

Dedicated to V. F. Mironov on His 60th Anniversary

Synthesis of 1,3-Diketo Derivatives of Calix[4]arene with Nonyl Substituents at the Lower Rim as Novel Efficient Sensibilizers of Tb³⁺ Luminescence

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Abstract—Novel bis- and tetra-1,3-diketo derivatives of calix[4]arene with nonyl substituents at the lower rim have been synthesized. Their conformational and tautomeric composition have been determined; spectral parameters and complex formation properties with Tb³⁺ have been studied. Substitution of two 1,3-diketo groups with bromine under going from tetra- to bis 1,3-diketone derivatives was resulted in twofold increase luminescence intensity in their terbium complexes. Lifetime of the excited state of the terbium luminescence of the corresponding complexes as well as lifetime of excited triplet level of the 1,3-diketone ligands have been determined.

Keywords: 1,3-diketone, calix[4]arene, terbium complex, luminescence

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1,3-Diketones are widely used as key reagents in the synthesis of heterocyclic compounds [1–4] including drugs [5]. 1,3-Diketones are popular chelating ligands and extracting agents for many transition metals [6, 7]. These compounds can sensitize IR and visible-range luminescence of lanthanides due to the “antenna” effect of the ligand [8, 9]. The introduction of several 1,3-diketo groups in the ligand molecule opens a possibility of preparation of complexes with unusual structure and improved stability as well as can significantly enhance the luminescent properties of the complexes [10]. In view of this, development of poly-1,3-diketones based on calix[4]arene platform is especially promising, since such framework can afford rigid complexes exhibiting additional antenna effect due to the presence of macrocyclic scaffold.

Methods of 1,3-diketones synthesis have been considered in detail in the available literature [11–13]. The methods applicable for the preparation of poly-1,3-

diketones have been reviewed in [14, 15]. The synthesis is based on the assembly of 1,3-diketo fragments from smaller blocks under relatively rigid conditions. Half of the described compounds have been prepared via the Claisen condensation of an ester and a ketone. The use of these methods is restricted by the possibility of competing reactions such as aldol and ester condensations under conditions of the Claisen condensation. Side reactions accompany the synthesis of poly-1,3-diketones via other methods as well; therefore, the yield of the target products is in general low.

Functionalization of bulky and heavy calix[*n*]arenes bearing several reactive sites is further complicated. The syntheses of derivatives of calix[5]arene and calix[6]arene with 1,3-diketo groups attached via their central atom to the lower rim of the macrocycle have been reported [16, 17]. Their preparation starts with bromination of bridging carbon atoms of calix[*n*]-

arenes. At the next stage, acetylacetone or dibenzoylmethane is added to the brominated derivative, and the mixture was refluxed in ionizing 2,2,2-trifluoroethanol. The yield of the reaction products was significantly reduced (from 51 to 10–23%) with the decrease in the size of the macrocycle and the increase in the volume of 1,3-diketone. Mono-1,3-diketo derivatives of calix[8]arene have been prepared as well [18]. Calix[4]arene distal-substituted at the upper rim by two 1,3-diketone groups has been prepared in high yield (74%) from the chloromethyl derivative and acetylacetone in the presence of potassium *tert*-butylate [19]. Unfortunately, the experimental conditions of the preparation of the key reagent, bis(chloromethyl) derivative, have not been reported. Synthesis of this compound can be accompanied by the formation of hardly separable derivatives of calix[4]arene differing in the substitution degree.

Using the reaction of nucleophilic substitution of halomethyl derivatives of calix[4]arenes with 1,3-diketone sodium salts, we have prepared tetra-1,3-diketo derivatives of calix[4]resorcin [20] and calix[4]arene [21] as well as bis-1,3-diketo derivatives of calix[4]arene unsubstituted at the lower rim [22]. Similarly, we have synthesized the tris-1,3-diketones based on mesitylene platform [23].

Extending this approach, we elaborated a new method of synthesis of bis-1,3-diketone derivatives of calix[4]arene with nonyl substituents at the lower rim of the macrocycle and prepared its tetrasubstituted analog. A special feature of the obtained bis-1,3-diketone derivatives of calix[4]arene is the presence of two bromine atoms instead of two 1,3-diketone groups. It was expected that the long alkyl substituents would improve the solubility of their lanthanide complexes in low-polar organic media, and the presence of bromine atoms in the bis-1,3-diketones could enhance the luminescence of the complexes due to the “heavy atom effect” [24].

Novel bis- and tetra-1,3-diketones **4**, **10** were synthesized from the unsubstituted at the upper rim calix[4]arene **1**. Addition of a solution of compound **1** in DMF to a suspension of NaH afforded the sodium salt of calix[4]arene, treatment of which with excess of 1-iodopropane gave the tetraalkyl derivative **2**. The interaction of the latter compound with excess of methyl chloromethyl ether in the presence of SnCl₄ yielded tetra(chloromethyl)calix[4]arene **3** in 70% yield (Scheme 1).

Tetra-1,3-diketone **4** was obtained via the addition of excess of acetylacetone sodium salt to a solution of compound **3** followed by heating during a day. Tetra-1,3-diketone of calix[4]resorcin has been prepared earlier via refluxing in 1,4-dioxane medium [20]. However, when compound **4** was prepared under the same conditions, MALDI TOF analysis of the reaction mixture revealed the presence of compound **4** (*m/z* 1400 [*M* + Na]⁺) along with several side products (**P_n**) (*m/z* 1274, 1316, and 1358 [*M* + Na]⁺). Likely, they were formed via splitting of 1,3-diketo moieties in the presence of catalytic amount of alkali.

