J Incl Phenom Macrocycl Chem (2008) 61:187–193
DOI 10.1007/s10847-008-9413-9

ORIGINAL ARTICLE

Synthesis of original capping calixarenes with DTPA fragment

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Received: 12 December 2007 / Accepted: 2 February 2008 / Published online: 21 February 2008

Abstract Calixarenes **5–8** capped with DTPA bridges were synthesized by condensation of the corresponding 1,3-(distal)-diaminocalixarenes and DTPA dianhydride in DMF. The chelating properties of the DTPA-calixarenes were evaluated towards europium and the resulting complexes were characterized by mass spectroscopy.

Keywords Calixarene · DTPA · Europium · Mass spectroscopy

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Introduction

Owing to the development of supramolecular chemistry, a number of calixarene-based ligands have been extensively studied for their coordination properties [1]. Moreover, the chemistry of these macrocycles is nowadays well known and efficient. Synthetic modifications can be realized on the lower and/or the upper rim with various functional chelating groups. The easy accessibility and the selective functionalizations at the phenolic hydroxy groups of calix[4]arenes have made this member of the series increasingly attractive for chemists involved in host-guest chemistry [2]. In particular, cation complexing ligands containing calix[4]arene building blocks have been synthesized to obtain more selective metal ion sensors. These molecules are generally O-substituted calix[4]arenes at lower rim with various chemical functionalities to ion recognition (carbamoylphosphine oxide [3], phosphine oxide [4], acid-amide [5], phosphonic acid [6], among others [7]).

Polyaminoacetic acid DTPA ligand is one of the most frequently employed chelating agents, because of the high stability of its metal complexes [8], particularly dedicated to the gadolinium complexation for MRI applications [9]. Surprisingly, to the best of our knowledge, combination of the architecture of calix[n]arenes with the chelating behaviour of polyaminoacetic acids such as DTPA or EDTA was not reported in the literature. Bitter tried to obtained calixarene-DTPA type ligands from the corresponding calix(aza)crowns [10], but the exhaustive alkylation of nitrogen atoms failed. We could only find cyclodextrin capped with DTPA prepared by condensation of aminocyclodextrin and DTPA anhydride. The preorganized ligands were used for lanthanide complexation [11].

We report here the synthesis of the calixarenes **5–8** capped by DTPA bridges and the preliminary study of their binding properties towards lanthanides.

Experimental section

General considerations

Starting materials and solvents were obtained from commercial suppliers and used without further purification. TLC: silica gel 60 F254. NMR spectra were recorded on DRX 300 Brücker FT spectrometers. Abbreviation was used as: s (singlet), d (doublet), dd (divided doublet), t (triplet), q (quadruplet), m (multiplet) and l (large). Mass spectra were recorded by electrospay at the Mass Spectrometry centre. Elementary analyses were performed by the Service Central d'Analyses, Vernaison (France).

Synthesis of 5,11,17,23-tetra(*tert*-butyl)-25,27-bis(3-aminopropoxy)-26,28-dihydroxycalix[4]arene **3**

p-tert-Butylcalix[4]arene (10 g, 15.4 mmol) and K_2CO_3 (2.34 g, 17 mmol) were heated at reflux for 1 h in acetonitrile (380 mL). *N*-(3-Bromopropyl)phthalimide (9.1 g, 33.9 mmol) was then added and the mixture heated to reflux for a additional 48 h. The solvent was evaporated in vacuo and the residue re-dissolved in chloroform. The solution was washed twice with water and brine and then dried. Evaporation of the solvent followed by precipitation from chloroform/methanol gave the desired compound as a white solid. Yield: 86%, 10.1 g; ^{1}H NMR (300 MHz, $CDCl_3$): 7.72–7.75 (m, 4 H, Phth), 7.56–7.60 (m, 4 H, Phth), 7.44 (s, 2 H, O*H*), 7.02 (s, 4 H Ar*H*), 6.77 (s, 4 H Ar*H*), 4.30 (d, 4 H, J = 13.0 Hz ArCH_2Ar), 4.09 (m, 8 H, CH_2N + OCH_2), 3.31 (d, 4 H, J = 13.0 Hz, ArCH_2Ar), 2.43 (quin, 4 H, J = 7.2 Hz, CH_2CH$_2$N), 1.27 (s, 18 H, *t*-Bu), 0.93 (s, 18 H, *t*-Bu).

