

Review Article

Application of Calixarenes as Macrocyclic Ligands for Uranium(VI): A Review

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Calixarenes represent a well-known family of macrocyclic molecules with broad range of potential applications in chemical, analytical, and engineering materials fields. This paper covers the use of calixarenes as complexing agents for uranium(VI). The high effectiveness of calix[6]arenes in comparison to other calixarenes in uranium(VI) separation process is also presented. Processes such as liquid-liquid extraction (LLE), liquid membrane (LM) separation, and ion exchange are considered as potential fields for application of calixarenes as useful agents for binding UO_2^{2+} for effective separation from aqueous solutions containing other metal components.

1. Introduction

In the last years an increasing interest in calixarenes as potential complexing agents for metals, among them actinides, is observed. It is supported by several reviews [1–3]. The present paper focuses on application of calixarenes for separation of uranium(VI) from competing metal ions in aqueous solutions.

Uranium plays an important role in generation of nuclear power. The selective isolation of uranium is of particular interest in the context of both energy resources and treatment of nuclear wastes. As a key element for production of the fuel for nuclear reactors, uranium, the more common element in the Earth's crust occurring in rocks, soil, and river and ocean waters [4], has to be extracted from the raw material in complex hydrometallurgical processes involving many separation steps. Processes such as acidic leaching, liquid-liquid extraction, or ion exchange are applied to obtain pure triuranium octaoxide (U_3O_8) from uranium ore. Since in most of uranium minerals uranium is accompanied by other heavy metals, postleaching solutions usually contain a mixture of different metallic ions that should be separated from UO_2^{2+} , the uranyl ion that forms complexes with various organic chelating agents. The separation can be achieved by

using of extracting agents that exhibit high specificity towards UO_2^{2+} and allowing selective uranium recovery.

Uranium(VI) has unique characteristics, namely, the extreme stability of the triatomic uranyl ion OUO^{2+} . This ion possesses very stable uranium(VI)-oxygen double bonds, leaving the oxygen atoms largely unreactive [5]. In crystalline structures, UO_2^{2+} is linear and is capable of forming complexes of coordinative bonds with host molecules containing five or six ligand groups, primarily oxygen atoms [6]. This suggests that a macrocyclic host molecule having a nearly coplanar arrangement of either five or six ligand groups would act as a specific ligand for UO_2^{2+} (i.e., as an uranophile).

In order to design a ligand that can selectively extract UO_2^{2+} , one has to overcome a difficult problem, that is, the ligand must discriminate strictly between UO_2^{2+} and other metal ions present in great excess in water or waste solution. Over the last three decades, a variety of studies have targeted molecular design and implementation of various polydentate compounds that serve effectively as uranium(VI) extracting agents, for example, a macrocyclic hexaketone, macrocyclic hexacarboxylic acid, and tridithiocarbamate synthesized by Tabushi et al. [7–9]. Shinkai and coworkers [10] applied

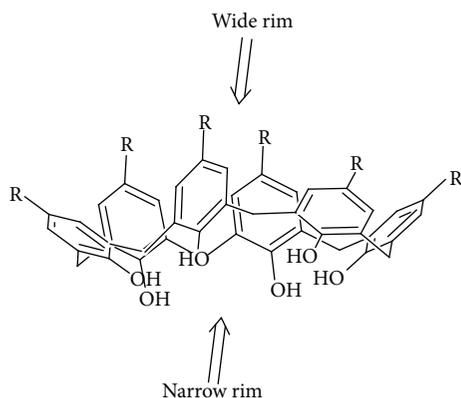


FIGURE 1: Illustration of the structure of calixarenes.

calixarenes for UO_2^{2+} complexation with efficient results in terms of stability and selectivity. The increasing interest in these macrocycles is not only due to their easy synthesis through well-established and simple methodologies [11], but also due to the possibility of shaping their basket through functionalization at the lower (narrow) or at upper (wide) rims (Figure 1).

Calixarenes are formed by paraphenolic units linked by methylene bridges ortho to OH functions. In addition, they can be easily functionalized to be more specific. The OR groups (chelating groups) on the lower rim are usually chosen for their affinity and selectivity towards a specific molecule or ion. On the other hand, the groups in paraposition on the upper rim can give hydrophilic or hydrophobic character to the molecule. These groups can also rigidify the conformation of calix[*n*]arene.

The extraction study of lanthanides and actinides showed that the calixarenes bearing ligands including P=O groups were more efficient than TBP (tributyl phosphate), TOPO (trioctylphosphine oxide), and CMPO (carbamoyl phosphonate) [12, 13]. The ligand concentration necessary to reach a given extraction yield was 10 to 100 times lower with the calixarenes than with the classical extractants.

Very interesting results were obtained in the study of toxicity of calixarenes [14]. The calix[6]arenes and calix[8]arenes functionalized with sulfonate group had the same level of toxicity as glucose. On the other hand, derivatives of *p*-sulfonato-calix[4]arenes showed slight toxicity, in contrast to calix[4]arene phosphonic acid derivatives which exhibited no effect on the cell growth of human fibroblast. It is worthy to remind that derivatives of *p*-sulfonato calix[6]arene and calix[8]arene analogs were investigated in radiotherapy [15]. Complexation studies of ^{230}U with these calixarenes showed that in vivo application of such compounds is not possible. The complexation of uranium(VI) was efficient, but serum proteins and carbonate led to the destruction of the desired complexes.

The ligands that can be used in chemical process of radioactive waste treatment should be resistant to chemical and radiolytic conditions. Although calixarenes were well

examined for their chemical stability under acidic and basic conditions, their behavior under irradiation conditions is still under investigation. It was found that after the exposure to the gamma radiation the ligands could change their properties. Mariani et al. [16] studied a derivative of calix[6]arenes. They observed that an absorbed dose above 100 kGy in the presence of air decreased the distribution coefficient for ^{241}Am and ^{152}Eu without significant influence on the selectivity in comparison to nonirradiated ligands. However, an absorbed dose up to 55 kGy in the presence of air caused an increase of the distribution coefficient for both metals. The same absorbed dose in the presence of nitrogen caused a decrease of the distribution coefficient. These results indicated how important the influence of oxidizing environment on radiolysis is.

2. Speciation of Uranium(VI) in Water

The speciation of uranium(VI) in aqueous solution is very important to understand the mechanism of extraction and to choose the appropriate extraction system. In aqueous solution, uranium(VI) exists as a linear UO_2^{2+} , and it forms stable complexes with both organic and inorganic ligands [17, 18]. Simulations [19, 20], calculations [21], and experiments [22, 23] suggest that in water, UO_2^{2+} is coordinated to five water molecules. The hydrolysis of uranium(VI) has been investigated by different techniques, for example, Raman spectroscopy [24], calorimetry, and potentiometry [25]. Moll et al. [26] investigated the structure of UO_2^{2+} as a function of pH with the aid of U L_{III}-edge EXAFS (extended X-ray absorption fine structure) spectroscopy. UO_2^{2+} forms strong complexes with OH^- . In slightly acidic solutions (pH 3 to 4), there are two dominated polynuclear complexes: $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$. In the pH region between 6–11, the uranium(VI) speciation is dominated by the precipitation of schoepite phases $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. In the presence of carbonate or atmospheric carbon dioxide, in the basic pH region uranyl-carbonate complexes: UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are formed [27].

The complexes of uranium(VI) with NO_3^- are the most fundamental species in the PUREX process (plutonium and uranium recovery by extraction), which is a liquid-liquid extraction method used to reprocess spent nuclear fuel. This is the most developed and widely used process in commercial reprocessing plants. Most of the unit operations in the PUREX reprocessing process are carried out in aqueous nitrate media. In aqueous nitrate the water molecules in the first hydration shell are replaced by the bidentate species NO_3^- as a function of increasing NO_3^- concentration at low pH [28]. With increasing HNO_3 concentration, coordination numbers (CN) increase from 5 to 6. The U(VI)- NO_3^- complexation system in HNO_3 undergoes the formation of a 5-fold bidentate coordination mononitrate complex, $[\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_3(\eta_2\text{-NO}_3)]^+$, and a 6-fold bidentate coordinated dinitrate complex, $[\text{U}^{\text{VI}}\text{O}_2(\text{H}_2\text{O})_2(\eta_2\text{-NO}_3)_2]^0$. The complexation of uranium(VI) by NO_3^- terminates with the formation of the trinitrate species, $[\text{U}^{\text{VI}}\text{O}_2(\text{NO}_3)_3]^-$.