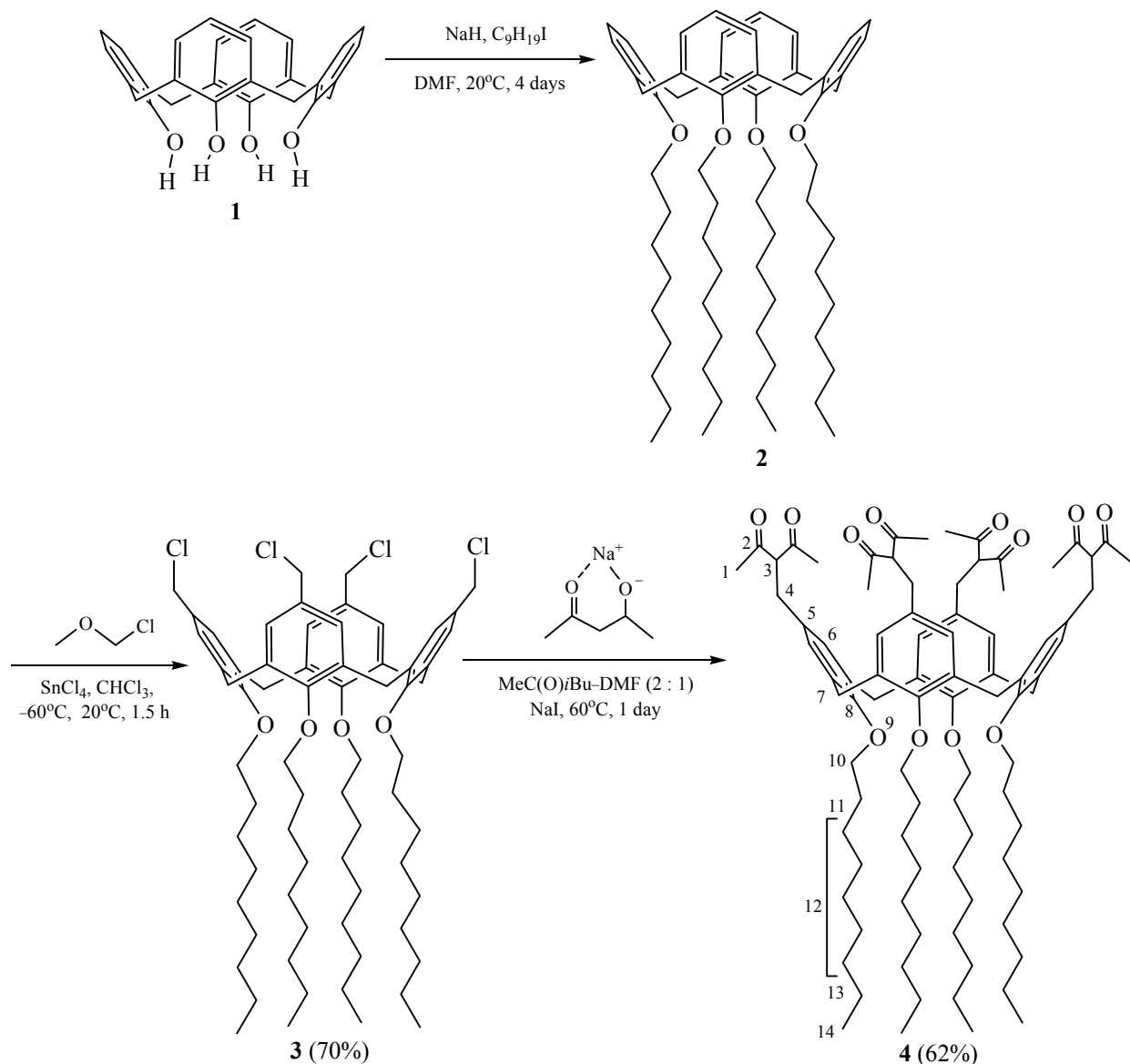
The possibility of such splitting of 1,3-dicarbonyl compounds is significantly increased in the case of the α -substituted derivatives [25, 26]. Formation of such products has been observed in the case of similarly substituted tris-1,3-diketones [27]. The trend is caused by the fact that the keto-enol equilibrium is shifted towards the keto form for the α -substituted compounds. In the enol form, the partially double carbon-carbon bond can be hardly split. Moreover, catalytic amount of alkali is bound by the enol form and cannot participate in the reaction [28].

The optimal conditions of the synthesis of α -substituted acetylacetone have been found as follows: the use of a 2 : 1 mixture of methyl isobutyl ketone and DMF in the presence of excess of NaI at 40–60°C [29]. As a result, tetra-1,3-diketone **4** was obtained in 62% yield (Scheme 1). Mass spectra of the reaction mixture and the spectra of the isolated product did not contain the signals of side products.

The synthesis of bis-1,3-diketone **10** involved the use of dibromo derivative **7** prepared via sequential transformation of calix[4]arene **1** into compounds **5–7** (Scheme 2) by means of protection-deprotection reactions [30]. Tetraalkyl derivative **8**, bis(chloromethyl)calix[4]arene **9**, and bis-1,3-diketone **10** were prepared similarly to compounds **2–4**.

Composition and structure of the prepared compounds were confirmed by the data of elemental analysis, NMR and IR spectroscopy, and mass spectrometry (MALDI TOF). The signals in the NMR spectra of the studied compounds were assigned from the 2D COSY, HSQC, and HMBC data (see the table). The spectra of compounds **2–4** and **8–10** contained the only signal of the bridging methylene carbon atoms (δ_C 30.1–31.6 ppm). According to the De Mendoza rule (δ_C 31±2 and 37±2 ppm for the *cone* and *1,3-alternate* isomers) [31], such values of the chemical shifts

Scheme 1.

