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Heterometallic Co^{III}–Ln^{III} (Ln = Gd, Tb, Dy) Complexes on a *p*-Sulfonatothiacalix[4]arene Platform Exhibiting Redox-Switchable Metal-to-Metal Energy Transfer

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Nuclear magnetic relaxation along with pH metric data have been used to reveal pH-dependent heterometallic Co^{III}–Ln^{III} (Ln = Gd, Tb, and Dy) complex formation on a *p*-sulfonatothiacalix[4]arene (TCAS) platform in aqueous solution. The previously obtained 1D and 2D ^1H NMR spectroscopic and X-ray data prove the outer sphere binding of the Co^{III} block with the upper rim of TCAS, whereas the Ln^{III} ion is coordinated with the phenolate groups of the lower rim of TCAS. The inclusive outer-sphere binding of Co^{III} tris(dipyridyl) and tris(ethylendiaminate) complexes with the upper rim of TCAS favors binding of the inner-sphere lanthanide ions through the lower rim of TCAS, whereas noninclusive binding of Co^{III} bis(histidinate) provides no effect on the binding of lanthanide ions. The emission properties of $[Co(dipy)_3]^{3+}$–Ln^{III} (Ln = Gd, Tb, Dy) complexes indicate the quenching of 4f luminescence by the 3d block. This quenching can be switched off by electrochemical Co^{III}/Co^{II} reduction with further switching on by reoxidation.

Introduction

Lanthanides with their well-defined energy levels provide high sensitivity to chemical environments due to the variety of energy exchange processes,[1] and d–f complexes are of particular importance from this point of view, as they can provide both efficient sensitizing[2–5] and quenching[6,7] of f luminescence. The main advantage of the use of d chromophores as an antenna or quencher for f luminescence is their kinetic and photochemical inertness.[3] The redox properties of the d block of d–f complexes provide a prerequisite condition of redox switching of f luminescence. The redox switchable luminescence is of particular importance in the development of logic gates and signaling systems.[8,9] Thus, it is interesting to use both the chromophore and redox properties of the d block to develop redox-switchable luminescent bimetallic d–f complexes on a *p*-sulfonatothiacalix[4]arene (TCAS) platform. The choice of TCAS as a platform for a heterometallic complex is conditioned by its versatile complexability, which has earned considerable attention during the last decades.[10–20] In particular, TCAS is well known to include both organic substrates and metal complexes into the cavity through its upper rim.[10–16] The upper rim of TCAS with four rigidly fixed sulfonate groups possesses good binding sites for metal ions.[17] The coordination of lanthanides through the sulfonate groups of TCAS is the predominant mode of binding in acidic media (pH 2–4), whereas at increased pH values (5–10) binding through the lower phenolate rim becomes more favorable.[18,19] It is interesting to note that TCAS with sulfur bridges exhibits more enhanced complexability towards lanthanide ions at pH 5–10 than its classic analogue (*p*-sulfonatocalix[4]arene) in aqueous solutions.[18] Moreover, the binding of the Tb^{III} ion through the lower rim of TCAS results in rather intense luminescence due to the energy transfer from the triplet levels of TCAS to the emission level of Tb^{III}.[18] It is also worth noting that the upper rim and cavity of TCAS are not taken up and able to include various guests when the metal ion is bound with its lower rim. The inclusion of an organic cation into the cavity along with metal-ion coordination by the hydroxy groups on the lower rim were estimated in both the solid state (from X-ray data[20]) and solutions.[19] It is worth noting that d metal complexes can be also bound by the upper rim of

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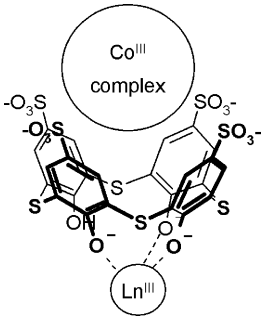
TCAS[11–13] and its classic analogue,[21,22] thus forming stable outer-sphere associates with calixarenes in both inclusive and noninclusive modes. The choice of Co^{III} complexes as d blocks is conditioned by their chromophoric properties and kinetic inertness, as well as by our previous data.[12,13] According to these data, the outer-sphere association with TCAS can be considered as a way to fix the Co^{III} block onto the TCAS platform, whereas the f center can be bound in the inner-sphere mode by the lower rim. Thus, the main goal of the work presented is to reveal the regularities of the formation of Co^{III}–Tb^{III} complexes on a TCAS platform with the Co^{III} complex included in the outer-sphere coordination mode and the Tb^{III} ion in the inner sphere coordination mode (Scheme 1) and to reveal the effect of the d block in both oxidized (Co^{III}) and reduced (Co^{II}) forms on Tb^{III}-centered luminescence. The series of Co^{III} complexes with various ligand environments, that is, $[Co(en)_3]^{3+}$ (en = ethylenediamine), $[Co(dipy)_3]^{3+}$ (dipy = dipyridyl), $[Co(His)_2]^{+}$ (His = L-histidinate), $[Co(en)_2C_2O_4]^{+}$, which are known[11,12] to form outer-sphere associates with TCAS, were chosen as the d blocks.



Scheme 1. Scheme of the heterometallic Co^{III}–TCAS–Ln^{III} complexes.

