Supporting information for

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

Niu Zhang,[a] Lu Zhang,[a] Xiaoqiang Qiao,*[a] Yongli Wang,[b] Hongyuan Yan[a] and Ligai Bai[a]

[a]Key Laboratory of Medicinal Chemistry and Molecular Diagnosis, Ministry of Education and Key Laboratory of Pharmaceutical Quality Control of Hebei Province, College of Pharmaceutical Sciences, Hebei University, Baoding 071002, China.

[b]Affiliated Hospital of Hebei University, Baoding 071000, China.

Materials and reagents

γ-Methacryloxypropyltrimethoxysilane (γ-MAPS) was purchased from Acros Organics (NJ, USA). Polyhedral oligomeric silsesquioxane methacryl substituted (POSS-MA) was obtained from Sigma-Aldrich (St. Louis, MO, USA). 1-Vinyl-3-octylimidazolium bromide (VOI) was from Shanghai ChengJie Chemical (Shanghai, China). Azobisisobutyronitrile (AIBN) was purchased from J&K Scientific (Beijing, China). Fused-silica capillary with 100 μm i.d. and 365 μm o.d. was obtained from Hebei Yongnian Optical Fiber Plant (Hebei, China). 1,4-Butanediol, 1-propanol, thiourea, benzene, toluene, ethylbenzene, propylbenzene, butylbenzene and dodecanol were from Tianjin Guangfu Fine Chemical Research Institute

(Tianjin, China). Triphenylamine, diphenylamine, 1,10-phenanthroline monohydrate, diphenyl, phenanthrene, m-terphenyl, triphenylene, 2-aminophenol, hydroquinone, m-dihydroxybenzene, catechol, 2-amino-4-chlorophenol, 1,2-diaminobenzene and 1-naphthylamine were purchased from Tianjin Kemiou Chemical Reagent (Tianjin, China). HPLC-grade acetonitrile (ACN) and methanol were obtained from Thermo Fisher Scientific (New York, USA). Water was purified by a Milli-Q system (Millipore, Molsheim, France).

Apparatus

Scanning electron microscopy (SEM) was performed on a Phenom pro desktop scanning electron microscope (Philips, Eindhoven, Netherlands). Fourier transform infrared (FT-IR) spectra were obtained on a Bruker Vertex 70 spectrometer (Bruker Optik GmbH, Ettlingen, Germany). Thermogravimetric analysis (TGA) was carried out on a TGA/SDTA851E system (Perkin-Elmer, Boston, USA). Pore size distribution was determined by mercury intrusion porosimetry on an AutoPore II 9220V instrument (Micromeritics Instrument, Atlanta, GA, USA). Element analysis was performed on a CE-440 elemental analyzer (EAI, Chicago, USA). HPLC experiments were carried out on a self-assembled c-LC system consisting of a Valco ten-port injection valve (Houston, USA) with a 2 μL sample loop, two intelligent P230II pumps (Dalian Elite Analytical Instrument, Dalian, China), a Knauer K-2520 UV detector (Berlin, Germany), and a HW-2000 workstation (Qianpu software, Shanghai, China). To obtain the nano-flow rate, a T-union connector was used for splitter by connecting one end to the blank capillary (78 cm×50 μm i.d.) while the other end was directly connected to the prepared hybrid monolithic column. At the end of the monolithic column, a detection window was made by removing the polyimide coat (about 2 mm) and the column was directly passed

on the detector. The split ratio was set at about 500:1.

Preparation of POSS-VOI hybrid monolithic column

Firstly, the bare capillary (100 μm i.d.) was flushed with 1.0 M NaOH for 3 h, washed with water until pH ~7.0, followed by 1.0 M HCl for 2 h and further washed with water until pH ~7.0. Secondly, the bare capillary was rinsed by methanol and dried by nitrogen stream at room temperature. Subsequently, 50% γ-MAPS methanol solution was filled into the capillary and submerged into the water bath for 12 h at 60 °C with both the two ends sealed with silicone rubbers. Finally, the capillary was flushed with methanol to remove the residuals, dried by nitrogen stream again, ready for further use.

