Preparation of ionogel-bonded mesoporous silica and its application in liquid chromatography

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Caption:

Figure S1. Characterization of (a) FTIR spectra of bare silica, SH-silica and C_{12}-AVImBF$_4$@SiO$_2$, (b) TGA curves of bare silica and C_{12}-AVImBF$_4$@SiO$_2$, (c) Nitrogen physisorption isotherm of C_{12}-AVImBF$_4$@SiO$_2$ measured at 77 K.

Figure S2. The pore distribution C_{12}-AVImBF$_4$@SiO$_2$ materials measured at 77K.

Figure S3. (a) Chromatograms of 5 polycyclic aromatic hydrocarbons under different temperatures and (b) effect of column temperature on the retention of five polycyclic aromatic hydrocarbons on C_{12}-AVImBF$_4$@SiO$_2$ column. Analytes: 1. benzene, 2. naphthalene, 3. fluorene, 4. phenanthrene, 5. fluoranthene. Mobile phase: MeOH/H_2O (60/40, v/v). UV detection at 254 nm. Column temperature was investigated from 5 ℃ to 65 ℃ with an interval of 10 ℃; Flow rate: 1.0 mL/min.

Figure S4. Structure of eight amino acid analytes.

Figure S5. Structures of seven nucleosides and nucleobases analytes.

Figure S6. The structures of six sulfonamides.

Figure S7. Chromatograms of five polycyclic aromatic hydrocarbons under different volume fraction of the aqueous phase in the mobile phase (a) on C_{12}-AVImBF$_4$@SiO$_2$ column and (b) on the C18 column. Mobile phase: MeOH/H_2O with different volume fraction of the aqueous phase in the the mobile phase. UV detection at 254 nm. Column temperature: 25 °C. Flow rate: 1.0 mL/min.

Figure S8. Chromatograms of (a) the intra-day repeatability of polycyclic aromatic hydrocarbons on the C_{12}-AVImBF$_4$@SiO$_2$ column, (b) the inter-day repeatability of nucleosides and nucleobases on the C_{12}-AVImBF$_4$@SiO$_2$ column and (c) reproducibility between two C_{12}-AVImBF$_4$@SiO$_2$ columns for nucleosides and nucleobases. UV detection at 254 nm. Column temperature: 25 °C. Flow rate: 1.0 mL/min.

Figure S9. Stability of polycyclic aromatic hydrocarbons on the C_{12}-AVImBF$_4$@SiO$_2$ column after using for more than 6 months. Analytes: 1. benzene, 2. naphthalene, 3. fluorene, 4. phenanthrene, 5. fluoranthene. Mobile phase: MeOH/H_2O (60/40, v/v). UV detection at 254 nm. Column temperature: 25 °C. Flow rate: 1.0 mL/min.

Table S1

Elemental analysis results of corresponding materials

Table S2

Summary report of nitrogen physisorption isotherms of bare silica and C_{12}-AVImBF$_4$@SiO$_2$ measured at 77K.

Table S3

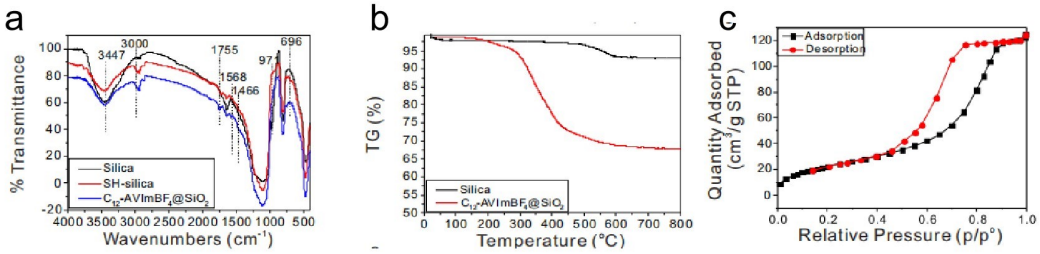
The values of ΔH and ΔS of van't Hoff plots.

