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Article

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Phosphine oxide-Chelated Europium(III) Nanoparticles for Ceftriaxone Detection

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Abstract The present work demonstrates the optimization of the ligand structure in the series of bisphosphine oxide and carbamoylphosphine oxide representatives for efficient coordination of Tb³⁺ and Eu³⁺ ions with the formation of the complexes exhibiting high Tb³⁺- and Eu³⁺-centered luminescence. The analysis of the stoichiometry and structure of the lanthanide complexes obtained by XRD method reveals the great impact of the bridging group nature between two phosphine oxide moieties on the coordination mode of the ligands with Tb³⁺ and Eu³⁺ ions. The bridging imido-group facilitates the deprotonation of imido-bisphosphine oxide ligand followed by the formation of triscomplexes. The spectral and PXRD analysis of the separated colloids indicates that the high stability of the tris-complexes provides their safe conversion into polystyrenesulfonate-stabilized colloids under the solvent exchange method. The red Eu³⁺-centered luminescence of the tris-complex exhibits the same specificity in the solutions and the colloids. The pronounced luminescent response on the antibiotics ceftriaxone allows to sense the latter in aqueous solutions with the LOD value equal to 0.974 µM.

Keywords: luminescent sensor; lanthanide-centered luminescence; bis-phosphine oxide; cephalosporins; Judd-Ofelt

Introduction

Luminescent lanthanide complexes have long attracting researchers due to their excellent optical properties. They are widely used as building blocks for luminescent nanomaterials for application in biomedical analysis, medical diagnosis, and cell imaging[1– 3]. Long luminescence lifetimes, sharp characteristic emission bands, and large Stoke's shifts allow getting rid of biological background autofluorescence, which is of great importance when biomedical experiments are conducted.

However, due to the difficulties with direct sensitization of Ln(III) luminescence organic ligands (L) are usually used to excite lanthanides indirectly mainly by ligands' triplet level[4–7]. Within the complex of Ln(III)-L, the efficiency of ligand-to-metal energy transfer governs the resulting brightness and, hence, luminescence performance in various applications. It is worth noting that 1,3-diketones demonstrated outstanding chelating properties towards all lanthanide series forming stable six-membered chelate rings[8–10]. Structural variability of beta-diketones gave rise to a number of Ln(III) complexes with the record optical properties due to the precise tuning of triplet energy level via simple change of substituents[11–13]. Moreover, a great number of such complexes was successfully converted into aqueous colloids through the solvent exchange technique[8,14]. However, 1,3-diketonates are pretty selective in sensitizing specific lanthanide ions. In this regard, the design of new ligands that can excite different metals of lanthanide series and nanomaterials exhibiting both diverse lanthanide-centered luminescence in the visible region of the spectrum, e.g., green or red, and good colloid properties simultaneously is a top challenge in current chemistry.

Phosphine oxides attracted great attention as promising extractants for 4(5)f-metal ions [15–20]. The chemistry of 1,3-bis-phosphine oxides is rapidly developing, which is mainly because bis-phosphine oxides are efficient ligands allowing diverse complexation with lanthanide ions[21–24]. It is worth noting the great impact of the structure of the group linking two phosphine oxides on the complexation mode. In particular, the chelation of lanthanide ions by imido-bis-phosphine oxides is followed by deprotonation[25– 27], while bis-phosphine oxides bridged via methylene group tend to form stable complexes with lanthanide ions without deprotonation[28,29]. A similar chelating ability towards lanthanide ions was previously demonstrated for the carbamovlphosphine oxide derivatives[30,31]. Having a valence of five, the phosphorus atom brings an additional option for introducing P-substituent compared to dicarbonyles. This makes carbamoylphosphine oxides (CMPO) and bisphosphine oxides beneficial in terms of structural variations and possible functional add-ons. Aryl-substituted phosphorus-containing ligands have recently been documented to grant substantial antenna-effect sensitizing luminescence of rare Earth elements (REE), which may surely be in demand in luminescence-related applications[32,33]. However, to the best of our knowledge, the applicability of such complexes in the development of nanosensors is very poorly documented in literature if any.

The wide applicability of lanthanide complexes in fluorescent sensing of residual amounts of drugs, including antibiotics, in water or biological fluids is well-known[34–40]. In this regard, the synthesis of new lanthanide complexes, where ligand-to-metal energy transfer is enough for sensitizing lanthanide-centered luminescence, and ligand-metal coordination bonds are tight enough for the safe conversion of the complexes into water-dispersible nanomaterial with high lanthanide-centered luminescence is a challenging scientific task.

Thus, the present work represents the already known [27] and [28] (a, b in Figure 1) and newly synthesized (c, d in Figure 1) as the ligands for Tb³⁺ and Eu³⁺ ions. Additional methoxyphenyl fragment was purposely introduced at the alpha-position to promote further build-ups, to control the lanthanide coordination center symmetry for additional boosting lanthanide-centered luminescence and for additional hydrophobic shielding of the inner-sphere of the lanthanide ions minimizing solvent-induced nonradiative relaxation. The synthesis of the complexes and their structural and spectral characterization in the solid state and solutions are described in detail in this work. The efficiency of converting the as-synthesized complexes into the aqueous PSS-stabilized colloids is correlated with the structures of the complexes and the ligands. The diverse physico-chemical techniques applied for the characterization of the ligands, complexes and the nanoparticles on molecular, supramolecular and nano-levels are focused on the ability of the ligands to sensitize the lanthanide-centered luminescence in both organic solutions and in the aqueous colloids. The applicability of the developed aqueous colloids as nanosensors will be demonstrated by their luminescent reply on ceftriaxone, which is the third generation of cephalosporin antibiotic widely applied in treating of such socially relevant bacterial infections as meningitis, pneumonia and many others[41–44].

Experimental section

Materials. All reagents were used as purchased from Sigma-Aldrich or Acros Chemicals and used without further purification. Solvents were purified by standard procedures before use. All reactions were run under an argon atmosphere unless in aqueous media. Ceftriaxone sodium from RUE Belmedpreparaty was used as purchased.

Syntheses. Ligand **a** was obtained by a procedure suggested by Magennis et al[26], and ligand **b** was synthesized by a method described by Maass et al [45]. Detailed synthetic procedures as well as their lanthanide complexes syntheses, $[Ln(a)_3]$ and $[Ln(b)_2(NO_3)_3]$, are given in SI. Synthetic protocols and characterization using ¹H NMR, IR spectra, ³¹P NMR, and ESI-MS for ligands **c** and **d** are described in detail in ESI.

Nanoparticles synthesis. For each system 0.5 mL of solution of the corresponding complex (C=3 mM) in acetonitrile was added dropwise via syringe plunger into 2.5 mL of PSS aqueous solution (1 g/L) containing NaCl (C = 0.5 M) while vigorously stirring (2200 rpm). Formation of fine white colloid was observed. To separate colloid nanoparticles from acetonitrile, the mixtures were centrifuged, supernatant removed and replaced with H₂O (V=3 mL). These operations were repeated twice. After each replacement of the solvent, the solutions were ultrasonicated for 10 min.