A solution of 25,27-diphthalimidopropoxy-*p-tert*-butylcalix[4]arene-26,28-diol (5 g, 4.9 mmol) in EtOH (100 mL) was refluxed with hydrazine (5 mL). After 8 h the solvent was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (150 mL), washed with water (2 × 50 mL), dried ($MgSO_4$) and the solvent was evaporated. The resulting powder was dissolved in chloroform (20 mL) and precipitated with hexane (40 mL) to give the pure diamine as a white powder, yield: 87%, 3.74 g. ^{1}H NMR (300 MHz, $CDCl_3$): 7.06 (s, 4 H, Ar*H*), 6.75 (s, 4 H, Ar*H*) 4.12 (d, J = 13 Hz, 4 H, ArCH_2 Ar), 4.07 (t, J = 5.8 Hz, 4 H, OCH$_2$), 3.21–3.30 (m, 8 H, ArCH_2Ar), 2.13 (m, J = 6.2 Hz, 4 H, CH$_2$CH_2CH$_2$), 1.23 (s, 18 H, *t*-Bu), 0.90 (s, 18 H, *t*-Bu).

*Synthesis of macrobicycles calix[4]arene-DTPA **5–8***

Triethylamine (4.1 mmol) was added to a solution of diaminocalixarenes (0.7 mmol) in 50 mL of dry DMF. A solution of DTPA dianhydride (0.7 mmol) in 20 mL of DMF was added dropwise and the resulting mixture was stirred at 80 °C during 6 days. After cooling to room temperature, a water/acetone mixture (50/50) was added and the resulting precipitate was filtered off, rinsed with acetone and dissolved in DMF. Addition of Et_2O led to a precipitate which was filtered off and dried under vacuum.

A mixture of **8a** and **8b** was obtained as a light pink powder.

8a: ^{1}H NMR (DMSO-d$_6$): 9.30 (s, 2 H, OH), 8.31 (s, 4 H, ArH), 7.11 (s, 2 H, NH), 7.10 (d, J = 7.2 Hz, 4 ArH), 4.89 (t, J = 7.2 Hz, 2 ArH), 4.22 (d, J = 13 Hz, 4 H, ArCH_2Ar), 3.99 (s, 6 H, OMe), 3.82 (s, 2 H, NCH_2CO$_2$H), 3.78 (s, 4 H, NCH_2CO$_2$H), 3.33–3.53 (m, 8 H, ArCH_2Ar and NCH_2CO), 2.79 (t, J = 4.5 Hz, 4 H, NCH_2CH$_2$N), 2.33 (t, J = 4.5 Hz, 4 H, NCH$_2$CH_2N).

ES–MS: 839 ([**8a** + H]$^+$). ES-MS: 1680 ([**8b** + H]$^+$).

5 was obtained as a light yellow powder (0.65 g, 81%).

^{1}H NMR (DMSO-d$_6$): 11.88 (s, 3COOH), 7.70–8.55 (sl, 4 H, NH + OH), 6.99 (s, 8 H, ArH), 2.20–4.40 (m, 34 H, ArCH_2Ar, OCH_2CH$_2$N, NCH_2CH$_2$N, NCH_2COOH), 1.03 (s, 18 H, *t*Bu), 0.99(s, 18 H, *t*Bu).

ES–MS: 1092 ([M + H]$^+$)

Anal. Calc. for C_{62} H_{85} N_5 O_{12}·2H_2O (1128.41): C 65.99, H 7.95, N: 6.21, O: 19.85 found C 66.12, H 7.82, N 6.19, O 19.98.

6 was obtained as a white powder (0.39 g, 65%).