Table S4

Intra-day and inter-day RSD of the retention time on C_{12}-AVImBF$_4$ @ SiO_2 column for 7 nucleosides and nucleobases compounds.

Instruments for materials characterization

Results and discussion: Influence of chromatographic conditions on retention behavior



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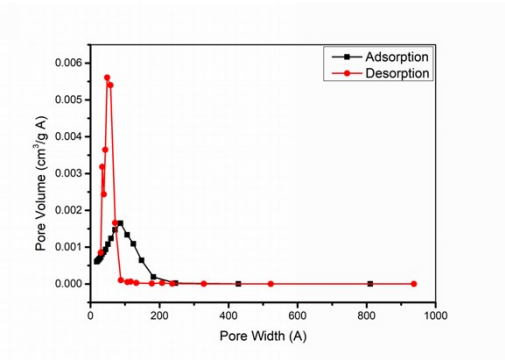

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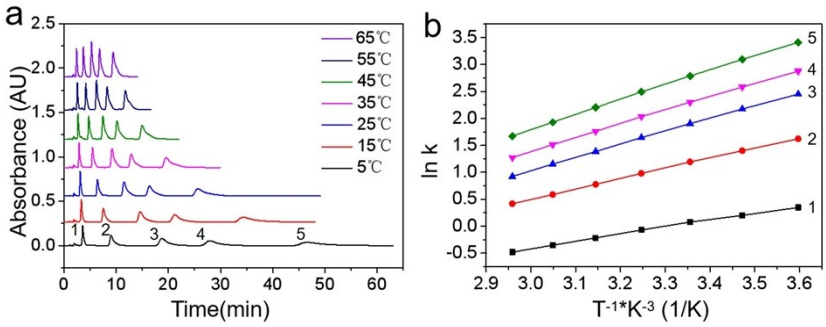

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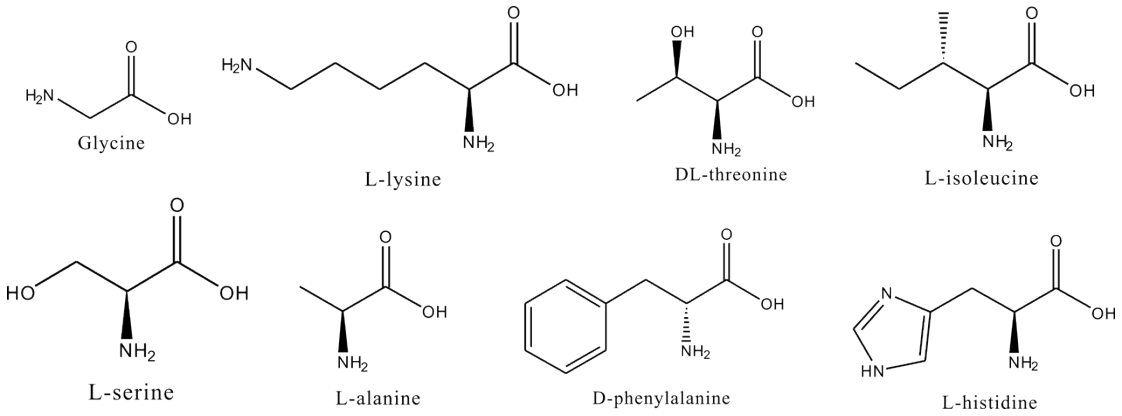