Methods. Mass spectra were recorded on an AmaZon X «Bruker» mass spectrometer. IR spectra were recorded on a Bruker Tensor-27 instrument for the samples in KBr pellets. NMR experiments were carried out on 400 MHz [400 MHz (¹H), 162 MHz (³¹P)] or 600 MHz [600 MHz (1H), 243 MHz (3P),] spectrometers equipped with a pulsed gradient unit capable of producing magnetic field pulse gradients in the z-direction of 53.5 G cm⁻¹. All spectra were acquired in a 5 mm gradient inverse broadband probe head. Chemical shifts (d) are expressed in parts per million relative to the residual ¹H signal of CDCl₃ and the signals are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (J) are in hertz (Hz). Excitation and emission spectra and luminescence decay curves were registered with Fluorolog-QM (Horiba). The transmission electron microscopy (TEM) was performed on a Hitachi HT7700 (tungsten filament, HV = 100 kV). amples were deposited on a 300 mesh copper grid with continuous carbon-formvar support film. XRD of crystals was performed with Bruker D8 QUEST. Detailed description can be found in supplementary material file. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using Cu radiation (40 kV, 40 mA) monochromated by the curved Johansson monochromator (λ Cu K α 1 1.5406 Å). Electron absorption spectra were registered with Analytic Jena SPECORD 50plus, for dynamic light scattering and zeta-potential measurements Malvern Zetasizer Nano ZS was utilized. Fundamental basis of Judd-Ofelt analysis [46,47] and corresponding formulas [48,49] are collected in supplementary material file.

Results and discussion

Synthesis of ligands c and d





X = N (c): 1.) 2 eq. Ph₂PCl, 2 eq. Et₃N, THF; 2.) H_2O_2 aq., acetone $0^{\circ}C$; X = C (d): 3.) 2 eq. Ph₂POEt, up to $200^{\circ}C$, neat;

Figure 1. Ligands synthesized for this study: *N*-(diphenylphosphoryl)-*P*,*P*-diphenylphosphinic amide (a), 2-(diphenylphosphoryl)-1-phenylethan-1-one (b), ((4-methoxyphenyl)methylene)bis(diphenylphosphine oxide) (c), *N*-(diphenylphosphoryl)-*N*-(4methoxyphenyl)-*P*,*P*-diphenylphosphinic amide (d). Synthetic routes employed in this work to synthesize new ligands c and d with *p*-methoxyphenyl substituent at *α*-position.

Ligands **a** and **b** were obtained and reported previously [26,45]. Both syntheses were reproduced in this work in order to synthesize a row of lanthanide(III) complexes to conduct a comparative study. Ligands **c** and **d** were obtained by known methods with some adjustments as depicted in Figure 1. In brief, ligand **c** was synthesized *via* interaction of 1-(dichloromethyl)-4-methoxybenzene and ethyl diphenylphosphinite, including Arbuzov rearrangement at high temperature neat till the reaction mixture solidifies. The desired ((4-methoxyphenyl)methylene)bis(diphenylphosphine oxide) **c** was obtained individually by recrystallization as a white poorly soluble solid. Ligand **d** was synthesized *via* oxidation of a crude reaction mixture of corresponding phosphine obtained as described by Ogawa et al [50]. The desired *N*-(diphenylphosphoryl)-*N*-(4-methoxyphenyl)-*P*,*P*-diphenylphosphinic amide **c** was obtained individually by two subsequent recrystallizations.

Synthesis of [Ln(L)x] complexes, $Ln=Eu^{3+}$, Tb^{3+} , L=a, b, c, x=1,2,3 and XRD data

Lanthanide complexes of bis-diphenylphosphine oxide amine (**a**) and 2-diphenylphosphineoxide-1-phenylethanone (**b**) were obtained previously and reproduced in this work in order to compare luminescent properties within the row of complexes.[27,28] X-Ray crystal structures of [Tb(**a**)₃] and [Eu(**b**)₂(NO₃)₃] are illustrated on the Figure 2a and 2b, respectively.



Figure 2. Comparison of the X-ray structures of complexes [Tb(a)₃] (a), [Eu(b)₂(NO₃)₃] (b), and [Tb(c)(NO₃)₃(H₂O)] (c). Metal atoms are shown as polyhedra. Hydrogen atoms are omitted for clarity. In the case of [Tb(a)₃], both molecules represented in the asymmetric cell are shown. (d) ORTEP of complex [Tb(c)(NO₃)₃(H₂O)] at the 50 % probability level for non-hydrogen atoms according to single-crystal X-ray diffraction. THF solvent molecules are omitted for clarity. Selected internuclear distances [Å]: Tb1–O1 2.3680(14), Tb1–O2 2.2949(13), Tb1–O1w 2.3532(18), Tb1–O11 2.4298(16), Tb1–O12 2.5068(15), Tb1–O21 2.4976(15), Tb1–O22 2.4872(15), Tb1–O31 2.4653(16), Tb1–O32 2.4351(15), P1–O1 1.5047(14), P2–O2 1.5001(14).

Single crystals of complex [Tb(c)(NO₃)₃(H₂O)] as colorless prisms were prepared by slow evaporation of a THF solution. The compound crystallizes in the monoclinic space group C2/c as a crystallosolvate with 2.5 THF molecules per complex. One complex molecule is present in the asymmetric cell. Its molecular structure is shown in Figure 2c,d and reflects the 1:1 stoichiometry. Nine-coordinated Tb atom is surrounded by one ligand c attached by bisphosphine oxide chelation through the P=O coordination, three ditopic NO₃- residues, and one water molecule. Interestingly, the [P=]O–Tb internuclear distances are notably different and equal to 2.3680(14) and 2.2949(13) Å. The internuclear distances between the Eu and coordinated oxygen atoms of NO₃- vary between 2.4298(16) and 2.5068(15) Å. Deposition number CCDC 2218909 contains the supplementary crystallographic data for compound Tb(c). These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

X-ray structures of previously studied $[Tb(a)_3]$ and $[Eu(b)_2(NO_3)_3]$, as well as the newly obtained $[Tb(c)(NO_3)_3(H_2O)]$, are presented in Figure 2a-c to illustrate the difference in the inner-sphere environment of the lanthanide ions in the complexes. In particular, the unsaturated coordination environment of Tb^{3+} ion in $[Tb(a)_3]$ by six oxygen atoms derives from the chelation of three imido-bis-phosphinates. The coordination polyhedron of $[Eu(b)_2(NO_3)_3]$ is filled by ten oxygen atoms arising from the coordination of both ligands and nitrates, and the nine oxygen atoms in the polyhedra of complex $[Tb(c)(NO_3)_3(H_2O)]$ also arises from the coordination of one organic ligand, three nitrates, and one water molecule. Complex $[Tb(a)_3]$ crystallizes with two molecules in the asymmetric cell. Although both molecules are situated at the crystallographic 3-fold proper rotating axes, they show different coordination modes, namely, trigonal prismatic and octahedral. Complexes $[Eu(b)_2(NO_3)_3]$ and $[Tb(c)(NO_3)_3(H_2O)]$ are located in general position in the crystals and, consequently, they are asymmetric.

