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Synthesis and properties of novel magnetic nanoparticles grafted with nitropyridine-substituted calix[4]arene derivative as Cr^{6+} extractant

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Abstract: A new calix[4]arene derivative, **3**, which functionalized at the lower rim with 2-(2-aminoethyl amino)-5-nitropyridine, was synthesized and characterized by a combination of FTIR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. Then the calix[4]arene **3** was grafted onto [3-(2,3-epoxypropoxy)propyl]trimethoxysilane-modified Fe_3O_4– nanoparticles (EPPTMS-MN) to produce new calixarene-adorned magnetic nanoparticles (MN-DiNoPy-Calix (**4**)). The structure of the calixarene-adorned magnetic nanoparticles **4** was determined by a combination of FTIR, TEM, and elemental analysis. Moreover, a study regarding the removal of toxic $HCr_2O_7^-$ anion from aqueous solution was also carried out with the calixarene-adorned magnetic nanoparticles in solid–liquid extraction studies.

Key words: Calixarene, proton-switchable, magnetic nanoparticles, dichromate anion, solid–liquid extraction

1. Introduction

Although it has a wide variety of industrial uses, chromium is highly toxic and hazardous to humans. Transmitted to the environment via effluents produced in processes such as textile dyeing, mining, photography, and steel fabrication,[1–4] chromium in the aqueous phase can occur in several oxidation forms. However, only the Cr(III) and Cr(VI) states are environmentally significant.[5] Chromium(III) provides essential micronutrients to various organisms, while chromium(VI) has extremely toxic and carcinogenic influences on biological systems due to the strongly oxidizing biological anions $Cr_2O_7^{2-}$ and $HCr_2O_7^-$.[6–8] Therefore, developing a method that uses low-cost materials to remove oxidized forms of Cr(VI) from contaminated wastewater is essential.

One recent challenge has been to develop receptors that selectively respond to the removal of toxic as well as carcinogenic ions, like Cr(VI), from contaminated water resources.[9–12] Among these receptors, calixarenes,[4,8] which are produced by a condensation reaction of phenol and formaldehyde, have been successfully employed as receptors for the extraction of dichromate anions from aqueous solutions.[13–17] Because of their unique structure, which provides host–guest complexability and unlimited functionalization properties, calixarenes[13,16] have been found to be magnificent supramolecular compounds.[18–20]

Although calixarene derivatives have been used as receptors for the removal of toxic ions such as dichromate anions, they have led to a separation concern arising from the final step of the extraction. Moreover, some calixarene derivatives might be soluble in the aqueous phase, which is when the wastewater is contaminated. To address these disadvantages, calixarene-grafted magnetic nanoparticles[4,16] have recently been developed so that calixarene derivatives may acquire magnetic properties that prevent their solubility in water.[21,22]

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In our previous study, a disubstituted calixarene derivative containing pyridinium units was synthesized and grafted onto Fe_3O_4 nanoparticles to use as receptor for the extraction of dichromate anions (see Figure 1). The magnetic nanoparticles-grafted calix[4]arenes were found to be effective ligands with maximum extraction capabilities of 69% (for **MN-Py-1**) and 53% (for **MN-Py-2**) at pH 3.5 with respect to their convenient complexability with dichromate anions.[23]