Results and Discussion

Kinetically inert coordinatively saturated octahedral complexes of Co^{III} exhibit efficient outer-sphere association with polyanions. Sulfonated calix[4]arenes fill the special place among polyanions, as the bowl-shaped cavity both preorganizes the ionized groups on the upper rim and provides the additional center for binding. Analysis of the 1D and 2D NMR spectroscopic data in solution and the X-ray data in the solid state prove that the well-defined cavity of *p*-sulfonatocalix[4]arene and its thia analogue can include the ethylendiaminate chelate ring of $[Co(en)_3]^{3+}$, whereas more bulky tris(chelates) $[Co(dipy)_3]^{3+}$ and $[Co(phen)_3]^{2+}$ are included by the fragments of the dipy chelate rings.[10,11] It is worth noting that the inclusion of the complex becomes less for $[Co(en)_2C_2O_4]^{+}$ or even insignificant for the *trans-i*-$[Co(His)_2]^{+}$ when the carboxylate groups are in the inner sphere of Co^{III}. Thus, the above-mentioned chelates of Co^{III} are good guests for the terbium complex of TCAS, as they provide various modes of binding (inclusive and noninclusive) with the upper rim, which is rather efficient (with $\log\beta \geq 4.5$) and practically pH independent.[11,12]

Formation of Co^{III}–Ln^{III} (Ln = Gd, Dy, Tb) Complexes Verified by NMR Spectroscopic Relaxation and pH Metric Data

The efficiency of NMR spectroscopic relaxation in the study of TCAS complex formation with Gd^{III} ions in aqueous solutions was proved in our previous studies.[19] The high molar relaxivity (R_1) of Gd^{III} enables NMR spectroscopic relaxation measurements to be performed in rather dilute Gd^{III}-containing aqueous solutions (2.0×10^{-4} M). Figure 1 shows the pH dependencies of R_1 in both binary Gd^{III}–TCAS and ternary Gd^{III}–TCAS–Co^{III} systems. As it was stated in our previous work,[19] R_1 data first show the relaxivity decrease at pH 5–7, followed by an increase at pH 8–10 by implying the two-step binding of Gd^{III} with TCAS. The first-step binding of TCAS (H_4XNa_4) with Gd^{III} is an equilibrium according to Equations (1) and (2), where complex $[Gd(H_2X)]^{3-}$ is minor and $[Gd(HX)]^{4-}$ is predominant. The second complexation step (pH 8–10) is conditioned by the superposition of the species formed according to the equilibrium outline in Equations (3) and (4).

$$Gd^{3+} + H_3X^{5-} = [Gd(H_2X)]^{3-} + H^+ \quad (1)$$

$$Gd^{3+} + H_3X^{5-} = [Gd(HX)]^{4-} + 2\,H^+ \quad (2)$$

$$[Gd(H_2O)_n(HX)]^{4-} = [Gd(OH)(H_2O)_{n-1}(HX)]^{5-} + H^+ \quad (3)$$

$$[Gd(HX)]^{4-} + H_2X^{6-} = [Gd(HX)_2]^{11-} + H^+, \quad (4)$$

where H_3X^{5-} is the penta anion of TCAS with four ionized sulfonate groups on the upper rim and one deprotonated phenolate group (pK_1 = 2.2[23]) on the lower rim.

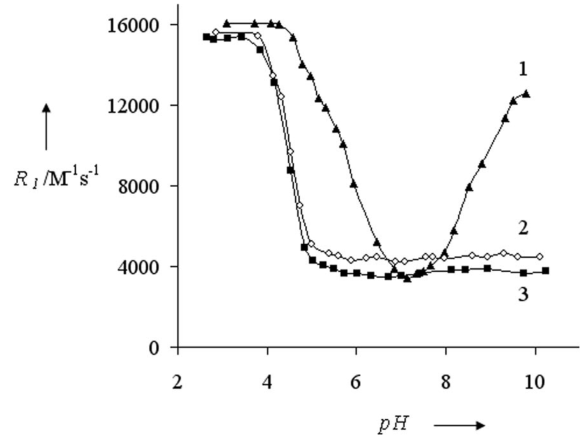


Figure 1. R_1 vs. pH dependence of the relaxivity in aqueous solutions of TCAS–Gd^{III} (▲) at $C(Gd^{III}) = 2.0 \times 10^{-4}$ M, C(TCAS) = 3.0×10^{-4} M; $[Co(en)_3]^{3+}$–TCAS–Gd^{III} (◇) at $C(Gd^{III})$ = 2.0×10^{-4} M, C(TCAS) = 3.0×10^{-4} M, $C([Co(en)_3]^{3+})$ = 3.0×10^{-4} M; $[Co(dipy)_3]^{3+}$–TCAS–Gd^{III} (■) at $C(Gd^{III})$ = 2.0×10^{-4} M, C(TCAS) = 3.0×10^{-4} M, $C([Co(dipy)_3]^{3+})$ = 3.0×10^{-4} M.

We recently found that the upper rim inclusion of tetramethylammonium (TEMA) occurs along with Gd^{III} coordination through the phenolate groups of TCAS.[19] The inclusion of tetramethylammonium into the cavity of TCAS in the ternary Gd^{III}–TCAS–TEMA system was found to favor the Gd^{III}–TCAS first complexation step at pH 5–7 [Equation (2)], which is apparent from the shift in R_1 versus pH curve to more acidic media. This effect indicates that TEMA inclusion results in an enhancement in the complexability of the phenolate groups of the lower rim towards the gadolinium ion. A similar effect is apparent from the relaxivity data in ternary systems containing $[Co(dipy)_3]^{3+}$ and $[Co(en)_3]^{3+}$ (Figure 1). The lack of the effect is evident for $[Co(His)_2]^+$, whereas ternary complex formation for $[Co(en)_2C_2O_4]^+$ is complicated by probable Gd^{III} coordination through the oxalate anion in the inner sphere of Co^{III}, as it is evident from the experimentally observed increase in R_1 at pH 5–6 (Figure 2).

