



Enhancement of molecular shape selectivity by in situ anion-exchange in poly(octadecylimidazolium) silica column

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ABSTRACT

This paper demonstrates that in situ anion exchange could be successfully applied as a new method for modifying the surface properties of a poly(octadecylimidazolium)-grafted silica stationary phase to tune and enhance selectivity. Specifically, the original stationary phase was prepared by surface-initiated radical chain-transfer polymerization of 1-vinyl-3-octadecylimidazolium bromide as an ionic liquid monomer; the Br⁻ counter anion was then exchanged for methyl orange *via* an in-column process. As evaluated *via* the separation of constrained isomers of polycyclic aromatic hydrocarbons (PAHs), the in situ exchange enhanced the molecular shape-selectivity performance. Enhanced selectivity was also confirmed using Standard Reference Material (SRM) 869b (column selectivity test mixture) and SRM 1647e (16 priority pollutant PAHs). The reproducibility of new column was tested *via* the separation of pyrene, triphenylene, benzo[*a*]anthracene and chrysene with methanol as eluent at 10 °C and the RSD values ($n = 12$) of the retention factors of them are within 0.27–0.77%.

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1. Introduction

Ionic liquids (ILs) [1] have attracted considerable research interest due to their unique physical and chemical properties such as low flammability, low vapour pressure, low melting point, and high thermal stability. In addition, there is a huge structural diversity of ILs with a nearly unlimited number of anion–cation combinations. This opens up the possibility of further tailoring the physico-chemical properties of ILs according to the specific requirements of an application [2]. In addition, ILs can be immobilized on silica [3], polymer [4], resin [5], hollow-fibre [6], multi-walled carbon nanotube [7], and zirconia nanoparticle [8] supports for applications as recycled catalysts [2,3], hybrid electrolytes [7,8], solid-phase extraction absorbents [9,10], and chromatographic packing materials [11], etc.

Recently, ILs were immobilized on fused-silica capillaries as a new separation material for gas chromatography (GC) [12,13] or capillary electrophoresis (CE) [14]. ILs have also been immobilized on silica gel as new stationary phases in high-performance liquid chromatography (HPLC) as an extension of the first report of bonding them to silica and their use for the separation of

alkaloids in 2004 [15]. Subsequently, we prepared two anion-exchange stationary phases based on *N*-methylimidazolium- and imidazolium-functionalized silica for the separation of inorganic and organic anions [16,17]. We also prepared two zwitterionic stationary phases based on sulfonate IL-modified silica for the simultaneous separation of anions and cations [18,19]. Stalcup et al. [20–22] synthesized IL-modified silica stationary phases and characterized them using the linear solvation energy relationship method. This previous research shows that these new phases are capable of presenting a variety of interactions including hydrophobic, electrostatic, π – π and hydrogen-bonding interactions for the separation of different analytes [15–24]. Actually, the adoption of the “ionic liquid” nomenclature to describe these phases has been somewhat controversial because covalent attachment to a solid support arguably reduces the parallels with true ionic liquids. However, ionic liquid analogues are useful because there are ample examples because of their structure designability.

The properties of IL-modified materials can be easily changed by modifying the anions [25,26]. Anion metathesis is commonly used in the chemistry of imidazolium moieties through which a large variety of anions can be introduced. For example, IL-modified carbon nanotubes with reversible, switchable solubility between aqueous and organic solvents were induced by anion exchange [7]. The conversion of IL-modified gold nanoparticles [27] or silica nanoparticle networks [28] from hydrophilic to hydrophobic is rendered possible by anion-exchange. In our previous report [29], ionic self-assembly was used to modify the counteranions

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of an ionic liquid-modified silica stationary phase to enhance chromatographic selectivity. Using this method, ultra-high selectivity towards polycyclic aromatic hydrocarbons (PAHs) could be induced.

In this study, *in situ* anion-exchange was used as a new and facile strategy to tune the shape selectivity towards constrained isomers of PAHs in an IL-modified silica column. *In situ* anion-exchange has some advantages in terms of simplicity of the synthetic step or the laboratory procedure of doing an in-tube approach rather than an anion-exchange reaction before packing the column. It should be noted that the anions were immobilized *via* ionic interaction which differs from common in-column coating immobilization through hydrophobic interaction [30]. As far as we know, there is no report of using *in situ* anion-exchange to tune the properties of a chromatographic column.

