Electronic Supporting Information

Polyhedral oligomeric silsesquioxane (POSS) -based multifunctional organic-silica hybrid monolith

Xucong Lin [a],*, Na Zheng [a], Jinzhen Wang [a], Xiao Wang [a], Yanqiong Zheng [a] and Zenghong Xie [a]

[a] *Institute of food safety and environmental monitoring, Fuzhou University, 350108, China.*

* Corresponding author: Xucong Lin

E-mail: xulin@fzu.edu.cn

Fax: +86-591-22866131; Tel: +86-591-22866131;

1. Experimental section

1.1 Materials and Chemicals

Vinylbenzyl trimethylammonium chloride (VBTA) and 3-trimethoxysilyl propyl methacrylate (γ-MAPS) were purchased from Acros (NJ, USA). Polyhedral oligomeric silsesquioxane-methacrylsub stituted (POSS-MA, n=8,10,12) was purchased from Sigma (St. Louis, MO, USA). Azobisisobutyronitrile (AIBN) was obtained from the Forth Chemical Reagent Plant (Shanghai, China) and recrystallized in ethanol before use. Cyclohexanol and dodecanol were purchased from Tianjin Chemical Plant (Tianjin, China). Uracil, uridine, adenine, adenosine, cytosine, cytidine and guanine were purchased from Sigma (St. Louis, MO, USA). Phenol, catechol, hydroquinone, pyrogallol, phloroglucinol, thiourea, N, N-dimethylenebisacrylamide, acrylamide, acetamide, N, N-dimethylformamide (DMF), formamide were of analytical grade (Chemical Reagent Plant, Shanghai, China). Benzoic acid (B), 4-hydroxybenzoic acid (4-HB), 3,4-dihydroxybenzoic acid (3,4-DHB), 3,4,5-trihydroxybenzoic acid (3,4,5-THB), PAHs were purchased from Aldrich (Milwaukee, WI, USA). Nucleobases, nucleoside and estrogens were purchased from Sigma (St. Louis, MO, USA). HPLC-grade methanol and ACN were purchased from Chemical Reagent Corporation (Shanghai, China). The fused-silica capillaries with a dimension of 100-μm ID (375-μm OD) were purchased from the Yongnian Optic Fiber Plant (Hebei, China).

1.2 Instrumentation

The experiments were performed on a cLC system (Unimicro Technologies, Pleasanton, CA, USA) equipped with a UV/Vis detector (190–600 nm), comprising a microvolume pumps, a microfluid manipulation module (including a six-port injector) with a splited pump flow, and a data acquisition module. Pressure was applied to the column inlet during the separation. In this experiment, the pump flow was splited with a ratio of 1:200 (v/v).

Scanning electron micrographs (SEM) of the monolithic columns were carried out on an XL30 E scanning electron microscope (Philips, The Netherlands).

1.3 Preparation of poly(POSS-MA -co- VBTA) monolith

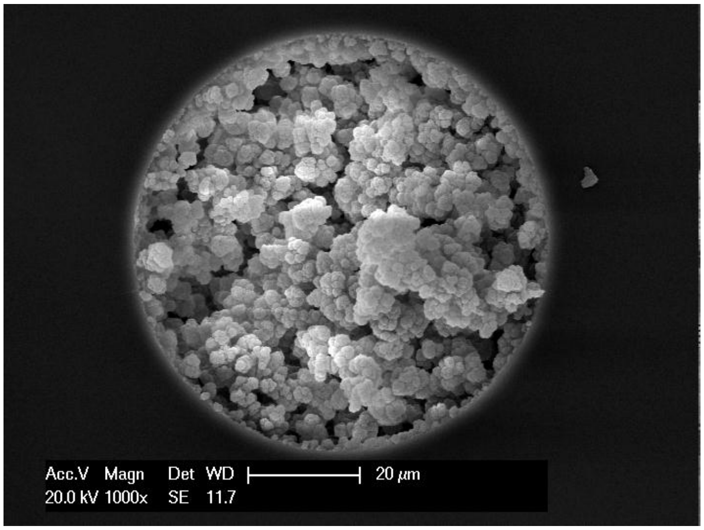
Prior to use, the inner wall of the capillary was firstly treated with λ-MAPS [S1]. Polymerization solutions were prepared from monomers and porogenic solvents. The mixtures of monomers (POSS-MA, VBTA) were weighed and dissolved in ternary porogenic solvents consisting of cyclohexanol, dodecanol and N,N-Dimethylformamide (see Table S1). AIBN (2.0 mg) was added to the porogenic solvents. The mixtures were vortexed and then ultrasonicated for 15 min respectively to obtain homogeneous solution. The polymerization mixture was kept in ice until it was injected into the capillary for 35-cm length. The capillary was plugged at both ends with silicone rubbers and submerged into a thermostatic bath at 55 ℃ for 12h. The obtained monolith was washed with methanol to flush out the residual reagents. A detection window was created at 1-2 mm at the end of the polymer bed. Finally, the column was cut to a total length of 50 cm with an effective length of 30 cm.