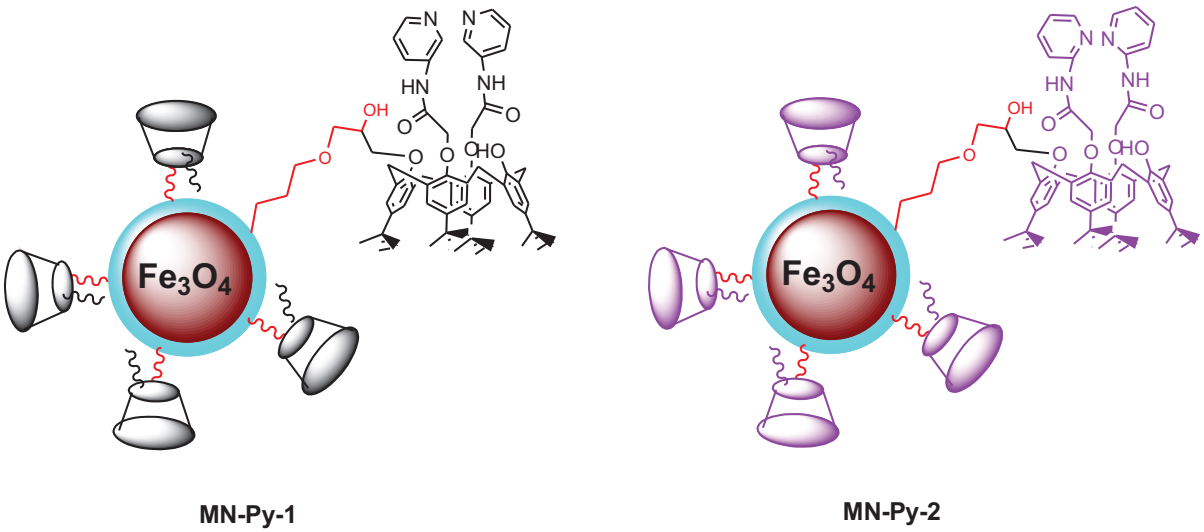


Figure 1. Structures of the magnetic nanoparticles-grafted calix[4]arenes (**MN-Py-1** and **MN-Py-2**).

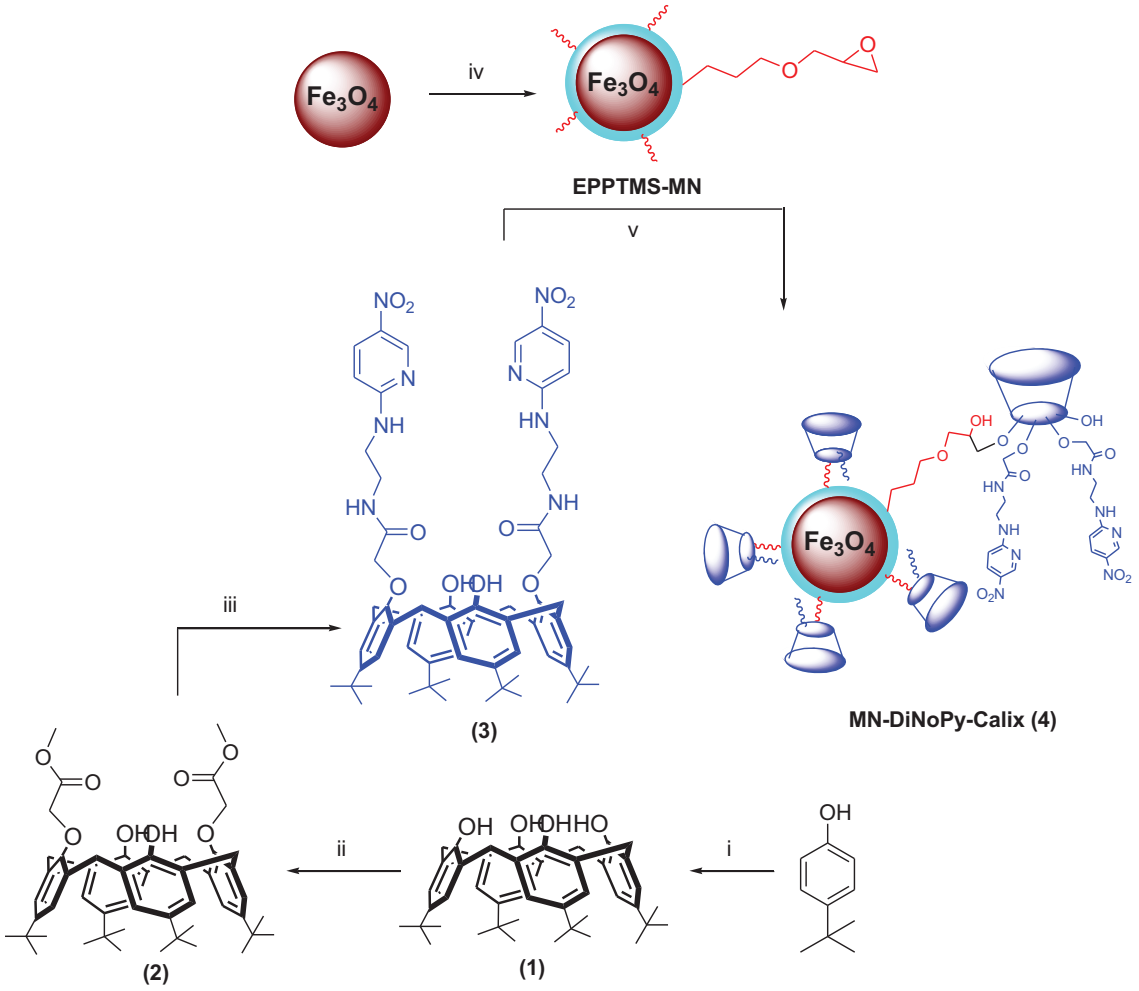
In the present study, we aimed to prepare new calixarene-grafted magnetic nanoparticles that would be used as potential receptors for the removal of toxic dichromate anions from aqueous solutions. For this purpose, the bis(nitropyridine)-substituted calix[4]arene **3** was synthesized and then immobilized onto silica-coated magnetic nanoparticles to easily form complexes with dichromate anions by means of electrostatic interactions and hydrogen bonding.

