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Syntheses of two diamine substituted 1,3-distal calix[4]arene-based magnetite nanoparticles for extraction of dichromate, arsenate and uranyl ions

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ABSTRACT

The synthesis of two new calixarene derivatives **4** and **5**, functionalized at the lower rim with 4-amino-1-benzylpiperidine to give diamide and diamine derivatives of *p-tert*-butylcalix[4]arene, is described. They were obtained by the reaction of both the diester derivative of *p-tert*-butylcalix[4]arene (**2**) and the dialkyl bromide derivative of *p-tert*-butylcalix[4]arene (**3**) with 4-amino-1-benzylpiperidine. The ^{1}H NMR spectra of calixarene derivatives show that **4** and **5** exist in the cone conformation. Moreover, these diamide and diamine derivatives of *p-tert*-butylcalix[4]arene (**4** and **5**) have been immobilized onto [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane-modified Fe_3O_4 magnetite nanoparticles to obtain calixarene-based magnetic nanoparticles **M-DADBP-Calix** (**6**) and **M-DABP-Calix** (**7**). The calix[4]arene immobilized materials were characterized by a combination of Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Thermogravimetric Analyses (TGA) and elemental analysis. Additionally, the studies regarding the removal of As(V)/Cr(VI) ions as well as U(VI) ion from aqueous solutions were also carried out by using these compounds in liquid–liquid/solid–liquid extraction experiments.

1. Introduction

Cr(VI) and inorganic arsenics, such as As(V) and As(III) are counted among the top 20 most hazardous substances.[1] It is well known that these oxyanions have become the most serious environmental pollutants.[2–4] Among them, arsenic is a well-documented carcinogenic causing various adverse health effects such as cancer and skin diseases even at sub-ppm levels.[4–7] About 150 million people are threatened by this serious health hazard from over 70 countries.[8,9] Typically in soils, arsenic occurs naturally at concentrations varying between 0.2 and 40 mg/kg. Recently, the use of pesticides, herbicides and wood preservatives containing arsenic has lead to an increase of its concentration in soils.[10,11]

In nature, chromium exists in the Cr(VI) and Cr(III) forms, which differ widely in their chemical properties and biological reactivities.[12,13] Many studies have indicated that Cr(VI), like As(V) is highly toxic, carcinogenic and harmful to humans, while Cr(III) is essential to mammals as it maintains effective glucose, lipid and protein metabolisms.[14]

Uranium is most commonly used as a nuclear fuel in fission reactors for civilian purpose.[15] In a nuclear accident, uranium is at the origin of severe internal contaminations by ingestion or inhalation.[15] In mammalian systems, the uranyl ion interacts with blood and low molecular weight complexing agents, such as citrates, bicarbonates and phosphates.[16]

Uranyl ions are extremely mobile and once entered into living bodies provoke inner irradiation which may cause cancers in the long term.[17] In this case, there has been increased special interest in uranium (VI), in particular uranyl ion analysis in the nuclear industry, especially in fuel separation and processing steps, composed of a few steps including leaching from ores, purification by ion exchange and solvent extraction, precipitation, reduction, etc.[18,19]

In the last decade, increased investigations with several types of iron oxide have been carried out in the field of nano-sized magnetic particles (generally maghemite, γ-Fe_2O_3, or magnetite, Fe_3O_4, single domains of about 5–20 nm in diameter).[20] Magnetite, Fe_3O_4, is a common magnetic iron oxide. Due to this feature, the separation process should be achieved quite easily and rapidly.

Recently, magnetic nanoparticles of iron oxide have shown great potential in many fields like bioseparation,[20,21] tumour hyperthermia,[22] magnetic resonance imaging (MRI), diagnostic contrast agents,[23] magnetically guided site-specific drug delivery agents,[24] biomolecules immobilization,[25,26] as well as support materials for some selective calixarene derivatives acting on arsenate or dichromate ions.[2,4,27]

Calixarenes, cyclic oligomers of phenolic units linked through the *ortho* positions, are a fascinating class of macrocycle. Chemical modification of *the upper* or *lower rim* has made this class of synthetic ionophores effective extractants for transferring anionic[28,29]

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and cationic ions[30,31] or neutral molecules from aqueous solution into an organic layer. These molecules are generally calix[4]arene derivatives containing amine or amide functions, capable of interacting with anions/cations by hydrogen bonds.[2,4,32]

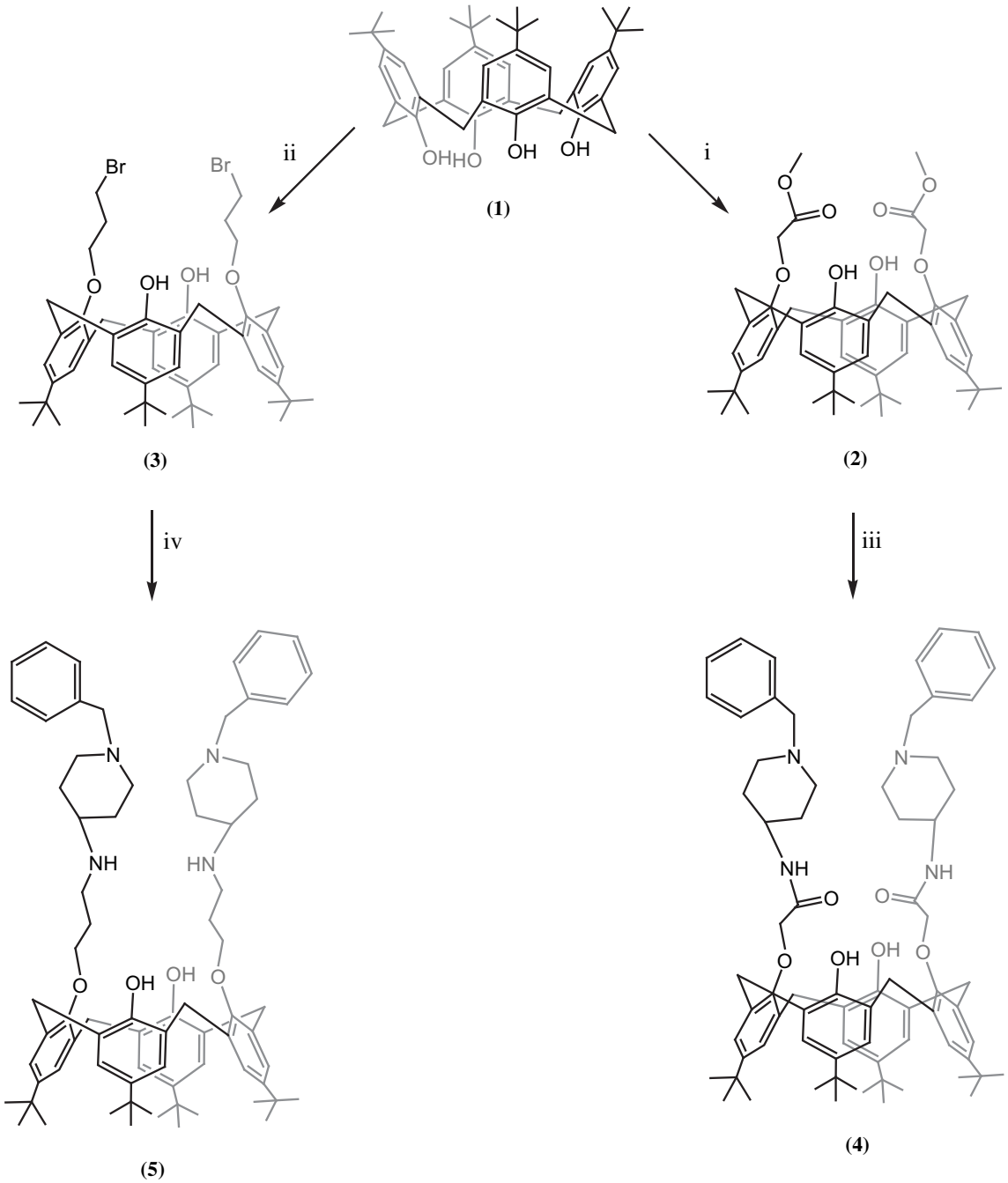
Until now, calixarene-based materials have seen increased use as uranophiles with either a pseudoplanar pentaco-ordinate or hexaco-ordinate structure.[33,34] It is well known that the high selectivity is attributed to the rigid skeleton of calix[5]arenes and calix[6]arenes towards the uranyl ion since these derivatives can provide the pre-organized hexa- or penta-coordination geometry required for the binding of UO_2^{2+}.[35]

Herein, we have synthesized two new calixarene derivatives and immobilized them onto the silica based iron oxide nanoparticles surface and then investigated their extraction capability towards arsenate/dichromate anions as well as uranyl cation by means of liquid liquid/solid–liquid extraction process.

