Electronic Supplementary Information for

A novel well-ordered mesoporous organosilica specialized for highly selective recognition of Pb(II) by host-guest interaction

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Experimental

1. Materials

The macrocyclic host molecule *cis*-di(aminocyclohexyl)-18-crown-6 was synthesized by ourselves. The experimental conditions and structure characterization can be seen in our previous paper.[1] Tetramethoxysilane (TMOS, 98%) and 3-chloropropyltrimethoxysilane (CPTMS, 97%) were supplied by Aldrich. Deionized water (resistivity > 18 MΩ·cm) was obtained from a Milli-Q water purification system. The analytical grade chemicals, such as sodium hydroxide, tetrahydrofuran, potassium iodide, and other reagents were commercially obtained and used as received without further purification.

2. Preparation of mesoporous precursor

Surfactant solution was prepared by adding cetyltrimethylammonium bromide (CTAB) (6.56 g, 18 mmol), NaOH (1.48 g, 37 mmol) and H_2O (252 g, 14 mol) into a 1 L flask followed with vigorous stirring. A mixture of tetramethoxysilane (TMOS) (15.2 g, 100 mmol) and 3-chloropropyltrimethoxysilane (CPTMS) (7.95 g, 40 mmol) was quickly added. After stirring at room temperature for 1 h, the mixture was heated to 90 °C for 24 h ageing. The product was isolated and the surfactant was removed by HCl/methanol extraction to obtain the mesoporous precursor.[2]

3. Preparation of DCH18C6-grafted mesoporous organosilica

1.5 g precursor and 2.0 g *cis*-di(aminocyclohexyl)-18-crown-6 were mixed in 150 mL THF, followed by the addition of 5.0 g K_2CO_3 and 2.0 g KI. Under N_2 protection, the mixture was heated to 80 °C for 6 h reflux with vigorous stirring. The solid was collected by vacuum filtration and washed alternately with deionized water and ethanol until the pH of the washing effluent was neutral and no K^+ was detected by atomic absorption spectroscopy. Then, the product was dried in 70 °C vacuum oven for 24 h.

4. Adsorption of Pb(II) in multicomponent solution

Batch adsorption experiment toward Pb(II) in solution containing various interference ions (Ba(II), Cd(II), Cr(III), Cu(II), Fe(III), Ni(II), Pd(II), Zn(II) and Zr(IV)) was performed in 25 °C

thermostat. The initial concentration of each metal ion is 100 mg/L. 0.05 g DCH18C6-grafted mesoporous organosilica was added into 5 mL stock solution. After vigorous agitating for 30 min, the aqueous phase was separated with 0.45 μm micro-pore filter. The residual amount of the Pb(II) in the solution was measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The removal rate of the metal ions was calculated based on material balance.

5. Hydrolytic stability study

200 mg DCH18C6-grafted mesoporous organosilica was mixed with 5 mL HNO_3 solution with the concentration of 0.1 or 1 mol/L in a glass-stopper tube. Then, the tube was mechanically shaken in a thermostated water bath at 25 ºC. The hydrolysis process lasted for 45 h. After separation, the mesoporous organosilica were repeatedly washed with deionized water to neutral and dried under vacuum at 60 ºC for 24 h. Elemental analysis of C, H and N was performed to examine the hydrolysis degree of the product.