^{1}H NMR (DMSO-d$_6$): 12.1 (s, 3COOH), 8.25 (sl, 4 H, OH + NH), 7.31 (d, J = 7, 4 Hz, ArH), 7.15–7.21 (m, 4 ArH), 6.95 (t, J = 7.2 Hz, ArH), 6.74–6.86 (m, 4 ArH), 2.61–4.68 (m, 34 H, ArCH_2Ar, NCH_2CH$_2$N, NCH_2COOH, OCH_2CH$_2$N, NCH_2C(O)).

ES–MS: 868 ([M + H]$^+$), 890 ([M + Na]$^+$).

Anal. Calc. for C_{46} H_{53} N_5 O_{12}·H_2O (885.97): C 62.36, H 6.26, N: 7.90, O: 23.47 found C 62.15, H 6.21, N 7.95, O 23.22.

7 was obtained as a white powder (0.3 g, 40%).

^{1}H NMR (DMSO-d$_6$): 7.93–8.62 (sl, 4 H, NH + OH), 7.1 (s, 8 H, ArH), (3.47) 4.17 (AB, J_{AB} = 13.1 Hz, 4 H, ArCH_2Ar), 3.99 (m, 4 H, OCH_2CH$_2$CH$_2$N), 2.89–3.62 (m, 26 H, ArCH_2Ar, OCH_2CH$_2$CH$_2$N, NCH_2CH$_2$N, NCH_2COOH), 2.18 (m, 4 H, OCH_2CH$_2$CH$_2$N), 1.18 (s, 18 H, *t*Bu), 1.13 (s, 18 H, *t*Bu).

ES–MS: 1120 ([M + H]$^+$).

Anal. Calc. for C_{64} H_{89} N_5 O_{12}·H_2O (1138.45): C 67.52, H 8.06, N: 6.28, O: 17.89 found C 67.86, H 7.93, N 6.28, O 17.89.

*General procedure for the preparation of europium complexes **9**(Eu)–**12**(Eu)*

A solution of $EuCl_3 \cdot 6H_2O$ (0.04 mmol) in 2 mL of DMF was added to a solution of the macrobicycle *p-tert*-butylcalix[4]arene-DTPA (1 eq.) in 3 mL of DMF. The resulting mixture was heated and stirred for 24 h, then concentrated. Diethyl ether was added and the formed precipitate was filtered off to give a light yellow solid.

ES–MS:

12 (Eu): 988.2, 989.2, 990.2, 991.2 et 992.2 uma ([**12** (Eu) + H]$^+$).

12′ $(Eu)_2$: 988.7, 989.7, 990.7, 991.7 et 992.7 uma ([**12′** $(Eu)_2$ + H]$^{2+}$/2).

9 (Eu): 1240.5, 1241.5, 1242.5, 1243.5 et 1244.5 uma [**9** (Eu) + H]$^+$.

10 (Eu): 1016.3, 1017.3, 1018.3, 1019.3, 1020.3 uma [**10** (Eu) + H]$^+$.

11 (Eu): 1268.7, 1269.7, 1270.5, 1271.5, 1272.4 uma [**11** (Eu) + H]$^+$.

Results and discussion

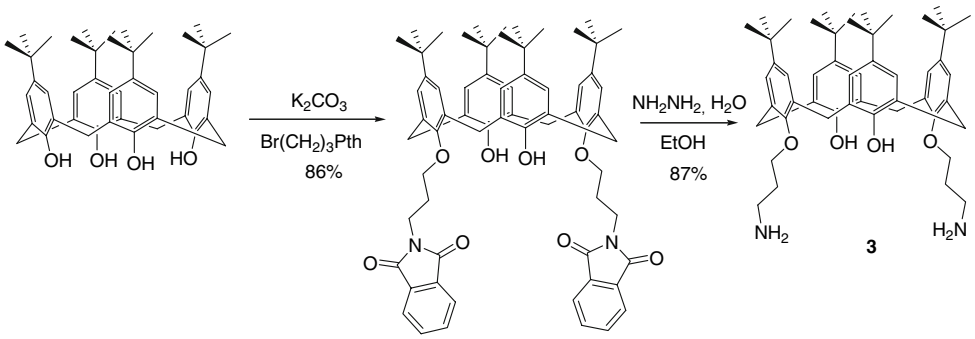
5,11,17,23-tetra(*tert*-butyl)-25,27-bis(3-aminopropoxy)-26,28-dihydroxycalix[4]arene **3** [12, 14] was previously prepared in two steps from the *p-tert*-butylcalix[4]arene (Scheme 1). Instead of preparing compound **3** in 3 steps according to Beer procedure [12], we firstly alkylated the *p-tert*-butylcalix[4]arene with N-(3-bromopropyl)phtalimide in acetonitrile and then deprotected the amino group with hydrazine. This way, we obtained the aminocalixarenes **3** in 75% overall yield.

