

Supplementary Information

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

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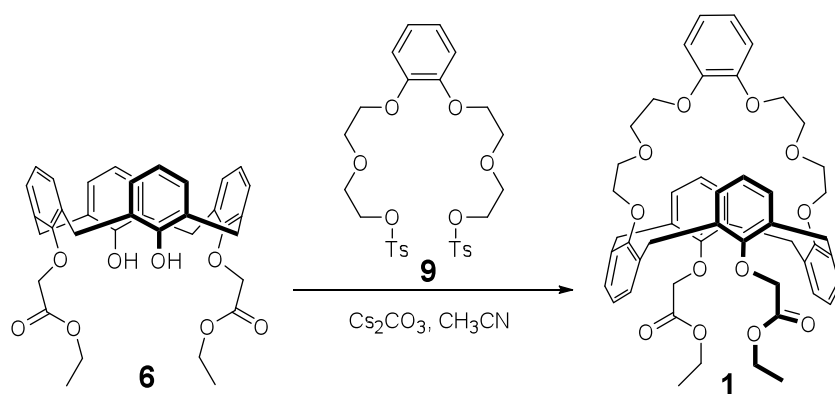
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SYNTHETIC DETAILS

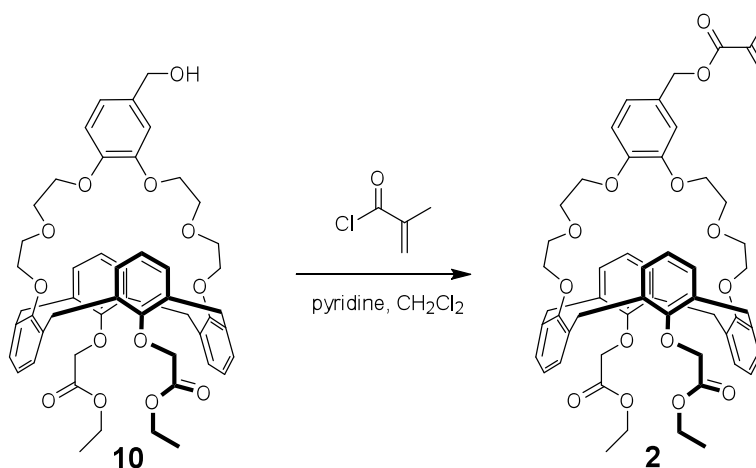
General Considerations. All solvents were dried before use according to standard procedures. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). All other reagents were purchased from Aldrich, Acros, or Fisher and used without further purification. Compounds **4 - 10** were prepared according to literature procedures.¹⁻⁴ NMR spectra were recorded on a Varian Mercury 400 spectrometer. Chemical shifts (δ) are given in ppm and are referenced to the residual protio solvent (¹H: CD₂Cl₂, 5.32 ppm and CDCl₃, 7.26 ppm; ¹³C: CD₂Cl₂, 53.5 ppm and CDCl₃, 77.2). GPC analyses were performed using a Waters HPLC system equipped with HR-1, HR-3, and HR-5 Styragel[®] 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 diester² **6** (0.50 g, 0.84 mmol), ditosylate **9** (0.55 g, 0.92 mmol) and Cs₂CO₃ (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 *en vacuo*. To the resulting colorless oil, CH₂Cl₂ (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 MgSO₄ and the solvent was removed *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). ^1H NMR (400 MHz, CDCl_3): δ 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, $\text{OCH}_2\text{CH}_2\text{O}$, $J = 4.80$ Hz), 4.09 (q, 4H, OCH_2CH_3 , $J = 7.20$ & 6.80 & 7.2 Hz), 4.05 (d, 4H, ArCH_2Ar , $J = 15.61$), 3.78 (d, 4H, ArCH_2Ar , $J = 16.41$), 3.75 (t, 4H, $\text{OCH}_2\text{CH}_2\text{O}$, $J = 5.20$ & 4.80 Hz), 3.71 (t, 4H, $\text{OCH}_2\text{CH}_2\text{O}$, $J = 6.00$ & 5.60 Hz), 3.50 (t, 4H, $\text{OCH}_2\text{CH}_2\text{O}$, $J = 6.00$ Hz), 3.34 (s, 8H, OCH_2CO), 1.22 (t, 6H, OCH_2CH_3 , $J = 7.20$ Hz). Note: J values were non-first order and were resolved. ^{13}C NMR (100 MHz, CD_2Cl_2): δ 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 ($\text{M} + \text{Na}$) $^+$ for $\text{C}_{50}\text{H}_{54}\text{O}_{12}\text{Na}^+$, 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_2Cl_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_2Cl_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 ^1H NMR spectroscopic analysis, compound **2** was judged to contain a small amount of an unidentified impurity. ^1H NMR (400 MHz, CDCl_3): δ 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, CH₂), 5.58 (s, 1H, CH₂), 5.15 (s, 2H, ArCH₂O), 4.16 (br t, 4H, OCH₂CH₂O), 4.09 (q, 4H, OCH₂CH₃, $J = 6.80$ & 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 CH₂), 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). $M_w = 28$ kDa; PDI = 2.1.

¹H NMR SPECTRA

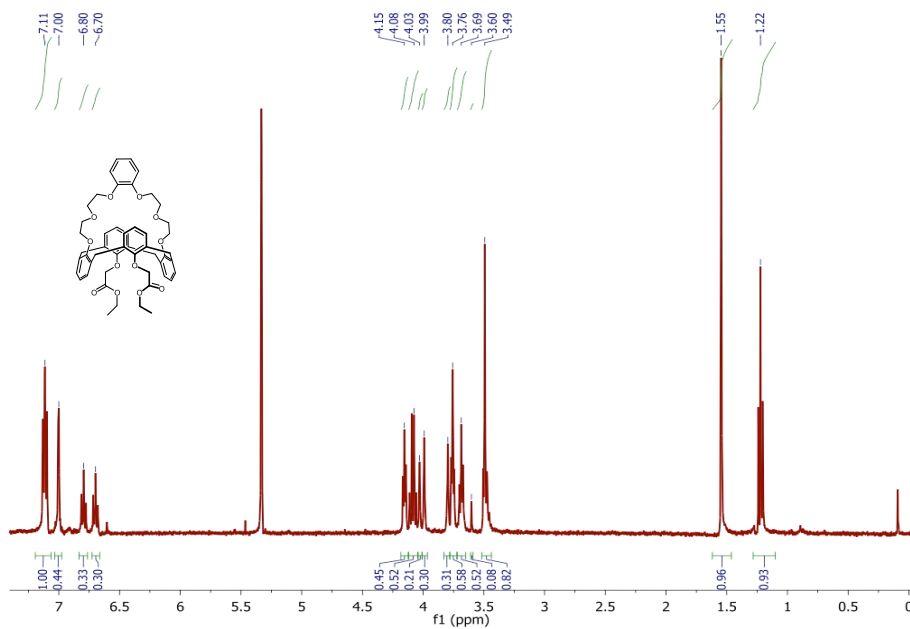


Figure S1. ¹H NMR spectrum of **1** (CD₂Cl₂).