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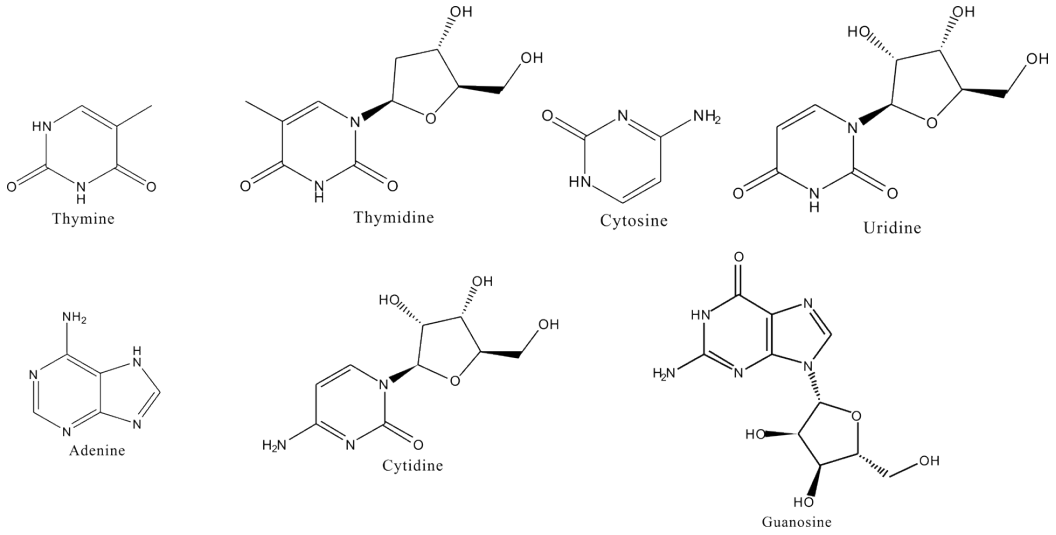
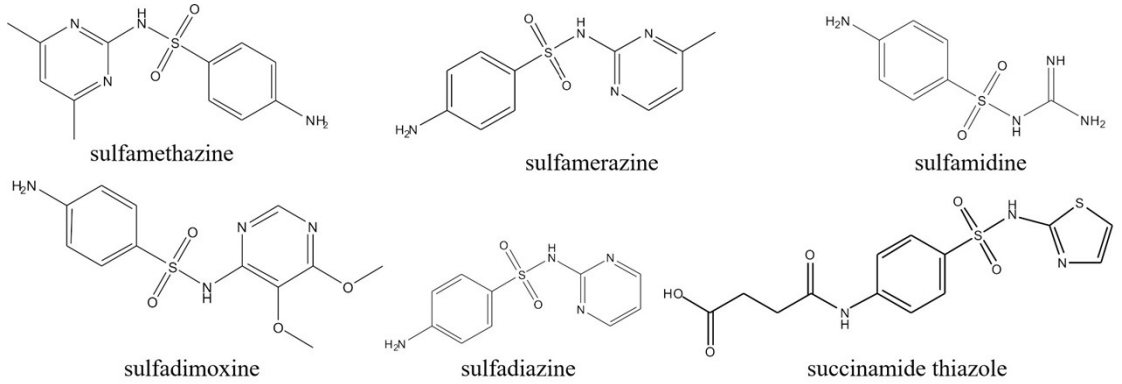


Figure S5. Structures of seven nucleosides/bases analytes.



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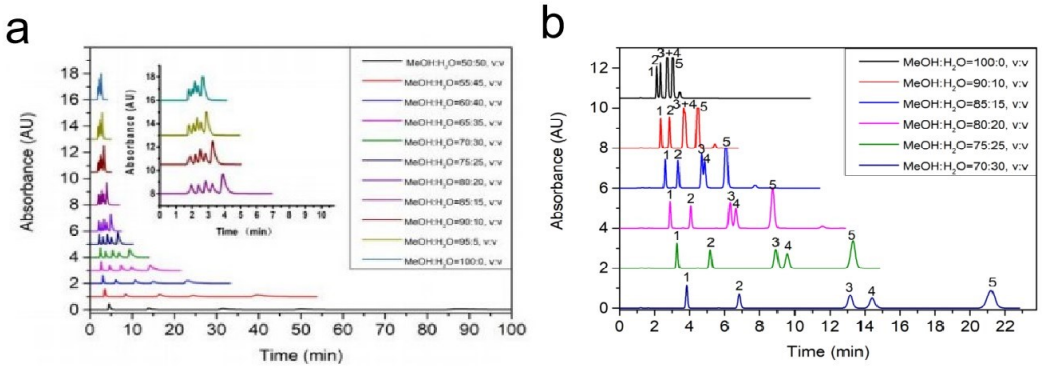