Acid leaching is the predominant process for uranium recovery from the uranium ores [29]. Sulphuric acid is used usually because of its low cost and availability. The UO_2^{2+} and SO_4^{2-} form monodentate and bidentate species in acidic aqueous solution [30]. At low concentration of sulfate and uranium, the predominated form is UO_2SO_4 with monodentate coordination structure of sulfate. The $\text{UO}_2(\text{SO}_4)_2^{2-}$ species becomes dominant with increasing concentration of SO_4^{2-} [30, 31]. In high concentration of SO_4^{2-} , the UO_2^{2+} is coordinated by two bidentate sulfate groups [30]. It is worthy to notice that the complexes of UO_2^{2+} with sulfate are stronger than with nitrate groups.

The study of the interaction between UO_2^{2+} and Cl^- ions showed that uranium(VI) exists only as UO_2^{2+} and UO_2Cl^+ in the NaCl solution with concentration below 1.5 M at low pH. At higher brine concentration, the further complexation of uranium(VI) with Cl^- takes place; so UO_2Cl_2 and UO_2Cl_3^- species can be formed. At very high concentration of NaCl, above 10 M, tetrachloro species $\text{UO}_2\text{Cl}_4^{2-}$ can be also present [32].

Uranyl phosphates and uranyl arsenate minerals constitute about one-third of the approximately two hundreds known uranium minerals [33]. The speciation in the UO_2^{2+} -water-phosphate system was also studied [34]. In the pH range from 2 to 5, two forms of species: $\text{UO}_2\text{H}_2\text{PO}_4^+$ and neutral $(\text{UO}_2)(\text{HPO}_4)$ exist. At pH above 6.5, negatively charged species $\text{UO}_2(\text{PO}_4)^-$ is also formed.

Uranium forms also several complex species with arsenate ions in water solution. TRLFS (time-resolved laser fluorescence spectroscopy) showed the presence of $\text{UO}_2\text{H}_2\text{AsO}_4^+$, $\text{UO}_2(\text{HAsO}_4)$ and $\text{UO}_2(\text{H}_2\text{AsO}_4)_2$ [35].

3. Structures and Conformational Analysis of Calix[6]arenes

The conformational flexibility of calix[6]arenes and presence of functional groups facilitates the binding of metal centers [36]. There are eight conformations of calix[6]arenes described in the literature [37]. They are called as distorted cone, compressed cone, pinched cone, double partial cone, winged, 1,2,3-alternate, 1,3,5-alternate, and distorted 1,2,3-alternate.

Until now few crystal structures of UO_2^{2+} with calix[6]arenes have been described. Calix[6]arenes similar to calix[8]arenes show smaller ability to form inclusion complexes than their lower homologues [38]. The first crystal structures of the uranium(VI) complex with calix[6]arene were reported by Thuéry et al. [39]. In the complex whose formula was $[(\text{UO}_2^{2+})(\text{H}_2\text{L}^{4-})]_2(\text{HNEt}_3^+)_2(\text{H}_3\text{O}^+)_2 \cdot 6\text{CH}_3\text{CN}$, where $\text{L} = p\text{-tert-butylcalix[6]arene}$, each UO_2^{2+} was bound to four oxygen atoms (two from each calixarene moiety). The mean value of O-U-O angle is 90° , suggesting that atom of uranium(VI) had octahedral centre of coordination. The conformation of the calix[6]arene was slightly distorted with respect to the usual pinched cone conformation of calix[6]arenes. The minus charge of the dimer was compensated by two protonated triethylamine

molecules and two hydronium ions. Triethylamine molecules were outside of the calixarene in comparison to hydronium ions, which were inside the cavity defined by each calixarene. In the complex hydrogen bonds were formed between the hydronium ions and two phenolic oxygen atoms nonbonded to the UO_2^{2+} and with the nitrogen atom of one acetonitrile molecule, which was included in the hydrophobic cavity of the calixarene.

Later, Thuéry and Masci [40] studied the hetero(tri- and tetra-)nuclear complexes of UO_2^{2+} and alkali metal (Li^+ and K^+) with *p-tert-butylhexahomotrioxacalix[6]arene* (L). The authors synthesized in the presence of lithium or potassium hydroxide the following complexes: $[(\text{UO}_2)_2\text{Li}(\text{OH})\text{L}(\text{py})][\text{Li}(\text{H}_2\text{O})_3(\text{py})] \cdot (\text{Hpy}) \cdot \text{H}_2\text{O} \cdot 4.5\text{py}$ and $[\text{UO}_2\text{K}(\text{LH}_3)(\text{H}_2\text{O})_2]_2 \cdot 14\text{py}$. The complex, which was obtained in the presence of lithium hydroxide, contained the trimetallic dianionic species, in which three cations were complexed in internal fashion. The two UO_2^{2+} were bound to three phenoxide groups and the central hydroxide ion. The lithium ion was bound to two phenoxide groups and one other oxygen atom and the pyridine molecule. The geometry of coordination center of uranium(VI) could be described as distorted square bipyramidal environment.

The complex, which was obtained in the presence of potassium hydroxide, was built of an asymmetric unit, which contains $[\text{UO}_2\text{K}(\text{LH}_3)(\text{H}_2\text{O})_2]_2$ heterobinuclear unit and pyridine solvent. UO_2^{2+} was bound to three phenoxide groups and the potassium ion to two phenol groups and one of ether groups of *p-tert-butylhexahomotrioxacalix[6]arene*. To obtain the usual square bipyramidal geometry around the uranium atom, the UO_2^{2+} completed its coordination sphere with a water molecule. The conformation of macrocycle could be described as a double partial cone. In comparison to the lithium complex, the potassium complex was dimeric.

The next crystal structure described in the literature was $[(\text{HO})\{\text{UO}_2(\text{calix[6]H}_4)(\text{dmsO})\}_3\text{H}] \cdot 11\text{MeCN} \cdot 6\text{H}_2\text{O}$ synthesized by Delaigue et al. [41]. The conformation of calixarene ligand in this complex could be described as distorted cones. The complex was trinuclear. Uranium atoms were linked in their equatorial planes symmetrically by a "hydroxyl" oxygen atom, disposed on a crystallographic 3-axis in cubic space group P2_13 . The equatorial plane of uranium(VI) was of five coordinates; one of these sites was occupied by DMSO oxygen. Next two sites were occupied by adjacent phenoxy-oxygen of calixarene ligand. In this case, UO_2^{2+} was bound to the calixarene in an external manner.

There have been well-known structures of uranium(VI) complexes with calixarenes in a solid state, but not in a solution. The two spectroscopic methods described below may overcome the analytical problems, providing insight into the structure of complexes studied.

TRLFS is a very selective and sensitive method for actinide and lanthanide analysis because it can offer the spectral and temporal resolution together. This method provides information on lifetime and spectral characteristic of species, which can be used to obtain the number of different species and their spectral identity [42]. TRLFS has been widely used to investigate the speciation of

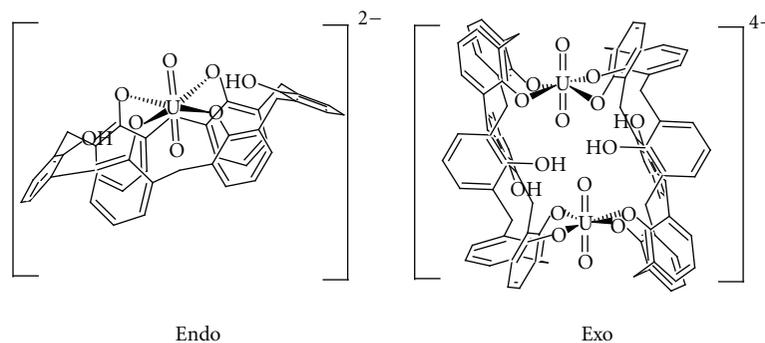


FIGURE 2: Endo- and exocavity binding in calix[6]arene.

the fluorescent metal ions, extracting quantitative and structural information from multiple TRLFS data measured as a function of chemical and physical parameters. The distinguishing ability of TRLFS relies on the fact that different chemical species of a fluorescent metal ion have different lifetimes of fluorescent and spectral shapes. The estimation of the number of different species, their concentrations, and their chemical or structural information from TRLFS data is a difficult task, due to overlapped spectra and similar fluorescence lifetimes. The development of statistical techniques such as two-way factor analysis (FA), evolving factor analysis (EFA) combined with multivariate curve resolution (MCR), or parallel factor analysis (PARAFAC) can overcome such difficulties [43]. TRLFS was used by Schmeide et al. [44] to study the complexation of uranium(VI) by calix[6]arenes in water and organic solvents.