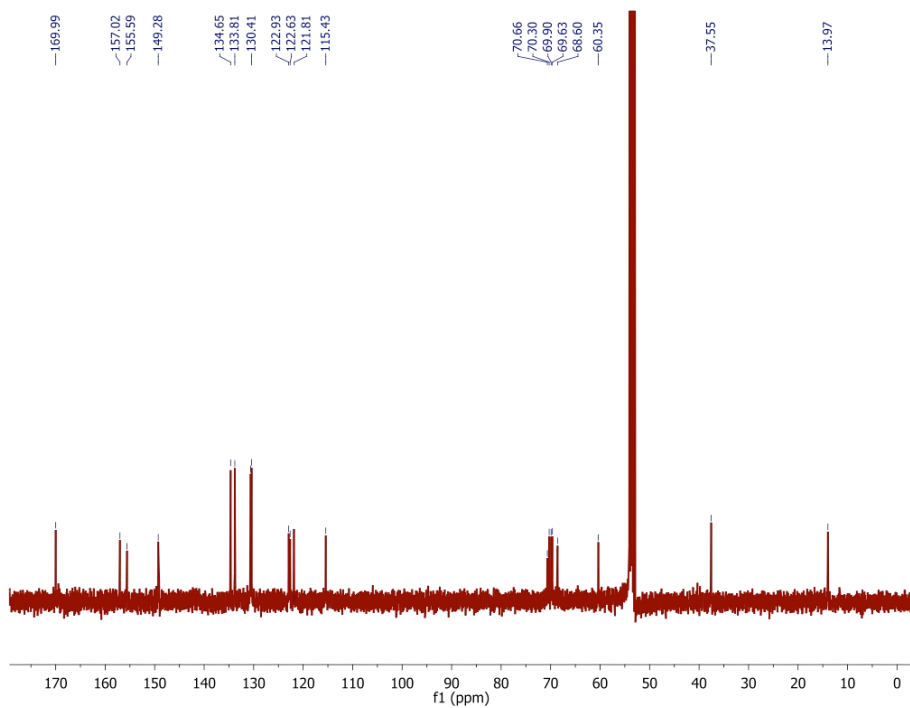


Figure S2. ¹³C NMR spectrum of **1** (CD₂Cl₂).

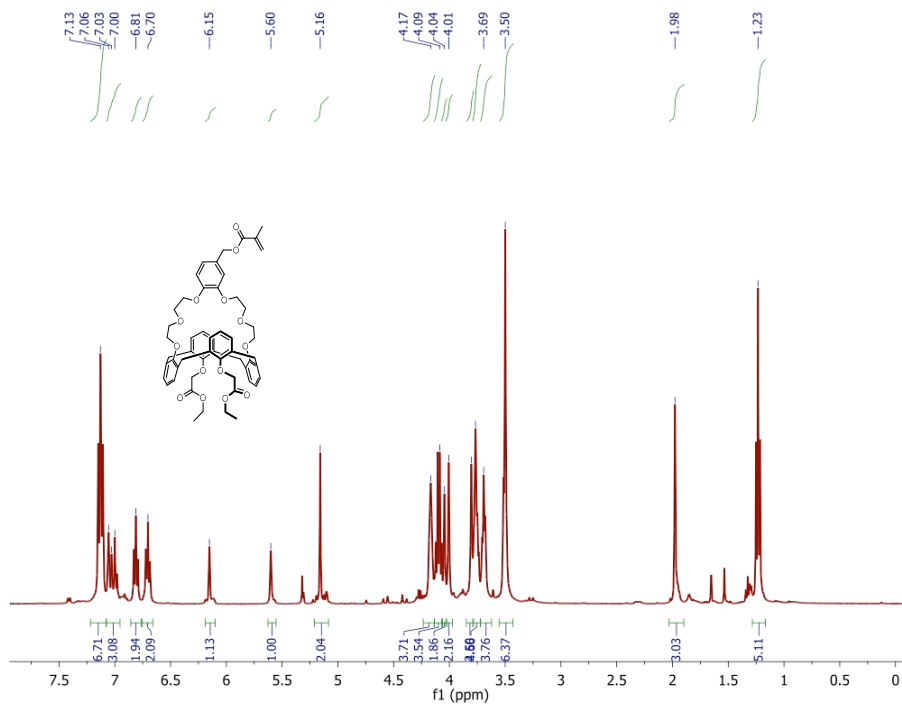


Figure S3. ^1H NMR spectrum of 2 (CD₂Cl₂).

