Supplementary Information

A Benzocrown-6-calix[4]arene Methacrylate Copolymer: Selective Extraction of Cesium Ions from a Multi-Component System

Brett M. Rambo, Sung Kuk Kim, Jong Seung Kim, Christopher W. Bielawski* and Jonathan L. Sessler*

Department of Chemistry & Biochemistry, The University of Texas, Austin, Texas 78712 (USA) and Department of Chemistry, Korea University, Seoul 136-701, South Korea

E-mail: bielawski@cm.utexas.edu; sessler@mail.utexas.edu

Synthetic Details S2–S4

General Considerations S2

Scheme S1. Synthesis of compound 1. S2

Scheme S2. Synthesis of compound 2. S3

Syntheses of 1 - 3. S2-S4

1H NMR Spectra S5–S8

Figure S1. 1H NMR spectrum of 1 (CD2Cl2). S5

Figure S2. 13C NMR spectrum of 1 (CD2Cl2). S5

Figure S3. 1H NMR spectrum of 2 (CD2Cl2) S6

Figure S4. 13C NMR spectrum of 2 (CD2Cl2) S6

Figure S5. 1H NMR spectrum of 3 (CD2Cl2) S7

Figure S6. 1H NMR spectrum of 3 after exposure to CsNO3 (200 mM) (CD2Cl2). S7

Figure S7. 1H NMR spectrum of 3 after exposure to CsBr (200 mM) (CD2Cl2). S8

Figure S8. 1H NMR spectrum of 3 after exposure to CsNO3 followed by precipitation (CD2Cl2). S8

Extraction Studies S9–S18

Quantification of Picrate Salt Extraction via UV/vis Spectroscopy. S9-S12

Analysis of Salt Extraction via 1H NMR Spectroscopy S13–S18

Inductively Coupled Mass Spectrometry S19-S20

References S21

S1
SYNTHETIC DETAILS

General Considerations. All solvents were dried before use according to standard procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). All other reagents were purchased from Aldrich, Acros, or Fisher and used without further purification. Compounds 4 - 10 were prepared according to literature procedures.\(^1\)-\(^4\) NMR spectra were recorded on a Varian Mercury 400 spectrometer. Chemical shifts (\(\delta\)) are given in ppm and are referenced to the residual protio solvent (\(^1\)H: CD\(_2\)Cl\(_2\), 5.32 ppm and CDCl\(_3\), 7.26 ppm; \(^1\)C: CD\(_2\)Cl\(_2\), 53.5 ppm and CDCl\(_3\), 77.2). GPC analyses were performed using a Waters HPLC system equipped with HR-1, HR-3, and HR-5 Styragel\(^\circledR\) columns arranged in series, a 1515 pump, and a 2414 RE detector; reported molecular weights are relative to polystyrene standards in DMF (0.01 LiBr) at 40 °C (column temperature). Thermogravimetric analyses were performed using a Mettler Toledo TGA/SDTA851e. UV/Vis data was collected using a Varian Cary 5000 UV/Vis spectrometer.

Scheme S1. Synthesis of compound 1.