EXAFS spectroscopy is a very useful method for structural studies of organometallic complexes in solution. This method can be used to probe a local structure providing information on the number of the adjacent atoms, their type, and their lengths from the absorbing atom. Using EXAFS measurements in the investigation of the complexes of calixarenes with metals was reported [45, 46].

It seems that the studies with spectroscopic techniques (EXAFS, TRLFS) could provide insight into the coordination models of novel calixarene complexes with uranium(VI).

4. Kinetic Studies of the Complexation Uranium(VI) with Calixarenes

Despite of very high selectivity $K_{\text{uranyl}}/K_{M^{n+}}$ and remarkably large stability constants, calixarenes have a very slow binding rate with uranium(VI) [47]. This is because uranium(VI) is a linear guest cation. In order to permit UO_2^{2+} to penetrate the calixarene ring first the exocomplex [16] is created and finally the endocomplex [48, 49] (Figure 2) is formed.

Nagasaki et al. [49] investigated the difference in the kinetics between the calixarene and noncyclic analog pentasodium 2,6-bis{[2-hydroxy-3-(2-hydroxy-3-methyl-5-sulfonate-(phenyl)methyl)-5-sulfonate(phenyl)]methyl}-4-sulfonate(phenol) (1) (Table 1). In case of the noncyclic ligand, the rate constants were greater than those for the cyclic ones. However, the examination of kinetic parameters

revealed that rapid equilibration in case of noncyclic analogs was not only due to the fast forward complexation rate but also due to the more enhanced reverse decomplexation rate. The surprising effect was observed with pentasodium 31,32,33,34,35-pentahydroxycalix[5]arene-5,11,17,23,29-pentasulfonate (2) that gave kinetic parameters much greater than those for hexasodium 37,38,39,40,41,42-hexahydroxycalix[6]arene-5,11,17,23,29,35-hexasulfonate (3). The authors reported that in contrast to calix[6]arene where at pH 6 all six OH groups were dissociated, in calix[5]arene only four groups were dissociated [49]. The remained groups dissociated scarcely at pH 9 to form the fully saturated pentacoordinate complex. In conclusion, the initial state and final state in the binding to UO_2^{2+} were both destabilized, and the calix[5]arene ring was a priori distorted. In this connection, Nagasaki et al. [49] pointed out that calix[5]arenes and the noncyclic analog are better extraction agents for UO_2^{2+} than calix[6]arenes. Later studies showed stable complexes of uranium(VI) with calix[6]arenes in exoconformation [39].

5. Application of Calixarenes in Separation of Uranium(VI)

5.1. Liquid-Liquid Extraction. The separation of metal ions from a solution and selective removal of particular cations are of interest in a variety of fields such as recovery of precious metal ions from the waste and hydrometallurgy. The separation methods that are often used include solvent extraction, chromatography, and membrane separation.

Two-phase solvent extraction of uranium(VI) with calixarene derivatives has been reported by several groups. This review concerns the uranophile properties of calix[5]arene and calix[6]arene derivatives.

Shinkai et al. [50] noticed that calix[5]arene and calix[6]arene had an ideal architecture for the design of uranophiles because the introduction of ligand groups into each benzene unit of these calixarenes exactly provided the required pseudoplanar penta- and hexacoordinate structures. They synthesized several water-soluble calixarene derivatives from calix[*n*]arenes ($n = 4, 5, 6$) (4, 2, and 3) (Table 1). They found that the

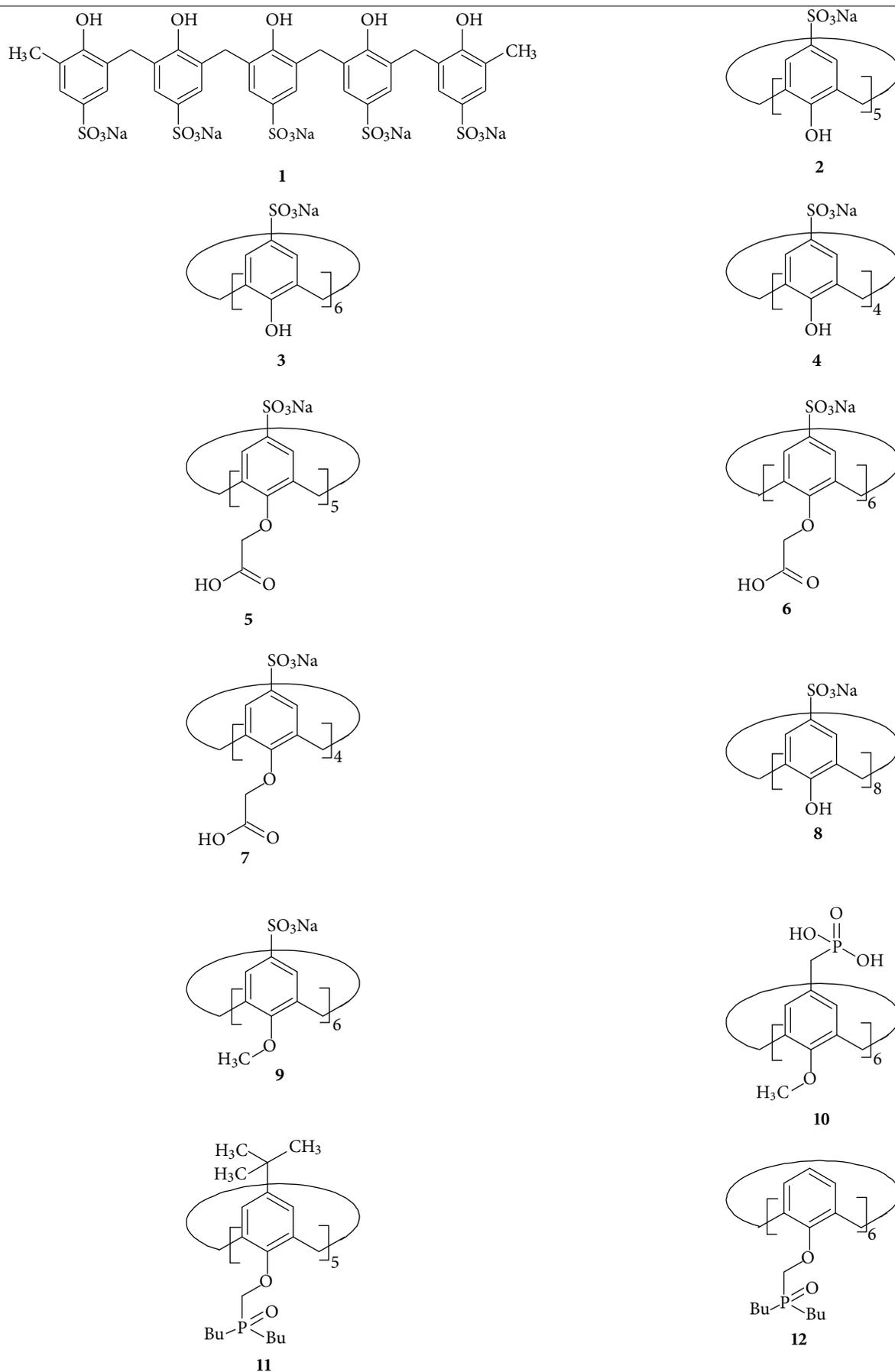
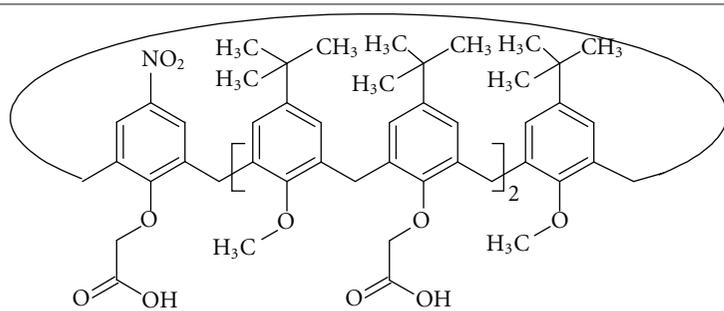
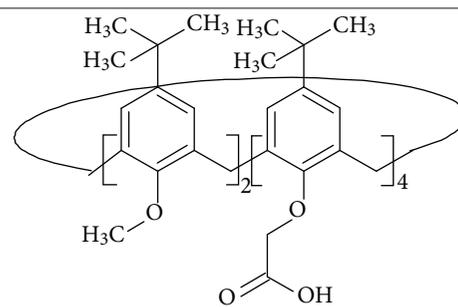
TABLE 1: The structures of noncyclic analog **1** and calixarene derivatives **2–34**.