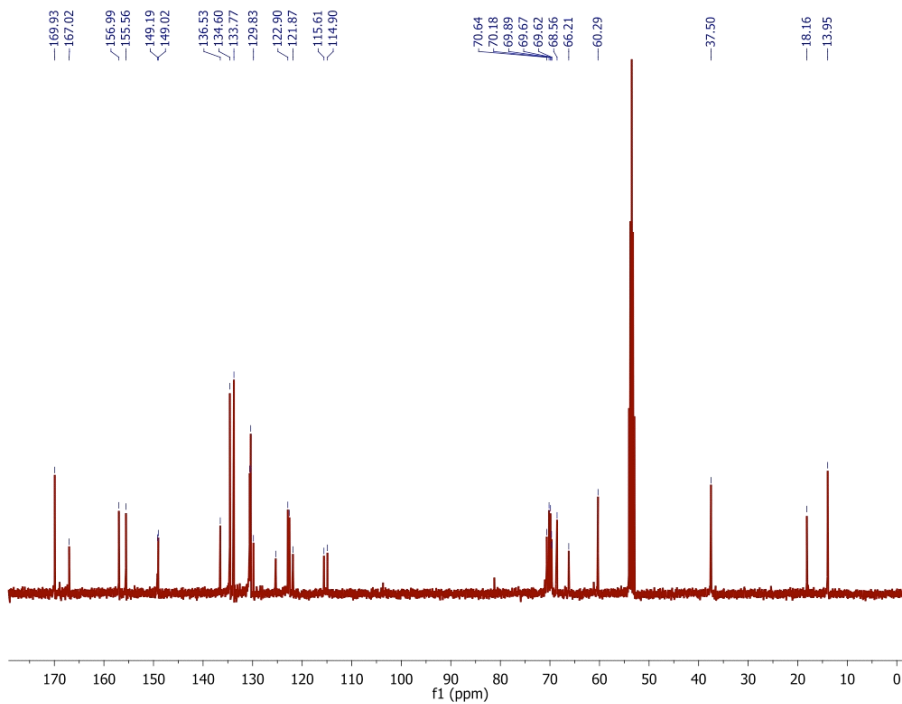


Figure S4. ^{13}C NMR spectrum of 2 (CD₂Cl₂).

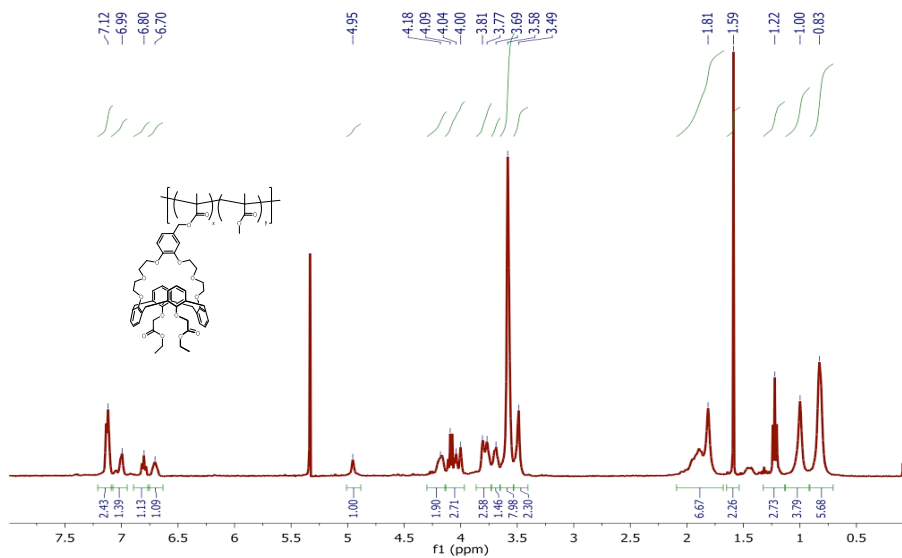


Figure S5. ^1H NMR spectrum of **3** (CD_2Cl_2).

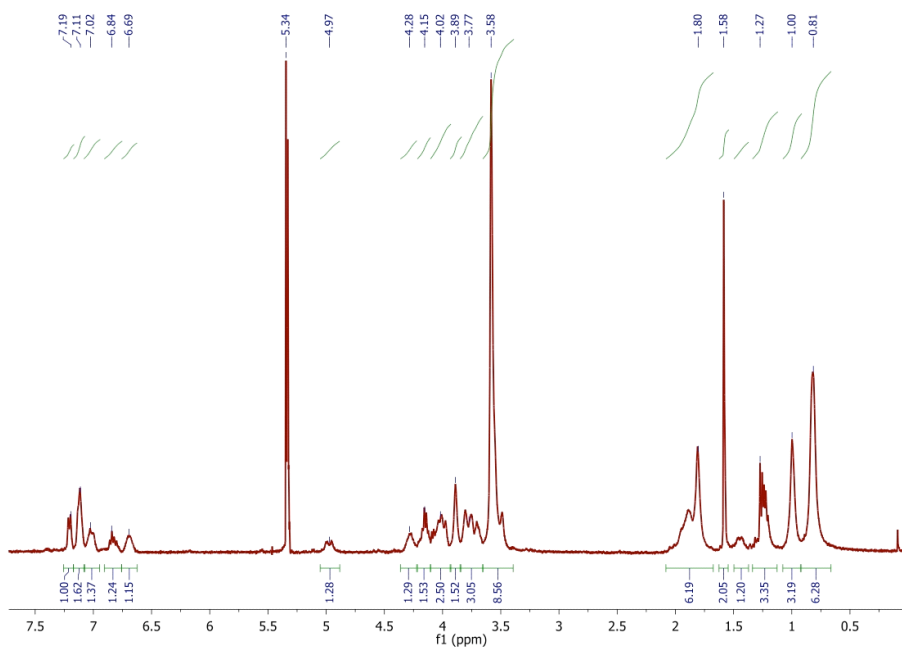


Figure S6. ^1H NMR spectrum of **3** after exposure to CsNO_3 (200 mM in D_2O) (CD_2Cl_2).

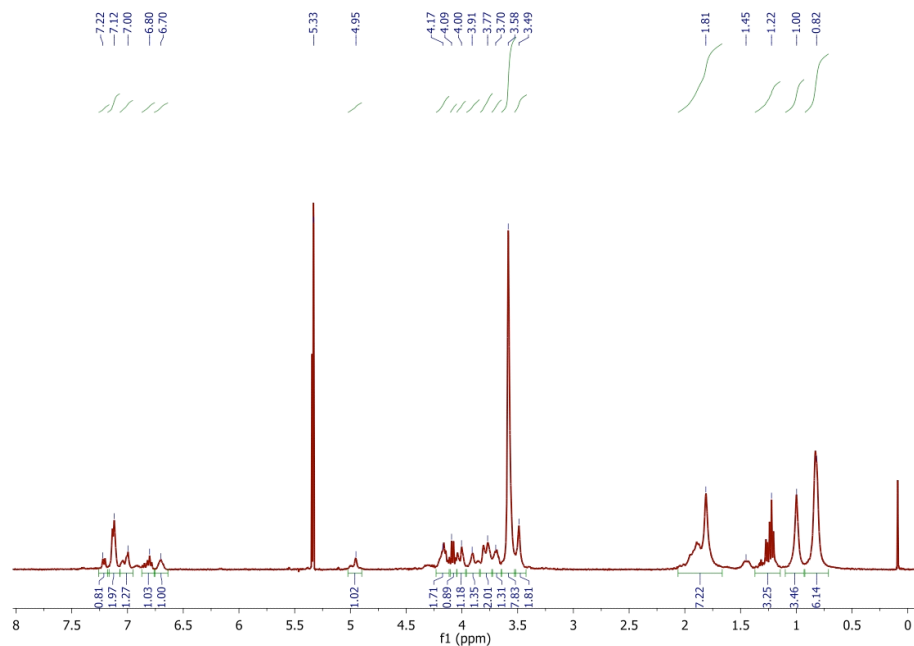


Figure S7. ¹H NMR spectrum of **3** after exposure to CsBr (200 mM in D₂O) (CD₂Cl₂).