2. Experimental

2.1. Materials and reagents

Poly(octadecylimidazolium)-grafted silica with bromide counteranions (SIL-Br) was synthesized, characterized, and packed into two stainless steel columns (150 mm × 4.6 mm i.d.). A poly(octadecylimidazolium)-grafted silica with methyl orange (MO) counteranions (SIL-MO) was derived from one of the SIL-Br columns *via in situ* anion-exchange in the column. Porous silica particles (YMC) with 5 μm diameters, average pore sizes of 12 nm, and a specific surface area (S_{BET}) of 300 m² g⁻¹ were used as a support. Two reference columns were used for comparison: a commercial monomeric octadecyl silica (C₁₈) column and a polymeric octadecyl silica (C₁₈) column. The monomeric C₁₈ (C₁₈-m) column (Inertsil, ODS-3, column size 150 mm × 4.6 mm i.d. with particle sizes of 5.5 μm, pore sizes of 10 nm, and surface area of 450 m² g⁻¹) was purchased from G. L. Sciences (Tokyo, Japan). The polymeric C₁₈ (C₁₈-p) column (150 mm × 4.6 mm i.d., Shodex, C18 P, particle sizes of 5 μm, pore sizes of 10 nm and surface area of 300 m² g⁻¹ with unreacted silanol group end caps) containing 17.5% C was obtained from Shodex (Tokyo, Japan).

3-Mercaptopropyltrimethoxysilane (MPS), 1-vinylimidazole (99%), and 1-bromooctadecane were purchased from Azmax (Chiba, Japan), TCI (Tokyo, Japan), and Wako (Osaka, Japan), respectively. Azobisisobutyronitrile (AIBN) was obtained from Nacalai Tesque, Inc. (Kyoto, Japan) and purified by recrystallization from methanol before use. Methyl orange (MO) dye was obtained from Kanto Chemical Co., Inc. (Kyoto, Japan). Standard Reference Material (SRM) 869b, which is a Column Selectivity Test Mixture for Liquid Chromatography, and SRM 1647e, which contains priority pollutant PAHs, were obtained from the Standard Reference Materials Program (NIST, Gaithersburg, MD). All other PAHs and alkylbenzenes were commercially available and used without purification.

2.2. Synthesis of Sil-MPS

Mercaptopropyl modified silica (Sil-MPS) was prepared by mixing activated silica (6.0 g) and excess 3-mercaptopropyltrimethoxysilane (3.0 g) in 30 mL of dry toluene. After the mixture was mechanically stirred and refluxed for 68 h, the reaction was stopped and cooled to room temperature. Sil-MPS was obtained after successive washing with large volumes of toluene, a methanol–water mixture, methanol, and ether and then drying under vacuum.

2.3. Synthesis of IL monomer

The synthesis of 1-vinyl-3-octadecylimidazolium bromide ([C₁₈VIm]Br) followed the same procedure in a previous report

[29]. In brief, 1-vinylimidazole was mixed with a slight excess of 1-bromooctadecane in acetonitrile and the mixture was stirred at 60 °C for three days. The product was precipitated in diethyl ether and dried under vacuum, resulting in a high yield of a white solid powder.

2.4. Synthesis of SIL-Br

The new poly(octadecylimidazolium)-grafted silica phase was prepared by grafting the IL monomers onto Sil-MPS through a surface radical chain-transfer polymerization method that was modified from a previous publication [29] (Fig. S1). First, 6.1 g of Sil-MPS was added to a 100 mL three-neck round-bottomed flask. Then, the same amount of [C₁₈VIm]Br was dissolved in 30 mL of chloroform and added to the flask. After 20 min of bubbling N₂ through the solution, 1% AIBN was added. The mixture was stirred at 60 °C for 32 h under an N₂ atmosphere. The obtained polymer-grafted silica was filtered and washed consecutively with chloroform, ethanol, ethanol–water, methanol, and diethyl ether. The resultant SIL-Br was either used for characterization or packed into two columns (150 mm × 4.6 mm i.d.) after being dried under vacuum.

2.5. Preparation of SIL-MO

SIL-MO was derived by modifying one of the packed SIL-Br columns *via in situ* anion exchange. An MO aqueous solution (10 mmol L⁻¹) was pumped into the SIL-Br column at a flow rate of 1 mL min⁻¹ at 30 °C until red waste liquid eluted from the column. This process was also monitored by the transition of the chromatographic baseline. The total time for the anion exchange was 68 min resulting in the exchange of the small inorganic counteranions (Br⁻) with large, strong organic anions (MO), i.e. the SIL-Br column was converted to a SIL-MO column. The column was then continuously flushed with a large volume of water and methanol until the waste solvent was colourless.