2. Results and discussion

2.1. Synthesis of new host molecules

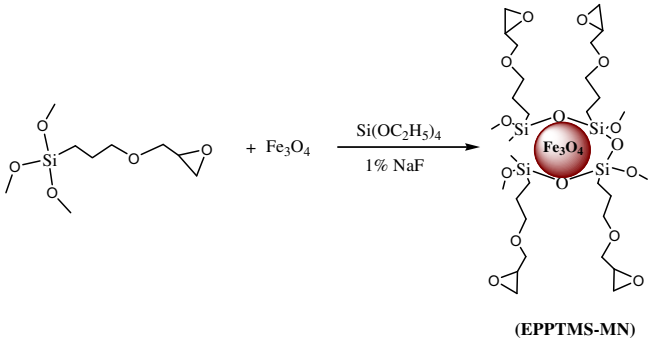
The main goal of this work was the design and synthesis of new calixarene derivatives (**4** and **5**) and exploration of their binding properties towards arsenate/dichromate anions and uranyl cations. Scheme 1 shows the route to the first target calixarene derivatives **4** and **5**. *p-tert*-Butylcalix[4]arene (**1**), diester derivative of *p-tert*-butylcalix[4]arene (**2**) and dialkyl bromide derivative of *p-tert*-butylcalix[4]arene (**3**) were synthesized by a modification of the



Scheme 1. The synthetic route for synthesis of **4** and **5**. Reaction conditions: (i) K_2CO_3, acetone, methyl bromo acetate; (ii) K_2CO_3, CH_3CN, NaI, 1,3-dibromopropane; (iii) toluene/methanol, 4-amino-1-benzylpiperidine; (iv) CH_3CN, K_2CO_3, NaI, 4-amino-1-benzylpiperidine.

literature route.[35–37] The substitution of diester derivative of *p*-*tert*-butylcalix[4]arene (**2**) was conducted in the presence of toluene/methanol with 4-amino-1-benzylpiperidine, which acts as a monoamine releasing agent with 20- to 48-fold selectivity for releasing dopamine versus serotonin,[38] to afford the cone conformer **DADBP-Calix** (**4**) in 54% yield. The formation of **DADBP-Calix** was confirmed by the appearance of the characteristic amide bands at about 1672 cm^{-1} and by the disappearance of the ester carbonyl band at 1750 cm^{-1} in the IR spectra. Reaction of dialkyl bromide derivative of *p*-*tert*-butylcalix[4]arene (**3**) with the 4-amino-1-benzylpiperidine in the presence of K_2CO_3 and NaI in CH_3CN gave the diamine derivative **DABP-Calix** (**5**) (42% yield). The ^1H NMR spectra of **4** or **5** have a typical AX pattern for the methylene bridge proton ($ArCH_2Ar$) of the calixarene moiety, respectively, at 3.42 and 4.15 ppm (J=13.2 Hz) or at 3.36 ppm (J=12.8 Hz) and 4.26 ppm (J=12.4 Hz), which demonstrates that the compound **4** and **5** exists in the cone conformation.[39]

It is well known that in extraction processes, separation is a time consuming task. In our previous studies,[4,29] we prepared silica based magnetic nanoparticles (see Scheme 2) and immobilized various calixarene derivatives onto its surface for easy separation of these from solvents by using a magnet. In view of this, in this study we immobilized two new calixarene derivatives **4** and **5** onto silica based magnetic nanoparticles surface (**EPPTMS-MN**) to prepare two new magnetic calixarene derivatives (**6** and **7**) as our second target (see Scheme 3). Binding properties of these calixarenes towards arsenate/dichromate anions and uranyl cations have been investigated. All new compounds have been characterized by ^1H NMR and IR spectroscopy, TGA, TEM and Elemental analyses techniques.



Scheme 2. Preparation of the **EPPTMS-MN**.

The magnetic (Fe_3O_4) nanoparticles and EPPTMS-modified Fe_3O_4 nanoparticles (**EPPTMS-MN**) were prepared according to the published procedures[4] (see Scheme 2). The immobilization of **4 or 5** onto **EPPTMS-MN** was carried out in the presence of NaH in THF/DMF to obtain magnetic calix[4]arene derivatives **6** or **7** (**M-DADBP-Calix or M-DABP-Calix**). The formation of **M-DADBP-Calix** or **M-DABP-Calix** (**6** or **7**) was confirmed by a combination of FTIR, TEM, TGA and elemental analysis.

In order to receive more direct information on the particle size and morphology, transmission electron microscopy (TEM) micrographs of pure Fe_3O_4 nanoparticles and magnetic calixarene derivatives (**M-DADBP-Calix** and **M-DABP-Calix**) were investigated (Fig. 1a–c). Observing the TEM micrographs (Fig. 1), nanoparticles formed dense aggregates due to the lack of any repulsive force between the magnetic nanoparticles, which is mainly due to the nano-size of the EPPTMS-modified Fe_3O_4, which is about 10±2 nm. This may be considered as indirect evidence that the magnetic core of the EPPTMS-modified magnetic particles consist of a single magnetic crystallite with a typical diameter of 8±3 nm, and that difference corresponds to the EPPTMS coating. After *p*-*tert*-butylcalix[4]arene immobilization, the dispersion of particles was improved greatly (Fig. 1b/c, for **6**/**7**), which can easily be explained by the electrostatic repulsion force and steric hindrance between the calix[4]arenes on the surface of Fe_3O_4 nanoparticles.

The thermal properties of **EPPTMS-MN** and magnetic calixarene derivatives (**M-DADBP-Calix** and **M-DABP-Calix**) were analyzed by the thermogravimetric method. The indication of coating formation on the magnetite nanoparticles surface can be obtained from the TGA measurement. Upon heating, the weight loss of EPPTMS-modified magnetite nanoparticles (**EPPTMS-MN**) was shown to be about 5% within a broad temperature range of 250 and 650 °C. The decomposition of both calix[4]arene units and 3-(2,3-epoxypropoxy)-propyl groups of **6** was observed as 22% between 325 and 550 °C. On the other hand, the weight loss of **7** indicated thermal degradation between 325 and 832 °C temperature ranges. The step arises from the decomposition of both calix[4]arene units and 3-(2,3-epoxypropoxy)-propyl groups (22% for **6**, 34% for **7**) (see Fig. 2).

FTIR spectroscopy was used to elaborate the structure of Fe_3O_4, EPPTMS-modified Fe_3O_4 and **CB-MN**s. The IR peak at 568 cm^{-1} belongs to the stretching vibration mode of Fe–O bonds in Fe_3O_4. Compared with the IR spectrum of EPPTMS-modified Fe_3O_4, the calix[4]arene derivatives (**6** and **7**) possessed peaks at 1646 cm^{-1} (for **6**) and 1648 cm^{-1} (for **7**), both of which are stretching vibrations of the amide carbonyl (N–C=O). The peaks at 1479, 1410 cm^{-1} (for **6**) and 1598, 1408 cm^{-1} (for **7**) are attributed to the bending vibration of the aromatic C=C bonds of the *p*-*tert*-butylcalix[4]arene derivatives. Additional peaks centered at 1044, 945, 789 cm^{-1} (for **6**), 1046, 950, 781 cm^{-1} (for **7**) and 1116, 1090, 955 cm^{-1} (for **EPPTMS-MN**) were most probably due to the symmetric and asymmetric stretching vibration of framework and terminal Si–O– groups (see Fig. 3a and b).