2. Results and discussion

2.1. Synthesis and characterizations of new receptors

The objective of this study was to synthesize bis(nitropyridine)-substituted calix[4]arene **3** and its magnetic nanoparticles (**MN-DiNoPy-Calix**). Moreover, their extraction attractions towards dichromate ions were evaluated for the first time. To achieve this goal, *p-tert*-butylcalix[4]arene **1** and its diester derivative **2** were synthesized according to procedures outlined previously.[24,25] The substitution of the diester derivative **2** at the lower rim was conducted with 2-(2-aminoethylamino)-5-nitropyridine to afford 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-nitropyridin-2-ylamino)ethyl**amino**carbonyl-methoxy)-26,28-dihydroxy calix[4]arene **3** (Scheme). The synthesized new compound **3** was fully characterized by a combination of FTIR, ^{1}H NMR, ^{13}C NMR, and elemental analysis techniques.

The FTIR spectra of the bis(nitropyridine)-substituted calix[4]arene **3** confirm its structure by its characteristic peaks at 1670 cm^{-1} belonging to the vibration stretch of C=O bonds, as well as at 1481 and 1291 cm^{-1}, which are stretching vibrations of the NO_2 group.



Scheme. Synthesis of **MN-DiNoPy-Calix**. Reaction conditions: i) HCHO, NaOH; ii) methylbromoacetate, K_2CO_3, CH_3CN; iii) 2-(2-aminoethylamino)-5-nitropyridine, CH_2Cl_2/CH_3OH; iv) 3-(2,3-epoxypropoxy)propyl]trimethoxysilane, tetraethyl orthosilicate, NaF, H_2O; v) NaH, THF/DMF.

As seen in the ^{1}H NMR spectrum of the bis(nitropyridine)-substituted calix[4]arene **3**, there are 2 doublets at 3.28 and 3.91 ppm (J = 13.2 Hz), which indicate compound **3** exists in the cone conformation (Figure 2). In addition, the protons of the amide group, and the aromatic protons of the pyridine appeared at 8.94 ppm (–NH), and 8.11 (ArH), 8.25 (ArH), and 8.79 ppm (ArH) in the ^{1}H NMR spectra (Figure 2). The ^{13}C NMR spectra present useful information about the structure of the bis(nitropyridine)-substituted calix[4]arene **3** by the peak at 169.72 ppm, which belongs to the C=O groups (Figure 3).

The iron oxide magnetic nanoparticles and epoxysilica-coated Fe_3O_4 nanoparticles (**EPPTMS-MN**) were prepared according to the literature.[4,26] **MN-DiNoPy-Calix** (**4**) was prepared by the immobilization of calix[4]arene **3** onto [3-(2,3-epoxypropoxy)-propyl]-trimethoxysilane-coated Fe_3O_4 nanoparticles (**EPPTMS-MN**) in the presence of NaH in THF/DMF (Scheme). The structure of the novel calix[4]arene-grafted magnetic nanoparticles **MN-DiNoPy-Calix** (**4**) was determined by a combination of FTIR, TEM, and elemental analysis techniques.

