-C10-OAc column and the PEG-20M column, but were consistent with those on the HP-5 and HP-35 column, proving the stronger π-π interaction between the 3D aromatic cavity of the P6A-C10-OAc stationary phase and the polar analytes. Meanwhile, H-bonding which exists between ester groups and polar analytes could result in longer retention time and different elution sequences during the separation processes between the P6A-C10-OAc stationary phase and the analytes with polar groups, such as the following elution sequences: 1,2,4-trimethylbenzene/hexanol (peaks 2/3, b.p. 168 ℃/151 ℃), dodecane/octanol (peaks 8/9, b.p. 216.3 ℃/196 ℃), methyl decanoate/2,3-dimethylaniline (peaks 14/15, b.p. 224 ℃/221 ℃), 2-methylnaphthalene/2-bromoaniline/2,3-dmethyl phenol (peaks 16/17/18, b.p. 241 ℃/227 ℃/218 ℃). Its high separation performance is due to its unique 3D aromatic skeleton with π-rich cavity, apolar long alkyl chains and polar ester group, and the comprehensive effect of its multiple molecular interactions (π-π stacking, H-bonding, dipole-dipole, and van der Waals forces) with a wide range of analytes.

Furthermore, the separation performance of the P6A-C10-OAc column was investigated by a wide variety of isomer mixtures, including alkylbenzenes, naphthalenes, halobenzenes, benzaldehydes, and phenols. As can be seen, the P6A-C10-OAc column achieved baseline resolution (R>1.5) of 14 aromatic isomers from nonpolar to polar with good peak shapes, demonstrating its ability to recognize aromatic isomers with slight differences in structure and physicochemical properties. Alkylbenzenes (Fig. 4a, b) and naphthalenes (Fig. 4c, d) without special functional groups were well separated on a column. This indicates that the P6A-C10-OAc stationary phase has high selectivity for substituted benzenes. This is attributed to the presence of slightly different π-π interactions between the three-dimensional aromatic skeleton and the single or multiple benzene rings of the analytes. In addition, the polar aromatic isomers with different substituents, such as halobenzenes (Fig. 4e–h), benzaldehydes (Fig. 4i–l), and phenols (Fig. 4m, n), were completely separated on the P6A-C10-OAc column. It is worth noting that benzaldehydes and phenols are analytes that are prone to tailing in GC separation, but they both obtain satisfactory peak shapes on the P6A-C10-OAc

Table 1 McReynolds constants of the P6A-C10-OAc, P5A-C10-OAc, and commercial HP-5, HP-35, and PEG-20M columns

Stationary phases	*X′*	*Y′*	*Z′*	*U′*	*S′*	General polarity	Average
P6A-C10-OAc	122	149	73	202	124	670	134
P5A-C10-OAc	119	136	159	240	115	769	154
HP-5	30	72	62	96	65	325	65
HP-35	98	151	144	228	178	800	160
PEG-20M	303	520	352	557	485	2217	443

X′, benzene; *Y′*, 1-butanol; *Z′*, 2-pentanone; *U′*, 1-nitropropane; *S′*, pyridine. Temperature: 120 ℃

