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Structure impact in antenna effect of novel upper rim substituted tetra-1,3-diketone calix[4]arenes on Tb(III) green and Yb(III) NIR-luminescence

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Abstract

Two novel calix[4]arene macrocyclic ligands functionalized with four 1,3-diketone groups at the upper and hydroxyl (**3**) or propyloxy-groups (**6**) at the lower rims were synthesized and characterized using NMR, IR spectroscopy, mass spectrometry and elemental analysis. UV-Vis spectrophotometry and ESI mass spectrometry studies indicate 1:1 complex formation of ligands **3** and **6** with Ln(III) (Ln=Tb, Yb) in alkaline DMF solutions resulted from coordination of Ln(III) with 1,3-diketonate groups. Luminescence study of Ln(III) complexes with **3** and **6** reveals significant difference in antenna effects of their deprotonated forms on both Tb(III)- and Yb(III)-centered luminescence. Comparison of ligand-centered emission for ligands **3** and **6** in alkaline media is assumed as a reason for the experimentally observed difference in sensitization pathways in Ln(III) complexes with **3** and **6**.

Keywords: calix[4]arene, 1,3-diketone, luminescence, NIR-emission, ytterbium(III), terbium(III), complexation.

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Introduction

Luminescent Ln(III) complexes attract great research attention due to their wide application as fiber amplifiers operating at telecommunication wavelength,¹ OLEDs²⁻⁴ as well as UV light converters transforming high energy UV irradiation to visible or NIR-emission,⁵ immune-fluorescent analysis and therapy,⁶ and information security.⁷ Usually, the small absorption of Ln(III) ions due to Laport forbiddance of 4f-4f transitions results in poor emission from the excited 4f levels under direct excitation unless powerful lasers are used. One of the most popular ways to overcome this limitation is complexation of Ln(III) ions with organic ligands that sensitize emission of the metal ion by the well-known antenna effect.⁸ However, NIR emitting lanthanide complexes with organic ligands often show low emission efficiencies compared to inorganic and cluster systems. Radiationless decay through high-frequency oscillators (O–H, N–H and C–H) resulting from organic ligands or the solvent molecules is the reason for quenching NIR luminescence.⁹

Many recent efforts have been made to synthesize the appropriate antenna-ligands for the Er(III) and Yb(III) NIR-luminescence according to the general requirements of the organic antenna – an energetically well-matched triplet state of the ligand or d-block chromophore to the first Ln(III) excited state, a rigid structure, and the number of O–H, N–H, C–H oscillators minimized via chelating or fluorination processes (for C-H bonds).¹⁰

1,3-Diketones have been reported as very promising antenna-ligands for Ln(III)-centered emission,^{11,12} where the rigidity of the complex structure is a reason for lesser radiationless decay.¹³⁻¹⁶ For example, the luminescence of the Ln(III) bis(1,3-diketone) dinuclear complex was found to be 11 times more intense than the luminescence of mononuclear analogues.¹³ Anchoring 1,3-diketone fragments to a cyclic calix[4]resorcinarene backbone was recently documented as a route for efficiently sensitizing Tb(III)-centered luminescence due to the rigidity of the complex structures or/and additional antenna effect provided by the cyclophane-based platform.¹⁷ The impact of the thiacalix[4]arene backbone in the antenna effect of its derivatives is exemplified in the literature.^{18,19}

From this point of view, 1,3-diketone groups anchored to the cyclophane platform is a prospective direction for the design of novel ligands for luminescent lanthanide(III) complex synthesis. However, there are only few papers devoted to synthesis of cyclophane-based 1,3-diketones. The recent report by Senthilvelan et al. introduces the synthesis of lower and upper rim substituted calix[4]arene derivatives with one 1,3-diketone group from an isoxazoline precursor in the presence of $Mo(CO)_6$ as a catalyst.²⁰ Low reaction yield, necessity for proper catalyst selection and disproportionation of the initial compounds can be noted as the main drawbacks of this synthetic route, restricting its application for the synthesis of poly-1,3-

diketones. A penta-substituted calix[5]arene with five 1,3-diketone groups attached to methylene carbon atoms is another example of a poly-1,3-diketone ligand. This ligand was obtained by heating pentabromine-substituted calix[5]arene with an excess of acetylacetone or dibenzoylacetone.²¹ The corresponding calix[6]arene ligand was synthesized in a similar way.²² It is worth noting that this synthesis requires the use of the ionizing solvent 2,2,2-trifluoroethanol, and results in a low yield (10-23%). An upper rim substituted calix[4]arene with four 1,3-diketone groups was obtained through the reaction of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2 λ^5 -dioxaphosphole with the tetraformylated calix[4]arene, followed by molecular rearrangement in methanol in 40% yield.²³ Reaction of chloromethylated calix[4]arene with 1,3-diketone groups at the upper rim, in a higher yield (74%)²⁴ than the above mentioned synthetic procedures. Our recent article¹⁷ reports the synthesis and luminescent properties of Tb(III) complexes of calix[4]resorcine cavitand, bearing four (acetylaceton-3-yl)methylene groups obtained through the corresponding tetrabromomethylated calix[4]resorcine cavitand, with a good yield (63%).

Herein, we report a synthetic route for novel tetra-substituted calix[4]arenes with 1,3diketone groups on the upper rim, and alkylated(6) or nonalkylated(3) on the lower rim of the macrocycle. Complex formation of 3 and 6 with Tb(III) and Yb(III) in alkaline DMF solution is also introduced in correlation with Tb(III)- and Yb(III)-centered luminescence of the complexes. The reasons for the different antenna effect of the ligands are also discussed. In particular, the impact of the macrocyclic backbone in the sensitizing effect of calix[4]arene tetra-diketone derivatives is not clear. Thus, comparison of the sensitizing effects of two structural counterparts 3 and 6 exhibiting different conformational flexibility is aimed at highlighting the impact of the calix[4]arene backbone in antenna effects of the tetra-1,3-diketone derivatives.

