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Controlling Structure Beyond the Initial Coordination Sphere: Complexation-Induced Reversed Micelle Formation in Calix[4]pyrrole-containing Diblock Copolymers

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Supporting Information Placeholder

ABSTRACT: A diblock copolymer containing a strapped calix[4]pyrrole-based ion pair recognition subunit has been synthesized via RAFT polymerization. As prepared, the polymer is hydrophobic and devoid of any particular morphological form. However, upon ion pair complexation, the copolymer self-assembles to generate reverse micelles in organic media. The reverse micelle formed in this way may be used to extract alkali cation and cesium halide anion salts from an aqueous source into an organic receiving phase. The polymer proved more effective as an extractant than the corresponding free ion pair receptor.

Controlling structure beyond the first coordination sphere through complexation is a current challenge in supramolecular chemistry.[1] It is being tackled elegantly through use of mechanically interlinked molecular systems,[2] and is becoming increasingly appreciated in the context of catalysis.[3] Long-range, complexation-based changes in order also provide the basis for certain stimulus-responsive polymers and self-assembled ensembles.[4] Remote structural effects are particularly important in the area of liquid-liquid extraction where recent work has served to highlight the role of higher order organized structures, such as micelles and reversed micelles, in determining the efficacy of a given molecular extractant.[5] However, actually controlling these effects has proved challenging.

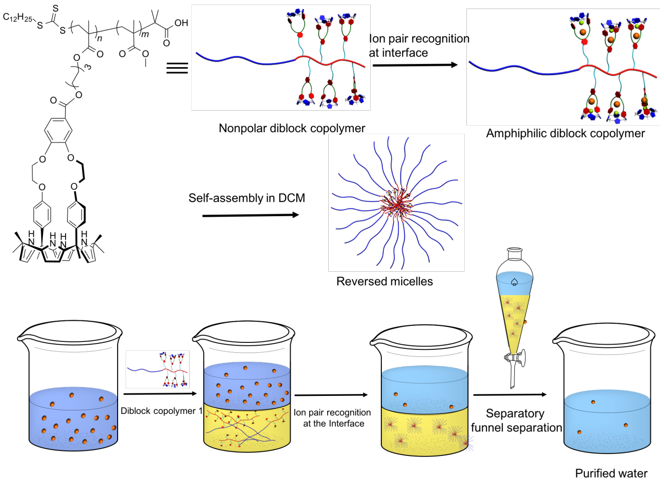
Recently, we showed that a free-standing calix[4]pyrrole-based ion pair receptor could be used to extract specific ion pairs from an aqueous source phase by means of ion pair complexation-induced micellization.[5b] Here, we report here a new diblock copolymer, poly(methyl methacrylate)-block-poly(SC4Py) (PMMA-b-PSC4Py; **1**) that contains both a crown ether-like cation recognition motif and a calix[4]pyrrole anion binding subunit. As prepared, diblock copolymer **1** is hydrophobic and lacking any well-defined structure. However, upon complexation with an appropriately chosen ion pair in dichloromethane solution or at an organic-water interface it becomes amphiphilic and self-assembles into multi-aggregated reversed micelles. Compared to the free-standing ion pair receptor on which it is based, namely the crown ether-functionalized calix[4]pyrrole **M1**, copolymer **1** is much more effective as an extractant for a range of test alkali cation and cesium halide anion salts.

In recent years, increasing effort has been devoted to the preparation of polymeric extractants.[6] For example, our group created copolymers containing calix[4]pyrroles and showed they could extract certain halide anion salts.[7] Piatek and co-workers used a polymer bearing heteroditopic side chain receptors to extract $NaNO_3$.[8] Flood and co-workers used polymers contained aryl-triazole-based anion receptors to extract chloride anion salts.[9] It is our view that such focused recognition and extraction tasks would benefit further from the use of ion pair receptors incorporated into the polymer.

