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Synthesis and photophysical properties of europium complexes with heterotopic hexadentate ligands based on 2,2′-bipyridyl-6,6′-dicarboxamide

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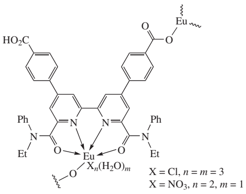
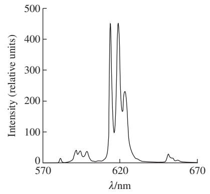
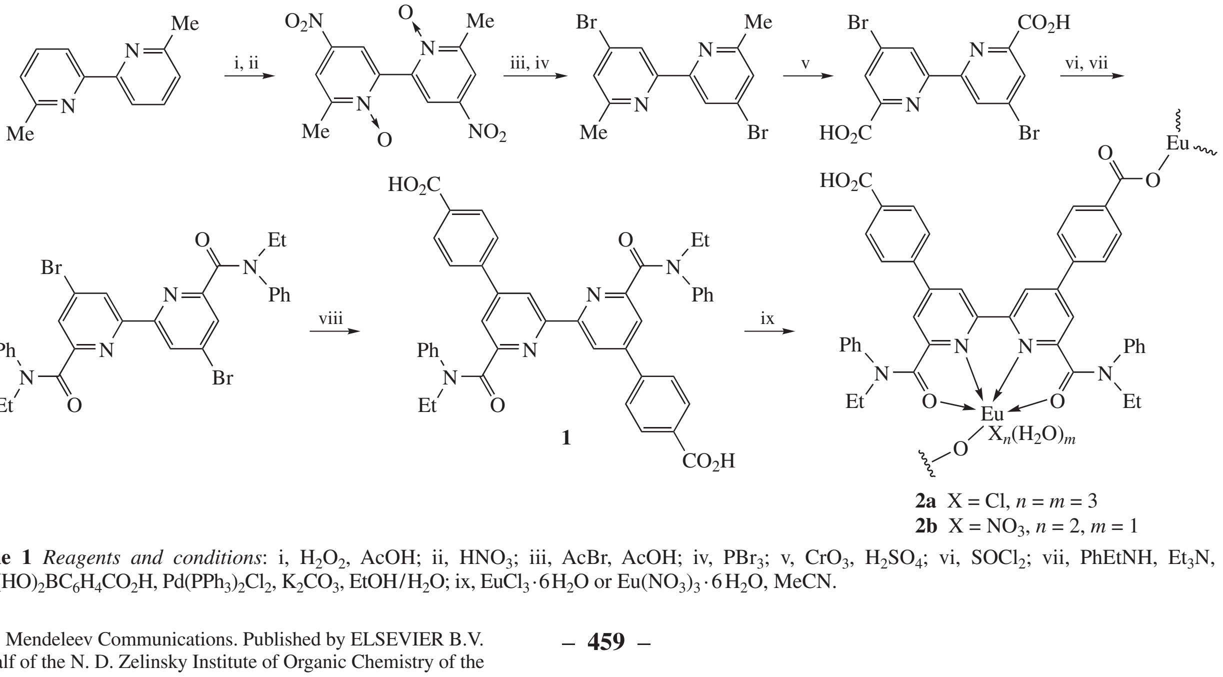
Europium complexes with heterotopic hexadentate ligands based on 2,2′-bipyridyl-6,6′-dicarboxamide exhibit bright long-lived luminescence at 618 nm as well as extremely low solubility ($<1\times10^{-4}$ M) in polar solvents.





Lanthanide luminescence is in focus of interests due to well resolved spectra with sharp emission lines, which finds applications in light emission devices, from lamp phosphors[1] to electroluminescent materials for OLED,[2] or functional bioassay materials.[3] Another application is the lanthanide complexes-doped polymers for solid-state dye lasers.[4] The compounds for potent laser generation should possess high photophysical properties. The fluorescence efficiency of lanthanide complexes is an important parameter, however, the fluorescence yield of the majority of these chelates is relatively low because of deactivation mostly by water molecules and the C–H bond vibrations of ligands and host matrix.[4] Introduction of low molecular weight Lewis bases can substantially increase the emission of lanthanide chelates.[5] Previously, we reported synthesis of bright luminescent complexes of europium and terbium with N,N′,O,O′-tetradentate heterocyclic diamide[6] exhibiting emissions at 618 and 535–555 nm. Incorporation of additional donor centers capable of bonding with lanthanide ion should enhance the luminescence efficiency and reduce deactivation by water molecules or high-frequency C–H vibrations of the ligand by saturation of the coordination vacancies of lanthanide ion. Here we report synthesis and spectral properties of europium complexes with hexadentate ditopic 2,2′-bipyridyl type ligand bearing two peripherial phenyl groups. Introduction of phenyl substituents is supposed to enhance photophysical properties of the complexes and provide rigid arrangement of the additional carboxylic groups, which can improve the relative intensity of the emission peak at 618 nm.