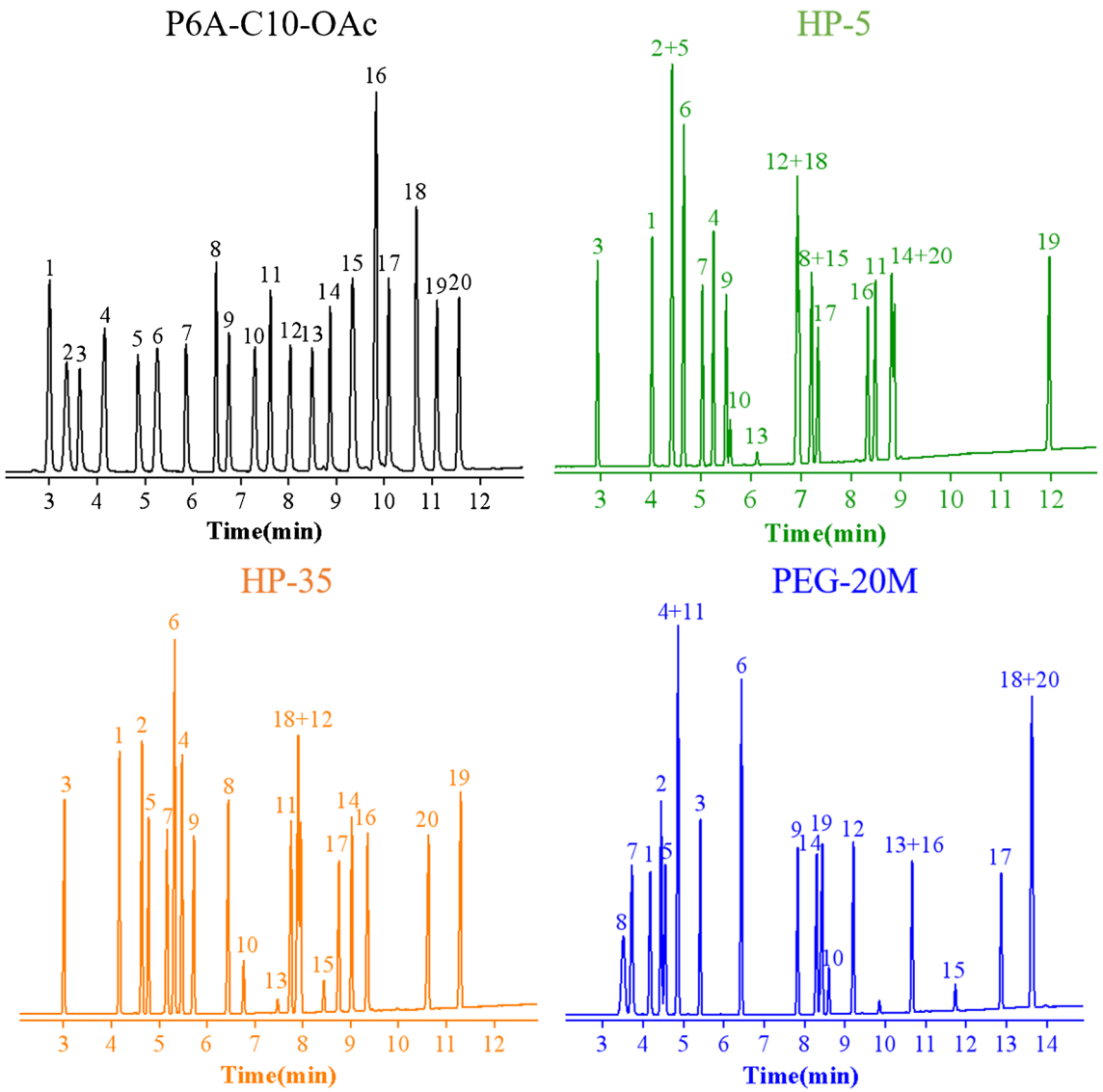

Fig. 3 Separations of the mixture of 20 analytes of diverse types on the P6A-C10-OAc, HP-5, HP-35, and PEG-20M capillary columns. Peaks: (1) 4-dodecane, (2) 1,2,4-trimethylbenzene, (3) *n*-hexanol, (4) 1,4-diethylbenzene, (5) octanone, (6) 1,4-dichlorobenzene, (7) 1-bromoheptane, (8) *n*-dodecane, (9) *n*-octanol, (10) *p*-methylbenzaldehyde, (11) *n*-tridecane, (12) 1,3-dibromobenzene, (13) *m*-chlorobenzaldehyde, (14) methyl enanthate, (15) 2,3-dimethylaniline, (16) 2-methylnaphthalene, (17) 2-bromoaniline, (18) 2,3-dimethyl phenol, (19) *n*-hexadecane, (20) *o*-bromonitrobenzene. Temperature program: 40 ℃ (1 min) to 160 ℃ at 10℃/min, flow rate at 0.6 mL/min

column [40, 41]. As can be noted, compared to the other columns, the P6A-C10-OAc column shows distinct advantages for separations of the isomers of alkylbenzenes and halogenated benzenes (diethylbenzene, ethyltoluene, dibromobenzene, chloronitrobenzene, bromonitrobenzene, bromobenzaldehyde, chlorobenzaldehyde, and nitrobenzaldehyde) in Table S1. The above findings evidenced the high separation capacity and good inertness of the P6A-C10-OAc column towards diverse types of analytes.

Xylene isomers consisted of *ortho*-xylene (*o*X), *para*-xylene (*p*X), *meta*-xylene (*m*X) and are mainly obtained from crude oil and widely applied in the petrochemical and medical industries [42]. They are important industrial raw materials for the preparation of phthalic anhydride, polyethylene terephthalate, and isophthalic acid. Separation of xylene isomers is difficult due to their similar physicochemical properties and molecular structure containing kinetic diameters, boiling points, and dipole moments [43]. The P6A-C10-OAc column was explored for its separation capability towards xylene isomers in comparison with the commercial HP-5, HP-35, and PEG-20M columns. As shown in Fig. 5a, the P6A-C10-OAc column baseline separated the xylene isomers and exhibited dramatically higher resolving capability than three commercial columns. Notably, the commercial HP-5, HP-35, and PEG-20M columns completely