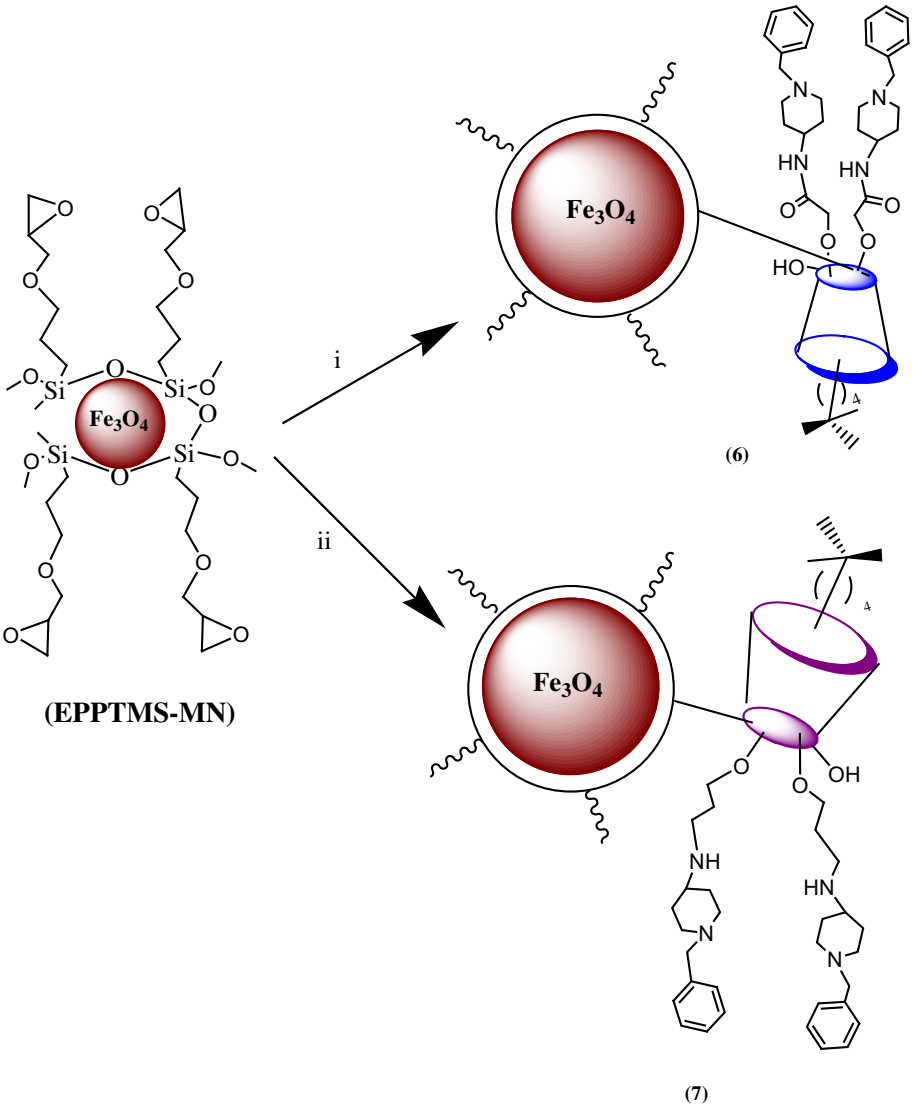
The elemental analysis results of **6** and **7**, given in Table 1, confirmed that the immobilization of calix[4]arene derivatives was accomplished. The amount of the loaded calix[4]arene derivatives **4** or **5** onto the polymeric support was evaluated from the results of elemental analysis. According to the elemental analysis, the resulting **6** and **7** contain 0.11% and 0.09% nitrogens corresponding to 0.32 mmol of **6**/g and 0.26 mmol of **7**/g of supports, respectively.

2.2. Two-phase solvent extractions

2.2.1. Dichromate anion. The removal of the dichromate anion from wastewater sources has gained high attention because of its highly toxic effects. It is well known that at pH<6, the oxyanions structure changes from the monomeric CrO_4^{2-} to the dimeric $HCr_2O_7^-$[40]. These oxides are potential sites for hydrogen bonding to the host molecule. For this purpose, we were interested in synthesizing two calix[4]arene derivatives at the lower rim, functionalized with 4-amino-1-benzylpiperidine as a host having proton-switchable binding lobes for extraction studies. A preliminary evaluation of the binding efficiencies of the hosts was carried out by liquid–liquid extraction of $Na_2Cr_2O_7$ from an aqueous solution at the range of pH 1.5–4.5. The binding efficiency of the diamine derivative **DABP-Calix** (**5**) was not evaluated due to its solubility in water at this pH range. The binding efficiencies of the other host (**DADBP-Calix**) were carried out by liquid–liquid extraction system of $HCr_2O_7^-$ from aqueous solution at different pH.

The extraction results (see Fig. 4) depicted that the diamide derivative **DADBP-Calix** (**4**) is an effective extractant at low pH between 1.5 and 4.5. The percentage of dichromate ions extracted was 23% when the pH of the aqueous solution was 1.5 and attained minimum 8% when pH of the aqueous solution increased to 4.5. The extractant **4** provides suitable binding sites for dichromate anions at the low pH due to the presence of protonable amine moieties.

Both to prevent solubility of **5** and to obtain a more rigid structure of **4** and **5**, the binding efficiencies of the magnetic calixarene derivatives (**M-DABP-Calix** and **M-DADBP-Calix**) were carried out by the solid–liquid extraction of $HCr_2O_7^-$ from an



Scheme 3. The synthetic routes for preparation of **6** and **7**. Reaction conditions: (i) **4**, NaH, THF/DMF; (ii) **5**, NaH, THF/DMF.

aqueous solution at different pH. The extraction results of **M-DADBP-Calix** (**6**) and **M-DABP-Calix** (**7**) are summarized in Fig. 5. These receptors (**6** and **7**) have increased the anion extraction ability of these compounds to a remarkable extent. It is clear that this pronounced increase is due to the more rigid structural features and protonation of the amine groups of **6** and **7**, which helps anion transfer. From the results, it is clear that these receptors (**6** and **7**) are more effective hosts for the removal of dichromate anions. Namely, the extraction data given in Fig. 5 indicates that the magnetic calix[4]arene derivatives (**6** and **7**) have notably increased the anion extraction ability. This increase can be explained by the fact that the magnetic calix[4]arene derivatives (**6** and **7**) are protonable in acidic conditions due to the presence of the amine groups and can easily form complexes with dichromate anions by electrostatic interactions and hydrogen bonding.

To understand the foreign anion effect on the dichromate anion, we examined the dichromate anion retentions of **4** by using different inorganic sodium salts (Cl^-, SO_4^{2-} and NO_3^-) as additives. The results given in Table 2 showed the retentions of dichromate anion with **4** in the presence of the other anions. The extraction of $Na_2Cr_2O_7$ with **4** was not affected greatly by the presence of the other sodium salts. Hence these new calixarene derivatives **4** could be used selectively in the presence of foreign anions.

2.2.2. Arsenate anion. For a molecule to be effective as a host, it is necessary that its structural features should be compatible with those of the guest anions. The arsenate species occur mainly in the form of $H_2AsO_4^-$ in the pH range between 3 and 6, while a divalent anion $HAsO_4^{2-}$ dominates at higher pH values (such as between pH 8 and 11). This is evident in the extraction of arsenate by calixarenes. In higher acidic conditions (pH 1–3) the arsenate ions will be protonated to generate the H_3AsO_4 form. Besides this, the monoanion ($H_2AsO_4^-$) will have a smaller free energy of hydration as compared to its dianionic form $HAsO_4^{2-}$. In brief, the arsenate ions ($H_2AsO_4^-$/$HAsO_4^{2-}$) are the dianions that have oxide moieties at the periphery of the anions. These oxides are potential sites for hydrogen bonding to the host molecule.