Compound 1. Under an argon atmosphere, calix[4]arene diester\(^2\) 6 (0.50 g, 0.84 mmol), ditosylate 9 (0.55 g, 0.92 mmol) and Cs\(_2\)CO\(_3\) (0.82 g, 2.52 mmol) in 100 mL of acetonitrile were heated to reflux.\(^4\) After heating at reflux for 24 h, the acetonitrile was removed \textit{en vacuo}. To the resulting colorless oil, CH\(_2\)Cl\(_2\) (50 mL) and 5% aqueous HCl (100 mL) were added, and the organic layer was separated and washed three times with 50 mL of water. The organic layer was dried over anhydrous MgSO\(_4\) and the solvent was removed \textit{en vacuo} to give a colorless oil. Column chromatography over silica gel (eluent: ethyl acetate/hexane (3/1 v/v)) afforded 1 as a
white solid (0.42 g; 59.1% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.13 (d, 4H, ArH, $J = 7.61$ Hz), 7.09 (d, 4H, ArH, $J = 7.61$ Hz), 7.00 (m, 4H, ArH), 6.79 (t, 2H, ArH, $J = 7.61$ Hz), 6.70 (t, 2H, ArH, $J = 7.61$ Hz), 4.17 (t, 4H, OCH$_2$CH$_2$O, $J = 4.80$ Hz), 4.09 (q, 4H, OCH$_2$CH$_3$, $J = 7.20$ & 6.80 & 7.2 Hz), 4.05 (d, 4H, ArCH$_2$Ar, $J = 15.61$), 3.78 (d, 4H, ArCH$_2$Ar, $J = 16.41$), 3.75 (t, 4H, OCH$_2$CH$_2$O, $J = 5.20$ & 4.80 Hz), 3.71 (t, 4H, OCH$_2$CH$_2$O, $J = 6.00$ & 5.60 Hz), 3.50 (t, 4H, OCH$_2$CH$_2$O, $J = 6.00$ Hz), 3.34 (s, 8H, OCH$_2$CO), 1.22 (t, 6H, OCH$_2$CH$_3$, $J = 7.20$ Hz). Note: $J$ values were non-first order and were resolved. $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 170.0, 157.0, 155.6, 149.3, 134.6, 133.8, 130.7, 130.4, 122.9, 122.6, 121.8, 115.4, 70.6, 70.3, 70.0, 69.6, 68.6, 60.3, 37.5, 14.0. HRMS (ESI) $m/z$ 869.35075 (M + Na)$^+$ for C$_{50}$H$_{54}$O$_{12}$Na$,^+$ found 869.35091.

**Scheme S2.** Synthesis of compound 2.

**Compound 2.** A 100 mL round bottom flask was charged with the calix[4]benzocrown-6 10 (0.82 g, 0.94 mmol),$^4$ pyridine (1.0 mL, 12.4 mmol), CH$_2$Cl$_2$ (50 mL), and a stir bar. After cooling the flask to 0 °C using an ice bath, methacryloyl chloride (0.18 mL, 1.91 mmol) was slowly added drop-wise via syringe.$^1$ The reaction mixture was then allowed to warm to ambient temperature over the course of 12 h. The reaction mixture was then quenched via the addition of water (1 mL) and the resulting mixture was extracted with CH$_2$Cl$_2$ (2 $\times$ 50 mL). The organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed en vacuo to give colorless oil. Column chromatography over silica gel (eluent: ethyl acetate/hexane (2/1 v/v)) afforded 2 as a white solid (0.80 g; 90.1% yield). On the basis of the $^1$H NMR spectroscopic analysis, compound 2 was judged to contain a small amount of an unidentified impurity. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.13 (d, 4H, ArH, $J = 7.61$ Hz), 7.09 (d, 4H, ArH, $J = 7.61$ Hz), 7.03 (s, 1H,
ArH), 7.04 (m, 2H, ArH), 6.80 (t, 2H, ArH, J = 7.61 Hz), 6.70 (t, 2H, ArH, J = 7.61 Hz), 6.15 (s, 1H, CH3), 5.58 (s, 1H, CH3), 5.15 (s, 2H, ArCH2O), 4.16 (br t, 4H, OCH3CH2O), 4.09 (q, 4H, OCH3CH3, J = 6.80 & 7.20 Hz), 4.04 (d, 4H, ArCH2Ar, J = 15.21), 3.78 (d, 4H, ArCH2Ar, J = 15.61), 3.74 (t, 4H, OCH2CH2O, J = 5.20 & 4.80 Hz), 3.71 (t, 4H, OCH2CH2O, J = 6.80 & 5.60 Hz), 3.50 (t, 4H, OCH2CH2O, J = 6.00 & 5.60 Hz), 3.33 (s, 8H, OCH2CO), 1.96 (s, 3H, CH3), 1.21 (t, 6H, OCH2CH3, J = 7.20 & 6.80 Hz). Note: J values were non-first order and were resolved. 13C NMR (100 MHz, CD2Cl2): δ 170.0, 167.0, 157.0, 155.5, 149.1, 149.0, 136.5, 134.6, 133.8, 129.8, 122.9, 121.8, 115.6, 114.9, 70.6, 70.2, 69.9, 69.7, 69.6, 68.6, 66.2, 60.3, 37.5, 18.2, 13.9. HRMS (ESI) m/z 967.43213 (M + Na)+ for C55H60O14Na+, found 967.38755.