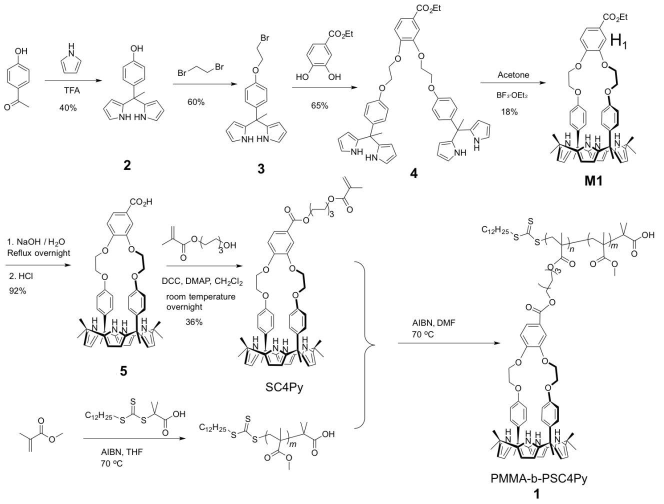
Relative to simple ion (anion or cation) receptors, ion pair receptors generally display enhanced affinities for the ions in question as the result of, e.g., allosteric effects and enhanced electrostatic interactions between the co-bound ions.[10,11] To date, ion pair receptors have seen use in such diverse areas as salt solublization,[12] ion extraction,[13] and through-membrane transport.[14] We were thus keen to test whether an appropriately designed diblock copolymer containing an ion pair receptor would prove effective as an ion pair extractant. Our thinking, shown in Scheme 1, was that ion pair recognition would favor micelle formation thus aiding the extraction process.

Such considerations led to the design of **1**, whose synthesis is shown in Scheme 2. First, the functionalized strapped-calix[4]pyrrole monomer, SC4Py was prepared via precursor **M1**. This latter species was extended to produce SC4Py. Since monomer SC4Py contains a pyrrole ring, it was deemed incompatible with most living polymerization strategies, such as atom transfer radical polymerization (ATRP).[15] Thus, it was subject to RAFT polymerization. First, the hydrophobic block PMMA was synthesized using S-1-dodecyl-s′-(α,α′-dimethyl-α″-acetic acid) trithio-carbonate (DDMAT) as a chain transfer agent (CTA). RAFT polymerization with SC4Py gave the PMMA-b-PSC4Py block copolymer **1** (Scheme 2).

Scheme 1. Diblock Copolymer **1** and Illustration of the Self-Assembly Processes giving Multi-aggregated Reversed Micelles.



Scheme 2. Synthetic route leading to a strapped calix[4]pyrrole-bearing diblock copolymer, PMMA-b-PSC4Py (**1**).



Prior to studying the effects of salts on the morphology of polymer **1**, its expected ion pair recognition features were studied using precursor **M1** as a model host system. Initial evidence that compound **M1** could act as an ion pair receptor for cesium fluoride (CsF) came from a single-crystal X-ray diffraction analysis of the CsF complex. Crystals were obtained via the slow evaporation of a $CHCl_3$ / CH_3OH solution in the presence of CsF.

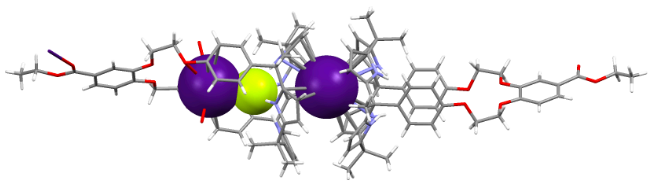


Figure 1. Single crystal structure of the complex **M1•**(CsF). The CsF is shown in space-filling representations. Other anions have been omitted for clarity. Cs purple, F light green.