2.6. Characterization

Since a new silica base was used and the synthetic method was modified, the MPS and octadecylimidazolium moieties grafted onto the silica were checked by elemental analysis and diffuse reflectance infrared Fourier transformation (DRIFT) spectra, as described previously [31].

2.7. Chromatographic conditions

The HPLC system (JASCO, Tokyo, Japan) consisted of an LC-NetII/ADC communication device, a DG-2080-53 3 line degasser, a PU-2080 Plus Intelligent HPLC pump, a UV-2075 Plus Intelligent UV/vis detector, and a Rheodyne injector with a 20 μL sample loop. All chromatographic data were obtained using a JASCO ChromNAV chromatography data system. A mixture of HPLC-grade methanol and Millipore water was used as components of the mobile phase. All samples were directly dissolved in methanol, and *in situ* anion exchange was done at room temperature. The chromatographic separation was executed at 10 °C using a column jacket with a circulator that features a heating and cooling system. A low temperature was selected not only to increase the column selectivity, but also considering the column stability. The flow rate was 1.0 mL min⁻¹, the detection wavelength was 254 nm, and the injection volume was 5 μL. The retention time of D₂O was used as the void volume (t_0) marker. The retention factors (k) of the analytes were calculated according to $k = (t_R - t_0)/t_0$, where t_R is the retention time of the analyte. The separation factor (α) is defined as the ratio of the retention factors of the two solutes being analyzed.

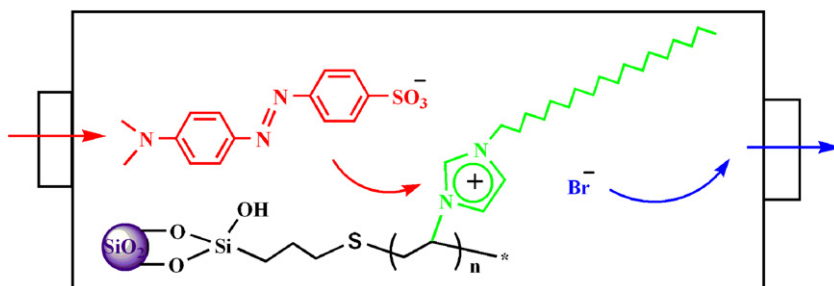


Fig. 1. Scheme of in situ anion-exchange reaction happened in poly(octadecylimidazolium)-grafted silica column.

The 1-octanol/water partition coefficients ($\log P_{o/w}$), which are usually used to represent molecular hydrophobicity, of the alkylbenzenes and PAHs were determined from the retention factor with the ODS column stated above using $\log P_{o/w} = 3.759 + 4.207 \log k$ ($r = 0.99997$) according to a procedure described in our previous work [32].

3. Results and discussion

3.1. Synthesis of SIL-Br and SIL-MO

First, the silica surface was modified with 3-mercaptopropyltrimethoxysilane. A long-chain IL monomer ($[C_{18}VIm]Br$) was prepared and then grafted onto the 3-mercaptopropyl silica by surface radical chain-transfer polymerization, as reported previously [29]. The obtained SIL-Br was packed into two columns; one of the columns was then modified by elution of MO solvent. After a certain volume of MO was poured into the column, the counteranions (bromide) were completely exchanged by MO to yield SIL-MO, as shown in Fig. 1. This method is different from a previously reported method that involved an anion-exchange reaction before packing [29]. Since the counterions were changed after packing in this experiment, the end point of the reaction is easy to discern from either the breakthrough curve or the colour of the waste solvent.

3.2. Characterizations

From elemental analyses, the contents of Sil-MPS and SIL-Br were determined to be C 3.13%, H 1.14% and C 20.05%, H 3.46%, N 1.83%, respectively. The surface coverages were calculated according to the following equations [18]:

$$\text{Sil-MPS} (\text{mmol m}^{-2}) = \frac{\%C}{36 \times (1 - \%C - \%H) \times S} = 3.03 \quad (1)$$

$$\text{SIL-Br} (\text{mmol m}^{-2}) = \frac{\%N}{28 \times (1 - \%C - \%H - \%N - \%Br) \times S} = 3.14 \quad (2)$$

where %C, %H, %N, and %Br represent the percentages of carbon, hydrogen, nitrogen, and bromide, respectively. %Br is calculated from %N with respect to the stoichiometric ratio (%N : %Br = 28:80; therefore, %Br = 5.23%). S is the specific surface area of the silica support ($300 \text{ m}^2 \text{ g}^{-1}$). The amounts of mercaptopropyl and octadecylimidazolium moieties attached to the silica surface were calculated to be 3.03 and $3.14 \mu\text{mol m}^{-2}$ for Sil-MPS and SIL-Br, respectively.

