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New Surface-Confined Ionic Liquid Stationary Phases with Enhanced Chromatographic Selectivity and Stability by Co-immobilization of Polymerizable Anion and Cation Pairs

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Experimental details

Materials and reagents

2-Acrylamido-2-methylpropane sulphonic acid (AMPS) and 1-vinylimidazole (99%) was purchased from TCI (Tokyo, Japan). 1-Bromooctadecane and sodium *p*-styrenesulphonate was obtained from Wako (Osaka, Japan). Azobisisobutyronitrile (AIBN) was obtained form Nacalai tesque, Inc. (Kyoto, Japan) and purified by recrystallization from methanol before use. 3-Mercaptopropyltrimethoxysilane (MPS) was purchased from Azmax (Chiba, Japan). Porous silica particles (diameter 5 μm, pore size 120 Å, specific surface area 300 $m^2\ g^{-1}$) were obtained from YMC (Kyoto, Japan). Standard Reference Material (SRM) 869b, Column Selectivity Test Mixture for Liquid Chromatography, and SRM 1647e, Priority Pollutant Polycyclic Aromatic Hydrocarbons, were obtained from the Standard Reference Materials Program (NIST, Gaithersburg, MD). Theophylline, uracil, uridine, adenosine, adenine, cytosine and guanosine were purchased from Sigma-Aldrich, Inc. All PAHs and alkylbenzenes were commercially available and used without any purification.

Synthesis of Sil-P(ImC_{18}-SS)

The first step is to synthesize [C_{18}VIm]Br monomer as reported in our previous work [1]. Simply, 1-vinylimidazole and 1-bromooctadecane were mixed and reacted in acetonitrile at 60 °C for three days. The obtained [C_{18}VIm]Br was recrystallized in cold diethyl ether and dried under vacuum, giving a white solid powder: yield 96.5%; [C_{18}VIm]Br ($C_{23}H_{43}BrN_2$): ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.38 (1H, s), 7.48-7.54 (2H, m), 7.26-7.32 (1H, d), 5.89-5.94 (1H, m), 5.43-5.46 (1H, d), 4.39-4.43 (2H, t), 1.92-2.00 (2H, m), 1.35-1.37 (2H, d), 1.25 (28H, s), 0.86-0.90 (3H, t).

And then, bromide was changed to be *p*-styrenesulphonate organic anion. [C_{18}VIm]Br (5.0 g) was mixed with excess sodium *p*-styrenesulphonate (2.5 g) in 50 ml of water. After stirred two days at room temperature, the solid was collected by filtration and washed by water, and then dried under

vacuum, giving a white fine powder: yield 91.9%; [C_{18}VIm]SS ($C_{31}H_{50}N_2O_3S$): ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.947 (1H, s), 7.84-7.86 (2H, d), 7.36-7.40 (2H, t), 7.23-7.27 (2H, d), 6.66-6.74 (1H, t), 5.74-5.79 (1H, d), 5.27-5.28 (1H, d), 4.17-4.21 (2H, t), 4.03 (3H, s), 1.94 (2H, s), 1.25 (30H, s), 0.86-0.90 (3H, t).

Third, mercaptopropyl modified silica (Sil-MPS-1) was prepared to obtain surface initiator as described before [2]. 6.0 g of silica gel was dispersed in toluene. 3.0 g of MPS and 30 ml of toluene was added and the mixture was refluxed for 36 h. The suspension was filtered and the solid was washed with toluene, methanol, water, methanol and diethyl ether successively.

At last, [C_{18}VIm]SS was grafted onto Sil-MPS-1 through a surface radical chain-transfer reaction as shown in Scheme 2. Sil-MPS-1 (2.8 g) was added to a three-neck round-bottomed container. 2.0 g of [C_{18}VIm]SS dissolved in chloroform and 1% of AIBN was added into the container. The mixture was stirred in nitrogen atmosphere at 60 °C for 30 h. The precipitates were filtered and washed with chloroform, methanol, and diethyl ether. After being dried under vacuum, Sil-P(ImC_{18}-SS) was confirmed by different characterized technologies or packed into a column for chromatographic applications.