Thus, the structure of ligands is of great impact on the complex structure. It is worth noting the conversion of the ligand from phosphine oxide to phosphonate forms as the reason for the formation of complex $[Tb(\mathbf{a})_3]$ with the coordinative unsaturated innersphere environment of the Tb³⁺ ion. A similar structure is revealed for some 1,3-diketonate complexes of lanthanides[51,52]. In turn, the substitution of N-H by N-R in the structure of \mathbf{d} (Figure 1) results in poor complexation. One can hypothesize that an impossibility of the deprotonation of ligand \mathbf{d} explains its poor ability to form complex, while the ability of the phosphine oxide representative **a** with N–H bridging moiety to deprotonate prerequisites its high complexing ability. The ligands **b** and **c** tend to chelate without deprotonation, which agrees well with the literature data [28,29]. The smaller electron donating properties of both bis-phosphine oxide **c** and ketophosphine oxide **b** vs. the anionic deprotonated form of ligand **a** result in the formation of the saturated coordination sphere due to the coordination of the nitrates and water molecule along with the organic ligands. The aforesaid difference in the coordination polyhedra can be of some impact on the lanthanide-centered luminescence of the complexes. It is also worth noting that the difference in the complex stoichiometry, which is 1:2 and 1:1 (metal-to-ligand ratio) for the ligands **b** and **c**, respectively, can be explained by additional steric constraints arising from the introduction of the bulky methoxyphenyl moiety in the ligand **c**.

Absorption and luminescent properties of Ln(c)

Absorption spectra of newly synthesized ligands **c** and **d** as well as their terbium complexes were recorded in CH₃CN (Figure 3a). Both ligands are characterized by an absorption band at 230 nm responsible for $\pi \rightarrow \pi^*$ transition. The spectrum of [Tb(**c**)(NO₃)₃(H₂O)] differs significantly from that of the ligand.



Figure 3. (a) UV-Vis absorption spectra of ligand **c** (1), **c** in the presence of triethylamine (2) and **c** in the presence of triethylamine and equimolar amount of terbium(III) (C=10⁻⁵ M). Excitation and emission spectra of $[Ln(\mathbf{a})_3]$ (1), $[Ln(\mathbf{b})_2(NO_3)_3]$ (2), $[Ln(\mathbf{c})(NO_3)_3(H_2O)]$ (3), $(Ln = Tb^{3+}$ (b); $Ln = Eu^{3+}$ (c)) ($C_{Ln}=10^{-5}$ M).

The as-synthesized terbium and europium complexes with ligands **a**, **b**, and **c** are well soluble in CH₃CN. Their luminescence spectra recorded at the same instrumental conditions revealed that terbium centers are more effectively sensitized by ligands **a** and **b** *vs* ligand **c** (Figure 3b). It is worth assuming that the tris-chelation of ligand **a** can be a reason for better sheltering of a coordination center from solvent molecules, while the inner-sphere nitrates in $[Tb(b)_2(NO_3)_3]$ and $[Tb(c)(NO_3)_3(H_2O)]$ can easily be substituted by the solvent molecules. However, the excited state lifetime (τ_{meas}) values calculated from the luminescence decay kinetic measurements (Table 1) remain high arguing against dissociation of the complexes $[Tb(b)_2(NO_3)_3]$ and $[Tb(c)(NO_3)_3(H_2O)]$.

The sensitivity to changes in symmetry and strength of the ligand field is the peculiar feature of the Eu³⁺-centered luminescence. The intensity ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions (R) is the well-known value allowing to follow the changes in the symmetry and strength of the ligand field around Eu³⁺ ions. This derives from the fact that the intensity of the dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ is hypersensitive to electric symmetry and strength of the ligand field around Eu³⁺ ions, while the magnetic dipole transition ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ is not affected by the surrounding charge distribution because it is parity-allowed, and its emission is often used as internal standard.[53] Thus, the R-values calculated through equation (1) are collected in Table 1 along with the τ -values calculated from the luminescence decay kinetic measurements.

$$R = \frac{I({}^{5}D_{0} \rightarrow {}^{7}F_{2})}{I({}^{5}D_{0} \rightarrow {}^{7}F_{1})}$$
(1)

The higher R, the lower the local symmetry around Eu³⁺ is with respect to an inversion center, since a high local symmetry strongly reduces the electric dipolar emission without affecting the magnetic dipolar one, and vice versa. Also, in many complexes, the ratio is high due to an increase in the covalency of Eu-ligand coordinative bonds, which lowers the symmetry.

Focusing our attention on Eu complexes, the PL emission spectra show a much different shape for the three analyzed complexes, as an indication of the different environment surrounding the rare earth ion. Indeed, the R-value is the highest for complex $[Eu(a)_3]$ as an indication of a low symmetry surrounding the rare earth ion. The opposite is observed for complexes $[Eu(b)_2(NO_3)_3]$ and $[Eu(c)(NO_3)_3(H_2O)]$, where the R-values

	R	Tau_rad (ms)	Tau_meas (ms)	PL efficiency
$[Tb(a)_3]$	-	-	2.20	
$[Tb(b)_2(NO_3)_3]$	-	-	4.79	
$[Tb(c)(NO_3)_3(H_2O)]$	-	-	3.05	
$[Eu(a)_3]$	11.22	1.49	1.5	0.93
$[Eu(b)_2(NO_3)_3]$	1.52	6.86	3.90	0.48
$[Eu(c)(NO_3)_3(H_2O)]$	1.38	7.40	4.20	0.62
$PSS-[Eu(\mathbf{a})_3]$	12.18	1.41	0.46	0.33
PSS- $[Eu(\mathbf{b})_2(NO_3)_3]$	1.17	8.10	3.50	0.43
$PSS[Eu(\mathbf{c})(NO_3)_3(H_2O)]$	0.86	10.13	3.33	0.33

barely exceed 1.0, thus, indicating that the magnetic transition intensity is similar to the electric dipolar one.

Table 1. Decay parameters for [Eu(L) _x] ir	n CH3CN
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The luminescence decay kinetics of the europium complexes also demonstrate the mono-exponential decay, which argues for a rather poor dissociation of the complexes. The lifetime results (Table 1) are in agreement with the previous considerations. Due to the forbidden nature of the internal 4f transitions, the probability of electric dipole recombination is low, resulting in long lifetimes in the millisecond range as it occurs for $[Eu(b)_2(NO_3)_3]$ and $[Eu(c)(NO_3)_3(H_2O)]$ complexes. However, when the surrounding environment introduces an asymmetric perturbation to the wave functions, this increases the dipole transition rate, reducing the radiative lifetime and increasing the electric dipole emission component. Thus, the calculated radiative lifetime reported in Table 1 is shorter for complex [Eu(a)₃] and longer for the other two. The measured lifetimes follow the same trend.

The lifetime results (Table 1) derived from corresponding luminescence decay curves (Figure 4) are in agreement with the difference in the inner-sphere environment of Eu^{3+} ions in the complexes with ligands **a**, **b**, and **c**. Due to the forbidden nature of the internal 4f transitions, the probability of electric dipole recombination is low, resulting in long lifetimes in the millisecond range as it occurs for $[Eu(b)_2(NO_3)_3]$ and $[Eu(c)(NO_3)_3(H_2O)]$ complexes. However, when the surrounding environment introduces an asymmetric perturbation to the wave functions, this increases the dipole transition rate, reducing the radiative lifetime and increasing the electric dipole emission component. Thus, the calculated radiative lifetime reported in Table 1 is shorter for complex $[Eu(a)_3]$, and longer for the other two. The measured lifetimes follow the same trend.