Reference

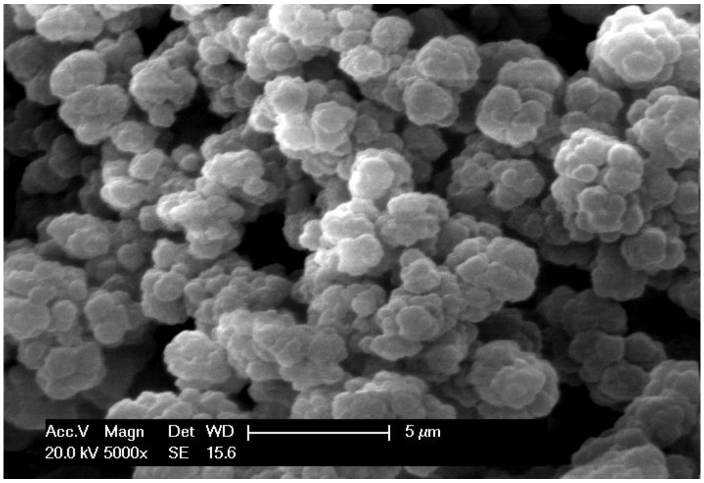
S1. B. Xiong, L. Zhang, Y. Zhang, and H. Zou, *J. High Resolut. Chromatogr.*, 2000, **23**，67-72.