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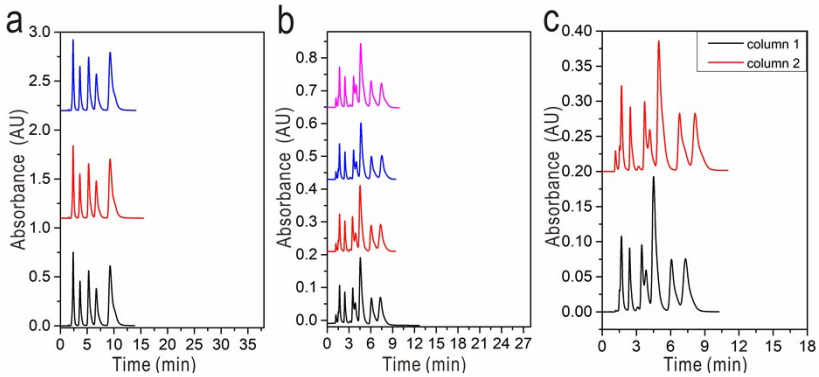

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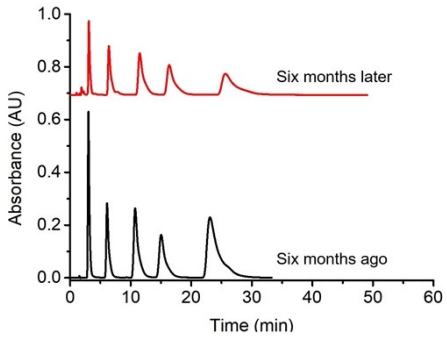

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Table S1

Elemental analysis results of corresponding materials

	N (%)	C (%)	H (%)
Silica	0.00	0.40	0.657
SH-silica	0.00	4.60	1.070
C_{12}-AVImBF$_4$@SiO$_2$	1.75	16.88	2.458

Table S2

Summary report of nitrogen physisorption isotherms of bare silica and C_{12}-AVImBF$_4$@SiO$_2$ measured at 77K.

		Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (Å)
C_{12}-AVIMBF$_4$@SiO$_2$	Adsorption	96	0.18	74
	Desorption	147	0.19	53
	Total	85	0.19	89
Bare silica	Adsorption	420	0.77	73
	Desorption	475	0.81	68
	Total	355	0.80	90

"The adsorption, and desorption of surface area, pore volume and pore size" are "BJH adsorption and desorption of surface area, pore volume and pore size". "Total of surface area, pore volume and pore size" refer to "BET Surface Area", "Single point adsorption total pore volume of pores less than 3412.896 Å width at p/p^o = 0.994318596" and "Adsorption average pore width (4V/A by BET)"

Table S3

The values of ΔH and ΔS of van't hoff plots.

Analytes	ΔS ($J \cdot mol^{-1}k^{-1}$)	ΔH ($kJ \cdot mol^{-1}$)	R^2
Benzene	-35.80	-10.80	0.996
Naphthalene	-43.17	-15.78	0.999
Fluorene	-51.18	-19.94	0.999
Phenanthrene	-51.13	-20.90	0.999
Fluoranthene	-53.07	-22.68	0.999

Table S4

Intra-day and inter-day RSD of the retention time on C_{12}-AVImBF$_4$ @ SiO$_2$ column for 7 nucleosides and nucleobases compounds.

