

## Experimental details

### Homogenous formation, quaternization of urea-functionalized imidazolyl silane and its immobilization onto silica for surface-confined ionic liquid stationary phases

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#### Chemicals

*N*-(3-Aminopropyl) imidazole (98%) was purchased from Alfa Aesar (Tianjin, China).  $\gamma$ -Isocyanatopropyltriethoxysilane (98%) and terphenyls were purchased from Aladdin Industrial Corporation (Shanghai, China). Triphenylene was supplied by TCI (Tokyo, Japan). 1-Bromooctadecane (99%), 11-bromoundecanoic acid (99%) and tribromophosphine (99%) were purchased from Sun Chemical Technology Co. Ltd. (Shanghai, China). 1-Bromooctane (99%) was purchased from Adamas Reagent Co. Ltd. (Shanghai, China). Octadecanol (99%), *o*-dichlorobenzene (98%) and phosphorus oxychloride (99%) were obtained from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). Anthracene (98%) was obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). Silica spheres (diameter 5  $\mu\text{m}$ , pore size 100 Å, specific surface area 400  $\text{m}^2\cdot\text{g}^{-1}$ ) were obtained from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, China). Anilines of analytical grade were commercially available from different suppliers. Methanol (MeOH), *iso*-propanol, tetrahydrofuran (THF) and acetonitrile (MeCN) of HPLC grade were used. Ultrapure water (18.3 M $\Omega$ ) was produced by a Millipore Direct-Q 3UV unit (Billerica, USA). *N,N*-Dimethyl formamide (DMF), toluene, *n*-hexane, acetic acid, sodium borohydride ( $\text{NaBH}_4$ ) of analytical grade and other necessary reagents were obtained from different origins. Anhydrous solvents were prepared by distillation over 3 Å molecular sieves.

#### Synthetic works

##### Synthesis of 9-(bromomethyl)anthracene

Anthracene was first converted to 9-formylanthracene by the method proposed in literature.<sup>1</sup> Briefly, anthracene (36 g, 0.21 mol), DMF (32 g, 0.44 mol), phosphorus oxychloride (56 g, 0.24 mol) and *o*-dichlorobenzene (40 mL) was mixed in a 250-mL flask under vigorous mechanical stirring. The suspension was heated at 100 °C for 2 h. The resulting solution of dark red colour was cooled to room-temperature and neutralized by copious amount of aqueous sodium acetate (120 g) solution (2 L). The yellow precipitate appeared after standing overnight, which was filtered and washed thoroughly by water and air-dried. Recrystallization of the yellow substance from 110 mL of acetic acid and subsequent washing by cold methanol (40 mL) afforded yellow needles of 9-formylanthracene (28 g, 65% yield). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  11.52 (1H, s), 8.97-8.99 (2H, d), 8.70 (1H, s), 8.05-8.07 (2H, s), 7.65-7.69 (2H, t), 7.52-7.56 (2H, t).

9-Formylanthracene was quantitatively reduced to 9-anthracenemethanol by  $\text{NaBH}_4$  in IPA/THF

binary solvent (v/v=1/1) and recrystallized from chloroform (white scaly crystal). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.46 (1H, s), 8.39-8.42 (2H, d), 8.00-8.02 (2H, d), 7.53-7.58 (2H, t), 7.45-7.50 (2H, t), 5.66 (2H, d).

9-Anthracenemethanol was brominated by tribromophosphine in toluene. Briefly, 9-anthracenemethanol (20.8 g, 0.1 mol) was suspended in 100 mL of toluene, to which triphosphine (30 g, 0.11 mol) in 50 mL of toluene was added dropwise at room temperature. A clean solution was obtained after the addition of tribromophosphine, which was further stirred overnight. Ice was added to the solution; the organic layer was washed by brine and water and dried over MgSO<sub>4</sub>. Evaporation of toluene gave yellow residue, which was recrystallized from toluene. Greenish yellow needles (AntBr) (25 g, 93% yield) were obtained. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.47 (1H, s), 8.28-8.30 (2H, d), 8.00-8.03 (2H, d), 7.58-7.62 (2H, d), 7.49-7.51 (2H, d), 5.60 (2H, s).

### Synthesis of *n*-octadecyl 11-bromoundecanoate

11-Bromoundecanoic acid (10.6 g, 40 mmol) was converted to acyl chloride using thionyl chloride and re-dissolved in 40 mL of toluene, which was added dropwise to a warm solution of octadecanol (10.55 g, 39 mmol) in toluene (110 mL) in 30 min. Nitrogen was bubbled throughout the reaction process. After addition, the reaction was allowed to continue at 90 °C overnight. Toluene was evaporated, an oil was obtained, which quickly solidified at room-temperature. Pure *n*-octadecyl 11-bromoundecanoate (EC29Br) was obtained by recrystallization from acetone twice as bright white flakes (16 g, 78% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 4.05 (t, 2H), 3.41 (t, 2H), 2.29 (t, 2H), 1.90-1.81 (m, 2H), 1.68-1.59 (m, 4H), 1.47-1.39 (m, 2H), 1.39-1.19 (m, 42H), 0.88 (t, 3H).