Results and discussion

Synthesis and characterization of tetra-1,3-diketone calix[4]*arenes* **3** *and* **6***.*

The synthetic routes for tetra-1,3-diketone calix[4]arenes **3** and **6** are presented in Scheme **1**. This approach has been successfully applied earlier for the preparation of tris-(1,3)-diketonyl)benzenes,²⁵ and tetra-1,3-acetylacetone derivative of calix[4]resorcinarene cavitand.¹⁷ According to the procedure, the prepared sodium salt of acetylacetone (NaAA) was added to corresponding tetrakis(halogenomethyl) derivative **2** or **5** in 1,4-dioxane and the reaction mixture was heated with stirring for several hours. The obtained new tetra-1,3-diketone derivatives **3** and **6** were characterized by ¹H NMR, ¹³C NMR, IR spectroscopy and MALDI-MS techniques.

It is worth noting that the nucleophilic substitution of calix[4]arene 2 proceeds even at room temperature, and completes in a rather short time in contrast to compound $5^{.17,25}$. The chlorine analogue of 2 is known to be a highly reactive compound, especially under basic conditions.^{26,27} It easily loses HCl to give the corresponding *p*-quinone methide which undergoes further transformations. The intensive reddening of the reaction mixture observed in 10-15 minutes after adding NaAA to calix[4]arene 2, is followed by the disappearance of color when the reaction was completed. These facts clearly indicate formation of an intermediate quinone structure in the solution. In spite of the differences in the reactive behavior of the initial compounds 2 and 5, the applied synthetic protocol afforded the target products 3 and 6 with high yields (65% and 77% respectively).



Scheme 1. Synthetic routes and structures of compounds 3 and 6. The similar numbering system of atoms is used in the experimental section.

The IR spectra of both tetra-1,3-diketones contain the doublet bands assigned to the v(C=O) vibrations (1724 and 1698 cm⁻¹ for **3**, 1720 and 1699 cm⁻¹ for **6**). The doublet character of the keto-carbonyl bands with similar intensities is caused by the syn- and anti-phase stretching vibrations of the carbonyl groups in the 1,3-diketone fragments.^{28,29} The absorption band at ~1600 cm⁻¹, reflecting both the stretching vibrations of multiple bonds of aromatic rings and the resonance vibrations of enol structures (v(C=O) and v(C=C)) is noticeably broadened and its intensity in both cases is ~0.5-0.7 of v(C=O) absorbance in Nujol. It is worth noting the lower intensity peak in this region (~0.1) in the IR spectrum of the previously reported calix[4]resorcine tetra-1,3-diketone, which results from the 5-10% of enol contribution according

to ¹H NMR spectroscopic data.¹⁷ Taking this into account, the IR spectra of **3** and **6** indicate the presence of a considerably higher percentage of enol form.

Stretching vibrations v(OH) for **6** are detected as a broad diffuse base under the v(CH) lines in the interval 2400—3300 cm⁻¹ with an uncertain maximum, which is characteristic for enol structures.^{30,28} In the case of calix[4]arene **3** having the non-substituted lower rim, this absorption is additionally masked under the broad and intensive dome-shaped v(OH) band with the maximum at ~ 3183 cm⁻¹, caused by vibrations of the hydroxyl groups of the calix[4]arene scaffold. The underfrequency for this band in comparison with v(OH)_{free} ~ 3500-3600cm⁻¹ reveals the participation of these groups in strong hydrogen bonding.²⁸

Assignment of signals in the NMR spectra was accomplished by means of 2D COSY, ${}^{1}H{-}{}^{13}C$ HSQC and ${}^{1}H{-}{}^{13}C$ HMBC experiments. The embedding of four 1,3-diketone fragments on the calix[4]arene backbone leads to a large number of spatial forms for these compounds. Ketoenol tautomerism of 1,3-diketone moieties is one more reason for the complication of spectral patterns in compounds **3** and **6**. Each of 1,3-diketone fragments in the compounds can exist both in enol and keto form. Furthermore, these tautomers may occupy different positions relative to each other, which undoubtedly lead to multiplication of peaks in the NMR spectra of compounds **3** and **6** in CDCl₃. Nevertheless, the use of two-dimensional NMR correlation spectroscopy techniques results in accurate identification of compounds **3** and **6**.

Calix[4]arenes and their derivatives can adopt four conformations, namely *cone*, *partial cone*, *1,3*- and *1,2-alternates*.^{31,32} The single narrow peak assigned to the methylene-bridged carbon atom is observed in the ¹³C NMR spectra of compounds **3** and **6**. This behavior is peculiar for *cone* or 1,3-*alternate* conformations. The choice between these spatial forms may be realized by the using "de Mendoza rule".³³ The obtained ¹³C chemical shifts determined for the bridged carbon atoms of **3** and **6** (δ ¹³C = 33.4 and 30.9 ppm respectively) evidence the *cone* isomer for the synthesized compounds. The chemical shift for the hydroxyl protons in the ¹H NMR spectrum of calix[4]arene **3** in CDCl₃ is 10.1 ppm and is almost the same as in the parent calix[4]arene **1** (10.19 ppm).³⁴ Thus, both the IR and NMR data indicate a circular hydrogen bond realized at the low rim of the compound **3**, similar to calix[4]arene **1**.³⁵

The chemical shifts of the OH groups protons (~16.7 - 16.9 ppm), belonging to 1,3diketone fragments of the compounds **3** and **6**, testify for a strong intramolecular hydrogen bonding. The amount of enol tautomer in CDCl₃ solution reaches 40% for **3** and 50% for **6**, essentially higher than for the mentioned above calix[4]resorcine derivative. This difference is obviously caused by the rigidity of the cavitand structure, and the sterical hindrances realized for the latter compound, which prevents the stabilization of the enol form.