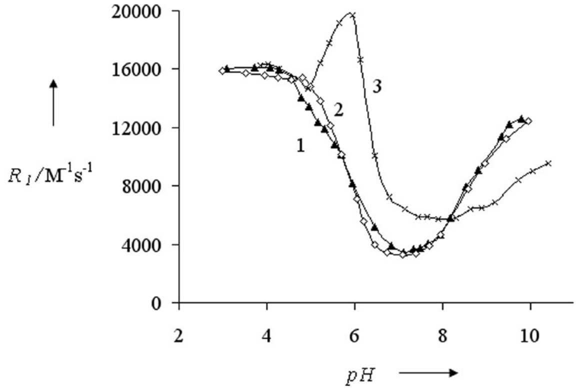


Figure 2. R_1 vs. pH dependence of the relaxivity in aqueous solutions of TCAS–Gd^{III} (▲) at $C(Gd^{III})$ = 2.0 × 10^{-4} M, C(TCAS) = 3.0 × 10^{-4} M; $[Co(His)_2]^+$–TCAS–Gd^{III} (◇) at $C(Gd^{III})$ = 2.0 × 10^{-4} M, C(TCAS) = 3.0 × 10^{-4} M, $C([Co(His)_2]^+)$ = 3.0 × 10^{-4} M; $[Co(en)_2C_2O_4]^+$–TCAS–Gd^{III} (×) at $C(Gd^{III})$ = 2.0 × 10^{-4} M, C(TCAS) = 3.0 × 10^{-4} M, $C([Co(en)_2C_2O_4]^+)$ = 3.0 × 10^{-4} M.

By analyzing the effect of the guests on the second step of complexation at pH 8–10 it is worth noting that the $[Co(dipy)_3]^{3+}$ and $[Co(en)_3]^{3+}$ complexes prevent an increase in the value of R_1 at pH 8–10 (Figure 1), indicating that ternary complex formation suppresses the second binding step [Equations (3) and (4)]. This effect is insignificant for $[Co(en)_2C_2O_4]^+$ and $[Co(His)_2]^+$ (Figure 2). According to our previous data, the outer-sphere association of $[Co(His)_2]^+$ with TCAS is not accompanied by the inclusion of histidinate moieties into the cavity of TCAS.[13] The presence of the oxalate dianion in the inner sphere of $[Co(en)_2C_2O_4]^+$ prevents its deep and efficient inclusion into the macrocycle.[13] So, the effect of the additional stabilization is apparent only for the $[Co(en)_3]^{3+}$ and $[Co(dipy)_3]^{3+}$ complexes, forming inclusion complexes with TCAS with high binding efficiency ($\log\beta \geq 4.5$).[12,13]

The NMR spectroscopic data in solution,[10] X-ray data in the solid state,[11,12] and quantum chemical calculations[34] indicate that the cavity is tuning up to provide the most efficient host–guest interaction. In particular, the pinched cone conformation becomes predominant in inclusion complexes both in the solid state and in solution, whereas cone conformation dominates for sulfonated calix[4]arene and its thia analogue with empty cavities.[10,24] Indeed, the inclusion capacity of calixarenes can be modified through rigidification of the lower rim,[25] and vice versa, definite preorganization of the phenolic rings should modify the preorganization of the phenolic groups on the lower rim. Thus, the conformational rigidification of the phenolic rings caused by their CH–π interactions with the Co^{III} complex is the most probable reason for the extra-favored Gd^{III} ion binding with the lower rim of TCAS, which results from inclusion of Co^{III} complexes into the cavity of TCAS.

The precipitation occurring in ternary solutions at higher concentrations (4.0 × 10^{-3} M) (no precipitation occurs in the corresponding binary solutions) brings another confirmation of ternary complex formation. The elemental analysis data confirms a 1:1:1 stoichiometry of the complex precipitated from neutral aqueous solutions, containing Gd^{III}, TCAS, and $[Co(dipy)_3]^{3+}$.

So, the outer-sphere binding of the Co^{III} complex provides the insertion of the Co^{III} block into the TCAS platform by the upper rim of the latter. It is worth noting that this binding mode is pH independent, whereas the inner-sphere binding of the Gd^{III} ion by the lower rim occurs in a definite pH range. According to our previous work,[19] the pH metric titration data have been successfully used to evaluate equilibrium constants for the reactions shown in Equations (1) (K_1) and (2) (K_2) for Gd^{III}. That is why the similar pH titration data have been performed for Tb^{III} and Dy^{III}. Taking into account the similarity of coordinative properties of neighboring lanthanide ions, it is rather awaited that the values log K_2 for Tb^{III}, Dy^{III}, and Gd^{III} ions are very similar (Table 1). Stability constants of $[Gd(HX)]^{4-}$, $[Tb(HX)]^{4-}$, and $[Dy(HX)]^{4-}$ calculated according to Equation (5) are rather high and similar within experimental error ($\log\beta_{Tb} = \log\beta_{Gd} = \log\beta_{Dy} = 13.0$).

$$\log\beta = \log K_2 + pK_1 + pK_2 + pK_3 \qquad (5)$$

Table 1. log K values for the equilibriums outline in Equations (1) and (2) for Gd^{III}, Tb^{III}, and Dy^{III}.

