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Facile one-pot preparation of imidazolium embedded C₈ hybrid monolith using polyhedral oligomeric silsesquioxane for capillary liquid chromatography

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In this study, a novel imidazolium embedded C₈ hybrid monolithic column based on polyhedral oligomeric silsesquioxane (POSS) was developed. With 1-vinyl-3-octylimidazolium bromide (VOI) as functional monomer, POSS-methacryl substituted (POSS-MA) as cross-linker, and azodiisobutyronitrile (AIBN) as thermal initiator, the monolithic column was facily prepared via "one-pot" process. The prepared column was characterized by scanning electron microscopy, Fourier transform infrared spectrometry, thermogravimetric analysis, and element analysis, respectively. Due to the introduction of VOI to the POSS-based monolith, the column efficiency reached 124,000 theoretical plates/m for separation of alkylbenzenes, outperforming the previous reported pentafluorobenzyl imidazolium bromide modified POSS hybrid monolithic column. Furthermore, high-efficiency separation of polycyclic aromatic hydrocarbons, aromatic amines, and even phenolic isomers was also achieved. All these results suggest the potential merits of the prepared hybrid monolithic column for separation of small molecules.

Over the past few decades, monolithic columns have received comprehensive attention and been widely used in a variety of fields, such as proteomics, metabolomics and enantioseparation researches.¹⁻⁵ Based on the chemical nature of the monoliths, monolithic columns can be mainly divided into three types: organic polymer-based monoliths, silica-based monoliths, and organic-silica hybrid monoliths. Since organic-silica hybrid monoliths combine both the merits of organic polymer-based monoliths and silica-based monoliths, such as easy preparation, wide pH range tolerance, and high stability,^{6,7} in recent years, a variety of hybrid monolithic

columns have been developed and further used for high efficiency separation of both small molecules and macromolecules.⁸⁻¹²

Polyhedral oligomeric silsesquioxane (POSS), firstly discovered by Scott in 1946, possesses unique three-dimensional cubic structure and nanoscale dimension (diameter: 0.5 nm). As an ideal alternative to the traditional alkoxysilane reagents (such as tetramethoxysilane and tetraethoxysilane), POSS, with the merits of good pH tolerance, excellent oxidation and temperature resistance characteristics, has been developed to fabricate novel hybrid materials and nanocomposites.¹³⁻¹⁶ Since it was firstly introduced to prepare monolithic column by Zou et al.,⁴ several novel hybrid monolithic columns based on octaglycidyl dimethylsilyl POSS (POSS-epoxy),¹⁷⁻²⁰ POSS-methacryl substituted (POSS-MA),²¹⁻²⁵ and sodium 3-mercapto-1-propanesulfonate modified octavinyl octasilsesquioxane (MPS-OVS)²⁶ were fabricated. For example, with POSS-epoxy and a variety of diamines as monomers, a series of hybrid monolithic columns with well-controlled 3D skeletons were prepared by Zou et al.; high-efficiency separation of alkylbenzenes, polycyclic aromatic hydrocarbons, phenols and anilines was achieved with the prepared columns.¹⁷ By the polycondensation of hydrolyzed alkoxysilanes and in situ reaction of (3-mercaptopropyl)trimethoxysilane with MPS-OVS, cage-like silica nanoparticles-functionalized hybrid monolith was facily prepared. The fabricated monolithic column displayed with both reversed-phase and cation-exchange chromatographic retention mechanisms; anilines and phenols were well separated via capillary electrochromatography.²⁶

Ionic liquid is a salt in liquid state, possessing many excellent characteristics, such as low vapour pressure, high thermal stability and favorable solvating properties for both polar and non-polar compounds.²⁷⁻²⁹ Imidazolium-based ionic liquid was firstly introduced as modified silica-based stationary phase by Jiang et al.³⁰ Recently, they have been exploited for preparation of novel monolithic columns.³¹⁻³³ Because multiple interactions, such as electrostatic, dipole-dipole, hydrogen bonding and π - π , could be produced by imidazolium ion

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liquids; phenols, alkylbenzenes, nucleic acid bases/nucleosides, peptides and proteins were efficiently separated by the prepared monolithic columns introduced with different imidazolium ionic liquids.^{34–36} However, monolithic columns with the combination of both the merits of POSS and ionic liquid have been rarely discussed.

