



Synthesis and characterization of novel macroporous silica-polymer-calixcrown hybrid supramolecular recognition materials for effective separation of cesium

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HIGHLIGHTS

- Two novel silica-based supramolecular recognition materials were synthesized.
- They were well characterized by SEM, TG, FT-IR, XRD, and ²⁹Si NMR.
- These materials exhibited excellent adsorption and high selectivity for Cs(I).
- They are very stable in the HNO₃ aqueous solution.

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ABSTRACT

Two novel macroporous silica-polymer-calixcrown hybrid supramolecular recognition materials, 25,27-bis(*n*-octyloxy)calix[4]arene-crown-6 (BnOCalix[4]C6)/SiO₂-P and 25,27-bis(*i*-octyloxy)calix[4]arene-crown-6 (BiOCalix[4]C6)/SiO₂-P were synthesized by in situ polymerization and impregnation techniques. The obtained materials were characterized by scanning electron microscope (SEM), particle size distribution, nitrogen adsorption–desorption isotherms, thermogravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectroscopy, ²⁹Si solid-state NMR, and powder X-ray diffraction (XRD). The adsorption of some typical fission and non-fission products Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), La(III), Y(III), Pd(II), Ru(III), Zr(IV), and Mo(VI) onto BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P in HNO₃ solution was investigated. The bleeding of the materials in HNO₃ solution was evaluated by analysis of total organic carbon (TOC). BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P exhibited excellent adsorption ability and high selectivity for Cs(I) over all the other tested metals.

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1. Introduction

The design of functional materials containing chelating agents for adsorption, ion exchange, catalysis, sensor, electronic, and optoelectronic devices is an exciting research area [1–5]. The immobilization of ion selective ligands to form porous polymer-supported reagents has been developed to apply in separation science [6–8]. But some disadvantages are obvious, such as low mechanical strength, low adsorption capacity, and poor resistance to acid and irradiation.

Recently, modification of inorganic silica by selective functionalization with various organic moieties has attracted more attention [9–11]. Porous silica-organic hybrid materials were mostly prepared either by co-condensation reaction of organosilanes [12–14] or post-synthetic grafting of organic moieties onto silica surfaces [15–17]. For example, Ye et al. [18] reported the covalent grafting dicyclohexano-18-crown-6 onto a silica precursor to synthesize strontium-selective polysiloxane resin. The above two methods exhibited chemical and thermal stability because of strong covalent bonding between the organic moieties and silica substrate. In addition, the pore surface-confined polymerization approach was reported by Choi et al. [19], where the monomers were polymerized in situ after impregnation into mesoporous silica. This method could flexibly tailor the coating of pore surface by changing the types of monomers and the degree of polymerization. But it is too difficult to introduce special recognition agents with complicated structures into the pores of silica by direct polymerization.

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To obtain ideal porous inorganic–organic hybrid materials at will, a synthetic method consisted of two steps, in situ polymerization step and vacuum impregnation step, has been developed in our previous work [20]. Firstly, an inert monomer, styrene, was initially introduced to copolymerize in situ with divinylbenzene in the surface of silica support to modify the hydrophilic surface of silica support. Then, more complicated and selective ligands were easily impregnated into the pores of silica to synthesize innovative organic–inorganic hybrid materials. Based on this method, we have prepared several macroporous silica-based recognition materials for palladium, lanthanide, actinide, cesium, and strontium separation [21–25]. One of successful examples is SPEC (Strontium/Cesium Partitioning from HLW by Extraction Chromatography) process [26–28]. It comprised of two macroporous silica-based supramolecular recognition materials, 1,3-[(2,4-diethylheptyl-ethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14)/SiO₂-P for Cs(I) and di-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6)/SiO₂-P for Sr(II), respectively. However, the organic ligand, Calix[4]arene-R14, is relatively complicated and difficult to synthesize. Additionally, some small modifiers, such as 1-octanol and tributyl phosphate (TBP), need to be introduced to help Calix[4]arene-R14 impregnate into the pores of silica during the synthesis process. It is necessary for us to design and screen new simple and efficient supramolecular hosts in the macroporous silica-based recognition materials. BnOCalix[4]C6 is a simpler calixarene-crown analog to Calix[4]arene-R14, which has similar long alkyl substituents in the lower rim. BiOCalix[4]C6 is synthesized for comparison to see how the branch alkyl group affects the properties.