After the in-column exchange of the counterions from Br^- to MO, the column would have to be unpacked to obtain the modified silica for characterizations; therefore, the modified silica was not directly characterized. The amount of methyl orange incorporated

into the phase could be estimated by knowing its concentration and the volume pumped through the column before breakthrough. However, in a previous study, we proved that most of the Br^- could be replaced by MO to form SIL-MO from the elemental analysis of SIL-MO obtained by the anion-exchange reaction before packing [29]. The conversion of SIL-Br to SIL-MO can also be confirmed by the significant enhancement of the selectivity towards isomers of PAHs, as described below.

The immobilization of MPS and the polymerization of octadecylimidazolium IL monomers were also confirmed by DRIFT spectroscopy. Differences in the wave numbers and intensities of the absorption bands are clearly observed in the spectra of Sil-MPS and SIL-Br, as shown in the supporting information (Fig. S2). The spectrum of SIL-Br features a group of peaks at 2923 and 2853 cm^{-1} , which are attributed to the C–H bond stretching of the long alkyl chains of octadecylimidazolium. The imidazolium group introduced by IL is clearly indicated by the characteristic imidazolium peaks at 1565 and 1463 cm^{-1} [3]. These results indicate that octadecylimidazolium could be successfully immobilized on the silica surface.

3.3. Retention mode

To evaluate the retention mode of the poly(octadecylimidazolium) columns (i.e. SIL-Br and SIL-MO), separation of a Tanaka test mixture including uracil, caffeine, phenol, butylbenzene, *o*-terphenyl, amylbenzene, and triphenylene was performed using C_{18} -m, C_{18} -p, SIL-Br, and SIL-MO columns with $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (8:2, v/v) as the mobile phase, as shown in Fig. 2. From the figure, it is evident that there are two primary differences in the performances of the C_{18} columns (Fig. 2a and b) and the poly(octadecylimidazolium) columns (Fig. 2c and d): (1) Using

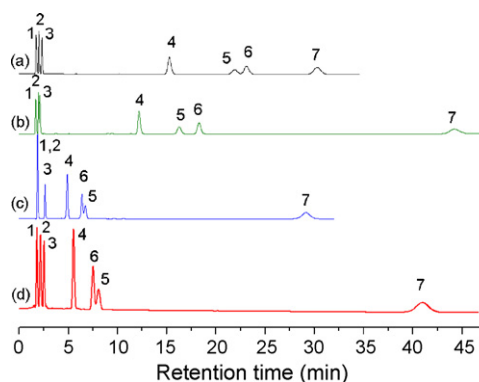


Fig. 2. Separation of Tanaka test mixture including uracil (1), caffeine (2), phenol (3), butylbenzene (4), *o*-terphenyl (5), amylbenzene (6), and triphenylene (7). Stationary phase: (a) C_{18} -m, (b) C_{18} -p, (c) SIL-Br and (d) SIL-MO. Mobile phase: $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (8:2, v/v). Flow-rate: 1.0 mL min^{-1} . Detection: UV 254 nm. Column temperature: 10°C . Injection volume: $5 \mu\text{L}$.

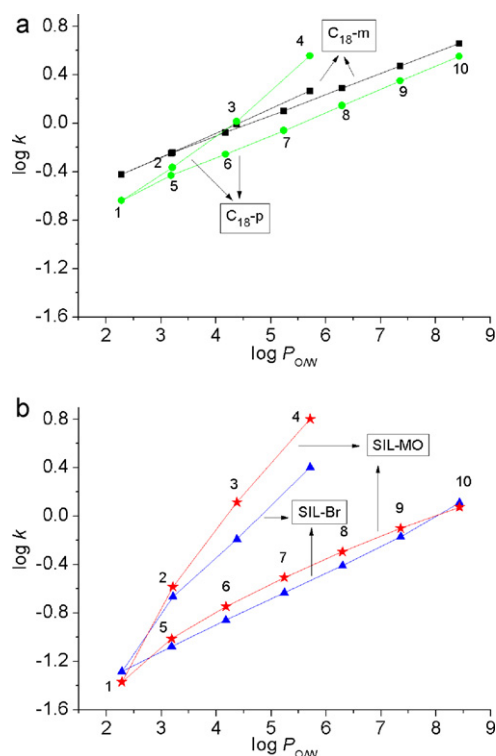


Fig. 3. The relationships of $\log k$ and $\log P_{o/w}$ for commercial columns including C_{18} -m (■) and C_{18} -p (●) (a) and new imidazolium columns including SIL-Br (▲) and SIL-MO (★) (Fig. 2b). Analytes: benzene (1), naphthalene (2), anthracene (3), naphthacene (4), ethylbenzene (5), butylbenzene (6), hexylbenzene (7), octylbenzene (8), decylbenzene (9), and dodecylbenzene (10). Mobile phase: 100% methanol. Other chromatographic conditions were the same as in Fig. 2.