The starting aminocalixarenes, 5,11,17,23-tetra(*tert*-butyl)-25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]arene **1** [12], 25,27-bis(2-aminoethoxy)-26,28-dihydroxycalix[4]arene **2** [13], were prepared through a cyano intermediate as previously described in the literature.

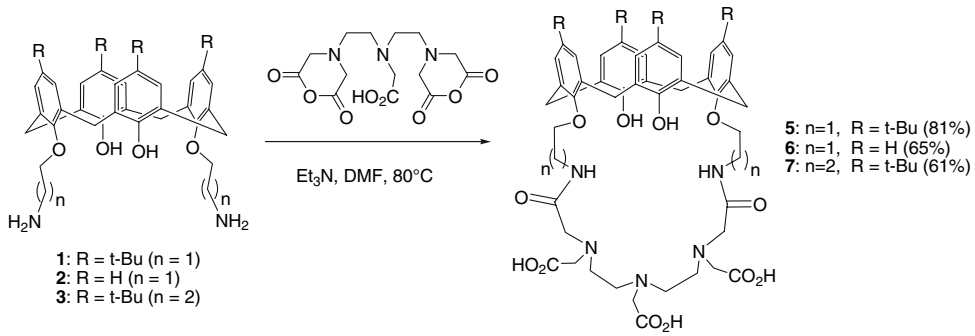
Condensation of the 1,3-(distal) bisaminocalixarene **1** with a stoechiometric amount of freshly prepared DTPA dianhydride [15] in dry DMF at 80 °C in the presence of Et_3N during 6 days afforded calixarene-DTPA **5** after precipitation and filtration in 81% yield (Scheme 2). Following the same procedure, calixarenes **6** and **7** were obtained in 65 and 61% respectively.

The structures of compounds **5**, **6** and **7** were established by NMR spectroscopy and electrospray mass spectrometry. ESMS is a powerful technique to analyze functionalized calix[n]arene [16]. Due to its "soft ionization" technique, the integrity of the molecules is readily kept during the ionization process. A special benefit for the ionization of calix[n]arenes comes from the extraordinary affinity of calix[n]arenes for alkali metal ions, especially Na^+, because of the chelating site of the macrocycle, DTPA fragment or interactions with phenolic oxygens of the macrocycle [2b]. Therefore, ESMS is a sensitive, reliable

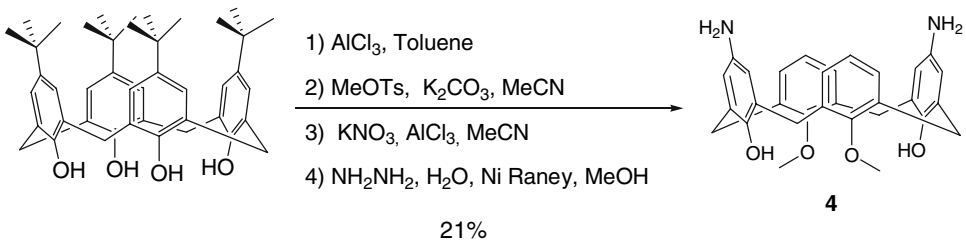
Scheme 1 Synthesis of diaminocalixarene 3