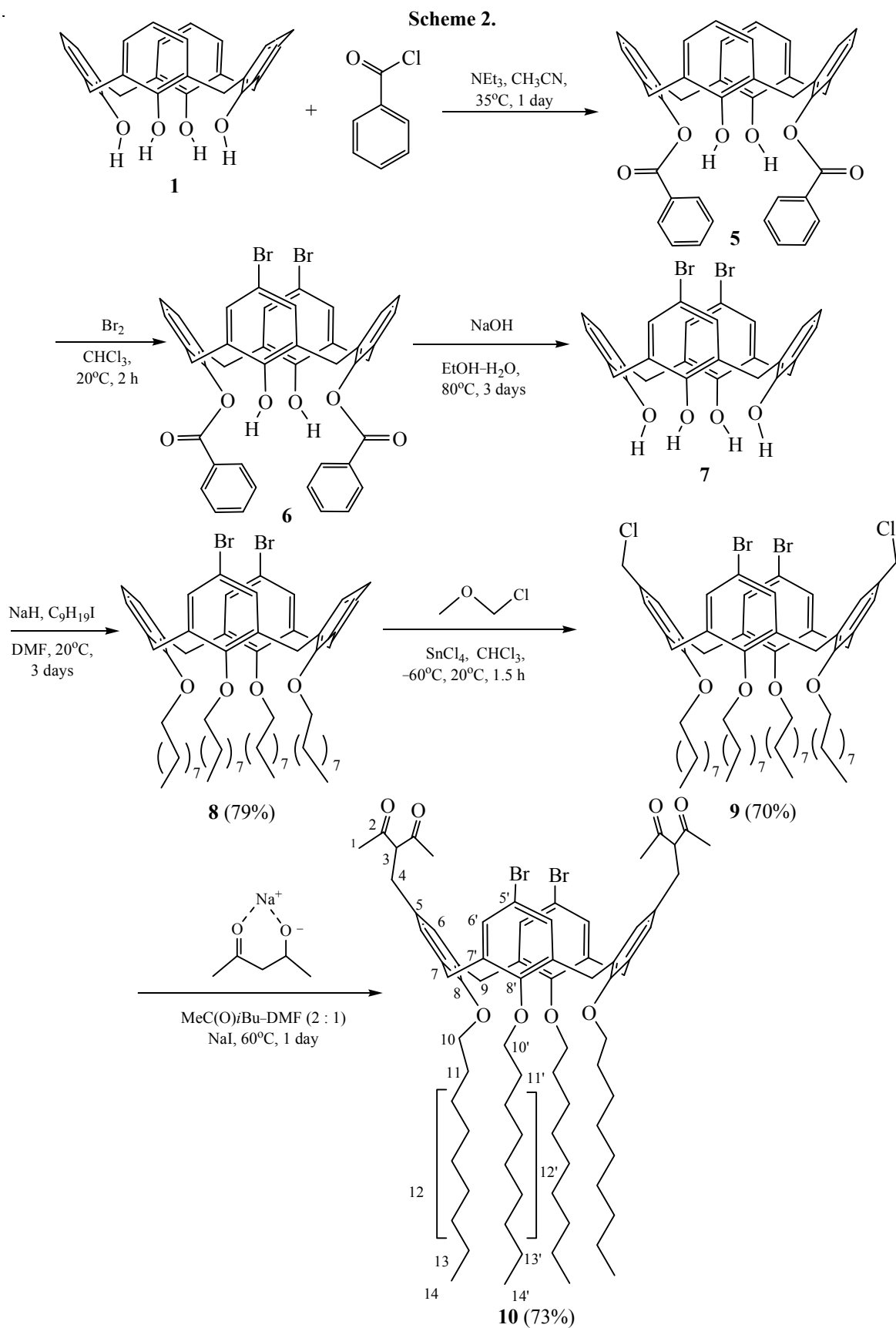


evidenced the *cone* conformer of the prepared calix[4]arenes. The enol form fraction in 1,3-diketones **4** and **10** (CDCl₃) equaled 33 and 38%, respectively. Hence, the exchange of the 1,3-diketone group with bromine atoms in compound **10** practically did not affect the amount of the enol form.

Keto groups of the 1,3-diketone fragments are revealed in the IR spectra as split $\nu(\text{C}=\text{O})$ bands at 1725 and 1699 cm⁻¹ (**4**), 1727 and 1701 cm⁻¹ (**10**). Relative intensity of the band at 1701 cm⁻¹ was reduced about twofold, because of lower content of the keto groups in the compound **10**.

Comparison of UV spectra of calix[4]arenes **4** and **10** (Fig. 1) revealed that the exchange of two 1,3-diketone groups with bromine atoms did not affect the position of the maximum of the major absorption band related to the π - π^* -electronic transition, yet the molar extinction coefficient was reduced [ϵ_{283} 1.07 × 10³ L mol⁻¹ cm⁻¹ (**4**), ϵ_{284} 0.79 × 10³ L mol⁻¹ cm⁻¹ (**10**)]. The spectra of both compounds contained the broad band around 310 nm which was due to the absorption of enol forms of 1,3-diketo fragments.

The addition of Et₃N or Tb(NO₃)₃ to the solutions of compounds **4** or **10** in DMF did not practically