	Gd^{III}	Tb^{III}	Dy^{III}
log K_1	–3.9 ± 0.2	–3.5 ± 0.1	–3.6 ± 0.1
log K_2	–8.8 ± 0.1	–8.8 ± 0.1	–8.9 ± 0.1

Though pK_3 can not be accurately estimated from pH-metric data it is close to 11,[23] and this value have been used to calculate logβ. So, Gd^{III}, Dy^{III} and Tb^{III} are bound with TCAS in the same pH range. Thus the adjustment of definite pH value in the ternary Co^{III}–TCAS–Ln^{III} (Ln = Gd, Tb, Dy) solution provide the heterometallic complexes with metal ions separated by TCAS as a spacer, which is the prerequisite condition for metal-to-metal energy exchange.

Luminescent Properties of $[Co(dipy)_3]^{3+}$–TCAS–Ln^{III} (Ln = Tb, Dy) Complexes

As it was mentioned above, the terbium complex with TCAS exhibits efficient luminescence.[18] The similarity of the binding modes and binding constants for TCAS–Ln^{III} (Ln = Gd, Tb, Dy) complexes enables the regularities for $[Co(dipy)_3]^{3+}$–TCAS–Gd^{III} complex formation to be used for the similar Tb^{III} and Dy^{III} complexes. The spectra of Tb^{III}- and Dy^{III}-centered luminescence were recorded by using excitation at 330 nm in much-more diluted solutions (C_{Ln} = 1.0×10^{-6} м, C_{TCAS} = 5.0×10^{-6} м) than those of the nuclear magnetic relaxation data (C_{Gd} = 2.0×10^{-4} м, C_{TCAS} = 3.0×10^{-4} м), which is why pH 8.5 was adjusted to achieve the saturation conditions of $[Ln(HX)]^{4-}$.

According to the data obtained (Supporting Information, Figure S1) the Dy^{III} complex with TCAS also exhibits luminescent properties, and the luminescent efficiency is less than in the case of Tb^{III} (the quantum yields of luminescence for the Tb^{III} and Dy^{III} complexes are ϕ = 0.141 and ϕ = 0.008).[26] According to Iki,[18] luminescent properties of Tb^{III}–TCAS are conditioned by the energy transfer from the triplet level of TCAS (T) to the emission level of Tb^{III} 20430 cm^{-1} ($^5D_4$). The emission level of Dy^{III} 20960 cm^{-1} ($^4F_{9/2}$)^1 is also below the triplet level of TCAS (21800 cm^{-1}, see Experimental Section). The excitation wavelength (330 nm) for Dy^{III}–TCAS is close to its absorbance peak (326 nm) and the own luminescence of TCAS at 440 and 470 nm decreases when TCAS is bound with Dy^{III}, thus confirming the efficiency of the TCAS–Dy^{III} energy transfer. It is well known that T(ligand)–Ln* energy flow can be optimized by adjusting the energy gap between the triplet level of the ligand and the emitting level of the lanthanide, otherwise back energy transfer becomes probable.[27] The energy gap between the triplet level of TCAS and the emission levels of Tb^{III} and Dy^{III} are 1370 and 840 cm^{-1}, which explains why the luminescence is less efficient in the latter case (Figure 3).

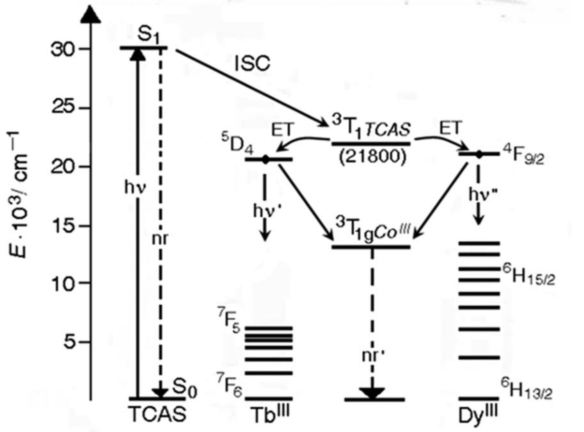


Figure 3. Energy diagrams for complexes $[Co(dipy)_3]^{3+}$–TCAS–Tb^{III} and $[Co(dipy)_3]^{3+}$–TCAS–Dy^{III}.