The starting 4,4′-bis(4-carboxyphenyl)-*N*,*N*′-diethyl-*N*,*N*′-diphenyl-2,2′-bipyridyl-6,6′-dicarboxamide **1** was synthesized by the Suzuki reaction from the corresponding 4,4′-dibromo-*N*,*N*′-diethyl-*N*,*N*′-diphenyl-2,2′-bipyridyl-6,6-dicarboxamide[7] using K_2CO_3 (aq.) as the base[8] (Scheme 1). The combination of alcohol–water mixture together with phase transfer catalyst Bu_4NBr allowed us to use simple palladium complex $Pd(PPh_3)_2Cl_2$ as a catalyst.



2a X = Cl, *n* = *m* = 3
2b X = NO_3, *n* = 2, *m* = 1

Scheme 1 *Reagents and conditions*: i, H_2O_2, AcOH; ii, HNO_3; iii, AcBr, AcOH; iv, PBr_3; v, CrO_3, H_2SO_4; vi, $SOCl_2$; vii, PhEtNH, Et_3N, THF; viii, $4\text{-}(HO)_2BC_6H_4CO_2H$, $Pd(PPh_3)_2Cl_2$, K_2CO_3, EtOH/H_2O; ix, $EuCl_3\cdot 6H_2O$ or $Eu(NO_3)_3\cdot 6H_2O$, MeCN.

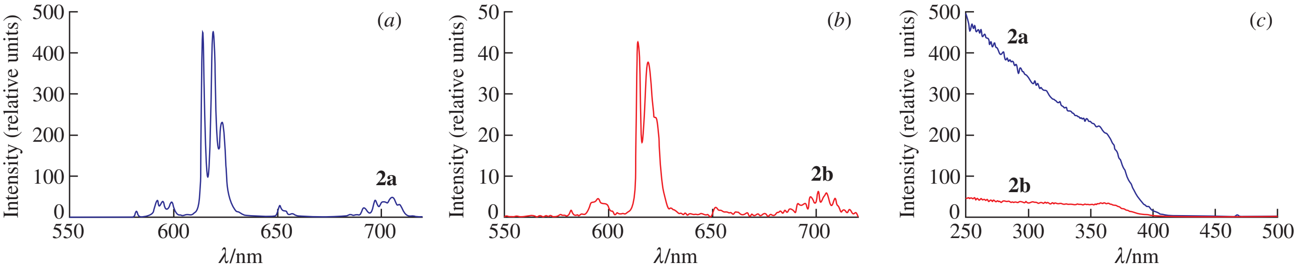


Figure 1 Luminescence (*a*), (*b*) emission (excitation at λ = 320 nm) and (*c*) excitation spectra (emission at λ = 618 nm) for the europium-based coordination polymers **2a** and **2b**.

The target polydentate ligand **1** was obtained in 85% yield[†] as white powder with poor solubility in most of the organic solvents excepting polar ones (DMSO, DMF). Its ^{1}H NMR spectrum shows well resolved signals of aromatic protons only at elevated temperature (55 °C) due to slow intramolecular rotation of aromatic fragments.

The europium complexes **2** with ligand **1** were prepared by the reaction of the latter with either europium chloride or nitrate salts (see Scheme 1).[‡] Complexes **2** are light grey compounds with extremely low solubility even in polar solvents (DMSO or DMF). For this reason, their ^{1}H NMR spectra in DMSO-d_6 solutions were recorded at 60 °C.

The coordination of the europium atom seems to occur both on bipyridine moiety and carboxylic group of the ligand. The strong upfield shift of the CH-protons of benzoic acid moieties observed for both complexes **2** testifies to the coordination of carboxylic group to the Eu atom. Moreover, the spectra reveal significant broadening of the signals due to the effect of europium ion. The determined composition of the complexes evidences the water molecules coordination to the metal ion or hydrogen bonding with the carboxylic groups.