the SIL-Br and SIL-MO columns, *o*-terphenyl was eluted later than amylybenzene, whereas the retention order is reversed using the C_{18} -m and C_{18} -p columns. (2) The selectivity towards *o*-terphenyl and triphenylene in the SIL-Br ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 8.48$) and SIL-MO ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 8.70$) columns is much higher than that in the C_{18} -m ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 1.78$) and C_{18} -p ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 3.42$) columns, which indicates that the SIL-Br and SIL-MO columns have high planar selectivity [33,34]. These characteristics were both derived from the incorporation of the imidazolium groups into the poly(octadecylimidazolium) columns.

The retention mode and the extent of hydrophobic interactions among the solutes and packing materials in HPLC could also be determined by retention studies using alkylbenzenes and PAHs as the solutes [35]. Similar results also could be found in the column modified by ionic self-assembly before packing in ref. [29]; however, since new kind of silica was used and different chain density of octadecylimidazolium was obtained here, the retention of alkylbenzenes and PAHs and their selectivity have some change. Fig. 3 shows the relationship between $\log k$ and $\log P_{o/w}$ for C_{18} -m, C_{18} -p, SIL-Br, and SIL-MO. It was observed that SIL-Br showed a higher retention of PAHs than alkylbenzenes. For instance, the $\log P_{o/w}$ of naphthacene (5.71) is much smaller than that of decylbenzene (7.36) but the $\log k$ value of naphthacene (0.40) is clearly higher than that of decylbenzene (0.11) when using SIL-Br. After the bromide counteranions were changed to MO to form SIL-MO, the difference between the $\log k$ values of naphthacene (0.80) and dodecylbenzene (0.08) increased. An inferior selectivity to PAHs and alkylbenzenes was found for C_{18} columns. Especially for C_{18} -m, the $\log k$ vs. $\log P_{o/w}$ plots for alkylbenzenes and PAHs were almost equivalent.

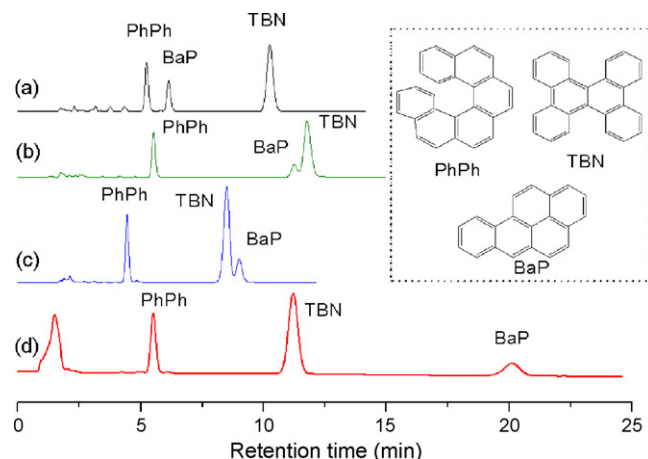


Fig. 4. Separation of SRM 869b test mixture with (a) C_{18} -m, (b) C_{18} -p, (c) SIL-Br and (d) SIL-MO columns with methanol as mobile phase at 10 °C. Chromatographic conditions are the same as in Fig. 3.

3.4. SRM 869b

SRM 869b, which is the column selectivity test mixture for LC, consists of phenanthro[3,4-*c*]phenanthrene (PhPh), tetrabenzonaphthalene (TBN), and benzo[*a*]pyrene (BaP) and was used to assess the shape-selectivity performance of the new columns [36,37]. In general, the later elution of BaP relative to TBN ($\alpha_{\text{TBN}/\text{BaP}} < 1$) indicates a polymeric-like retention behaviour with high shape selectivity. The reverse result ($\alpha_{\text{TBN}/\text{BaP}} > 1$) indicates monomeric-like retention behaviour and low shape selectivity such as in C_{18} -m ($\alpha_{\text{TBN}/\text{BaP}} = 1.93$), as shown in Fig. 4. From the figure, we can see that SIL-Br and SIL-MO both presented polymeric-like enhanced selectivity and SIL-MO ($\alpha_{\text{TBN}/\text{BaP}} = 0.56$) shows a much higher selectivity than SIL-Br ($\alpha_{\text{TBN}/\text{BaP}} = 0.93$). The alkyl chain densities of SIL-Br.