Figure 4. Luminescence decay curves for [Eu(L)x] (a) and PSS-[Eu(L)x] (b) in logarithmic scale (L=a(1), b(2), c(3)).

Synthesis of PSS-[Ln(L)x] nanoparticles, L=a, b, c, x=1,2, 3, Ln=Tb, Eu

Chasing applicability for biomedical purposes the complexes were converted to water colloids according to the solvent change method [8], where the precipitated species are incorporated into the PSS capsules through an electrostatic attraction. Thus, the charge of the precipitated species is of great impact on the efficacy of the incorporation. The surface charge of the colloidal species can be measured by measuring their electrokinetic potential (ζ) values. Dropwise addition of the complexes in the acetonitrile solution (C = 1 mM) to water results in the formation of the colloids, which were characterized by measurements of their size and ζ -values (Table 2). These values were measured for the colloids formed from the Eu³⁺ complexes with the ligands (Table 2). The positive ζ -values of the colloids formed formed from complexes [Eu(**b**)₂(NO₃)₃] and [Eu(**c**)(NO₃)₃(H₂O)] are rather anticipated, since the surface exposed complex units can undergo partial degradation, most probably, due to release of nitrate anions. The significant negative surface charging of the colloids from complex Eu(a)³ also argues for its partial degradation, while the significant basicity of the released deprotonated ligand triggers a formation of hydroxyls under the interaction with water molecules.

Name	Size (nm)	PDI	ζ (mV)
$[Eu(\mathbf{a})_3]$	1305.0 ± 62.7	0.199 ± 0.182	-32.9 ± 0.6
$[Eu(b)_2(NO_3)_3]$	878.6 ± 28.9	0.659 ± 0.016	35.7 ± 0.5
$[Eu(c)(NO_3)_3(H_2O)]$	1922.0 ± 133.5	0.265 ± 0.157	28.3 ± 1.2
$PSS-[Eu(\mathbf{a})_3]$	314.9 ± 11.2	0.272 ± 0.006	-27.1 ± 0.7
$PSS-[Eu(\mathbf{b})_2(NO_3)_3]$	522.2 ± 58.3	0.549 ± 0.040	-67.1 ± 0.8
$PSS_{-}[Eu(c)(NO_{2})_{2}(H_{2}O_{2})]$	$6/6.9 \pm 68.5$	0.561 ± 0.038	-620 + 23

It is worth noting that the nanoprecipitation of the complexes in the solutions of PSS and NaCl results in the formation of the aqueous colloids, which are manifested by the average size values less than those of the nanoprecipitates formed in the aqueous solutions. The PSS-stabilized colloids exhibit high colloid stability, while their uncoated counterparts aggregate and precipitate within several hours. The efficient incorporation of the nanoprecipitates into the PSS-based aggregates is rather anticipated for the lanthanide complexes with ligands **b** and **c**, since their nanoprecipitates of complex [$Eu(a)_3$] into the aggregates is rather unusual. However, we can keep in mind the high concentration of the counterions derived from the high concentration level of NaCl in the PSS solutions, which can facilitate the incorporation of the [$Eu(a)_3$]-based nanoprecipitates into the PSS-capsules.

Table 3. The equilibrium Eu³⁺ concentrations in the aqueous colloids and the supernatants after the phase separation and the washing procedure along with the percentage of Eu³⁺ in the colloids and supernatants.

	Introdu ced	Remain compose coll	within the sition of loids	C_{Ln} in su	upernatant 1	C_{Ln} in su	pernatant 2	Total loss	of Ln(III)
	мМ	мМ	%	мМ	%	мМ	%	мМ	%
$PSS-[Eu(\mathbf{a})_3]$	0.5	0.344	68.94	0.13	26.50	0.023	4.55	0.155	31.05
$PSS-[Eu(\mathbf{b})_2(NO_3)_3]$	0.5	0.108	21.69	0.37	73.49	0.024	4.82	0.392	78.31
PSS-[Eu(\mathbf{c})(NO ₃) ₃ (H ₂ O)]	0.5	0.116	23.29	0.38	37.67	0.007	1.38	38.36	76.71

The efficacy of the complex transformation from the acetonitrile solutions into the PSS-stabilized colloids can be followed by the partial leaching of the lanthanide ions. Thus, the equilibrium concentrations of the lanthanide ions were measured in the aqueous colloids and two first supernatants after the phase separation and the washing procedure

(for more details see the experimental section). The percentage of the conversion calculated from the data is represented in Table 3 for the complexes $[Eu(L)_x]$. The most efficient conversion is observed for $[Eu(a)_3]$, which indicates poor leaching of Eu^{3+} ions from the nanoprecipitates. The leaching is more pronounced for complexes $[Eu(b)_2(NO_3)_3]$ and $[Eu(c)(NO_3)_3(H_2O)]$, which correlates with the less tight binding of Eu^{3+} ions by ligands **b** and **c** than by ligand **a**. It is worth mentioning that ligands **b** and **c** tend to coordinate without deprotonation, while the tightest binding of Eu^{3+} by ligand **a** is due to its deprotonation, which enforces the coordination bonds in $[Eu(a)_3]$.

Figure 5a illustrates morphology of of PSS-[Eu(\mathbf{a})₃] colloids dried on the formvar coated substrate. There are 35-70 nm particles of PSS stuffed by multiple 2-8 nm sized cores built of [Eu(\mathbf{a})₃] complexes. Such plum-duff architecture is the key to more efficient sensing compared to PSS- PSS-[Eu(\mathbf{b})₂(NO₃)₃] and [Eu(\mathbf{c})(NO₃)₃(H₂O)] colloidal species (Figure S1) due to highly developed surface. The produced colloids exhibit Eu³⁺-centered luminescence (Figure 5b). The R-values of the colloids follow the similar tendency as for the complexes in solutions (Table 1). Thus, the specific R-value of [Eu(\mathbf{a})₃] in the acetonitrile solution and in PSS-stabilised colloids argues for the similarity in the inner-sphere environment of Eu³⁺ ion in both molecular and colloidal forms. The excited state lifetime values of the colloids (Table 1) also reveal the specificity of [Eu(\mathbf{a})₃] similar with the complexes in the solutions. The aforesaid agrees well with the safe conversion of [Eu(\mathbf{a})₃] complexes into the colloids (Table 3).



Figure 5. (a) TEM image of PSS-[Eu(**a**)₃]. (b) Excitation and emission spectra of PSS-[Eu(**L**)_x] (L=a, b, c, x=3,2,1 correspondingly). (c) Simulated PXRD pattern out of single crystal data of [Eu(**a**)₃] (2) in comparison to dried PSS-[Eu(**a**)₃] PXRD pattern (1). (d) PXRD patterns of dried PSS-[Eu(**a**)₃] (1) and ligand **a** (2).

