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Removal of Anions from Aqueous Media by Means of a Thermoresponsive Calix[4]pyrrole Amphiphilic Polymer

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Abstract: To address the challenge of removing unwanted anions from aqueous media under extraction-free conditions we have prepared a thermoresponsive amphiphilic polymer with pendent calix[4]pyrrole (C4P) receptors. Because of its amphiphaticity, this polymer self-assembles into micelles in water. These micelles contain the C4P receptors buried in a hydrophobic core. This allows uptake of various cesium anions into the micelles. Due to the thermal-responsiveness of the hydrophilic block chain, the anion-bearing micelles precipitate in water upon heating. Simple filtration allows their removal from the aqueous environment, thus allowing for effective water purification. Treating the anion-trapped micelles with acidic aqueous solution leads to the competition-induced release of the bound anion and thus recycling the polymeric material.

Many anionic species constitute major environmental pollutants. There is thus a clear and widely appreciated need for materials capable of recognizing, capturing, and removing these deleterious anionic species from water.^[1] A venerable technique currently being explored for the removal of potentially harmful anions from aqueous environments is liquid-liquid extraction.^[2] This approach typically relies on the use of a privileged extractant to facilitate the transfer of a given anion from one liquid phase to another liquid phase (usually from an aqueous source phase to an organic receiving phase).^[3] The extractant can be either a free anion receptor (i.e., a small molecule) or a polymer bearing one or more ion receptors.^[3–5] Polymeric systems offer certain advantages in that they are 1) usually easy to isolate from solutions or mixtures, and 2) often benefit from multivalency effects.^[4] In early work, Sessler and Bielawski used poly-(methyl methacrylate) (PMMA) polymers functionalized with calix[4]pyrroles (C4Ps; structure in Scheme 1) as pendent anion receptor groups to extract halides,^[4a] ion pairs,^[4b] and dianions^[4c] from aqueous environments. Recently, we showed that a polystyrene (PS) polymer bearing pendent Schiff-base

macrocycles could be used to extract phosphate anions from water.^[4d] Separately, Piatek reported that a heteroditopic side-chain receptor incorporated within a copolymer could be used to extract NaNO₃.^[4e] Flood demonstrated that PMMA copolymers bearing aryl-triazoles as anion recognition groups could be used to extract chloride from water.^[4f] In all cases, two phase liquid-liquid extraction approaches were employed. While impressive results have been obtained, the requirement for an organic receiving phase raises concerns that a potential secondary pollutant (the non-aqueous solvent) could be introduced into the environment under conditions of field use. Here, we report a thermoresponsive amphiphilic polymer bearing pendent C4P receptors that allows representative test anions to be captured and removed from water without the need for organic solvents. As detailed further below, this purification sequence involves 1) the capture of anion salts from aqueous media in the form of self-assembled micelles, 2) warming to induce micelle precipitation, and 3) removal of the anion-bound micelles from the aqueous medium via filtration. The original polymer may be regenerated by treating with an acid, followed by dialysis and drying. This permits repeated cycles of anion removal and water purification.

In previous studies, C4P was found to form a discrete 1:1 complex with the Cs⁺ cation in its anion bound conformer.^[5a, 5b] C4Ps have also been shown to act as extractants for various cesium halide anion salts under conditions of liquid-liquid extraction.^[5b] In certain cases, the organic receiving phase could be back extracted with an acidic aqueous solution allowing the system to be recycled.^[3b] In recent years, considerable progress has been made in the area of CsNO₃ extraction as required for the remediation of radioactive tank waste.^[5c, 5d] However, the broader problem of being able to selectively remove cesium cations from aqueous media containing less hydrophobic anions, such as chloride anions as would be found in the case of ¹³⁷Cs⁺ contaminated sea water, remains unsolved.^[5] We were thus keen to develop a polymeric material that permitted the removal of cesium halide anion salts from aqueous source phases without recourse to liquid-liquid extraction protocols. A further goal was to create systems that could be used to capture effectively anionic dyes from water since such anions could be considered as easy-to-visualize surrogates for organic pollutants.