2. Results and discussions

2.1 Supporting Figures



(a) 1000×



(b) 5000×

Fig.S1 SEM of the cross section of the column B

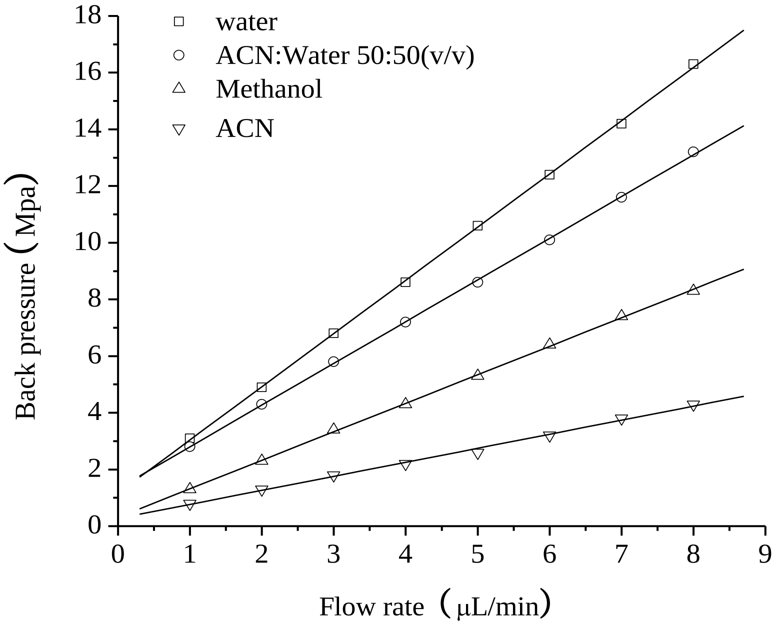


Fig.S2 Dependence of column pressure on the flow rate in different mobile phase

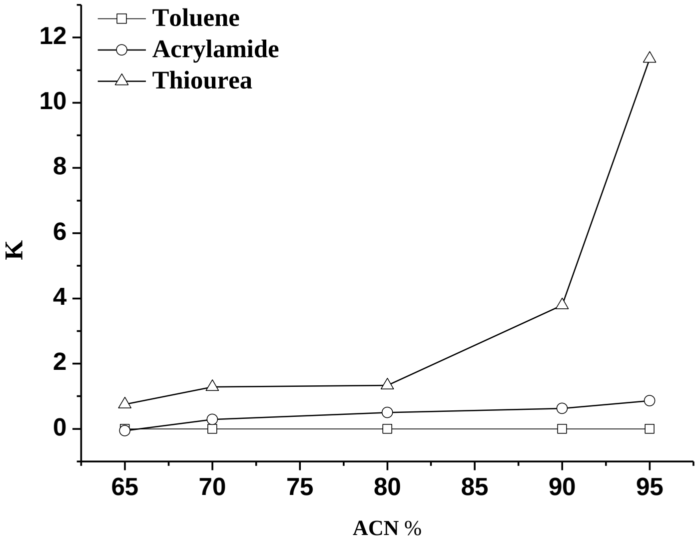


Fig. S3 Plots of retention times versus ACN content

Experimental conditions: mobile phase, 5 mmol/L ammonium formate buffer pH 5.0; supplement pressure: 0.9 MPa; pump flow rate: 0.1 mL /min; detection wavelength: 214 nm. Solutes: □. Toluene; O. Acrylamide; Δ. Thiourea

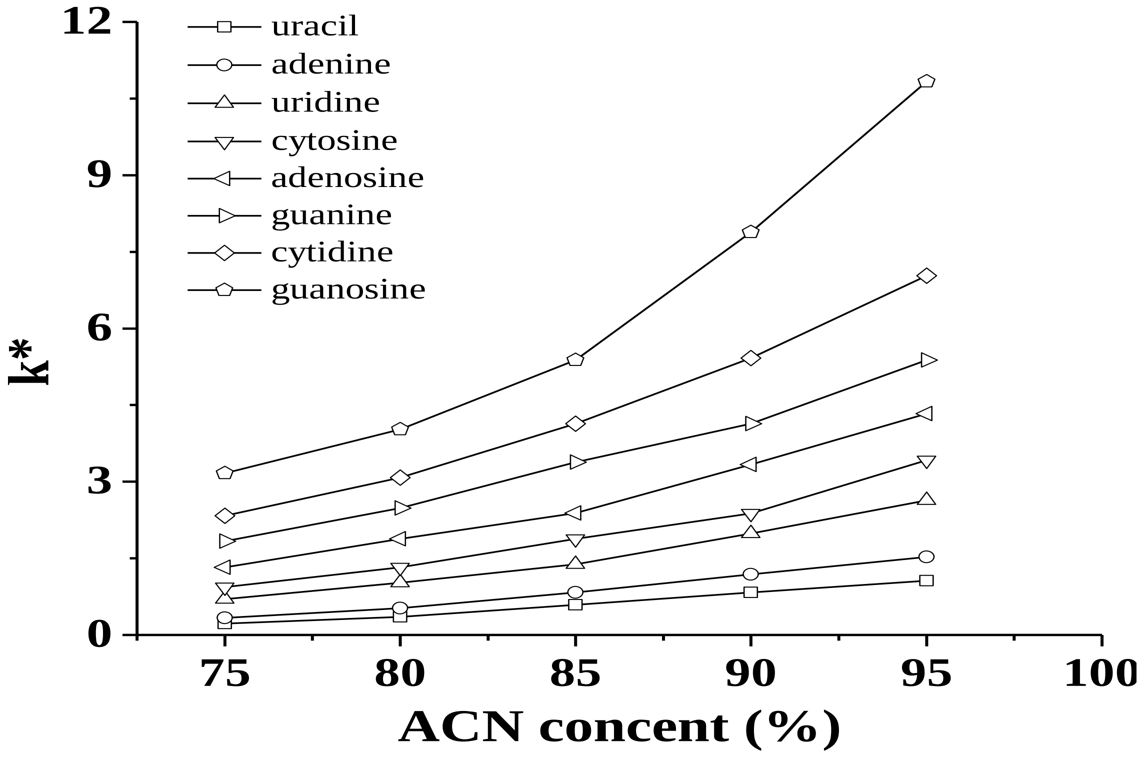


Figure S4. Effect of ACN content on the retention factor (k).

Experimental conditions: 5 mmol/L ammonium formate（pH 4.5）in ACN/Buffer (v/v).