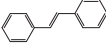


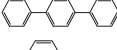






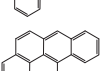


3.5. Selectivity towards PAH isomers

Since poly(octadecylimidazolium) columns showed very high shape selectivity towards PAHs, they should be ideal for the separation of constrained isomers of PAHs. The retention factors (k) and separation factors (α) of some PAH isomers using C_{18} -m, C_{18} -p, SIL-Br, and SIL-MO columns are compared in Table 1. From the results, it is evident that SIL-Br shows a higher selectivity than the monomeric ODS column (C_{18} -m) and sometimes a higher or comparable selectivity than the polymeric ODS column (C_{18} -p). However, SIL-MO presents considerably higher selectivity towards isomers than C_{18} -p. For example, the selectivities towards *m*-terphenyl and *p*-terphenyl were 1.03, 1.43, 1.44, and 3.28 for C_{18} -m, C_{18} -p, SIL-Br, and SIL-MO, respectively. The best separation of the PAH isomers including pyrene, triphenylene, benzo[*a*]anthracene, chrysene and naphthacene was obtained using the SIL-MO column (figure not shown).

3.6. SRM 1647e

A high selectivity towards constrained isomers is beneficial for the separation of PAHs. Fig. 5 shows the separation of SRM 1647e, which is composed of 16 priority pollutant PAHs, using C_{18} -m, C_{18} -p, SIL-Br and SIL-MO columns with methanol as the eluent. Some position isomer pairs such as phenanthrene and anthracene and benzo[*a*]anthracene and chrysene could not be separated by C_{18} -m, C_{18} -p, or SIL-Br. However, the 16 PAHs were completely separated using SIL-MO under the same chromatographic conditions. The complex mixture is resolved in less than 35 min with SIL-MO working in isocratic conditions, which is the common separation

Table 1
Retention factors (k) and separation factor (α) of PAH isomers.

PAH isomers	Structure	C ₁₈ -m		C ₁₈ -p		SIL-Br		SIL-MO	
		k	α	k	α	k	α	k	α
<i>cis</i> -Stilbene		0.75	(1)	0.49	(1)	0.17	(1)	0.23	(1)
<i>trans</i> -Stilbene		0.78	1.04	0.66	1.36	0.38	2.15	0.62	2.69
<i>o</i> -Terphenyl		0.88	(1)	0.55	(1)	0.19	(1)	0.30	(1)
<i>m</i> -Terphenyl		1.20	1.36	0.94	1.70	0.48	2.49	0.71	2.34
<i>p</i> -Terphenyl		1.24	1.41	1.34	2.44	0.69	3.63	2.32	7.73
Phenanthrene		0.94	(1)	0.93	(1)	0.62	(1)	0.92	(1)
Anthracene		0.99	1.05	1.03	1.12	0.64	1.04	1.30	1.42
Pyrene		1.44	(1)	1.71	(1)	1.20	(1)	1.83	(1)
Triphenylene		1.57	1.09	2.05	1.20	1.64	1.37	2.63	1.44
Benzo[<i>a</i>]anthracene		1.60	1.11	2.31	1.35	1.73	1.44	3.69	2.02
Chrysene		1.63	1.13	2.49	1.46	1.81	1.51	4.92	2.69
Naphthacene		1.85	1.28	3.60	2.11	2.52	2.10	6.37	3.48
Benzo[<i>e</i>]pyrene		2.45	(1)	4.18	(1)	3.34	(1)	5.85	(1)
Benzo[<i>a</i>]pyrene		2.65	1.09	5.27	1.26	3.91	1.17	10.16	1.74