The POSS-VOI hybrid monolithic column was prepared via "one-pot" approach. A prepolymerization mixture comprising of POSS-MA (as cross-linker), VOI (as functional monomer), AIBN (as initiator) and 1-propanol (as porogenic solvent) was firstly mixed in a 2 mL vial. After it was ultrasonicated for 15 min, the formed homogeneous solution was directly injected into the pretreated capillary via a syringe, followed by submerging into the water bath for 15 h at 55 °C with both the two ends sealed with silicone rubbers. Finally, the prepared hybrid monolithic column was flushed with methanol for 2 h, ready for use. Furthermore, the bulk hybrid monolith which was used for subsequent characterization by FT-IR, thermogravimetric analysis, mercury intrusion porosimetry, and element analysis was also prepared. The preparation conditions were the same as that for the preparation of the hybrid monolithic column except that the prepolymerization mixture directly polymerized in a 2 mL vial.

Chromatographic conditions

The monolithic column (100 μm i.d.) with a total length of 39 cm (effective length of 30 cm) was used for chromatographic separation under isocratic elution. The column temperature was room temperature. The separation of alkylbenzenes, phenols and aromatic amines was performed with ACN-water as the mobile phase and UV detection at 214 nm while the separation of polycyclic aromatic hydrocarbons was performed with ACN-water as the mobile phase and UV detection at 254 nm.

Calculation

The permeability (*K*) which reflects the external porosity and through-pore size of the monolithic columns can be calculated based on the Darcy's equation [1]:

$$K = \frac{F \times \eta \times L}{\Delta P \times \pi \times \mathrm{r}^2}$$

Where *F* (m^3/s) is the flow rate of the mobile phase, η (Pa s) is the dynamic viscosity of the mobile phase, *L* (m) is the column length, ΔP (Pa) is the backpressure of the monolithic columns, and *r* (m) is the inner radius of the monolithic columns. Herein, ACN was used as the mobile phase and the corresponding value of η is 0.38 Pa s [2].

Retention factor (*k*) can be calculated based on the formula:

$$k = \frac{t_R - t_0}{t_0}$$

where t_R and t_0 represent the retention time of the analytes and the void time, respectively.

Resolution (*R*) which indicates the separation degree of the two adjacent peaks in HPLC can be calculated based on the formula:

$$R = \frac{t_{R_2} - t_{R_1}}{(W_2 + W_1)/2}$$

where t_{R1} and t_{R2} are the retention time of the adjacent peaks 1 and 2 , W_1 and W_2 are the peak width of the adjacent peaks 1 and 2.

Tailing factor (T) which reflects the symmetry of the peaks in HPLC can be calculated based on the formula:

$$T = \frac{W_{0.05\mathrm{h}}}{2A}$$

where $W_{0.05h}$ is the peak width at one-twentieth of the peak height, A is the distance between the leading edge of the peak and the perpendicular dropped from the peak maximum at one-twentieth of the peak height.

Column efficiency (N) which reflects the column performance can be calculated based on the formula:

$$N = 5.54(\frac{t_R}{W_{1/2}})^2$$

where t_R is the retention time of the analytes, $W_{1/2}$ is the peak width at half height.

The parameters of resolution, tailing factor and column efficiency can be automatically calculated via the HW-2000 Workstation (Qianpu software, Shanghai, China). Furthermore, the log P values of the analytes can be calculated via the software Chemical Office 2004.

Notes and references

[1] S. Shen, F. Ye, C. Zhang, Y. Xiong, L. Su and S. Zhao, *Analyst*, 2015, **140**, 265-271.

[2] Y. Wang, Q. Deng, G. Fang, M. Pan, Y. Yu, S. Wang, *Anal. Chim. Acta*, 2012, **712**, 1-8.