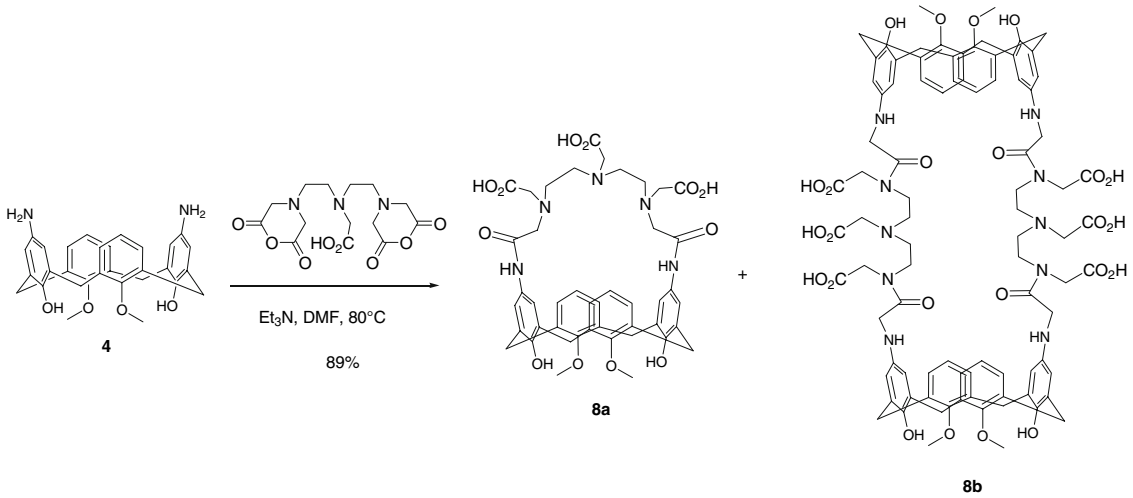


Scheme 2 Synthesis of calixarene-DTPA 5–7



Scheme 3 Synthesis of diaminocalixarene 4





Scheme 4 Condensation of diaminocalixarene 4 with DTPA dianhydride

and convenient method for the study of calix[n]arene systems. Using ESMS only the [1 + 1] macrocycle was detected and we could not detect the [2 + 2].

The cone conformation was deduced from the presence of resonance signals at 31–32 ppm for **5**, **6** and **7** corresponding to the methylene groups Ar*CH*$_2$Ar [17]. ^{1}H NMR of **5** and **6** are complex due to some overlapping CH_2 signals from the DTPA moieties. Nevertheless the ^{1}H NMR and HSQC of **7** confirmed the cone conformation by the presence of an AB system for the Ar*CH*$_2$Ar protons located at 3.48 and 4.17 ppm.

Later, we focused our attention on the functionalization of the upper rim. We prepared compound **4** [18] in 4 steps according to the literature. After the removal of *tert*-butyl groups with aluminium chloride (75%), the 25,27-dimethoxycalix[4]arene was prepared by regio and stereospecifique O-alkylation (86%). The next step was the nitration with potassium nitrate and aluminium chloride in acetonitrile (59%). Finally compound **4** was obtained by reduction of the nitro group with hydrazine (Scheme 3). In this four steps synthesis the limiting step was the reduction of the nitro group to an amino-function. Therefore we explored several other reducting methods (H_2, Pd/C, 1 atm, CH_2Cl_2/MeOH, Δ; H_2, Pd/C, 20 atm, CH_2Cl_2/MeOH, Δ; $NH_2NH_2{\cdot}H_2O$, $FeCl_3{\cdot}6H_2O$, methoxyethanol; $NH_2NH_2{\cdot}H_2O$, Pd/C, EtOH, Δ; $SnCl_2$ 1-methyl-2-pyrrolidinone, Δ) but none of them gave rise to better results than the first one (56%).

According to previously described conditions, the reaction of compound **4** with DPTA unit afforded two products. ESMS analysis reveals that we have a mixture of **8a** and **8b** corresponding to the expected calixarene and biscalixarene (Scheme 4). This phenomenon was also observed by Brunet in a similar case during the reaction of bis-pyrazolylpyridine with DTPA [19].