Our previous data demonstrate that the inclusion of Co^{III} complexes causes insignificant changes in the absorption spectrum of TCAS.[12,13] Similar analysis reveals that the changes are also insignificant in the case of ternary Co^{III}–TCAS–Tb^{III} complex formation. Thus, the experimentally observed quenching of Tb-centered luminescence, which is dependent on the concentration of $[Co(dipy)_3]^{3+}$ is the result of energy transfer between f- and d containing blocks. The choice of $[Co(dipy)_3]^{3+}$ as a quencher of Tb^{III} luminescence is determined by comparative stability[28] and kinetic inertness[29] of its reduced form among the above-mentioned Co^{III} complexes. In particular, the potential of the Co^{III}/Co^{II} couple for $[Co(dipy)_3]^{3+}$ is the most positive, and the reduction of $[Co(dipy)_3]^{3+}$ provides reversible waves in the CV curves, whereas reduction of other Co^{III} complexes is nonreversible and occurs in a much more cathodic region.[28] Thus, $[Co(dipy)_3]^{3+}$ is a convenient Co^{III} block from the viewpoint of the development of redox-dependent quenching. Figure 4a illustrates the quenching of Tb-centered luminescence induced by $[Co(dipy)_3]^{3+}$. Analysis of the luminescence quenching versus Co^{III} concentration (Figure 4b) indicates that this process is not diffusion controlled,[6] but is derived from the binding of the quencher (Co^{III} complex) along with f-luminescent ion through spacer–TCAS. The quenching observed can be ascribed to

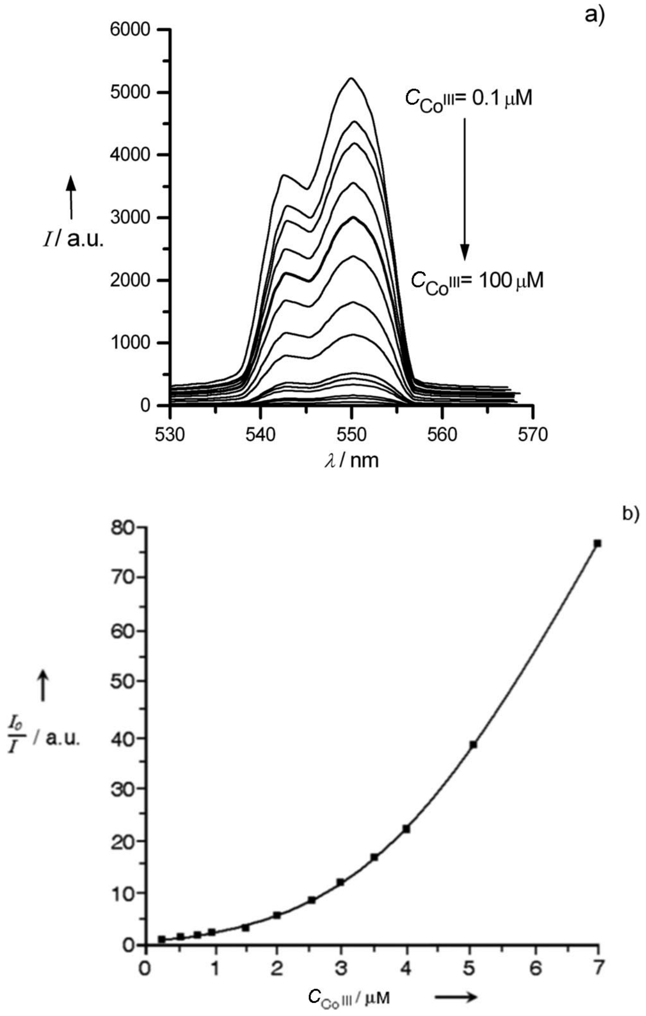


Figure 4. The spectra of Tb-centered luminescence of Tb^{III}–TCAS [C(Tb^{III}) = 1.0×10^{-6} м, C(TCAS) = 5.0×10^{-6} м] complex in aqueous solutions prior and after the addition of various amounts of $[Co(dipy)_3]^{3+}$ [C(Co^{III}) = 1×10^{-7} to 1×10^{-5} м] (a); dependence of the luminescence quenching (I_0/I, where I_0 and I are the luminescence intensity prior and after the addition of $[Co(dipy)_3]^{3+}$) vs. the concentration of Co^{III} (b).

overlap of the absorption bands of the Co^{III} blocks with the spectral range of the narrow-line emission of Tb^{III}.[6,30] The absorbance spectra of d^6 low-spin Co^{III} octahedral complexes are caused by intraligand charge-transfer transitions (for [Co(dipy)$_3$]$^{3+}$) and d–d transitions from $^1A_{1g}$ to $^1T_{1g}$,$^1T_{2g}$ excited levels, as well as triplet levels $^3T_{1g}$,$^3T_{2g}$.[25] Thus, the presence of $^3T_{1g}$,$^3T_{2g}$ triplet levels of Co^{III} complexes, lying under the emission levels of Tb^{III} and Dy^{III}, provide the probability of Ln*–Co^{III} energy transfer, which quenches the f-centered emission. The luminescence lifetime of the Tb^{III}–TCAS complex (0.726 ms) is close to the similar value obtained by Iki[18] and shortens up to 0.693 ms when [Co(dipy)$_3$]$^{3+}$ is bound with the Tb^{III}–TCAS complex.