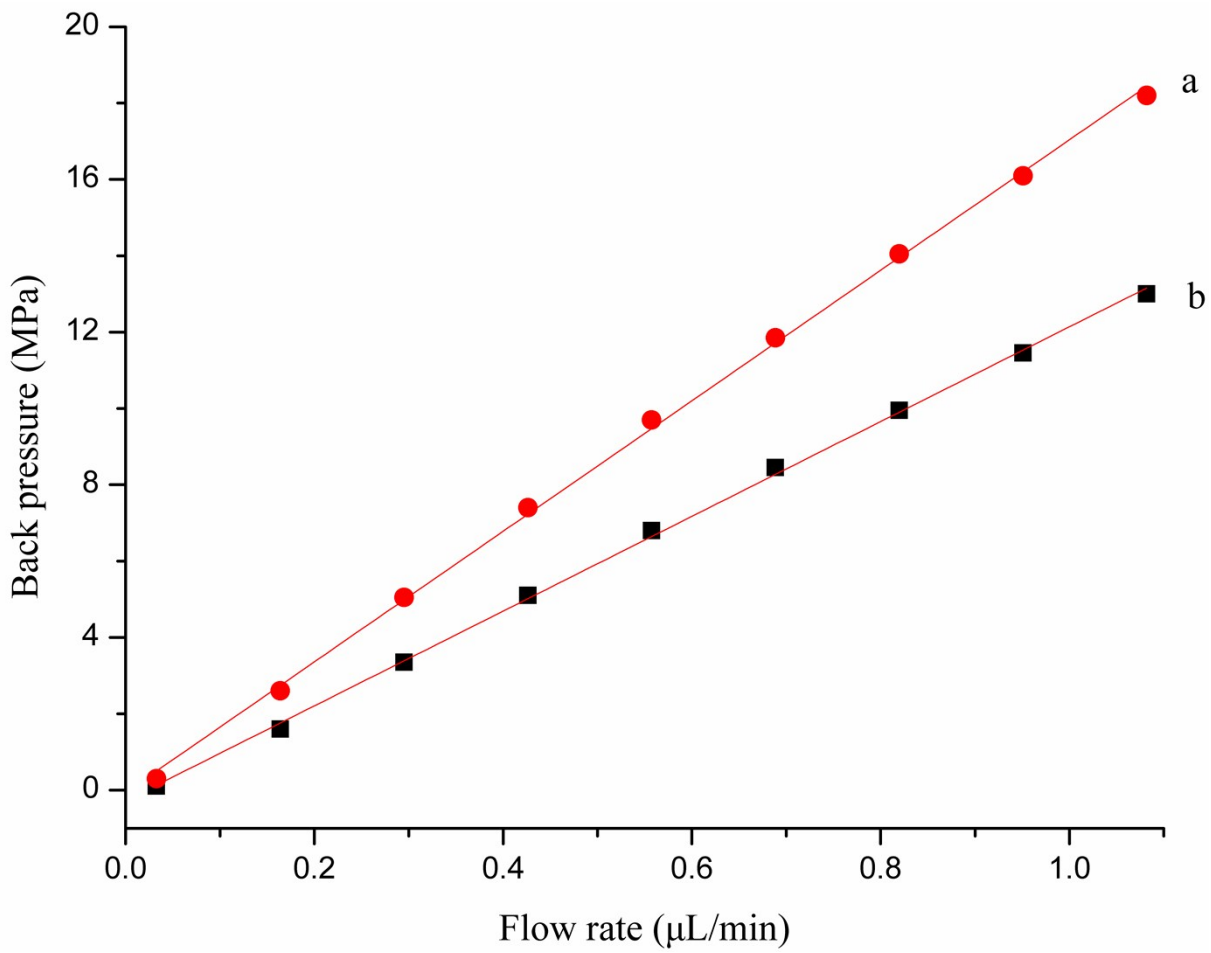

Fig. S1 Back pressure against flow rate of the prepared POSS-VOI hybrid monolithic column. Experimental conditions: effective length, 30 cm × 100 μm i.d.; mobile phase, methanol for (a) and ACN for (b).