A preliminary evaluation of the extraction efficiencies of **DADBP-Calix** (**4**) has been carried out by the liquid–liquid extraction of arsenate ions from an aqueous solution into dichloromethane at the range of pH 3.5–7.0. The extraction result depicts that arsenate anion is efficiently extracted by **4** at pH 3.5–4.5. This is not a surprising result because extractant **4** contains the appropriate proton switchable amine binding sites for arsenate anions at different pH.

From the extraction results, the maximum extraction values (90% for **4**) occurs at pH 3.5 (see Fig. 6), which indicate that the best interaction between this ligand and arsenate ions occurs at this pH.

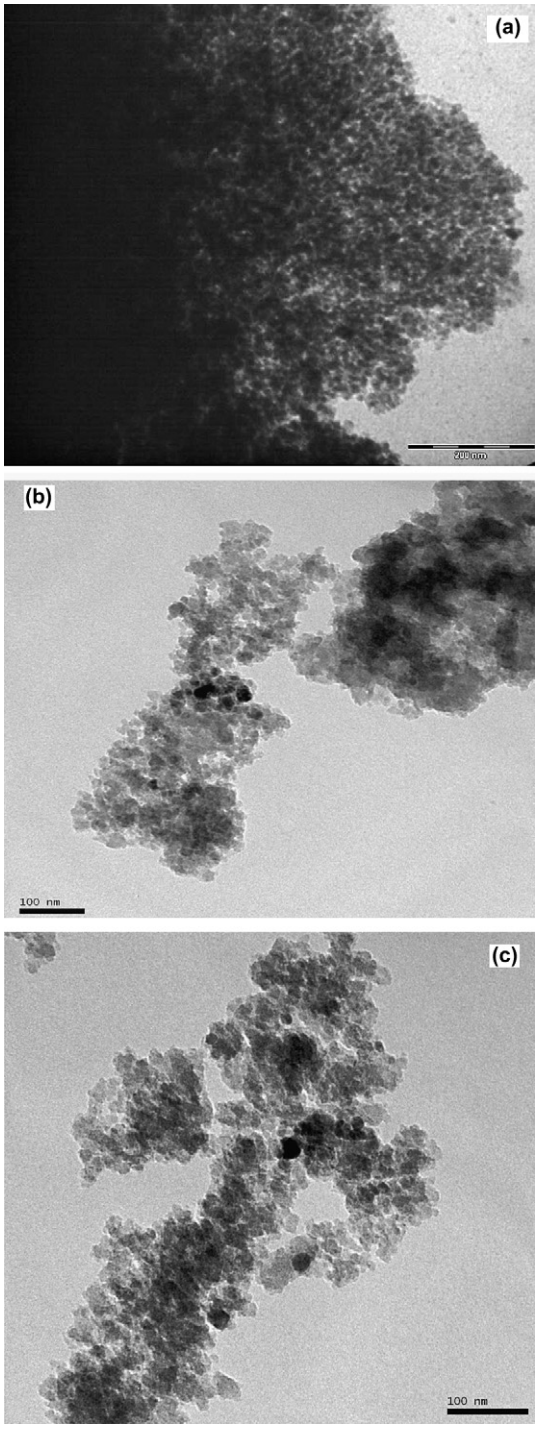


Fig. 1. TEM micrographs of (a) pure Fe_3O_4 nanoparticles, (b) **6**, (c) **7**.

These interactions include electrostatic interaction and hydrogen bonding between protonable amine and the oxygens of arsenate anions.[2,27]

The extraction binding efficiencies of **M-DADBP-Calix** (**6**), **M-DABP-Calix** (**7**) and **EPPTMS-MN** were carried out by solid–liquid extraction studies. The extraction results of **M-DADBP-Calix** (**6**), **M-DABP-Calix** (**7**) and **EPPTMS-MN** are summarized in Fig. 7. Magnetic ligands **6** and **7** contain amine groups, which are protonable in acidic conditions and easily form complexes with arsenate anions by electrostatic interactions and hydrogen bonding. Although, the magnetic support material **EPPTMS-MN** is hardly protonated under more acidic condition due to containing ether moieties, bearing magnetic property support extracts arsenate ion with 18% in the pH range of 3.5–4.5. The mainly maximum extraction value (91% for **6** and 73.8% for **7**) occurs at pH 3.5. This is reflected in these receptors (**6** and **7**), which have increased the arsenate ion extraction. The proposed interaction of **6** with these anions is given in Scheme 4.

2.2.3. Uranyl cation. The mobility of U(VI) is enhanced in oxidizing environments by the formation of uranyl (UO_2^{2+}), which hydrolyzes to form a number of aqueous hydroxyl species.[41] The hydrolysis reactions of UO_2^{2+} are listed in Table 3 according to the literature.[42]

It is well known that through a hydrolysis process, uranium may form a series of aqua-complexes, such as $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$.[43,44] The ratio of these species depends on the concentration of uranyl ions, concentration and on the pH of the solution. Over the 1.3–4.0 pH interval the predominant species are UO_2^{2+}, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$.[45] Increasing pH over 4.0, uranium adsorption decreases because in this range, the soluble complexes of uranyl ions are the predominant species.[46] At pH<4, only a low amount of non-hydrolyzed UO_2^{2+} ions are adsorbed. At pH<6, the uranyl contaminant solution results in the formation of uranium(VI)–hydroxo or uranium(VI)–aquo-complexes. At pH 5.3 the cationic uranium(VI) species, UO_2^{2+} and UO_2OH^+, are predominant in solution and the competition of protons, regarding cation exchange, is relatively low.[47,48]

Although several studies have been published regarding the host molecules, which act as complex for cations and anions, there is no example of a magnetic calixarene nanoparticles receptor that act as a host for the uranyl cation. Herein, we have designed the two new calixarene receptors (**DADBP-Calix** and **DABP-Calix**) and have also prepared their magnetic derivatives (**M-DADBP-Calix** and **M-DABP-Calix**) to convert into more rigid structural feature and primarily investigated their extraction capability towards U(VI). A preliminary evaluation of the extraction efficiencies of **DADBP-Calix** (**4**) and **DABP-Calix** (**5**) has been performed by liquid–liquid extraction of $UO_2(OAc)_2 \cdot 2H_2O$ from water into dichloromethane at different pH values. The extraction data (Fig. 8) showed that the maximum percentage of U(VI) extracted was almost the same (74%) both for **4** and **5** when the pH of the aqueous solution was 5.5 (for **4**) or 7.0 (for **5**).

The conversions of **4** and **5** into the magnetic derivatives **M-DADBP-Calix** and **M-DABP-Calix** have increased the uranyl extraction ability. This increase can be explained by the fact that the calixarene derivatives in the polymeric matrix may have gained a more rigid and appropriate structure, which assists the transfer of U(VI) when compared with monomers. The role of the silica based magnetic nanoparticles backbone was used to convert rigid structures of **4** and **5**. This implies a better preorganization of the immobilized calixarenes (**6** and **7**), which occurs with a cooperative effect of the amine groups and a number of donor atoms. This cooperative effect may improve extraction ability.

The solid–liquid extraction results show that **6** and **7** are the effective ligands for the removal of U(VI) in aqueous solution at pH 5.5–8.5 (see Fig. 9). The maximum sorption values of the magnetic calixarene derivatives occur at pH 8.0 (62% for **6**) and at pH 8.5 (61% for **7**).