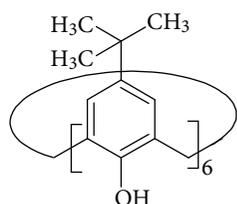
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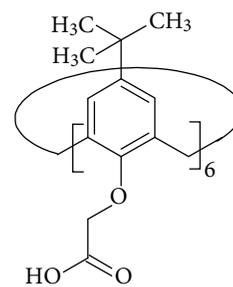
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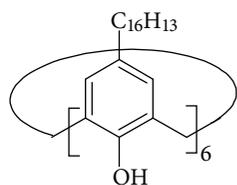
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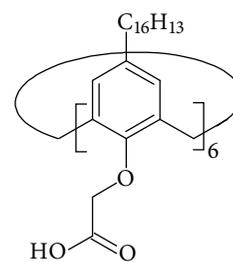
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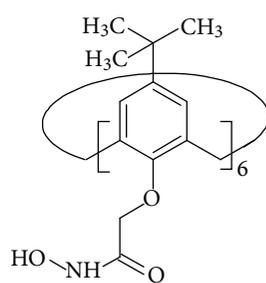
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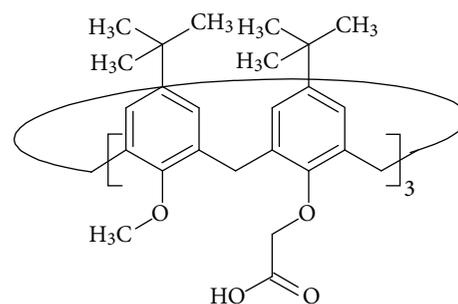
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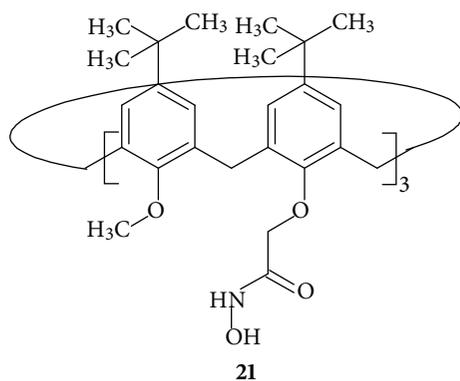
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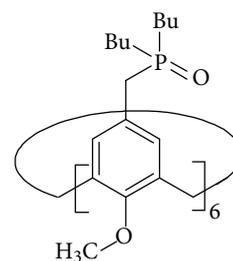
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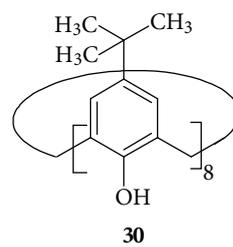
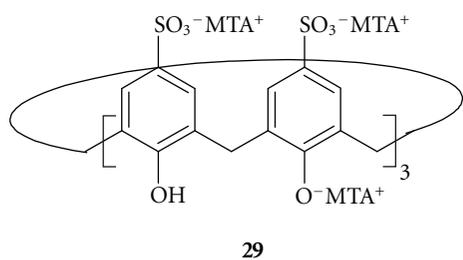
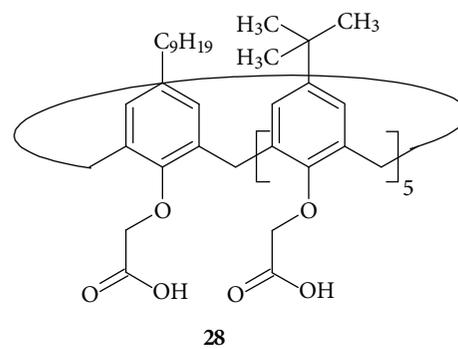
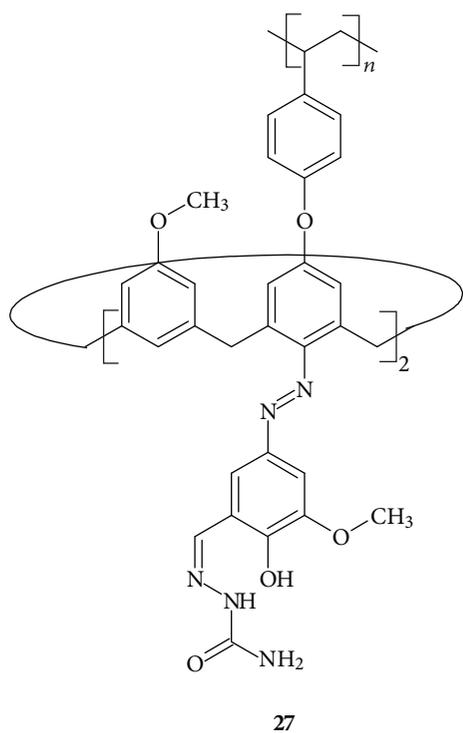
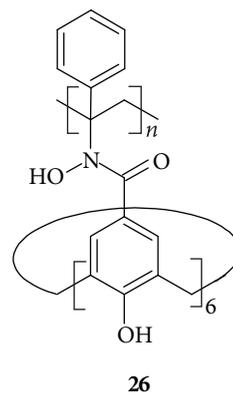
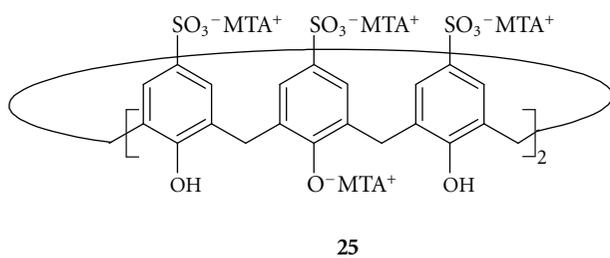
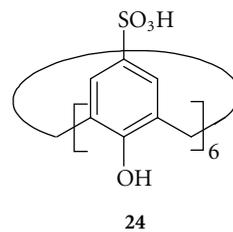
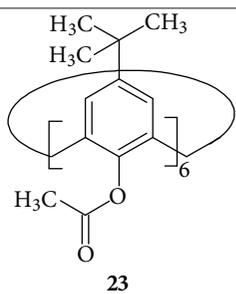
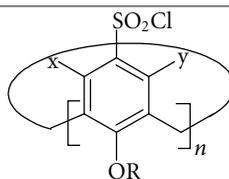
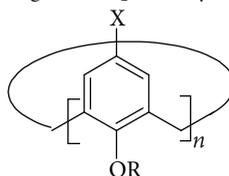


