

# New Strategy for Drastic Enhancement of Selectivity via Chemical Modification of Counter Anions in Ionic Liquid Polymer Phase

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A new strategy for the design of a new chromatographic stationary phase via simple modifications of the counter anions in poly(ionic liquid)-grafted silica phase based on ionic self-assembly technology is proposed. The phase with methyl orange dye as counter anions exhibits ultra-high selectivity towards shape-constrained isomers.

Ionic liquids (ILs) are organic molten salts with a melting point close to or below room temperature.<sup>1</sup> Further, their properties can be tailored via the modification of ions.<sup>2</sup> In recent years, ILs have attracted considerable attention from both academic and industrial research communities due to their unusual chemical and physical properties.<sup>3</sup> ILs have also been investigated as components of polymeric matrixes and polymerization media.<sup>4</sup> Lu et al. recently reported the design of a photosensitive material as liquid crystalline alignment layers constructed by coupling poly(ionic liquid) (PIL) and a photosensitive unit, azobenzene dye methyl orange (MO), based on an ionic self-assembly (ISA) technology.<sup>5</sup> Today, ISA and other non-covalent strategies—hydrogen bonding, coordination binding, and acid-base interactions, namely, self-assembly or self-organization processes—are becoming important frontiers of materials research conducted for designing new materials.<sup>6</sup>

On the other hand, in high-performance liquid chromatography (HPLC), ILs have played various roles in facilitating chromatographic separation either as mobile-phase additives or as stationary phases.<sup>7</sup> In this paper, we report a new strategy to tune the selectivity by simple modifications of the counter anions in the polymerized IL phase. Ultra-high selectivity during the separation of the geometrical isomers of polycyclic aromatic hydrocarbons (PAHs) can be obtained by using MO dye as counter anions in the PIL-grafted silica phase. Commercial MO was selected as the building unit because it is capable of photoisomerization, and moreover, it is the essence of liquid crystal materials.<sup>8</sup> The ordered arrangement of an MO molecule can be expected to achieve unique selectivities; however, accomplishing the covalent attachment of MO to a matrix is a very complex task.<sup>9</sup>

In this study, a long-chain IL monomer 1-vinyl-3-octadecylimidazolium bromide [ $C_{18}VyIm$ ]Br was prepared; this monomer was then polymerized on mercaptopropyl-functionalized silica through surface radical chain-transfer polymerization. The obtained PIL-grafted silica (Sil-PIm $C_{18}$ -Br) was further self-assembled with MO to form Sil-PIm $C_{18}$ -MO, as shown in scheme 1. Sil-PIm $C_{18}$ -MO was packed into a



**Scheme 1** Synthesis of poly(ionic liquid)-grafted silica stationary phase.

stainless column (150 × 4.6 mm, i.d.) for HPLC. Another PIL-grafted silica Sil-PIm $C_{18}$ -Br-1 was also prepared and packed as a reference column.

The processes of polymerization and ISA were confirmed using characterization techniques including elemental analysis, thermo-gravimetric analysis, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. From the elemental analysis results, the amounts of mercaptopropyl and IL moieties attached to the silica surface were calculated as 3.50  $\mu\text{mol m}^{-2}$  and 3.74  $\mu\text{mol m}^{-2}$  for Sil-MPS and Sil-PIm $C_{18}$ -Br, respectively. After ISA, the carbon percent increased from 9.87% for Sil-PIm $C_{18}$ -Br to 13.52% for Sil-PIm $C_{18}$ -MO. In the DRIFT spectra, the signals at 2923 and 2852  $\text{cm}^{-1}$  arose from C-H stretches. Further, the peaks near 1562 and 1467  $\text{cm}^{-1}$  can be attributed to the character of imidazolium. In the case of Sil-PIm $C_{18}$ -MO, additional characteristic signals of MO are evident at 1604, 1518, and 1362  $\text{cm}^{-1}$ . Further, differential scanning calorimetry (DSC) was conducted to investigate the thermal behaviour of this material. However, the curve did not show any structural thermal transitions between 10 and 90 °C. This might be due to its rigid molecular structure.<sup>5</sup> A detailed description of the apparatus and experimental procedure are given in Electronic Supporting Information (ESI).