The foreign cation effect on the U(VI) retention of **4** and **5** in the presence of different metal cations (Fe^{3+}, Ca^{2+}, K^+ and Na^+) was also examined. The results showed that the selective retention of U(VI) with **4** and **5** was affected by the presence of other cations (see Table 4). The extraction of U(VI) with **4** and **5** was affected by the presence of Fe^{3+} and Ca^{2+} cations. On the other hand, the extraction percentages of U(VI) was not affected by the presence of Na^+ and K^+ cations. In conclusion, all calixarene derivatives could be used selectively in the presence of cations like Na^+ and K^+ ions.

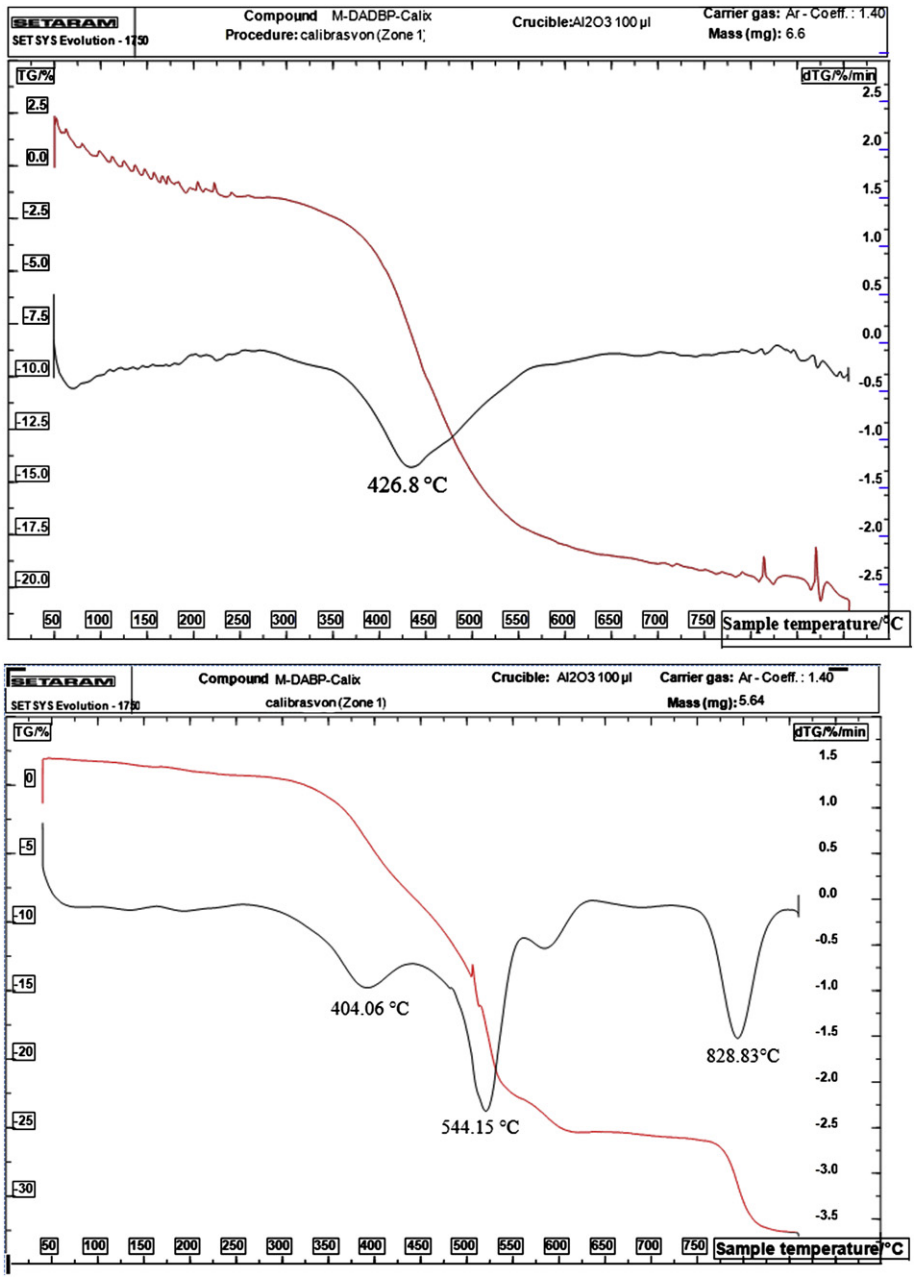


Fig. 2. TG and their first derivatives (dTG) of **6** and **7**.

3. Conclusion

In summary, two new calixarene derivatives (**4** and **5**) were synthesized and then immobilized onto the silica based magnetic nanoparticles surface (**EPPTMS-MN**) to impact both more rigid structural features and to prevent solubility of the compounds. This immobilization provides an efficient way to improve the separation capability of the calixarene compositae silica carriers due to their magnetic properties. Additionally, extraction capability of these new calixarene derivatives were investigated towards As(V), Cr(VI) and U(VI) ions. The complexation studies by these ions showed that these calixarene derivatives were effective extractants for the removal of As(V), Cr(VI) and U(VI) from the aqueous solution. The extraction results reflect that the complexation of arsenate/dichromate anions and the uranyl cation depends on the structural properties of the receptors, such as stability or rigidity, proton-switchable ability and hydrogen binding ability.

4. Experimental

4.1. Apparatus

Melting points were determined on a Gallenkamp apparatus in a sealed capillary glass tube and are uncorrected. ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer. IR spectra were obtained on a Perkin–Elmer 1605 FTIR spectrometer using KBr pellets. UV–vis spectra were obtained on a Shimadzu 160A UV–vis spectrophotometer. Elemental analyses were performed using a Leco CHNS-932 analyzer. Thermogravimetric analyses (TGA) was carried out with Seteram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from room temperature to 900 °C at a heating rate of 10 °C/min under argon atmosphere with a gas flow rate of 20 mL/min. An Orion 410A+ pH metre was used for the pH measurements.

