



# New macrocyclic ligand incorporated organosilicas: Co-condensation synthesis, characterization and separation of strontium in simulated high level liquid waste

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## ABSTRACT

A new category of organosilica adsorbents functionalized with macrocyclic ligand *cis*-dicyclohexano-18-crown-6 (*cis*-DCH18C6) were synthesized for selective strontium separation. The *cis*-DCH18C6 molecule, well-known as an excellent complexing agent of strontium, was elaborately modified for immobilization in the organosilica matrix by co-condensation. <sup>13</sup>C and <sup>29</sup>Si solid-state NMR, XPS, FT-IR, ESEM, and elemental analysis were employed to characterize the structure and surface morphology of the organosilicas. Due to the improved surface properties and supramolecular recognition to the ion, the functionalized organosilicas showed favorable adsorption capacity and selectivity to the strontium in HNO<sub>3</sub> media. The sample of Crown-75 showed a high distribution coefficient (185.3 cm<sup>3</sup>/g) of strontium in 1 mol/L HNO<sub>3</sub> solution. For practical purpose, the separation of strontium in the simulated high level liquid waste (HLLW) from the spent fuel of a light water reactor (LWR) was investigated. The *K<sub>d</sub>*S of strontium as well as dozens of other metals present in the HLLW were obtained. Moreover, the radiolytic and hydrolytic stability of the organosilicas was evaluated. It revealed that the organosilicas had excellent resistance against gamma-ray irradiation and nitric acid treatment. These novel DCH18C6-functionalized organosilicas possess a promising future for the separation of the strontium in radioactive liquid waste.

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## 1. Introduction

From the beginning, the development of nuclear energy has been facing the people's concern over the safety of nuclear technology. The nuclear accident in Fukushima last March triggered a new wave of public panic and made the nuclear safety a more imperative issue. Meanwhile, a great mass of the radioactive waste produced during the reprocessing of spent fuels, though not as urgent as sudden accidents, is also a potential threat [1,2]. Strontium-90, having a half-life of 28.5 years, is one of the main long lived nuclides and heat generators present in the high level liquid waste (HLLW) [3]. The separation of strontium prior to vitrification will not only help to effectively lower the volume of nuclear waste, but also reduces the risk of matrix deformation caused by the radiated heat during the long term storage [4–6].

Extractants with strong complexing ability and selectivity play an important role in the efficient separation of the target elements. It has been found that a macrocyclic ligand *cis*-dicyclohexano-18-crown-6 (*cis*-DCH18C6), as well as its *tert*-butyl substituted derivative, exhibited favorable extraction ability and selectivity

towards Sr(II) ion [7,8]. The use of these crown ethers greatly accelerated the research on the separation of strontium from radioactive stream. Several methods like ion exchange, solvent extraction and extraction chromatography have been developed [9–16]. As the radioactive liquid waste contains miscellaneous ions and substantial amount of acid, ion exchange is not considered as a good choice for nuclide separation, because of its poor selectivity and slow adsorption kinetics. Widely accepted are the latter two methods, which attract more and more attentions in recent years [17,18].

Extraction chromatography, also called solid state extraction, is characterized by loading the complexing agents onto an inert solid support material [19–21]. Extraction chromatography has the advantage of minimal organic diluents utilization, less waste accumulation and compact equipment, which makes it a promising alternative for replacing solvent extraction toward metal separation in radioactive liquid waste [22,23]. The researchers in Argonne National Laboratory prepared a novel Sr-selective extraction chromatographic resin (Sr-Spec, abbreviation for Strontium Specific) by impregnating a 1-octanol solution containing DtBuCH18C6 into an inert polymeric support (XAD-7) [24]. This innovative work opened a new period in radiostromium separation and analysis. Thereafter, Rodríguez et al. modified the Sr-resin and made an attempt to

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separate the  $^{90}\text{Sr}$  in the waste from Spanish nuclear power plants [25]. Typical researches on the crown ether loaded chromatographic material in the past decade were continuously reported by Zhang et al. They developed the DtBuCH18C6 impregnated macroporous silica-based polymeric composite and proposed the SPEC process for chromatographic separation the Sr(II) in HLLW [26–28]. Except for the complexing agent, the support materials are also of significance in the extraction chromatography. Many natural and composite materials can be utilized as substrate for the loading of the extractant molecules. Among them, silica-based adsorbents have gained more attention owing to their excellent thermal and hydrolytic stability [29–31].

Nevertheless, up to now, almost all the chromatography resins for Sr(II) separation in the literature were developed based on physical methods, such as impregnation or inclusion. The crown ether molecules were immobilized into the substrate material by van der Waals force or hydrogen bond. Though having advantage of simple operation, the resins suffered from the leak of extractant during the adsorption and elution, which resulted in an obvious decrease of separation efficiency in cycle use [32].