Electronic absorption spectroscopy

Electronic absorption spectra of both ligands are characterized by the main absorption peak at 290 nm arising from the $\pi \rightarrow \pi^*$ transition and a shoulder at 310-320 nm, which should be assigned to enolic forms of the 1,3-diketone groups (Fig. 1). Changes in electronic absorption spectra of the ligands under basification and complex formation with lanthanides are exemplified in Figure 1 by Tb(NO₃)₃.



Fig. 1. Absorption spectra of L ($C_L=0.025 \text{ mM}$) in DMF (1); L in alkalized DMF ($C_{TEA}=0.1 \text{ mM}$) (2); L with Tb(NO₃)₃ ($C_L=C_{Tb}=0.025 \text{ mM}$) in alkalized DMF: $C_{TEA}=0.1 \text{ mM}$ (3). L = **3** (a) and **6** (b).

The basification of DMF solutions of the both calixarenes with triethylamine (TEA) affects their absorption spectra (Fig.1). This effect significantly increases when both $Tb(NO_3)_3$ and TEA are added to the ligands **3** and **6** (Fig.1). A similar tendency is observed for $Yb(NO_3)_3$ (Fig. S1 in ESI). The observed changes clearly point to complex formation of the lanthanide ions with **3** and **6** in alkaline conditions. The spectral changes at various ligand:TEA ratios were measured in order to optimize this value for efficient complex formation of the ligands with Tb(III) and Yb(III). This would avoid any interference caused by their hydrolysis at higher pH. The obtained spectral data are analysed graphically by means of absorption intensities at 320 and 306 nm for **3** and **6**, respectively (Fig. S2 in ESI). The optimal ligand:TEA ratio is 1:4 for Tb(III) and 1:2 for Yb(III). This agrees well with their coordination capacities and hydrolysis constants, which both tend to increase from Tb(III) to Yb(III) in accordance with the lanthanide contraction effect.

The spectral data measured at various concentrations of the ligands were analyzed by Job plotting (Fig. 2) in order to evaluate the stoichiometry of the complex formation in DMF solutions of the ligands at constant TEA:ligand ratio. The obtained results indicate the predominance of 1:1 stoichiometry for both ligands (Fig.2).



Fig. 2. The Job plot profiles for the DMF solutions at varied Ln:L molar ratio [Ln]+[L]=0.15 mM. L:TEA concentration ratio remaining at the 1:2 (a) and 1:4 (b) level. Ln=Yb (a), Tb (b). L = **3** (1), **6** (2).

ESI mass spectrometry

Mass spectrometry is another useful tool for the complex formation study. ESI spectra provide evidence of 1:1 complexes of Tb(III) and Yb(III) in alkaline DMF solutions of **6** (Fig.3). In particular, the signals at m/z^- 1336.5 and m/z^- 1321.6 are revealed in the spectra of alkaline DMF solutions of **6** in the presence of Yb(NO₃)₃ and Tb(NO₃)₃, respectively (Fig.3). The signals are related to 1:1 anionic complexes with dianion (**6**²⁻) and two nitrate anions, namely [Yb³⁺(NO₃)₂(**6**²⁻)]⁻ and [Tb³⁺(NO₃)₂(**6**²⁻)]⁻. The changes in the electronic absorption spectra of DMF solutions of **6** and the lanthanide nitrates under the basification (Fig.1b) point to deprotonation of two 1,3-diketone groups as the reason for the complex formation with the lanthanide ions. The smaller peak at m/z^- 1384.6 assigned to [Tb³⁺(NO₃)₃(**6**)]⁻ indicates the equilibrium between various 1:1 complexes in solution. The isotopic patterns for all peaks are in good agreement with the predicted isotopic distribution patterns (see insets).



Fig. 3. ESI spectra of calix[4]arene **6** with Yb(NO₃)₃ (a) and Tb(NO₃)₃ (b) in alkaline DMF solutions ($C_L=C_{Yb(III)}=0.05$ mM at 0.1 mM TEA; $C_L=C_{Tb(III)}=0.05$ mM at 0.2 mM TEA) at negative mode. Inset represents isotopic distribution patterns.

In the case of **3** and the lanthanide nitrates in alkaline DMF solution, ESI spectra (Fig. 4) reveal no peaks in negative mode, which can be assigned to the complexes. Nevertheless, peaks at m/z^+ 1102.4 and m/z^+ 1117.4 in the ESI spectra of the solutions indicate the formation of $[(\text{Tb}^{3+}\text{DMF})(3^{2-})]^+$ and $[(\text{Yb}^{3+}\text{DMF})(3^{2-})]^+$ in alkaline DMF solutions.

Thus, the ESI spectra confirm the 1:1 complex formation of ligands 3 and 6 with lanthanide ions in alkalized DMF solutions.



Fig. 4. ESI spectra of calix[4]arene **3** with Yb(NO₃)₃ (a) and Tb(NO₃)₃ (b) in alkaline DMF solutions ($C_L=C_{Yb(III)}=0.05$ mM at 0.1 mM TEA; $C_L=C_{Tb(III)}=0.05$ mM at 0.2 mM TEA) in positive mode. Inset represents isotopic distribution patterns.