Atom	2		3		4 ^b		8		9		10 ^{b,c}	
	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C	¹ H	¹³ C
1					2.1 m (1.9 m)	23.4 (22.9)					2.19 c, 2.14 s (q), 2.13 s (e)	30.7 (23.5)
2					16.78 m (OH)	204.3 (192.1)					16.85 s (q) (OH), 16.84 s (e) (OH)	204.2 (192.1)
3					3.89 c	70.7 (109.2)					4.08 t (³ J=7.9)	70.5 (109.2)
4			4.312 s	46.8	2.82 m (3.41 m)	34.0 (29.1)			4.33 c	46.7	3.1 d (³ J=7.9) (3.66)	34.4 (32.6)
5	6.57 m	122.0		131.1		131.3	6.65 m	122.6		131.4		131.8 (134.0)
5'					6.84 m (6.8 m)	128.5 (127.6)						115.1
6	6.61 m	128.3	6.67 s	128.8		128.5	6.65 m	128.6	6.66 c	128.8	6.86 s (q), 6.84 s (e), 6.78 s (e)	129.5 (128.2)
6'							6.80 c	130.9	6.81 c	131.1	6.36 m	130.4
7		135.4		135.3		135.2		134.6		134.9		130.5 (130.4)
7'												137.1
8		156.8		156.9		155.2		56.6		156.9		156.2 (156.0)
8'								155.9		155.9		135.8 154.7
9	3.16 (H _{eq}) 4.46 (H _{ax}) d(² J=13.3)	31.2	3.15 (H _{eq}) 4.42 (H _{ax}) d(² J=13.3)	31.1	4.36 br.d (H _{eq}) 3.05 br.d (H _{ax})	30.1	3.13 (H _{eq}) 4.42 (H _{ax}) d(² J=13.3)	31.1	3.12 (H _{eq}) 4.39 (H _{ax}) d(² J=13.3)	31.1	3.07 m, 4.36 m	31.6
10	3.89 t (³ J=7.4)	75.3	3.89 t (³ J=7.5)	75.6	3.86 m	75.5	3.89 t (³ J=7.5)	75.6	3.86 m	75.6	4.01 m	75.3
10'												
	1.92 m	30.6	1.91 m	30.5	2.0 m	30.7	1.91 m	30.4	1.89 m	30.4	1.93–1.85 m	30.2–30.5
11/11'												
2/12'	1.39 m	26.6	1.39 m	26.6	1.31 m	26.0–34.0	1.39 m	26.6	1.37 m	26.5	1.32 m	22.8–32.3
	1.32 m	22.9–32.2		22.2–32.4			1.33 m	22.9–32.1	1.31 m	22.9–32.1		
13/13'												
14/14'	0.91 t (³ J=6.9)	14.3	0.91 t (³ J=6.9)	14.3	0.91 m	14.3	0.92 t (³ J=6.9)	14.3	0.90 t (³ J=6.9)	14.3	0.91 t (³ J=6.9)	14.3

^a Numeration of atoms is shown in the scheme. ^b Assignment for the enol form of 1,3-diketone is given in parentheses. ^c (k) and (e) correspond to the keto and enol forms of the adjacent 1,3-diketone substituents.

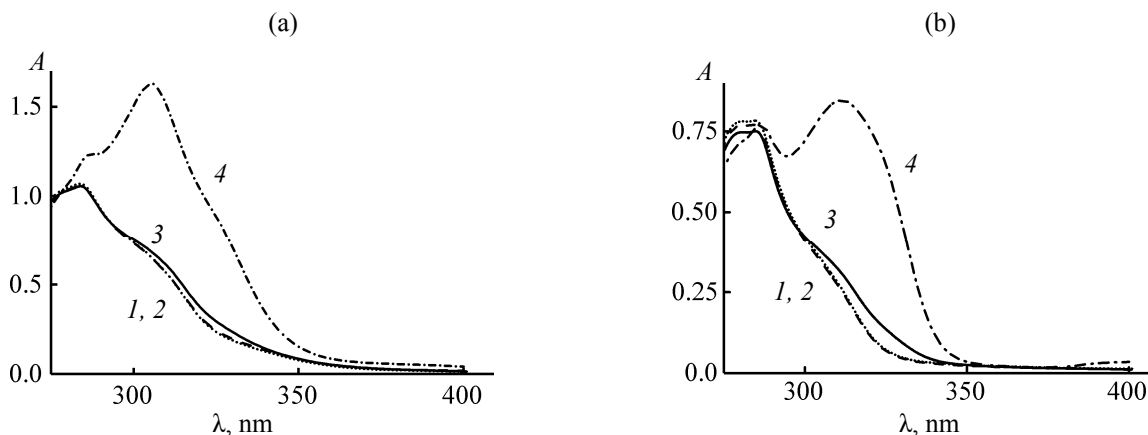


Fig. 1. UV spectra of solutions of compounds **4** (a, 1) and **10** (b, 1) in DMF after addition of Et_3N (2), $\text{Tb}(\text{NO}_3)_3$ (3), Et_3N , and $\text{Tb}(\text{NO}_3)_3$ (4) ($[\text{L}] = [\text{Tb}^{3+}] = 0.1 \text{ mmol/L}$, $[\text{Et}_3\text{N}] = 0.4 \text{ mmol/L}$).

affect the electronic absorption spectra. However, their simultaneous addition led to a significant increase of the absorption around 310 nm, due to the accumulation of the enol form of the ligand during the complex formation. We have earlier demonstrated that when 1,3-diketo groups are fixed at the calix[4]arene scaffold [21] (especially at the rigid cavitant of calix[4]resorcin [20]), the equilibration time during the complex formation is significant. This fact is due to noticeable deceleration of the keto-enol transformation in the α -substituted 1,3-diketones as compared to the unsubstituted analogs. Therefore, in this study we assured the equilibration before recording the spectra of the complexes solution.

Stoichiometry of the formed Tb^{3+} complexes with bis-1,3-diketones **4** and **10** was determined by the

analysis of their absorption spectra using the isomolar series method (the Job's method) (Fig. 2). The position of the maximum in the plots evidenced the formation of the 1 : 1 complex.

To determine the number of deprotonated groups of compounds **4** and **10** involved in the coordination with Tb^{3+} ion, we performed the UV-spectrophotometric titration. The obtained results were presented in as the plots of ΔA as a function of the Et_3N -L molar ratio, with $\Delta A = A - A_0$, A and A_0 being the absorbances in alkaline and neutral acidic solutions in DMF, respectively (Fig. 3). The obtained data evidenced the participation of two chelate groups in the coordination with Tb^{3+} ions.