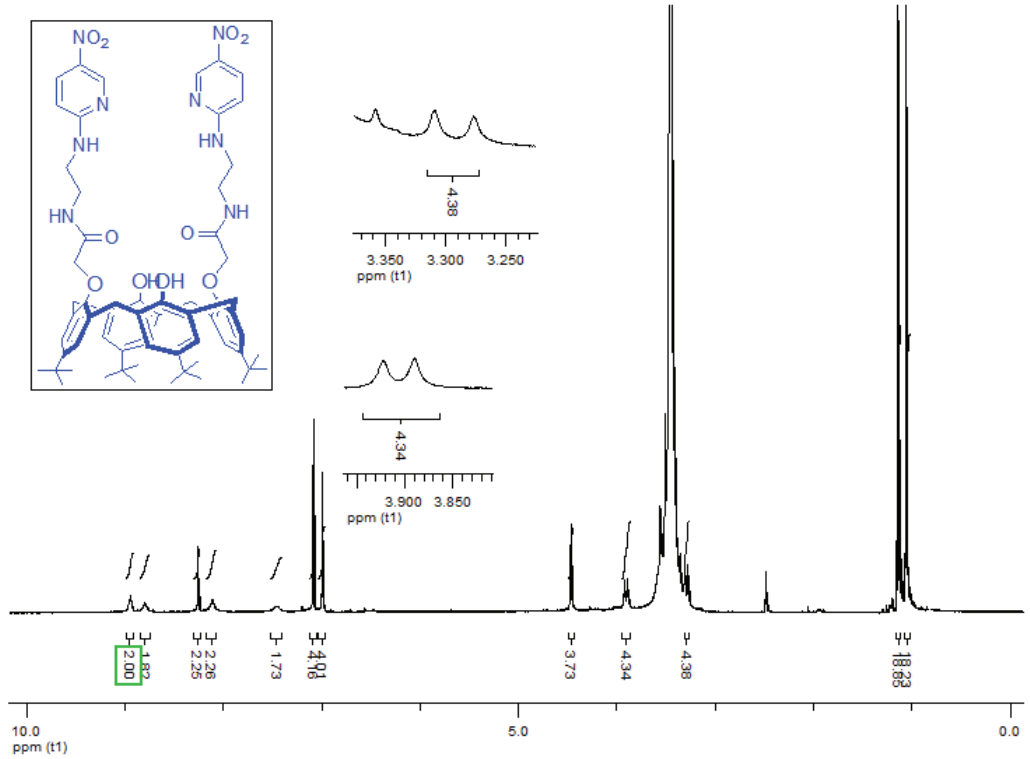


Figure 2. [1] H NMR spectrum of the bis(nitropyridine)-substituted calix[4]arene **3**.

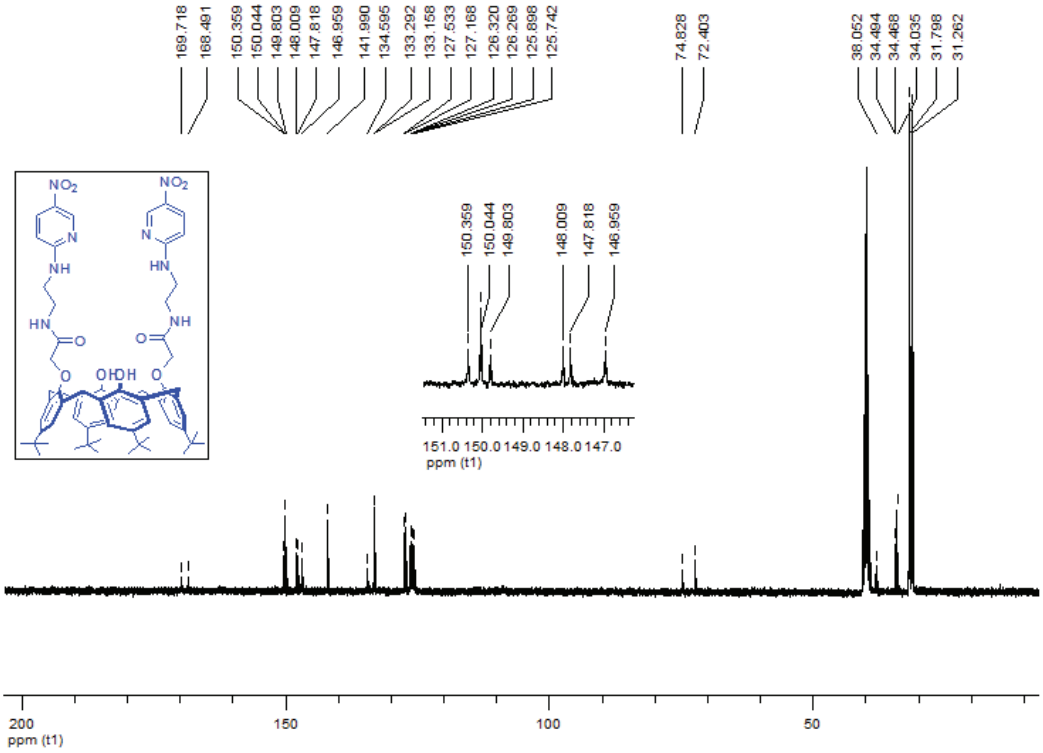


Figure 3. [13] C NMR spectrum of the bis(nitropyridine)-substituted calix[4]arene **3**.