6. Characterization

Solid-state NMR ^{13}C and ^{29}Si spectra were obtained with a Bruker AV300 Spectrometer with the cross-polarization/magic-angle spinning (CP/MAS) technique. X-ray photoelectron spectroscopy (XPS) measurement for the mesoporous organosilicas was performed using a PHI-5300 ESCA instrument. Spectra calibration was determined by setting the main C1s component due to C-C/C-H bonds at 284.8 eV. Powder X-ray diffraction (PXRD) data were collected on a D8 Discover using a Cu Kα radiation at room temperature. N_2 adsorption measurements were performed with a NOVA 3200e Surface Area & Pore Size Analyzer. Samples were dried at 120 ºC vacuum environment for at least 4 h before the nitrogen adsorption experiments. Surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Thermogravimetric analysis (TGA) was carried out on a SDT (Simultaneous DSC and TGA) Q600, TA Instruments. Samples were heated from 25 to 800 ºC at 5 ºC/min under nitrogen. Elemental analysis of C, H and N was performed on Elementar Vario EL III. Mass spectra were recorded by Perkin-Elmer API3000 LC/MS/MS spectrometry system. The size and distribution of the samples was measured by MALVERN 2000 laser particle analyzer. Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Thermo Jarrel Ash mod. IRIS Advantage) and Atomic Absorption

Spectroscopy (HITACHI Z-2000) were employed to determine the concentration of the metal ions. The morphology of the mesoporous organosilicas was recorded by JEM-2010 high-resolution transmission electron microscopy (HRTEM).
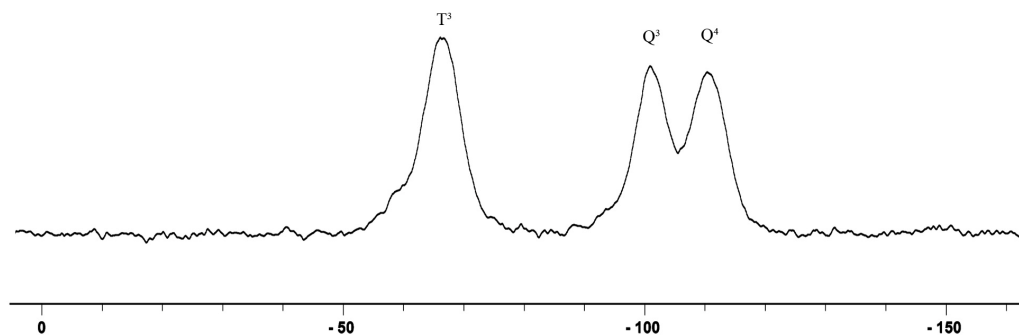
Supporting figures