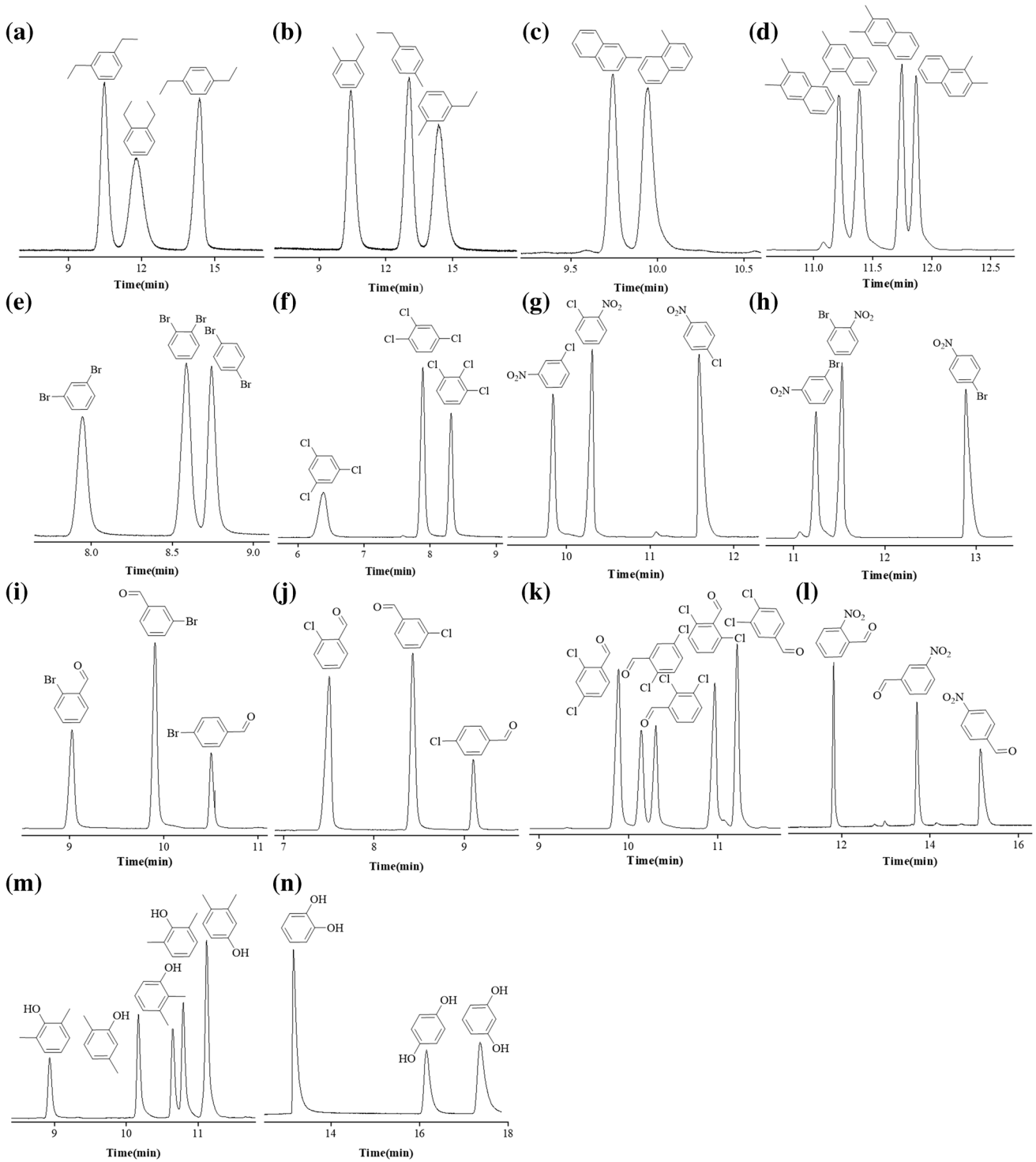

Fig. 4 Separations of isomer mixtures of **a** diethylbenzene, **b** ethyltoluene, **c** methylnaphthalene, **d** dimethylnaphthalene, **e** dibromobenzene, **f** trichlorobenzene, **g** chloronitrobenzene, **h** bromonitrobenzene, **i** bromobenzaldehyde, **j** chlorobenzaldehyde, **k** dichlorobenzaldehyde, **l** nitrobenzaldehyde, **m** xylenol, and **n** hydroquinone on the P6A-C10-OAc column. GC conditions: 40 ℃ (1 min) to 160 ℃ at 10 ℃/min, flow rate at 0.6 mL/min

overlapped the *p*X (b.p. 138.1 ℃) and *m*X (b.p. 139.1 ℃). In Fig. 5b and c, the P6A-C10-OAc column completely resolved the isomers of diethylbenzene and ethyltoluene, proving its advantageous distinguishing capability for the critical pair through stronger π-π stacking interactions with alkylbenzenes due to unique 3D aromatic skeleton.