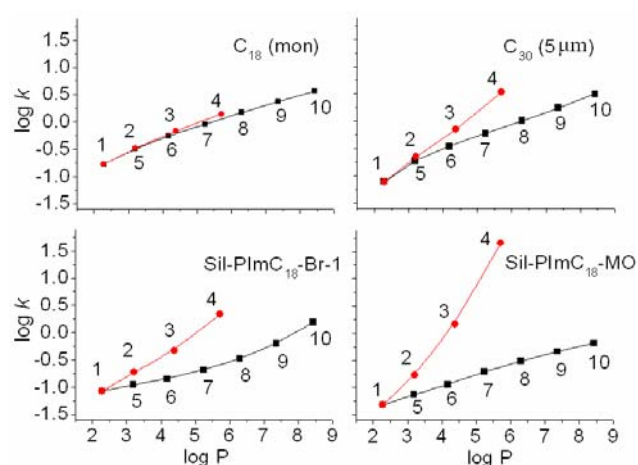
A comparison between the retention behaviours of alkylbenzenes and PAHs could be used to evaluate the retention mode of the packing materials in HPLC. Fig. 1 shows a comparison of the relationships between  $\log k$  and  $\log P$  for  $C_{18}$  (mon),  $C_{30}$  (5  $\mu\text{m}$ ), Sil-PIm $C_{18}$ -Br-1, and Sil-PIm $C_{18}$ -MO columns. Compared with the other three columns, Sil-PIm $C_{18}$ -MO showed considerably higher retention for PAHs than for alkylbenzenes. For instance,  $\log P$  for naphthacene (5.71) was smaller than that for dodecylbenzene (8.43), but the  $\log k$  value for naphthacene (1.65) was considerably higher than that for dodecylbenzene (-0.18).

When Sil-PIm $C_{18}$ -MO is applied for the separation of PAHs

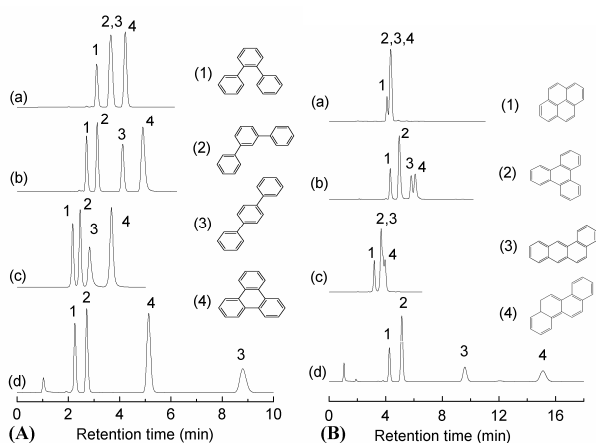
**Table 1** Separation factors ( $\alpha$ ) of geometrical isomers for various stationary phases.

Columns	<i>trans</i> -/ <i>cis</i> -stilbene	<i>m</i> -/ <i>o</i> -terphenyl	<i>p</i> -/ <i>m</i> -terphenyl	chrysene/ benzo[ <i>a</i> ]anthracene	anthracene / phenanthrene	benzo[ <i>a</i> ]pyrene/ benzo[ <i>e</i> ]pyrene
C <sub>18</sub> (mon) <sup>a</sup>	1.08	1.52	1.03	1.00	1.08	1.07
C <sub>18</sub> (poly) <sup>a</sup>	1.33	1.70	1.26	1.03	1.20	1.26
C <sub>30</sub> (3 $\mu$ m) <sup>b</sup>	1.58	1.52	1.82	1.07	1.19	1.36
C <sub>30</sub> (5 $\mu$ m) <sup>b</sup>	1.64	1.58	1.85	1.07	1.20	1.36
Sil-ODA <sub>25</sub> <sup>a</sup>	2.15	1.86	1.90	1.08	1.22	1.27
Sil-DSG <sup>a</sup>	3.04	1.95	4.29	1.23	1.31	1.31
SiImBr <sup>c</sup>	1.68	1.91	0.98	1.02	n.d.	n.d.
Sil-PImC <sub>18</sub> -Br-1 <sup>b</sup>	1.87	2.03	1.60	1.07	1.06	1.23
Sil-PImC <sub>18</sub> -MO <sup>b</sup>	3.65	2.28	8.45	1.72	2.16	2.94

