Polyhedron 118 (2016) 30-36

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Novel neutral lanthanide complexes of 5-aryl-2,2'-bipyridine-6'-carboxylic acids with improved photophysical properties



Dmitry S. Kopchuk^{a,b,*}, Alexey P. Krinochkin^a, Dmitry N. Kozhevnikov^{a,b}, Pavel A. Slepukhin^{a,b}

^a Ural Federal University, 19, Mira St., 620002 Yekaterinburg, Russian Federation
^b Postovsky Institute of Organic Synthesis of RAS (Ural Division), 22/20, S. Kovalevskoy/Akademicheskaya St., 620990 Yekaterinburg, Russian Federation

ARTICLE INFO

Article history: Received 17 May 2016 Accepted 20 July 2016 Available online 30 July 2016

Keywords: 5-Aryl-2,2'-bipyridine-6'-carboxylic acids Luminescence Lanthanide complexes aza-Diels-Alder reaction 1,2,4-Triazine

ABSTRACT

By means of "1,2,4-triazine" strategy new 2,2'-bipyridine-type lanthanide ligands, i.e. 5-aryl-2,2'-bipyridine-6'-carboxylic acids and its cycloalkane-annulated derivatives, i.e. 6-(4-aryl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl)picolinic acids, have been synthesized, and their luminescent neutral lanthanide complexes have been prepared. Due to the presence of an annulated cyclopentene fragment the last ligand lanthanide complexes exhibited high solubility in non-polar solvents. In comparison with early published chelates the herein reported complexes exhibit improved photophysical properties in nonpolar solvents namely more pronounced bathochromic shift in absorption spectra and higher europium luminescence quantum yields. The structures of two europium complexes have been confirmed based on X-ray diffraction analysis.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The creation of electroluminescent materials [1] is one of the important uses of neutral luminescent lanthanide complexes. In order to provide the high luminescence intensity of the resulted lanthanide complex the first coordination sphere of the lanthanide cation needs to be fully saturated [2]. In addition, these complexes should be stable, able to sublime in vacuum or to be soluble in non-polar solvents for the aim of doping semiconductive polymers.

Diketonate-based lanthanide complexes [3] are the most commonly used for the creation of electroluminescent materials. However, the complexes of such ligands have a number of drawbacks; in particular, they may suffer from a poor photostability upon UV irradiation [4]. Also in this aspect such ligands as 2,2'-bipyridine-6-carboxylic acid derivatives [5,6] as well as their aza-analogs [7] should be mentioned. Their neutral lanthanide complexes [Ln (L)₃] (L = 2,2'-bipyridine-6-carboxylate) with high quantum efficiency of a lanthanide luminescence are potentially useful as components for OLEDs. However, according to the literature, in most cases such complexes have low solubility in organic solvents, which complicates their practical use. Recently, we have demonstrated the possibility for the significant increasing of the solubility of these chelates by means of the cyclopentene moiety annulation to one of the pyridine rings (the general formula of these ligands is shown in Fig. 1, structure **A**) [8]. Such a possibility has been achieved through the use of so-called "1,2,4-triazine" synthetic approach towards the oligopyridine ligands [9], and the cycloalkane ring annulation to the pyridine ligand can be easily carried out by means of aza-Diels–Alder reaction with 1-morpholinocyclopentene as a dienophile. Thus obtained neutral europium complexes exhibited the luminescence lifetime values up to 1.1 ms and the quantum yield of luminescence of europium cation up to 11%, which can be considered as a moderate result.

It should be noted that these complexes demonstrated absorption maxima in short wavelengths, i.e. in a range of 295–309 nm, which may be attributed to the possible hampering of the conjugation between the aromatic substituent (β -position) and the bipyridine moiety due to the steric hindrances caused by the presence of the carboxyl group in an α -position of pyridine ring. As a result the aromatic substituent is not coplanar towards 2,2'-bipyridine moiety. We have assumed that by the transfer of the carboxyl group from one pyridine ring to another within the 2,2'-bypyridine moiety will possibly increase the conjugation and thus improves the photophysical properties of the resulting complexes. In this work, we are pleased to report the approach towards 5-aryl-2,2'-bipyridine-6'-carboxylic acids as a new ligands for luminescent neutral lanthanide complexes and results of our studies of the photophysical properties for these complexes.



Corresponding author at: Ural Federal University, 19, Mira St., 620002
 Yekaterinburg, Russian Federation. Fax: +7 343 374 0458.
 E-mail address: dkopchuk@mail.ru (D.S. Kopchuk).



Fig. 1. The structure of the previously described ligands for neutral lanthanide complexes (**A**) and the structure of the ligands reported in this paper (**B**).