Luminescence spectra of Tb^{3+} solutions in the presence of Et_3N and compounds **4**, **10** as well as

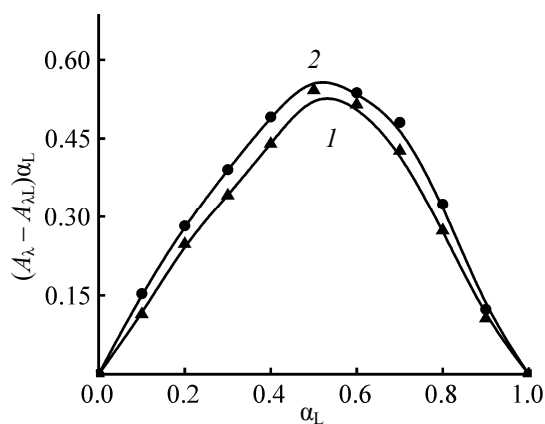


Fig. 2. Job's plots at different molar ratios of ligands **4** (1) or **10** (2) to $\text{Tb}(\text{NO}_3)_3$ in DMF. λ 305 (**4**) and 310 nm (**10**). ($[\text{Tb}^{3+}] + [\text{L}] = 0.1 \text{ mmol/L}$, $\text{L}:\text{Et}_3\text{N} = 1:4$; $\alpha_L = [\text{L}]/([\text{L}] + [\text{Tb}^{3+}])$).

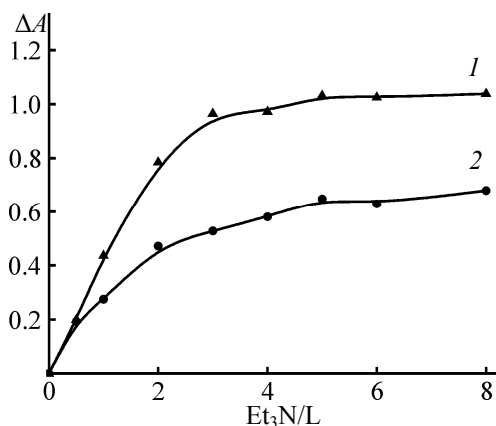


Fig. 3. The change in absorbance of compounds **4** (λ 305 nm, 1) and **10** (λ 310 nm, 2) in the presence of $\text{Tb}(\text{NO}_3)_3$ ($[\text{4}] = [\text{10}] = [\text{Tb}^{3+}] = 0.1 \text{ mmol/L}$) at different Et_3N -L molar ratio in DMF.

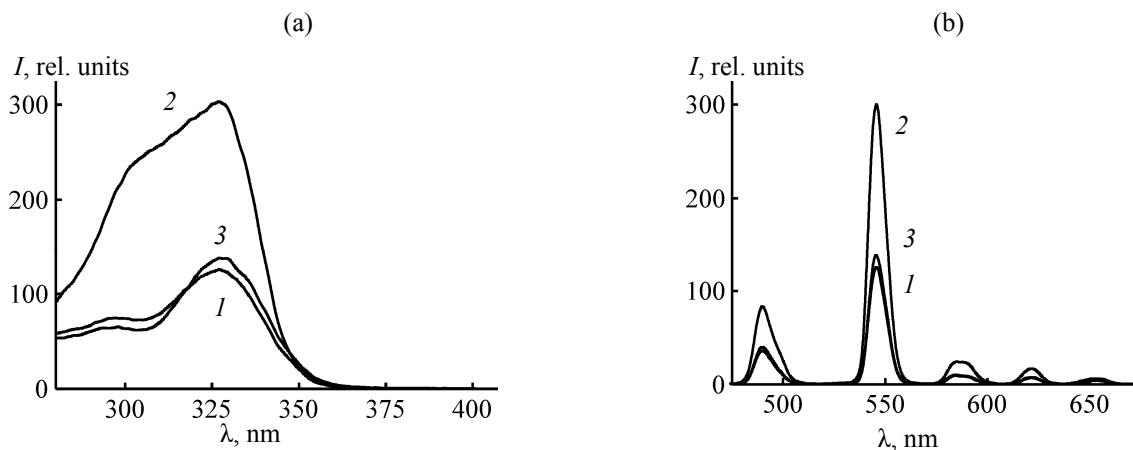


Fig. 4. Excitation (λ_{em} 545 nm) (a) and luminescence (λ_{ex} 327 nm) (b) spectra of Tb^{3+} complexes with ligands **4**, **10**, and **11** (1–3) in DMF ($[Tb^{3+}] = [L] = 0.1$ mmol/L, $[Et_3N] = 0.4$ mmol/L).

analog of compound **4** containing propyl groups at the lower rim of calix[4]arene instead of nonyl ones (**11**, Fig. 4) reflected the difference in the structures of the ligands and complexes. Intensity of luminescence of the complexes with ligands **4** and **11** was close, due to the similarity of the substituents at the upper rim of calix[4]arene, whereas the length of the alkyl substituents at the lower rim did not affect the mentioned properties. The exchange of two 1,3-diketone groups (**4**) with bromine atoms (**10**) resulted in more than twofold (≈ 2.4) increase in the luminescence intensity at λ 545 nm. As was noted above, both ligands formed similar 1 : 1 complexes with Tb^{3+} , and only two of the 1,3-diketo groups were involved in the coordination.

Excitation of the metal ion in coordination compounds of lanthanides occurs via the intramolecular energy transfer from the coordinated ligands containing chromophores [32]. In detail, after absorption of a photon, the ligands being first excited in the singlet state and then are transformed into the triplet state via intercombinatory conversion. The excitation energy is transferred to the emission level of the lanthanide ion via radiationless mechanism, and then is emitted via luminescence. The efficiency of the energy transfer from the ligands to the ion mainly depends on the energy gap between the lower triplet state of the ligands (T_1) and the emission level of the lanthanide ion. In Tb^{3+} complexes, efficient energy transfer is possible if the energy gap between the T_1 state and the emission level 5D_4 of Tb^{3+} ion, $\Delta E[T_1 - ^5D_4(20500 \text{ cm}^{-1})]$, should be of $2500\text{--}4000 \text{ cm}^{-1}$ [33], and the $\Delta E(S_1 - T_1)$ value should be about 5000 cm^{-1} [34, 35]. It is

important to notice that the luminescence spectra of Tb^{3+} solutions in the presence of Et_3N and ligands **4**, **10**, and **11** in DMF contained no bands of the ligand emission, evidencing efficient energy transfer in the complexes.