The dried PSS-[Eu(\mathbf{a})₃] colloids were analysed by PXRD method (Figure 5 c, d). The PXRD pattern of the colloids was compared with the PXRD pattern simulated out of

single crystal data of $[Eu(\mathbf{a})_3]$ (Figure 5c) in order to prove composition of PSS- $[Eu(\mathbf{a})_3]$ colloids. The vast majority of reflections in diffractograms of $[Eu(\mathbf{a})_3]$ and PSS- $[Eu(\mathbf{a})_3]$ coincides. At the same time, comparative analysis of the difractograms of the powder samples of PSS- $[Eu(\mathbf{a})_3]$ colloids and ligand **a** represented in Figure 5d reveals no coincidence between the PXRD patterns of ligand **a** and PSS- $[Eu(\mathbf{a})_3]$. This allows us to conclude that the nanoparticles contain a pure crystalline phase of the complex without an admixture of the separately precipitated ligand phase.

Detection of ceftriaxone using PSS-[Eu(a)₃] colloids

The high chemical stability of $[Eu(\mathbf{a})_3]$ and relative hydrophobicity ensured efficient transformation of $[Eu(\mathbf{a})_3]$ into PSS- $[Eu(\mathbf{a})_3]$, which makes these colloids the most promising basis for reliable sensing of substrates. Short screening of antibiotics was performed for PSS-[Eu(**a**)₃] water dispersions in terms of possible luminescent response. No quenching was observed for penicillins and fluoroquinolones exemplified by amoxicillin and ciprofloxacin, respetively. In the meanwhile, the presence of micromolar amounts of ceftriaxone resulted in significant changes of emission intensity. Main europium band at 612 nm demonstrated quenching for the factor of 7.23 when $87.5 \,\mu$ M ceftriaxone is added (Figure 6a). Deviation of Io/I from linear law in Stern-Volmer coordinates indicates mixed, static and dynamic, mechanism of quenching, which is typical for dark complexes formation (Figure 6b).[54,55] Limit of detection (LOD) calculated as $3\sigma/S$ (where σ is standart deviation for blank experiments and S is a slope of linear segment of luminescence intensity vs. concentration of analyte) is equal to 0.974 μ M, which is comparable to the previously reported values (Table 4). For comparative purposes the luminescent response of PSS- $[Eu(b)_2(NO_3)_3]$ to ceftriaxone was also monitored (Figure S2). The latter colloids demonstrate a less sensitive response to the substrate, which can be explained by their mixed composition.



Figure 6. (a) Gradual quenching of Eu³⁺ luminescence within the composition of PSS-[Eu(**a**)₃] colloids in the presence of increasing amounts of ceftriaxone (C= 57.4 μM). (b) I/I₀ values *vs*. concentration of ceftriaxone, I₀ and I are the luminescence intensities of PSS-[Eu(**a**)₃] colloids without and in the presence of certain concentration of ceftriaxone, respectively (1). Tangent for curve (1) in low-concentration region taken for LOD calculation.

 Table 4. LOD values of ceftriaxone detection for various luminescent nanomaterials/compounds reported in the literature.

Luminescent compound	LOD (M)		
CdSe/CdS/ZnS quantum dots[56]	1×10^{-6}		
ceftriaxone converted into a fluorescent compound[57]	$3,5 \times 10^{-8}$		

Chemiluminescence emission generated from the oxidation of	
ceftriaxone sodium[58]	$4.5 imes 10^{-8}$
Ceftriaxone converted into a fluorescent product[59]	$2,3 imes 10^{-9}$
carbonized blue crab shell carbon dots[60]	$9.0 imes 10^{-9}$
chicken drumstick-derived carbon dots[61]	4,4 ×10 ⁻¹⁰
Graphene quantum dots in a molecularly imprinted polymer MIP-	
GQDs[62]	$1,8 \times 10^{-10}$
L-cysteine (Cys) coated CdS QDs[63]	$1.3 imes 10^{-9}$
L-cysteine capped ZnS (L-Cys-ZnS) QDs [64]	$9,0 imes10^{-8}$
Our paper	$9,7 imes 10^{-7}$

Conclusion

Summarizing, the present work demonstrates the three representatives of bis-phosphine oxides and carbamoylphosphine oxide as ligands for Tb³⁺ and Eu³⁺ ions. The nature of brigding group between phosphine oxide moieties is of great impact on the complex structure. The specificity of imido-group as the bridging one between two phosphine oxide moieties manifested by the possibility of conversion of imido-bisphosphine oxides to their phosphonate form is the reason for the formation of complexes $[Ln(a)_3]$ (Ln=Eu³⁺, Tb³⁺) with the coordinative unsaturated inner-sphere environment of the Ln³⁺ ion. The carbamoylphosphine oxide and bis-phosphine oxide ligands with methylene bridging groups are efficiently coordinated to Ln³⁺ ions without deprotonation, while the complex ability is poor for the ligand possessing N-R bridging group. The coordination of the ligands with the Ln³⁺ ions results in the efficient sensitization of both Tb³⁺- and Eu³⁺-centered luminescence. The ligand environment in [Ln(a)₃] complexes provides the specific ligand field symmetry, which is manifested by the specific spectral pattern and excited state lifetime value of $[Eu(\mathbf{a})_3]$. Moreover, the high stability of $[Ln(\mathbf{a})_3]$ complexes provides their safe conversion into $PSS-[Ln(\mathbf{a})_3]$ colloids, while the lanthanide complexes with carbamoylphosphine oxide and bis-phosphine oxide ligands suffer from the partial degradation under the synthesis of the PSS-stabilized colloids. The red luminescence of PSS- $[Eu(\mathbf{a})_3]$ fitting to the wavelengths range of the so-called biological window exhibit the pronounced luminescent response on the antibiotics ceftriaxone, which allows to sense the latter in aqueous solutions with the LOD value equal to $0.974 \,\mu$ M.

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References

- Comby, S.; Surender, E.M.; Kotova, O.; Truman, L.K.; Molloy, J.K.; Gunnlaugsson, T. Lanthanide-functionalized nanoparticles as MRI and luminescent probes for sensing and/or imaging applications. *Inorg. Chem.* 2014, 53, 1867–1879, doi:10.1021/ic4023568.
- Zairov, R.; Mustafina, A.; Shamsutdinova, N.; Nizameev, I.; Moreira, B.; Sudakova, S.; Podyachev, S.; Fattakhova, A.; Safina, G.; Lundstrom, I.; et al. High performance magneto-fluorescent nanoparticles assembled from terbium and gadolinium 1,3diketones. *Sci. Rep.* 2017, 7, doi:10.1038/srep40486.
- 3. Bünzli, J.G.C.G. Lanthanide light for biology and medical diagnosis. J. Lumin. 2016, 170, 866–878, doi:10.1016/j.jlumin.2015.07.033.

