Supplementary Materials: Extraction Property of *p-tert*-butylsulfonylcalix[4]arene Possessing Irradiation Stability towards Cesium(I) and Strontium(II)

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1. Synthesis of *p*-tert-butylthiacalix[4]arene (TC4A)

The synthesis scheme for preparation of *p-tert*-butylthiacalix[4]arene is presented in Figure S1. TC4A was synthesized as follows. A mixture of *p-tert*-butylphenol (32.25 g), elemental sulfur S⁸ (13.75 g), and NaOH (4.43 g) in diphenyl ether (30 mL) was stirred under nitrogen. The stirred mixture was heated gradually to 230 °C over a period of 4 h and kept at this temperature for a further 4 h with concomitant removal of the evolving hydrogen sulfide with a slow stream of nitrogen. The product was cooled to ambient temperature and diluted with toluene (20 mL), and washed with sulfuric acid solution (0.5 mol·L⁻¹) and deionized water to give a grayish yellow suspension liquid. Then, the precipitate was collected by filtration, recrystallized from chloroform (170 mL) and dried in vacuum (60 °C, 4 h) to give a white powder product (yield 53%). Electrospray ionization mass spectrometry (ESI-MS): m/z 719.4 [M – H]⁻. Melting point (Mp): 320–324 °C. ¹H nuclear magnetic resonance (¹H NMR) (CDCl₃): δ 1.22 (s, 36H, C(CH₃)₃), 7.66 (s, 8H, ArH), 9.61 (s, 4H, OH). IR (KBr): 3324 (OH), 2961, 1395, 1364 (C(CH₃)₃).



Figure S1. Synthesis of *p*-tert-butylthiacalix[4]arene.

2. Synthesis of *p-tert*-butylsulfonylcalix[4]arene (SC4A)

The synthesis scheme for preparation of *p-tert*-butylsulfonylcalix[4]arene (SC4A) is presented in Figure S2. SC4A was synthesized as follows. Acetic acid (25 mL) and NaBO₃·4H₂O (2.57 g) were added to the solution of TC4A (1.8 g) in chloroform (30 mL). After the mixture was stirred at 55 °C for 4 days, the product was extracted with chloroform (45 mL × 3). A white powder SC4A (yield 78%) was obtained by recrystallized from methanol and dried in vacuum. ESI-MS: *m*/*z* 847.2 [M – H]⁻. Mp: 399–400 °C. ¹H NMR (CDCl₃): δ 1.22 (s, 36H, C(CH₃)₃), 8.12 (s, 8H, ArH). IR (KBr): 3324 (OH), 2961, 1395, 1364 (C(CH₃)₃), 1330, 1160 (SO₂).



Figure S2. Synthesis of *p*-tert-butylsulfonylcalix[4]arene.

3. Synthesis of *p-tert*-butysulfonylcalix[4]arene Tetraacetate (SC4AOEt)

The synthesis scheme for preparation of *p-tert*-butysulfonylcalix[4]arene (SC4AOEt) is presented in Figure S3. SC4A was synthesized as follows. A mixture of TC4A (5.0 g), K₂CO₃ (6.0 g), and KI (0.45 g) in 100 mL of anhydrous acetone was stirred under nitrogen. After the stirred mixture was heated and kept refluxing for 1 h, ethyl chloroacetate (5.3 mL) was added. Acetone was removed and the rest of materials dissolved in water. The reaction mixture obtained was separated into an aqueous layer and an organic layer. The organic phase was sufficiently washed 3 times with water and then dried over magnesium sulfate. Oil materials were obtained by filtration, and the oil materials were treated with ethyl alcohol to give raw products. Thereafter, the white products *p-tert*-butylthiacalix[4]arene tetraacetate (TC4AOEt, yield 61%) were obtained by recrystallization with dichloromethane (60 mL). ESI-MS: m/z 1183.1 [M + Na]⁺. Mp: 173–175 °C. ¹H NMR (CDCl₃): δ 1.12 (brs, 36H, C(CH₃)₃), 1.31 (t, 12H, CH₃), 4.26 (q, 8H, OCH₂CH₃), 5.49 (s, 8H, CH₂COOEt), 7.83 (s, 8H, Ar-H). IR (KBr): 2961, 1395, 1364 (C(CH₃)₃), 1740 (C=O), 1185, 1116 (C–O–C), 1060 (C–O).

TC4AOEt (1.0 g), acetic acid (20 mL) and hydrogen peroxide (30%, 10 mL) in 10 mL of chloroform was heated to reflux for 5 days. After being cooled to ambient temperature, the reaction was evaporated to dryness and the residue was distributed between chloroform (15 mL) and a saturated aqueous solution of NaHSO₃ (30 mL × 2). The organic layer was dried over MgSO₄ and evaporated under reduced pressure. The crystallization gave white platelets product (yield 85%). ESI-MS: m/z 1215.1 [M + Na]⁺. Mp: 330–333 °C. ¹H NMR (CDCl₃): δ 1.14 (brs, 36H, C(CH₃)₃), 1.33 (t, 12H, CH3), 4.26 (q, 8H, OCH₂CH₃), 5.50 (s, 8H, CH₂COOEt), 7.87 (s, 8H, Ar–H). IR (KBr): 2961, 1395, 1364 (C(CH₃)₃), 1741 (C=O), 1330, 1160 (SO₂), 1186, 1116 (C–O–C), 1061 (C–O).



Figure S3. Synthesis of *p-tert*-butylsulfonylcalix[4]arene tetraacetate.

4. ¹H NMR of SC4A and Extracted Species

The ¹H NMR spectra of SC4A, SC4A-Cs(I) and SC4A-Sr(II) complexes were presented in Figure S4.



