

## Synthesis of lariat organochalcogenoethers based on azacalix[3]arenes for the potentiometric detection of $[\text{UO}_2]^{2+}$ ions

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Respectfully dedicated in honor of Professor Sakae Uemura (Kyoto University, Japan) on the occasion of his 65th birthday

**Abstract**—The syntheses of organochalcogen-supported azacalix[3]arenes are described in a one-pot manner in satisfactory yields. A remarkably selective potentiometric response was accomplished for uranyl ions over a variety of other metal ions, including alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ), alkaline-earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ), transition and heavy metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ) using an ion-selective electrode based on compound **3** incorporated into a polymeric (PVC) membrane.

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The design and synthesis of new polyfunctional organochalcogen donors offers possibilities to create molecular structures for functional materials and devices for future application such as chemical sensors to recognize toxic metal ions. In fact, incorporation of organochalcogen species in a conventional host molecule can be greatly rewarding in contrast to the native host molecule.<sup>1,2</sup> In continuation of our research activities in the area of organochalcogen chemistry<sup>3</sup> we became interested in designing sterically hindered organochalcogen-bearing donor molecules anticipating that these, in combination with other heteroatoms might exhibit interesting behaviour and have new applications in chemistry.

To this end, we recently reported the synthesis of acyclic ligand systems bearing (N,  $\text{Se}_2/\text{Te}_2$  and O, N, Se/Te) donor combinations and their complexation behaviour.<sup>3a</sup> It was realized that judiciously positioned chalcogen atoms in a multifunctional core can substantially reduce the flexibility of the ligand architecture with respect to their lighter congeners (O and S) and ensure the possibility that the designed molecular species would retain their solid-state structures in solution<sup>3a,c</sup> and thus can be tailored for specific applications. Additionally, the results

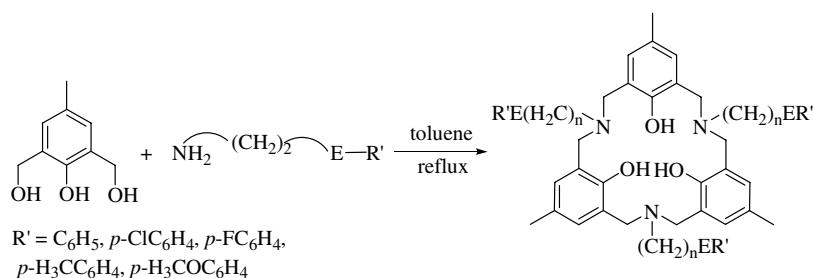
obtained by us with our acyclic system bearing (N,  $\text{Se}_2/\text{Te}_2$ ) donor functionalities have shown dramatic enhancement in  $\text{Pd}^{2+}$  ion affinity in the presence of various other metal ions and hence they can be applied exclusively in sensors and separation processes used in host–guest and analytical chemistry.<sup>4</sup>

The organochalcogen supported azacalix[3]arenes<sup>5</sup> were prepared by thermal condensation of 2,6-di-hydroxy-4-methylphenols with organochalcogenoalkyl amines. We obtained the desired products **1–12** exclusively, in greater than 60% yields (Scheme 1) without any templating bases. Another possibility is that the starting amine, which may be protonated, could act as a templating agent. There was no indication of the formation of any lower or higher analogues under these conditions. We believe that the good yields obtained in the coupling reaction and absence of any polymeric or acyclic species may be due to either intramolecular Se...N bonding of the primary organochalcogenoamine which facilitates the cyclization or intramolecular hydrogen bonding between the phenolic –OH and –NH<sub>2</sub> group of the primary organochalcogenoamines.

The products were obtained as viscous oils after column chromatography and were identified by means of <sup>1</sup>H NMR, <sup>13</sup>C NMR and FAB-MS spectroscopy and these studies revealed the formation of organochalcogen-supported azacalix[3]arenes, exclusively. As has been reported, the specificity of azacalixarenes, in contrast