**Copolymer 3.** A 100 mL round bottom Schlenk flask was charged with 2 (0.566 g, 0.60 mmol), methyl methacrylate (0.64 mL, 6.0 mmol), THF (10 mL), 2,2'-azobisisobutyronitrile (10.8 mg, 0.066 mmol), and a stir bar. After placing the reaction vessel under an atmosphere of argon, it was heated to 70 °C. After 24 h, the vessel was cooled to room temperature and the reaction mixture was added drop-wise to a separate vessel containing an excess of rapidly stirred cold methanol. The precipitated solids were collected by filtration and dried under reduced pressure to afford of the desired material as a white solid (876 mg; 75% yield). 1H NMR (400 MHz, CD2Cl2): δ 0.83 (br, polymer backbone CH3), 1.00 (br, polymer backbone CH3), 1.21 (br t, 6H), 1.81 (br, polymer backbone CH3), 3.48 (br, 8H, calixarene -OCH3), 3.58 (br, 3H, PMMA OCH3), 3.69 (br, 8H, calixarene -OCH2), 3.77 (br, 4H, calixarene –OCH2), 4.00 (br, 4H), 4.09 (br, 4H), 4.19 (br, 10H), 4.95 (br s, 2H, calixarene CH2), 6.70 (br, 2H, Ar-H), 6.80 (br, 2H, Ar-H), 6.99 (br, 4H, pyrrole NH), 7.12 (br, 8H, Ar-H). Mw = 28 kDa; PDI = 2.1.
**S5**

**1H NMR SPECTRA**

*Figure S1.* $^1$H NMR spectrum of 1 (CD$_2$Cl$_2$).

*Figure S2.* $^{13}$C NMR spectrum of 1 (CD$_2$Cl$_2$).
Figure S3. $^1$H NMR spectrum of 2 (CD$_2$Cl$_2$).

Figure S4. $^{13}$C NMR spectrum of 2 (CD$_2$Cl$_2$).
Figure S5. $^1$H NMR spectrum of $\text{3 (CD}_2\text{Cl}_2$).

Figure S6. $^1$H NMR spectrum of $\text{3 after exposure to CsNO}_3$ (200 mM in D$_2$O) (CD$_2$Cl$_2$).
**Figure S7.** $^1$H NMR spectrum of 3 after exposure to CsBr (200 mM in D$_2$O) (CD$_2$Cl$_2$).

**Figure S8.** $^1$H NMR spectrum of 3 after exposure to CsNO$_3$ in D$_2$O, followed by precipitation (CD$_2$Cl$_2$).
EXTRACTION STUDIES

Quantification of Cesium, Sodium, and Potassium Picrate Salt Extraction via UV/vis Spectroscopy. The quantity of picrate salt ([M+ picrate]₀ = 0.02 mM) remaining in the aqueous phase after independent exposure to dichloromethane solutions of 1 ([I]₀ = 6 mM), 3 ([calix[4]arene]₀ = 6 mM), 4 ([calix[4]pyrrole]₀ = 6 mM) and a PMMA homopolymer ([MMA]₀ = 60 mM) was measured using UV/Vis spectroscopy. Extraction of picrate salts was performed by vigorously mixing 1 mL of the aforementioned extractant solutions with 3 mL of an aqueous solution of picrate salt for 30 min. The resulting mixture was then centrifuged to separate the aqueous and organic layers. After separation, 2 mL of the aqueous phase was removed and analyzed by UV-Vis spectroscopy (see Figure S9 – S11). To determine the concentration of picrate in the aqueous layer, a calibration curve was generated (Figure S12) using known concentrations of cesium picrate in water. The percent extraction (%E) was calculated using Eq. 1 (Table S1 – S3; also see main text).