To address the above challenges, polymer **P1** (poly(*N*-isopropylacrylamide)-*b*-poly(calix[4]pyrrole-co-methyl methacrylate) or PNIPAM-*b*-P(C4P-co-MMA) was prepared (Scheme 1a). Briefly, PNIPAM **P0** (Supporting Information) was used as a macro-chain-transfer agent (macro-CTA) to initiate the reversible addition-fragmentation chain transfer (RAFT) polymerization^[6] of a mixture of C4P and MMA monomers (Figures S1–S2 in the Supporting Information). Polymer **P2**, lacking the C4P receptor, was prepared in a similar manner (see Scheme 1a for structure). As inferred from ¹H NMR spectral studies and gel-permeation chromatography (GPC) (*M*_{n,NMR} = 10490 g/mol, *M*_{n,GPC} = 10220 g/mol, PDI = 1.18), polymer **P1** is

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characterized by an NIPAM/MMA/C4P repeat unit value of 50:25:4. For the control polymer, **P2**, ($M_{n,NMR} = 8880$ g/mol, $M_{n,GPC} = 8660$ g/mol, PDI = 1.16), the corresponding NIPAM/MMA repeat unit value is 50:30 (Figure S3, SI).

Polymer **P1** was designed to be amphipathic. Thus, when added to an anion-containing aqueous medium, it was expected to adopt a micelle-like structure due to the presence of both hydrophilic PNIPAM and hydrophobic P(C4P-co-MMA) chains.^[7] Under conditions of micelle formation, the hydrophobic C4P receptor units present in **P1** (but not **P2**) are expected to be largely buried within the hydrophobic micellar core and thus in an environment that favors receptor-anion interactions (Scheme 1c). Both **P1** and **P2** incorporate thermal-responsive hydrophilic PNIPAM chains.^[8] In typical PNIPAM polymers intra/intermolecular hydrogen bonding interactions between the chains dominates at high temperature leading to aggregation at higher temperatures.^[8a] It was thus anticipated that upon warming in water the micelles formed from **P1** and **P2** would precipitate. Filtration would then allow removal of the anion-containing micelles from the medium. This, in turn, would provide effective removal of the bound anion from the aqueous medium without the need for contact with an organic solvent. Exposure to dilute acid was then expected to induce release of the bound anions.^[3b] Dialysis (to remove residual acid and salts) and drying would then give the polymeric material suitable for reuse. Experimental support for these contentions now follows.

Scheme 1. a) Chemical structures and cartoon representations of the polymeric materials used in this study. b) Schematic representation of the receptor anion + counter cation ion-pairing and acid-induced disassembly. Cartoon representations of c) anion removal from water by use of polymer **P1** containing C4P receptors, and d) sequence used to regenerate **P1**.

Prior to testing the ability of polymers **P1** and **P2** to remove anions from aqueous environments, their self-assembly and thermal-responsive behavior in water was examined using dynamic light scattering (DLS), transmission electron microscopy (TEM), 1H NMR spectroscopy, and turbidity measurements. As shown in Figures S4 and S5, DLS analyses of **P1** in water revealed that the intensity-averaged hydrodynamic diameter changes with the concentration of **P1**. At low concentrations (1.0×10^{-6} – 4.0×10^{-5} M), the diameter is 7–10 nm. However, as the concentration is raised to 6.0×10^{-5} , the average diameter increases to 45–55 nm, leading to the inference that self-assembled aggregates are being formed.^[7] A TEM study of **P1** at 1.0×10^{-4} M (Figure S4) revealed the presence of spherical micelles with an average diameter of around 45 nm.^[7] Moreover, only peaks corresponding to the PNIPAM protons were readily observed in the 1H NMR spectrum of **P1** recorded in D_2O (Figure S6, SI) supporting that the hydrophobic P(C4P-co-MMA) portion of the micelle is largely shielded from the aqueous environment.^[9]