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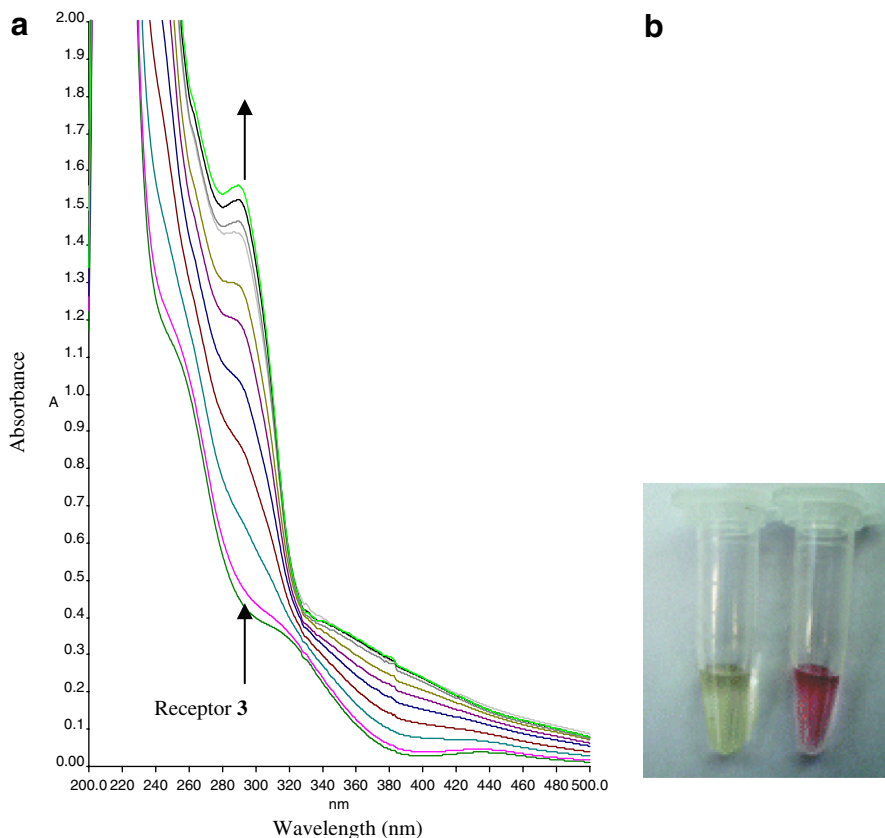


**Scheme 1.** Reagents and conditions: E = Se,  $n = 2$ ,  $\text{R}' = p\text{-H}_3\text{COC}_6\text{H}_4$ , **1** (70%); E = Se,  $n = 2$ ,  $\text{R}' = p\text{-H}_3\text{CC}_6\text{H}_4$ , **2** (73%); E = Se,  $n = 2$ ,  $\text{R}' = p\text{-FC}_6\text{H}_4$ , **3** (65%); E = Se,  $n = 2$ ,  $\text{R}' = \text{C}_6\text{H}_5$ , **4** (60%); E = Se,  $n = 2$ ,  $\text{R}' = p\text{-ClC}_6\text{H}_4$ , **5** (67%); E = Se,  $n = 3$ ,  $\text{R}' = p\text{-H}_3\text{CC}_6\text{H}_4$ , **6** (70%); E = Se,  $n = 3$ ,  $\text{R}' = \text{C}_6\text{H}_5$ , **7** (62%); E = Se,  $n = 3$ ,  $\text{R}' = p\text{-H}_3\text{COC}_6\text{H}_4$ , **8** (71%); E = Te,  $n = 2$ ,  $\text{R}' = p\text{-FC}_6\text{H}_4$ , **9** (63%); E = Te,  $n = 2$ ,  $\text{R}' = p\text{-H}_3\text{CC}_6\text{H}_4$ , **10** (69%); E = Te,  $n = 3$ ,  $\text{R}' = p\text{-FC}_6\text{H}_4$ , **11** (65%); E = Te,  $n = 3$ ,  $\text{R}' = p\text{-H}_3\text{CC}_6\text{H}_4$ , **12** (69%).

to classical calixarenes and homocalixarenes, leads to complexes without addition of a basic reagent. Indeed, the complexing phenolic groups are transferred to the amine group, which results in a poly-zwitterionic form of the ligand being the complexing species.<sup>6</sup> In addition, it has also been demonstrated that when dissolved in a basic solution, calixarenes unmodified on the lower rim can behave as poly-aryloxide ligands for the complexation of lanthanide and actinide ( $\text{UO}_2^{2+}$ ) ions.<sup>7</sup> The azacalixarenes in the present study contain nitrogen in the macrocyclic ring as well as chalcogen donors in lariat arms which could provide additional binding sites for guests. Hence, complexation studies of these molecules were evaluated.

Initial studies were performed on the detection of  $\text{UO}_2^{2+}$  in the presence of a variety of metal ions, including alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ), alkaline-earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ), transition and heavy metal ions ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{3+}$ ) each at a concentration of  $10^{-4}$  M in methanol.

