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Selective recognition and extraction of the uranyl ion from aqueous solutions with a recyclable chelating resin⁺

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An ion exchange polymer **1**, incorporating a chelating ligand engineered for the uranyl ion was prepared and its ability to remove uranium from aqueous solutions was studied. The chelating module was shown to form a 1 : 1 complex with the uranyl ion in solution. Comparisons of **1** with the standard imidodiacetate chelating resin, Chelex 100 were performed in uranyl extraction experiments. **1** effectively extracts uranyl ion from aqueous solutions, including spiked seawater, and is fully recyclable for at least 15 extraction cycles.

Introduction

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Since their initial discovery over 100 years ago, ion exchange polymers have found many uses in industrial processes, catalysis, analytical chemistry, and metal binding.1 To improve selectivity for metal ions, polymeric materials impregnated with chelating groups have been developed.2,3 Among the first commercially available chelating resins, and perhaps the most widely studied, are the polystyrene-supported imidodiacetates, Dowex A-1 and Chelex 100.4 Generally, the imidodiacetate ligand binds a range of divalent metal ions forming two fivemembered ring chelates upon complexation.⁵ For instance, Chelex 100 has been employed in columns to separate metal mixtures, in batch mode to remove various metal ions from aqueous solutions, and analytically to determine the concentration of aqueous metal ions. While Chelex 100 has found an assortment of applications, pH and ionic strength of the matrix can greatly diminish the extraction efficiency and selectivity for a desired metal ion.

The selective recovery of the uranyl ion—whether it be for environmental remediation, nuclear waste processing,⁶ or harvesting for energy production—is an ongoing challenge. The prospect of tapping the Earth's oceans for their vast quantities of uranium has inspired many research programs and recent success has been realized with metal–organic frameworks (MOFs)⁷ and amidoxime-laden fibers.^{8,9} Chelex 100 has also been used to recover uranium from aqueous systems,¹⁰ although the desired selectivity is precluded by the preferences of the imidodiacetate ligand for the alkali earth metals and various other divalent metal cations. In general, extraction is often thwarted by the abundance of other metal cations and the relatively low concentration of the targeted uranyl ion at 3 ppb.

The geometry of the linear uranyl ion limits coordination about its equator to 4-6 donor atoms¹¹ and its shape provides a means for effecting selectivity.12 Careful ligand design has revealed unique reactivity at the otherwise inert uranyl oxygen atoms13 and has also allowed for the controlled self-assembly of large polyhedra.14 Here we report a chelating resin-tailored to the uranyl ion-for extraction from aqueous systems of varying concentration, pH and ionic strength. The chelate is a rigid preorganized ligand that surrounds the uranyl ion with three carboxylates derived from Kemp's triacid¹⁵ (6 donor atoms), forming a stable 1 : 1 complex in solution.16 The application of Kemp's triacid derivatives has proved useful in selective recognition of heterocycles,17 especially nucleic acid components,18 and the key structural notion-convergent functional groupsshould provide the same advantage for ions. The new polymer (1) is completely recyclable with no detectable aging and shows unusual activity for a carboxylate ligand in solutions of high ionic strength. The activity of 1 for uranyl extraction compares favorably with Chelex 100.

Results and discussion

Synthesis of UO2 chelating monomers 7a and 8

The synthesis of the chelating monomer is shown in Fig. 1 and begins with a Pd(0)-catalyzed Sonogashira reaction between

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[†] Electronic supplementary information (ESI) available: Additional experimental details, synthesis and characterization of ligands **7a** and **8**, synthesis and characterization of recyclable chelating resin **1**, solution behavior of **7a** and **8** with the uranyl ion, detailed extraction studies of Chelex 100 and **1** buffered at pH 5 with acetate–acetic acid, detailed extraction studies of **1** uranyl solutions buffered at pH 5 with acetate–acetic acid, and recovery of the uranyl ion from **1**. See DOI: 10.1039/c3sc51507a



Fig. 1 Synthesis of chelating monomers **7a** and **8**. *Reagents and conditions*: (a) Pd(PPh₃)₄, Cul, TEA, 90 °C, 24 h, 92%; (b) Pd/C, H₂, MeOH, rt, 24 h, 96%; (c) (CH₂O)_n, AcOH/HBr, ZnBr₂, 90 °C, 3 days, 77%; (d) DMSO, KCN, rt, 24 h, 96%; (e) HCl/AcOH, reflux, 48 h; (f) MeOH, SOCl₂, reflux, 2 h, 80% from (e); (g) Boc₂O, DCM, TEA, rt, 19 h, 81%; (h) N₂H₄, EtOH, reflux, 2 days, 93%; (i) **6**, pyr, DMAP, 80 °C, 18 h, 89%; (j) TFA (5%) in DCM, rt, 3 h, 99%; (k) imidazole-1-sulfonyl azide hydrochloride, K₂CO₃, MeOH, rt, 19 h, 91%.