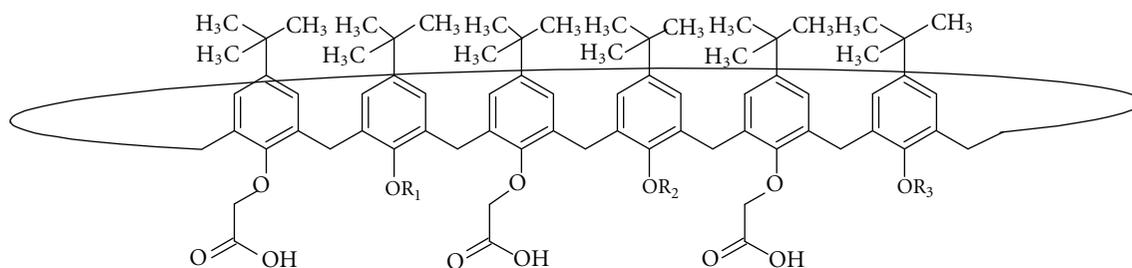
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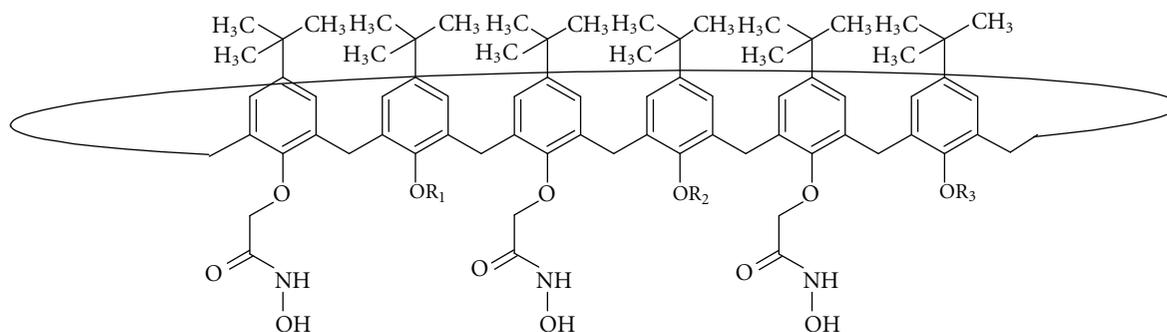
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 $n = 6-8$; R = e.g., H, CH₂OH; x, y = e.g., H, alkyl

32

 $n = 2-8$; R = R', CONH(OH); X = H, R'' or SO₃M; R', R'' = lower hydrocarbon; M = H or monovalent metal

33



34

R_n = H, halogen, acetyl, amino, phosphate, nitro, sulfate, carboxyl, carboxylic, thiocarboxylic, carbamate, thiocarbamate radical, alkyl C1-C60, alkenyl C2-C60, alkynyl C2-C60, cycloalkyl C13-C12, cycloalkyl with at least one ethylenic or acetylenic unsaturation, aryl, naphthyl, aryl(C1-C30 Alkyl), (C1-C30 Alkyl)Aryl, and R₁ = R₂ = R₃ or R₁ = R₂ ≠ R₃ or R₁ ≠ R₂ = R₃ or R₁ ≠ R₃ = R₂ or R₁ ≠ R₃ ≠ R₂.

UO₂²⁺-complexes formed by pentasodium 31,32,33,34,35-penta(carboxymethoxy)calix[5]arene-5,11,17,23,29 pentasulfonate (5) and hexasodium 37,38,39,40,41,42-hexa(carboxymethoxy)calix[6]arene-5,11,17,23,29,35-hexasulfonate (6) had high stability (Table 2, entries 5 and 6) and furthermore, that these ligands showed also an unusual high selectivity for uranium(VI) (Table 3). It is worthy to notice that tetrasodium 25,26,27,28-tetrahydroxycalix[4]arene-5,11,17,23-tetrasulfonate (4) and tetrasodium 25,26,27,28-tetra(car-

boxymethoxy)calix[4]arene-5,11,17,23-tetrasulfonate (7) were not efficient as complexing ligand of UO₂²⁺ (Table 2, entries 4 and 7).

It is interesting that the stability constants for UO₂²⁺ octasodium 50,51,52,53,54,55,56,57-octahydroxycalix[8]arene-5,11,17,23,29,35,41,47-octasulfonate (8) (Table 2, entry 8) were comparable with those for calixarenes 2 and 3 (Table 2, entries 2 and 3). It is well known that the calix[8]arene ring is more flexible than the smaller calixarene rings [55, 56].

TABLE 2: Stability constants ($K_{\text{uranyl}}^{\text{a}}$) for the complexes of UO_2^{2+} and calixarene derivatives at 25°C.

Entry	Extraction agent	$\log K_{\text{uranyl}}$	Medium	pH	Reference
1	1 ^b	17.7	carbonate buffer	10.4	[49]
2	2	18.9	10^{-2} M carbonate	10.4	[50]
3	3	19.2	10^{-2} M carbonate	10.4	[50]
4	4	3.2	10^{-2} M carbonate	6.5	[50]
5	5	18.4	10^{-2} M carbonate	10.4	[50]
6	6	18.7	10^{-2} M carbonate	10.4	[50]
7	7	3.1	10^{-2} M carbonate	6.5	[50]
8	8	18.7 ($\log K_1$) ^c 18.1 ($\log K_2$) ^c	carbonate buffer	10.4	[49]
9	9	3.2	10^{-2} M carbonate	6.5	[50]
10	10	16.3	10^{-2} M carbonate	10.4	[51]
11	10	17.5	10^{-2} M carbonate	11.5	[51]
12	11	2.7	methanol	—	[52]
13	11	3.72	acetonitrile	—	[52]
14	12	3.26	methanol	—	[52]
15	12	3.6	acetonitrile	—	[52]
16	13	9.93	methanol	—	[53]
17	14	14.2	methanol	—	[54]

^a $K_{\text{uranyl}} = [\text{UO}_2^{2+} \cdot \text{Extraction agent complex}] / [\text{UO}_2^{2+}][\text{Extraction agent}]$.

^bNoncyclic extractant **1**.

^c $K_1 = [\text{UO}_2^{2+} \cdot \mathbf{8} \text{ complex}] / [\text{UO}_2^{2+}][\mathbf{8}]$, $K_2 = [(\text{UO}_2^{2+})_2 \cdot \mathbf{8} \text{ complex}] / [\text{UO}_2^{2+}][\text{UO}_2^{2+} \cdot \mathbf{8} \text{ complex}]$.

TABLE 3: Selectivity factor for UO_2^{2+} ($K_{\text{uranyl}}/K_{\text{M}^{n+}}$).

Entry	Extraction agent	Metal (M^{n+})	$K_{\text{uranyl}}/K_{\text{M}^{n+}}$	Reference
1	3	Mg^{2+}	$>10^{17}$	[50]
2	3	Ni^{2+}	$10^{17.0}$	[50]
3	3	Zn^{2+}	$10^{13.7}$	[50]
4	3	Cu^{2+}	$10^{10.6}$	[50]
5	5	Mg^{2+}	$>10^{17}$	[50]
6	5	Ni^{2+}	$10^{15.3}$	[50]
7	5	Zn^{2+}	$10^{13.1}$	[50]
8	5	Cu^{2+}	$10^{12.0}$	[50]

Although the phenolic oxygens are not suitably arranged for coordination to UO_2^{2+} , the flexibility would allow and induce fit-type complexation with UO_2^{2+} . In contrast, K_{uranyl} for noncyclic compound **1** (Table 2, entry 1) was somewhat smaller than those values for cyclic extractant **2** and **3** (Table 2, entries 2 and 3). The calix[4]arenes **4** and **7** could not form the stable uranyl complexes at pH range from 3 to 7. In neutral-to-basic region, the calix[5]arene **2** and calix[6]arene **3** form with UO_2^{2+} the stable 1:1 complexes, whereas the calix[8]arene **8** forms a 2:1 UO_2^{2+} : complex. It is necessary to note that the complexation study was carried out in carbonate medium where the main species is $\text{UO}_2(\text{CO}_3)_3^{4-}$. The carbonate ligands are replaced by calixarene ligands during the reaction [49, 50].

Hexasodium 37,38,39,40,41,42-hexamethoxycalix[6]-arene-5,11,17,23,29,35-hexa-sulfonate (**9**) had a low stability constant (Table 2, entry 9), on the contrary to the compound

6 (Table 2, entry 6) substituted with the carboxymethoxy group in the narrow rim. This indicates that carboxylate groups on the edge of the calixarene **6** are responsible for the UO_2^{2+} binding.

The binding properties of phosphorylated calixarene derivatives bearing phosphonate or phosphine oxide groups either at the wide or narrow rim have been investigated towards UO_2^{2+} [51, 52]. A high stability constant was observed for complex of UO_2^{2+} with 37,38,39,40,41,42-hexamethoxy-5,11,17,23,29,35-hexakis(phosphonomethyl)-calix[6]arene (**10**) (Table 2, entries 10 and 11). The complexes of 31,32,33,34,35-pentakis(dibutylphosphinylmethoxy)-5,11,17,23,29-penta(*p-tert*-butyl)calix[5]arene (**11**) and 37,38,39,40,41,42-hexakis(dibutylphosphinylmethoxy)calix[6]-arene (**12**) with uranium(VI) had a lower stability (Table 2, entries 12–15). The complexation was carried out in two different solvents: methanol, whose properties are close to

TABLE 4: Solvent extraction of UO_2^{2+} at 30°C.