Addition of these metal ions to azacalix[3]arene **3** in the absence of  $\text{UO}_2^{2+}$  resulted in no change in the UV–vis spectrum. Addition of  $\text{UO}_2^{2+}$  led to the appearance of a peak at 290 nm as shown in Figure 1a, indicating the ability of **3** to selectively complex  $\text{UO}_2^{2+}$  despite the presence of other metal ions. Moreover, the colorimetric sensing ability of the receptors in the presence of  $\text{UO}_2^{2+}$



**Figure 1.** (a) Spectral changes associated with the formation of a  $\text{UO}_2^{2+}$  complex with **3**. The arrow shows the increase in the observed absorbance at 290 nm on each addition of a solution of  $[\text{UO}_2(\text{NO}_3)_2]$  ( $2 \times 10^{-3}$  M) in methanol to a solution of **3** in methanol (concentration =  $5 \times 10^{-4}$  M); (b) Colorimetric response; yellowish-green to red on addition of a methanolic solution of  $\text{UO}_2^{2+}$  ions.

ions was also observable by the naked eye as shown in Figure 1b. The azacalix[3]arenes in the present investigation possess three N, O and Se or Te binding sites and showed selectivity towards  $\text{UO}_2^{2+}$  ions in the presence of various alkali, alkaline-earth transition and heavy metal ions under nearly neutral conditions. An attempt to trap  $\text{Hg}^{2+}$  was unsuccessful instead, leading to a precipitate<sup>8</sup> of RE–Hg–ER from a mixture of species **3** or **9**. The merging of N–CH<sub>2</sub> and Se–CH<sub>2</sub> protons in the  $\text{UO}_2^{2+}$  complex indicates the involvement of N in bonding to  $\text{UO}_2^{2+}$ . At the same time, a single sharp peak at  $\delta$  311.13 ppm in the <sup>77</sup>Se NMR spectrum of representative species **7** was split into a multiplet in the uranyl complex which gives an indication of the weaker interactions of selenium in coordination geometry. At this stage we were unable to resolve the structural aspects of the complex molecules<sup>9</sup> due to the unavailability of suitable crystals for X-ray structure determinations. However, physicochemical studies favour the formation of chalcogen-supported azacalixarenes and their receptivity towards  $\text{UO}_2^{2+}$  species.

The organochalcogen-substituted form of the calix[3]arene isolated herein determined the binding of uranyl ions in the presence of competing  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  ions. The selective binding of  $\text{UO}_2^{2+}$  ions by **3** in the presence of other metal ions results from the fact that **3** provides a pseudoplanar, hexacoordinate geometry which suits  $\text{UO}_2^{2+}$  exclusively. Any weakly bound metal complexes with other metal ions, if formed, would have fast dissociation kinetics in this preorganized structure and would be unresolved due to their rapid dissociation in solution. Previous work<sup>7</sup> on the synthesis of  $\text{UO}_2^{2+}$ -specific ligands, so-called ‘*uranophiles*’,<sup>10,11</sup> presumed that the ligands providing essentially planar pentagonal or hexagonal donor atom arrays would be most appropriate, given that such geometries, common in  $\text{UO}_2^{2+}$  complexes, are not well known for other metal ions.

The potentiometric sensing ability of the receptors with ions of alkali, alkaline earth metals and heavy metal ions have also been monitored. In preliminary experiments, ionophore **3** was used as a potential neutral carrier for the preparation of a PVC membrane ion-selective electrode for a variety of metal ions. The potentiometric response curves obtained for individual metal ions with ionophore **3** are given in Figure 2.

Uranyl ions gave a better response compared to the other metal ions studied.<sup>12</sup> For ionophore **3** to act as an efficient ion-carrier in uranyl-selective sensors it should fulfill certain conditions. It should be selective towards uranyl ions over other metal ions and demonstrate rapid exchange kinetics across the PVC membrane. Ion-selective electrodes (ISEs) for metal ions including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Fe}^{3+}$  were found to give sub-Nernstian potentiometric responses with very narrow linear ranges of concentration. The uranyl ion-selective electrode (EI) based<sup>13</sup> on ionophore **3** exhibited a near-Nernstian slope of 28.69 mV per decade over a

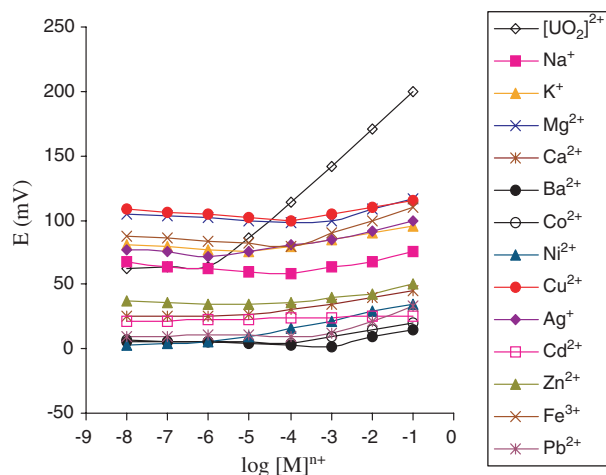


Figure 2. Response of a uranyl ion templated electrode and the most likely interfering ions.

wide linear concentration range of  $1.0 \times 10^{-1}$ – $5.0 \times 10^{-6}$  M with an internal reference solution,  $1.0 \times 10^{-2}$  M  $[\text{UO}_2(\text{NO}_3)_2]$  in methanol. The detection limit of the electrode (EI) was found to be  $1.99 \times 10^{-6}$  M. It was clear from the results obtained in preliminary experiments that ionophore **3** acts as an efficient ion-carrier for the preparation of a PVC membrane based ion-selective electrode for the determination of  $[\text{UO}_2]^{2+}$  ions.