There are two CsF complexes in the asymmetric unit (Figure 1 and Figures S28 and S29, Supporting Information). In both complexes, the fluoride anion is hydrogen bonded to the four pyrrole N-H protons of the cone-shaped calix[4]pyrrole subunit. In one complex (ca. 50% occupancy) the Cs^+ ion is coordinated directly to the F^- ion and is found within the cavity of the macrocyclic receptor. In the other complex, the Cs^+ cation is bound within the bowl-like pockets created by the pyrrole rings of two adjacent calix[4]pyrroles.

The ability of **M1** to bind cesium fluoride in solution was probed *via* ^1H NMR spectroscopy using a mixture of $CDCl_3$ and CD_3OD (9:1, v/v) as the solvent (Figure S17). In a first study, receptor **M1** was dissolved in $CD_3OD/CDCl_3$ (1:9, v/v) and was subject to titration with between 0.25 and 1.00 equiv of CsF. Under these conditions, two sets of resonances are seen for all the proton signals (Figure S17). At the point where 1.0 equiv of CsF has been added, the NH proton signals are downfield-shifted and split into a doublet (reflecting ^1H–^{19}F coupling). At this juncture in the titration, the ß-pyrrolic protons are seen to resonate at higher field (Figure S17), as do the benzene CH protons, especially H_1. These findings are interpreted in terms of the fluoride anion being bound to the calix[4]pyrrole NH protons with the cesium cation being held within the electron rich cup of the calix[4]pyrrole (rather than the crown ether ring). Thus, under these conditions and at this stoichiometry the solution phase structure recapitulates only one of the complexes seen in the solid state (cf. Figure 1).

Further addition of CsF beyond one stoichiometric equiv induces gradual downfield shifts in the aromatic proton signals of the benzene subunit, particularly H_1 (Figure S17). These ^1H NMR spectral changes are ascribed to the complexation of a second cesium cation by the crown ether subunit. The addition of ≥1.0 equiv of CsF to **M1** also leads to an upfield shift in the NH proton signals (Figure S17). Such upfield shifts are consistent with the presence of interactions between a cesium cation complexed by the crown ether moiety and the bound fluoride anion.

The ion pair complexation seen in the case of the model system **M1** led us to consider whether diblock copolymer **1** could be used to promote the formation of supramolecular aggregates via presumed ion pair complexation. As prepared, copolymer **1** displays no amphiphile-like features (Figures S19 and S22). However, when treated with CsF in CH_2Cl_2, the polymer becomes amphiphlic, as evidenced by dynamic light scattering (DLS), transmission electron microscopy (TEM), and energy dispersive X-ray analyses (EDX) studies. This change in character is ascribed to recognition of the CsF by the strapped calix[4]pyrrole subunits, rendering those portions of the diblock copolymer polar and the overall system amphiphilic (cf Scheme 1).

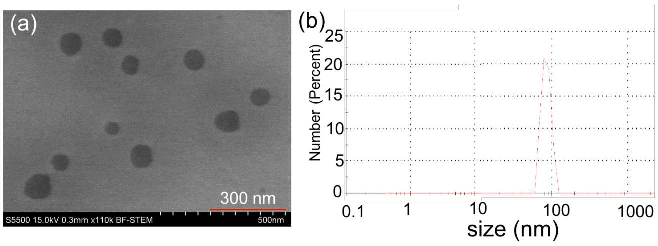


Figure 2. (a) TEM images of the aggregates formed by treating diblock copolymer **1** in dichloromethane with CsF (b) DLS results corresponding to (a). The concentration of the copolymer is 2 mg/mL and that of CsF is 1 mM.

Dynamic light scattering (DLS) analyses were then carried out so as to probe the relationship between the presumed ion pair complexation and the observed self-assembly. At low CsF-to-calix[4]pyrrole ratios (below 0.4 based on the number of sites), the average size of the ensembles were found to range from 3 nm to 10 nm. This was taken as evidence that little aggregation is occurring. As the relative ion pair concentration increases, larger nanoparticles are formed (Figure 2 and S18). Presumably, this reflects the fact that more ions are binding to the appended calix[4]pyrrole subunits, rendering the polymer more amphiphilic.