Entry	Extraction agent	Ex%	Organic phase	pH	Reference
1	15	4.6	<i>o</i> -dichlorobenzene	8.0	[57]
2	15	0	<i>o</i> -dichlorobenzene	10.0	[57]
3	16	100	<i>o</i> -dichlorobenzene	8.0	[57]
4	16	93.3	<i>o</i> -dichlorobenzene	10.0	[57]
5	17	22.5	<i>o</i> -dichlorobenzene	8.0	[57]
6	17	0	<i>o</i> -dichlorobenzene	10.0	[57]
7	18	100	<i>o</i> -dichlorobenzene	8.0	[57]
8	18	90.0	<i>o</i> -dichlorobenzene	10.0	[57]
9	15	100	chloroform	5.9	[57]
10	19	100	chloroform	5.9	[58]

those of water and acetonitrile, which is a medium-polarity solvent.

37,39,41-tris[(methoxycarbonyl)methoxy]-38,40,42-trimethoxy-35-nitro-5,11,17,23,29-penta-(*tert*-butyl)calix[6]arene (**13**) and 37,38,39,40-tetrakis(carboxymethoxy)-41,42-dimethoxy-5,11,17,23,29,35-hexa(*tert*-butyl)calix[6]arene (**14**) showed strong binding properties with UO_2^{2+} in methanol (Table 2, entries 16 and 17) [53, 54].

It is worthy to notice that calix[5]arene **5**, **11** and calix[6]arene **9**, **12** formed a 1 : 1 UO_2^{2+} : calixarene complex. However, this stoichiometry was not necessarily in agreement with that of the extracted complexes.

The selectivity of uranophiles can be evaluated by competitive binding with other metal cations. The results are presented in Table 3.

Shinkai et al. [57, 58] extended the concept of uranophile calixarenes to two-phase solvent extraction. 37,38,39,40,41,42-hexahydroxy-5,11,17,23,29,35-hexa(*p*-*tert*-butyl)calix[6]arene (**15**) and 37,38,39,40,41,42-hexahydroxy-5,11,17,23,29,35-hexahexylcalix[6]arene (**17**) showed very low extractability (Table 4, entries 1, 2, 5, and 6). On the other hand, hydrophobic hexacarboxylate derivatives of calix[6]arene: 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexa(*p*-*tert*-butyl)calix[6]arene (**16**), 37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexahexylcalix[6]arene (**18**), and 37,38,39,40,41,42-hexakis(*N*-hydroxycarbamoylmethoxy)-5,11,17,23,29,35-hexa(*p*-*tert*-butyl)calix[6]arene (**19**) were used to extract UO_2^{2+} efficiently and selectively from water into organic media (Table 4).

Examination of Table 4 reveals that **16** and **18** (entries 3, 4, 7, and 8) exhibited excellent extractability (Ex%). The slight decrease in extractability at higher pH was attributed to the hydrolysis of $\text{UO}_2(\text{CH}_2\text{CO}_2)_2$. The low extractability for **15** and **17** was thus attributed to the $\text{p}K_a$ of the OH groups, which is sensitive to the nature of parasubstituents. The values were lowered by electron-withdrawing groups for example, sulfonate group, so ligands such as **2** and **3** were able to associate well with UO_2^{2+} at neutral to slightly basic pH [50]. In contrast, the $\text{p}K_a$ values of **15** and **17** were too high to use them as uranophiles in this pH region. Also in contrast, as the $\text{p}K_a$ values of **16** and **18** were scarcely affected by the nature

of the parasubstituents, they behaved as excellent uranophiles at pH 8–10 [57].

On the other hand, the compound **19**, bearing hydroxamate groups on the lower rim, was an excellent uranophile even in the acidic pH region (Table 4, entry 10). This pH dependence was correlated with the dissociation of the hydroxamic groups and binding to UO_2^{2+} .

It is worth noting that calixarene-based uranophiles from **15** to **18** did not leak out into the aqueous phase. It was confirmed on the basis of spectrophotometric method [57]. The main difference between the homogeneous aqueous system and two-phase solvent-extraction system is that the species extracted into the organic phase must be “neutral” [59]. The above findings suggest, therefore, that calix[6]arene⁶⁻ bearing carboxylic or hydroxamic groups on the lower rim, for example, **16** and **19** formed a 1 : 1 complex with UO_2^{2+} , and the resultant complex $[(\mathbf{16})\cdot\text{UO}_2^{2+}]^{4-}$ or $[(\mathbf{19})\cdot\text{UO}_2^{2+}]^{4-}$ was neutralized by two UO_2^{2+} adsorbed as counteranions [57, 58].

In Table 5, the selectivity of hydrophobic calix[6]arenes is shown. Although calix[6]arenes **15**, **16**, and **19** could efficiently extract UO_2^{2+} from aqueous solution to organic phase, the selectivity factors in two-phase solvent extraction were not so excellent as those obtained with **3** in aqueous system (Table 3). Much more excellent selectivity factors in solvent extraction of UO_2^{2+} were observed when 37,39,41-tris(carboxymethoxy)-38,40,42-trimethoxy-5,11,17,23,29,35-hexa(*p*-*tert*-butyl)calix[6]arene (**20**) was applied [60]. Extractability of **20** was a little inferior to those of **16** and **19** but reached nearly 100% at pH 7.

37,39,41-tris(*N*-hydroxycarbamoylmethoxy)-38,40,42-trimethoxy-5,11,17,23,29,35-hexa(*p*-*tert*-butyl)calix[6]arene (**21**) was shown as more efficient as the carboxylate one (**20**) for UO_2^{2+} extraction [61]. The complex formed in the organic phase was $(\mathbf{21})\cdot(\text{UO}_2^{2+})$ with an apparent extraction constant equal to 7.1×10^{-5} M ($I = 0.04$ M).

Further, the compound **21** has been found as an extractant molecule for selective separation of plutonium(IV) from uranium(VI) [62]. Both elements were selectively extracted depending on the aqueous phase pH (Table 6). At the first step, 93% of plutonium was extracted at pH 2 by **21**

TABLE 5: Solvent extraction of UO_2^{2+} in the presence of competing metal cations at 30°C and at pH 5.9.

Entry	Extraction agent	M^{n+}	$[\text{M}^{n+}]/[\text{UO}_2^{2+}]$	Ex%	Organic solvent	Reference
1	16	Mg^{2+}	5000 ^a	72	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
2	16 /MTA ⁺ Cl ^{-c}	Mg^{2+}	5000 ^a	100	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
3	16	Mg^{2+}	1000 ^a	100	CHCl ₃	[58]
4	19	Mg^{2+}	1000 ^a	100	CHCl ₃	[58]
5	20	Mg^{2+}	943.4 ^b	92	CHCl ₃	[60]
6	16	Ni^{2+}	12.5 ^a	93	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
7	16 /MTA ⁺ Cl ^{-c}	Ni^{2+}	12.5 ^a	100	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
8	16	Ni^{2+}	50 ^a	77	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
9	16 /MTA ⁺ Cl ^{-c}	Ni^{2+}	50 ^a	100	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
10	19	Ni^{2+}	10 ^a	77	CHCl ₃	[58]
11	15	Ni^{2+}	10 ^a	98	CHCl ₃	[58]
12	20	Ni^{2+}	2.4 ^b	98	CHCl ₃	[60]
13	20	Ni^{2+}	9.4 ^b	98	CHCl ₃	[60]
14	16	Zn^{2+}	36.5 ^a	63	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
15	16 /MTA ⁺ Cl ^{-c}	Zn^{2+}	36.5 ^a	90	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
16	16	Zn^{2+}	60 ^a	51	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
17	16 /MTA ⁺ Cl ^{-c}	Zn^{2+}	60 ^a	84	<i>o</i> -Cl ₂ C ₆ H ₄ ^d	[57]
18	15	Zn^{2+}	12 ^a	51	CHCl ₃	[58]
19	19	Zn^{2+}	12 ^a	96	CHCl ₃	[58]
20	20	Zn^{2+}	6.9 ^b	98	CHCl ₃	[60]
21	19	Fe^{3+}	10 ^a	66	CHCl ₃	[58]
22	19	Fe^{3+}	1 ^a	100	CHCl ₃	[58]

^a $[\text{UO}_2(\text{CH}_3\text{CO}_2)_2] = 0.020 \text{ mmol dm}^{-3}$.