To determine the position of the T_1 state of the ligands in the complexes, we prepared analogous solutions of the Gd^{3+} complexes. Since the gap between the ground state $^8S_{7/2}$ and the first excited state $^6P_{7/2}$ was large ($\sim 32000 \text{ cm}^{-1}$), Gd^{3+} ion could not take the energy of triplet state of the ligands. The presence of heavy paramagnetic ion Gd^{3+} in the complexes led to the acceleration of intercombinatory conversion and, hence, the increase in the ratio between the yield of phosphorescence to that of fluorescence of the organic part of the complexes [36]. Therefore, the phosphorescence of ligands can be observed for such compounds at low temperature. Since the atomic number, ionic radius, and paramagnetic parameters of Tb^{3+} and Gd^{3+} ions are close, it was expected that the change of Tb^{3+} ion with Gd^{3+} only slightly affects the rate of the intercombinatory conversion in the ligand surrounding.

Phosphorescence spectra of solutions of the Gd^{3+} complexes with ligands **4** and **10** recorded 100 μs after the excitation by the laser impulse (excitation at 337 nm) at 143 K (Fig. 5) consist of broad bands with maxima at 470 and 456 nm, respectively. To determine precisely the position of the maximum of the 0–0 transition corresponding to energy of the T_1 state of the ligands [36], the phosphorescence spectra were deconvoluted into individual Gaussian bands. The 0–0 transition for the Gd^{3+} complexes corresponds to the maxima at 442 (22624 cm^{-1}) (**4**) and 429 nm (23310 cm^{-1})

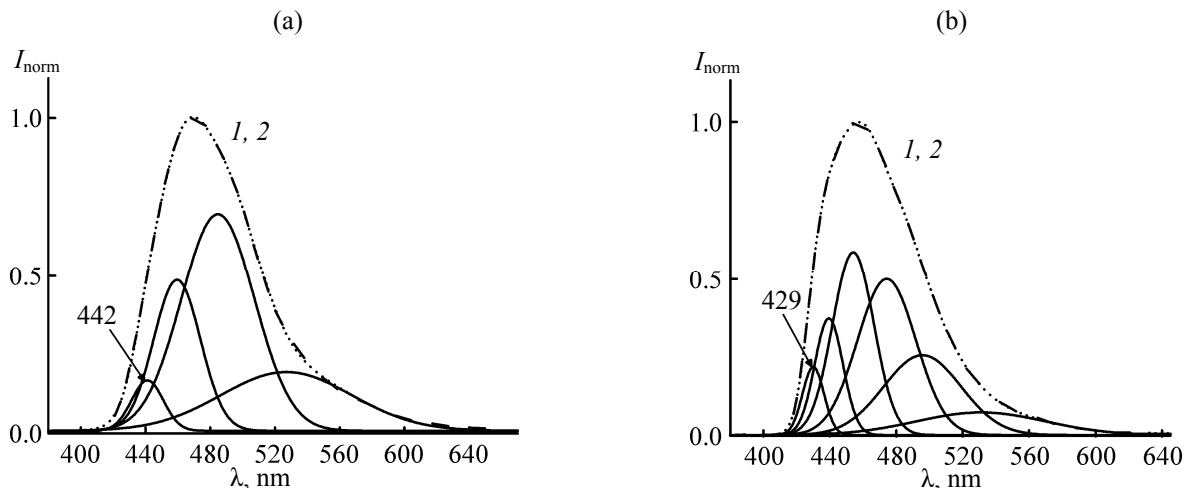


Fig. 5. Deconvolution of time-resolved phosphorescence spectra (delay 100 μs , λ_{ex} 337 nm, 143 K) of Gd^{3+} complexes with ligands **4** in DMF (a) and **10** (b) into individual Gaussian bands. [Gd^{3+}] = [L] = 1 mmol/L, [Et_3N] = 4 mmol/L; (I) experimental spectrum and (2) envelope curve.

(10). Analysis of kinetic curves of fluorescence (Fig. 6) gave the average time of the phosphorescence decay, 558 (**4**) and 865 μs (**10**).

Comparison of phosphorescence spectra and kinetics of solutions of Gd^{3+} complexes with ligands **4** and **10** showed that in the latter case the energy of the ligand T_1 state was higher by 680 cm^{-1} , and the average time of phosphorescence decay was longer by 307 μs . The major pathway of the luminescence decay of the Tb^{3+} complexes is the reverse energy transfer from the emission level $^5\text{D}_4$ of the Tb^{3+} ion to the T_1 state of the ligands. This phenomenon is usually observed for the Tb^{3+} complexes with ligands exhibiting the energy of the triplet level below 22300 cm^{-1} [33].

Based on the obtained data, we suggested that the increase in the intensity of luminescence of Tb^{3+} complex with **10** in comparison with the Tb^{3+} complex with **4** was due to the more efficient transfer of energy from the T_1 state of the ligands to the emission level $^5\text{D}_4$ of the Tb^{3+} ion resulting from the increase in the energy gap $\Delta E(T_1 - ^5\text{D}_4)$ and, hence, deceleration of the reverse energy transfer. Moreover, the average lifetime of complex with ligand **10** (τ 114 μs) was somewhat longer in comparison with the other complex (τ 98 μs) (detected at 545 nm). Another reason for the enhancement of the antenna effect of the terbium complex with ligand **10** compared to ligand **4** could be the more efficient energy transfer from the singlet level of the ligand to the triplet one, resulting

from the heavy atom effect (introduction of bromine atoms) [37–40]. Moreover, the exchange of hydrogen with halogen atom tends to reduce the radiationless dissipation of the excitation energy caused by high-frequency vibrations of the C–H bonds.