Herein, imidazolium embedded C₈ hybrid monolithic column is reported and facilely fabricated via “one-pot” approach using 1-vinyl-3-octylimidazolium bromide (VOI) as functional monomer and POSS-MA as cross-linker, as shown in Fig. 1. To the best of our knowledge, for the first time, imidazolium-based ionic liquid VOI is introduced into the POSS matrix so as to fabricate a novel hybrid monolithic column (POSS-VOI). Since the prepared monolithic column has combined both the merits of POSS and imidazolium ionic liquid, thus, high-efficiency separation can be achieved.

The composition of the prepolymerization is important for fabrication of the monoliths. Therefore, the effects of porogenic solvent and the ratio of functional monomer to cross-linker were investigated, as summarized in Table 1. With toluene and dodecanol as the porogenic solvents, transparent gel-like polymer was obtained (Column A). Porous polymer could be obtained with 1-propanol and 1,4-butanediol as the porogenic solvents (Column B). However, the polymer was very fluffy (permeability: $95.1 \times 10^{-14} \text{ m}^2$). By further reducing the content of 1,4-butanediol (Column C) or increasing the content of POSS-MA (Column D), the polymers were almost the same as the Column B. However, the permeability of the columns dramatically decreased to $11.6 \times 10^{-14} \text{ m}^2$ from $95.1 \times 10^{-14} \text{ m}^2$. When single porogenic solvent 1-propanol was used, the permeability of the column further decreased to $0.45 \times 10^{-14} \text{ m}^2$ (Column E). With further increasing the content of VOI, the pore diameter became bigger and the permeability of Column F increased to moderate $1.25 \times 10^{-14} \text{ m}^2$.²⁴ Furthermore, the column efficiency of Column F reached 124,000 theoretical plates/m for separation of benzene. By comprehensive consideration of the results mentioned above, the conditions for preparation of Column F were used for subsequent experiments, including of 24.0 mg of POSS-MA, 12.5 mg of VOI, 150 μL of 1-propanol, and 1 mg of azobisisobutyronitrile (AIBN). The detailed preparation procedures are shown in the ESI.†

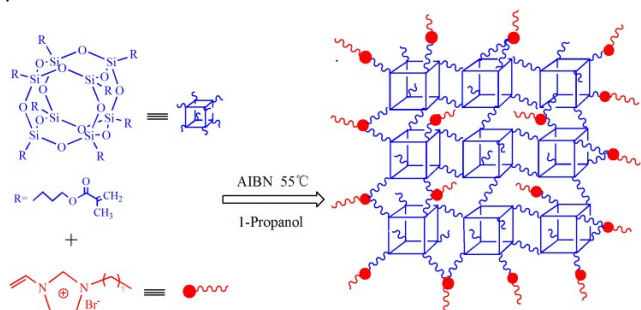


Fig. 1 Preparation of POSS-VOI hybrid monolithic column.

Table 1 The composition of polymerization mixture for preparation of POSS-VOI hybrid monolithic columns

Column	POSS-MA (mg)	VOI (mg)	Toluene (μL)	Dodecanol (μL)	1-Propanol (μL)	1,4-Butanediol (μL)	Permeability ($\times 10^{-14} \text{ m}^2$)
A	24.0	12.5	150	40	0	0	-
B	24.0	12.5	0	0	130	40	95.1
C	24.0	12.5	0	0	150	20	25.8
D	32.0	12.5	0	0	130	40	11.6
E	32.0	12.5	0	0	150	0	0.45
F	24.0	12.5	0	0	150	0	1.25

Scanning electron microscopy (SEM) was firstly used to characterize the prepared POSS-VOI hybrid monolithic column and the cross-sectional images with different magnifications are shown in Fig. 2. The prepared POSS-VOI monolithic column displays with homogeneous porous structure and the materials are well attached to the inner capillary wall without any disconnection (Fig. 2a and 2b). Furthermore, porous structure including large through-pores (about 1 μm) and continuous microglobules (about 0.5 μm) are observed (Fig. 2c and 2d). The total intrusion volume, median pore diameter (volume), and porosity are respectively 3.62 mL/g, 796.7 nm and 83.41% by mercury intrusion porosimetry.