The ES–MS spectrum showed two peaks at m/z 840 and 1679.6 mass units corresponding to the [**8a** + H]$^+$ and [**8b** + H]$^+$ species. Pure compound **8a** could be obtained by slow precipitation in DMF and was isolated by filtration. ^{1}H NMR measured in DMSO-d_6 showed that calixarene is in the cone conformation. A singlet at 8.31 ppm points out the presence of aromatic protons of the substituted core in upper rim, a doublet at 7.16 ppm corresponding to *meta* protons on the non substituted aromatic core and 6.89 ppm for the proton at the *para* position.

The chelating behaviour of macrocycles **5**, **6**, **7**, **8a** and **8b** was then evaluated towards europium complexation. Based on molecular modelling of **7** and its europium

complex (HyperChem, MM + and AM1), [**7** (Eu)] structure would be obtained in cône conformation which showed that the DTPA macro ring of **7** would adequately embrace the metal without any interaction with the calixarene moiety (Fig. 1), assuming nine-coordination of the metals by means of the three carboxylates and aliphatic amines as already published for DTPA-lanthanide complexes [20].

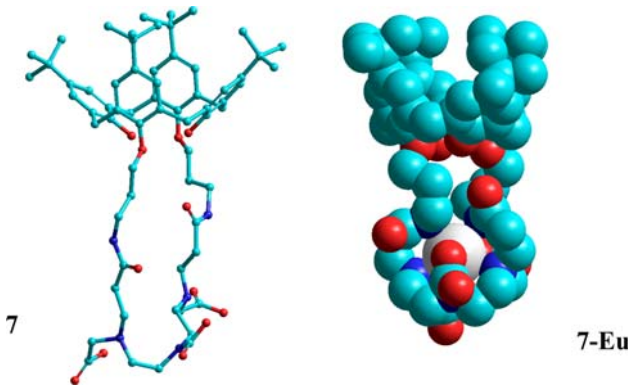
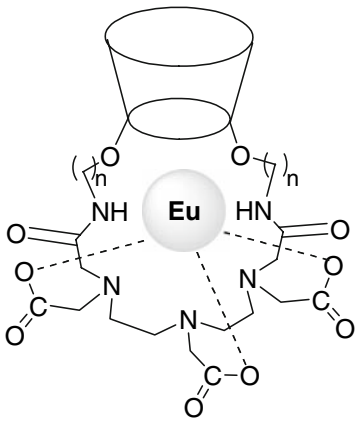


Fig. 1 Molecular model of **7** and its europium complex

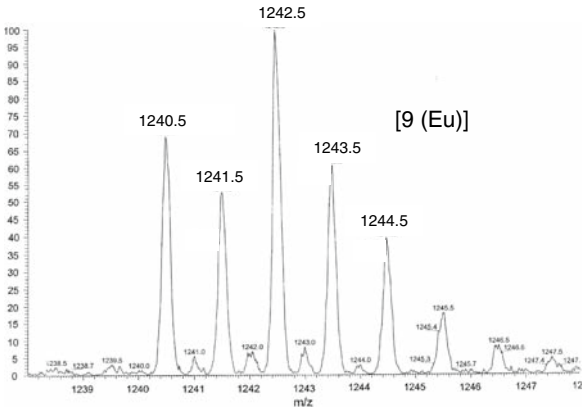
Due to their low solubility in most solvents including acidic aqueous medium, the europium complexes were prepared by addition of calixarenes previously solubilized in DMF to a solution of $EuCl_3$ in DMF. After 24 h under stirring at 60 °C, Eu(III) complexes precipitated in the reaction mixture and were collected by filtration. Characterizations of the europium complexes were done by electrospray mass spectrometry (Figs. 2 and 3).