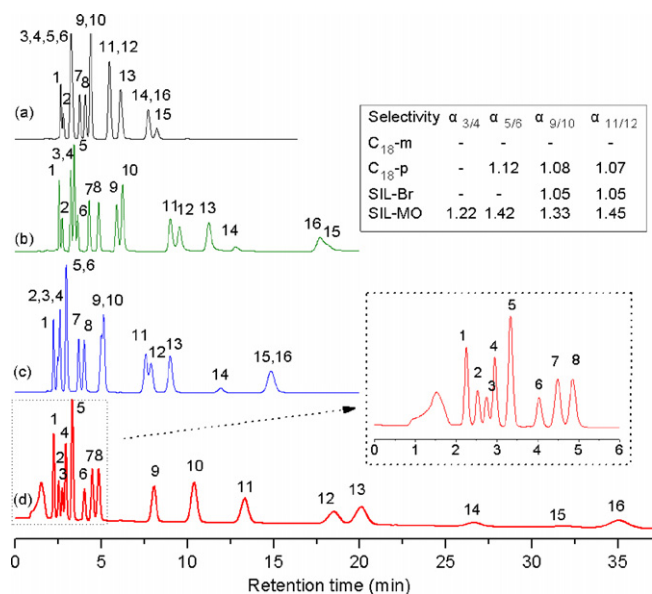


Fig. 5. Separation of the 16 Priority Pollutant PAHs (SRM 1647e) with (a) C₁₈-m, (b) C₁₈-p, (c) SIL-Br and (d) SIL-MO columns with methanol as mobile phase at 10°C. Key: naphthalene (1), acenaphthylene (2), acenaphthene (3), fluorine (4), phenanthrene (5), anthracene (6), fluoranthene (7), pyrene (8), benzo[*a*]anthracene (9), chrysene (10), benzo[*b*]fluoranthene (11), benzo[*k*]fluoranthene (12), benzo[*a*]pyrene (13), dibenzo[*a,h*]anthracene (14), benzo[*ghi*]perylene (15), indeno[1,2,3-*cd*]pyrene (16). Chromatographic conditions are the same as in Fig. 3.

time when working in gradient elution mode with conventional columns. The separation factors of some key sets for all columns are noted in Fig. 5.

3.7. Retention mechanism

Compared with a common C₁₈ column, poly(octadecylimidazolium)-grafted silica phases (i.e. SIL-Br and SIL-MO) not only have long octadecyl chains to increase the hydrophobic interactions, but also contain charged polar imidazolium groups to incorporate interactions such as π - π and hydrogen-bonding interactions. As described above, high planar selectivity towards *o*-terphenyl and triphenylene were obtained both in the SIL-Br ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 8.48$) and SIL-MO ($\alpha_{\text{triphenylene}/o\text{-terphenyl}} = 8.70$) because of the imbedded imidazolium. After the in situ anion exchange from bromide to MO, large organic azobenzene anions were imported. Interestingly, MO not only resulted in the incorporation of additional hydrophobic and π - π interactions, but also increased the order of the original long C₁₈ chains [38]. We know that increased ordering and greater shape selectivity also could be caused by increasing the ligand density of stationary phases. However, as shown in Table S1 (ESI), octadecylimidazolium phases have similar alkyl chain density compared with commercial phase (C₁₈-p), this enhanced selectivity should be induced by the combination of octadecylimidazolium and MO.