	Intra-day (RSD, %)			Inter-day (RSD, %)
	1	2	3	
6-Chlorouracil	0	0.24	0.44	0.21
Thymidine	0.17	0.17	0	0.42
Thymine	0.30	0	0.29	0.77
Uridine	0.27	0.10	0.10	0.85
Adenine	0.23	0	0.15	0.51
Hypoxanthine	0.23	0	0.29	0.32
Inosine	0.28	0	0.31	0.26

Instruments for materials characterization

The obtained materials were characterized by fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), scanning electron microscopy (SEM), transmission electron microscopic (TEM), energy dispersive spectroscopy (EDS), thermogravimetric analysis (TGA) and N_2 adsorption/desorption experiments. The EA data were recorded on a Vario EL elemental analyzer (Elementar, Germany). The SEM images were taken from JSM6701F (JEOL, Japan). The FT-IR spectra were collected from an IFS 120HR fourier transform infrared spectrometer (Bruker, Germany). The TEM images were obtained from tecnai G2 TF20 transmission electron microscope (FEI, USA). The TGA of the stationary phases was collected on a STA-449 C thermogravimetric analyzer (Netzsch, Germany) in N2. The N2 adsorption surface areas were measured on an ASPS 2010 analyzer (USA).

Influence of chromatographic conditions on retention behavior

1. The effect of buffer concentration, pH value and mobile phase ratio on retention behaviour

We use different concentrations of ammonium acetate aqueous solution as the aqueous mobile phase to increase the ionic strength of the system, inhibit the dissociation of ionic compounds and optimize retention [1]. When other chromatographic conditions remain unchanged, the retention factors (k) of the analytes decrease with the increase of the buffer concentration in the mobile phase (Figure 3a). When keeping the other chromatographic conditions constant except the pH value of the buffer in the mobile phase, the retention factors (k) are the largest when the pH value of the buffer approaches 7 (Figure 3b). But these rules are exceptions for DL-threonine and L-serine, which have a larger and the longest retention time at the smallest buffer concentration. It also has the smallest retention time at the pH closest to neutral. The reason may be that the structures of these two amino acids both contain two hydroxyl groups (Figure S4). The dihydroxy structure easily forms intramolecular hydrogen bonds, making these two amino acids show different trends from the other six amino acids. As the volume fraction of the aqueous phase in the mobile phase increases, the retention factors (k) of the analytes increases (Figure 3c), so it can preliminarily be determined that retention is through hydrophilic interaction [2, 3].

2. The effect of column temperature on retention behavior

As an important condition that can affect the retention of hydrophobic analytes, the effect of the column temperature is mainly related to the enthalpy of analytes transfer between the stationary phase and the mobile phase. The van't hoff plot was often utilized to explore the relationship between column temperature and retention factor. We studied the thermodynamics of PAH separation in the temperature range of 5 to 65 °C. It is found that as the column temperature increases, the retention time of the analytes are greatly reduced, which indicates that the separation process is exothermic (Figure S3a). The van't hoff plot of the analytes showed a good linear correlation, indicating that the interaction mechanism did not change during the separation process (Figure S3b). Analysis from the values of ΔH and ΔS shows that

the retention of the analyte is not solely controlled by ΔH or ΔS (Table S3). This shows that the separation process is controlled by both of them.

[1] A. Czyrski, J. Sznura, The application of Box-Behnken-Design in the optimization of HPLC separation of fluoroquinolones, Sci. Rep. 9 (2019).
[2] T. L. Chester, The combination of partition, size exclusion, and hydrodynamic models in chromatography, and application to bonded phases on porous supports, J. Chromatogr. A 1620 (2020).
[3] M. Fourdinier, S. Bostyn, R. Delepee, H. Fauduet, Interest of a chemometric approach in understanding the retention behaviour of three columns in hydrophilic interaction liquid chromatography: Application to the separation of glycerol carbonate, glycerol and urea, Talanta , 81 (4-5) (2010) 1281-1287.