^b $[\text{K}_4\text{UO}_2(\text{CO}_3)_3] = 0.106 \text{ mmol dm}^{-3}$.

^cMTA⁺Cl⁻ methyltriocylammonium chloride, $[\text{MTA}^+\text{Cl}^-] = 1.0 \text{ mmol dm}^{-3}$.

^d*o*-dichlorobenzene.

TABLE 6: Successive extractions of Pu(IV) and U(VI) by **21** (extraction (%)) at each step).

	First step pH 2.0	Second step pH 5.0	Reference
Pu(IV) extraction (%) ^a	93	8	[62]
U(VI) extraction (%) ^a	0	99	[62]

^aOrganic solvent: 1,2,3,4-tetrahydronaphthalene.

without extraction of uranium. Then, increasing the pH of the aqueous phase to pH 5 allowed the quantitative extraction of uranium(VI) by **21**. However, it should be noted that at this pH, more than 8% of the remaining plutonium(IV) was also extracted. It is necessary to note that the Pu(IV) is a spherical cation of Pu^{4+} , not a *trans*-dioxo cation like PuO_2^{2+} which is isostructural with the UO_2^{2+} .

The extraction mechanism of UO_2^{2+} by calixarene **20** has been studied in a two-phase solvent-extraction system [63]. The competition between calix[6]arene and other complexing anions, such as phosphate or sulfate, has been investigated. The results showed that UO_2^{2+} extraction was independent of the cation concentration, whatever the pH and the ionic strength were. The UO_2^{2+} -calixarene extraction constant was higher than that of the UO_2^{2+} -anion complexation.

Liquid-liquid extraction experiments of UO_2^{2+} from nitric acid into *m*-nitrobenzotrifluoride (*m*-NBTF) with phosphorylated calix[5]arene and calix[6]arene derivatives were carried out [52]. The distribution coefficients *D* obtained were shown to depend on the concentration of nitric acid in the aqueous phase (Table 7). The *D* values decreased when the nitric acid concentration increased. This behavior was consistent with a competition between the metal ions and proton, as was seen with TOPO and phosphorylated extractant [52]. The values of the distribution coefficients determined for the calixarenes were even smaller than those of TOPO. Only the hexamer 37,38,39,40,41,42-hexamethoxy-5,11,17,23,29,35-hexakis-(dibutyl-phosphinyl-methyl)-calix[6]arene (**22**) extracted UO_2^{2+} much better than TOPO.

A synergistic effect was observed for the extraction of uranium(VI) when acetate solution was extracted with toluene containing *p*-tert-butylcalix[6]arene (**15**) or 37,38,39,40,41,42-hexaacetoxy-5,11,17,23,29,35-hexa(*p*-tert-butyl)calix[6]arene (**23**) and thenyltrifluoroacetone (HTTA) [64]. Also, the presence of alkali metal ions strongly influenced the extraction of UO_2^{2+} by calixarene. This kind of extraction was advantageous for the separation of metal ions efficiently. Thus, whereas the calix[6]arene **15** and **23** studied display a very poor affinity for the UO_2^{2+} (Table 8, entries 1 and 2), these ligands behaved as very efficient

TABLE 7: Extraction of UO_2^{2+} from nitric acid solutions into *m*-NBTF by phosphorylated calixarenes. Distribution coefficients D^a .

Entry	Extraction agent	Nitric acid concentration (M)					Reference
		0.1	0.3	1	3	6	
1	11	0.24	0.32	0.49	0.23	0.15	[52]
2	12	7.5	3.1	1.69	1.22	0.84	[52]
3	22	21	16.8	12.1	8.6	4.0	[52]
4	TOPO ^b	8.3	5.9	1.23	0.19	0.09	[52]

^a D : distribution coefficient, $D = [\text{UO}_2^{2+}]_{\text{org}}/[\text{UO}_2^{2+}]_{\text{aq}}$.

^b**TOPO**: trioctylphosphine oxide.

TABLE 8: The synergistic coefficients of UO_2^{2+} ^a.

Entry	System (pH)	D^b	SF ^c	Reference
1	5×10^{-3} M 15 (pH 6.5)	3.380	—	[64]
2	5×10^{-3} M 23 (pH 5.0)	0.035	—	[64]
3	5×10^{-3} M 15 + 5×10^{-3} M HTTA (pH 6.5)	8.931	1.343	[64]
4	5×10^{-3} M 23 + 5×10^{-3} M HTTA (pH 5.0)	10.240	2.905	[64]

^a $[\text{Na}^+] = 0.04$ M.

^b D : distribution coefficient, $D = [\text{UO}_2^{2+}]_{\text{org}}/[\text{UO}_2^{2+}]_{\text{aq}}$.

^cSF: synergistic factor, $\text{SF} = D_{\text{syn}}/(D_{\text{HTTA}} + D_{\text{CALIX}})$, where D_{syn} is the distribution coefficient of the synergistic mixture.

extracting agents for this ion in the presence of HTTA (Table 8, entries 3 and 4). The extraction was strongly dependent on pH. The extraction decreased from pH 1 to pH 3 for acetatocalixarene/toluene/HTTA/sodium ion system began to increase from pH 4, and it was saturated at around pH 5.0 showing about 90% extractability. The synergistic effect was observed in the systems at $\text{pH} > 5$.

The strong ability of calixarene nanoemulsion to extract UO_2^{2+} was found by Spagnul et al. [65, 66]. They designed an oil-in water emulsion, taking advantage of the small droplet size offering a large contact surface with contaminated aqueous medium. The calixarene **20** nanoemulsion extracted up to 80% of uranium. It is important that the calixarene nanoemulsion effect was observed after a very short time of contact with uranium-contaminated solution. The calixarene nanoemulsion appeared to be a very promising system for uranium skin decontamination [65].

The reactivity of several calixarene derivatives as strong uranophiles could be utilized for sensitive electrochemical measurements of minor concentrations of UO_2^{2+} in aqueous solution [67]. 37,38,39,40,41,42-Hexahydroxy-5,11,17,23,29,35-hexasulfonic-calix[6]arene (**24**): cysteamine monolayer assembled on gold electrode was utilized for the determination of UO_2^{2+} down to 1 ppm.

Jung et al. [68] studied the scavenging of UO_2^{2+} using 4-sulfonic calix[6]arene **24** in the presence of goethite (iron oxyhydroxide). Goethite was selected because of its strong affinity to UO_2^{2+} and its abundance in natural soil [69]. After adsorption of UO_2^{2+} onto goethite, its extraction with the compound **24** in aqueous environment was studied. The results indicated that UO_2^{2+} was almost completely extracted around pH 10.5 when U(VI): calixarene ratio was 1 : 3.

5.2. Extraction with Liquid Membranes. In order to selectively remove and recover metals from aqueous solution, the membrane-based processes are still being developed.

The selective transport of UO_2^{2+} across the liquid membrane with hydrophobic derivative of calix[6]arene **16** as the carrier was studied by Shinkai et al. [57]. The authors examined the transport rate from H_2O (source phase)-organic solvent- H_2O (receiving phase). They found that the rate determining step was the UO_2^{2+} release from organic solvent to the receiving aqueous phase. The extent of UO_2^{2+} transport was efficiently controlled by the changes in pH and temperatures.

Later Kondo et al. [70] investigated selective transport of UO_2^{2+} through a bulk liquid membrane (BLM) containing hydrophobic ion associate of methyltrioctylammonium and hydroxycalix[6]arene-*p*-sulfonates (**25**) diluted in chloroform. The authors observed that the extraction rate of UO_2^{2+} increased with increasing pH in the source phase as well as with increasing temperature in the temperature range 15–55°C. This effect could be explained by increasing the concentration of dissociated carrier **25**. The developed system was not suitable for temperatures higher than 55°C since bubbles were generated in the membrane and sometimes the boiling solvent broke the layer structure of the interfaces of both aqueous phases with the membrane. The other ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Fe^{3+} , La^{3+} , Eu^{3+} , and Lu^{3+} , are not transported through the BLM, and therefore UO_2^{2+} can be separated selectively.