In order to elaborate the structure of **MN-DiNoPy-Calix** (**4**), FTIR spectroscopy was used. Its characteristic peaks appeared at 1456 and 1411 cm^{-1}, which are stretching vibrations of the aromatic C=C bonds, and a peak at 1634 cm^{-1} belonging to C=O groups. The characteristic vibration bend of N–O and Fe–O groups centered at 1479 cm^{-1} (N–O stretch) and 560 (Fe–O stretch) can also be found. Additional peaks of **MN-DiNoPy-Calix** (**4**) that appeared at 1107, 958, and 799 cm^{-1} may result from the symmetric and asymmetric vibration bends of framework and terminal Si–O groups (Figure 4).

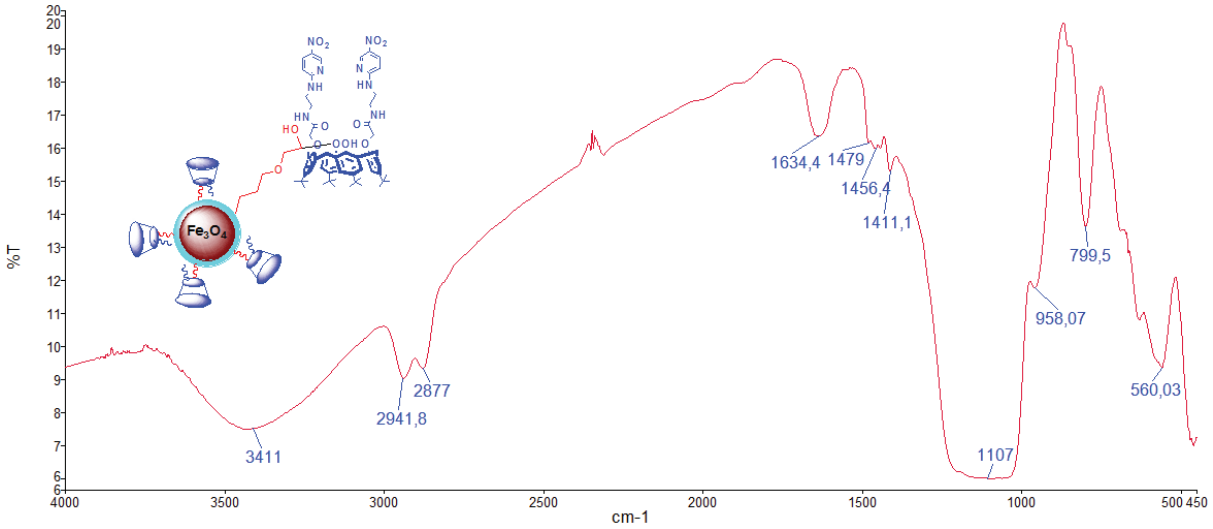


Figure 4. FTIR spectra of **MN-DiNoPy-Calix** (**4**).

Transmission electron microscopy (TEM) analysis of pure Fe_3O_4 nanoparticles (Figure 5a) and **MN-DiNoPy-Calix** (Figure 5b) was used, respectively, to obtain more direct information about particle size and morphology (Figure 5). As seen in the micrographs, **MN-DiNoPy-Calix** has a distinctly different morphology