Redox Switching of Tb^{III} Luminescence by the Reduction of the [Co(dipy)$_3$]$^{3+}$ Block

According to our previous data,[11] the reduction of [Co(dipy)$_3$]$^{3+}$ bound with TCAS is reversible in aqueous DMSO solutions. It is still reversible in aqueous solutions (Table 2). Both in aqueous DMSO[12] and in aqueous media the reduction potential exhibits a cathodic shift when [Co(dipy)$_3$]$^{3+}$ is ion paired with TCAS (Table 2). According to Equation (6), the residual between the potentials of the Co^{III}/Co^{II} couples of free and ion paired with TCAS [Co(dipy)$_3$]$^{3+}$ enables the difference between free energies of binding of TCAS with [Co(dipy)$_3$]$^{3+}$ and [Co(dipy)$_3$]$^{2+}$ to be evaluated.

$$\Delta G_0{}^1 - \Delta G_0{}^2 = \Delta\Delta G_0 = F(E_0{}^2 - E_0{}^1) \quad (6)$$

where $\Delta G_0{}^1$ and $\Delta G_0{}^2$ are the free energies of the binding of [Co(dipy)$_3$]$^{3+}$ and [Co(dipy)$_3$]$^{2+}$ with TCAS (H_3X^{5-}) in J mol^{-1}, $E_0{}^1$ and $E_0{}^2$ are the standard potentials of the Co^{III}/Co^{II} couples for unbound and bound with TCAS [Co(dipy)$_3$]$^{3+}$, and F is the Faraday number, 96500 A s mol^{-1}.

Taking into account the correlation between the free energy and the binding constant, a value of –6.8 kJ mol^{-1} for $\Delta\Delta G_0$ indicates more than a 10-fold decrease in the binding constant of TCAS on going from [Co(dipy)$_3$]$^{3+}$ to its reduced form. Such a decrease indicates that the reduction of the Co block results in substantial dissociation of the outer sphere associate with TCAS.

The reduction of Tb^{III} occurs in a much more cathodic region than that of the Co^{III}/Co^{II} couple (it cannot be detected in the available potential range) and thus does not influence the reduction of the Co^{III} block. The potential of the Co^{III}/Co^{II} couple in the heterometallic [Co(dipy)$_3$]$^{3+}$–TCAS–Tb^{III} complex is very close to the similar value for the [Co(dipy)$_3$]$^{3+}$–TCAS complex and the reduction is still reversible (Table 2). Electrolysis for 20 min results in complete reduction of [Co(dipy)$_3$]$^{3+}$, which is evident from the spectrophotometric data (no further spectral changes were revealed after this time; Supporting Information, Figure S2).

The kinetic lability of [Co(dipy)$_3$]$^{2+}$ in aqueous solutions[29] may result in whole or partial destruction of [Co(dipy)$_3$]$^{2+}$ during the performance of electrolysis, thus making this process irreversible. To evaluate the extent of the reversibility of the process, CV curves were recorded before and after bulk electrochemical reduction and reoxidation of the heterometallic system (Supporting Information, Figure S3). The CV data for the reduced heterometallic system reveal reversible oxidation peak with $E_{p,ox}$ = +0.08 V, $E_{p,rered}$ = –0.01 V. The comparison of current peak intensities of the CV curves before and after electrolysis indicates substantial (up to 75%) destruction of [Co(dipy)$_3$]$^{2+}$, which is evident from the corresponding decrease in the current peak intensity after the electrolysis. The performance of CV in the reoxidized heterometallic solution reveals the peak of reduction of Co^{III} ($E_{p,red}$ = 0.0 V, $E_{p,reox}$ = +0.08 V) with the current peak intensity being similar to that of the reduced heterometallic system.

The fluorimetric measurements of heterometallic solutions before and after reduction (Figure 5) indicate that Tb luminescence is switched off in the initial [Co(dipy)$_3$]$^{3+}$–TCAS–Tb^{III} system and reestablishes its intensity up to the intensity of the homometallic Tb^{III}–TCAS complex when [Co(dipy)$_3$]$^{3+}$ is reduced to [Co(dipy)$_3$]$^{2+}$. Taking into account the above-mentioned electrochemical data, it should be noted that the redox switching on of the Tb-centered luminescence is conditioned by several reasons. The first is the change in the metal-centered energy levels on going from low-spin Co^{III} to high-spin Co^{II}.[31] The second is the

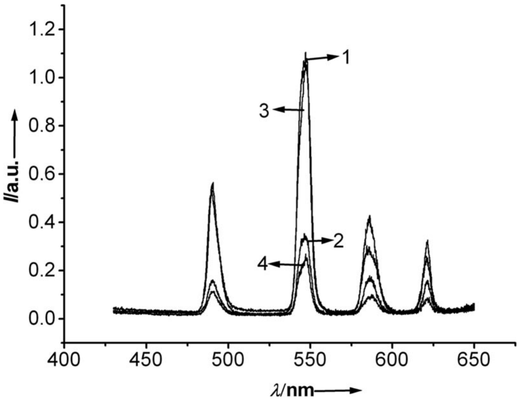


Figure 5. The luminescence spectra of the TCAS–Tb^{III} complex (1), [Co(dipy)$_3$]$^{3+}$–TCAS–Tb^{III} (2), [Co(dipy)$_3$]$^{2+}$–TCAS–Tb^{III} after the reduction of [Co(dipy)$_3$]$^{3+}$ (3), [Co(dipy)$_3$]$^{3+}$–TCAS–Tb^{III} after reoxidation of Co^{II} (4). C(Tb^{III}) = 5.0×10^{-7} M, C(TCAS) = 5.0×10^{-7} M, C([Co(dipy)$_3$]$^{3+}$) = 5×10^{-7} M, pH = 9, $\lambda_{excit.}$ = 330 nm.

Table 2. CV data for reduction of [Co(dipy)$_3$]$^{3+}$ in aqueous solutions and in the presence of TCAS and TCAS–Tb^{III} (potentials are determined vs. Ag/0.01 M AgCl).