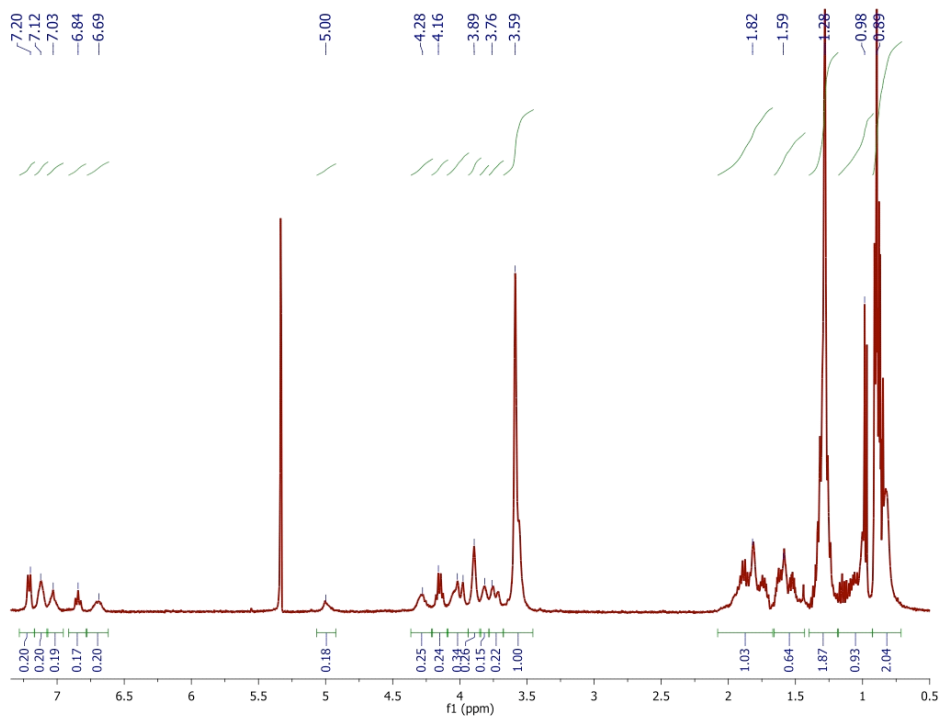


Figure S8. ¹H NMR spectrum of **3** after exposure to CsNO₃ in D₂O, followed by precipitation (CD₂Cl₂).

EXTRACTION STUDIES

Quantification of Cesium, Sodium, and Potassium Picrate Salt Extraction via UV/vis Spectroscopy. The quantity of picrate salt ($[M^+ \text{ picrate}]_0 = 0.02 \text{ mM}$) remaining in the aqueous phase after independent exposure to dichloromethane solutions of **1** ($[1]_0 = 6 \text{ mM}$), **3** ($[\text{calix}[4]\text{arene}]_0 = 6 \text{ mM}$), **4** ($[\text{calix}[4]\text{pyrrole}]_0 = 6 \text{ mM}$) and a PMMA homopolymer ($[\text{MMA}]_0 = 60 \text{ mM}$) was measured using UV/Vis spectroscopy.⁵ 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).

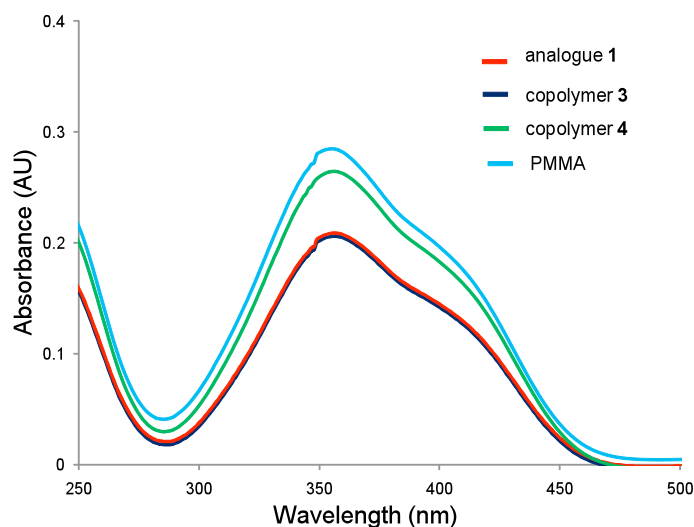


Figure S9. UV-Vis spectra of the aqueous phase recorded after solutions of cesium picrate (3 mL; 0.02 mM) in water were exposed to CH_2Cl_2 solutions of **1**, **3**, **4**, and PMMA (solutions were prepared at 6 mM except for PMMA which was prepared at 60 mM with respect to calix[4]arene, calix[4]pyrrole, 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

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

^a $[\text{Cesium picrate}]_0 = 0.02 \text{ mM}$. ^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.

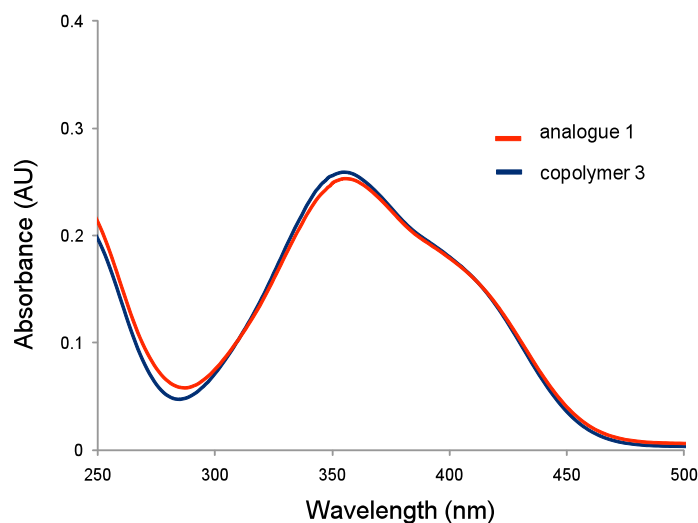


Figure S10. UV-Vis spectra of the aqueous phase recorded after solutions of sodium picrate (3 ml; 0.02 mM) in water were exposed to CH_2Cl_2 solutions of **1** and **3** (1 mL; 6 mM each).