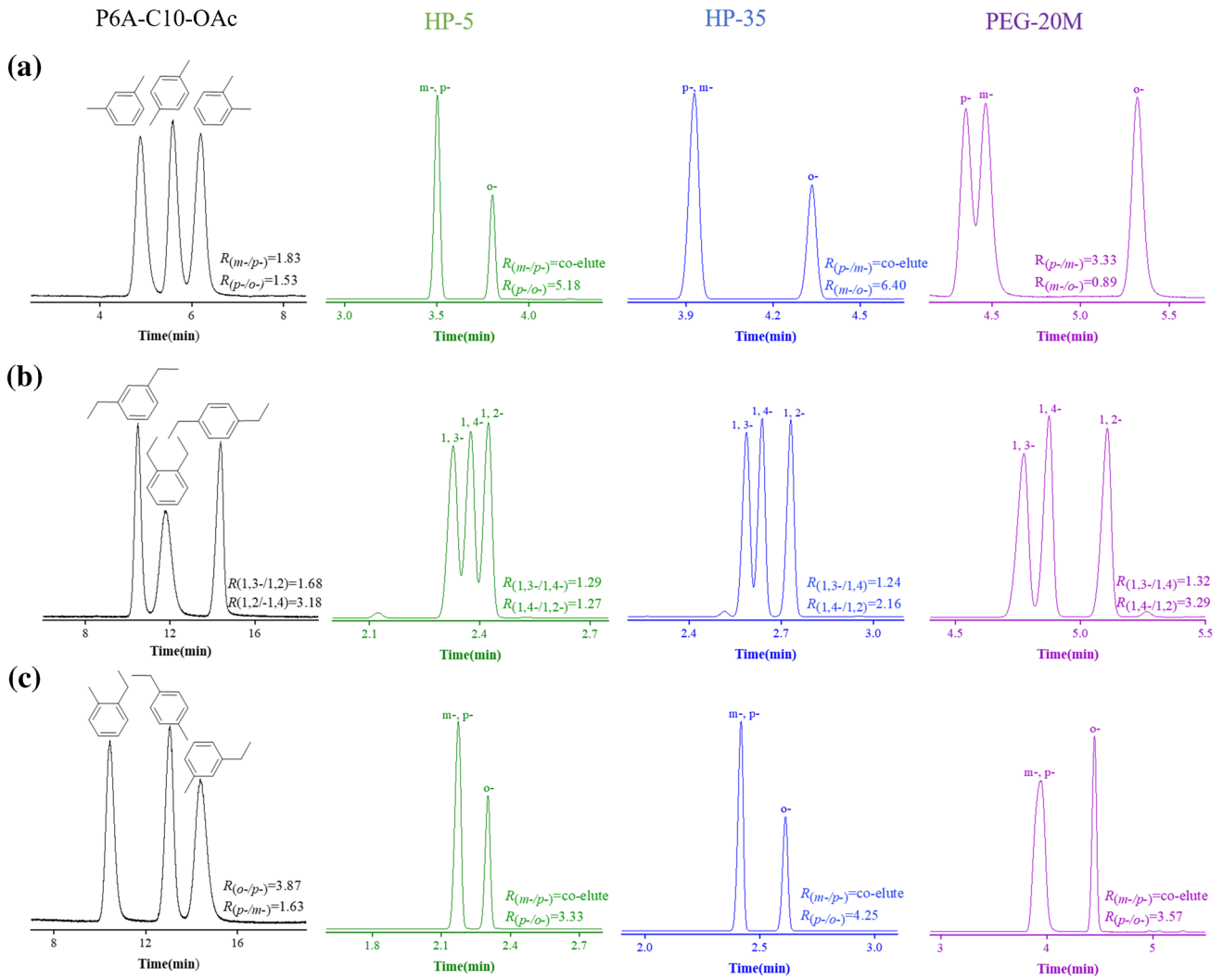

Fig. 5 Separations of isomer mixtures of **a** xylene, **b** diethylbenzene, and **c** ethyltoluene on the P6A-C10-OAc, HP-5, HP-35, and PEG-20M columns. GC conditions: 40 ℃ (1 min) to 160 ℃ at 10 ℃/min, flow rate at 0.6 mL/min

Then, the P6A-C10-OAc column was further explored on its separation capability for halobenzenes, as shown in Fig. 6a for chloronitrobenzenes, Fig. 6b for bromonitrobenzenes, Fig. 6c for bromobenzaldehydes, and Fig. 6d for chlorobenzaldehydes, respectively. The P6A-C10-OAc column baseline resolved all the halobenzenes isomers ($R > 1.5$) while HP-5 column coeluted *p*-/*o*-bromonitrobenzene ($R = 0$) and partially overlapped *p*-/*o*-chloronitrobenzene ($R = 1.41$), *m*-/*p*-bromonitrobenzene ($R = 1.41$), *o*-/*m*-bromobenzaldehyde ($R = 1.21$), *m*-/*p*-bromobenzaldehyde ($R = 0.60$), *o*-/*m*-chlorobenzaldehyde ($R = 1.08$), and *m*-/*p*-chlorobenzaldehyde ($R = 0.87$); HP-35 column partially overlapped *p*-/*o*-bromonitrobenzene ($R = 1.41$) and *m*-/*p*-bromobenzaldehyde ($R = 1.02$); and PEG-20M column completely overlapped *m*-/*p*-bromobenzaldehyde ($R = 0$) and *m*-/*p*-chlorobenzaldehyde ($R = 0$). For the P6A-C10-OAc stationary phase, additional π-π stacking and CH-π interactions from the pillararene framework may also contribute to the high resolving capability of the halobenzene isomers besides the dipole-dipole, H-bonding, and halogen bonding interactions from the polar ester groups. This result indicated the outstanding resolving ability of the P6A-C10-OAc column for the aromatic isomers varying from apolar to polar nature.