PNIPAM bears analogy to known thermoresponsive polymers that are soluble in water below a lower critical solution temperature (LCST), which become insoluble when the temperature exceeds their LCST.^[8] The thermoresponsive behavior of **P1** was studied by turbidity measurements. Specifically, the transmittance of an aqueous solution of **P1** was studied as a function of temperature (Figure S10). It was found that the transmittance of an aqueous solution containing **P1** dropped gradually from 100 to 0% as the temperature increased, with an LCST of 34.8 °C. On this basis we conclude that **P1** is soluble in water at room temperature but will precipitate upon heating over its LCST. Similar self-assembly and thermal responsive behavior was seen in the case of the control polymer **P2** that lacks the C4P domains (Figures S7–S10, SI).

As a first test of whether **P1** could be used to capture various anions in aqueous media, 21 mg (2.0×10^{-3} M) of **P1** (effective concentration of the C4P repeat units = 8.0×10^{-3} M) was added to aqueous solutions of, respectively, CsF, CsCl, CsBr, CsI, and CsNO₃ (1.0 mL, 5.0×10^{-4} M each). It was expected that changes in concentration would be reflected in differences in the solution conductivity (SI, Figure S11). As shown in Figure 1a, the conductivity of CsF, CsCl, and CsBr solutions decreased after completing the proposed anion sequence consisting of micelle formation, warming (50 °C), and filtration as shown in Scheme 1. Based on the linear correlation between conductivity and concentration (SI, Figure S11), plots of the change in concentration (Figure 1b) and net percentage of anion salt removed by **P1** (Figure 1c) could be constructed. On this basis, it was concluded that under the test conditions described above **P1** was able to remove CsBr (39%) in preference over CsCl (32%) and CsF (16%). This selectivity order stands in contrast with the relative anion affinities seen in dichloromethane $F^- > Cl^- > Br^-$.^[10a]

Rather, it is in accord with what would be predicted based on the Hofmeister bias^[10b] and the relative anion hydration energies.^[4a] However, these latter effects are not fully determinative. For instance, the relatively poorly hydrated anion salts, CsI and CsNO₃, were not removed appreciably from the aqueous source phase by **P1**. We ascribe this finding to the fact that C4P has little affinity for either the iodide or nitrate anion.^[5b,10a]

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Figure 1. a) Conductivity and b) corresponding concentration changes of various inorganic salt solutions (each at an initial concentration of 5.0×10^{-4} M and a volume of 1 mL) before and after treatment with polymer **P1** (2.0×10^{-3} M). The values in b) were calculated based on the correlation between the solution conductivity and the concentration. c) Percentage of various inorganic salts (initial conc. = 5.0×10^{-4} M in each) removed by **P1** (2.0×10^{-3} M), respectively, after completing the sequence of micelle formation, warming, and filtration outlined in Scheme 1.

DLS analyses (Figure S12, SI) revealed that when **P1** (2.0×10^{-3} M) was added to aqueous solutions of these inorganic salts (1.0 mL, 5.0×10^{-4} M each) assemblies were formed with an average diameter in the range of 40–50 nm. In contrast, little evidence of aggregate formation was seen both before and after the addition of **P1** and after completing the warming, precipitation, and filtration sequence (average particle size 0.2–0.4 nm).

Polymer **P2** was prepared as a control. It resembles **P1** but lacks the C4P receptor. When **P2** (18 mg; 2.0×10^{-3} M) was also added to aqueous solutions of, respectively, CsF, CsCl, CsBr, CsI, and CsNO₃ (1.0 mL, 5.0×10^{-4} M each) little appreciable change in the conductivity was observed (SI, Figure S13). This system was thus not considered to be an effective extractant. However, as expected given its amphipathic nature, evidence of micelle formation was also seen in the case of **P2** as inferred from DLS analyses (Figure S14, SI).