On the basis of SPEC process, two novel macroporous silica-polymer-calixcrown hybrid supramolecular recognition materials, BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P, were synthesized and characterized by SEM, particle size distribution, nitrogen adsorption-desorption isotherms, TGA, FT-IR, ²⁹Si NMR, and XRD. To investigate the recognition behavior of BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P, the adsorptions of Na(I), K(I), Rb(I), Cs(I), Sr(II), Ba(II), La(III), Y(III), Pd(II), Ru(III), Zr(IV), and Mo(VI) were performed.

2. Experimental

2.1. Reagents and materials

Alkali metals nitrates M^INO₃ (M^I = Na, K, Rb and Cs.), alkaline earths nitrates M^{II}(NO₃)₂ (M^{II} = Sr and Ba), RE(NO₃)₃·6H₂O (RE = La and Y), and (NH₄)₆Mo₇O₂₄·4H₂O were of analytical grade. Ruthenium(III) nitrosyl nitrate solution with 1.5% (w/v) of Ru(III) was provided by Alfa Co., Ltd., USA. The concentrations of the tested elements were around 5.0 × 10^{−3} M. Methanol, dichloromethane, and other inorganic/organic reagents were of analytical grade, used without further purification. Two macrocyclic supramolecular recognition agents, 25,27-bis(*n*-octyloxy) calix[4]arene-crown-6 (BnOCalix[4]C6) and 25,27-bis(*i*-octyloxy)calix[4]arene-crown-6 (BiOCalix[4]C6) were synthesized according to a procedure reported previously (Scheme 1) [29]. Their structures and purities were confirmed by ESI-MS, ¹H NMR, ¹³C NMR, TG-DSC, and elemental analysis. The detailed characterization data are shown as follows:

BnOCalix[4]C6: Melting point, 97.85 °C. ¹H NMR (CDCl₃, 500 MHz): δ = 0.913–0.941 ppm, t, OCH₂(CH₂)₆CH₃, 6H; δ = 1.149–1.362 ppm, m, OCH₂(CH₂)₆CH₃, 24H; δ = 3.389–3.454 ppm, m; ArOCH₂CH₂OCH₂CH₂OCH₂, 8H; δ = 3.489–3.508 ppm, t, ArOCH₂CH₂OCH₂CH₂OCH₂, 4H; δ = 3.590–3.614 ppm, t, OCH₂(CH₂)₆CH₃, 4H; δ = 3.654–3.672 ppm, t, ArOCH₂CH₂OCH₂CH₂OCH₂, 4H; δ = 3.715 ppm, s, ArO(CH₂CH₂O)₂CH₂, 4H; δ = 3.781 ppm, d,

ArCH₂Ar, 8H; δ = 6.765–6.795 ppm; δ = 6.823–6.853 ppm, t, ArH para, 4H; δ = 7.015–7.029 ppm, 7.081–7.096 ppm, d, ArH meta, 8H. ESI-MS: (M+NH₄)⁺ 868.7, (M+Na)⁺ 873.6, (M+K)⁺ 889.5. Anal. Cal. for C₄₈H₆₂O₈(%): C, 76.20; H, 8.76; O, 15.04; Found: C, 76.19; H, 8.74; O, 15.07.