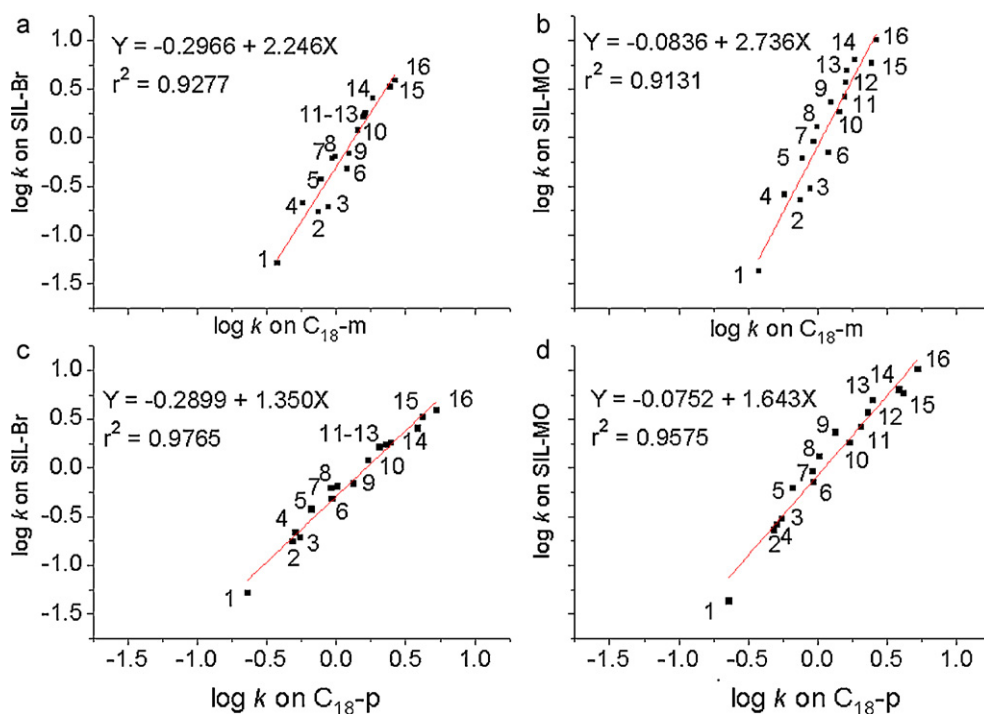


Fig. 6. Correlations between $\log k$ values of (a) C_{18} -m vs. SIL-Br, (b) C_{18} -m vs. SIL-MO, (c) C_{18} -p vs. SIL-Br, (d) C_{18} -p vs. SIL-MO. Elutes: benzene (1), *cis*-stilbene (2), *o*-terphenyl (3), naphthalene (4), *trans*-stilbene (5), *m*-terphenyl (6), phenanthrene (7), anthracene (8), *p*-terphenyl (9) pyrene (10), triphenylene (11), benzo[*a*]anthracene (12), chrysene (13), naphthacene (14), benzo[*e*]pyrene (15), benzo[*a*]pyrene (16). Chromatographic conditions are the same as in Fig. 3.

Fig. 6 shows the plots of the $\log k$ values of (a) C_{18} -m vs. SIL-Br, (b) C_{18} -m vs. SIL-MO, (c) C_{18} -p vs. SIL-Br and (d) C_{18} -p vs. SIL-MO. Linear regression analyses indicate that the retention behaviour of SIL-Br and SIL-MO were correlated more closely with that of C_{18} -p than that of C_{18} -m. Compared with the high correlation coefficient of SIL-Br and C_{18} -p ($r^2 = 0.977$), a lower correlation coefficient was obtained for SIL-MO and C_{18} -p ($r^2 = 0.958$), which should be due to the better shape selectivity of SIL-MO towards PAHs than C_{18} -p.

SIL-MO is a new column synthesized by *in situ* anion-exchange. Compared with a complex covalent-bonding reaction, anion-exchange is a very facile and unique method for preparing a new column. MO, which is an important imported part of the phase, was immobilized by ionic bonding between imidazolium and sulfonate and co-existent hydrophobic interactions between octadecyl chains and azobenzene groups. The reproducibility of the SIL-MO column was tested *via* the separation of pyrene, triphenylene, benzo[*a*]anthracene and chrysene. The overlapped

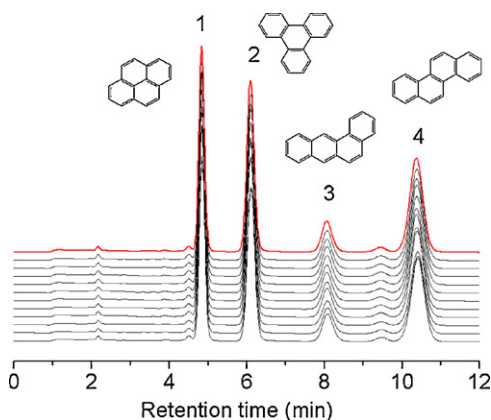


Fig. 7. The reproducibility test of SIL-MO column at the separation of pyrene (1), triphenylene (2), benzo[*a*]anthracene (3) and chrysene (4) with methanol as eluent at 10 °C. Chromatographic conditions are the same as in Fig. 3.

chromatograms are shown in Fig. 7 and the RSD values ($n = 12$) of the retention factors are within 0.27%–0.77%. This indicates that the column is qualified for use for the separation of PAHs using these chromatographic conditions.

4. Conclusions

In this paper, *in situ* anion-exchange as a new self-assembly strategy was used to tune the counter anions of poly(octadecylimidazolium)-grafted silica column. The retention mode was evaluated by the separation of a Tanaka test mixture and the retention studies using alkylbenzenes and PAHs. Compared with commonly used commercial octadecyl columns, poly(octadecylimidazolium) columns not only have an octadecyl chain, but also contain functionalized imidazolium groups to impart additional interactions such as π - π and hydrogen-bonding interactions to the analytes. After bromide was replaced by methyl orange in the column, enhanced molecular shape selectivity was confirmed by separations of SRM 869b and SRM 1647e. *In situ* anion-exchange could also be used as a new method for synthesizing other ionic columns to modify the surface of the stationary phase and tune the chromatographic performance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2011.10.065](https://doi.org/10.1016/j.chroma.2011.10.065).

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