The ability of **P1** to capture organic anions in water was also studied. C4P is known to bind organic anion, such as ArCOO^- and ArO^- (as their Cs^+ salts).^[4c,5a,5c] Therefore, dyes **3** and **4** (coumarin derivatives, Figure 2a) were selected for this study. UV/Vis spectroscopy experiments provided support for the notion that the process of Scheme 1 was effective in the case of these anionic dyes and polymer **P1** (SI, Figures 2a, S15, and S16).

Figure 2. a) Chemical structures of dyes **3** and **4**. UV-vis spectra of b) **3** and c) **4** (each at an initial concentration of 5.0×10^{-5} M in a sample volume of 1 mL) upon treatment with polymer **P1** (2.0×10^{-4} M). d) Absorption intensity and e) corresponding concentration changes of **3** and **4** (each at an initial concentration of 5.0×10^{-5} M in a sample volume of 1 mL) seen upon treatment with polymer **P1** (2.0×10^{-4} M). These values were calculated based on the correlation between the solution absorption intensity and the concentration (λ_{max} of 285 nm for **3**, and λ_{max} of 365 nm for **4**). f) Percentage of **3** and **4** (initial conc. of each = 5.0×10^{-5} M) removed by **P1** (2.0×10^{-4} M), respectively, after completing the purification sequence outlined in Scheme 1.

As can be seen from Figure 2b, a mixture of **3** (5.0×10^{-5} M) and **P1** (2.0×10^{-4} M) shows an absorption feature that is slightly enhanced compared to that of **3** only ($A = 1.08$ at λ_{max} of 285 nm vs. $A = 1.00$ at λ_{max} of 285 nm). We ascribe these spectral changes to the formation of micelles. Their presence reduces the transmittance of the aqueous solution, resulting in an increase of the absorption.^[7] DLS analyses revealed morphological changes consistent with micelle formation (Figures S18 and S19, SI). After heating (50 °C) and filtration, the absorbance intensity of the resulting solution was lower than that of the original solution containing **3** (Figure 2d, $A = 0.375$ at a λ_{max} of 285 nm vs. $A = 1.00$ at a λ_{max} of 285 nm). These spectral changes are ascribed to the capture of **3** by the C4P subunits in **P1** and concomitant formation of micelles. Similarly, in the case of dye **4**, the absorbance intensity of the solution also increased when **P1** was added (Figure 2c, $A = 0.991$ at a λ_{max} of 365 nm vs. $A = 0.909$ at λ_{max} of 365 nm). After heating (50 °C) and filtration, the absorbance intensity of the resulting solution was again lower than that of the original solution of **4** (Figure 2d, $A = 0.464$ at a λ_{max} of 365 nm vs. $A = 0.909$ at a λ_{max} of 365 nm). Only modest changes in spectral intensity were seen in the initial and final solutions of **3** and **4** upon treatment with **P2** (Figure S17, SI).

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A linear correlation between the solution absorbance intensity and concentration was observed for aqueous solutions of **3** and **4** (Figures S15 and S16, SI). The concentration of **3** and **4** in aqueous solution before and after subjecting to treatment with polymers **P1** and **P2** could thus be calculated using the UV/Vis spectroscopy data shown in Figures 2b and 2c. As shown in Figure 2e, after treatment with **P1**, the concentration of **3** decreased from 5.0×10^{-5} M to 1.88×10^{-5} M, and that of **4** decreased from 5.0×10^{-5} M to 2.56×10^{-5} M. Thus, under these experimental conditions, the removal efficiencies for **3** and **4** displayed by **P1** were 62.5% and 48.9%, respectively (Figure 2f). The difference in removal efficiency is consistent with the differences in the anion binding affinities of these two dyes for C4P.^[11] In the case of **P2**, removal efficiencies of only 10.8% for **3** and 9.6% for **4** were seen, respectively (Figure S17, SI). We therefore conclude that the process outlined in Scheme 1 may be used to remove test anionic dyes from an aqueous source phase and that the presence of an anion receptor within polymer **P1** plays a critical role in mediating the process.