Fig. S1. ^{29}Si MAS NMR spectra of the DCH18C6-grafted mesoporous organosilicas. The three regions of major intensity centered at -110.2 ppm (Q^4), -102.2 ppm (Q^3) and -67.5 ppm (T^3) correspond to $Si(-O-)_4$, $EtOSi(-O-)_3$ and $RSi(-O-)_3$ silicate species.
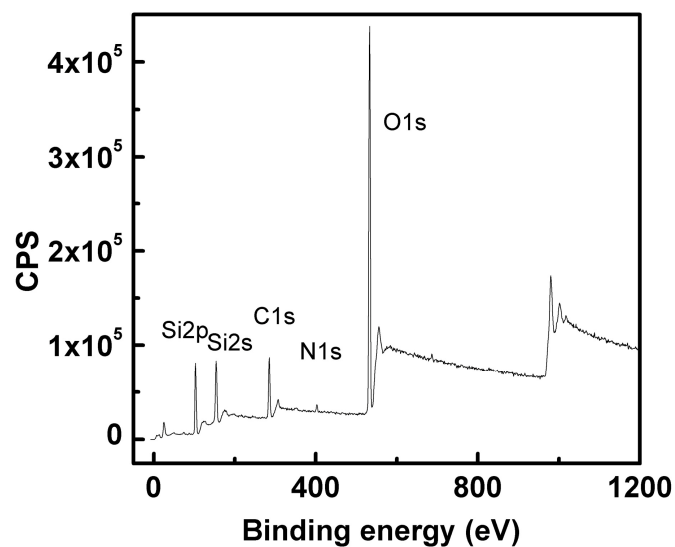
Fig. S2. XPS survey scan of the DCH18C6-grafted mesoporous organosilica. The spectra were calibrated by setting the main C1s component due to C-C/C-H bonds at 284.8 eV. Signals of Si 2p, Si 2s, C 1s, N 1s and O 1s were recorded. According to the peak analysis, the amount of the N element was calculated to be 1.86%, which is higher than that obtained by elemental analysis. The difference in the results implies that the macrocyclic host molecules are mainly grafted on the surface of the mesoporous organosilica.
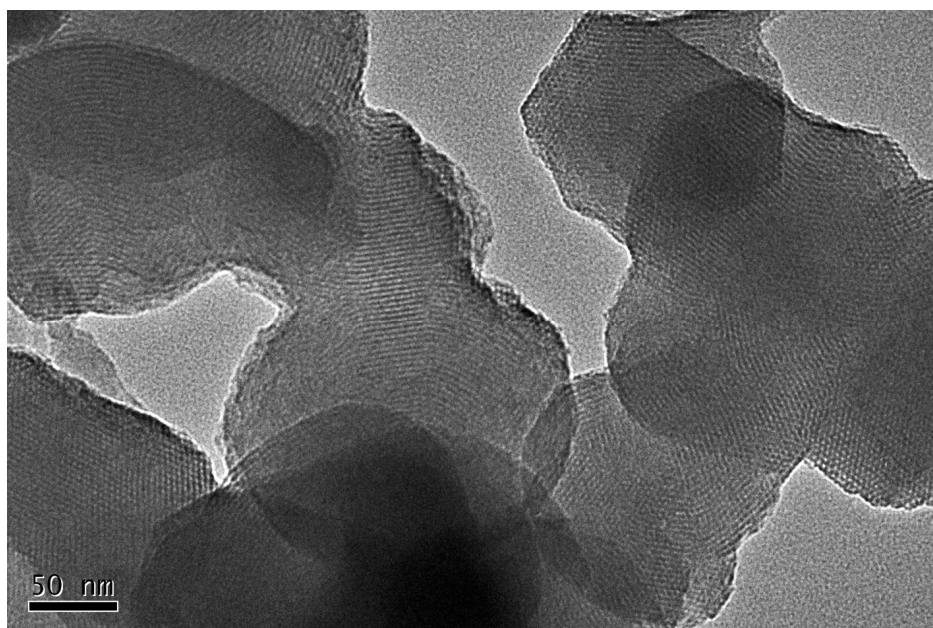
Fig. S3. TEM image of the mesoporous organosilica. In the whole visual range, uniform mesoporous structure can be clearly observed.
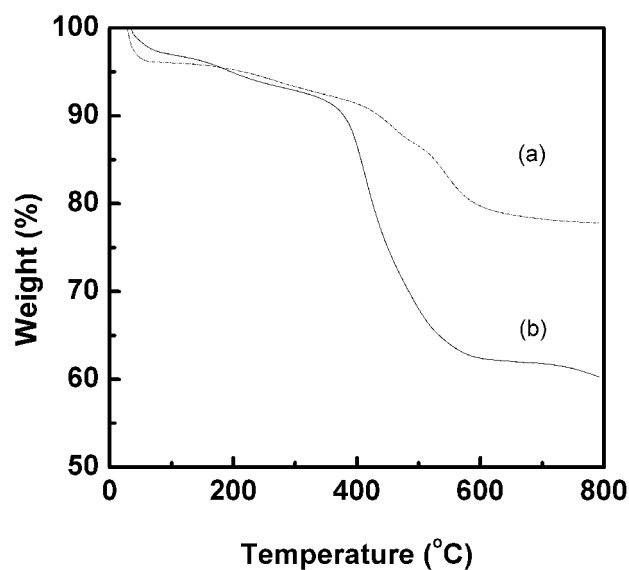
Fig. S4. TGA curves of the mesoporous organosilica precursor (a) and DCH18C6-grafted product (b). It can be seen that there is only a slight weight loss (~ 5%) due to the evaporation of the residual solvent occurred around 200 ^{o}C, indicating that the samples have satisfactory thermal stability. Further increase of temperature results the decomposition of the macrocyclic host groups as well as other organic components such as residual ethoxy groups. The difference in weight loss between the precursor and grafted product approximately corresponds to the DCH18C6 molecules immobilized in the mesoporous organosilica.