- Podyachev, S.N.; Sudakova, S.N.; Zairov, R.R.; Syakaev, V. V.; Masliy, A.N.; Dusek, M.; Gubaidullin, A.T.; Dovzhenko, A.P.; Buzyurova, D.N.; Lapaev, D. V.; et al. Modulating the Inclusive and Coordinating Ability of Thiacalix[4]arene and Its Antenna Effect on Yb3-Luminescence via Upper-Rim Substitution+. *Molecules* 2022, 27, 6793, doi:10.3390/molecules27206793.
- 5. Metlin, M.T.; Ambrozevich, S.A.; Metlina, D.A.; Vitukhnovsky, A.G.; Taydakov, I.V. Luminescence of pyrazolic 1,3-diketone <math altimg="si0042.gif" overflow="scroll"> <msup> <mrow> <mi>Pr</mi> </mrow> <mrow> <mn>3</mn> <mo>+</mo> </mrow> </msup> </math> complex with 1,10-phenanthroline. *J. Lumin.* **2017**, *188*, 365–370, doi:10.1016/j.jlumin.2017.04.058.
- 6. Emelina, T.B.; Kalinovskaya, I.V.; Mirochnik, A.G. Europium(III) complex with powerful antenna ligands: Interligand interaction. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2019**, 207, 222–228, doi:10.1016/j.saa.2018.09.012.
- Metlin, M.T.; Goryachii, D.O.; Datskevich, N.P.; Asanov, R.K.; Aminev, D.F.; Metlina, D.A.; Taidakov, I. V. Photo- and Electroluminescent Properties of the Yb3+ Complex with Pyrazole-Substituted 1,3-Diketone and 1,10-Phenanthroline. *Bull. Lebedev Phys. Inst.* 2021, 48, 139–143, doi:10.3103/S1068335621050055.
- 8. Podyachev, S.N.; Zairov, R.R.; Mustafina, A.R. 1,3-Diketone Calix[4]arene Derivatives-A New Type of Versatile Ligands for Metal Complexes and Nanoparticles. *Molecules* **2021**, *26*, 1–29, doi:10.3390/molecules26051214.
- Reid, B.L.; Stagni, S.; Malicka, J.M.; Cocchi, M.; Hanan, G.S.; Ogden, M.I.; Massi, M. Lanthanoid β-triketonates: a new class of highly efficient NIR emitters for bright NIR-OLEDs. *Chem. Commun.* 2014, *50*, 11580–11582, doi:10.1039/C4CC04961F.
- Mironov, L.Y.; Sveshnikova, E.B.; Ermolaev, V.L. Energy transfer from the singlet levels of diketones and dyes to lanthanide ions in nanoparticles consisting of their diketonate complexes. *Opt. Spectrosc.* 2014, *116*, 933–940, doi:10.1134/S0030400X14060162.
- 11. Clegg, J.K.; Li, F.; Lindoy, L.F. Oligo-β-diketones as versatile ligands for use in metallo-supramolecular chemistry: Recent progress and perspectives. *Coord. Chem. Rev.* **2022**, *455*, 214355, doi:10.1016/j.ccr.2021.214355.
- 12. Podyachev, S.N.; Gimazetdinova, G.S.; Sudakova, S.N.; Shamsutdinova, N.A.; Lapaev, D. V.; Syakaev, V. V.; Gubaidullin, A.T.; Nagimov, R.N.; Mustafina, A.R. Influence of upper rim dibromo-substitution in bis-1,3-diketone calix[4]arenes on spectral properties of ligands and their lanthanide complexes. *Tetrahedron* **2017**, *73*, 5397–5407, doi:10.1016/j.tet.2017.07.043.
- 13. Brites, C.D.S.; Lima, P.P.; Carlos, L.D. Tuning the sensitivity of Ln3+-based luminescent molecular thermometers through ligand design. *J. Lumin.* **2016**, *169*, 497–502, doi:10.1016/j.jlumin.2015.01.025.
- 14. Zairov, R.R.; Dovzhenko, A.P.; Podyachev, S.N.; Sudakova, S.N.; Kornev, T.A.; Shvedova, A.E.; Masliy, A.N.; Syakaev, V. V.; Alekseev, I.S.; Vatsouro, I.M.; et al. Role of PSS-based assemblies in stabilization of Eu and Sm luminescent complexes and their thermoresponsive luminescence. *Colloids Surfaces B Biointerfaces* **2022**, *217*, 112664, doi:10.1016/j.colsurfb.2022.112664.
- 15. Pradhan, S.; Swain, N.; Prusty, S.; Sahu, R.K.; Mishra, S. Role of extractants and diluents in recovery of rare earths from waste materials. *Mater. Today Proc.* 2020, *30*, 239–245, doi:10.1016/j.matpr.2020.01.288.
- Safiulina, A.; Borisova, N.; Grigoriev, M.; Baulin, D.; Baulin, V.; Tsivadze, A. Design of Extractants for F-Block Elements in a Series of (2-(Diphenylphosphoryl)methoxyphenyl)diphenylphosphine Oxide Derivatives: Synthesis, Quantum-Chemical, and Extraction Studies. *Molecules* 2021, 26, 2217, doi:10.3390/molecules26082217.
- 17. Batchu, N.K.; Li, Z.; Verbelen, B.; Binnemans, K. Structural effects of neutral organophosphorus extractants on solvent extraction of rare-earth elements from aqueous and non-aqueous nitrate solutions. *Sep. Purif. Technol.* **2021**, 255, 117711, doi:10.1016/j.seppur.2020.117711.
- Kukkonen, E.; Virtanen, E.J.; Moilanen, J.O. α-Aminophosphonates, -Phosphinates, and -Phosphine Oxides as Extraction and Precipitation Agents for Rare Earth Metals, Thorium, and Uranium: A Review. *Molecules* 2022, 27, 3465, doi:10.3390/molecules27113465.
- 19. Nazarova, A.; Padnya, P.; Cragg, P.J.; Stoikov, I. [1]Rotaxanes based on phosphorylated pillar[5]arenes. *New J. Chem.* **2022**, *46*, 2033–2037, doi:10.1039/D1NJ05461A.
- Nazarova, A.A.; Yakimova, L.S.; Padnya, P.L.; Evtugyn, V.G.; Osin, Y.N.; Cragg, P.J.; Stoikov, I.I. Monosubstituted pillar[5]arene functionalized with (amino)phosphonate fragments are "smart" building blocks for constructing nanosized structures with some s- and p-metal cations in the organic phase. *New J. Chem.* 2019, *43*, 14450–14458, doi:10.1039/C9NJ03539G.
- Aslandukov, A.N.; Utochnikova, V. V.; Goriachiy, D.O.; Vashchenko, A.A.; Tsymbarenko, D.M.; Hoffmann, M.; Pietraszkiewicz, M.; Kuzmina, N.P. The development of a new approach toward lanthanide-based OLED fabrication: new host materials for Tbbased emitters. *Dalt. Trans.* 2018, 47, 16350–16357, doi:10.1039/C8DT02911C.
- 22. Platt, A.W.G. Lanthanide phosphine oxide complexes. Coord. Chem. Rev. 2017, 340, 62–78, doi:10.1016/j.ccr.2016.09.012.
- 23. Casey, K.C.; Brown, A.M.; Robinson, J.R. Yttrium and lanthanum bis(phosphine-oxide)methanides: Structurally diverse, dynamic, and reactive. *Inorg. Chem. Front.* 2021, *8*, 1539–1552, doi:10.1039/d0qi01438a.
- Kariaka, N.; Litsis, O.; Kolomzarov, Y.; Gawryszewska, P.; Smola, S.; Rusakova, N.; Trush, V.; Sliva, T.; Amirkhanov, V. Luminescent thin films based on N-(diphenylphosphoryl)benzamide EuIII and TbIII complexes for light emitting diode technology. *Chem. J. Mold.* 2018, 13, 54–62, doi:10.19261/cjm.2018.473.
- Davis, D.; Carrod, A.J.; Guo, Z.; Kariuki, B.M.; Zhang, Y.-Z.; Pikramenou, Z. Imidodiphosphonate Ligands for Enhanced Sensitization and Shielding of Visible and Near-Infrared Lanthanides. *Inorg. Chem.* 2019, 58, 13268–13275, doi:10.1021/acs.inorgchem.9b02090.
- 26. Magennis, S.W.; Parsons, S.; Pikramenou, Z. Assembly of Hydrophobic Shells and Shields around Lanthanides. *Chem. A Eur. J.* **2002**, *8*, 5761–5771, doi:10.1002/1521-3765(20021216)8:24<5761::AID-CHEM5761>3.0.CO;2-H.
- 27. Magennis, S.W.; Parsons, S.; Corval, A.; Woollins, J.D.; Pikramenou, Z. Imidodiphosphinate ligands as antenna units in luminescent lanthanide complexes. *Chem. Commun.* **1999**, 61–62, doi:10.1039/a808046a.