To demonstrate the effect of the cavity sizes of pillararenes on their separation performance, the separation capability of the P6A-C10-OAc column was investigated by xylene, diethylbenzene, and ethyltoluene isomers in comparison with the P5A-C10-OAc column. As shown in Fig. 7, the P6A-C10-OAc column achieved baseline resolution for all isomers, whereas the P5A-C10-OAc column completely coeluted three pairs of *m*-/*p*-xylene, *o*-/*p*-diethylbenzene, and *m*-/*p*-ethyltoluene. Therefore, the cavity sizes of pillararenes have significant impact on their separation performance, and larger P6A has better shape matching selectivity with substituted benzenes [44].

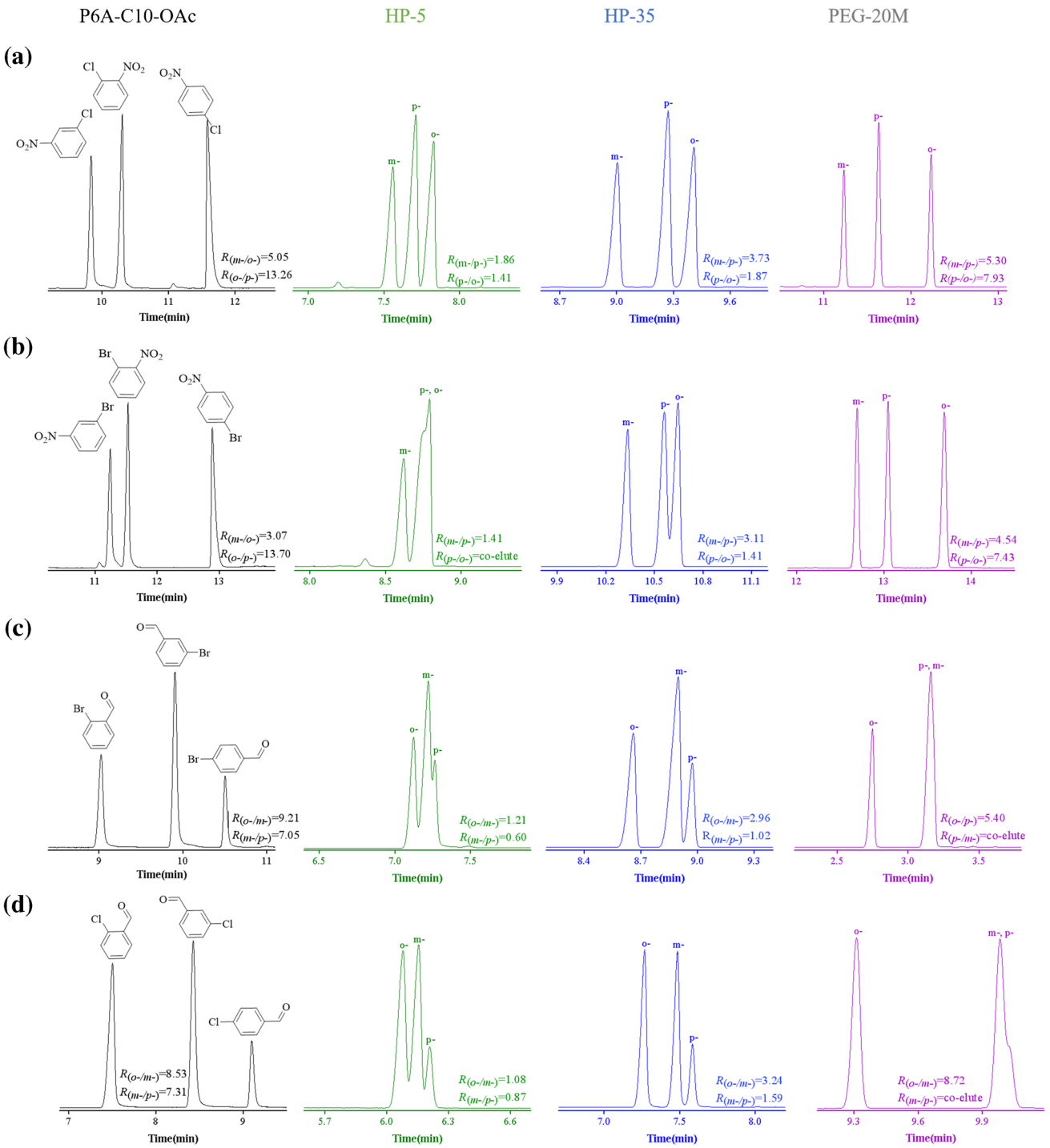

Fig. 6 Separations of isomer mixtures of **a** chloronitrobenzene, **b** bromonitrobenzene, **c** bromobenzaldehyde, and **d** chlorobenzaldehyde on the P6A-C10-OAc, HP-5, HP-35, and PEG-20M columns. GC conditions: 40 ℃ (1 min) to 160 ℃ at 10 ℃/min, flow rate at 0.6 mL/min

The practical application of the capillary column is also an important index to estimate its performance, we used the P6A-C10-OAc column to detect the isomer impurities in the reagent samples. Figure 8 shows the results for the determination of isomer impurities in the three reagent samples of geraniol, *cis*-decahydronaphthalene, and 2-chloroaniline. Table 2 summarizes their content results by the method of peak area normalization. As shown, the measured purity of the samples was consistent with their labeled values. The results proved the great potential of the P6A-C10-OAc column for the determination of the sample purities in GC.