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

Extractant ^b	Absorbance ^c (AU)	Na picrate remaining (μM)	Na picrate extracted (μM)	E^d (%)
1 (6 mM)	0.253	18.58	0.42	2.10 ± 1.00
3 (6 mM)	0.259	18.98	0.02	0.10 ± 0.05

^a $[\text{Sodium picrate}]_0 = 0.019 \text{ mM}$. ^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.

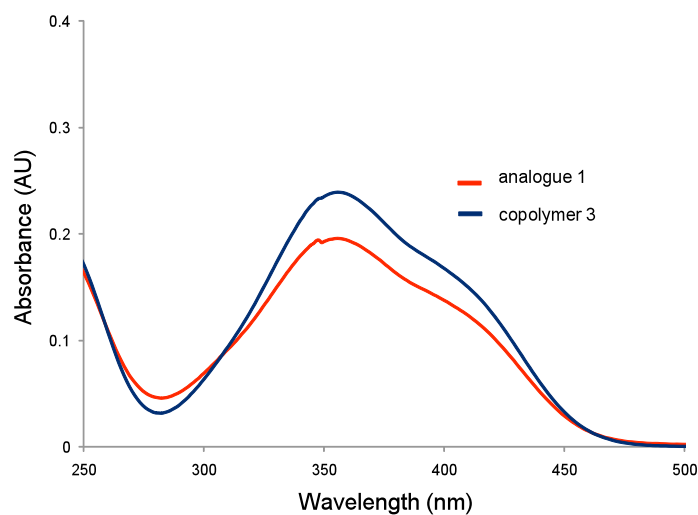


Figure S11. UV-Vis spectra of the aqueous phase recorded after solutions of potassium picrate (3 ml; 0.019 mM) in water were exposed to CH_2Cl_2 solutions of **1** and **3** (1 mL; 6 mM each).

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

Extractant ^b	Absorbance ^c (AU)	K picrate remaining (μM)	K picrate extracted (μM)	E^d (%)
1 (6 mM)	0.196	14.73	4.27	22.47 \pm 2.30
3 (6 mM)	0.240	17.70	1.30	6.83 \pm 0.70

^a $[\text{Potassium picrate}]_0 = 0.019 \text{ mM}$. ^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.

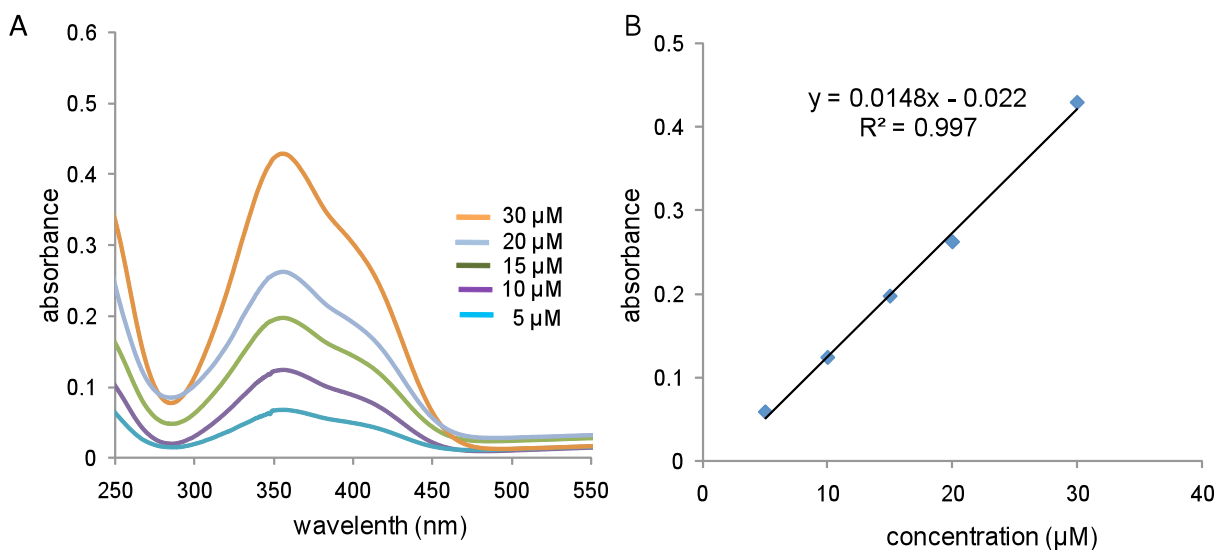


Figure S12. (A) UV-Vis absorbance spectra of aqueous cesium picrate at various concentrations (*i.e.*, 5 – 30 μM). (B) Plot of the absorbance at 356 nm (*i.e.*, λ_{max} of cesium picrate) as a function of concentration.

Analysis of Salt Extraction via ^1H 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** ($[\text{calix}[4]\text{arene}]_0 = 6 \text{ mM}$ in CD_2Cl_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, $[\text{calix}[4]\text{arene}]_0 = 6 \text{ mM}$ 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 ^1H NMR spectroscopy. Subsequently, CsNO_3 (100 mM) was added to the inorganic salt solution and the extraction capabilities were analyzed by ^1H NMR spectroscopy (Figure 17C). Further, in a separate study copolymer **3** (1 mL, $[\text{calix}[4]\text{arene}]_0 = 6 \text{ mM}$ 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 ^1H NMR spectroscopy. Subsequently, CsNO_3 (100 mM) was added to the inorganic salt solution and the extraction capabilities were analyzed by ^1H NMR spectroscopy (Figure S20B). For further studies utilizing mixtures of various inorganic salts, see main text.