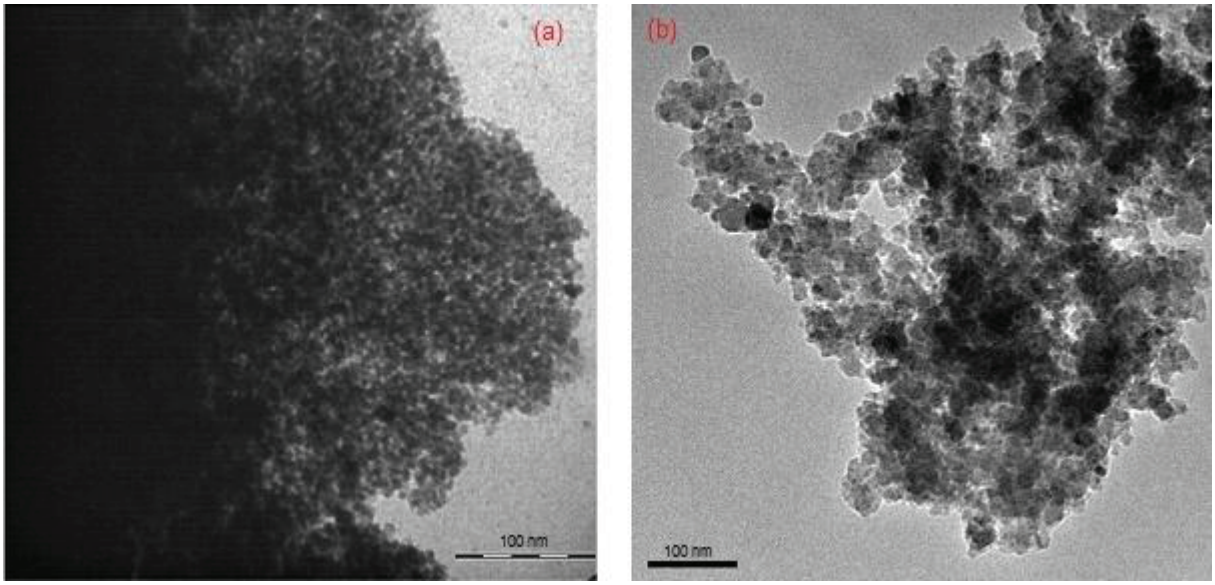


Figure 5. TEM micrographs of (a) pure Fe_3O_4 nanoparticles, (b) **MN-DiNoPy-Calix** (**4**).

than Fe_3O_4 nanoparticles; the latter have a single magnetic crystallite with a typical size range of 8 ± 3 nm. After immobilization of the bis(nitropyridine)-substituted calix[4]arene **3**, an increase in the particle dispersion was observed (Figure 5b). This increase might have been due to the electrostatic repulsion force and steric hindrance between the bis(nitropyridine)-substituted calix[4]arene units on the surface of Fe_3O_4 nanoparticles.

The elemental analysis results of **MN-DiNoPy-Calix** confirmed that the bis(nitropyridine)-substituted calix[4]arene **3** was successfully grafted onto **EPPTMS-MN** (Table). The results showed that **MN-DiNoPy-Calix** contains 0.42% nitrogen corresponding to 2.40 mmol of **MN-DiNoPy-Calix**/g of support.

Table. Elemental analysis results of **EPPTMS-MN** and **MN-DiNoPy-Calix**.

	C (%)	H (%)	N (%)	Bound amount (mmol/g)[a]
EPPTMS-MN	13.20	2.61	-	-
MN-DiNoPy-Calix	14.53	2.90	0.42	2.40

[a]Calculated according to the N content.

2.2. Dichromate anion extraction studies

It is well known that dichromate anions ($Cr_2O_7^{2-}$/$HCr_2O_7^-$) provide good potential interactions with host molecules, which have proton-switchable binding lobes and/or can form hydrogen-bonding sites.[16,27] An initial study of the extraction was carried out by liquid–liquid extraction of $Na_2Cr_2O_7$ from an aqueous solution at a range of pH 1.5–4.5 in the presence of receptor **3**. However, the binding affinity of receptor **3** was not investigated because of the solubility of receptor **3** in water in the range of pH 1.5–4.5. In order to prevent water solubility of receptor **3** and to acquire magnetic properties that enable easy separation of the receptor, the bis(nitropyridine)-substituted calix[4]arene **3** was grafted onto epoxy-silica–coated magnetic nanoparticles. The resulting **MN-DiNoPy-Calix** was tested as receptor **4** for the extraction of the dichromate anion from an aqueous solution by means of solid–liquid extraction at a range of pH 1.5–4.5.

The extraction results of receptor **4** (**MN-DiNoPy-Calix**) are summarized in Figure 6. It was found that receptor **4** was an effective host for the removal of dichromate anions. Because of the more rigid structural features and the proton-switchable capability of the pyridine units of **MN-DiNoPy-Calix**, dichromate anion extraction from an aqueous solution was achieved (Figure 6). Indeed, the highest extraction capacity by receptor **4** was observed in acidic nature, which confirmed that receptor **4** was protonated. These protonated units played an important role in forming complexes with $HCr_2O_7^-$ by electrostatic interactions and hydrogen bonding.

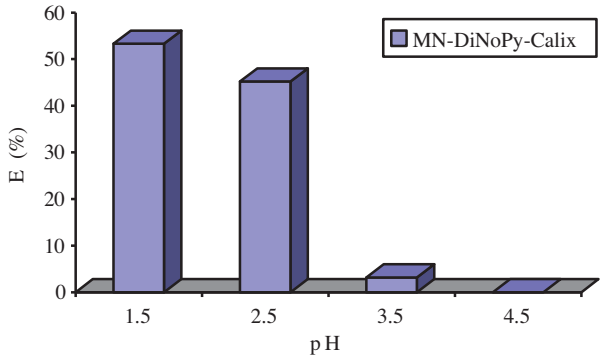


Figure 6. Extraction percentages of dichromate anion with **MN-DiNoPy-Calix** at pH 1.5–4.5 (solid phase, sorbent = 25 mg (**MN-DiNoPy-Calix**), aqueous phase, $Na_2Cr_2O_7 = 1.0 \times 10^{-4}$ M (10 mL) at 25 °C for 1 h).

