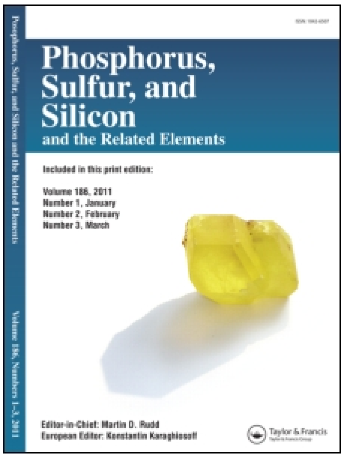

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Organochalcogen-Supported Azacalix[3]arenes as Membrane Sensor for Potentiometric Determination of Uranyl Ions

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An one-pot syntheses of organochalcogen-supported azacalix[3]arenes and their behavior toward metal ions sensing was investigated by spectrochemical (UV-vis, ^1H NMR and ^{77}Se NMR) methods. The azacalix[3]arenes prepared have shown better potentiometric response for uranyl ions compared to alkali (Na^+, K^+), alkaline-earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), transition and heavy metal (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}) 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.

Keywords Azacalix[3]arenes; host–guest systems; ion-selective electrode; O, N, Se/Te donor combinations; potentiometric sensors; uranyl ions

INTRODUCTION

Incorporation of organochalcogen moiety in a conventional host molecule offers newer possibilities to create novel structural motif for functional materials and devices and may be greatly rewarding for imminent application such as chemical sensors in contrast to native host molecule.[1–4] In continuation to our research activities in the area of organochalcogen chemistry, we recently reported the synthesis of acyclic ligand systems bearing (O, N, Se/Te) donor combinations and their complexation behavior.[5,6] To this end, It was realized that rationally positioned heavier chalcogen (Se or Te) atoms in a polyfunctional molecular core can significantly decrease the flexibility of the molecular architecture with respect to their lighter congeners (O and S) and ensure the possibility that the designed molecular species would preserve their solid-state structures in solution and thus can

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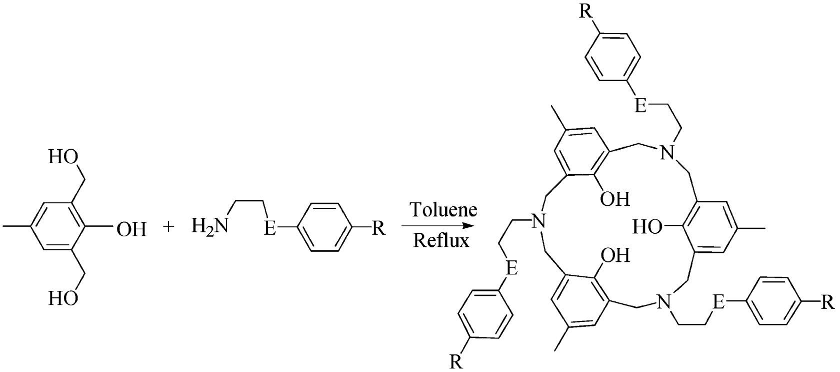
have diverse reactivity patterns than those for its close lighter congener sulfur. To examine the validity of our approach, we now describe herein the synthesis of cyclic systems bearing (O, N, S/Se/Te) donor combinations, i.e., organochalcogen-supported azacalix[3]arenes and their potential application as efficient ion- carriers for the preparation of PVC membrane based ion selective electrodes for the determination of uranyl ions. The organochalcogen supported azacalix[3]arenas were prepared by the condensation of 2,6-di-hydroxy-4-methylphenol with organochalogenoalkyl amines. The optimized reaction conditions led to the isolation of the desired products (**1-7**) exclusively as viscous mass in > 60% yields (Scheme 1).



SCHEME 1 Reagents and conditions: E = Se, R = p-FC6H4, **1** (65%); E = Te, R = p-FC_6H_4, **2** (63%); E = S, R = p-FC_6H_4, **3** (67%); E = Se, R = C_6H_5, **4** (61%); E = Te, R = C_6H_5, **5** (67%); E = S, R = C_6H_5, **6** (64%); E = Se, R = p-ClC_6H_4, **7** (69%).

They were identified by means of ^{1}H NMR, ^{13}C NMR, ^{77}Se NMR, UV-vis and FAB-MS spectroscopy and these studies revealed the formation of organochalcogen supported azacalix[3]arenes, exclusively. The azacalixarenes in the present study contain -OH group in core and nitrogen in the periphery of the cyclic ring followed by chalcogen (Se or Te) donors in side arms thus could provide attractive binding sites for guests. An optimized structure for **1** revealed a funnel shaped structure (Figure 1) and may reveal an appealing complexation-recognition behavior for guest molecules.