N-(4-pentynyl)phthalimide and 5-iodo-*meta*-xylene. The resulting alkyne was fully reduced, and the aromatic ring of **2** was subsequently functionalized by bromomethylation. Nucleophilic displacement of the bromides with KCN gave **3** in excellent yield. The cyano and phthalimide groups were hydrolyzed under acidic conditions, then Fischer esterification provided **4** in 80% yield over two steps. The primary amine of **4** was protected with di-*tert*-butyl dicarbonate (Boc) and subsequent treatment with hydrazine afforded **5**. The anhydride acid chloride of Kemp's triacid,¹⁵ **6** smoothly acylated **5** and installed the carboxylic acid chelating groups of **7a**. Removal of the Boc group with TFA afforded **7b** and copper catalyzed conversion of the resulting primary amine to the alkyl azide with imidazole-1-sulfonyl azide hydrochloride¹⁹ completed the synthesis of monomer **8** in **11** linear steps, on multi-gram scale.

The binding pocket of **8** (ref. 16) features three organized carboxylates that converge on the uranyl ion through bidentate interactions, and N–H bonds directed toward one of the uranyl oxygens. The aromatic ring is modified for attachment (*via* a click reaction) to an appropriately functionalized solid support. However, with either **7a** or **8**, we had the opportunity to study the binding of uranyl in solution prior to immobilization. The ¹H NMR spectrum of ligand **8** in methanol-d₄ is shown in Fig. 2. Treatment of **8** with sodium acetate (NaOAc) results in a broadening of the signals, but upon addition of 1 equivalent of uranyl nitrate, the signals shift and sharpen. Upon complex formation with uranyl, the benzylic protons (highlighted by an asterisk in the figure) are shifted upfield by ~0.5 ppm and split



Fig. 2 (a) ¹H NMR spectrum of uranyl ligand **8**. (b) ¹H NMR spectrum of uranyl ligand **8** with 3.1 equiv. of NaOAc added. (c) ¹H NMR spectrum of uranyl ligand **8** with 3.1 equiv. of NaOAc and 1 equiv. of uranyl nitrate added. The inset highlights the diagnostic benzylic protons (marked by an asterisk).

into an A,B quartet and a singlet. Due to symmetry, in the locked, rigid conformation of the complex, the protons on two of the benzylic arms are diastereotopic, giving rise to the observed splitting. In fact, when less than 1 equivalent of uranyl ion is added to a basic solution of **8**, separate signals appear for uncomplexed deprotonated ligand (Fig. 2b) and complex (Fig. 2c). This behavior suggests that **8** is in slow exchange with the complex on the NMR timescale, and augurs well for high affinity to the uranyl ion. The ¹H NMR solution studies also show that Boc-protected ligand **7a** behaves identically to **8** and their respective complexes persist upon treatment with additional uranyl ion (Fig. S1–S4†).

Next, we immobilized the highly hydrophobic ligand 8 on a solid support. Because resin swelling impacts the reactivity of the bound functional groups, we chose a polyethylene glycol (PEG) containing resin to assure our material would swell in aqueous conditions, giving maximum exposure of the ligands to solution.²⁰ A TentaGel resin offers this on a minimally crosslinked polystyrene core.21 The combination of the PEG groups and low crosslinking ensures the desired swelling properties over an array of solvents and conditions. Initial attempts to immobilize our chelating ligand involved a reductive amination with amine 7b and an aldehyde-functionalized TentaGel.²² But the desired aminated product was obtained in widely variable and irreproducible yields. Perhaps the low solubility of 7b, which is essentially a large, hydrophobic amino acid was to blame. When the primary amine of 7b was converted to the azide 8, its solubility in organic media greatly improved.

Synthesis of recyclable chelating resin 1 and UO₂ extraction

A TentaGel resin functionalized with a primary amine 9 (~0.48 mmol g⁻¹) was acylated with propiolic acid using *N*-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) in CH_2Cl_2 (Fig. 3).²³ The use of EEDQ as the coupling reagent was critical for clean amide bond formation as traditional carbodiimides led to a dark red-purple impurity that was formed rapidly and trapped within the resin. Presumably, the colored



Fig. 3 Synthesis of recyclable chelating resin **1** and schematic of **1:UO**₂. *Reagents and conditions:* (a) DCM, propiolic acid (3 equiv.), EEDQ (3 equiv.), $-10 \degree C 4$ h, then warm to rt; (b) **8** (2 equiv.), Hünig's base (50 equiv.), [Cu(MeCN)₄] PF₆ (0.1 equiv.), rt, 20 h, 70%.

impurity arises from polymerization of the propiolic acid, but with EEDQ the resin maintained its pale yellow appearance. The reaction's progress was conveniently monitored using IR by following the developing amide stretching frequency. The azide ligand **8** was reliably attached to the alkyne-functionalized TentaGel **10** *via* a copper-catalyzed azide–alkyne cycloaddition reaction (CuAAC).²⁴ The use of copper(1) iodide as a catalyst led to discoloration of the resin, but tetrakis(acetonitrile)copper(1) hexafluorophosphate provided **1** as a pale yellow resin. Again, IR showed the appearance of new carbonyl stretches (carboxylic acids, amides, and imides) that mostly overlap in one broad peak (see ESI†). Resin **1** was analyzed by elemental analysis; the final loading of the ligand was ~0.22 mmol g⁻¹ (70% conversion) as determined by mass gain and amount of **8** recovered.²⁵