- 28. Leach, E.G.; Shady, J.R.; Boyden, A.C.; Emig, A.L.; Henry, A.T.; Connor, E.K.; Staples, R.J.; Schaertel, S.; Werner, E.J.; Biros, S.M. X-ray crystallographic, luminescence and NMR studies of phenacyldiphenylphosphine oxide with the Ln(iii) ions Sm, Eu, Gd, Tb and Dy. *Dalt. Trans.* 2017, 46, 15458–15469, doi:10.1039/c7dt02678a.
- 29. Lees, A.M.J.; Platt, A.W.G. Complexes of Lanthanide Nitrates with Bis(diphenylphosphino)methane Dioxide. *Inorg. Chem.* 2003, 42, 4673–4679, doi:10.1021/ic0342954.
- Turanov, A.N.; Karandashev, V.K.; Artyushin, O.I.; Peregudov, A.S.; Khvostikov, V.A.; Bondarenko, N.A. Extraction Properties of Diphenyl{[N-(2-diphenylphosphinylethyl)-N-alkyl]carbamoylmethyl}phosphine Oxides in Nitric Acid Solutions. *Russ. J. Inorg. Chem.* 2020, 65, 905–913, doi:10.1134/S0036023620060248.
- 31. Turanov, A.N.; Karandashev, V.K.; Yarkevich, A.N. Novel Bis(diphenylcarbamoylmethylphosphine oxide) Ligand for Effective Extraction of Actinides and Lanthanides from Nitric Acid Solutions. *Solvent Extr. Ion Exch.* **2022**, *40*, 493–517, doi:10.1080/07366299.2021.2001973.
- 32. Bryleva, Y.A.; Artem'ev, A. V.; Glinskaya, L.A.; Rakhmanova, M.I.; Samsonenko, D.G.; Komarov, V.Y.; Rogovoy, M.I.; Davydova, M.P. Bright photo- and triboluminescence of centrosymmetric Eu(<scp>iii</scp>) and Tb(<scp>iii</scp>) complexes with phosphine oxides containing azaheterocycles. *New J. Chem.* **2021**, *45*, 13869–13876, doi:10.1039/D1NJ02441H.
- Xu, H.; Yin, K.; Huang, W. Synthesis, photophysical and electroluminescent properties of a novel bright light-emitting Eu3+ complex based on a fluorene-containing bidentate aryl phosphine oxide. *Synth. Met.* 2010, 160, 2197–2202, doi:10.1016/j.synthmet.2010.08.009.
- Davydov, N.; Zairov, R.; Mustafina, A.; Syakayev, V.; Tatarinov, D.; Mironov, V.; Eremin, S.; Konovalov, A.; Mustafin, M. Determination of fluoroquinolone antibiotics through the fluorescent response of Eu(III) based nanoparticles fabricated by layer-by-layer technique. *Anal. Chim. Acta* 2013, 784, doi:10.1016/j.aca.2013.04.054.
- Shamsutdinova, N.; Zairov, R.; Mustafina, A.; Podyachev, S.; Sudakova, S.; Nizameev, I.; Kadirov, M.; Amirov, R. Interfacial interactions of hard polyelectrolyte-stabilized luminescent colloids with substrates. *Colloids Surfaces A Physicochem. Eng. Asp.* 2015, 482, 231–240, doi:10.1016/j.colsurfa.2015.05.013.
- Makedonskaya, M.I.; Veselova, I.A.; Kalmykov, S.N.; Shekhovtsova, T.N. Novel biosensing system for the simultaneous multiplex fluorescent determination of catecholamines and their metabolites in biological liquids. *J. Pharm. Biomed. Anal.* 2018, 156, 133–141, doi:10.1016/j.jpba.2018.04.026.
- Wang, X.; Chang, H.; Xie, J.; Zhao, B.; Liu, B.; Xu, S.; Pei, W.; Ren, N.; Huang, L.; Huang, W. Recent developments in lanthanidebased luminescent probes. *Coord. Chem. Rev.* 2014, 273–274, 201–212, doi:10.1016/j.ccr.2014.02.001.
- 38. Rahbar, N.; Abbaszadegan, P.; Savarizadeh, A. A sensitive fluorescent sensing strategy for nanomolar levels of metformin using graphitic carbon nitride nanosheets as nanofluoroprobe. *Anal. Chim. Acta* **2018**, *1026*, 117–124, doi:10.1016/j.aca.2018.04.007.
- Zairov, R.R.; Dovzhenko, A.P.; Podyachev, S.N.; Sudakova, S.N.; Masliy, A.N.; Syakaev, V. V.; Gimazetdinova, G.S.; Nizameev, I.R.; Lapaev, D. V.; Budnikova, Y.H.; et al. Rational design of efficient nanosensor for glyphosate and temperature out of terbium complexes with 1,3-diketone calix[4]arenes. *Sensors Actuators B Chem.* 2022, 350, 130845, doi:10.1016/j.snb.2021.130845.
- Zairov, R.R.; Nagimov, R.N.; Sudakova, S.N.; Lapaev, D. V.; Syakaev, V. V.; Gimazetdinova, G.S.; Voloshina, A.D.; Shykula, M.; Nizameev, I.R.; Samigullina, A.I.; et al. Polystyrenesulfonate-coated nanoparticles with low cytotoxicity for determination of copper(II) via the luminescence of Tb(III) complexes with new calix[4]arene derivatives. *Microchim. Acta* 2018, 185, 4–13, doi:10.1007/s00604-018-2923-2.
- Marais, O. Le traitement par ceftriaxone des méningites bactériennes chez l'enfant est efficace. Option/Bio 2011, 22, 4, doi:10.1016/S0992-5945(11)70829-7.
- 42. Tiltnes, T.S.; Kehrer, M.; Hughes, H.; Morris, T.E.; Justesen, U.S. Ceftriaxone treatment of spondylodiscitis and other serious infections with Cutibacterium acnes. *J. Antimicrob. Chemother.* **2020**, *75*, 3046–3048, doi:10.1093/jac/dkaa259.
- Han, Y.; Yin, Y.; Dai, X.; Chen, S.; Yang, L.; Zhu, B.; Zhong, N.; Cao, W.; Zhang, X.; Wu, Z.; et al. Widespread Use of High-dose Ceftriaxone Therapy for Uncomplicated Gonorrhea Without Reported Ceftriaxone Treatment Failure: Results From 5 Years of Multicenter Surveillance Data in China. *Clin. Infect. Dis.* 2020, 70, 99–105, doi:10.1093/cid/ciz170.
- 44. File, T.M.; Eckburg, P.B.; Talbot, G.H.; Llorens, L.; Friedland, H.D. Macrolide therapy for community-acquired pneumonia due to atypical pathogens: outcome assessment at an early time point. *Int. J. Antimicrob. Agents* **2017**, *50*, 247–251, doi:10.1016/j.ijantimicag.2017.01.043.
- 45. Maass, J.S.; Wilharm, R.K.; Luck, R.L.; Zeller, M. Photoluminescent properties of three lanthanide compounds of formulae LnCl3(diphenyl((5-phenyl-1H-pyrazol-3-yl)methyl)phosphine oxide)2, Ln = Sm, Eu and Tb: X-ray structural, emission and vibrational spectroscopies, DFT and thermogravimetric studies. *Inorganica Chim. Acta* 2018, 471, 481–492, doi:10.1016/j.ica.2017.11.049.
- 46. Judd, B.R. Optical absorption intensities of rare-earth ions. Phys. Rev. 1962, 127, 750–761, doi:10.1103/PhysRev.127.750.
- 47. Ofelt, G.S. Intensities of crystal spectra of rare-earth ions. J. Chem. Phys. 1962, 37, 511–519, doi:10.1063/1.1701366.
- Malba, C.; Sudhakaran, U.P.; Borsacchi, S.; Geppi, M.; Enrichi, F.; Natile, M.M.; Armelao, L.; Finotto, T.; Marin, R.; Riello, P.; et al. Structural and photophysical properties of rare-earth complexes encapsulated into surface modified mesoporous silica nanoparticles. *Dalt. Trans.* 2014, 43, 16183–16196, doi:10.1039/c4dt00760c.
- 49. Werts, M.H. V.; Jukes, R.T.F.; Verhoeven, J.W. The emission spectrum and the radiative lifetime of Eu3+ in luminescent lanthanide complexes. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542–1548, doi:10.1039/b107770h.