As desired, the purification efficiencies could be increased by subjecting the source phase to several rounds of treatment. For instance, when fresh batches of **P1** (2.0×10^{-4} M each) were used to extract sequentially an initial 5.0×10^{-5} M solution of **3** (Figure S20, SI) an order of magnitude decrease in the concentration of **3** could be achieved within five cycles (final concentration of **3** = 4.75×10^{-6} M).

An appealing feature of the present approach is that the polymeric extractant may be reused. Specifically, it was found that treating the precipitates formed by mixing solutions of **P1** and **3** as detailed above with 0.2 M aqueous HNO_3 (1 mL) at r.t. serves to produce micelles that resemble those seen initially (Scheme 1d). Presumably, these changes reflect first recognition and then the proton-induced release of the bound anionic guest from the C4P receptor. Subjecting to dialysis (to remove residual acid and the released dye) and drying under high vacuum then yielded a regenerated form of the polymer, **P1-r-1** (Scheme 1d). This regenerated material was tested for its ability to remove **3** from an aqueous source phase under conditions identical to those employed in the case of **P1** and found to be essentially as effective (Figure 3 and Scheme S1, SI). The polymer could be recycled several times by generating **P1-r-2**, **P1-r-3**, **P1-r-4**, and **P1-r-5** using the same regeneration procedure used to produce **P1-r-1** (Figure 3 and Scheme S1, SI). Again, the removal efficiencies (Figure 3d) of these regenerated polymers were competitive with those seen for **P1**; cf. Figure 2. We thus conclude that the polymeric material of this study may be used effectively through at least five cycles.

The regeneration of polymer **P1** is not limited to dye salts such as **3**. For instance, we found that release could be carried out effectively in the case of CsBr (Figure S21, SI). Moreover, the effective removal of CsBr from contaminated water could be realized through recycling this polymeric material through half a dozen cycles (Figure S22, SI).

Figure 3. a) UV-vis spectra, b) absorption intensity and c) corresponding concentration changes of independent freshly prepared aqueous solutions of **3** (5.0×10^{-5} M) recorded before and after treatment with **P1-r-1**, **P1-r-2**, **P1-r-3**, **P1-r-4**, and **P1-r-5**, respectively. d) Percentage of **3** (initial conc. = 5.0×10^{-5} M in H_2O ; sample volume = 1 mL) removed by **P1-r-1**, **P1-r-2**, **P1-r-3**, **P1-r-4**, and **P1-r-5**, respectively. Here, r means regenerated. A polymer concentration of 2.0×10^{-4} M was used in all cases.

In conclusion, an amphiphilic polymer **P1** containing both a hydrophilic segment and a hydrophobic part containing C4P units was prepared. It was found to self-assemble into micelle-like structures in water. Adding polymer **P1** to aqueous solutions containing cesium anion salts led to anion capture within micelles, presumably as the result recognition by the incorporated C4P units. Heating the solution causes the micelles to precipitate from the aqueous medium. The resulting anion-containing precipitates could then be removed by filtration allowing effective removal of the test anions. Since it avoids the use of organic solvents, we suggest that the present strategy could have a role to play in the development of new water purification processes.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: amphiphilic polymers • anion recognition • calixpyrroles • thermoresponsiveness • water purification

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COMMUNICATION

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Removal of Anions from Aqueous Media by Means of a Thermoresponsive Calix[4]pyrrole Amphiphilic Polymer

Adding a thermoresponsive amphiphilic polymer containing calix[4]pyrrole to an anionic aqueous solution, followed by heating and filtration, allows for the removal of test anion from an aqueous source phase without the use organic solvents, as required by more traditional liquid-liquid extraction-based approaches.