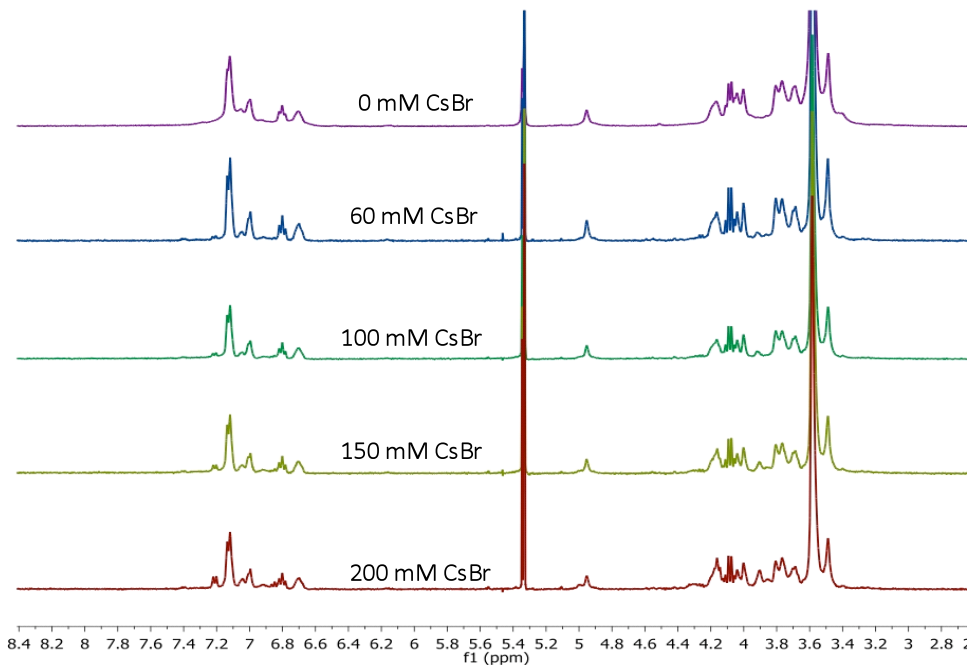


Figure S13. ¹H NMR spectra (8.4 – 2.8 ppm) of copolymer **3** in CD₂Cl₂ recorded after exposure to aqueous cesium bromide at different concentrations.

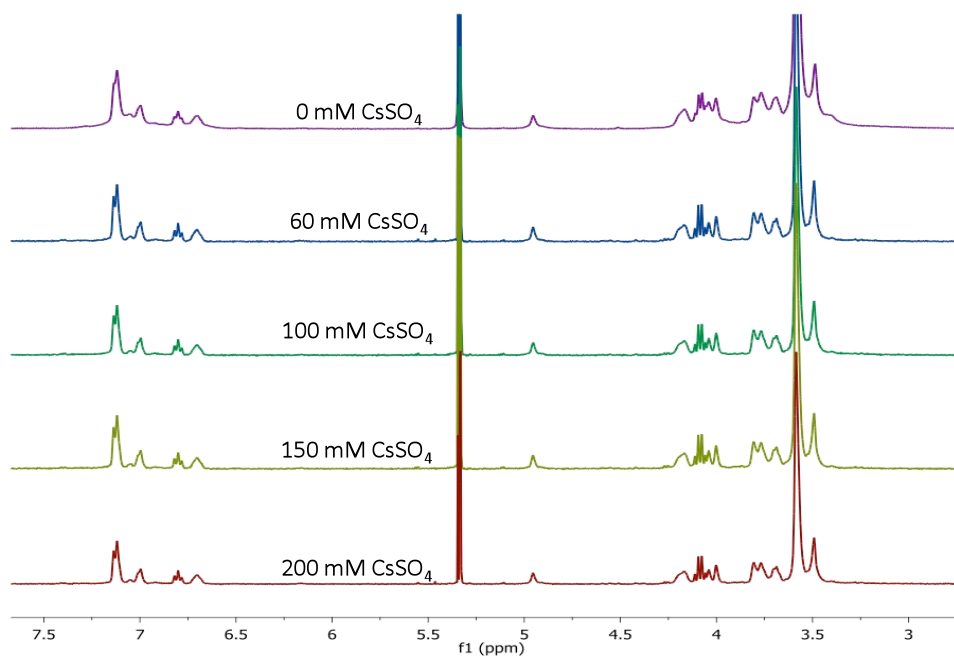


Figure S14. ¹H NMR spectra (7.5 – 3.0 ppm) of copolymer **3** in CD₂Cl₂ recorded after exposure to aqueous cesium sulfate at different concentrations.

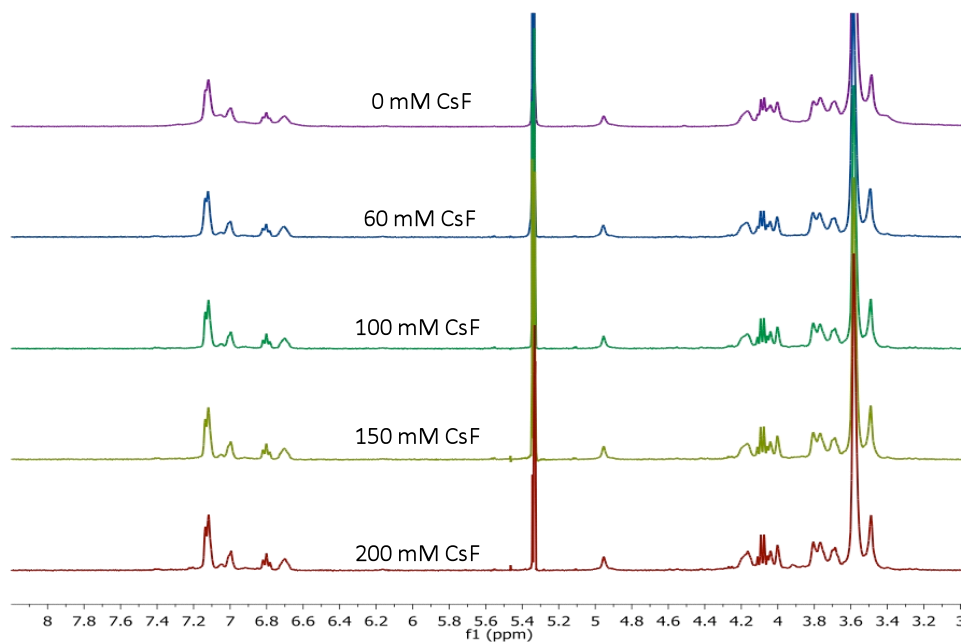


Figure S15. ^1H NMR spectra (8.0 – 3.0 ppm) of copolymer **3** in CD_2Cl_2 recorded after exposure to aqueous cesium fluoride at different concentrations.