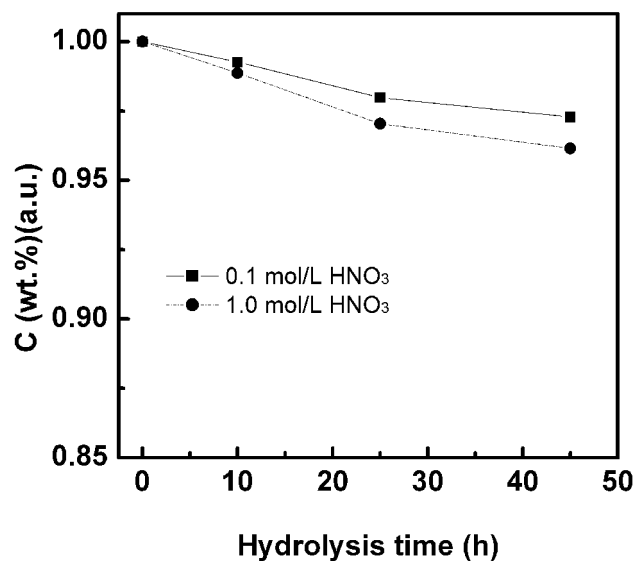
Fig. S5. Evaluation of hydrolytic stability of the DCH18C6-grafted mesoporous organosilica in 0.1 and 1.0 mol/L HNO_3 solutions. To avoid the interference of nitric acid, elemental analysis of carbon, rather than nitrogen, was measured for degradation evaluation of the sample. After treatment in the HNO_3 solutions for 45 h, there are only 2.7% and 3.8% of weight loss, implying that the DCH18C6-grafted mesoporous material is stable enough during hydrolysis treatment.
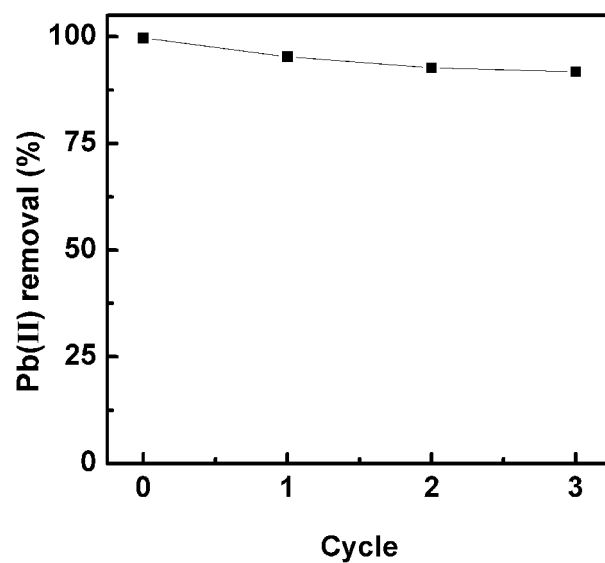
Fig. S6. Reusability evaluation of the macrocyclic host grafted mesoporous organosilica for Pb(II)

removal. The initial concentration of Pb(II) is 100 mg/L, and phase ratio was set as 0.01 g/1 mL.

The loaded metal was eluted by 0.1 mol/L HNO$_3$ solution for adsorbent regeneration. After the 4th

adsorption experiment, the mesoporous adsorbent still had a removal rate of 91.8%.

Supporting table

Table S1. Characterization of surface and pore structure for the DCH18C6-grafted mesoporous

organosilicas

Sample	BET surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
mesoporous precursor	854.9	3.828	0.146
DCH18C6-grafted product	81.01	3.433	0.079

Supporting references

1. G. Ye, F. Bai, J. Wei, J. Wang and J. Chen, *J. Hazard. Mater.*, 2012, **225-226**, 8.

2. M. H. Lim and A. Stein, *Chem. Mater.*, 1999, **11**, 3285.