Figure S4. ¹H NMR of SC4A and extracted species in CDCl₃: (**a**) SC4A; (**b**) SC4A-Cs(I) complex; and (**c**) SC4A-Sr(II) complex. Conditions: T = 298 K, [SC4A]₍₀₎=1 × 10⁻³ M, [Metal]_(a) = 1 × 10⁻⁴ M, contact time = 60 min, pH = 6, shaking speed: 150 rpm. SC4A-Cs(I) complex and SC4A-Sr(II) complex were dried in air.

5. Extraction of Mg(II), Ca(II) and Ba(II) with SCA4

The extraction of alkaline earth metals Mg(II), Ca(II) and Ba(II) with SC4A was conducted. The results were presented in Figure S5.



Figure S5. Dependence of the distribution ratio (*D*) of metals onto SC4A with a change in [SC4A]. Conditions: T = 298 K, pH = 6, [Metal]_(a) = 1 × 10⁻⁴ M, contact time = 60 min, shaking speed: 150 rpm.

6. The IR of SC4A for Different Irradiated Dose

SC4A samples A, B, C, D, and E absorbed 0, 1.0×10^4 , 1.0×10^5 , 5.0×10^5 , and 1.1×10^6 Gy irradiated dose, respectively. The IR spectra of them were presented in Figure S6.



Figure S6. The IR of SC4A for different irradiated dose, irradiated dose: (**A**) 0 Gy; (**B**) 1.0×10^4 Gy; (**C**) 1.0×10^5 Gy; (**D**) 5.0×10^5 Gy; and (**E**) 1.1×10^6 Gy.

7. MS Spectra of Irradiated SC4A

The MS spectra of SC4A samples A, B, C, D, and E were presented in Figure S7.







Figure S7. The MS spectra of SC4A before and after irradiation, irradiated dose: (**A**) 0 Gy; (**B**) 1.0×10^4 Gy; (**C**) 1.0×10^5 Gy; (**D**) 5.0×10^5 Gy; and (**E**) 1.1×10^5 Gy.

8. TG Curves of SC4A before and after Irradiation

The TG curves of SC4A samples A, B, C, D, and E were presented in Figure S8.



Figure S8. TG curves of SC4A before and after irradiation, irradiated dose: (**A**) 0 Gy; (**B**) 1.0 × 10⁴ Gy; (**C**) 1.0 × 10⁵ Gy; (**D**) 5.0 × 10⁵ Gy; and (**E**) 1.1 × 10⁶ Gy.

9. The UV-Visible Spectra of SC4A before and after Irradiation

The UV-visible spectra of SC4A samples A, B, C, D, and E were presented in Figure S9.



Figure S9. The UV-visible spectra of SC4A before and after irradiation in CHCl₃, irradiated dose: (**A**) 0 Gy; (**B**) 1.0×10^4 Gy; (**C**) 1.0×10^5 Gy; (**D**) 5.0×10^5 Gy; and (**E**) 1.1×10^5 Gy.

10. The ¹H NMR Spectrogram of SC4A before and after Irradiation

The 1H NMR spectrogram of SC4A samples A, B, C, D, and E were presented in Figure S10.



Figure S10. The ¹H NMR spectrogram of SC4A before and after irradiation, irradiated dose: (**A**) 0 Gy; (**B**) 1.0×10^4 Gy; (**C**) 1.0×10^5 Gy; (**D**) 5.0×10^5 Gy; and (**E**) 1.1×10^5 Gy.

11. The Distribution Ratio (*D*) of Mg(II), Ca(II) and Ba(II) onto SC4A with the Change in Contact Time

The extractions of alkaline earth metals Mg(II), Ca(II) and Ba(II) with SC4A were conducted with the change in contact time. The results were presented in Table S1.

Table S1. The distribution ratio (*D*) of Mg(II), Ca(II) and Ba(II) onto SC4A with the change in contact time.

Distribution Ratio (D)					
Time (min)	Mg(II)	Ca(II)	Ba(II)		

5	2.81	31.32	5.80
10	3.57	42.90	10.25
15	4.08	48.3	15.13
20	4.18	>48	17.52
40	4.20	>48	17.31
60	4.23	>48	18.10
80	4.21	>48	17.94

12. Calculations of ln D_{Cs}

The extraction equilibrium of Cs(I) can be expressed as follows:

$$Cs^{+}_{(a)} + SC4A_{(o)} \rightleftharpoons Cs \cdot SC4A_{(o)} + H^{+}_{(a)}$$
(S1)

The conditional extraction equilibrium constant, Kex1, in Equation (S1) is described as:

$$K_{\text{ex}} = [Cs \cdot SC4A_{(0)}] [H^{+}]_{(a)} / ([Cs^{+}]_{(a)} [SC4A]_{(0)})$$
(S2)

The distribution coefficient *D*_{Cs} is defined as:

$$D_{Cs} = [Cs \cdot SC4A]_{(0)}/[Cs^{\dagger}]_{(a)}$$
(S3)

According to Equations (S2) and (S3), the relationship between the distribution ratio and the extraction constant can be described as:

$$\ln D_{C_s} = \ln K_{ex} + \ln [SC4A]_{(o)} - \ln [H^+]_{(a)}$$
(S4)

Thus, the change in the enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) during the extraction procedure can be calculated using the Arrhenius law and the Gibbs–Helmholtz equation:

$$d \ln K_{ex} / d T = \Delta H^{\circ} / (RT^2)$$
(S5)

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{S6}$$

Then, ln *D*_{Cs} can be calculated using the following equation:

$$\ln D_{\rm Cs} = -\Delta H^{\circ}/(\rm RT) - \ln [\rm H^{+}]_{(a)} + \ln [\rm SC4A]_{(o)} + \Delta S^{\circ}/\rm R$$
(S7)