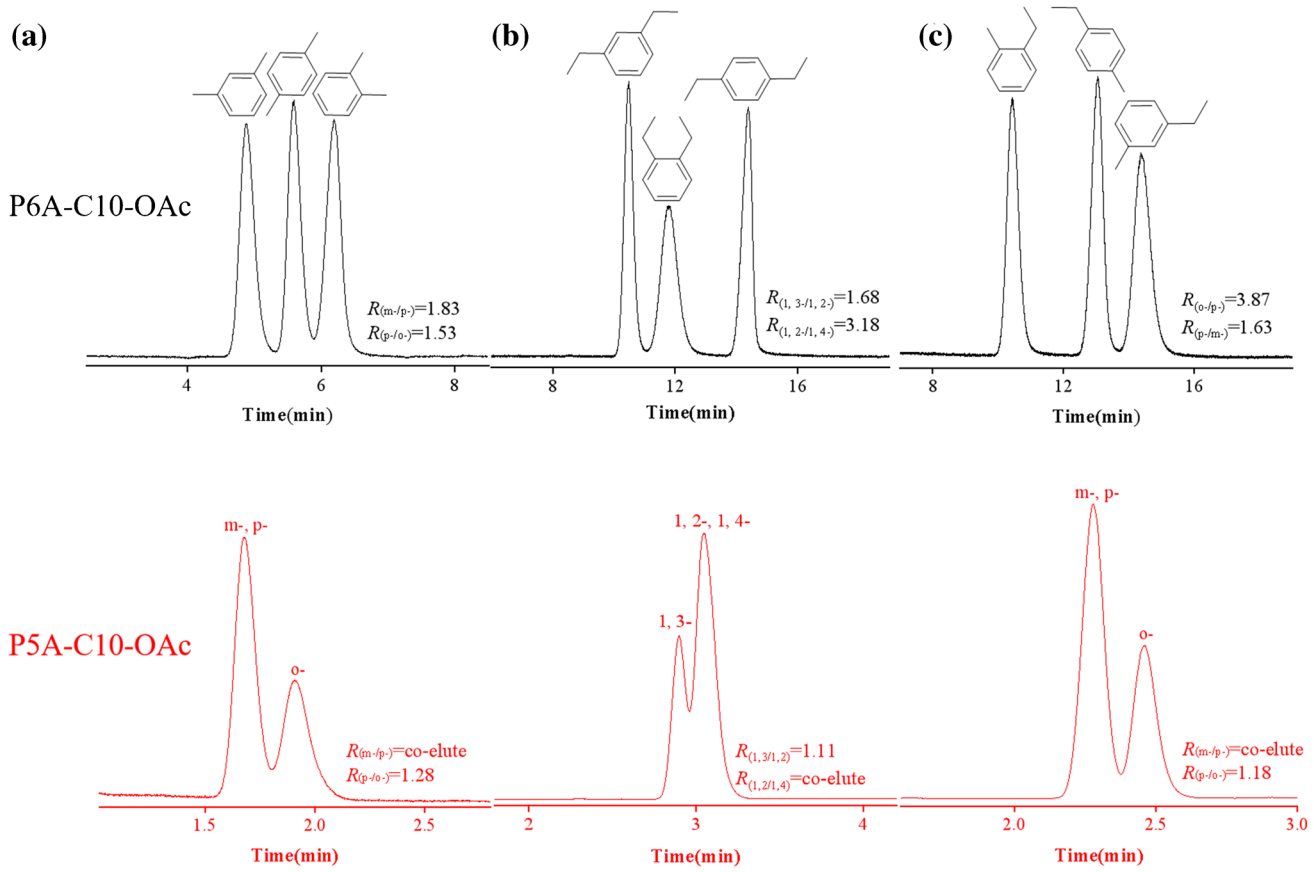

Fig. 7 Separations of isomer mixtures of **a** xylene, **b** diethylbenzene, and **c** ethyltoluene on the P6A-C10-OAc and P5A-C10-OAc columns. GC conditions: 40 ℃ (1 min) to 160 ℃ at 10 ℃/min, flow rate at 0.6 mL/min