BiOCalix[4]C6: Melting point, 106.56 °C. ¹H NMR (CDCl₃, 500 MHz): δ = 0.846–0.876 ppm, t, OCH₂CH(CH₂CH₃)(CH₂)₂CH₂CH₃, 6H; δ = 0.925–0.953 ppm, t, OCH₂CH–(CH₂CH₃)(CH₂)₂CH₂CH₃, 6H; δ = 1.289–1.356 ppm, m, OCH₂CH(CH₂CH₃)(CH₂)₂CH₂CH₃, 16H; δ = 1.783 ppm, m, OCH₂CH(CH₂CH₃)(CH₂)₂CH₂CH₃, 2H; δ = 1.494 ppm, m, OCH₂CH(CH₂CH₃)(CH₂)₂CH₂CH₃, 4H; δ = 3.374–3.397 ppm, t, ArOCH₂CH₂OCH₂CH₂–OCH₂, 20H; δ = 3.774 ppm, s, ArCH₂Ar, 8H; δ = 6.682 ppm, δ = 6.770–6.799 ppm, t, ArH para, 4H; δ = 7.013–7.027 ppm, 7.122–7.137 ppm, d, ArH meta, 8H. ESI-MS: (M+H)⁺ 851.1, (M+NH₄)⁺ 868.3. Anal. Cal. for C₄₈H₆₂O₈(%): C, 76.20; H, 8.76; O, 15.04; Found: C, 76.17; H, 8.77; O, 15.06.

A macroporous silica-based SiO₂-P particles support was developed according to Ref [20]. The monomers, styrene, and divinylbenzene, were copolymerized in situ and coated onto the pores of the silica particles. The letter P in the SiO₂-P means the styrene-divinylbenzene copolymer.

2.2. Synthesis of BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P

Prior to the synthesis of BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P, the silica-polymer supports were washed with concentrated HNO₃ for ten times and then in the boiling water for 24 h for three times to ensure that the supports would not leak anything. Additionally, the SiO₂-P particles were treated actively by acetone and methanol three times. The synthesis procedure of the BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P hybrid materials was described as follows: 2.0 g (2.35 mmol) of supramolecular recognition agents were dissolved with 30 mL of dichloromethane in a 100 mL glass-stopped flask, then, 4.0 g activated SiO₂-P particles were added under shaking. After the resulting mixture was stirred mechanically using an EYELA N-1001 Model rotary evaporator (Tokyo Rikakikai Co., Ltd., Japan) over 90 min at room temperature, it was moved into a water bath controlled using an EYELA SB-2000 Model temperature controller (Tokyo Rikakikai Co., Ltd., Japan) and stirred for about 180 min at 318 K to impregnate the supramolecular recognition agents into the pores of the SiO₂-P particles. After drying in a vacuum drying oven at 318 K overnight, macroporous silica-polymer-calixcrown hybrid supramolecular recognition materials, BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P, were obtained. The mole amounts of supramolecular hosts in these two hybrid materials are 0.45 mmol/g determined by TG-DSC technique.

2.3. Characterization of BnOCalix[4]C6/SiO₂-P and BiOCalix[4]C6/SiO₂-P

A scanning electron microscope (SEM, FEI Sirion 200, Netherlands) was used for morphological analysis. The particle size distribution was studied by a laser particle size analyzer (LS-230 Coulter, USA). The nitrogen adsorption-desorption isotherm was determined using an Omnisorp 100CX system (Beckman Coulter Co., USA) at liquid-nitrogen temperature. The specific surface area was calculated from the linear part of the Brunauer–Emmett–Teller (BET) equation. The pore diameter distribution was obtained using the Barrett–Joyner–Halenda (BJH) model. The thermogravimetric analysis (TGA, TA Instrument Universal V4.2E, USA) was carried out in the flowing O₂ gas from room temperature to 1000 °C at a heating rate of 10 °C/min. The Fourier transform infrared (FT-IR, Nicolet Nexus 670, USA) spectra were recorded using the KBr self supported pellet technique. Powder X-ray diffraction (XRD, PANalytical X'pert

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