Complex	$E_{p,red}$(Co^{III}/Co^{II})	$E_{p,reox}$(Co^{II}/Co^{III})	$E_{1/2}$(Co^{III}/Co^{II})	I_p
[Co(dipy)$_3$]$^{3+}$	0.09 V	0.15 V	0.12 V	2.5 µA
[Co(dipy)$_3$]$^{3+}$ + TCAS	0.02 V	0.08 V	0.05 V	2.0 µA
[Co(dipy)$_3$]$^{3+}$ + TCAS-Tb^{III}	0.02 V	0.08 V	0.05 V	0.5 µA

partial dissociation of the $[Co(dipy)_3]^{2+}$–TCAS ion pair, and the third is the partial dechelation of $[Co(dipy)_3]^{2+}$ due to its kinetic lability. According to electrochemical data only, 25% of the reduced Co^{II} is in the form of $[Co(dipy)_3]^{2+}$, whereas the residual is represented by some dechelated related forms of Co^{II}. Thus, the reoxidation should lead to partial switching off of the Tb-centered luminescence. It is rather unexpected that Tb-centered luminescence intensity of the reoxidized heterometallic system is close to the value of the initial $[Co(dipy)_3]^{3+}$–TCAS–Tb^{III} complex. Taking into account that only 25% of Co^{III} is in the form of $[Co(dipy)_3]^{3+}$ some related forms (dechelated for example) provide the similar quenching effect on TCAS–Tb^{III} luminescence. Though the fluorimetric data look like reversible redox switching, the electrochemical data reveal the extent of irreversibility conditioned by the duration of the electrolysis process. Thus, to make the redox switching reversible, one should shorten the duration of preparative reduction and reoxidation.

Conclusions

Summarizing the data obtained it should be concluded that both the outer-sphere and inner-sphere binding of the Co^{III} complex and the lanthanide ion with *p*-sulfonatothiacalix[4]arene provides heterometallic Co^{III}–TCAS–Ln^{III} (Ln = Tb Gd, Dy) complexes. The inclusive outer-sphere binding of Co^{III} complexes with the upper rim of TCAS favors binding of the inner-sphere lanthanide ions through the lower rim of TCAS, whereas noninclusive binding of the Co^{III} complex provides no effect on the binding of lanthanide ions. The emission properties of heterometallic Co^{III}–Tb^{III} complexes reveal that TCAS serves as a spacer between metal centers, thus favoring the switching off of the Tb-centered luminescence by $[Co(dipy)_3]^{3+}$. The bulk electrochemical reduction with subsequent reoxidation results in the switching on and off of the Tb-centered luminescence of the heterometallic system. A lot of poly- and heterometallic complexes have been obtained on calix[*n*]arene platforms.[32,33] Nevertheless the use of outer-sphere binding modes, along with inner-sphere binding modes, as driving forces for heteronuclear complex formation has an advantage in comparison with inner-sphere binding only. In particular, it enables definite clamping of the required metal centers (d and f) on the upper and the lower rims without a variety of structures due to the competition between metal ions for binding seats. Because the results obtained show energy transfer between the d and f blocks, the easy and controlled variation of redox, chromophoric, and emission properties of the d block is applicable in the design of supramolecular systems exhibiting active response on external input.

Experimental Section

Materials: Literature methods were used to synthesize TCAS[34] and the cobalt complexes $[Co(en)_3]Cl_3$,[35] $[Co(dipy)_3](ClO_4)_3$,[36] $[Co(His)_2]Cl$,[37] $[Co(en)_2C_2O_4]Cl$.[38] $Tb(NO_3)_3$, $Gd(NO_3)_3$, and $Dy(NO_3)_3$ were commercially available from Acros Organics. Stock solutions of $Ln(NO_3)_3$ (Ln = Tb, Gd, Dy) were prepared by dissolving the appropriate amounts of their salts $Ln(NO_3)_3{\cdot}nH_2O$ of analytical grade in doubly distilled water with further standardization with EDTA at pH 6 by using xylenol orange as an indicator.[39]

Gd^{III}–TCAS–Co^{III}: The ternary complex was precipitated and separated from an aqueous (pH 6) mixture of $[Co(dipy)_3](ClO_4)_3$, TCAS, and $Gd(NO_3)_3$. The pH of the solution was adjusted by sodium hydroxide. The concentration ratio of components was 1:1:1 ($C = 4.0\times10^{-3}$ M). The yellow precipitate was collected after filtering, washing, and drying. Elemental analysis was conducted with a CHNS/O Analyzer PE2400 Series II (Perkin–Elmer). $C_{54}H_{34}CoGdN_6NaO_{16}S_8(H_2O)_{16}$ (1806.79): calcd. C 35.88, H 3.68, N 4.65; found C 36.55, H 3.82, N 4.71.