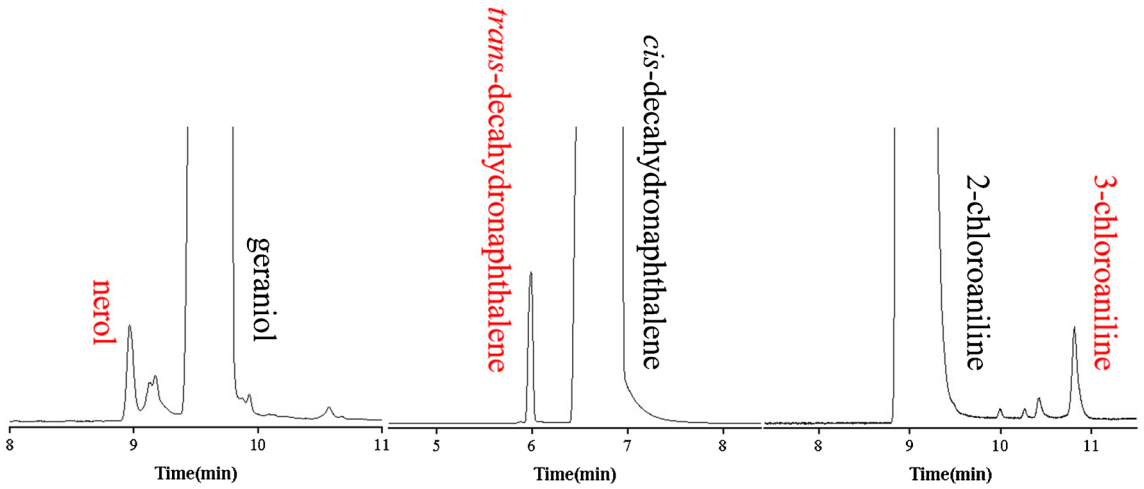

Fig. 8 Applications of the P6A-C10-OAc column for the determination of minor isomer impurities in the real samples of geraniol, *cis*-decahydronaphthalene, and 2-chloroaniline. Temperature program: 40 ℃ (keep 1 min) up to 160 ℃ (keep 5 min) at 10 ℃/min and flow rate: 0.6 mL/min

Table 2 The results of the analysis of isomer impurities in commercial reagent samples by the P6A-C10-OAc column

Samples	Labeled purity (%)	Measured purity (%)	Isomer impurity	Content (%)
Geraniol	97%	98.67%	Nerol	0.49%
cis-Decahydronaphthalene	98%	98.35%	*trans*-Decahydronaphthalene	1.19%
2-Chloroaniline	99%	99.94%	3-Chloroaniline	0.001%