Synthesis of Sil-P(VIm-AMPS)

Ionic liquid monomer couple (VIm-AMPS) was synthesized using a modified way as described in the reference [3]. 2-Acrylamido-2-methylpropane sulphonic acid (AMPS) and equimolar 1-vinylimidazole (VIm) was solved in water separately and then mixed at room temperature. The mixture was stirred continuously for 4 h. The aqueous solution was then dried with a vacuum rotary evaporator at 40 °C. The transparent viscous liquid was obtained after dried in vacuum with a high yield. The ^{1}H NMR spectrum of the monomer is shown in the supporting information. Integration confirmed a stoichiometric ratio of VIm and AMPS. VIm-AMPS ($C_{12}H_{19}N_3O_4S$): ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.38 (1H, s), 7.64 (1H, s), 7.53-7.55 (3H, d), 7.27-7.33 (1H, m), 6.12-6.14 (2H, d), 5.73-5.18 (1H, m), 5.36-5.55 (2H, m), 3.21 (2H, s), 1.62 (6H, s). It is noted to say that because of the activity of VIm-AMPS, it should be used early after it was obtained.

Mercaptopropyl modified silica (Sil-MPS-2) was prepared with a similar way for Sil-MPS-1. VIm-AMPS was copolymerized on the Sil-MPS-2 by surface-initiated chain-transfer reaction and Sil-P(VIm-AMPS) was obtained. The reaction condition is nearly the same as in the preparation of

Sil-P(ImC_{18}-SS). The only difference is that the reaction time is 6 h.

Characterizations

^{1}H NMR spectra for ionic liquid monomers were determined by a JNM-LA400 instrument (JEOL, Tokyo, Japan) at 400 MHz using $CDCl_3$ as the solvent at 25 ˚C. The composition of the copolymer grafted on silica was determined by elemental analysis using a Yanaco CHN Corder MT-6 apparatus (YANACO Co., Ltd., Kyoto, Japan). Diffuse reflectance infrared Fourier transformation (DRIFT) spectra were performed on a FT/IR–4100 with an accessory DR PRO410-M (JASCO Co., Ltd, Tokyo, Japan) in the range of 4000–400 cm^{-1}. Thermogravimetric analysis was conducted on a Seiko Exstar 6000 TG/DTA 6200 thermal analyzer (Seiko Instruments Inc., Chiba, Japan) in static air from 35 to 800 ˚C with a heating rate of 10 ˚C min^{-1}.

Chromatographic conditions

Sil-P(ImC_{18}-SS) were packed into a stainless-steel column (150 × 4.6 mm I.D.) by Masis, Inc. (Aomori, Japan). Sil-P(VIm-AMPS) was packed into a stainless-steel column (150 × 4.6 mm I.D.) by ourselves, using hexane as the propulsive solvent. Monomeric ODS (Inertsil ODS-3, 150 × 4.6 mm i.d.) used as the reference column was obtained from GL Science (Tokyo, Japan). HPLC-graded methanol and acetonitrile were used as components of the mobile phase. Millipore water was used during the experiments. The analytes were directly dissolved in methanol. The chromatographic system (JASCO, Tokyo, Japan) consisted of a 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 by a JASCO ChromNAV Chromatography Data System. The column temperature was controlled at using a column jacket with a circulator having a heating and cooling system. The flow-rate was 1.0 ml min^{-1}, the detection wavelength was UV 254 nm, and the injection volume was 5 μl. The retention time of D_2O was used as the void volume (t_0) marker (The absorption for D_2O was measured at 400 nm, which is actually considered as the injection shock). The retention factor (k) of an analyte was calculated according to the equation: $k = (t_R\text{-}t_0)/t_0$, where t_R is the retention time of the analyte. The separation factor (α) is the ratio of the retention factors for the two solutes being analyzed. The 1-octanol/water partition coefficient (log $P_{o/w}$), usually used to represent molecular hydrophobicity, was determined from the

retention factor with the ODS column stated above as log $P_{o/w}$ = 3.759 + 4.207 log k (r = 0.99997), according to the procedure described in our previous work [4].