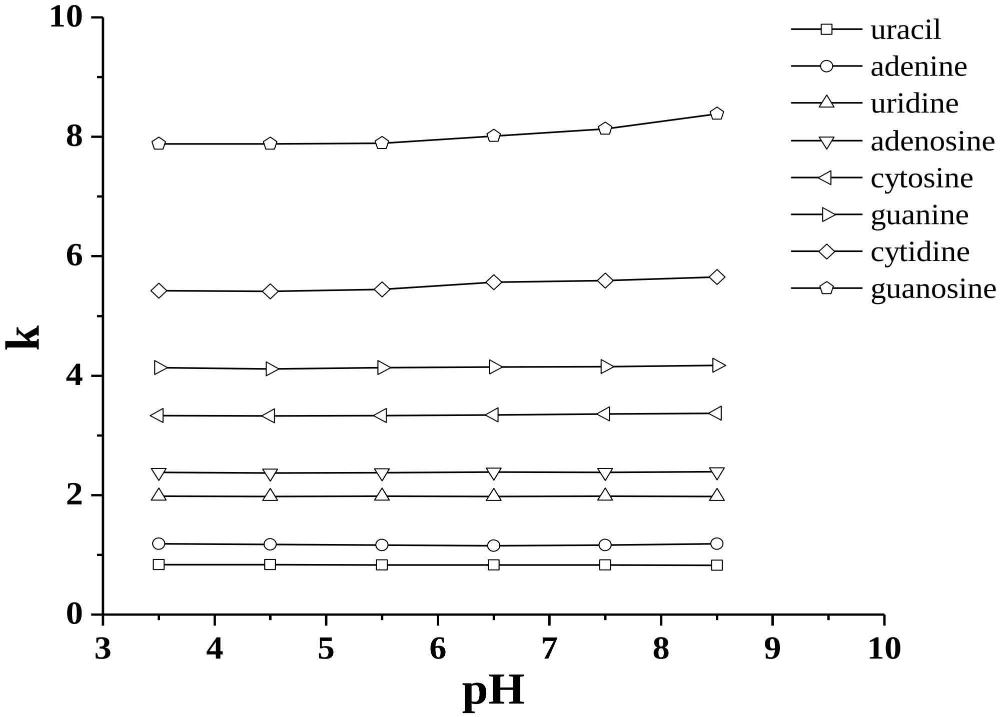


Figure S5. Effect of pH on the retention factor (k).

Experimental conditions: mobile phase: 5 mmol/L ammonium formate buffer in ACN/Buffer (85/15, v/v)

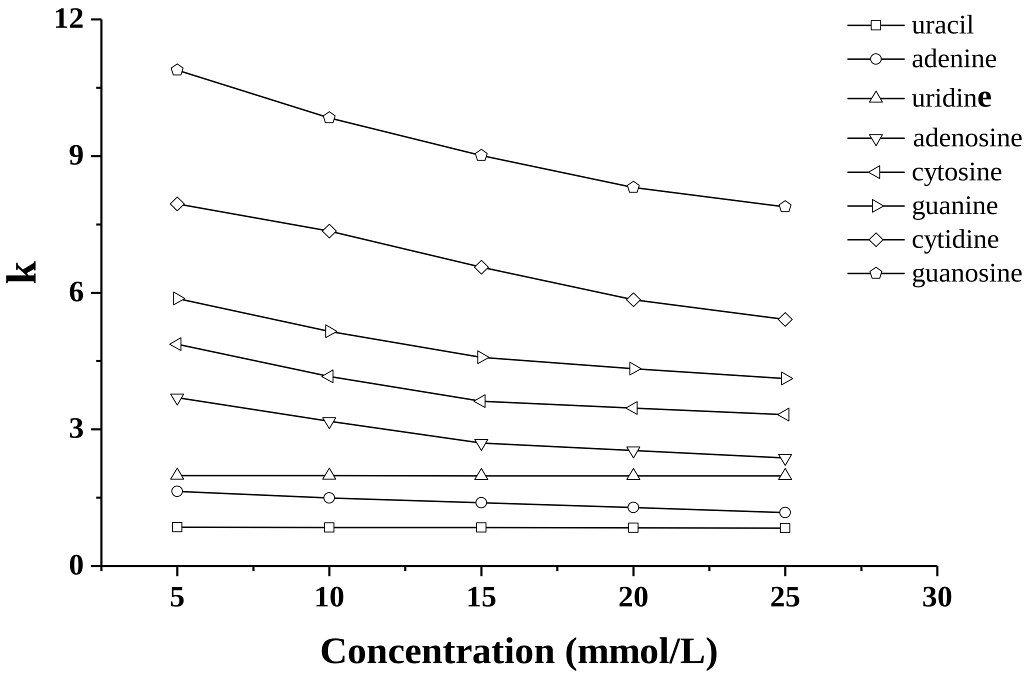


Figure S6. Effect of salt concentration on the retention factor (k).