![UV-Vis spectra](image)

**Figure S9.** UV-Vis spectra of the aqueous phase recorded after solutions of cesium picrate (3 ml; 0.02 mM) in water were exposed to CH₂Cl₂ solutions of 1, 3, 4, and PMMA (solutions were prepared at 6 mM except for PMMA which was prepared at 60 mM with respect to calix[4]arene, calix[4]pyrrole, or PMMA monomer, respectively).
Table S1. Liquid-liquid extraction data obtained by exposing aqueous solutions of cesium picrate to dichloromethane solutions of 1, 3, 4, and PMMA (*cf.* Figure S9).\(^a\)

<table>
<thead>
<tr>
<th>Extractant(^b)</th>
<th>Absorbance(^c) (AU)</th>
<th>Cs picrate remaining (µM)</th>
<th>Cs picrate extracted (µM)</th>
<th>(E^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (6 mM)</td>
<td>0.204</td>
<td>15.27</td>
<td>4.73</td>
<td>23.7 ± 2.4</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>0.204</td>
<td>15.27</td>
<td>4.73</td>
<td>23.7 ± 2.3</td>
</tr>
<tr>
<td>4 (6 mM)</td>
<td>0.264</td>
<td>19.32</td>
<td>0.68</td>
<td>3.4 ± 1.0</td>
</tr>
<tr>
<td>PMMA (60 mM)</td>
<td>0.281</td>
<td>20.47</td>
<td>0</td>
<td>0.0 ± 1.0</td>
</tr>
</tbody>
</table>

\(^a\) [Cesium picrate]_0 = 0.02 mM. \(^b\) The initial concentrations in dichloromethane are listed in parenthesis and refer to the concentration of calix[4]arene moieties (1 and 3), the concentration of the calix[4]pyrrole moieties (4), or the concentration of the MMA repeat unit (PMMA). \(^c\) The absorbance intensity was measured at 365 nm in water. \(^d\) Determined according to Eq. 1. The error values given represent the deviations seen in replicate (at least duplicate) measurements.

**Figure S10.** UV-Vis spectra of the aqueous phase recorded after solutions of sodium picrate (3 ml; 0.02 mM) in water were exposed to CH\(_2\)Cl\(_2\) solutions of 1 and 3 (1 mL; 6 mM each).
### Table S2. Liquid-liquid extraction data obtained by exposing aqueous solutions of sodium picrate to dichloromethane solutions of 1 and 3 (cf. Figure S10). \(^a\)

<table>
<thead>
<tr>
<th>Extractant (^b)</th>
<th>Absorbance (^c) (AU)</th>
<th>Na picrate remaining (µM)</th>
<th>Na picrate extracted (µM)</th>
<th>(E) (^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (6 mM)</td>
<td>0.253</td>
<td>18.58</td>
<td>0.42</td>
<td>2.10 ± 1.00</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>0.259</td>
<td>18.98</td>
<td>0.02</td>
<td>0.10 ± 0.05</td>
</tr>
</tbody>
</table>

\(^a\) [Sodium picrate] \(_0\) = 0.019 mM. \(^b\) The initial concentrations in dichloromethane are listed in parenthesis and refer to the concentration of calix[4]arene moieties (1 and 3). \(^c\) Measured at 365 nm in water. \(^d\) Determined according to Eq. 1. The error values given represent the deviations seen in replicate (at least duplicate) measurements.