Modeling of possible coordination modes of lanthanide ions with 3 and 6 in alkaline media Structural diversity of the ligands (Scheme 1) may be the reason for different coordination environment of lanthanide ions in their complexes with 3 and 6. As it was abovementioned the lower rim of 3 is phenolic, while it is alkyl-substituted for 6, which is the only structural

difference between the ligands. It is worth noting that coordination of lanthanide ions via 1,3diketone groups is more thermodynamically favorable than the coordination via phenolate groups in alkaline media. Nevertheless, deprotonation of lower phenolic rim is the well-known reason for conformational shift of calix[4]arenes.^{36,37} The *cone* conformation of calix[4]arenes in neutral media is favored by the efficient hydrogen bonding of the phenolic groups, while their deprotonation in alkaline media induces the conformation shift towards *partial cone*, *1,2-* and *1,3-alternates*.

Structural modeling of complexes was performed with the use of MOPAC 2012 software with the aim to illustrate diversity of binding modes of lanthanide ions via 1,3-diketonate groups, when calix[4]arene backbone is in different conformations. The possible complex structures represented in Scheme 2 indicate the similar coordination of lanthanide ions via two chelating 1,3-diketonate groups for all calix[4]arene conformers.



Scheme 2 Possible modes of binding of Tb(III) cations to molecule 3. The structures are obtained after SPARKLE/PM7 optimization (for details see subsection 'Quantum-chemical computations').

Luminescence spectroscopy

The electronic absorption spectra of the Tb(III) and Yb(III) complexes (Fig.1) indicate efficient feeding of the singlet excited levels, while the energy from singlet levels can be transferred to lanthanide-centered excited level through the intersystem crossing. Triplet excited state is considered as the main pathway in ligand-to-lanthanide energy transfer in 1,3-diketonate complexes of lanthanides.³⁸

The energy gap between triplet level of ligand and excited state of Tb(III) is of great impact in sensitizing Tb(III)-centered luminescence. Thus, the sensitizing abilities of ligands **3** and **6** were confirmed by measuring intra-ligand emission for Gd(III) counterparts of the Tb(III)

complexes in alkaline DMF solutions (Fig. 5). The emission bands of Gd(III) complexes with ligands 3 and 6 arise from ligand-centered luminescence. Although both emission bands are widened the energy of the triplet levels for ligands 3 and 6 can be compared. The results indicate that the triplet levels of 3 are underlying those of ligand 6 (Fig. 5). Moreover, the intensity of the intra-ligand emission is significantly greater for ligand 6 than for 3, while the intensity of the intraligand electronic absorption is greater for 3 than for 6 (Fig.1). This disagreement indicates that intersystem crossing is more efficient for 6 versus 3 in their complexes with Gd(III). Taking into account that intersystem crossing is the main pathway of triplet levels excitation, the different antennae effects of ligands 3 and 6 on Tb(III)-centered luminescence is rather anticipated.



Fig. 5. Luminescence spectra of Gd-L alkalized DMF solutions. L=**3** (2), **6** (1). C_L=C_{Gd(III)}=4.5 mM, C_{TEA}=18 mM, λ_{ex} =350 nm. The red color Y axis refers to emission magnitude for the spectrum of Gd-**3**.

Luminescence spectra of the alkalized DMF solutions of ligands **3** and **6** in the presence of Tb(NO₃)₃ are characterized by the peaks peculiar to Tb(III)-centered emission (emission bands at 494 nm, 545 nm and 587 nm, which are assigned to ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$, ${}^{5}D_{4} \rightarrow {}^{7}F_{4}$ transitions) under the excitation at λ =325 nm (Fig. 6). The luminescence spectra reveal the difference between ligands **3** and **6** in their antenna-effects on Tb(III)-centered luminescence.



Fig. 6. Excitation (a) and luminescence spectra (b) of alkalized DMF solutions of Tb(III) with ligands **3** (1) and **6** (2). $C_L=C_{Tb(III)}=0.1$ mM, $C_{TEA}=0.4$ mM, $\lambda_{ex}=325$ nm.

The results (Figs. 6, 7) point to ligand **6** being the more efficient antenna for Tb(III)centered luminescence than ligand **3** due to higher lying triplet levels, which facilitates the energy transfer to ${}^{5}D_{4}$ level of Tb(III). The lower lying triplet levels of **3** versus **6** should be noted as a reason for less efficient feeding of ${}^{5}D_{4}$ level in Tb(III) complexes with **3** versus **6**. It is worth noting that measurements of excited state lifetimes (τ) confirm the difference in the steady state luminescence. In particular, τ is about 0.15 ms for Tb(III) complexes with **6**, while it decreases to 0.09 ms in the case of **3** (the corresponding luminescence decay curves are represented in Fig. S3 in ESI).

It is well-known that ${}^{2}F_{5/2}$ level of Yb(III) is much lower than ${}^{5}D_{4}$ level of Tb(III). Thus, abilities of the ligands to sensitize Yb(III)-centered luminescence may differ from those for Tb(III). The luminescence measurements in alkaline DMF solutions of Yb(III) complexes with ligands **3** and **6** reveal Yb(III)-centered NIR-luminescence at 976 nm arisen from ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition (Fig. 7). The results indicate rather poor Yb(III)-centered luminescence in the solutions of **3**, while the antenna effect of ligand **6** is more significant.



Fig. 7. Excitation (a) and luminescence spectra (b) of alkalized DMF solutions of Yb(III) with ligands **3** (1) and **6** (2). $C_L=C_{Yb(III)}=0.1$ mM, $C_{TEA}=0.4$ mM, $\lambda_{ex}=325$ nm.