To ascertain the morphology of the aggregates formed in the presence of CsF, transmission electron microscopy (TEM) analyses of the amphiphilic form of **1** were performed on air-dried samples (Figure 2a). The TEM analyses proved consistent with the formation of spherical aggregates with an average diameter of about 90 nm, as would be expected for the formation of multi-micelle aggregates (MMAs) (Figure 2a).

EDX analyses of the micelles formed from amphiphile **1** were carried out by scanning a small area of the surface of the micelle and the blank background. The spectrum recorded from the micelle surface revealed peaks corresponding to Cs and F, as well as those for the carbon support (Figure 3b). In contrast, no discernible Cs or F signals were observed in the spectrum of the background (Figure 3d). This result is taken as evidence that CsF ion pairs are incorporated into the calix[4]pyrrole subunits within the multi-micelles formed upon exposure of amphiphile **1** to CsF.

We next sought to address the question of whether the diblock copolymer **1** could extract simple salts from an aqueous source phase. Toward this end, 5 ml dichloromethane solutions of polymer **1** for which the effective calix[4]pyrrole concentration was 2.0 mM, were contacted with 5 mM solutions of, respectively, CsF, CsCl, CsBr, KF, and NaF (5 mL each). It was expected that extraction-induced changes in the ion concentrations of the aqueous phases would be reflected in differences in the solution conductivity (SI, Figure S15). The conductivity of all five solutions decreased as a function of time. For example, the conductivity of the CsF solution decreased from 580 to 360 μS/cm after 30 h of liquid-liquid extraction, with a leveling off then being observed (Figure 4a). The higher overall extraction values for CsCl compared to CsF is consistent with the relative aqueous solvation energies (ΔG_h) of chloride and fluoride anions ($\Delta G_h = -465$ kJ mol^{-1} for F$^-$, –340 kJ mol^{-1} for Cl$^-$, –315 kJ mol^{-1} for Br$^-$).[16]

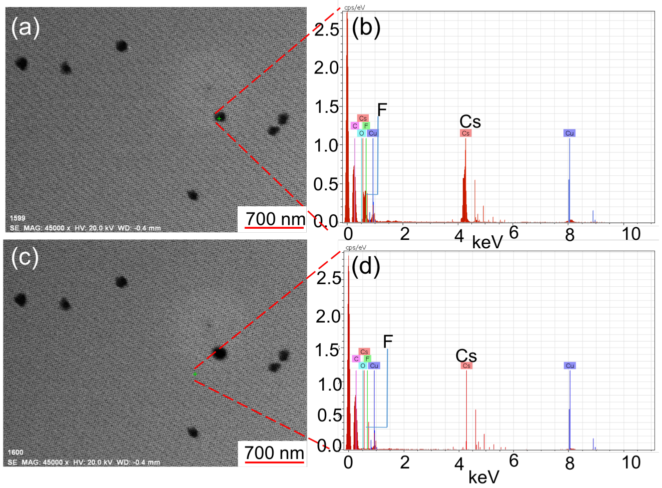


Figure 3. TEM-EDX studies of the aggregates formed upon exposure of amphiphile **1** to CsF in dchloromethane. (a-b) Spectrum recorded from the micelle surface; (c-d) spectrum recorded from the background. The concentration of the copolymer is 2 mg/mL and [CsF] = 1 mM.

A similar study looking at the cations was carried out. For this purpose, CsF, KF, and NaF were studied. As shown in Figure 4a, polymer **1** was found to extract cesium fluoride much more effectively than other fluoride salts. This finding, which is in accord with the hydration energies ($\Delta G_h = -245$ kJ mol^{-1}, −295 kJ mol^{-1}, and −365 kJ mol^{-1} for Cs$^+$, K$^+$, and Na$^+$, respectively),[16] leads us to suggest that these materials may ultimately enable the separation of cesium halide salts from aqueous mixtures.