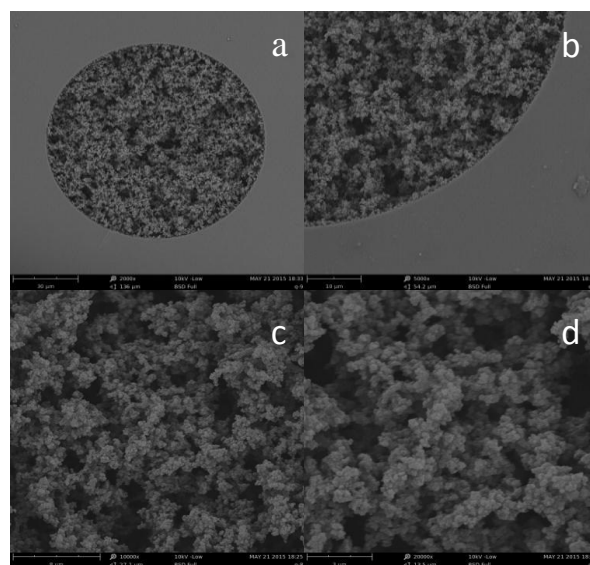


Fig. 2 SEM images of the cross-section of POSS-VOI hybrid monolithic column. Magnification: (a) 2000 \times , (b) 5000 \times , (c) 10000 \times , and (d) 20000 \times .

Fourier transform infrared (FT-IR) spectra provide a further proof that the POSS-VOI hybrid monolithic column was successfully prepared. The FT-IR spectra of POSS-MA, VOI and the prepared POSS-VOI hybrid monolithic column are shown in Fig. 3a. Bands around 1720 and 1639 cm^{-1} in POSS-MA could attribute to C=O and C=C double bonds of methacryl group, respectively. Bands 2927 and 2854 cm^{-1} in the spectrum of VOI could attribute to C–H stretching vibration of methyl and methylene groups while bands 1570 and 1550 cm^{-1} could ascribe to C=N stretching vibration of imidazolium ring. In the spectrum of POSS-VOI, Bands 1720, 1570 and 1550 cm^{-1} respectively attributing to POSS-MA and VOI could be

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simultaneously observed indicating that the POSS-VOI hybrid monolithic column was successfully fabricated. Element analysis was further used to characterize the prepared monolithic column and the elemental contents are C 45.11%, H 6.57% and N 1.70%, respectively. Thus, the bonded amount of VOI to the prepared monolithic column is 0.61 mmol/g based on the content of nitrogen element. Moreover, thermogravimetric analysis of the prepared monolithic column was simultaneously performed. As shown in Fig. 3b, an endothermic mass loss begins to aggravate around 270 °C indicating excellent thermostability of the prepared monolithic column. From the back pressure vs flow rate curves (Fig. S1, ESI[†]), the POSS-VOI hybrid monolithic column displays with good mechanical strength.