In order to see the interfering effect of other anions on dichromate anion retention of the receptor (**MN-DiNoPy-Calix**), different inorganic sodium salts (SO_4^{2-}, Cl^-, and NO_3^-) were additionally mixed with the solution at pH 1.5. The results given in Figure 7 clearly indicate that the receptor (**MN-DiNoPy-Calix**) is a selective extractant for the extraction of $Na_2Cr_2O_7$ owing to the small difference obtained in the extraction value of $Na_2Cr_2O_7$ with **MN-DiNoPy-Calix** by the presence of other anions.

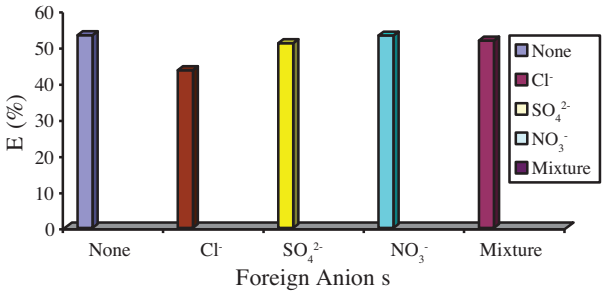


Figure 7. Dichromate retention results of the receptor (**MN-DiNoPy-Calix**) in the presence of interfering anions (Cl^-, SO_4^{2-}, and NO_3^-) at pH 1.5. Averages and standard deviations calculated for data received from 3 independent extraction experiments. Sodium dichromate, 1×10^{-4} M; ligand, 1×10^{-3} M; NaCl, 1×10^{-2} M; Na_2SO_4, 1×10^{-2} M; $NaNO_3$, 1×10^{-2} M; 1 h, 25 °C.

3. Experimental

3.1. General remarks

An Ez-Melt apparatus in a sealed capillary was used to determine all melting points of the synthesized compounds. NMR spectra were recorded on a Varian 400 MHz spectrometer, indicating chemical shifts as ppm relative to an internal standard tetramethylsilane ($\delta = 0.0$). FT-IR spectra were recorded with a PerkinElmer 100 spectrometer. A Shimadzu 160A UV-vis apparatus was used to analyze absorbance of Cr^{6+} in aqueous solutions. For the pH measurements, an Orion 410A+ pH meter was used. Elemental analyses were performed on a Leco CHNS-932 analyzer.

3.2. Synthesis

Compounds **1** and **2**[24,25] and Fe_3O_4 and **EPPTMS-MN**[4,26] were prepared according to the literature methods. The synthesis of compound **3** and the immobilization of compound **3** onto **EPPTMS-MN** in order to produce **MN-DiNoPy-Calix** (**4**) are herein reported for the first time.

3.2.1. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-nitropyridin-2-ylamino)ethylaminocarbonyl-methoxy)-26,28-dihydroxycalix[4]arene 3

To a solution of diester derivative **2** (1 g, 1.261 mmol) in 18 mL of a mixture of CH_2Cl_2/CH_3OH (2/1, v/v) was added 2-(2-aminoethylamino)-5-nitropyridine, followed by stirring at room temperature for 34 h. The reaction mixture was monitored by TLC (CH_2Cl_2), and the volatile components were removed under reduced pressure. The crude product was washed with water to adjust pH to 7.0 and then dried in an oven. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3OH, 10/1). Yield: 52%, mp 274–275 °C. FTIR (ATR) cm^{-1}: 3450 (–OH), 3380 (–NH), 1670 (C=O), 1481 (N–O asymmetric stretch), 1291 (N–O symmetric

stretch). ^{1}H NMR (400 MHz, DMSO): δ1.06 (s, 18H, Bu^t), 1.14 (s, 18H, Bu^t), 3.28 (d,4H, J= 13.2 Hz, ArCH$_2$Ar), 3.35–3.58 (m, HOD shielded, 10H, –CH$_2$– and Ar–NH), 3.91 (d,4H, J = 13.2 Hz, ArCH$_2$Ar), 4.47 (s, 4H, OCH$_2$), 6.99 (s, 4H, ArH), 7.08 (s, 4H, ArH), 7.46 (brs, 2H, OH), 8.11 (brs, 2H, ArH), 8.25 (s, 2H, ArH), 8.79 (brs, 2H, ArH), 8.94 (brs, 2H, NH) (see Figure 2). ^{13}C NMR (100 MHz, DMSO): δ 31.26 (–*C*H$_3$, Bu^t), 31.80 (–*C*H$_3$, Bu^t), 34.04 (Ar–*C*H$_2$–Ar), 34.47 (–*C*, Bu^t), 34.49 (–*C*, Bu^t), 38.05 (–N–*C*H$_2$), 72.40 (ArN–*C*H$_2$), 74.83 (O–*C*H$_2$), 125.74 (Ar*C*), 125.90 (Ar*C*), 126.29 (Ar*C*), 127.17 (Ar*C*), 127.53 (Ar*C*), 133.16 (Ar*C*), 133.29 (Ar*C*), 134.59 (Ar*C*), 141.99 (Ar*C*), 146.96 (Ar*C*), 147.91 (O–*C*Ar), 150.04 (O–*C*Ar), 168.49 (N–*C*Ar, Pyr), 169.72 (*C*=O) (see Figure 3). Anal. Calcd. for C$_{62}$H$_{76}$N$_8$O$_{10}$: C, 68.11; H, 7.01; N, 10.25. Found (%): C, 68.26; H, 6.97; N, 10.32.