In summary, the syntheses of chalcogen-supported azacalix[3]arenes are described by coupling 2,6-dihydroxy-4-methylphenols with organochalogenoalkyl amines, which are ideally suited for selectively detecting  $\text{UO}_2^{2+}$  ions. The azacalix[3]arenes prepared have shown better potentiometric response for uranyl ions compared to other metal ions and thus can act as efficient ion-carriers for the preparation of PVC membrane based ion-selective electrodes for the determination of uranyl ions. Further investigations and elaboration of this ligand architecture are presently underway in our laboratories.

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- A general procedure was followed for the preparation of **1–12**. A mixture of 2,6-dihydroxymethyl-4-methylphenol (1 mol) and corresponding organochalcogenyl amine (1 mol) in 50 mL of toluene was refluxed for 24 h. Water generated during the reaction was removed azeotropically. After complete removal of toluene, the residual oily material was refluxed for an additional 24 h and the viscous mass thus obtained was purified by column chromatography with hexane:ethyl acetate mixture (80:20) to afford a yellow coloured viscous oil with yield >60%. Characterization data for **3**: Yellow viscous liquid (yield, 65%).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (br, s, 3H), 6.77 (br, 15H), 3.87 (s, 12H), 3.01 (t, 6H,  $J$  6.3 Hz), 2.87 (t, 6H,  $J$  6.6 Hz), 2.20 (s, 9H); MS(FAB)  $m/z$  ( $\text{M}^+$ , 1052).  $^{77}\text{Se NMR}$  ( $\text{CDCl}_3$ , 57.25 MHz):  $\delta$  292.12. Analysis for **7**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (br, 9H, 8.5 Hz), 6.89 (d, 6H,  $J$  8.4 Hz), 6.69 (s, 6H), 3.67 (s, 12H), 2.81 (t, 6H,  $J$  6.6 Hz), 2.57 (m, 6H), 2.19 (s, 9H), 1.84 (t, 6H,  $J$  6.6 Hz); MS(FAB)  $m/z$  ( $\text{M}^+$ , 1040),  $^{77}\text{Se NMR}$  ( $\text{CDCl}_3$ , 57.25 MHz):  $\delta$  311.13. Analysis for **11**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (br s, 6H), 6.82 (br s, 12H), 3.67 (s, 12H), 2.78 (t, 6H,  $J$  6.6 Hz), 2.45 (m, 6H), 2.21 (s, 9H), 1.98 (t, 6H,  $J$  6.2 Hz). MS(FAB)  $m/z$  ( $\text{M}^+$ , 1240). Analysis for **12**:  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43(d, 6H,  $J$  8.1 Hz), 6.92 (d, 6H,  $J$  8.0 Hz), 6.82 (br s, 6H), 3.79 (s, 12H), 2.74 (t, 6H,  $J$  6.6 Hz), 2.42 (m, 6H), 2.29 (s, 9H), 2.22 (s, 9H), 1.94 (t, 6H,  $J$  6.2 Hz); MS(FAB)  $m/z$  ( $\text{M}^+$ , 1228).
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- The pH dependence of uranyl ions ( $\text{UO}_2$ ) $^{2+}$  ISE (E1) was examined over the pH range 1–13 at a ( $\text{UO}_2$ ) $^{2+}$  ion concentration of  $1.0 \times 10^{-3}\text{ M}$ . The potential was found to remain constant from pH 1.99 to 5.40. Beyond pH 5.40, the potential was found to decrease due to the formation of hydroxyl complexes of uranyl ions. At pH <1.99, the membrane suffered strong interference from hydrogen ions due to protonation of the ionophore.
- Different plasticizers were used to study their effect on the potentiometric response of the electrode (E1). The plasticizers used in the present study were tributyl phosphate (TBP), dioctylsebacate (DOS), *o*-nitrophenyl octyl ether (*o*-NPOE), dibutylphthalate (DBP), bis-(2-ethylhexyl)adipate (DOA), dioctyl phthalate (DOP). Electrode (E1) with TBP as plasticizer was selected for further studies, as it gave a near-Nernstian slope over a wide concentration range, as compared to other membrane electrodes.