The nature of water molecules bonding in the complexes can be elucidated by measurements of their luminescence.[§] In the lanthanide coordination complexes, the luminescence of the metal ion can be efficiently quenched by water molecules coordination. Luminescence spectra of the complexes under study showed typical europium emission lines in the red region corresponding to transitions $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_J$ (J = 0, 1, 2, 3, 4) (Figure 1). The main europium luminescence band ($^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$) was splitted into three components for both complexes: 614 (the most intense), 619 and 623.5 nm. The spectra differed only in intensity (**2a** >> **2b**) and the ratios of these resolved components. The luminescence lifetimes, the internal quantum efficiency and the ratio between the integral intensities of the band located at 614–624 and that at 595 nm (9.4 for **2a** and 8.7 for **2b**) did not differ markedly.[6,9]

Luminescence kinetics for both compounds deviated from monoexponential decay is typical of coordination compounds in solutions. The experimental data showed that at room temperature luminescence kinetics consist of two components: fast (before 1 ms) and slow (after 1.5 ms) (Figure 2). We approximated the experimental decays with two exponents. This luminescence decay behaviour corroborates with the theory of energy migration in heterogeneous environment of solid solutions of organic compounds. The initial part of the decay kinetics was analyzed within existing triplet-triplet annihilation models.[10] The best

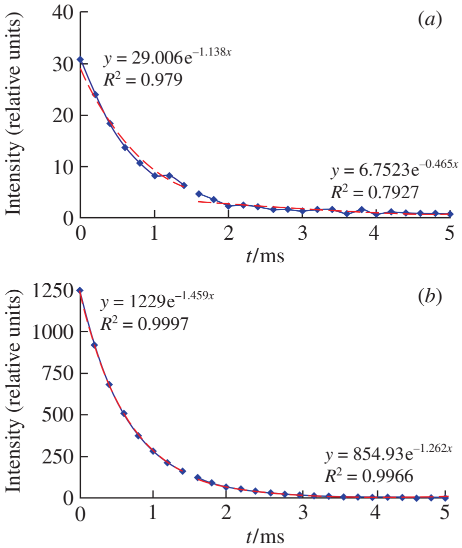


Figure 2 Luminescence kinetics in millisecond range for the europium-based complexes (*a*) **2a** and (*b*) **2b**. Excitation wavelength 320 nm.

[†] *4,4′-Bis(4-carboxyphenyl)-*N,N′*-diethyl-*N,N′*-diphenyl-2,2′-bipyridyl-6,6-dicarboxamide* **1**. 4,4′-Dibromo-*N*,*N*′-diethyl-*N*,*N*′-diphenyl-2,2′-bipyridyl-6,6-dicarboxamide (7.0 g, 11.5 mmol), 4-carboxyphenylboronic acid (6.0 g, 36 mmol), K_2CO_3 (30 g), $PdCl_2(PPh_3)_2$ (400 mg, 5 mol%) and Bu_4NBr (1.6 g, 40 mol%) were refluxed in EtOH (80 ml)/H_2O (30 ml) mixture for 4 h. After that, the reaction mixture was poured into water (200 ml) acidified to pH 2 with HCl and filtered. The solvent was removed and the dark residue was dissolved in 400 ml of CH_2Cl_2–MeOH (2 : 1) mixture. The resulting solution was passed through celite to give 10.65 g of crude product. The brown powder was dissolved under reflux in 400 ml of Pr^{i}OH–DCM–MeOH (1 : 2 : 1) mixture. After cooling, the sludge-like precipitate was filtered off and discarded, and the volume of the filtrate was reduced by boiling at 78 °C to 60 ml. Its cooling to room temperature gave 4.42 g of pure product. The standing overnight afforded additional crop (2.35 g) of pure **1**. Yield 6.77 g (85%). ^{1}H NMR (600.1 MHz, DMSO-d_6, 55 °C) δ: 1.21 (t, 3H, *J* 7.02 Hz), 3.98 (q, 2H, *J* 7.03 Hz), 7.02 (t, 1H, *J* 7.11 Hz), 7.15 (t, 2H, *J* 7.34 Hz), 7.18–7.31 (m, 3H), 7.85 (d, 2H, *J* 7.89 Hz), 7.97 (br. s, 1H), 8.19 (d, 2H, *J* 7.61 Hz). ^{13}C NMR (100.6 MHz, DMSO-d_6, 55 °C) δ: 166.57, 166.39, 154.19, 153.40, 147.77, 142.52, 140.34, 131.70, 129.86, 128.49, 127.24, 126.93, 126.14, 121.84, 118.13, 44.30, 12.38. MS (MALDI-TOF), *m*/*z*: 729 $[M+K]^+$, 691 $[M+H]^+$.

[‡] *Complexes of 4,4′-bis(4-carboxyphenyl)-*N,N′*-diethyl-*N,N′*-diphenyl 2,2′-bipyridyl-6,6-dicarboxamide with Eu* **2**. Ligand **1** (0.691 g, 1 mmol) was suspended in refluxing acetonitrile (120 ml). The corresponding europium salt hydrate $EuCl_3 \cdot 6H_2O$ or $Eu(NO_3)_3 \cdot 6H_2O$ (1 mmol) was carefully added to the boiling suspension. The reaction mixture was refluxed for 6 h. The solid ligand dissolved during the reflux and a new precipitate formed. After cooling to room temperature, the pale brownish solid was filtered off, washed with hot acetonitrile and air dried.