This tendency is in good agreement with the observation that revealed for the Tb(III)centered luminescence. The worse feeding of the triplet level of **3** versus **6**, which is evident from intensities of the corresponding ligand-centered luminescence (Fig. 5) is a main reason for the difference in antenna effects of **3** and **6**. Moreover, radiationless decay arisen from energy stock to high-frequency oscillators of the ligand is more important for Yb(III) than for Tb(III) complexes. Thus, the increase of radiationless decay in Yb(III) complexes with **3** versus **6** due to more conformation flexibility in alkaline media should be assumed as one more cause for the observed difference. It is also worth noting that Yb(III)-centered emission spectra are resolved with additional transitions at lower energy that correspond to the degeneracy of the ²F_{7/2} ground state due to crystal field effects of the ligands.^{39,40}

The probability of the intersystem crossing is more favorable when the vibrational levels of the two excited states overlap. Since the overlapping is greatly affected by structural or conformational changes⁴¹ the reasons for different conformation behavior of structurally similar ligands 3 and 6 are worth discussing. Both ligands 3 and 6 adopt *cone*-conformation in neutral solutions, while their conformation behavior tends to differentiate in alkaline solutions. The lack of intermolecular hydrogen bonding along with more easy conformation transformations make ligand 3 in alkaline media adopting *alternate* to *cone* conformations, which are represented by Scheme 2 c,d,e. Bulky substituents of ligand 6 restrict conformation shifts from *cone* (Scheme 2 a,b) to *alternate* conformations (Scheme 2 c,d,e).^{31,42} These tendencies are in good agreement with the experimentally observed difference in ligand-centered luminescence for Gd(III) complexes of ligands 3 and 6. The work of Iki¹⁹ should be mentioned for accurate correlation between the conformation of calix[4]arene backbone and its triplet level energy. Unfortunately, all precipitates separated from the solutions of lanthanide complexes are amorphous, which excludes the structure evaluation by X-ray analysis. Nevertheless, difference in the intraligand emission for ligands 3 and 6 correlates with the well-known effects of lower rim deprotonation or alkoxy-substitution on conformation behavior of calix[4]arene derivatives. Moreover, the obtained results highlight conformation shift of calix[4]arene backbone as convenient tool to tune antenna effect of calix[4]arene derivatives.

Summary

The obtained results introduce facile synthetic route for novel calix[4]arene macrocyclic ligands functionalized with four 1,3-diketone groups at the upper rim and hydroxyl (**3**) or propyl (**6**) groups at the lower rim on the basis of nucleophilic substitution of calix[4]arene. Their ability to form 1:1 complexes with Tb(III) and Yb(III) in alkaline DMF solutions through coordination via 1,3-diketonate groups is revealed from spectroscopic measurements. The sensitizing of Tb(III)-centered luminescence confirms the complex formation of both ligands

with Tb(III) in the solutions, although points to significant difference in antenna-effects of 3 and 6. The intra-ligand emission revealed from luminescence measurements of Gd(III) complexes with **3** and **6** indicates the inconvenient energy gap between triplet level of ligand **3** and ${}^{5}D_{4}$ level of Tb(III) as main reason for worse antenna-effect of 3 versus 6. Ligands 3 and 6 exhibit different conformation behavior in alkaline DMF solutions due to well-known effects of lower rim deprotonation and alkoxy-substitution on conformation behavior of calix[4]arene derivatives. Structural modeling of the complexes illustrates that bis-chelating of the lanthanide ions via two diketonate-groups is favorable coordination mode for all conformations of calix [4] arene backbone. In the case of Yb(III)-centered luminescence the ligand 6 is also a better sensitizer than 3, although the feeding of lower energy level ${}^{2}F_{5/2}$ of Yb(III) must be insensitive to the difference in triplet level energy of **3** and **6**. Both greater radiationless decay contribution and less efficient feeding of the triplet level of **3** should be assumed as reasons for the observed tendency. The obtained results point to conformation behavior of calix[4]arene backbone as one more cause affecting lanthanide-centered luminescence in lanthanide complexes with calix[4]arene derivatives and can be utilized for the design of new highly luminescent lanthanide complexes.

Experimental

Reagents and materials

Acetylacetone was distilled before use. 1,4-Dioxane and toluene were purified by distillation over metallic sodium. N,N-Dimethylformamide (DMF) (Acros Organics) was distilled over P_2O_5 . CDCl₃ (99.8% isotopic purity) from Aldrich was used for NMR spectroscopy. Ytterbium(III) nitrate pentahydrate (Yb(NO₃)₃·5H₂O) (Aldrich Chemistry), triethylamine (TEA) (Acros Organics) were used as commercially received without further purification. Other commercial reagents were used as received.

The sodium salt of acetylacetone was synthesized by addition of excess Na (metal plates) to acetylacetone in absolute toluene. After stirring the mixture at 50 °C for 4 h the precipitate was decanted from residues of unreacted sodium, washed with diethyl ether, and dried *in vacuo*. $T_{decomp.} > 198$ °C.

Methods

Microanalyses of C and H were carried out with a EuroVector CHNS-O Elemental Analyser EA3000. Melting points of compounds were measured with a Boetius hotstage apparatus. MALDI mass spectra were detected on a Bruker Ultraflex III MALDI-TOF/TOF mass spectrometer. ESI measurements were performed using an AmazonX ion trap mass spectrometer in positive and negative mode. NMR experiments were performed on a Bruker AVANCE-600

spectrometer at 303K equipped of a 5 mm diameter broadband probe head working at 600.13 MHz in ¹H and 150.864 MHz in ¹³C experiments. Chemical shifts in ¹H and ¹³C spectra were reported relative to the solvent as internal standard (CDCl₃ δ (¹H) 7.27 ppm, δ (¹³C) 77.2 ppm). Assignment of NMR signals was accomplished by means of 2D COSY, ¹H–¹³C HSQC and ¹H–¹³C HMBC experiments. The pulse programs of the COSY, HSQC and HMBC experiments were taken from Bruker software library. IR absorption spectra were recorded on a Vector-22 Bruker FT-IR spectrophotometer with a resolution of 4 cm⁻¹ as Nujol emulsions and KBr pellets of compounds.