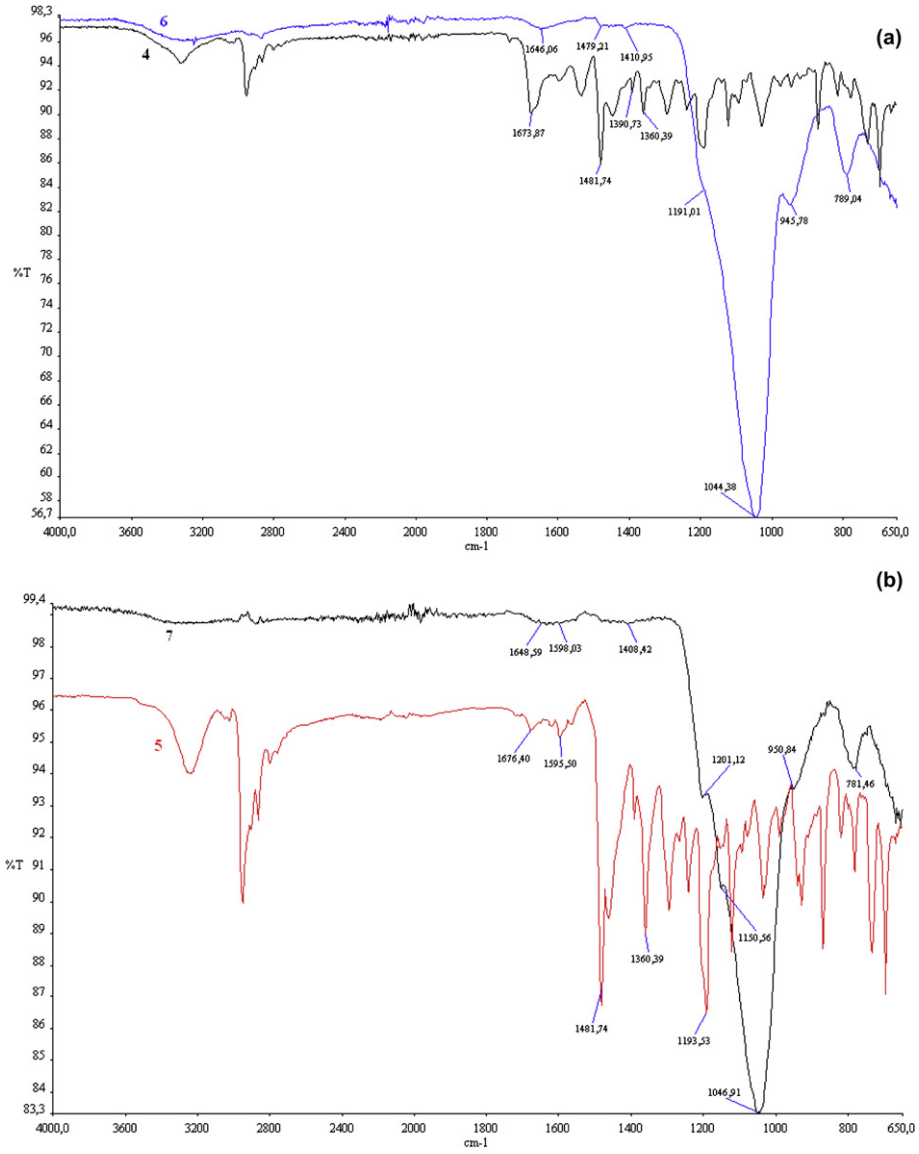


Fig. 3. (a) The IR spectrum of **4** and **6**. (b) The IR spectrum of **5** and **7**.

Table 1
Results of elemental analysis for **EPPTMS-MN**, **6** and **7**

	C (%)	H (%)	N (%)	Bounded amount[a] (mmol/g)
6	15.09	3.12	0.11	~0.32
7	12.69	2.77	0.09	~0.26
EPPTMS-MN	13.20	2.61	—	—

[a] Calculated according to the N content.

4.2. Materials

TLC analyses were carried out on DC Alufolien Kieselgel 60 F_{254} (Merck). Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). All reactions, unless otherwise noted, were conducted under a nitrogen atmosphere. All starting materials and reagents used were of standard analytical grade from Merck or Aldrich and used without further purification. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. CH_2Cl_2 was distilled from $CaCl_2$, while MeOH was distilled over Mg and stored over molecular sieves. All commercial grade solvents were distilled, and then stored over molecular sieves. The drying agent employed was anhydrous magnesium sulfate. All aqueous solutions were prepared

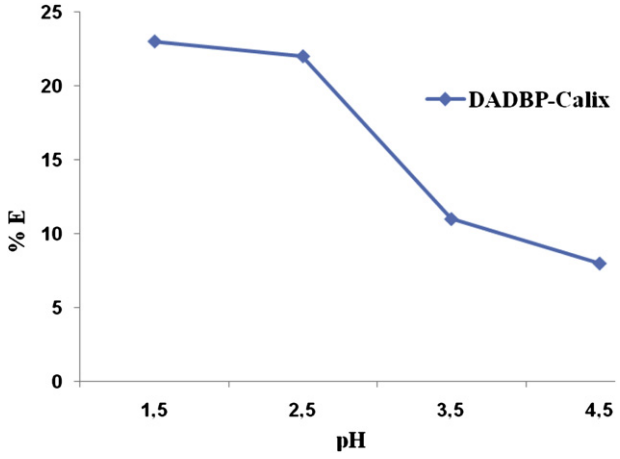


Fig. 4. Extraction percentages of dichromate anion with **4** at pH 1.5–4.5. (H_2O/CH_2Cl_2: 10/10 (v/v); sodium dichromate 1×10^{-4} M; ligand: 1×10^{-3} M, 1 h. 25 °C).

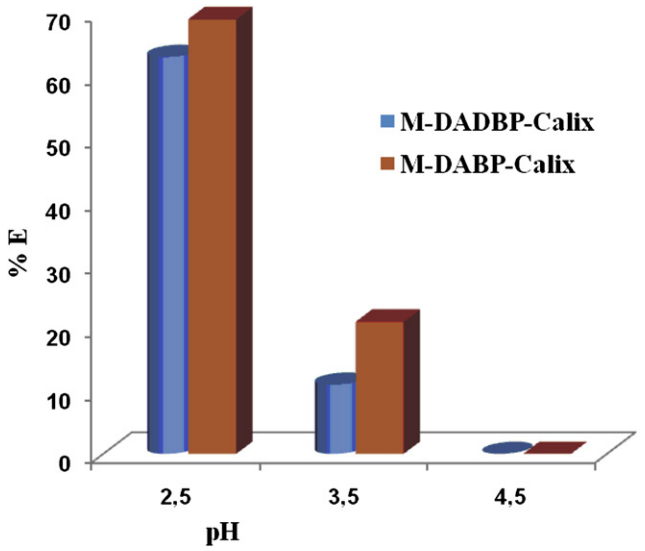


Fig. 5. Extraction percentages of dichromate anion with **6** and **7** at pH 2.5–4.5. (Solid phase, sorbent=25 mg (**6**,**7**), aqueous phase, $Na_2Cr_2O_7$=1.0×10^{-4} M (10 mL) at 25 °C for 1 h).

Table 2
Dichromate retention results of **4** pH 1.5, in the presence of foreign anions (Cl^-, SO_4^{2-} and NO_3^-) and their mixtures

	Different anions				
	None	Cl^-	SO_4^{2-}	NO_3^-	Mixture
4	23	22.77	22.69	20.32	18.21

[Sodium dichromate]=1.0×10^{-4} M; ligand **4**=1.0×10^{-3} M at 25 °C, pH 1.5.
The concentration of different anions=1.0×10^{-2} M.

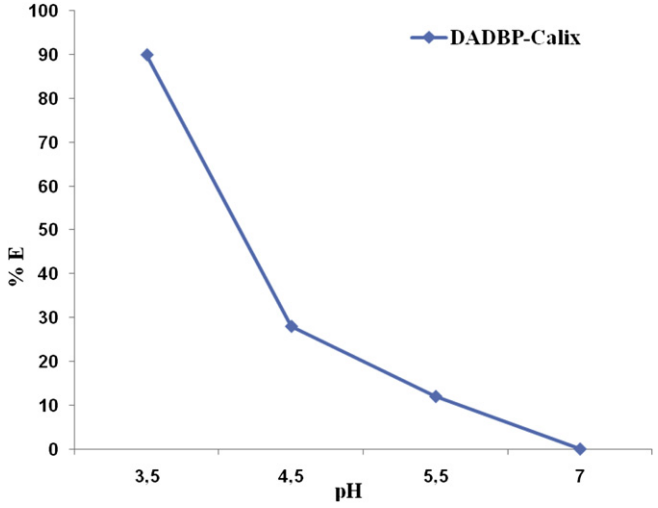


Fig. 6. Extraction percentages of arsenate anion with **4** pH 3.5–7.0. (H_2O/CH_2Cl_2: 10/10 (v/v); Na_2HAsO_4=1×10^{-5} M; ligand: 1.10^{-3} M, 1 h. 25 °C).

with deionized water that was passed through a Millipore milli-Q Plus water purification system. Anions were used as their sodium salts. Ammonium molybdate solution (3.15×10^{-2} M), methyl violet solution (4.5×10^{-5} M) and hydrochloric acid solution (6.85 M) were prepared by dissolving the reagents in doubly distilled water. Arsenazo III, uranyl acetate dihydrate were purchased from Fluka. Standard stock solution of 0.9787 μg/mL uranium (VI) was prepared by dissolving the appropriate amounts of uranyl acetate dihydrate in deionized water. A stock

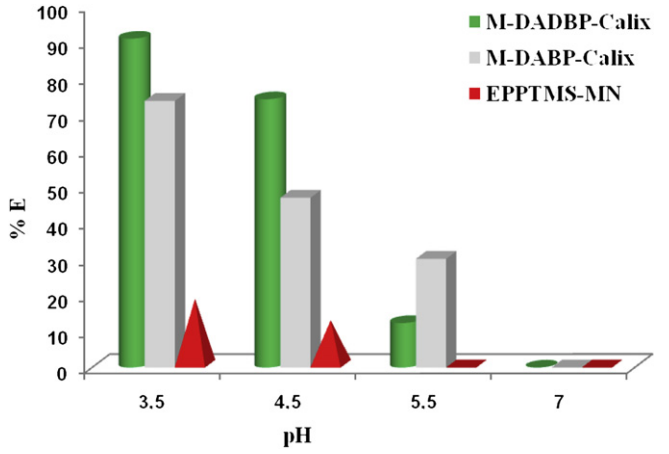


Fig. 7. Extraction percentages of arsenate anion with **6** and **7** at pH 3.5–7.0. (Solid phase, sorbent=25 mg (**6**,**7**), aqueous phase, Na_2HAsO_4=1.0×10^{-5} M (10 mL) at 25 °C for 1 h).