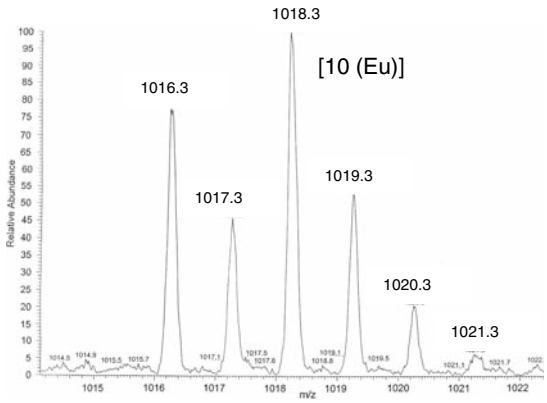
Mass spectra data of complexes [**9** (Eu)], [**10** (Eu)] and [**11** (Eu)] showed only the mass peaks corresponding to the mono-charged species with the isotope distribution of Eu as described in Table 1.

In the case of the mixture of compound **8a** and **8b**, the mass spectra data of the complexes [**12** (Eu)] and [**12′** $(Eu)_2$] confirmed our first observation about their synthesis.



[**9** (Eu)] n= 2 with tert-butyl group,
[**10** (Eu)] n= 2 without tert-butyl group
[**11** (Eu)] n= 3 with tert-butyl group





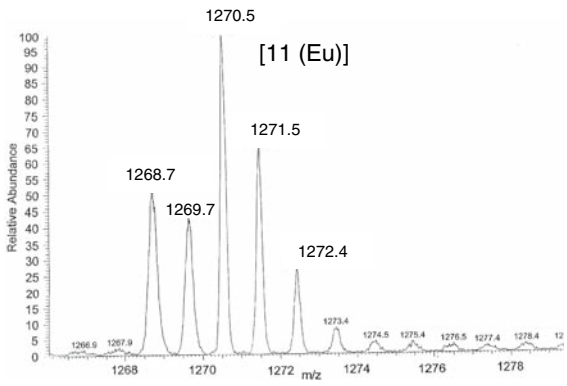


Fig. 2 Mass spectra of complexes [**9** (Eu)], [**10** (Eu)] and [**11** (Eu)]

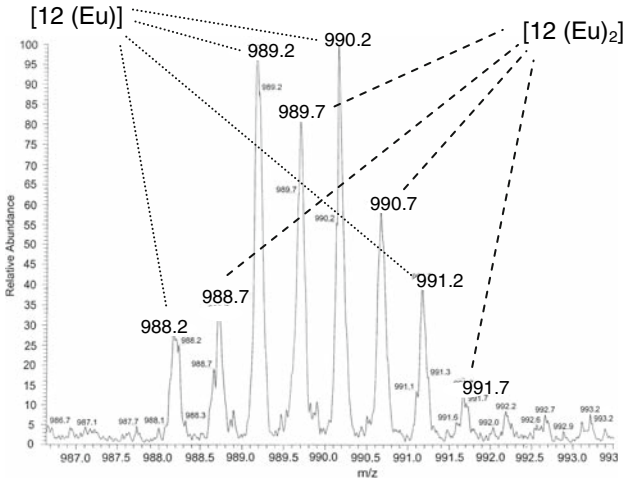


Fig. 3 Mass spectrum of complexes [**12** (Eu)] + [**12′** $(Eu)_2$]

Table 1 Mass spectra data of the (DTPA)calixarenes-europium complexes

Complexes	Mass peaks of the mono-charged species	Mass peaks of the di-charged species
[**9** (Eu)]	1240.5, 1241.5, 1242.5, 1243.5, 1244.5	
[**10** (Eu)]	1016.3, 1017.3, 1018.3, 1019.3, 1020.3	
[**11** (Eu)]	1268.7, 1269.7, 1270.5, 1271.5, 1272.4	
[**12** (Eu)] and [**12′** $(Eu)_2$]	988.2, 989.2, 990.2, 991.2, 992.2	988.7, 989.7, 990.7, 991.7, 992.7

Conclusion

In conclusion, we described the synthesis of original macrocycles, containing DTPA moieties. We made the corresponding europium complexes. These compounds might also be used for gadolinium complexation and studied for MRI application.

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