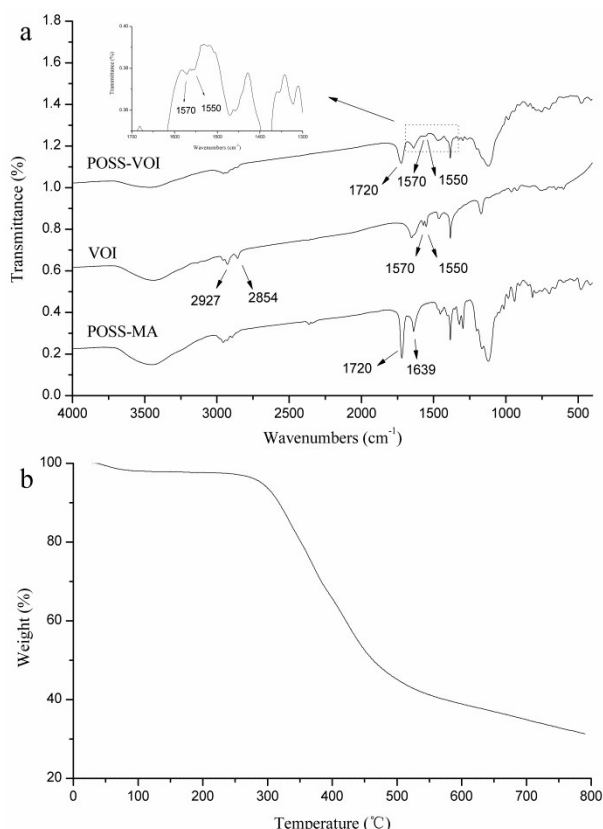


Fig. 3 Characterization of POSS-VOI hybrid monolithic column. (a) FT-IR spectra of POSS-MA, VOI and POSS-VOI hybrid monolithic column; (b) Thermogravimetric curve of POSS-VOI hybrid monolithic column.

With benzene as the mode analyte, the reproducibility for preparation of POSS-VOI hybrid monolithic column was investigated via the relative standard deviation (RSD) of the chromatographic retention time. The run-to-run ($n=7$) and day-to-day ($n=3$) repeatabilities for benzene are respectively 1.0% and 2.2% while the column-to-column ($n=3$) and batch-to-batch ($n=3$) repeatabilities are 2.4% and 8.7%, respectively. These results demonstrate the effectiveness and practicability for fabrication of the POSS-VOI hybrid monolithic column.

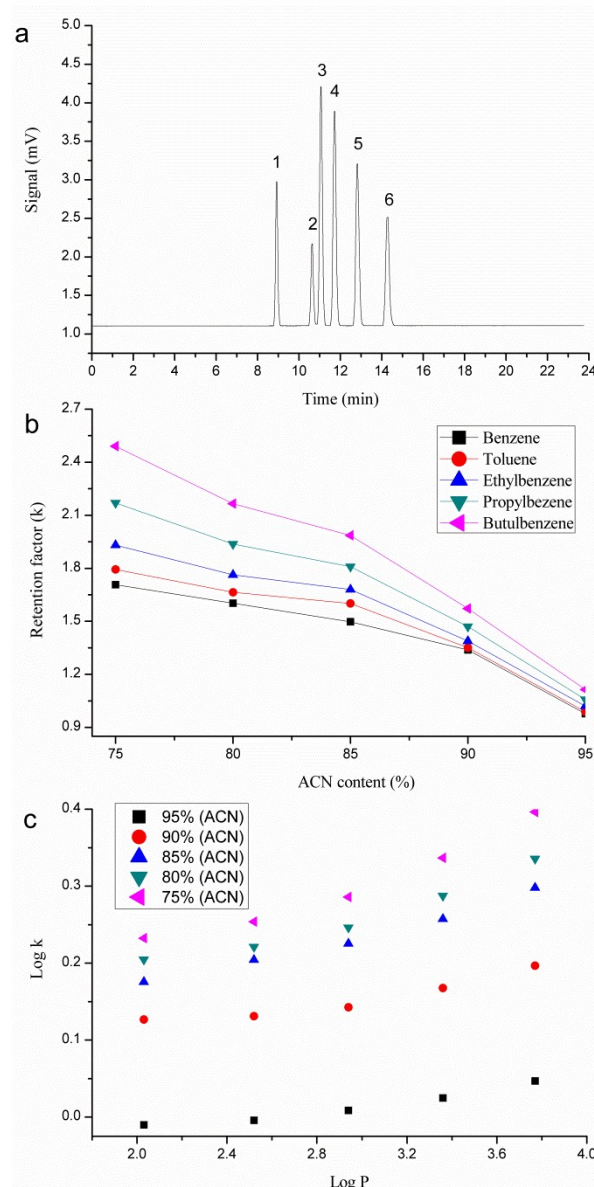


Fig. 4 Separation chromatogram of alkylbenzenes on the prepared POSS-VOI hybrid monolithic column (a). Analytes: 1, thiourea; 2, benzene; 3, toluene; 4, ethylbenzene; 5, propylbenzene; 6 butylbenzene. Effects of ACN content in eluent on k (b) and the relationship between $\log k$ and $\log P$ (c) of benzene, toluene, ethylbenzene, propylbenzene, butylbenzene on the prepared POSS-VOI hybrid monolithic column. Experimental conditions: effective length, 30 cm \times 100 μ m i.d.; mobile phase, ACN/H₂O (72/28, v/v) for (a) or with corresponding volume fractions for (b) and (c); flow-rate, 120 μ L/min (before split); detection wavelength, 214 nm.