We tested extraction of the uranyl ion from aqueous solutions with resin 1 at varying concentrations, pH and ionic strength, as well as in the presence of other metal cations. For comparison, all extraction experiments were run in parallel with an equimolar amount of Chelex 100.²⁶ The first extraction studies were carried out in a 0.1 M acetate buffer at pH 5 with a uranyl concentration of 400 ppm (Table 1). Each sample was agitated on a nutating mixer for 18 hours, the solution was collected, and the resin was washed several times with deionized water. The samples were then dried under vacuum, and the complexed uranyl ion was removed from 1 by treatment with 0.5 M HNO₃. The uranyl concentration of the acidic solution was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and reported as percent uranyl

Table 1 Extraction of UO₂ solutions with 1 and Chelex 100

U solutions	Resin 1 (% recovery) ^a	Chelex 100 (% recovery) ^a
400 ppm U (pH 5 acetate) ^{b} 400 ppb U (pH 5 acetate) ^{c} 400 ppb U (pH 8.4 seawater) ^{c}	$egin{array}{c} 85 \pm 4 \ 77 \pm 4 \ 83 \pm 2 \end{array}$	88 ± 4 96 \pm 4 10 \pm 6

 a Uncertainties are 2 standard deviations for three replicate samples. b Both resins exposed to 1 mL U solution. c Both resins exposed to 7 mL U solution.

recovered (Tables S1–S12†). Both Chelex 100 and resin 1 extract a similar quantity of uranyl ion under these conditions.

The concentration of UO_2^{2+} was then dropped 1000-fold to 400 ppb. To aid analysis at this dilution, each sample of resin was exposed to 7 mL uranyl solution and treated as before. Again both resins were capable of extracting the uranyl ion, although Chelex 100 outperforms 1 under these conditions: acetate buffer at pH 5. Using seawater spiked with 400 ppb uranyl ion (pH 8.4) revealed a marked difference between the two resins. Resin 1 maintains its capacity to extract uranyl ion while the efficiency of Chelex 100 drops significantly. The high concentrations of the other cations in seawater (Na⁺, Ca²⁺, K⁺, Mg²⁺)²⁷ effects the selectivity of Chelex 100 and the salt matrix slows down the chelating reaction.28 The imidodiacetate ligands of Chelex 100 are exposed and well suited to interact with the other cations at superior concentrations found in seawater. However, these competitors show no effect on the ability of 1 to extract uranyl ion. The well-defined, preorganized binding pocket of 1 disfavors interactions with these cations, and preference for uranyl ion is retained. The IR spectra of the respective uranyl complexes of 7a, 8, and 1 display similar stretches for the uranyl ion, suggesting that once immobilized, the ligand behaves as it did in solution (see ESI[†]). Additionally, both resins were tested on unspiked seawater, at its natural uranyl concentration of 3.3 ppb (see ESI[†]) and neither 1 nor Chelex 100 was capable of extracting uranyl in detectable amounts.

The stability of **1** to the uranyl recovery conditions (0.5 M HNO_3) was determined by subjecting a single sample to multiple extractions at a uranyl concentration of 400 ppm in



Fig. 4 Repetitive extraction–release cycles of the uranyl ion from resin **1** at 400 ppm in acetate buffer (pH 5). No statistically significant degradation of the resin was detected after 15 cycles.





acetate buffer at pH 5 (Fig. 4, S5, and Table S13[†]). The extraction/acid release was repeated a total of 15 times with no loss of extraction efficiency, showing that **1** is completely recyclable and insensitive to treatment with acid.

The rate of uranyl uptake by **1** was also examined at 400 ppm in acetate buffer at pH 5 (Fig. 5). For this purpose, the concentration of uranyl ion remaining in solution was monitored with ICP-AES over time. After 2.5 minutes, 48% of the uranyl ion is removed from solution (Table S14†) and extraction is complete after 40 minutes (85% uranyl extracted) with no additional uptake observed after a period of 24 hours.

Conclusions

We have developed a new ion exchange resin **1**, engineered for extraction of uranyl ion from aqueous solutions. The behavior of resin precursors **7a** and **8** were determined in solution prior to incorporation into a solid support. A **1** : **1** binding stoichiometry between the rigid monomers and the uranyl ion is indicated. Both resin **1** and Chelex 100 performed well in acetate buffer at pH 5 while only resin **1** maintained its uranyl extraction efficiency in seawater and allows it to function in the presence of other cations. Resin **1** was also fully recyclable, showing no degradation after 15 extraction–release cycles. A full selectivity series of **1** for a variety of transition metals will be reported in due course.

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