A facilitated selective transport of UO_2^{2+} across a BLM with the compound **15** in chloroform as ion carrier was studied by Ramkumar et al. [71] as well. With this system uranium(VI) with crown ethers as UO_2^{2+} -18C6 was effectively

separated from Cu^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+} . They confirmed that the transport of UO_2^{2+} increased with the increase of the acidity of the receiving solution. The use of excess of crown ether 18C6 in proportion to calixarene (100:1) allowed decreasing pH in the receiving phase without loose of the extraction yield. It was caused by better solubility of uranyl ion in the membrane phase. The hydrophobic crown ether 18C6 plays a role in the absorption of uranyl ion into hydrophobic phase by bonding to coordination sphere of the metal ion. The authors [71] suggested that crown ether is involved in the secondary coordination sphere of the uranyl-calixarene complex.

5.3. Ion Exchange and Chelating Resin. The separation of Th^{4+} , Ce^{4+} , and UO_2^{2+} by polymer supported calix[6]arene hydroxamic acid **26** as a novel chelating resin was investigated by Trivedi et al. [72]. The novel resin was stable against light, air, water, and temperature up to 210°C . With this system, Th^{4+} , Ce^{4+} , and UO_2^{2+} were effectively separated by changing pH of sorption or phase elution. The yield of the recovery at pH 6.5 of the sorption was $(99.1 \pm 0.3)\%$ for Th^{4+} (in this pH region thorium ions were not sorbed), $(98.2 \pm 0.2)\%$ for Ce^{4+} with 0.1 M HCl as an eluent, $(97.6 \pm 0.2)\%$ for UO_2^{2+} with 2 M HCl as an eluent.

A similar experiment was done by Jain et al. [73]. They studied the possibility of preconcentration of UO_2^{2+} and Th^{4+} by using Merrifield chloromethylated resin anchored with calix[4]arene-*o*-vanillinsemicarbazone (**27**). The experiments showed that the UO_2^{2+} can be separated from Th^{4+} and also from La^{3+} , Cu^{2+} , and Pb^{2+} .

Schmeide et al. [74] studied the separation of UO_2^{2+} from aqueous solution by mono-*p*-nonyl-penta-*p*-*tert*-butyl-calix[6]arene hexacarboxylic acid (**28**) modified textiles. The best results were obtained for separation of UO_2^{2+} at pH 7 (97.8%) and pH 5 (94.9%). They studied also the influence of other ions such as sodium, potassium, magnesium, and sulfate on the separation of UO_2^{2+} by calixarene modified textiles. They found that neither at pH 5 nor at pH 7 a change of the separation yield of UO_2^{2+} was observed. A different situation was observed in the case of calcium- and carbonate-rich waters. At pH 5 there was no significant change, but at pH 7 UO_2^{2+} separation was reduced from 92% to 9%. This was due to the formation of aqueous complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$.

Koga et al. [75] used silica gel particles impregnated with ion associates containing sulfonatocalix[6]arene ions **29** and methyltriethylammonium ions. They investigated adsorption properties for metals Mg^{2+} , Ca^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Sr^{2+} , Ba^{2+} , and UO_2^{2+} either at pH 5 or 7; then these metals were eluted by dilute sulfuric acid. That complex-type adsorbents exhibited large and selective adsorptivities for UO_2^{2+} and Ba^{2+} . The best adsorptivity for UO_2^{2+} was observed at pH 7.

Ayata and Merdivan [76] showed that silica gel loaded with *p*-*tert*-butylcalix[8]arene (**30**) could be a potential agent for preconcentration of uranium(VI).

The best adsorption of uranium(VI) was observed in the pH range from 5 to 7. At lower pH, the adsorption was

low because of the competition of hydronium ions with the UO_2^{2+} for the adsorption sites. At higher pH, uranium(VI) becomes hydrolysed to form oligomeric species (see Section 2).

6. The Potential Industrial Application of Calix[6]arenes for Uranium(VI)

The well-known high affinity of the calixarenes to UO_2^{2+} make base for industrial use of them as reagents for the recovery of uranium from water solutions or removal from liquid waste generated from uranium mining and processing.

The patent from 1988 [77] concerns the use of calixarenes as adsorbent for UO_2^{2+} . This adsorbent consisted of polyethyleneimine, which had calixarene residue **31** bonded to the side chain by SO_2Cl groups. It was characterized by an excellent affinity and selectivity.

In 1992, the patent for a calixarene derivative **32** [78] was published. This new compound has been useful as a host compound. Another ion or neutral compound could be bound in its cavity. Such compounds have shown excellent adsorption properties even at low pH which indicates that they can be used for adsorption and selective recovery of uranium(VI) from sea water or waste water, and so forth.

The invention described in American patent [79] was related to supported liquid membranes. The supporting materials contain the novel calixarenes with formula **33** and **34**, which can be used for analytical measurements of uranium, americium, and plutonium. The main function of these materials is to extract the above-mentioned actinides from complex matrices, such as biological media.

7. Conclusions

Calix[6]arenes represent a family of macrocyclic molecules with a broad range of potential applications in chemical, analytical, and engineering materials fields. Low toxicity of these compounds makes them useful in applications of green chemistry and eco-friendly industrial processes.

The present paper demonstrated that calix[6]arenes act as very good uranophiles in different fields including separation processes (e.g., solvent extraction, membrane transport, and chromatographic process). They may be useful for extracting UO_2^{2+} from solutions after leaching of uranium ores, sea water, radioactive waste, or natural soil. It was revealed that calixarenes bearing ligands including P=O groups are more efficient than TBP (tributyl phosphate), TOPO (trioctylphosphine oxide), and CMPO (carbamoylphosphonate) for extraction of lanthanides and actinides. Application of such extracting agents enables the use of 10 to 100 times lower ligand concentrations necessary to reach an assumed extraction yield than with the other existing extractants. Extensive literature studies showed that extraction ability and selectivity of calixarene derivatives is closely related to their structural arrangement. Easy functionalization of these compounds enables simple engineering of the calixarene derivatives and preparation of the materials of good affinity to specific forms of uranium like UO_2^{2+} .

The concept of uranophile calixarenes for liquid-liquid extraction and BLMs was studied with different calixarenes modified at the narrow and wide rims. The high effectiveness of calix[6]arenes in the process of separation of uranium(VI) from aqueous solutions was shown. It is necessary to notice that many factors, such as pH, temperature, presence of other metal ions and counter ions, and the kind of solvent applied, affect the performance of the extraction of UO_2^{2+} . In most of the processes described above, the halogenated solvents were used. They are not acceptable in the industrial chemistry due to their cost and toxicity.

Ion exchange seems powerful technique, which can be used to separate uranium from other chemical substances. Similar to solvent extraction and BLMs transport, it uses the reversible reaction causing all UO_2^{2+} to be reextracted. The advantages of ion exchange technique are lack of the organic solvent and the possibility of the control of the composition of the solutions by change of the eluent pH.

Acknowledgment

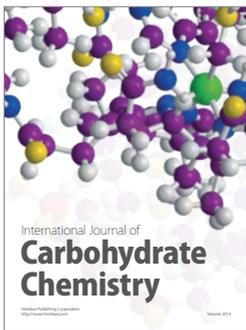
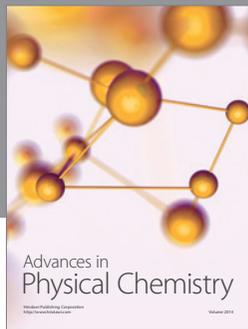
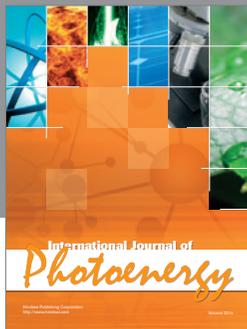
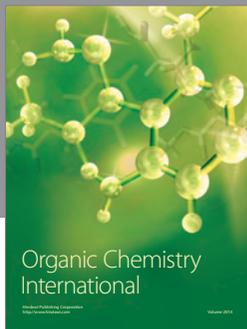
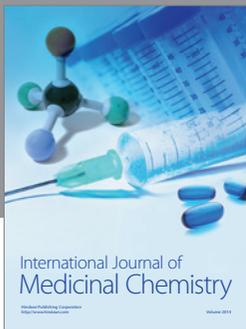
The studies were supported by the Operative Programme Innovative Economy: Analysis of the Possibility of Uranium Supply from Domestic Resources (POIG 01.01.02-14-094-09-00).

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