NMR Relaxation Measurements: The spin-lattice relaxation times T_1 of water molecule protons were measured by the spin echo method[40] by using a Bruker Minispec mq20 pulse NMR spectrometer (19.65 MHz, 298 K). Nuclear magnetic relaxation measurements were performed in aqueous solutions. The concentration ratio of components in binary Gd^{III}–TCAS and ternary Gd^{III}–TCAS–Co^{III} systems was 1:1.5 and 1:1.5:1.5, respectively. The observed proton spin-lattice relaxation rate $(1/T_1)_{obs}$ in aqueous solution containing Gd^{III} is an additive sum of two main contributions (diamagnetic and paramagnetic) according to Equation (7).

$$(1/T_1)_{obs} = (1/T_1)_d + (1/T_1)_p \tag{7}$$

The first, measured in the absence of paramagnetic ion, is usually equal to 0.4 s^{-1}. The paramagnetic contribution $(1/T_1)_p$ normalized by the concentration of paramagnetic species (C_M) is known as the relaxivity (R_1) can be found according to Equation (8), and it is used to characterize changes in the coordination environment or mobility of Gd^{III} ions.

$$R_1 = 1/C_M\ (T_1)_p \tag{8}$$

Photophysical Measurements: The luminescence spectra were performed in deaerated conditions with a SDL-1 (SDL-2) spectrofluorometer (LOMO Association, St.-Petersburg, Russia) by using a combination of a xenon lamp (XBO 150) and a monochromator (Lot-Oriel) for excitation and a polychromator with a cooled CCD matrix as a detector system (Lot-Oriel, Instaspec IV). Emission and excitation spectra were measured in 1-cm path length quartz cell. The decays were analyzed with Origin 7.0. The luminescence quantum yields (ϕ) were obtained by the method described by Haas and Stein[41] with quinine sulfate ($\phi = 0.546$ in 1 M H_2SO_4) as the standard for Tb^{III} and Dy^{III} complexes. The measured values were corrected for the refractive indices. The luminescence lifetime (τ) data were obtained by means of a SDL-1 spectrofluorimeter (LOMO Association, St. Petersburg, Russia) with a LGI-21 nitrogen laser (pulse duration of 8–10 ns at a wavelength of 337 nm) and analyzed by iterative deconvolution and nonlinear least-squares method.[42] The triplet level position of TCAS was obtained from the phosphorescence spectrum of lutecium complex with TCAS at 77 K. The concentration of Tb^{III} was maintained at 1.0×10^{-6} M, TCAS at 5.0×10^{-6} M, and the concentrations of the Co^{III} complexes were varied from 1.0×10^{-7} to 1.0×10^{-5} M. Tris buffer was used to adjust pH values to 8.5.

Electrochemical Measurements: Cyclic voltammograms (CV) were recorded by using a PI-50–1 potentiostat with a N307/2 XY-recorder. The potential scan rate was 100 mV s^{-1}. A glass-carbon electrode (d = 2 mm) pressed in Teflon served as a working electrode. The electrode was polished prior to each measurement. The potentials were measured versus Ag, AgCl/0.1 M KCl in aqueous solutions at $C([Co(dipy)_3]^{3+}) = 1.5 \times 10^{-3}$ M, $C(TCAS) = 2.0 \times 10^{-3}$ M in binary system. More diluted solutions were required to prevent the precipitation in the heterometallic system; thus, $C([Co(dipy)_3]^{3+}) = 5 \times 10^{-4}$ M, $C(TCAS) = 7 \times 10^{-4}$ M, and $C(Tb^{III}) = 5 \times 10^{-4}$ M were used. The required pH values (pH 7 in binary and pH 9 in ternary systems) were adjusted by Tris buffer. The bulk electroreduction of the $[Co(dipy)_3]^{3+}$ block was achieved by 20 min electrolysis of aqueous solution $\{C([Co(dipy)_3]^{3+}) = 2.5 \times 10^{-4}$ M, $C(TCAS) = 2.5 \times 10^{-4}$ M, $C(Tb^{III}) = 2.5 \times 10^{-4}$ M, pH = 9, V = 20 mL, T = 295 K$\}$ in unshared glass electrolyzer on a cylindrical glassy carbon fabric (ca. 10 cm^2) under argon in galvanostatic mode at controlled potentials of the first reduction peak of $[Co(dipy)_3]^{3+}$ with permanent stirring by magnetic stirrer. A Pt wire was used as a counter electrode. The reoxidation was carried out in the similar way at controllable oxidation peaks of $[Co(dipy)_3]^{2+}$. The flourimetric measurements before and after bulk electrolysis were performed on a spectrofluorometer FL3–221-NIR Jobin Jvon at $C([Co(dipy)_3]^{3+}) = 5.0 \times 10^{-7}$ M, $C(TCAS) = 5.0 \times 10^{-7}$ M, $C(Tb^{III}) = 5.0 \times 10^{-7}$ M, pH = 9. These concentration conditions have been achieved by the dilution of the reduced and reoxidized solutions.

The pH metric measurements were carried out in a thermostatically controlled cell at 25 ± 0.1 °C by use of an "I-130 Ionomer" meter with the error being less than 0.05 pH units. KOH (1.0×10^{-2} M) solution was used as the titrant. The pH meter was calibrated by a series of buffer solutions. The pH titration of TCAS ($C = 2.0 \times 10^{-3}$ M) and mixture of TCAS and $Ln(NO_3)_3$ (Ln = Gd, Tb, Dy) in concentration ratio of 1:1 were recorded in the range of pH 3.0–11.0. No extra salts were added in pH measurements to maintain definite value of ionic strength in order to avoid undesirable association equilibriums. pK values of TCAS (pK_1 = 2.19, pK_2 = 8.37, pK_3 ca. 11.0) are close to the literature data.[23]

Supporting Information (see footnote on the first page of this article): Luminescence spectra, absorbtion spectra, and CV curves of selected systems studied.

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