<sup>a</sup> Taken from ref. 10a. <sup>b</sup> Methanol as eluent. <sup>c</sup> Taken from ref. 10b.



**Fig. 1** The relationships of  $\log k$  and  $\log P$  for alkylbenzenes (Squares) and PAHs (Circles) with C<sub>18</sub> (mon), C<sub>30</sub> (5  $\mu$ m), Sil-PImC<sub>18</sub>-Br-1 and Sil-PImC<sub>18</sub>-MO columns. Mobile phase: methanol. Solutes: (1) benzene, (2) naphthalene, (3) anthracene, (4) naphthacene, (5)–(10) ethyl-, butyl-, hexyl-, octyl-, decyl-, and dodecylbenzenes. Mobile phase: methanol. Temperature: 10 °C.

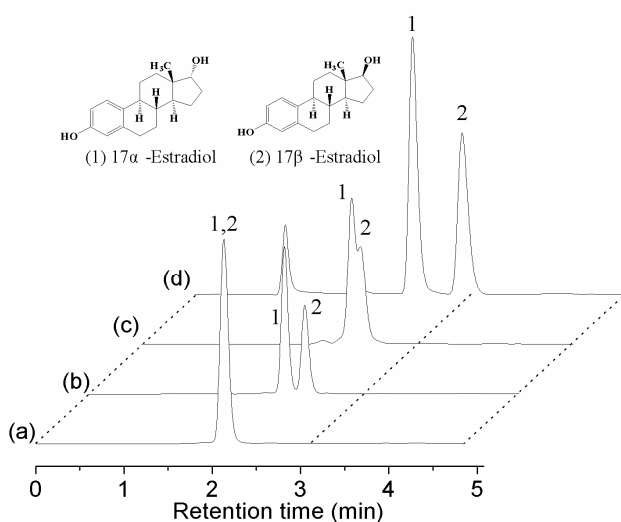


**Fig. 2** Separations of two mixtures contained geometrical isomers with C<sub>18</sub> (mon) (a), C<sub>30</sub> (5  $\mu$ m) (b), Sil-PImC<sub>18</sub>-Br-1 (c) and Sil-PImC<sub>18</sub>-MO (d) columns. Mixtures (A): (1) *o*-terphenyl, (2) *m*-terphenyl, (3) *p*-terphenyl and (4) triphenylene; (B): (1) pyrene, (2) triphenylene, (3) benzo[*a*]anthracene and (4) chrysene. Other chromatographic conditions are the same as in Fig. 1.

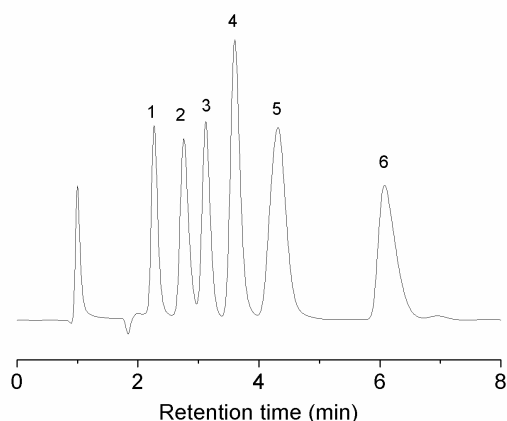
in a reversed phase mode, we encounter various specific selectivities. As shown in Table 1, Sil-PImC<sub>18</sub>-MO has considerably higher selectivity towards geometrical isomers than any other columns, including some extremely useful columns.<sup>10</sup> For example,  $\alpha = 8.45$  was obtained for a mixture of *p*- and *m*-terphenyls in Sil-PImC<sub>18</sub>-MO, while  $\alpha = 1.60$  in Sil-PImC<sub>18</sub>-Br-1. Both *p*- and *m*-terphenyls possess the same number of carbon atoms and p-electrons, but their molecular planarity is completely different. *p*-Terphenyl is slightly twisted (almost planar), but more slender (linear) than *m*-terphenyl. No similar enhancement of the selectivity was observed in C<sub>18</sub> and C<sub>30</sub> columns. Enhanced selectivity was clearly observed in the separation of two mixtures of isomers, as shown in Fig. 2.