### Characterizations

The <sup>1</sup>H NMR spectra were recorded on a Varian INOVA-400M instrument (Varian, USA) at 400 MHz using tetramethylsilane reference. The carbon, hydrogen and nitrogen contents of the silica adsorbents were determined by elemental analysis using a Vario EL III elemental analyzer (Hanau, Germany). Wettability tests of the stationary phases were carried out on a Dataphysics OCA 20 contact angle measuring and contour analysis unit (Filderstadt, Germany), the contact angle of each silica sample was measured twice to give average value. The infrared spectra were collected on a Bruker IFS120HR Fourier-transform spectrometer (Ettlingen, Germany).

### Chromatographic conditions

All the stationary phases were suspended in 1,4-dioxane and slurry-packed into stainless steel column (150×4.6 mm I.D.) at a liquid pressure of 60 MPa for 15 minutes. All the HPLC tests were run on a Shimadzu Essentia system (Kyoto, Japan) composed of LC-15C binary pumps, SPD-15C UV detector, CTO-15C column oven and a Rheodyne 7725i injector with 20 μL sample loop (Cotati, CA, USA). The columns were used at 30 °C with flow rate of 1.00 mL·min<sup>-1</sup>, the UV detection wavelength was 254 nm. MeOH and water were filtered through 0.45 μm membrane and ultrasonically degassed prior to use. The analytes were dissolved in MeCN and stored in refrigerator. A Shimadzu WondaSil C18-WR column (diameter: 5 μm, pore size: 100 Å, pore volume: 1.05 mL·g<sup>-1</sup>, surface area: 450 m<sup>2</sup>·g<sup>-1</sup>, carbon loading: 14 %, end-capped, 150 mm × 4.6 mm I.D.) was

used as reference column. The dead time of each column was determined by the signal of pure water.