Control extraction studies involving **M1** and PMMA were then carried out using conditions analogous to those employed for amphiphile **1**. In contrast to what was seen for the block copolymer, model compound **M1** proved relatively ineffective as an extractant or any of the salts considered in the present study (Figure 4a,b) with no evidence of extraction being seen in the case of PMMA alone (Figure 4c). On this basis, we suggest that the combined use of an ion pair recognition and a polymer backbone that is capable of undergoing ion pair-induced micelle formation can lead to improvements in extraction relative to the corresponding receptor system alone.

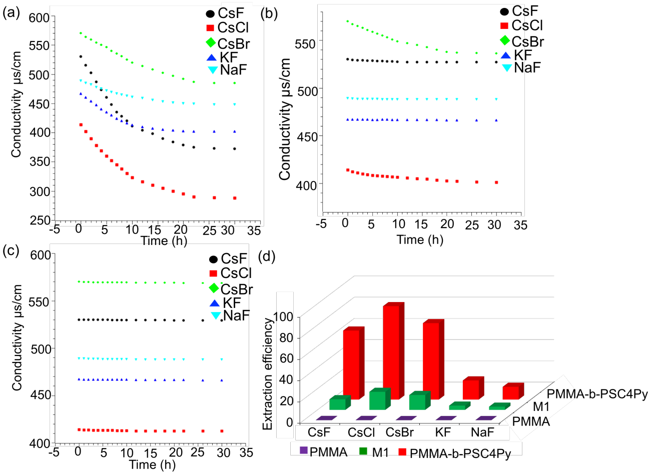


Figure 4. Conductivity of aqueous inorganic salt solutions (5 mL each at an initial concentration of 5 mM) after liquid-liquid extraction with various extractants (effective calix[4]pyrrole concentration: 2 mM) at different analysis times. (a) PMMA-b-PSC4Py; (b) **M1**; (c) PMMA. (d) Extraction efficiency[17] recorded after 30 h using the conditions of studies (a-c).

In summary, a diblock copolymer, containing a calix[4]pyrrole-derived ion pair receptor has been synthesized. Upon complexation with simple ion pairs in dichloromethane solution or at an organic-aqueous interface, the amphiphile polymer **1** self-assembles into reversed micelles that remain within the organic phase. The present diblock copolymer proved capable of extracting ion pairs into an organic receiving phase more effectively than the control calix[4]pyrrole-based ion pair receptor **M1**. This result underscores the potential benefits of polymer-based approaches to extraction, as well as the specific use of systems that allow control over structure beyond the first coordination sphere.

ASSOCIATED CONTENT

Supporting Information: Experimental details and characterization data. Cif files for **M1** (CCDC number: 1845439); and **M1**+ CsF (CCDC number: 1845440). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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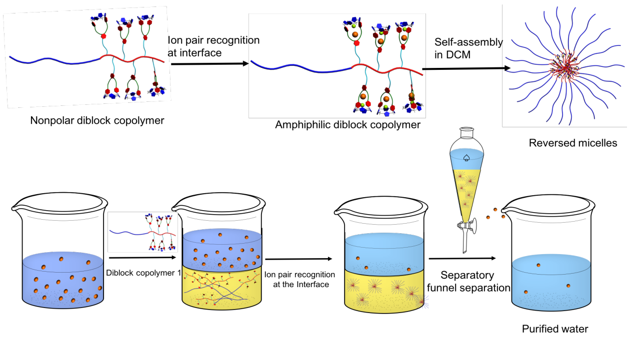
(17) Extraction efficiencies are reported as the percent (%) of extractant populated with various salts after contacting with a corresponding aqueous salt solution.

TOC Graphic


Ion pair recognition
at interface
Self-assembly
in DCM
Nonpolar diblock copolymer
Amphiphilic diblock copolymer
Reversed micelles
Diblock copolymer 1
Ion pair recognition
at the Interface
Separatory
funnel separation
Purified water