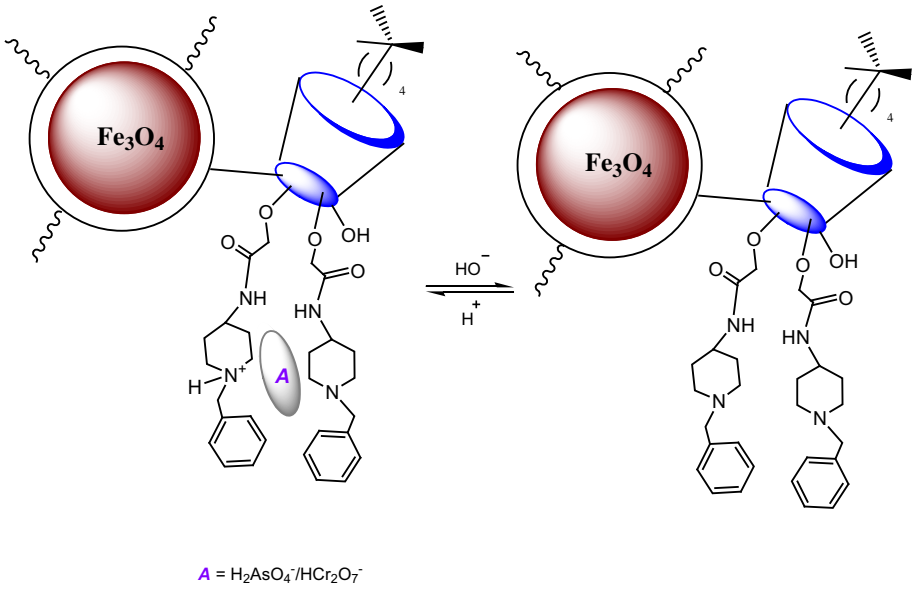
arsenazo III solution (0.01%) was prepared by dissolving reagent. Adjusting the pH values of the working solutions was carried out using 5 M of sodium acetate buffer to determination of UO_{22+} in aqueous solution.

4.3. Synthesis

The compounds **1**–**3** were synthesized by procedures published in the literature.[35–37] Silica based magnetic nanoparticles (**EPPTMS-MN**) was synthesized in our previously study.[4] Compounds **4** and **5** and magnetic derivatives of calix[4]arene (**6** and **7**) are herein reported for the first time.

*4.3.1. Synthesis of p-tert-butylcalix[4]arene diamide **DADBP-Calix** (**4**).* The diester derivative of *p-tert*-butylcalix[4]arene **2** (2.0 g, 2.52 mmol) was dissolved in toluene/methanol [2/1] (33 mL). 4-Amino-1-benzylpiperidine (4.8 g, 25.22 mmol) was added into this solution and the reaction mixture was stirred and heated at reflux. The reaction was monitored by using combinations of TLC and IR. After 10 days, most of the solvent was evaporated under reduced pressure and the resulting solid was dissolved in dichloromethane and washed three times with distilled water. The crude product was purified by column chromatography (SiO_2, EtOAc/*n*-hexane; 2:1). Yellow powder 54% yield mp: 195–197 °C. The IR spectral data is as (KBr disk) cm^{-1}: 1672 (amide carbonyl band, N–C=O). ^{1}H NMR (400 MHz $CDCl_3$): δ 1.06 (s, 18H, ^{t}Bu), 1.28 (s, 18H, ^{t}Bu), 1.64 (q, 8H, *J*=10.6 Hz, $-CH_2-$), 2.15 (t, 8H, *J*=11.2 Hz, $-CH_2-$), 3.42 (d, 4H, *J*=13.2 Hz, Ar$-CH_2-$Ar), 3.44 (s, 4H, $-CH_2-$), 3.89 (m, 2H, –CH–), 4.15 (d, 4H, *J*=13.2 Hz, Ar$-CH_2-$Ar), 4.55 (s, 4H, $-CH_2-$), 6.94 (s, 4H, ArH), 7.08 (s, 4H, ArH), 7.27 (m, 10H, ArH), 7.83 (s, 2H, –OH), 8.97 (d, 2H, *J*=7.6 Hz, –NH–). Anal. Calcd for $C_{72}H_{92}N_4O_6$: C, 77.94; H, 8.36; N, 5.05. Found (%); C, 78.02; H, 8.28; N, 5.10.

*4.3.2. Synthesis of p-tert-butylcalix[4]arene diamine **DABP-Calix** (**5**).* To a solution of dialkyl bromide of *p-tert*-butylcalix[4]arene (**3**) (1.0 g, 1.12 mmol) in CH_3CN (30 mL) were added K_2CO_3 (1.6 g, 11.58 mmol), NaI (0.7 g, 4.67 mmol) and 4-amino-1-benzylpiperidine (4.8 mL, 25.48 mmol) and the reaction mixture was stirred and heated at reflux. The reaction was monitored by using a TLC. After 97 h, the reaction mixture was filtered and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (150 mL) and the organic layer extracted three times with water. The combined organic phases were dried (anhydrous $MgSO_4$), the solvent was removed under reduced pressure; and the crude product was purified by column chromatography (SiO_2, $CHCl_3$/MeOH; 10:1).



Scheme 4. The suggested complexation phenomena of arsenate and dichromate ion with **6**.

Table 3
Equilibrium constants

Reaction	Log *K*
Aqueous speciation	
$UO_2^{2+}+H_2O=UO_2(OH)^{+}+H^{+}$	−5.20[a]
$2UO_2^{2+}+2H_2O=(UO_2)_2(OH)_2^{2+}+2H^{+}$	−5.62[a]
$3UO_2^{2+}+5H_2O=(UO_2)_3(OH)_5^{+}+5H^{+}$	−15.55[a]
$UO_2^{2+}+3H_2O=UO_2(OH)_3^{-}+3H^{+}$	−21.0[a]
Ion exchange reactions	
$UO_2^{2+}+2X^{-}=UO_2X_2$	30.9[b,c]
$UO_2(OH)^{+}+X^{-}=UO_2(OH)X$	8.6[c]
$(UO_2)_3(OH)_5^{+}+X^{-}=(UO_2)_3(OH)_5X$	−1.75[c]

[a] Literature.[42]
[b] Fixed relative to Na^+ constant.
[c] Literature.[41]

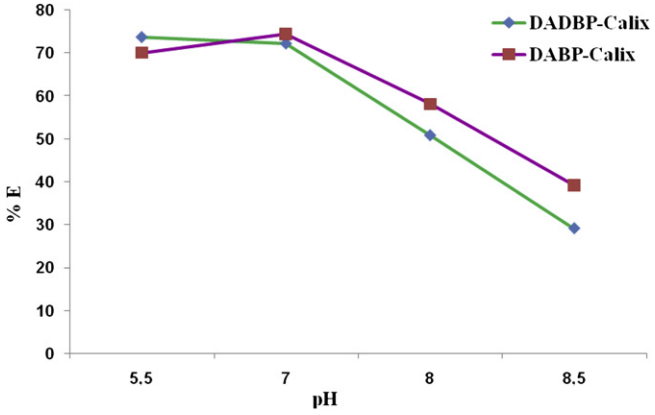


Fig. 8. The extraction percentages of uranyl cation with **4** and **5** at pH 5.5–8.5. (10 mL, 1.15×10^{-5} M) $UO_2(AcO)_2\cdot2H_2O$, calix[4]arene derivatives (10 mL of 1×10^{-3} M solution of **4** or **5** in CH_2Cl_2), 175 rpm, 25 °C for 1 h.