References for ESI

1 H. Qiu, M. Takafuji, T. Sawada, X. Liu, S. Jiang and H. Ihara, *Chem. Commun.*, 2010, **46**, 8740.

2 A. K. Mallik, T. Sawada, M. Takafuji and H. Ihara, *Anal. Chem.*, 2010, **82**, 3320.

3 M. Yoshizawa, W. Ogihara and H. Ohno, *Polym. Adv. Technol.*, 2002, **13**, 589.

4 H. Ihara, T. Sagawa, Y. Goto and S. Nagaoka, *Polymer*, 1999, **40**, 2555.

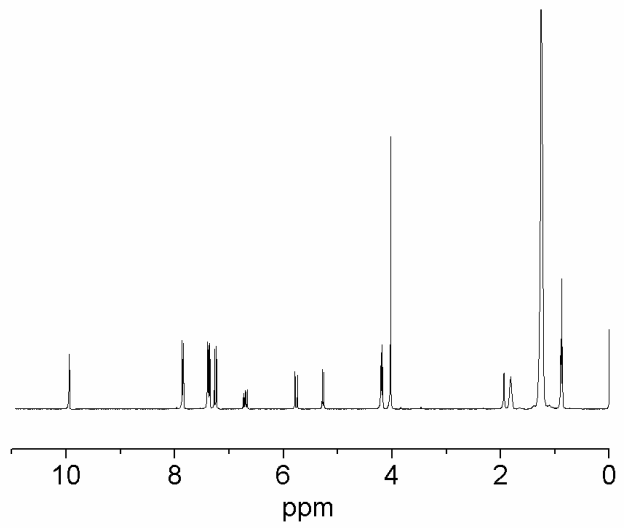


Fig. S1 ^{1}H NMR of [C_{18}VIm]SS.

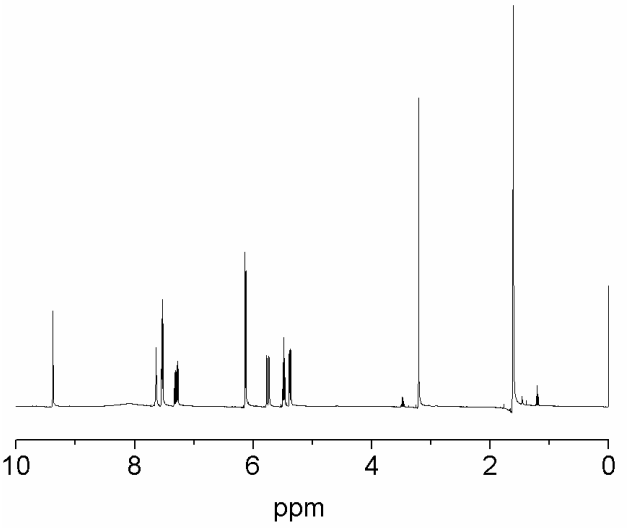


Fig. S2 ^{1}H NMR of VIm-AMPS.

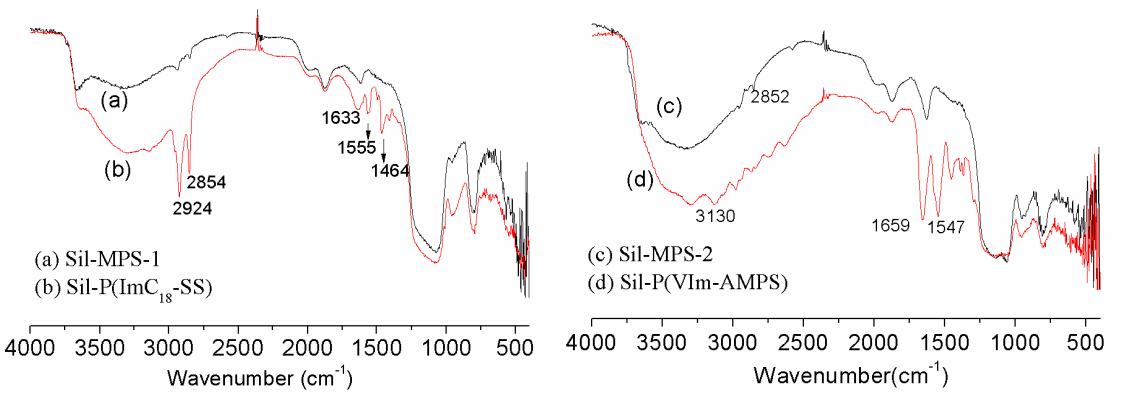


Fig. S3 DRIFT spectra of (a) Sil-MPS-1 and (b) Sil-P(ImC_{18}-SS), (c) Sil-MPS-2 and (d) Sil-P(VIm-AMPS).