The steady-state luminescence spectra were recorded on a spectrofluorometer Cary Eclipse (Agilent Technologies) in 10 mm quartz cuvettes. Excitation of samples was performed at 325 nm, and emission detected at 545 nm (for terbium luminescence) and 976 nm (for ytterbium luminescence) with a 6 nm slit width for both excitation and emission. Time-resolved measurements were performed using the following parameters: time per flash-49.00 ms, flash count-200 ms, initial delay-0.05 ms and sample window-2 ms. The normalized fluorescence decay curves are presented in Fig. S3 in ESI.

UV-VIS spectra were recorded on a Lambda 35 spectrophotometer (Perkin-Elmer) in 10 mm quartz cuvettes. The Job plotting was done from monitoring of the absorbance at $(A_{\lambda} - A_{\lambda L})$, where $A_{\lambda L}$ is absorbance at 320 nm for **3** and 306 nm for **6**.

Quantum-chemical computations. Structural modeling of complexes was performed with the use of MOPAC 2012 software.⁴³ The PM7 semiempirical method was applied⁴³ using of Sparkle/PM7 Lanthanide Parameters⁴⁴ for the Modeling of Tb(III) complexes, which allowed us to minimize computational time and resources and to maintain the accuracy comparable to non-empirical approaches.

Synthesis

The synthetic routes, the structural formulae and numbering of atoms of the investigated compounds are shown in Scheme 1. The calix[4]arene $1,^{34}$ 25,26,27,28-tetra-propoxycalix[4]arene $4,^{45}$ and their 5,11,17,23-tetrakis(halogenomethyl) derivatives 2^{36} and 5^{46} were obtained as described in the literature.

Synthesis of 5,11,17,23-tetrakis[(acetylaceton-3-yl)methyl)]-25,26,27,28-tetrahydroxycalix[4]arene (3). A mixture of the sodium salt of acetylacetone (NaAA) (0.92 g, 7.5 mmol) and 5,11,17,23-tetrakis(bromomethyl)-25,26,27,28- tetrahydroxycalix[4]arene 2 (1.19 g, 1.5 mmol) in anhydrous dioxane (40 mL) was stirred at 35 °C under an argon atmosphere for 3 h. Thereafter, dioxane was distilled off under reduced pressure. The residue was acidified with 1 M HCl (40 mL). After addition of CH_2Cl_2 (40 mL) the mixture was vigorously stirred. The organic layer was separated, washed several times with water, dried over MgSO₄ and concentrated by

distillation. Solvent residues were removed at 80 °C *in vacuo*. After foaming, the product **3** was obtained as a straw color powder (0.84 g) in 65% yield. Mp: 89-90 °C. ¹H NMR (600.13 MHz, CDCl₃, 303K, ppm), δ : 16.7-16.9 (m, OH_{enol}), 10.10 (4H, H(10)), 6.80 (8H, H(6)), 4.19 (4H, H(9)eq), 3.93_{ket} (t, ³*J*=5.3 Hz, 4H for keto form, H(3)_{ket}), 3.46 (4H, H(9)_{ax})), 3.44_{en}(s, 4H for enolic form H(4)) and 2.95_{ket} (d, ³*J* = 5.3 Hz, 8H for keto form, H(4)), 2.12_{ket}, 2.03_{en} (m, 24 H, H(1)). ¹³C NMR (150.9 MHz, CDCl₃, 303 K, ppm) δ : 203.5_{ket}, 191.9_{en} C(2); 147.6 C(8); 129.3 C(6); 128.6 C(7); 129.7 C(5); 108.4_{en}, 70.5_{ket} C(3); 33.3_{ket}, 32.1_{en} C(4); 31.9 C(9); 29.8_{ket}, 23.4_{en} C(1). IR (nujol, cm⁻¹): v = 3183 (vbr, v(OH)), 3000-2800 (v(CH), (v(CH₂) and (v(CH₃) for KBr pellet), 1724, 1698 (v(C=O)), 1603 (v(C=O) and v(C=C)), 1458 (v(Ph)), 1377, 1357, 1245, 1224, 1147 (v_{as}(CCC)), 1077, 1021, 950 (v_s(CCC)). HR-MALDI-MS: *m/z* calcd for C₅₂H₅₆O₁₂⁺ [M+Na]⁺ 895.3664, found 895.3670. Calcd for C₅₂H₅₆O₁₂: C, 71.54; H, 6.47. Found: C, 71.86; H, 6.43.