### Figure S11. UV-Vis spectra of the aqueous phase recorded after solutions of potassium picrate (3 ml; 0.019 mM) in water were exposed to CH\(_2\)Cl\(_2\) solutions of 1 and 3 (1 mL; 6 mM each).
Table S3. Liquid-liquid extraction data obtained after exposing aqueous solutions of potassium picrate to dichloromethane solutions of 1 and 3 (cf. Figure S11).\(^a\)

<table>
<thead>
<tr>
<th>Extractant(^b)</th>
<th>Absorbance(^c) (AU)</th>
<th>K picrate remaining (µM)</th>
<th>K picrate extracted (µM)</th>
<th>(E^d) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (6 mM)</td>
<td>0.196</td>
<td>14.73</td>
<td>4.27</td>
<td>22.47 ± 2.30</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>0.240</td>
<td>17.70</td>
<td>1.30</td>
<td>6.83 ± 0.70</td>
</tr>
</tbody>
</table>

\(^a\) [Potassium picrate]\(_0\) = 0.019 mM. \(^b\) The initial concentrations in dichloromethane are listed in parenthesis and refer to the concentration of calix[4]arene moieties (1 and 3). \(^c\) Measured at 365 nm in water. \(^d\) Determined according to Eq. 1. The error values given represent the deviations seen in replicate (at least duplicate) measurements.

Figure S12. (A) UV-Vis absorbance spectra of aqueous cesium picrate at various concentrations (i.e., 5 – 30 µM). (B) Plot of the absorbance at 356 nm (i.e., \(\lambda_{\text{max}}\) of cesium picrate) as a function of concentration.
**Analysis of Salt Extraction via $^1$H NMR Spectroscopy.** Initial extraction studies were performed by exposing aqueous solutions (1 mL) of various salts (*i.e.*, CsNO$_3$, CsBr, CsSO$_4^-$, CsF, CsCl, KNO$_3$, and NaNO$_3$) at different concentrations (0 – 200 mM) to 1 mL of solutions of copolymer 3 ([calix[4]arene]$_0$ = 6 mM in CD$_2$Cl$_2$) as described in the main text. The spectra of these studies are shown in Figure S13 – S20. In a second set of studies, we probed the selectivity of copolymer 3, as well as the ability of this system to extract CsNO$_3$ in the presence of other inorganic salts. Copolymer 3 (1 mL, [calix[4]arene]$_0$ = 6 mM solution) was exposed to a 1 mL aqueous solution containing various cesium salts (*e.g.*, CsF, CsCl, and CsSO$_4$; 100 mM initial concentration with respect to each salt; see Figure S17A) and analyzed by $^1$H NMR spectroscopy. Subsequently, CsNO$_3$ (100 mM) was added to the inorganic salt solution and the extraction capabilities were analyzed by $^1$H NMR spectroscopy (Figure 17C). Further, in a separate study copolymer 3 (1 mL, [calix[4]arene]$_0$ = 6 mM solution) was exposed to a 1 mL aqueous solution containing various nitrate salts (*i.e.*, KNO$_3$ and NaNO$_3$; 100 mM initial concentration with respect to each salt; see Figure S20A) and analyzed by $^1$H NMR spectroscopy. Subsequently, CsNO$_3$ (100 mM) was added to the inorganic salt solution and the extraction capabilities were analyzed by $^1$H NMR spectroscopy (Figure S20B). For further studies utilizing mixtures of various inorganic salts, see main text.
Figure S13. $^1$H NMR spectra (8.4 – 2.8 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous cesium bromide at different concentrations.

Figure S14. $^1$H NMR spectra (7.5 – 3.0 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous cesium sulfate at different concentrations.
**Figure S15.** $^1$H NMR spectra (8.0 – 3.0 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous cesium fluoride at different concentrations.

**Figure S16.** $^1$H NMR spectra (7.6 – 2.6 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous cesium chloride at different concentrations.
Figure S17. $^1$H NMR spectra (7.5 – 0 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to D$_2$O solutions of A) CsF, CsCl, and CsSO$_4$ (all salts 100 mM) B) Cs, CsCl, CsSO$_4$, and CsBr (all salts 100 mM) C) CsF, CsCl, CsSO$_4$, CsBr, and CsNO$_3$ (all salts 100 mM). Mixtures were agitated for 30 min and separated via centrifugation prior to analysis.