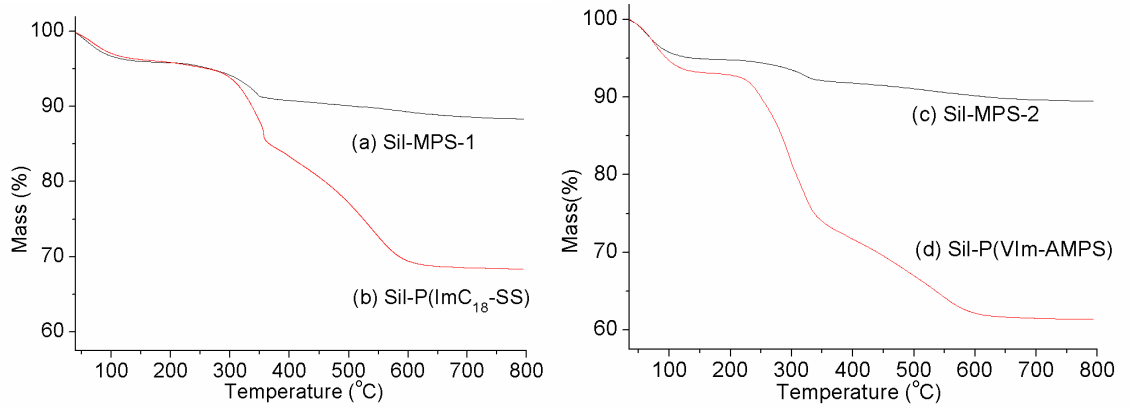


Fig. S4 Thermogravimetric curves of (a) Sil-MPS-1 and (b) Sil-P(ImC_{18}-SS), (c) Sil-MPS-2 and (d) Sil-P(VIm-AMPS).

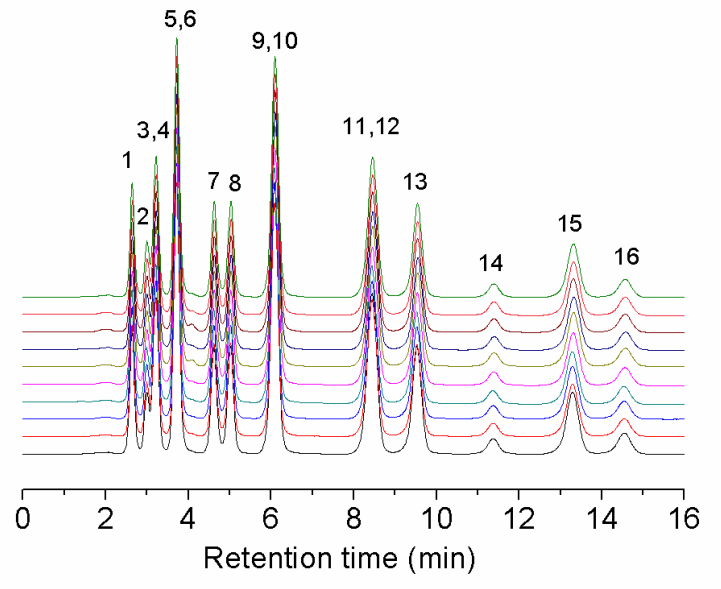


Fig. S5 The overlapped chromatograms the separation of 1647e. Chromatographic conditions are the same as in Fig. S6. The reproducibility of the method was determined for Sil-P(ImC_{18}-SS) column using the mixture of 1647e injected 10 times continuously. The RSD values (n = 10) of the retention factors of the analytes were 0.19–0.73%.