Synthesis of 5,11,17,23-tetrakis[(acetylaceton-3-yl)methyl)]-25,26,27,28-tetrapropoxycalix[4]arene (6). 5,11,17,23-Tetrakis(chloromethyl)-25,26,27,28-tetra-propoxycalix[4]arene 5 (0.4 g, 0.5 mmol) and the sodium salt of acetylacetone (NaAA) (0.38 g, 3.1 mmol) were mixed in anhydrous dioxane (30 mL). The suspension was refluxed with stirring for 24h under argon. Then dioxane was distilled off and the residue acidified with 1 M HCl (20 mL). After addition of CH₂Cl₂ (40 mL), the mixture was vigorously stirred. The organic layer was separated, washed twice with water, dried over MgSO₄ and concentrated. Solvent residues were removed at 80 °C in vacuo. After foaming, the product 6 was obtained as a straw color powder (0.41g) with the yield 77%. Mp: 80-83 °C. ¹H NMR (600.13 MHz, CDCl₃, 303 K, ppm), δ: for enol form: 16.7-16.9 (m, OHen), 6.4-6.6 (8H, H(6)), 4.41 (4H, H(9)eq), 3.82 (4H, for keto form H(3)), 3.79 (m, 8H, H(10)), 3.39 (m, 4H for enolic form H(4)) and 2.85_{ket} (m, 8H for keto form, H(4)), 3.09 (4H, H(9)_{ax}), 2.14_{en} and 2.09_{ket} (m, 24 H for keto and enolic forms, H(1)), 1.94 (m, 8H, H(11)); 1.01 (m, 12H, H(12)). ¹³C NMR (150.9 MHz, CDCl₃, 303 K, ppm) δ, enol form: 204.1_{ket}, 191.9_{en} C(2), 155.4 C(8), 135.2 C(7), 131.3 (C6)_{en} and 128.2 C(6)_{ket}, 128.5 C(5), 109.2_{en}, 70.3_{ket} C(3), 77.8 C(10), 34.0 ket, 31.1 en C(4); 29.8 C(9), 29.7 ket, 23.4 en C(1); 23.3 C(11), 10.5 C(12). IR (nujol, cm⁻¹): v = 3405 (overtone (v(C=O)), 3000-2800 (v(CH), (v(CH₂) and (v(CH₃) for KBr pellet), 1720, 1699 (v(C=O)), 1603 (v(C=O) and v(C=C)), 1465 (v(Ph)), 1378, 1359, 1304, 1254, 1221, 1146 ($v_{as}(CCC)$), 1067, 1041, 1007, 964 ($v_{s}(CCC)$). HR-MALDI-MS: m/z calcd for $C_{64}H_{80}O_{12}^{+}$ [M+Na]⁺ 1063.5542, found 1063.5553. Calcd for C₆₄H₈₀O₁₂: C, 73.82; H, 7.74. Found: C, 73.94; H, 7.98.

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- 1. Kuriki, K.; Koike, Y.; Okamoto, Y. Chemical Reviews 2002, 102, 2347-2356.
- 2. Martins, J. P.; Martín-Ramos, P.; Coya, C.; Álvarez, A. L.; Pereira, L. C.; Díaz, R.; Martín-Gil, J.; Ramos Silva, M. *Materials Chemistry and Physics* **2014**, *147*, 1157-1164.
- 3. Reid, B. L.; Stagni, S.; Malicka, J. M.; Cocchi, M.; Hanan, G. S.; Ogden, M. I.; Massi, M. *Chemical Communications* **2014**, *50*, 11580-11582.
- 4. Reid, B. L.; Stagni, S.; Malicka, J. M.; Cocchi, M.; Sobolev, A. N.; Skelton, B. W.; Moore, E. G.; Hanan, G. S.; Ogden, M. I.; Massi, M. *Chemistry – A European Journal* **2015**, *21*, 18354-18363.
- 5. van der Ende, B. M.; Aarts, L.; Meijerink, A. *Physical Chemistry Chemical Physics* 2009, *11*, 11081-11095.
- 6. Shi, M.; Ding, C.; Dong, J.; Wang, H.; Tian, Y.; Hu, Z. *Physical Chemistry Chemical Physics* **2009**, *11*, 5119-5123.
- 7. Tyler, B.; Jeevan, M.; May, P. S.; Jon, K.; William, C.; Krishnamraju, A.; Swathi, V.; QuocAnh, N. L. *Nanotechnology* **2012**, *23*, 185305.
- 8. Sabbatini, N.; Guardigli, M.; Lehn, J.-M. Coordination Chemistry Reviews 1993, 123, 201-228.
- 9. Biju, S.; Eom, Y. K.; Bunzli, J.-C. G.; Kim, H. K. *Journal of Materials Chemistry C* **2013**, *1*, 6935-6944.
- 10. Bunzli, J.-C. G.; Piguet, C. Chemical Society Reviews 2005, 34, 1048-1077.
- Sukhikh, T. S.; Bashirov, D. A.; Kuratieva, N. V.; Smolentsev, A. I.; Bogomyakov, A. S.; Burilov, V. A.; Mustafina, A. R.; Zibarev, A. V.; Konchenko, S. N. *Dalton Transactions* 2015, 44, 5727-5734.
- 12. Binnemans, K. In *Handbook on the Physics and Chemistry of Rare Earths;* Karl A. Gschneidner, J.-C. G. B.; Vitalij, K. P. Eds.; Elsevier, 2005; pp. 107-272.
- Bassett, A. P.; Magennis, S. W.; Glover, P. B.; Lewis, D. J.; Spencer, N.; Parsons, S.; Williams, R. M.; De Cola, L.; Pikramenou, Z. *Journal of the American Chemical Society* 2004, *126*, 9413-9424.
- 14. Yuan, J.; Sueda, S.; Somazawa, R.; Matsumoto, K.; Matsumoto, K. *Chemistry Letters* 2003, *32*, 492-493.
- 15. Irfanullah, M.; Iftikhar, K. Inorganic Chemistry Communications 2009, 12, 296-299.
- 16. Yang, C.; Luo, J.; Ma, J.; Lu, M.; Liang, L.; Tong, B. Dyes and Pigments **2012**, *92*, 696-704.
- Shamsutdinova, N. A.; Podyachev, S. N.; Sudakova, S. N.; Mustafina, A. R.; Zairov, R. R.; Burilov, V. A.; Nizameev, I. R.; Rizvanov, I. K.; Syakaev, V. V.; Gabidullin, B. M.; Katsuba, S. A.; Gubaidullin, A. T.; Safiullin, G. M.; Dehaen, W. *New Journal of Chemistry* 2014, *38*, 4130-4140.
- Safiullin, G. M.; Nikiforov, V. G.; Davydov, N. A.; Mustafina, A. R.; Soloveva, S. Y.; Lobkov, V. S.; Salikhov, K. M.; Konovalov, A. I. *Journal of Luminescence* 2015, *157*, 158-162.
- 19. Kajiwara, T.; Katagiri, K.; Hasegawa, M.; Ishii, A.; Ferbinteanu, M.; Takaishi, S.; Ito, T.; Yamashita, M.; Iki, N. *Inorganic Chemistry* **2006**, *45*, 4880-4882.
- 20. Senthilvelan, A.; Tsai, M.-T.; Chang, K.-C.; Chung, W.-S. *Tetrahedron Letters* **2006**, *47*, 9077-9081.
- 21. Kogan, K.; Biali, S. E. The Journal of Organic Chemistry 2009, 74, 7172-7175.
- 22. Kogan, K.; Columbus, I.; Biali, S. E. *The Journal of Organic Chemistry* **2008**, *73*, 7327-7335.
- 23. Jiang, X.-F.; Cui, Y.-X.; Yu, S.-Y. Synlett 2014, 25, 1181-1185.
- 24. Fujimoto, K.; Shinkai, S. *Tetrahedron Letters* **1994**, *35*, 2915-2918.
- 25. Podyachev, S. N.; Sudakova, S. N.; Galiev, A. K.; Mustafina, A. R.; Syakaev, V. V.; Shagidullin, R. R.; Bauer, I.; Konovalov, A. I. *Russian Chemical Bulletin* **2006**, *55*, 2000-2007.