Here, we report a novel kind of organosilica adsorbent with the macrocyclic ligand DCH18C6 covalently-attached on the substrate for the selective separation of strontium. Organic functionalization of silica can be achieved either by post-synthesis grafting (PSG) or by co-condensation. However, the former method can only afford a limited load of extractant molecules, and sharp decrease of the specific surface area usually happens during the post-grafting process, which will sacrifice the adsorption capacity toward the target metal [33]. To overcome the disadvantage, in this study, a series of macrocyclic ligand functionalized organosilicas were synthesized via a co-condensation method. The synthesis, structure characterization and surface morphology were detailed, the adsorption behavior toward Sr(II) in  $\text{HNO}_3$  solutions was examined. To meet the practical challenge, the separation ability of the functionalized organosilicas toward Sr(II) in the simulated high level liquid waste (HLLW) was investigated for the first time. Moreover, the radiolytic stability as well as the thermal and hydrolytic properties of the functionalized organosilicas was comprehensively evaluated.

## 2. Experimental

### 2.1. Chemicals

Di-*n*-butyltin dilaurate (DBTL, 95%), dibenzo-18-crown-6 (DB18C6, >98%) and palladium on activated carbon (Pd/C, 10%) were purchased from Alfa Aesar. Tetraethoxysilane (TEOS, 98%) and 3-chloropropyltriethoxysilane (CPTES, 97%) were supplied by Aldrich. The ruthenium catalyst used for the hydrogenation reaction was prepared following Pichler's method [34]. Deionized water (resistivity >18 M $\Omega$  cm) was obtained from a Milli-Q water purification system. The analytical grade chemicals, such as strontium nitrate, hydrazine hydrate, tetrahydrofuran, potassium iodide, and other reagents were commercially obtained and used as received without further purification.

**Table 1**

Composition of the simulated high level liquid waste (HLLW) from a light water reactor (LWR) nuclear power plant (acidity: 1 mol/L  $\text{HNO}_3$ ).

Element	Concentration (g/L)	Element	Concentration (g/L)
Ba	0.379	Nd	2.000
Cd	0.037	Ni	0.046
Cr	0.062	Pd	0.303
Cs	0.449	Rb	0.069
Fe	0.237	Ru	0.451
Mo	0.674	Sr	0.142
Na	1.136	Zr	0.100

The composition of the simulated high level liquid waste (HLLW) used in this study is shown in Table 1. The concentration of the metal elements is equivalent to that in the real HLLW after the reprocessing of the spent fuels from a typical light water reactor (LWR) nuclear power plant. The spent fuels are designed to have a burn up of 55,000 MWd/T followed with 8-year cooling. The acidity of the simulated HLLW was adjusted to be 1 mol/L, which was determined by acid–base titration.

### 2.2. Characterization

$^1\text{H}$  NMR spectra of the monomers were recorded by a JOEL JNM-ECA600 NMR spectrometer. Solid-state NMR  $^{13}\text{C}$  and  $^{29}\text{Si}$  spectra were obtained with a Bruker AV300 Spectrometer with the cross-polarization/magic-angle spinning (CP/MAS) technique. Nicolet Nexus 470 FT-IR was used to record the infrared (IR) spectra in KBr matrix in the range 4000–400  $\text{cm}^{-1}$ . X-ray photoelectron spectroscopy (XPS) measurement for the functionalized 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.  $\text{N}_2$  adsorption measurements were performed with a NOVA 3200e Surface Area & Pore Size Analyzer. Samples were dried at 120 °C 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 °C at a rate of 5 °C/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 Spectrometry (HITACHI Z-2000) were employed to determine the concentration of the metal ions. The morphology of the organosilicas was recorded by FEI Quanta 200 environmental scanning electron microscopy (ESEM).

### 2.3. Synthesis of monomers and functionalized organosilicas

4,4'-Di(aminocyclohexyl)-18-crown-6 [1]. The synthesis of *cis*-di(aminocyclohexyl)-18-crown-6 was started with dibenzo-18-crown-6 molecule [0] according to a three-stage procedure, namely, nitration, reduction and catalytic hydrogenation. The synthesis procedure and the structural characterization have been detailed in our earlier work [33].

4,4'-Bis((3-(triethoxysilyl)propyl)amino)dicyclohexyl-18-crown-6 [2]. 2.01 g compound [1] (5 mmol) was dissolved in 150 mL tetrahydrofuran (THF). 1.38 g potassium carbonate (10 mmol) and 1.66 g potassium iodide (10 mmol) were added into the solution. Then, with nitrogen protection and vigorous stirring, 3-chloropropyltriethoxysilane (CPTES) (2.40 g, 10 mmol) was dropwise added. The mixture was heated under reflux for 5 h, and the solid salt was separated by filtration. The crude product with brown color was obtained from the filtrate after removing the THF under vacuum. The product was purified via a procedure similar to that reported by Dubois et al. [35]. The brown oil was dissolved in 50 mL  $\text{CCl}_4$ . After filtration, the filtrate was collected for concentration. The residue was taken up in 40 mL ether twice. After evaporation of the ether, the resulting foam was washed with 15 mL pentane and dried under vacuum at room temperature for 10 h. The final product was obtained by extracting the foam with 50 mL hot pentane, followed by the removal of the solvent. Yield: 47%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.79–3.70 (q, 12H), 3.67–3.54 (m, 16H), 3.08 (m, 4H), 2.69 (m, 6H), 1.95–1.86 (m, 4H), 1.60–1.52 (m, 8H),

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