In summary, we have elaborated the methods of synthesis of novel tetra- and bis-1,3-diketone derivatives of calix[4]arene containing long-chain nonyl substituents at the lower rim. Both ligands efficiently sensitize luminescence of Tb^{3+} in DMF solution. Exchange of two 1,3-diketone groups with bromine atoms led to more than twofold increase in the intensity of Tb^{3+} luminescence in its complexes with retaining of the stoichiometry.

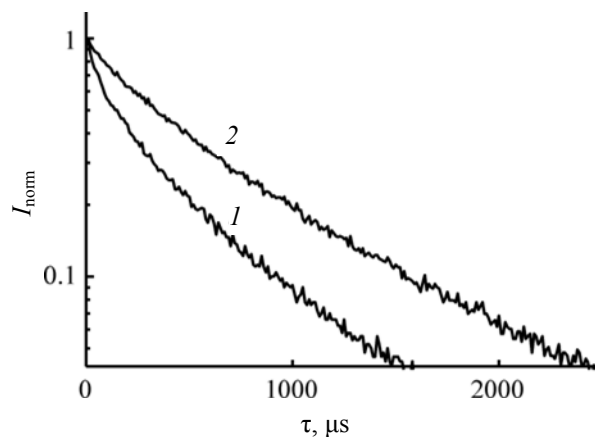


Fig. 6. Normalized kinetic curves of phosphorescence of Gd^{3+} complexes with ligands **4** (1) and **10** (2) in DMF (emission at 470 and 456 nm, respectively) at 143 K. [Gd^{3+}] = [L] = 1 mmol/L, [Et_3N] = 4 mmol/L.

EXPERIMENTAL

Commercial chemicals were used as received: CDCl_3 (99.8%, Aldrich), SnCl_4 (99%, Aldrich), $\text{C}_3\text{H}_7\text{I}$ (99%, Acros organics), $\text{C}_9\text{H}_{17}\text{I}$ (99%, Acros organics), dimethoxymethane (99.5%, Acros organics), and acetyl chloride (98%, Aldrich). Solvents CHCl_3 ("chemical pure") and methyl isobutyl ketone ("pure") were distilled over P_2O_5 under argon. DMF ("chemical pure") was twice distilled under reduced pressure over P_2O_5 . Sodium salt of acetylacetonate was prepared as described elsewhere [23].

The compounds purity was confirmed by means of TLC on Merk 60F-254 plates using a VL-6.LC ultra-violet lamp (254 nm). Melting points were determined using a Boëtius heating stage. IR spectra of emulsions in Vaseline oil were recorded using a Vector-22 Bruker spectrometer. Mass spectra (MALDI) were obtained using a Finnigan MALDI-TOF Dynamo mass spectrometer. Elemental analysis (C, H, Br, and Cl) was performed using a CHN-3 analyzer. NMR spectra were recorded using an AVANCE-600 Bruker spectrometer [600.1 (^1H) and 150.9 MHz (^{13}C)] at 303 K. Chemical shifts of ^1H and ^{13}C were reported relative to the residual signals of the solvent. NMR spectra were assigned using the data of 2D NMR COSY, HSQC, and HMBC experiments performed using standard impulse sequences from the instrument library.

UV spectra were recorded using a Lambda 35 spectrophotometer (Perkin Elmer) with bandwidth 2 nm using 10 mm quartz cells. The complex formation of the prepared compounds with Tb^{3+} ions and stoichiometry of the formed complexes were studied by means of the isomolar series method (the Job's method) and spectrophotometric titration monitoring the change in the absorbance of the solutions at the wavelength of the complexes absorption. Luminescence spectra were recorded using a Cary Eclipse spectrofluorimeter at 25°C using 10 mm quartz cells, the bandwidth was 5 nm.

Time-resolved phosphorescence spectra and the curves of the phosphorescence decay were obtained using an automated optical spectrometer based on a MDR-23 monochromator and a FEU-100 photoelectron multiplier [42]. An LGI-21 impulse nitrogen laser was used as the excitation source. The spectral measurements were performed in a cryostat with uviol windows. The cell was cooled to 143 K with nitrogen vapor. Temperature was monitored using a Testo 735-2 multifunctional thermometer (accuracy ± 0.3 K).

Calix[4]arenes **1** [42] and **5–7** [30] were prepared as described elsewhere.

Methyl chloromethyl ether. A mixture of dimethoxymethane (91 mL, 1.03 mol), acetyl chloride (70 mL, 0.98 mol), and zinc chloride (20 mg) was heated at 50°C during 0.5 h. The heating was then switched off, and the mixture was stirred during 3 h at room temperature. A solution of methyl chloromethyl ether (≈ 6.5 mol/L) in methyl acetate was stable during 1 year when stored at 5–7°C. The prepared solution was used for the synthesis of chloromethyl derivatives **3** and **9** without further purification.

25,26,27,28-Tetra(non-1-yloxy)calix[4]arene (2). A solution of 25,26,27,28-tetrahydroxycalix[4]arene **1** (3 g, 7 mmol) in 100 mL of anhydrous DMF was added to a suspension of NaH (60% in mineral oil, 1.7 g, 42 mmol, pre-washed in hexane). The mixture was vigorously stirred during 0.5 h, then 1-iodononane was added (14.0 mL, 70 mmol), and stirring was continued during 4 days under argon. 200 mL of 2 mol/L aqueous HCl solution was then added, and the reaction products were extracted with dichloromethane (2×150 mL). The organic layer was separated off, twice washed with water, and dried over MgSO_4 . The solution was filtered, and the solvent was distilled off. The residue was kept in vacuum at 80°C, and then methanol was added. The precipitate was decanted several times, triturated in methanol into powder, filtered off, and dried. Yield 5.8 g (89%), mp 39–45°C. Mass spectrum, m/z : 952.0 [$M + \text{Na}$] $^+$, 968.0 [$M + \text{K}$] $^+$. Found, %: C 83.02; H 10.23. $\text{C}_{64}\text{H}_{96}\text{O}_4$. Calculated, %: C 82.70; H 10.41.