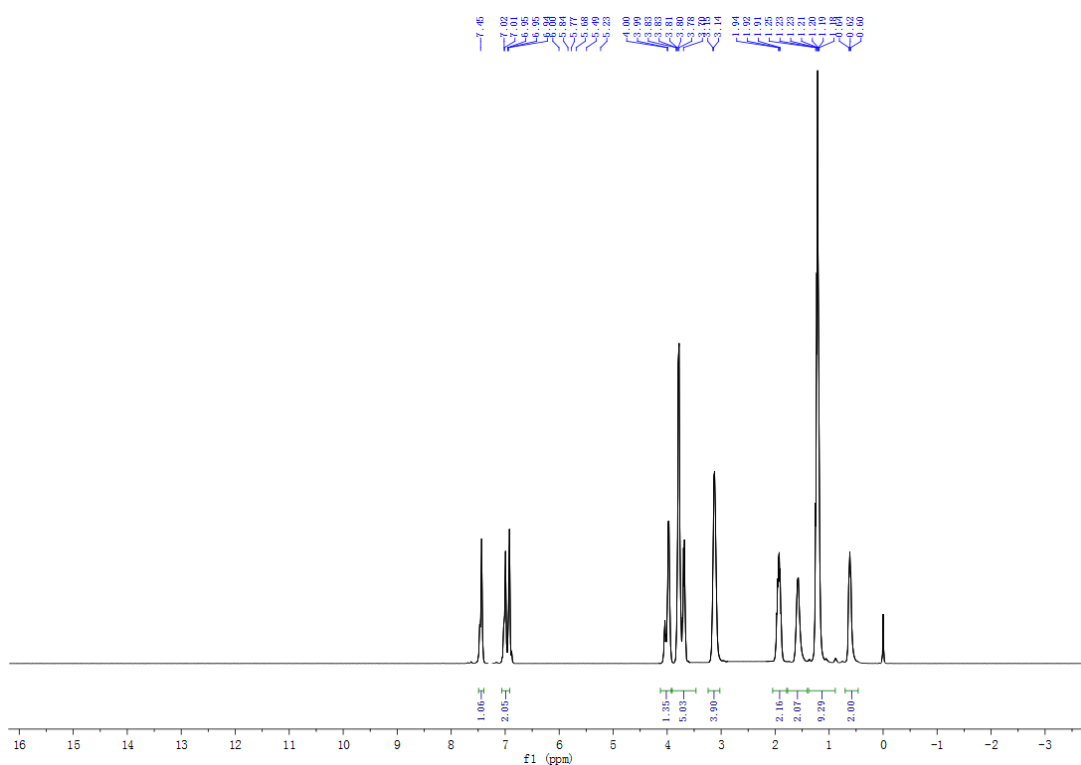


Fig. S1 <sup>1</sup>H NMR spectrum of UIm

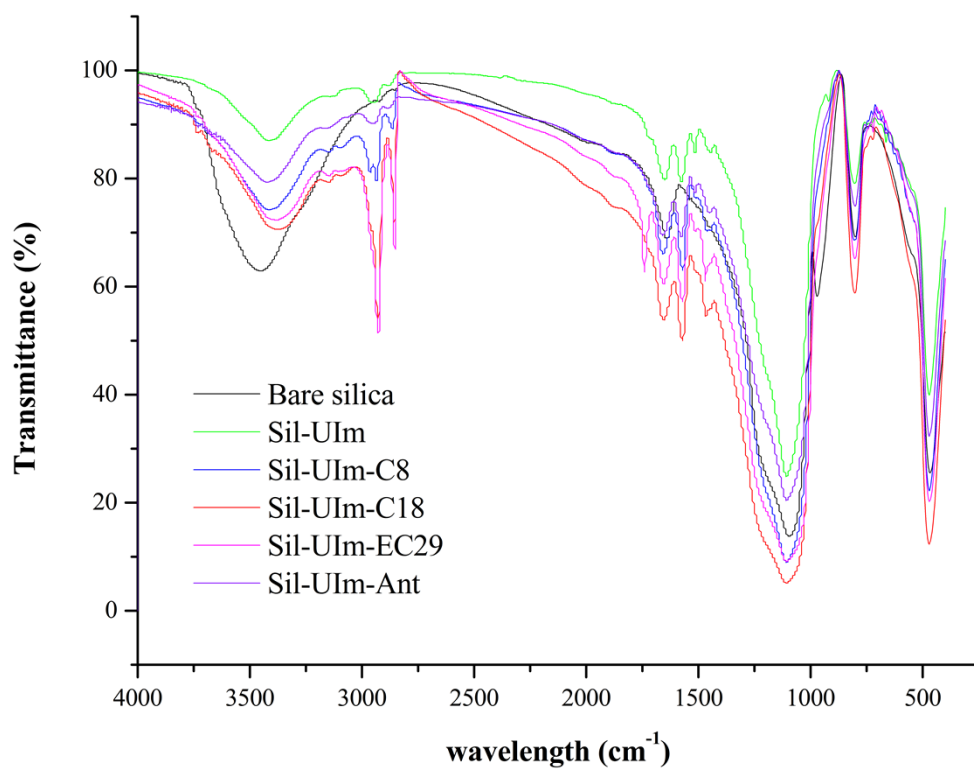


Fig. S2 Infrared Spectra of bare silica and modified silica

No.	Material	Elemental analysis						Contact angle (°)
		C%	N%	H%	Experimental C/N ratio	Theoretical C/N ratio	Surface coverage ( $\mu\text{mol}\cdot\text{m}^2$ )	
1	Sil-UIm	12.10	5.53	2.03	2.18	2.14	3.70	57.4
2	Sil-UIm-C8	14.78	3.76	2.40	3.92	3.86	2.25	94.7
3	Sil-UIm-C18	18.67	3.22	1.95	5.80	6.00	1.98	108.4
4	Sil-UIm-EC29	23.26	3.36	3.57	6.91	8.36	1.89	157.3
5	Sil-UIm-Ant	8.00	2.17	1.27	3.67	5.14	0.81	53.8

Table S1. Elemental analyses and surface properties of Sil-UIm and Sil-UIm-R.

Table S2 Selectivity factors for isomer terphenyls and triphenylene on different stationary phases.

Stationary phases	Selectivity factor ( $\alpha$ )			
	$\alpha_{m\text{-terphenyl}/o\text{-terphenyl}}$	$\alpha_{p\text{-terphenyl}/m\text{-terphenyl}}$	$\alpha_{\text{triphenylene}/p\text{-terphenyl}}$	$\alpha_{\text{triphenylene}/o\text{-terphenyl}}$
Sil-UIm <sup>a</sup>	1.82	1.01	1.16	2.84
Sil-UIm-C8 <sup>b</sup>	2.18	1.15	1.73	4.34
Sil-UIm-C18 <sup>c</sup>	2.03	1.15	2.02	4.74
Sil-UIm-EC29 <sup>c</sup>	2.62	1.41	2.54	9.37
Sil-UIm-Ant <sup>b</sup>	1.43	1.14	1.64	2.65
WondaSil C18 <sup>c</sup>	1.37	1.00	1.01	1.37

a: mobile phase was MeOH/water = 50/50 (v/v).

b: mobile phase was MeOH/water = 70/30 (v/v).

c: mobile phase was MeOH/water = 90/10 (v/v).

### **Reference**

1. E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, 1953, 75, 989-991.