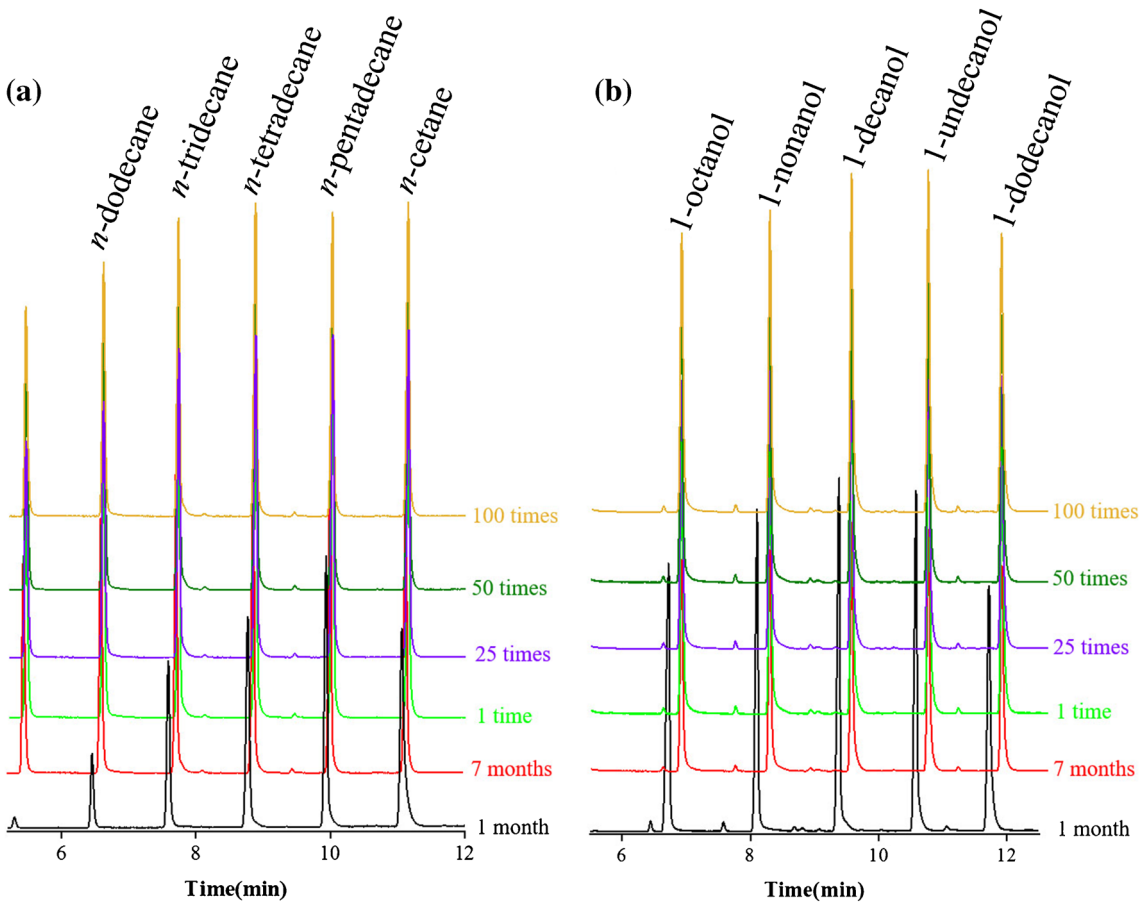

Fig. 9 The repeatability and durability of the P6A-C10-OAc column for the separation of **a** *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, and *n*-cetane and **b** 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, and 1-dodecanol. Temperature program: 40 ℃ (keep 1 min) up to 160 ℃ (keep 5 min) at 10 ℃/min and flow rate: 0.6 mL/min

Repeatability and durability of the P6A-C10-OAc column

The repeatability and durability of the P6A-C10-OAc column were investigated. Figure 9 shows the chromatograms of *n*-alkanes (*n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, *n*-hexadecane) and alcohols (1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol) obtained when the P6A-C10-OAc column was used for 1 month and 7 months, and after the column was subjected to 1, 25, 50, and 100 injections. There was no obvious change in the retention time of *n*-alkanes and alcohols, and the RSD of the retention time was less than 0.18% (Table 3), indicating the good repeatability and durability of the P6A-C10-OAc column.

Table 3 Repeatability of the P6A-C10-OAc capillary column on the retention time

Analytes	Retention time (min)				RSD (%)
	1 time	25 times	50 times	100 times	
n-Dodecane	6.602	6.602	6.604	6.606	0.03
n-Tridecane	7.724	7.724	7.725	7.725	0.07
n-Tetradecane	8.873	8.872	8.873	8.873	0.06
n-Pentadecane	10.020	10.023	10.022	10.021	0.01
n-Hexadecane	11.146	11.147	11.148	11.147	0.07
1-Octanol	6.889	6.884	6.884	6.882	0.04
1-Nonanol	8.242	8.237	8.237	8.236	0.03
1-Decanol	9.493	9.490	9.489	9.457	0.18
1-Undecanol	10.671	10.667	10.667	10.665	0.02
1-Dodecanol	11.794	11.792	11.793	11.791	0.01

Conclusion

This work describes the separation performance of the polar ester groups functionalized pillar[6]arene (P6A-C10-OAc) as the stationary phase for GC separations. As demonstrated, the P6A-C10-OAc column exhibits high-resolution performance for a wide range of analytes and isomers mainly through π-π stacking, CH-π, H-bonding, dipole-dipole, halogen-bonding, and dispersion interactions. Particularly, it achieved baseline resolution of the challenging isomers of xylenes, diethylbenzenes, ethyltoluenes, and halobenzenes and shows distinct advantages over the commercial HP-5, HP-35, and PEG-20M columns. Furthermore, we demonstrate that the cavity size of pillararenes plays an important role in the efficient separation of aromatic isomers. This work demonstrates the great potential of pillararenes as highly selective stationary phases for GC separations.

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Author contribution Yanli Song: investigation, methodology, formal analysis, visualization, validation, writing—original draft, writing—review and editing. Wen Li: investigation, methodology, formal analysis, validation. Mengyi Ba: methodology, visualization. Yuanyuan Zhang: validation, formal analysis. Haixin Liu: visualization, formal analysis. Xiang Xu: methodology, investigation. Haoyu Su: methodology, investigation. Zhiqiang Cai: conceptualization, methodology, supervision, resources, funding acquisition, writing—review and editing. Xianming Liu: methodology, supervision. Tao Sun: conceptualization, methodology, supervision, resources, funding acquisition, writing—review and editing.

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Declarations

Competing interests The authors declare no competing interests.

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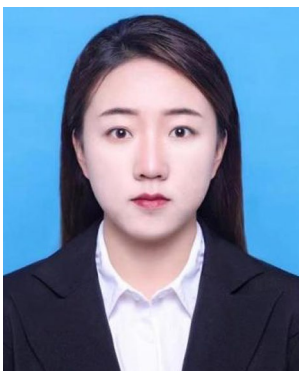

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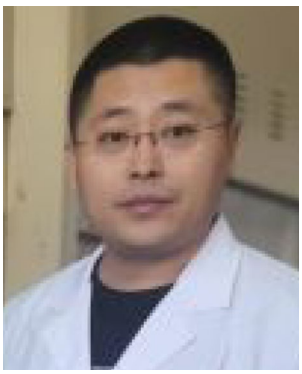

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