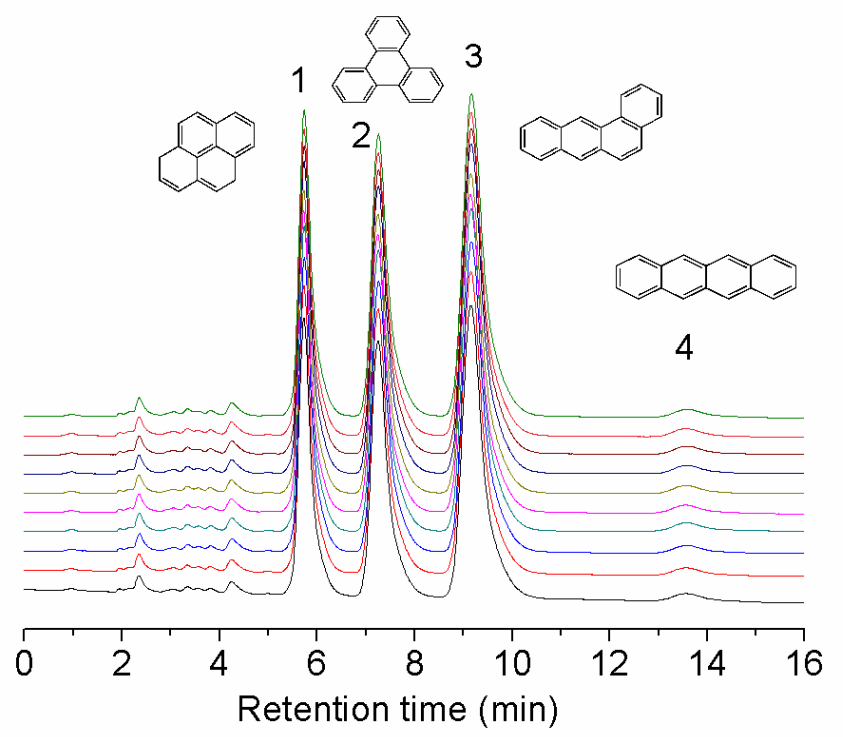
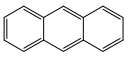
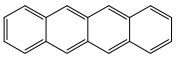
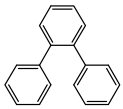
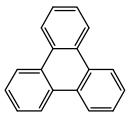
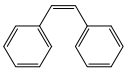
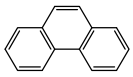
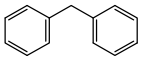
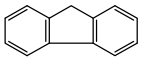


Fig. S6 The overlapped chromatograms the separation of four-ring PAH isomers with Sil-P(VIm-AMPS) column using methanol: water=(70/30, v/v) as mobile phase at 30 °C. The RSD values (n = 10) of the retention factors of the analytes were 0.28–0.51%.

Table S1. Retention and separation factors of PAHs for Sil-P(ImC_{18}-SS), SiImBr and ODS.[a]

PAHs	Structure	Sil-P(ImC_{18}-SS)		SiImBr		ODS	
		k	α	*k*	α	*K*	α
Benzene		0.13		0.17		0.62	
			3.51		2.46		1.81
Naphthalene		0.45		0.42		1.13	
			2.88		2.21		2.01
Anthracene		1.30		0.93		2.28	
			2.86		2.15		2.17
Naphthacene		3.73		2.01		4.94	
o-Terphenyl		0.67		0.66		2.56	
			5.04		3.89		1.57
Triphenylene		3.38		2.56		4.02	
cis-Stilbene		0.53		0.42		1.77	
			2.43		1.84		1.08
Phenanthrene		1.29		0.75		1.91	
Diphenylmethane		0.44		0.38		1.44	
			2.03		1.44		1.26
Fluorene		0.90		0.54		1.82	

[a] The data of SiImBr was cited from ref. 4(c). Other chromatographic conditions were the same as in Fig. 1.

Table S2 The retention factors of bases obtained at the separation of different mobile phase with Sil-P(VIm-AMPS) column.

Mobile phase	**10%**[a]	**5%**[b]	**100%**[c]
Caffeine	0.12	0.25	9.65
5-Bromouracil	0.16	0.37	0.37
Theophylline	0.28	0.44	3.18
Thymine	0.36	0.67	0.37
Thymidine	0.56	1.02	0.94
Purine	1.28	2.54	0.70
Uridine	1.45	2.65	0.16
Adenosine	1.94	4.62	1.90
Adenine	1.96	5.05	1.05
Xanthosine	3.73	11.86	-
Cytosine	4.13	12.06	0.35
Cytidine	6.62	19.93	0.21
Guanosine	7.88	29.93	0.74

[a] 20 mM ammonium acetate: acetonitrile= (10/90, v/v). [b] 20 mM ammonium acetate: acetonitrile= (5/95, v/v). [c] 20 mM ammonium acetate.