The shape selectivity performance of Sil-PImC<sub>18</sub>-MO was also assessed by SRM 869b, the column selectivity test mixture for liquid chromatography.<sup>11</sup> This material consists of three PAHs with planar and non-planar shapes. In general, the late elution of benzo[*a*]pyrene (BaP) relative to tetrabenzonaphthalene (TBN) indicates enhanced column selectivity towards geometrical isomers. The selectivity coefficient of TBN/BaP can be used as a measure of this property. The chromatogram of the SRM 869b test mixture (see Fig. S3, ESI) indicated that Sil-PImC<sub>18</sub>-MO exhibited polymer-like retention behaviour with ultra-high shape selectivity ( $\alpha_{\text{TBN/BaP}} = 0.26$ ). Ultra-high shape selectivity could have good applications in the separation of certain compounds having the same configuration. We know that the 17 $\alpha$ -estradiol and 17 $\beta$ -estradiol pair is one of the most difficult pairs of isomers in chromatographic separation.<sup>12</sup> However, in Sil-PImC<sub>18</sub>-MO, this pair was easily separated within 3 min even with methanol as the eluent, as shown in Fig. 3; six steroids including 17 $\alpha$ -estradiol and 17 $\beta$ -estradiol were successfully separated within 7 min with methanol/water (9:1) as the eluent, as shown in Fig. 4.

In summary, we demonstrated that PIL-grafted silica could be easily obtained by surface radical-chain transfer polymerization, and furthermore, counter anions could be simply modified by ionic self-assembly to tune the property of the phase; the phase with dye as counter anions exhibits ultra-high shape selectivity for PAHs. However, buffer solvents



**Fig. 3** Comparison of the separation of 17 $\alpha$ -estradiol and 17 $\beta$ -estradiol with C<sub>18</sub> (mon) (a), C<sub>30</sub> (5  $\mu$ m) (b), Sil-PlmC<sub>18</sub>-Br-1 (c) and Sil-PlmC<sub>18</sub>-MO (d) columns. Other chromatographic conditions are the same as in Fig. 1.



**Fig. 4** Separation of six steroids including (1) prednisolone, (2) estriol, (3) 17 $\alpha$ -estradiol, (4) testosterone, (5) 17 $\beta$ -estradiol and (6) estrone with Sil-PlmC<sub>18</sub>-MO column. Mobile phase: methanol/water (9:1). Other chromatographic conditions are the same as in Fig. 1.

could not be used as the eluent because the stationary phase was combined by anions and cations through ionic interactions. Nevertheless, such stationary phases still have sufficiently attractive advantages in the separation of hydrophobic shape-constrained isomers. The enhanced selectivity may be a result of the highly ordered arrangement between the C<sub>18</sub> chain and rigid azobenzene in Sil-PlmC<sub>18</sub>-MO due to the molecular interactions. Multiple interactions including hydrophobic effect and aromatic interaction between the PAHs and the functionalized groups (azobenzene and imidazolium) in the stationary phase were observed. Our experiments offer a new possibility for the design of complex functional materials for applications to chromatography and

electrochemistry conducted using ISA, which are not otherwise easy to synthesize by traditional chemical approaches. Work is currently underway to investigate more detail separation applications and more different counter anions for the modification of IL phases.

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## Notes and references

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