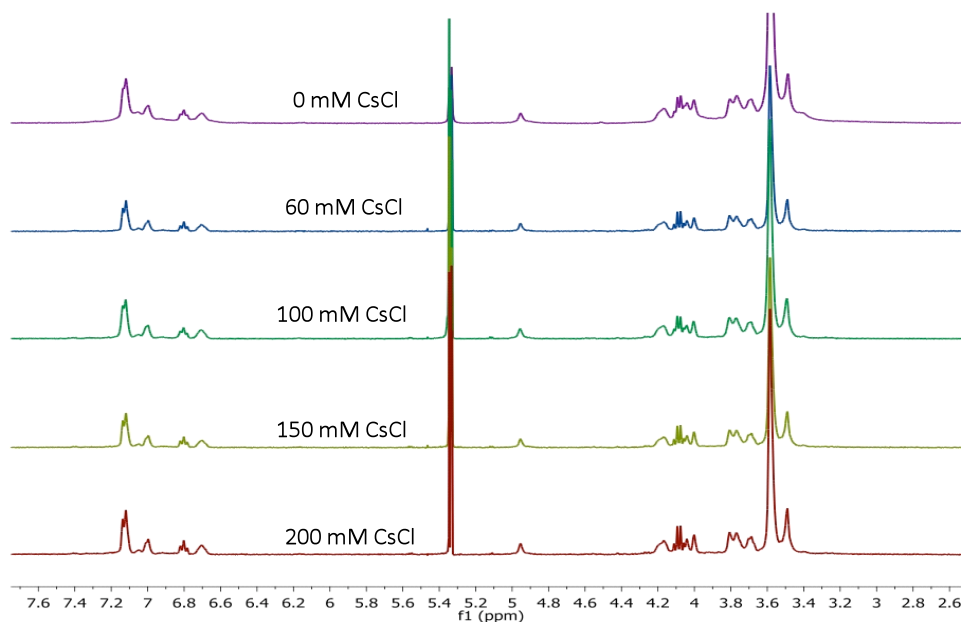


Figure S16. ^1H NMR spectra (7.6 – 2.6 ppm) of copolymer **3** in CD_2Cl_2 recorded after exposure to aqueous cesium chloride at different concentrations.

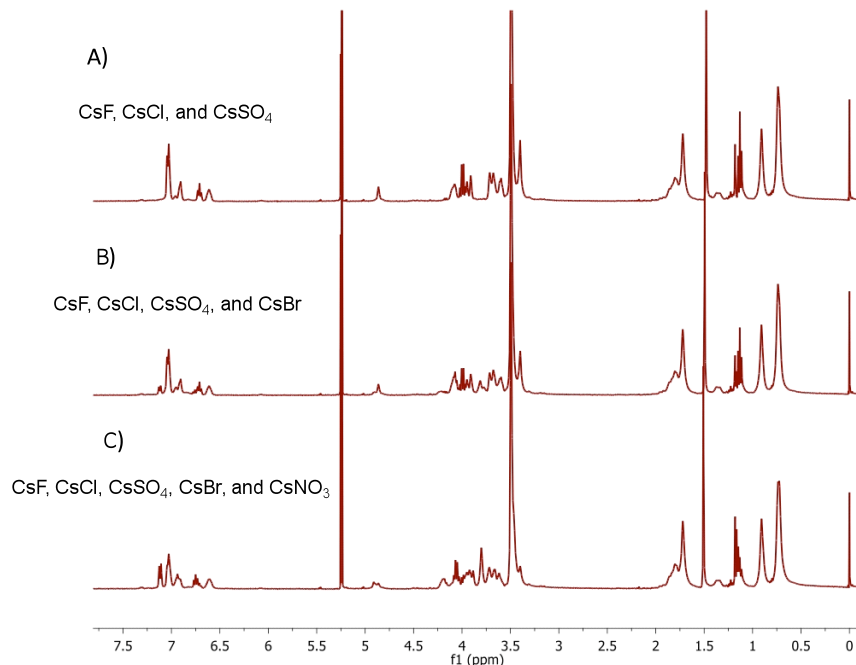


Figure S17. ^1H NMR spectra (7.5 – 0 ppm) of copolymer **3** in CD_2Cl_2 recorded after exposure to D_2O solutions of A) CsF, CsCl, and CsSO₄ (all salts 100 mM) B) Cs, CsCl, CsSO₄, and CsBr (all salts 100 mM) C) CsF, CsCl, CsSO₄, CsBr, and CsNO₃ (all salts 100 mM). Mixtures were agitated for 30 min and separated *via* centrifugation prior to analysis.

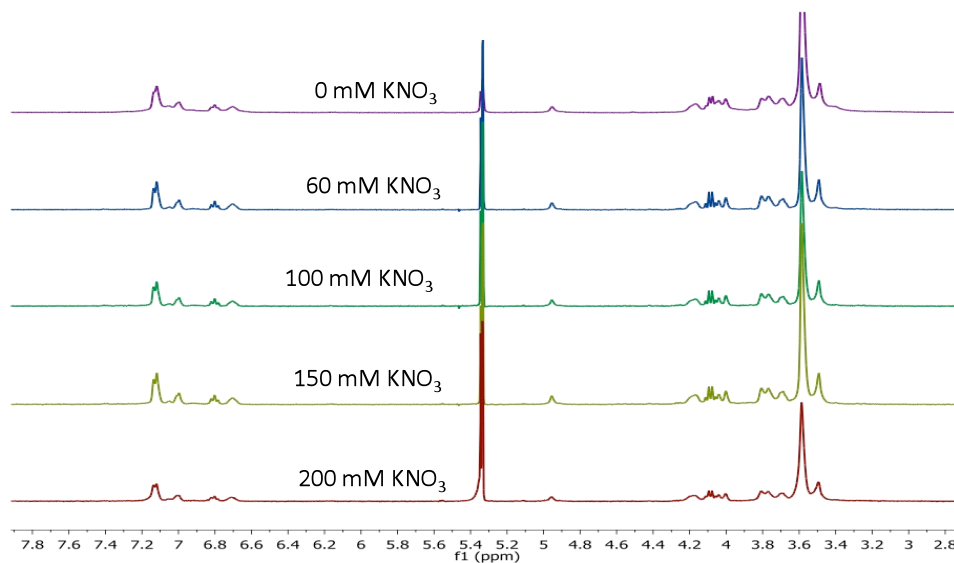


Figure S18. ^1H NMR spectra (7.8 – 2.8 ppm) of copolymer **3** in CD_2Cl_2 recorded after exposure to aqueous potassium nitrate at different concentrations.