The azacalix[3]arenes in the present investigation showed exemplary selectivity towards UO_2^{2+} ions in the presence of various alkali(Na^+, K^+), alkaline-earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), transition (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Fe^{3+}) and heavy metal (Cd^{2+}, Hg^{2+} and Pb^{2+}) ions under nearly neutral conditions. Addition of a solution of UO_2^{2+} ion

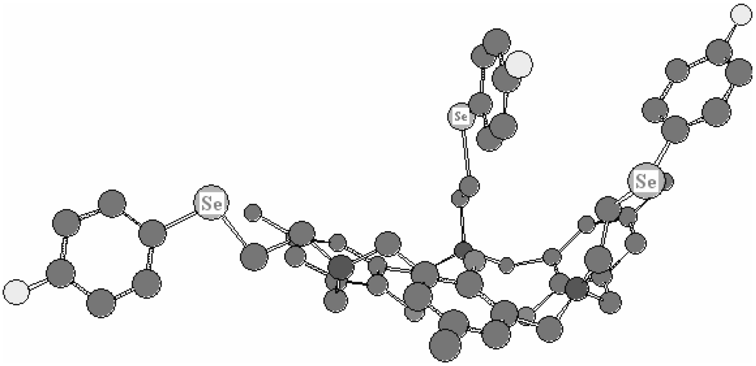
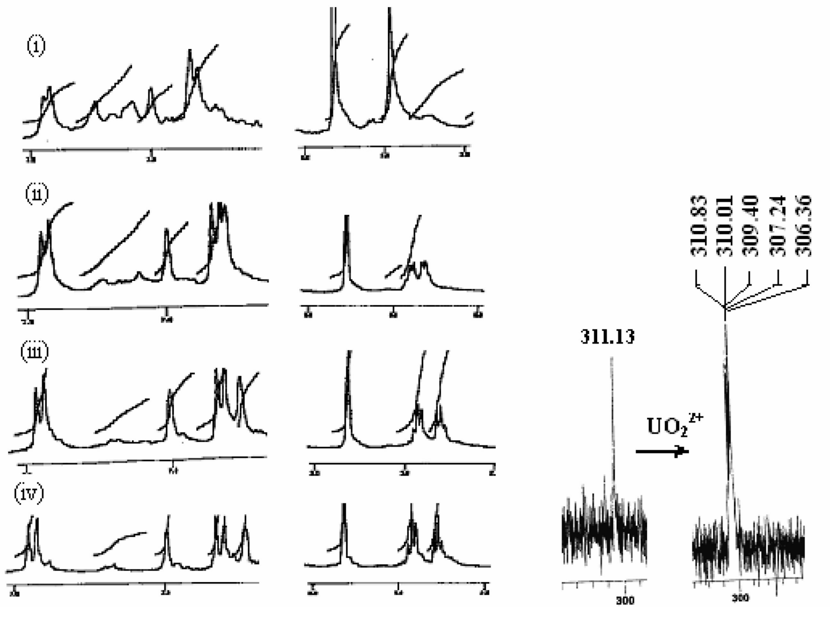


FIGURE 1 Energy minimized structure for species **1**.

to a solution of **1** gave a visual color change (Colorimetric response; yellowish-green to red on addition of a methanolic solution of UO_2^{2+} ions). as well as significant changes in UV-vis spectra, while other metal ions including alkali (Na^+, K^+), alkaline-earth (Mg^{2+}, Ca^{2+}, Ba^{2+}), transition and heavy metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}) induced no or much smaller color or spectral changes. ^1H NMR titrations of **1** with UO_2^{2+} were also carried out in order to understand the nature and extent of possible interactions taking place in solution state (Figure 2a).

The merging of N-CH2 and Se-CH2 protons in the UO_2^{2+} complex indicates the involvement of N in bonding to UO_2^{2+}. At the same time, a single sharp peak at δ 311.13 ppm in the ^{77}Se NMR spectrum of representative species **1** was split into a multiplet in the uranyl complex, which gives an indication of the weaker interactions of selenium in coordination geometry (Figure 2b). 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 **1** was used as a potential neutral carrier gave a better response for uranyl ions compared to the other metal ions studied. The uranyl ion selective electrode based on ionophore 1 exhibited a near-Nernstian slope of 28.69 mV per decade over a wide linear concentration range of $1.0 \times 10^{-1} - 5.0 \times 10^{-6}$ M with an internal reference solution, 1.0×10^{-2} M $[UO_2(NO_3)_2]$ in methanol. The pH dependence of uranyl ions $(UO_2)^{2+}$ ISE (**1**) was examined over the pH range 1–13 at a $(UO_2)^{2+}$ ion concentration 1.0×10^{-3} 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 (Figure 3).



(a) (b)

FIGURE 2 Spectral changes in the (a) ^{1}H NMR and (b) ^{77}Se NMR spectrum of the species **1** upon addition of uranyl nitrate solution (CD_3OD).

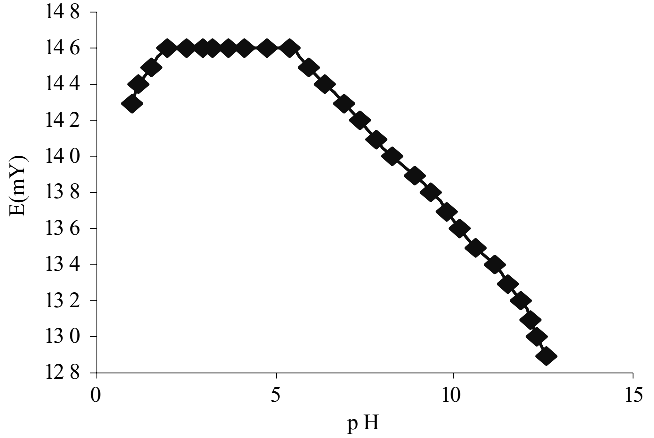


FIGURE 3 Effect of pH on $(UO_2)^{2+}$-ISE (**1**) at 1.0 × 10^{-3} M $[UO_2(NO_3)_2]$ solution.

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 UO_2^{2+} ions.

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