For **2a**: yield 0.70 g (70%). ^{1}H NMR (400 MHz, DMSO-d_6, 60 °C) δ: 1.56 (t, 3H, *J* 7.34 Hz), 3.96 (q, 2H, *J* 6.36 Hz), 6.83 (d, 2H, *J* 8.07 Hz), 7.01 (t, 1H, *J* 6.97 Hz), 7.14 (t, 2H, *J* 5.87 Hz), 7.18–7.32 (m, 3H), 7.79 (d, 4H, *J* 8.19 Hz), 8.04 (s, 1H), 8.06 (s, 1H). Found (%): C, 50.12; H, 3.60; N, 5.75. Calc. for $C_{42}H_{40}Cl_3EuN_4O_9$ (%): C, 50.29; H, 4.02; N, 5.59.

For **2b**: yield 0.827 g (84%). ^{1}H NMR (400 MHz, DMSO-d_6, 60 °C) δ: 1.12 (t, 3H, *J* 6.60 Hz), 3.89 (q, 2H, *J* 6.48 Hz), 6.92 (t, 1H, *J* 5.99 Hz), 6.96–7.08 (m, 3H) 7.08–7.25 (m, 3H), 7.38 (br. s, 2H), 7.66 (br. s, 1H), 7.78 (br. s, 1H). Found (%): C, 51.30; H, 3.58; N, 8.63. Calc. for $C_{42}H_{36}EuN_6O_{13}$ (%): C, 51.23; H, 3.68; N, 8.53.

[§] The photoluminescence emission and excitation spectra were collected in the solid state at room temperature using a Hitachi 7000 luminescence spectrometer with a spectral slitwidth of 1 nm.

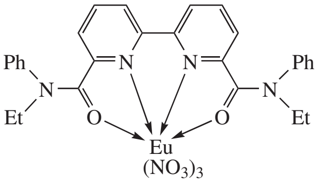
Table 1 The luminescence characteristics for complexes **2** and **3**.

Compound	$I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$	$I_{total}/I(^5D_0 \rightarrow {}^7F_1)$	τ_{obs}/ms	τ_R/ms	Φ_{Eu} (%)	$I(^5D_0 \rightarrow {}^7F_2)/I_{total}$[a]
2a	8.7	12.1	0.77	1.51	51	0.71
2b	7.8	12.0	0.67	1.53	43	0.48
3	5.3	7.8	1.24	2.34	53	0.67

[a] Relative intensity of the $^5D_0 \rightarrow {}^7F_2$ transition.

possible agreement can be achieved only in a static model implying inhomogeneous distribution of the triplet molecules in the matrix. The lifetime values are given in Table 1. The lifetimes are covered by typical values for the europium complexes which contain no water molecules directly coordinated by metal ion.[11] So we can expect that both of compounds hold water by intermolecular interactions rather than by coordination with metal ion.

The efficiency of excitation transfer from a light-absorbing chromophore to the europium ion is characterized by internal quantum yield Φ_{Ln}.[12] The calculation of Φ_{Ln} can be useful for the optimization of the organic chromophore structure, as it specifies the efficiency of the individual steps leading to the photosensitized luminescence of lanthanide complexes. Starting from the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition in a vacuum[12] and the ratio of the total area of the Eu emission spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ band (I_{total}/I_{MD}), we calculated the radiative lifetimes τ_R for complexes **2a** and **2b** (see Table 1). The photophysical properties of the complexes of type **2** were compared with those for complex **3**[6] lacking phenyl substituents in pyridine moieties.



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The internal quantum yields are close to each other for all studied complexes, which confirms that the main excitation transfer proceeds from organic ligand and that the nature of counter-ion does not affect this process significantly. The quantum yield value also supports a high degree of energy transfer since the closely related 2,2′-bipyridyl-6,6′-dicarboxylate and phenanthroline complexes show fivefold lower energy utilization effectiveness.[9] However, luminescence intensity for complexes **2a**,**b** is higher than that of complex **3**, and the ratio between intensities of the main band located at 614–624 nm the minor one at 595 nm is also higher. Therefore, insertion of additional phenyl rings into the bipyridyl system induces the asymmetry of the metal ion coordination and thus enhances the relative intensity of $^5D_0 \rightarrow {}^7F_2$ transition for complex **2a**. The latter is crucial for laser generation applications.

In conclusion, two new europium-based complexes presumably polymeric by nature have been synthesized in high yields. Excitation spectra, luminescence lifetimes and internal luminescence yields were similar for both compounds, which confirms the proposed coordination mode. The strong luminescence at 614–624 nm was observed. The relative intensity of these peaks is tenfold greater than that of 595 nm band, which makes it possible to consider this new type of europium complexes with hexadentate polytopic ligand as a good candidate for laser generation applications.

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