- 50. Ogawa, T.; Kajita, Y.; Wasada-Tsutsui, Y.; Wasada, H.; Masuda, H. Preparation, Characterization, and Reactivity of Dinitrogen Molybdenum Complexes with Bis(diphenylphosphino)amine Derivative Ligands that Form a Unique 4-Membered P–N–P Chelate Ring. *Inorg. Chem.* **2013**, *52*, 182–195, doi:10.1021/ic301577a.
- Stabnikov, P.A.; Pervukhina, N. V.; Kuratieva, N. V.; Kryuchkova, N.A.; Korolkov, I. V.; Urkasym kyzy, S.; Sysoev, S. V.; Babailov, S.P. New polymorphic modification of Y, Ho, Tm and Lu tris-2,2,6,6-tetramethyl-heptane-2,4-dionates: Structure, volatility and luminescence. *Polyhedron* 2021, 198, 115077, doi:10.1016/j.poly.2021.115077.
- 52. Huang, S.; Sysoev, S.V.; Stabnikov, P.A.; Pervukhina, N.V.; Korolkov, I.V.; Mosyagina, S.A. Crystal structures of trisdipivaloylmetanates of Tm3+ and Yb3+. *Jiegou Huaxue* 2018, *37*, 640–644, doi:10.14102/j.cnki.0254-5861.2011-1792.
- 53. Levy, D.; Reisfeld, R.; Avnir, D. Fluorescence of europium(III) trapped in silica gel-glass as a probe for cation binding and for changes in cage symmetry during gel dehydration. *Chem. Phys. Lett.* **1984**, *109*, 593–597, doi:10.1016/0009-2614(84)85431-7.
- 54. Bünzli, J.-C.G.C.G. On the design of highly luminescent lanthanide complexes. *Coord. Chem. Rev.* 2015, 293–294, 19–47, doi:10.1016/j.ccr.2014.10.013.
- Rusakova, N.V.; Kost, S.S.; Mustafina, A.R.; Amirov, R.R.; Zairov, R.R.; Solovieva, S.E.; Antipin, I.S.; Konovalov, A.I.; Korovin, Y.V. Spectral-luminescence and magnetic relaxation properties of lanthanide-p-sulfonatothiacalix[4]arenes in aqueous solution of surfactants. *Russ. Chem. Bull.* 2008, *57*, doi:10.1007/s11172-008-0088-6.
- Karpov, V.M.; Spektor, D. V.; Beklemishev, M.K. Determination of ceftriaxone by the fluorescence quenching of quantum dots using binding with polyethyleneimine. J. Anal. Chem. 2016, 71, 519–526, doi:10.1134/S1061934816050051.
- 57. Shah, J.; Jan, M.R.; Shah, S.; Naeem, M. Spectrofluorimetric Protocol for Ceftriaxone in Commercial Formulation and Human Plasma After Condensation with Formaldehyde and Ethyl Acetoacetate. *J. Fluoresc.* **2011**, *21*, 2155–2163, doi:10.1007/s10895-011-0917-0.
- 58. Zhang, D.; Ma, Y.; Zhou, M.; Li, L.; Chen, H. Determination of ceftriaxone sodium in pharmaceutical formulations by flow injection analysis with acid potassium permanganate chemiluminescence detection. *Anal. Sci.* 2006, 22, 183–186, doi:10.2116/analsci.22.183.
- 59. Shah, J.; Jan, M.R.; Shah, S.; Inayatullah Development and validation of a spectrofluorimetric method for the quantification of ceftriaxone in pharmaceutical formulations and plasma. *Luminescence* **2013**, *28*, 516–522, doi:10.1002/bio.2487.
- Pourmahdi, N.; Sarrafi, A.H.M.; Larki, A. Carbon Dots Green Synthesis for Ultra-Trace Determination of Ceftriaxone Using Response Surface Methodology. J. Fluoresc. 2019, 29, 887–897, doi:10.1007/s10895-019-02400-5.
- 61. Narimani, S.; Samadi, N. Rapid trace analysis of ceftriaxone using new fluorescent carbon dots as a highly sensitive turn-off nanoprobe. *Microchem. J.* **2021**, *168*, 106372, doi:10.1016/j.microc.2021.106372.
- Chullasat, K.; Kanatharana, P.; Bunkoed, O. Nanocomposite optosensor of dual quantum dot fluorescence probes for simultaneous detection of cephalexin and ceftriaxone. *Sensors Actuators B Chem.* 2019, 281, 689–697, doi:10.1016/j.snb.2018.11.003.
- Samadi, N.; Narimani, S. An ultrasensitive and selective method for the determination of Ceftriaxone using cysteine capped cadmium sulfide fluorescence quenched quantum dots as fluorescence probes. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2016, 163, 8–12, doi:10.1016/j.saa.2016.03.014.
- 64. Qu, J.; Zhu, Z.; Bai, X.; Qu, J. Determination of Ceftriaxone Sodium by Fluorescence Probes of L-Cysteine Capped ZnS Quantum Dots. *Nanosci. Nanotechnol. Lett.* **2013**, *5*, 1051–1057, doi:10.1166/nnl.2013.1666.