	19
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26.	Gutsche, C. D.; Nam, K. C. Journal of the American Chemical Society 1988 , 110, 6153-6162.
27.	Almi, M.; Arduini, A.; Casnati, A.; Pochini, A.; Ungaro, R. <i>Tetrahedron</i> 1989 , <i>45</i> , 2177-2182.
28.	Bellamy, L. J. The Infrared Spectra of Complex Molecules; Springer Netherlands, 1980.
29.	Nakanishi, K. Journal of Pharmaceutical Sciences 1963, 52, 716-716.
30.	Yin, D.; Liu, B.; Zhang, L.; Wu, M. Journal of Nanoparticle Research 2011, 13, 7271-7276.
31.	Gutsche, C. D. In <i>Calixarenes: An Introduction (2);</i> Cambridge Ed.; The Royal Society of Chemistry, 2008; pp. 88-93.
32.	Asfari, MZ. <i>Calixarenes 2001</i> ; Kluwer Academic Publishers: Dordrecht: The Netherlands, 2001.
33.	Jaime, C.; De Mendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C. <i>The Journal of Organic Chemistry</i> 1991 , <i>56</i> , 3372-3376.
34.	Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. <i>The Journal of Organic Chemistry</i> 1985 , <i>50</i> , 5802-5806.
35.	Lang, J.; Deckerová, V.; Czernek, J.; Lhoták, P. <i>The Journal of Chemical Physics</i> 2005, <i>122</i> , 044506.
36.	Guo, TD.; Zheng, QY.; Yang, LM.; Huang, ZT. <i>Journal of inclusion phenomena</i> and macrocyclic chemistry 2000 , <i>36</i> , 327-333.
37.	Mustafina, A.; Gruner, M.; Gubaidullin, A.; Katsyuba, S.; Skripacheva, V.; Zvereva, E.; Kleshnina, S.; Habicher, WD.; Soloveva, S.; Konovalov, A. <i>Supramolecular Chemistry</i> 2010 , <i>22</i> , 203-211.
38.	Wang, X.; Yan, Q.; Chu, P.; Luo, Y.; Zhang, Z.; Wu, S.; Wang, L.; Zhang, Q. <i>Journal of Luminescence</i> 2011 , <i>131</i> , 1719-1723.
39.	Ziessel, R. F.; Ulrich, G.; Charbonnière, L.; Imbert, D.; Scopelliti, R.; Bünzli, JC. G. <i>Chemistry – A European Journal</i> 2006 , <i>12</i> , 5060-5067.
40.	Lapadula, G.; Bourdolle, A.; Allouche, F.; Conley, M. P.; del Rosal, I.; Maron, L.; Lukens, W. W.; Guyot, Y.; Andraud, C.; Brasselet, S.; Copéret, C.; Maury, O.; Andersen, R. A. <i>Chemistry of Materials</i> 2014 , <i>26</i> , 1062-1073.
41.	Cao, J.; Xie, ZZ. Physical Chemistry Chemical Physics 2016, 18, 6931-6945.
42.	Lang, J.; Vágnerová, K.; Czernek, J.; Lhoták, P. Supramolecular Chemistry 2006, 18, 371-381.
43.	MOPAC 2012, Stewart, J. J. P., 2012.
44.	Dutra, J. D. L.; Filho, M. A. M.; Rocha, G. B.; Freire, R. O.; Simas, A. M.; Stewart, J. J. P. <i>Journal of Chemical Theory and Computation</i> 2013 , <i>9</i> , 3333-3341.
45.	Dondoni, A.; Marra, A.; Scherrmann, MC.; Casnati, A.; Sansone, F.; Ungaro, R. <i>Chemistry – A European Journal</i> 1997 , <i>3</i> , 1774-1782.
46.	Nagasaki, T.; Sisido, K.; Arimura, T.; Shinkai, S. Tetrahedron 1992, 48, 797-804.