5,11,17,23-Tetra(chloromethyl)-25,26,27,28-tetra(non-1-yloxy)calix[4]arene (3). Methyl chloromethyl ether (23 mL, 0.15 mol, c 6.5 mol/L) was added to a solution of calix[4]arene **2** (2.8 g, 3 mmol) in 100 mL of anhydrous CHCl_3 under argon. The reaction mixture was cooled to –60°C, then tin tetrachloride (2.8 mL, 24 mmol) was added dropwise, and the mixture was stirred during 0.5 h at –60 to –30°C. Cooling was then switched off, and the solution was kept at room temperature during 1 h. 100 mL of cool water was added to the reaction mixture, the organic layer was separated off, twice washed with water, and dried over MgSO_4 . The solution was filtered, and the solvent was distilled off. Viscous residue was crystallized from acetonitrile. Yield 2.37 g (70%), white powder, mp 127–131°C. Mass spectrum, m/z : 1144 [$M + \text{Na}$] $^+$, 1160 [$M + \text{K}$] $^+$. Found, %: C 73.08; H 8.83; Cl 12.93.

$C_{68}H_{100}Cl_4O_4$. Calculated, %: C 72.71; H 8.97; Cl 12.62.

5,11,17,23-Tetra[(2,4-dioxopent-3-yl)methyl]-25,26,27,28-tetra(non-1-yloxy)calix[4]arene (4). A mixture of compound **3** (0.5 g, 0.45 mmol) and NaI (0.4 g, 2.7 mmol) was stirred at $\approx 40^\circ\text{C}$ in a mixture of methyl isobutyl ketone (8 mL) and DMF (4 mL) under argon to complete dissolution of the salt. Sodium salt of acetylacetone (0.33 g, 2.7 mmol) was added, and the mixture was stirred during 1 day at 60°C . The solvent was removed, 20 mL of 2 mol/L aqueous solution of HCl was added, and the product was extracted with dichloromethane (2×20 mL). The organic layer was separated off, twice washed with water and then with 10% solution of $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL), and dried over MgSO_4 . The solution was filtered, and the solvent was removed. Yield 0.31 g (62%), light yellow powder, mp $50\text{--}60^\circ\text{C}$. IR spectrum, ν , cm^{-1} : 3400 (OH), 1725 and 1699 (CO), 1467 [$\delta(\text{CH}_2)$], 1357 [$\delta(\text{CH}_3\text{CO})$], 1220 (CCOC). Mass spectrum, m/z : 1400 [$M + \text{Na}$] $^+$, 1416 [$M + \text{K}$] $^+$. Found, %: C 75.95; H 9.16. $C_{88}H_{128}O_{12}$. Calculated, %: C 76.70; H 9.36.

5,17-Dibromo-25,26,27,28-tetra(non-1-yloxy)-calix[4]arene (8) was prepared similarly to compound **2** using 5,17-dibromo-25,26,27,28-tetrahydroxycalix[4]arene **7** (0.87 g, 1.5 mmol), 1-iodononane (3.0 mL, 15 mmol), and NaH (0.48 g, 60%, 12 mmol). The reaction was performed in 40 mL of anhydrous DMF during 3 days. Yield 1.29 g (79%), light yellow powder, mp $62\text{--}68^\circ\text{C}$. Mass spectrum, m/z : 1108 [$M + \text{Na}$] $^+$, 1124 [$M + \text{K}$] $^+$. Found, %: C 70.46; H 8.82; Br 14.17. $C_{64}H_{94}Br_2O_4$. Calculated, %: C 70.70; H 8.71; Br 14.70.

5,17-Dibromo-11,23-bis(chloromethyl)-25,26,27,28-tetra(non-1-yloxy)calix[4]arene (9) was prepared similarly to compound **3** using methyl chloromethyl ether (5.7 mL, 37 mmol, c 6.5 mol/L), compound **8** (1 g, 0.92 mmol), and tin tetrachloride (0.65 mL, 5.52 mmol) in 50 mL of anhydrous CHCl_3 . Yield 0.76 g (70%), white powder, mp $55\text{--}61^\circ\text{C}$. Mass spectrum, m/z : 1203 [$M + \text{Na}$] $^+$. Found, %: C 67.25; H 7.92. $C_{66}H_{96}Br_2Cl_2O_4$. Calculated, %: C 66.94; H 8.17.

5,17-Dibromo-11,23-bis[(2,4-dioxopent-3-yl)methyl]-25,26,27,28-tetra(non-1-yloxy)calix[4]arene (10) was prepared similarly to compound **4** using NaI (0.135 g, 0.9 mmol), compound **9** (0.36 g, 0.3 mmol), and sodium salt of acetylacetone (0.11 g, 0.9 mol). The reaction was performed in a mixture of methyl isobutyl ketone (6 mL) and DMF (3 mL). Yield 0.3 g (73%), light brown oily substance. IR spectrum, ν , cm^{-1} : 3408

(OH), 1727 and 1701 (CO), 1456 [$\delta(\text{CH}_2)$], 1380 and 1356 [$\delta(\text{CH}_3\text{CO})$], 1222 and 1198 (CCOC). Mass spectrum, m/z : 1310 [$M + \text{H}$] $^+$, 1332 [$M + \text{Na}$] $^+$, 1348 [$M + \text{K}$] $^+$. Found, %: C 69.45; H 8.63; Br 11.78. $C_{76}H_{110}Br_2O_8$. Calculated, %: C 69.60; H 8.45; Br 12.19.

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