Experimental conditions: mobile phase: 5 mmol/L ammonium formate buffer in ACN/Buffer (85/15, v/v)

2.2 Supporting Tables

Table. S1 Different porogen used in the preparation hybrid silica monolith

Porogen solvent mixture	homogeneity	permeability	column efficiency	mechanical stability
toluene-dodecanol	good	poor	n/a	n/a
1,4-butanediol-N-propanol	poor	n/a	n/a	n/a
methanol- dodecanol	good	good	poor	poor
N,N-Dimethylformamide - dodecanol	good	good	poor	poor
N,N-Dimethylformamide-Cyclohexanol - dodecanol	good	good	good	good

Table. S2 Composition of the polymerization solutions for hybrid silica monolith [a)]

Column designation	Porogen [b)]	Monomers		Permeability[c)] (K×$10^{-13}$$m^2$)	k^*_{thiourea}	N_{max}[d)] (plates/m)
	Dodecanol （μL)	VBTA (mg)	POSS-MA (mg)			
A	270	40	10	2.36	0.93	39000
B	250	40	10	1.19	1.32	78000
C	230	40	10	0.23	1.34	35000
D	250	40	8	1.36	1.32	62000
E	250	40	6	1.61	1.26	48000
F	250	30	10	1.41	1.18	53000
G	250	20	10	1.81	1.01	42000
H	250	50	20	n/a	n/a	n/a

Experimental conditions: mobile phase, 5 mmol/L ammonium formate buffer pH 5.0 in ACN/buffer (85/15, v/v); supplement pressure: 0.9 MPa; pump flow rate: 0.1 mL/ min; detection wavelength: 214 nm.

a). Other preparation condition: AIBN, 2mg;

b). N,N-Dimethylformamide, 10μL. The value of cyclohexanol and dodecanol was 330μL.

c). The permeability was measured by using 80/20 (v/v) acetonitrile/bufferr.

d) The column efficiency of thiourea.

n/a: The measurements could not be made because the columns were not applicable.

Table. S3 Reproducibility of retention time and column efficiency

	Retention time (% RSD)			Column efficiency (% RSD)		
	Thiourea	Uracil	Cinnamic	Thiourea	Uracil	Cinnamic
run to run[a)] (n=6)	0.9	2.0	1.6	1.5	2.6	2.1
day to day[a)] (n=5)	1.5	2.5	2.3	2.3	3.1	2.9
column to column[b)] (n=6)	2.8	3.4	3.1	2.9	3.6	3.3
batch-to-batch (n=4) [c)]	3.4	4.1	3.8	3.5	4.6	4.1

a) The % RSD of run-to-run and day-to-day was calculated by the same column.

b).The meaning of column-to-column (n = 6) was that the columns were prepared from three batches and each batch contained two columns.

c) The meaning of batch-to-batch (n = 6) was that the monoliths were prepared from four batches and every batch contained three columns.

Table S4 α(ribose) values of four nucleoside in different monoliths

Column designation	α(ribose)				Reference
	$k_{(uridine)}$/ $k_{(uracil)}$	$k_{(adenosine)}$/ $k_{(adenine)}$	$k_{(cytidine)/}$ $k_{(cytosine)}$	$k_{(guanosine)}$/ $k_{(guanine)}$	
Column B[a)]	2.34	2.27	1.74	1.59	S3
Amide-80	1.81	1.18	1.52	1.49	S4
ZIC-HILIC	2.53	1.08	1.71	1.75	S4

a. Column B was the obtained optimum poly(POSS-MA-co-VBTA) column.;

α(ribose) defined as $k_{(nucleoside)}$ /$k_{(nucleic\ base)}$

S3: This manusript.

S4: Y. Kawachia, T. Ikegamia, H. Takuboa,1, Y. Ikegamib, M. Miyamotoa and N. Tanaka, *J. Chromatogr. A*, 2011, **1218**: 5903- 5919