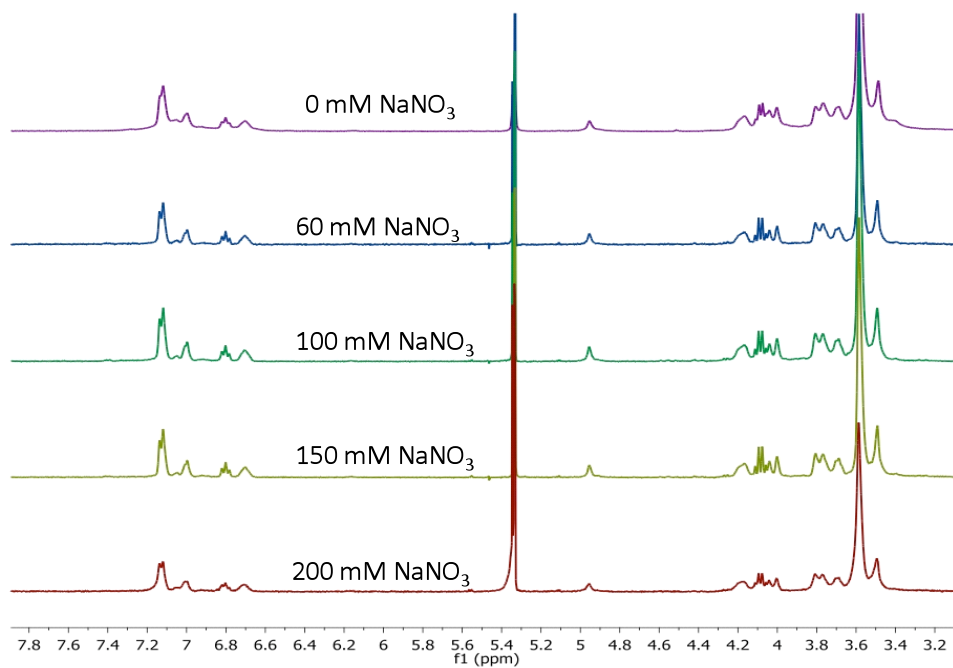


Figure S19. ¹H NMR spectra (7.8 – 3.2 ppm) of copolymer **3** in CD₂Cl₂ recorded after exposure to aqueous sodium nitrate at different concentrations.

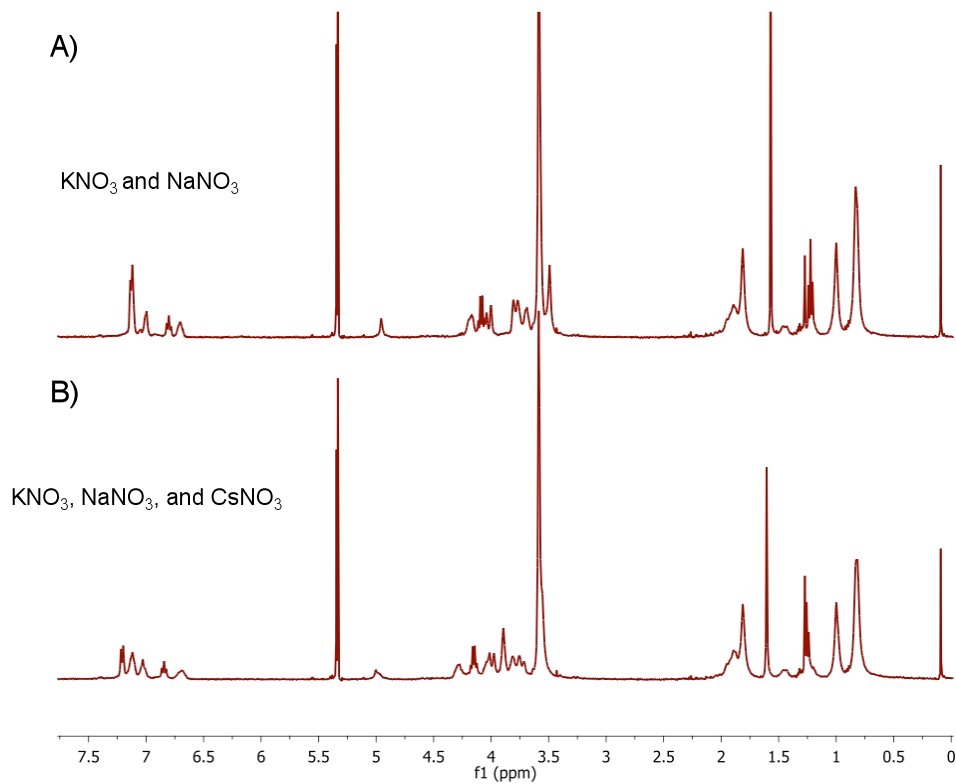


Figure S20. ^1H NMR spectra (7.5 – 0 ppm) of copolymer **3** in CD_2Cl_2 recorded after exposure to D_2O solutions of A) KNO_3 and NaNO_3 (all salts 100 mM) and B) KNO_3 , NaNO_3 and CsNO_3 (all salts 100 mM). Mixtures were agitated for 30 min and separated *via* centrifugation prior to analysis.

INDUCTIVELY COUPLED MASS SPECTROMETERY

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.

Extractant	Salt	³³ Na (ppb)	³⁹ K (ppb)	¹³³ Cs (ppb)	Receptor Bound^b (%)
3 (6 mM)	CsF	3,160	170	100	0 ± 1
3 (6 mM)	CsCl	3,400	130	90	0 ± 1.1
3 (6 mM)	CsBr	3,630	110	530	10 ± 1.4
3 (6 mM)	CsSO ₄	4,530	110	70	0 ± 0.9
3 (6 mM)	CsNO ₃	4,250	100	2300	60 ± 7
3 (6 mM)	NaNO ₃	4,090	130	5	0 ± 1.0 ^c
3 (6 mM)	KNO ₃	3,810	100	1	0 ± 1.1 ^c
3 (6 mM; precipitated)	CsNO ₃	4,000	110	2360	60 ± 6

^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

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