Alkylbenzenes, including benzene, toluene, ethylbenzene, propylbenzene and butylbenzene, were firstly used to evaluate the chromatographic performance of the prepared POSS-VOI hybrid monolithic column. Solvent methanol was used as the void time marker in the experiments. With 72% acetonitrile (ACN)/28% H₂O as the mobile phase, baseline separation

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the five compounds was achieved, as shown in Fig. 4a. The column efficiency reached 124,000 theoretical plates/m (Table 2). In a recent work, Xu et al. prepared a pentafluorobenzyl imidazolium bromide modified POSS hybrid monolithic column and the column efficiency for separation of alkylbenzenes was about 72,000 theoretical plates/m.³⁷ Obviously, the developed POSS-VOI hybrid monolithic column exhibits excellent chromatographic performance compared with the pentafluorobenzyl imidazolium bromide modified monolithic column. Furthermore, the column efficiency of the prepared POSS-VOI hybrid monolithic column is also higher than the recent reported 1,4-bis(mercaptoacetoxymethyl) butane (BMAB) modified POSS (POSS-BMAB) hybrid monolithic column¹¹ with 73,000 theoretical plates/m for benzene. Moreover, the developed POSS-VOI hybrid monolithic column indicates with good symmetry and asymmetry factors ranging from 0.97 to 1.12 were observed.

Alkylbenzenes are typically hydrophobic compounds. Thus, the retention mechanism of the prepared POSS-VOI hybrid monolithic column was investigated with benzene (log P: 2.03), toluene (log P: 2.52), ethylbenzene (log P: 2.94), propylbenzene (log P: 3.36) and butylbenzene (log P: 3.77). Log P is the logarithm of the partition coefficient of the analytes in octanol to water which reflects the hydrophobicity of the analytes. As shown in Fig. 4b, the retention factors (*k*) of these compounds rapidly decrease when the volume fractions of ACN in eluent increase to 95 from 75%, indicating typical reversed-phase liquid chromatography (RPLC) retention characteristic. The relationship between log *k* and log P further verifies the RPLC retention mechanism of the prepared POSS-VOI hybrid monolithic column. As shown in Fig. 4c, when the volume fractions of ACN in eluent are respectively 75, 80, 85, 90 and 95%, a gradual increment of retention is observed with the increment of hydrophobicity of these compounds.

The developed POSS-VOI hybrid monolithic column was further used for separation of polycyclic aromatic hydrocarbons, phenols and aromatic amines. The representative chromatogram for separation of polycyclic aromatic hydrocarbons (1,10-phenanthroline monohydrate, diphenyl, phenanthrene, m-terphenyl and triphenylene) is shown in Fig. 5a. With 90% ACN/10% H₂O as the mobile phase, baseline separation of the five compounds was achieved and

the maximum column efficiency reached 134,000 theoretical plates/m. Moreover, high-efficiency separation of phenols (2-aminophenol, hydroquinone, m-dihydroxybenzene, catechol and 2-amino-4-chlorophenol) was also achieved (Fig. 5b) and the resolution of isomers hydroquinone, m-dihydroxybenzene and catechol reached 4.97 and 4.76. Thus, the prepared POSS-VOI hybrid monolithic column displays with good planar selectivity. Especially, basic aromatic amines, including triphenylamine, 1,2-diaminobenzene, 1-naphthylamine and diphenylamine, were baseline-separated with 85% ACN/15% H₂O as the mobile phase while the peaks were all symmetric without apparent peak tailing (Fig. 5c).