3.2.2. Immobilization of 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-nitropyridin-2-ylamino)ethylaminocarbonyl-methoxy)-26,28-dihydroxycalix[4]arene onto silica-coated Fe_3O_4-nanoparticles MN-DiNoPy-Calix

A mixture of the bis(nitropyridine)-substituted calix[4]arene **3** (0.35 g, 0.32 mmol) and NaH (0.06 g, 2.5 mmol) in a solution of THF/DMF (20 mL, 3/1, v/v) was stirred at room temperature for 30 min. **EPPTMS-MN** (0.35 g) was added to the reaction mixture, followed by refluxing for 5 days. The mixture was separated via magnetic separation and washed with DMF 3 times to remove the excess dipyridine amide-substituted calix[4]arene **3**, and then washed with 1 M HCl solution and water to neutralize it. The nanoparticles obtained were dried under vacuum. Yield: 0.52 g. FTIR (KBr disk) cm^{-1}: 3411, 1634 (C=O), 1479 (N–O asymmetric stretch), 1456 and 1411 (C=C stretch), 1107, 958, and 799 (Si–O stretch), 560 (Fe–O stretch) (Figure 4).

3.3. Extraction experiments

Extraction studies were carried out using an aqueous solution of Na$_2$Cr$_2$O$_7$ (1.0×10^{-4} M) and the calixarene derivative (1.0×10^{-3} M solution of **3** in CH$_2$Cl$_2$ for liquid–liquid extraction, 25 mg of **MN-DiNoPy-Calix** (**4**) for solid–liquid extraction). A mixture of Na$_2$Cr$_2$O$_7$ (10 mL, 1.0×10^{-4} M) and the calixarene derivative (10 mL, 1.0×10^{-3} M solution in CH$_2$Cl$_2$ for liquid–liquid extraction, 25 mg of **MN-DiNoPy-Calix** (**4**) for solid–liquid extraction) was shaken in a stoppered flask at 175 rpm at 25 °C for 1 h. For the determination of the residual dichromate concentration, a UV-Visible spectrophotometer was used, and absorbance readings were measured at 346 nm as described previously.[4,13,27] The pHs of the dichromate solutions were adjusted by using diluted HCl and KOH solution at 25 °C, and the percent extraction (E%) was calculated[27] 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 anion before and after the extraction, respectively.

4. Conclusion

A new bis(nitropyridine)-substituted calix[4]arene **3** was synthesized and grafted onto the surface of epoxy-silica–coated magnetic nanoparticles to create more rigid structural features and to prevent water solubility

of the bis(nitropyridine)-substituted calix[4]arene **3**. In addition, the extraction capability of new calixarene-adorned magnetic nanoparticles, **MN-DiNoPy-Calix** (**4**), was investigated with regard to dichromate anions. In our previous studies we observed that the magnetic nanoparticles-grafted calix[4]arenes were selectively functionalized with amino pyridine units (see Figure 1), and extracted dichromate anion in maximum extraction capabilities at 69% (for **MN-Py-1**) and 53% (for **MN-Py-2**) at pH 3.5.[23] However, when using **MN-DiNoPy-Calix** (**4**) as an extractant, the maximum percentage of dichromate removal reached 54% at pH 1.5. These findings clearly illustrate that the calixarene-adorned magnetic nanoparticles, which bear amino pyridine units, have an affinity towards dichromate anions. The binding abilities of **MN-DiNoPy-Calix** with dichromate clearly depend on the rigid structural properties, proton-switchability, and hydrogen-binding ability. In addition, allowing calixarene compounds to acquire magnetic properties would bring new insight into the removal of toxic and hazardous materials from water because they can be easily separated by using an external magnet.

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