Figure S18. $^1$H NMR spectra (7.8 – 2.8 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous potassium nitrate at different concentrations.
Figure S19. $^1$H NMR spectra (7.8 – 3.2 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to aqueous sodium nitrate at different concentrations.
Figure S20. $^1$H NMR spectra (7.5 – 0 ppm) of copolymer 3 in CD$_2$Cl$_2$ recorded after exposure to D$_2$O solutions of A) KNO$_3$ and NaNO$_3$ (all salts 100 mM) and B) KNO$_3$, NaNO$_3$ and CsNO$_3$ (all salts 100 mM). Mixtures were agitated for 30 min and separated via centrifugation prior to analysis.
**INDUCTIVELY COUPLED MASS SPECTROMETRY**

**General Procedure.** An aqueous solution (1 mL) of the targeted salt (*e.g.*, CsNO₃, 200 mM) was exposed to 1 mL of extractant (*e.g.*, copolymer 3; [calix[4]arene]₀ = 6 mM) in CH₂Cl₂. Extraction was then performed as described above. The organic layer was removed, evaporated to dryness, and the extractants were digested using 30% hydrogen peroxide in sulfuric acid. The digested product was evaporated to dryness, dissolved in a known amount of aqueous 2% nitric acid and then filtered through a 0.2 µ syringe filter. Cesium concentrations were then determined using an Agilent 7500ce quadrupole spectrometer using the following conditions: 1500 W forward RF power, 4W reflected RF power, 15 L/min plasma gas flow, 0.9 L/min auxiliary gas flow, 0.90 L/min carrier nebulizer gas flow, 0.10 L/min make-up gas flow, spray chamber cooled to 2 °C, and peristaltic pump speed of 0.1 rpm. The Na⁺ and K⁺ cation concentrations were analyzed using an octopole collision-reaction system, with He being employed as a collision gas to remove matrix and plasma-related interferences, and to limit detected intensities. Key results are given in Table S4 and are described in the main text.
Table S4. Results from an ICP-MS analysis\(^a\) of the ability of copolymer 3 to extract various inorganic salts.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Salt</th>
<th>(^{33}\text{Na}) (ppb)</th>
<th>(^{39}\text{K}) (ppb)</th>
<th>(^{133}\text{Cs}) (ppb)</th>
<th>Receptor Bound(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 (6 mM)</td>
<td>CsF</td>
<td>3,160</td>
<td>170</td>
<td>100</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>CsCl</td>
<td>3,400</td>
<td>130</td>
<td>90</td>
<td>0 ± 1.1</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>CsBr</td>
<td>3,630</td>
<td>110</td>
<td>530</td>
<td>10 ± 1.4</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>CsSO(_4)</td>
<td>4,530</td>
<td>110</td>
<td>70</td>
<td>0 ± 0.9</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>CsNO(_3)</td>
<td>4,250</td>
<td>100</td>
<td>2300</td>
<td>60 ± 7</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>NaNO(_3)</td>
<td>4,090</td>
<td>130</td>
<td>5</td>
<td>0 ± 1.0(^c)</td>
</tr>
<tr>
<td>3 (6 mM)</td>
<td>KNO(_3)</td>
<td>3,810</td>
<td>100</td>
<td>1</td>
<td>0 ± 1.1(^c)</td>
</tr>
<tr>
<td>3 (6 mM; precipitated)</td>
<td>CsNO(_3)</td>
<td>4,000</td>
<td>110</td>
<td>2360</td>
<td>60 ± 6</td>
</tr>
</tbody>
</table>

\(^a\) Reported concentrations are after dilution with a known amount of aqueous 2\% nitric acid. The error values given represent the deviations seen in replicate (at least duplicate) measurements. \(^b\) Receptor bound refers to the percentage of the total possible receptor sites populated with cesium after exposure to an aqueous solution of a Cs salt. \(^c\) Calculated percentage of bound receptor in the case of sodium and potassium was achieved by subtracting the sodium and potassium levels found in the blank controls.
References


5. Extraction of sodium and potassium picrate was only quantified in the case of extractants 1 ([I]₀ = 6 mM) and 3 ([calix[4]arene]₀ = 6 mM).