Yellow powder 42% yield mp: 161–162 °C. ^{1}H NMR (400 MHz $CDCl_3$): δ 1.19 (s, 18H, ^{t}Bu), 1.22 (s, 18H, ^{t}Bu), 1.66 (m, 8H, $-CH_2-$), 2.05 (t, 8H, J=11.2 Hz, $-CH_2-$), 2.26 (m, 4H, $-CH_2-$), 2.36 (m, 4H, $-CH_2-$), 3.36 (d, 4H, J=12.8 Hz, Ar$-CH_2-$Ar), 3.45 (m, 2H, $-CH-$), 3.52 (s, 4H, $-CH_2-$), 3.56 (t, 2H, J=6.4 Hz, $-NH$), 4.01 (t, 4H, J=4.8 Hz, $-CH_2-$), 4.26 (d, 4H, J=12.8 Hz, Ar$-CH_2-$Ar), 7.00 (s, 4H, ArH), 7.08 (s, 4H, ArH), 7.26 (s, 2H, $-OH$), 7.32 (m, 10H, ArH). Anal. Calcd for $C_{74}H_{100}N_4O_4$: C, 80.10; H, 9.08; N, 5.05. Found (%); C, 79.94; H, 9.11; N, 5.07.

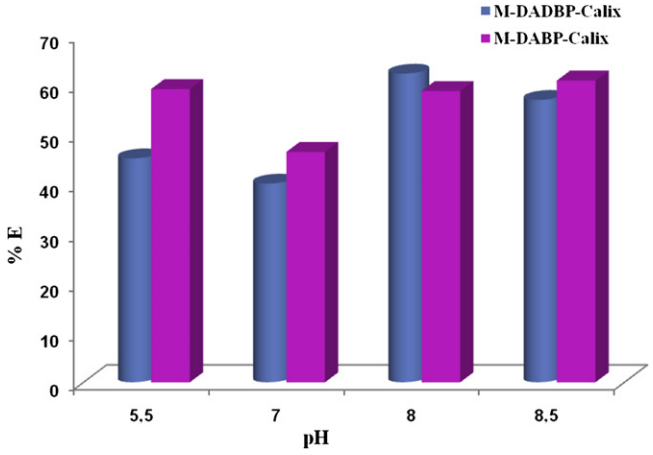


Fig. 9. Extraction percentages of uranyl cation with **6** and **7** at pH 5.5–8.5 (10 mL, 1.15×10^{-5} M) $UO_2(AcO)_2\cdot2H_2O$, magnetic calix[4]arene nanoparticles (25 mg of **6** or **7**), 175 rpm, 25 °C for 1 h.

Table 4
Uranyl retention results of **4** (pH 5.5) and **5** (pH 7.0), in the presence of foreign cations (Fe^{3+}, Ca^{2+}, Na^+ and K^+)

	Different cations				
	None	Fe^{3+}	Ca^{2+}	Na^+	K^+
4	73.7	0	14.6	73.0	73.4
5	74.5	0	14.8	73.8	74.1

Uranyl acetate dihydrate=1.15×10^{-5} M; **4** or **5**=1.0×10^{-3} M at 25 °C.
The concentration of different cations=1.15×10^{-3} M.

*4.3.3. General procedure for the preparation of magnetic p-tert-butylcalix[4]arene derivatives **M-DADBP-Calix** (**6**) and **M-DABP-Calix** (**7**).* A mixture of functionalized *p-tert*-butylcalix[4]arene derivative (**4** or **5**) (0.3 g) and NaH (0.05 g) in a solution of THF/DMF (20 mL, 3/1) was stirred for 30 min then **EPPTMS-MN** (0.9 g) was added, and the solution heated under reflux for 5 days. After magnetic separation, the resulting compound was washed with dichloromethane three times to remove excess of functionalized

p-tert-butylcalix[4]arene derivative, then washed with water and dried under vacuum.

For **6**: the IR spectral data is as (KBr disk) cm^{-1}: 3251, 1646 (amide C=O), 1479, 1410 (aromatic C=C), 1191, 1044, 945, 789 (Si–O) and 572 (Fe–O).

For **7**: the IR spectral data is as (KBr disk) cm^{-1}: 3424, 1648 (amine band), 1598, 1408 (aromatic C=C), 1150, 1046, 950, 781 (Si–O) and 574 (Fe–O).

4.4. Extraction studies

4.4.1. Dichromate/arsenate anion extraction studies. The extraction capacities of the synthesized calixarene derivatives (**4**–**7**) were determined by the following technique.[2] An aqueous solution (10 mL) containing $Na_2Cr_2O_7$ or Na_2HAsO_4 solution at a concentration of 1.0×10^{-4} M and calixarene derivative (10 mL of 1×10^{-3} M solution of **4** or **5** in CH_2Cl_2 for liquid–liquid extraction, 25 mg of **6** or **7** for solid–liquid extraction) were mixed in a stoppered flask that was shaken at 175 rpm at 25 °C for 1 h. The ligands were separated before measurements. The residual dichromate concentration was determined spectrophotometrically by UV–vis analysis at 346 nm as described previously.[49] The concentration of arsenate ion remaining in the aqueous phase was determined spectrophotometrically at 610 nm as described previously.[50] The effect of pH was studied by adjusting the pH of the aqueous solutions using diluted HCl and KOH solutions at 25 °C. The experiments were performed in triplicate.

The percent extraction (E %) was calculated according to Eq. 1;

$$(E\%) = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

where A_0 and A are the initial and final concentrations of the dichromate/arsenate or uranyl ion before and after the extraction, respectively.

4.4.2. Uranyl cation extraction studies. Into a vial was pipetted an aqueous solution (10 mL) containing $UO_2(AcO)_2\cdot2H_2O$ at a concentration of 1.15×10^{-5} M, a few drops of 0.01 M KOH/HCl solution in order to obtain the desired pH at equilibrium and maintain the ionic strength, and calix[4]arene derivatives (10 mL of 1×10^{-3} M solution of **4** or **5** in CH_2Cl_2 for liquid–liquid extraction, 25 mg of **6** or **7** for solid–liquid extraction). The mixture was vigorously agitated in a stoppered glass vial with a mechanical shaker for 2 min, then was shaken at 175 rpm at 25 °C for 1 h. The ligands were separated before measurements. The residual uranyl concentration of aqueous solute was determined spectrophotometrically.[51]

Blank experiments showed that no uranyl extraction occurred in the absence of calixarene. The uranyl cation in aqueous phase measured at 652 nm (for pH 5.5–8.5). The percent sorption (E %) was calculated[52] according to the above equation.

4.5. Selectivity studies

4.5.1. Anion selectivity studies. Selectivity studies of **4**–**7** were performed in the presence of different sodium salts nitrate (NO_3^-), sulfate ($SO_{4^{2-}}$) and chloride (Cl^-) anions since they could be present more than dichromate anions in aqueous solutions. For this purpose, anions were used as corresponded with one hundred-fold of dichromate anion concentration and determined according to the literature.[2]

4.5.2. Cation selectivity studies. Selectivity studies of **4**–**7** were performed in the presence of Fe^{3+}, Ca^{2+}, K^+ and Na^+ cations since they could be present more than uranyl cation in aqueous solutions. For this propose, cations were used as corresponded with one hundred-fold of uranyl cation concentration.

Acknowledgements

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