Table 2 Separation parameters of alkylbenzenes in the prepared POSS-VOI hybrid monolithic column

Analytes	Retention time (min)	Resolution	Tailing factor	Column efficiency (plates/m)
Benzene	10.6	1.74	0.97	124,000
Toluene	11.1	2.51	1.09	107,000
Ethylbenzene	11.7	3.85	1.09	101,000
Propylbenzene	12.8	4.64	1.12	103,000
Butylbenzene	14.3	-	1.11	103,000

Conclusions

In summary, a novel imidazolium embedded C₈ hybrid monolithic column based on polyhedral oligomeric silsesquioxane was facilely prepared via "one-pot" approach. The method for the preparation of the monolithic column is simple, convenient and the novel monolithic column displays with good separation ability for alkylbenzenes, polycyclic aromatic hydrocarbon, aromatic amines and even phenolic isomers in RPLC model, outperforming the previous reported pentafluorobenzyl imidazolium bromide modified POSS hybrid monolithic column. In the future work, we hope to prepare a series of POSS-based monolithic columns by introducing of ionic liquids with different characteristics so as to achieve high-efficiency separation of both small molecules and macromolecules with multiple retention mechanisms.

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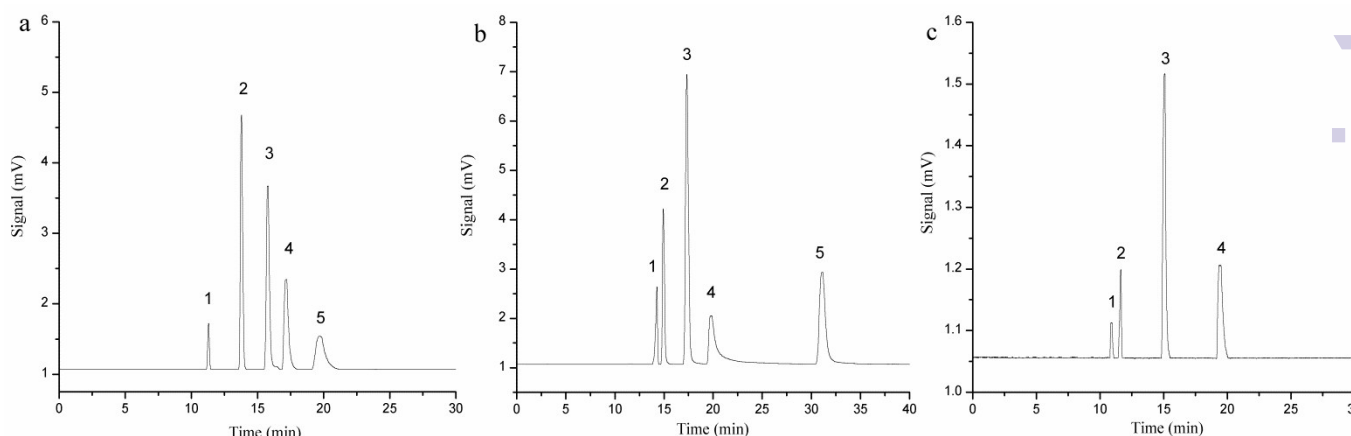


Fig. 5 Separation chromatograms of polycyclic aromatic hydrocarbons (a), phenols (b), and aromatic amines (c) on the prepared POSS-VOI hybrid monolithic column. Experimental conditions: effective length, 30 cm \times 100 μ m i.d.; mobile phase, ACN/H₂O (90/10, v/v) for (a), ACN/H₂O (73/27, v/v) for (b), and ACN/H₂O (85/15, v/v) for (c); flow rate, 160 μ L/min; detection wavelength, 254 nm for (a) and 214 nm for (b) and (c). Peaks for (a): 1, 1,10-phenanthroline monohydrate; 2, diphenyl; 3, phenanthrene; 4, m-terphenyl; 5, triphenylene. Peaks for (b): 1, 2-aminophenol; 2, hydroquinone; 3, m-dihydroxybenzene; 4, catechol; 5, 2-amino-4-chlorophenol. Peaks for (c): 1, triphenylamine; 2, 1,2-diaminobenzene; 3, 1-naphthylamine; 4, diphenylamine.

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