2. Experimental

All reagents were purchased from commercial sources and used without further purification. NMR spectra were recorded on a Bruker Avance-400 spectrometer, 298 K, digital resolution ±0.01 ppm, using TMS as internal standard for ¹H and ¹³C NMR or CFCl₃ for ¹⁹F NMR. Infrared spectra were measured on a Bruker Alpha FTIR spectrometer with an ATR accessory (ZnSe). UV–Vis spectra were recorded on Lambda 45 spectrophotometer (Perkin Elmer). Luminescence spectra were recorded on a Cary Eclipse spectrofluorometer (Varian). Mass spectra were recorded on a MicrOTOF-Q II mass spectrometer (Bruker Daltonics) with electrospray ionization. Elemental analysis were performed on a PE 2400 II CHN-analyzer (Perkin Elmer). Hydrazones of isonitrosoacetophenones 1 [12], 6-metoxycarbonylpyridine-2-carbaldehyde [13], 3-(6-metoxycarbonyl-2-pyridyl)-6-(4-methoxyphenyl)-1,2,4-triazine **2c** [11] were synthesized as described in literature.

2.1. General method for the synthesis of triazines 2

The corresponding hydrazone **1** (15 mmol) was solved in ethanol (30 ml) and solution of the 6-metoxycarbonylpyridine-2-carbaldehyde (2.48 g, 15 mmol) in ethanol (25 ml) was added. The resulting mixture was kept at room temperature for 12 h. The precipitate was filtered off, washed with ethanol and dried. Then the obtained intermediate was suspended in acetic acid (50 ml) and mixture was heated to reflux two times. Solvent was removed under reduced pressure. Ethanol (30 ml) was added to the residue; the resulting crystals of **2** were filtered off, washed with ethanol and dried. The next step without addition purification.

2.2. General method for synthesis of bipyridines 3b,d

The corresponding triazine **2** (5 mmol) was suspended in *o*-xylene (25 ml), 2,5-norbornadiene (0.46 ml, 4.5 mmol) was added and the resulting mixture was refluxed for 19 h with addition of 2,5-norbornadiene (0.46 ml, 4.5 mmol) every 7 h. Solvent was removed under reduced pressure. The product was isolated by column chromatography (chloroform, R_f = 0.25). Solvent from containing product fractions was removed under reduced pressure. The residue was recrystallized from ethanol.

2.3. General method for synthesis of bipyridines 4

Corresponding triazine **2** (3 mmol) was suspended in *o*-xylene (35 ml), 1-morpholinocyclopentene (0.96 ml, 6 mmol) was added and the resulting mixture was refluxed for 2 h. Then addition portion of 1-morpholinocyclopentene (0.48 ml, 3 mmol) was added and mixture was refluxed for 1 h. Solvent was removed under reduced pressure, the product was isolated by column chromatography (chloroform, R_f = 0.25). Solvent from containing product

fractions was removed under reduced pressure. The residue was recrystallized from ethanol.

2.4. General method for synthesis of acids 6, 7

The corresponding ester **3** or **4** (1.5 mmol) and NaOH (0.12 g, 3 mmol) were suspended in ethanol (60 ml) and the resulting mixture was refluxed for 30 min and then kept at room temperature for 3 h. Ethanol (40 ml) was removed under reduced pressure, hydrochloric acid (5 N) was added to adjust pH = 2. The precipitate was filtered off, washed with ethanol and water, dried in vacuum.

2.5. General method for synthesis of lanthanide complexes

Corresponding acid **6** or **7** (0.35 mmol) was suspended in methanol (40 ml), sodium hydroxide (14 mg, 0.35 mmol) was added and the resulting mixture was refluxed until clear solution was obtained. Then mixture was cooled to room temperature and chloride of corresponding lanthanide (0.117 mmol) was added. Mixture was kept at room temperature for 2 h. Solvent was removed under reduced pressure; water (20 ml) was added to the residue. The precipitate was filtered off, washed with water, dried in vacuum and solved in mixture methanol–DCM (1:1, 30 ml). Unsolved part was filtered off, solvents were removed under reduced pressure. The product was dried in vacuum.

3. Results and discussion

It is obvious that for achievement of the proposed synthetic goal the same '1,2,4-triazine' synthetic methodology can be used. In order to improve the solubility of the resulting lanthanide complexes the introduction of fused cyclopentene fragment into bipyridine ligand has been proposed. The choice of 5-aryl-2,2'bipyridine-6'-carboxylic acids as target ligands (Fig. 1, structure **B**) has been made based on their synthetic accessibility. Apart from that the introduction of an additional aromatic substituent in the β -position of the adjacent pyridine ring will not cause significant steric hindrances for the coordination of the lanthanide cation.

The key precursors for the synthesis of the target ligands are 6aryl-3-(2-pyridyl)-1,2,4-triazines substituted at the 6-position of the pyridine ring with any functional group which can be further transformed into carboxylic group. Based on the analysis of published data on possible methods for the synthesis of 6-aryl-3-(6-R-2-pyridyl)-1,2,4-triazines, for instance substituted at the position 6' by hydroxymethyl [10], methyl [11], or ester [11] group we have selected 6'-ester-substituted 1,2,4-triazines in a view of the lower complexity of the synthesis (Scheme 1, compound **C**).

For the synthesis of 1,2,4-triazine precursors **C** of target ligands **B** two methods are possible (Scheme 1). In particular, according to our previously reported method [10] in first path cyclization between isonitrosoacetophenones hydrazones **D** [12] and 6-methoxycarbonylpyridine-2-carbaldehyde **E** can be used. The 6-methoxycarbonylpyridine-2-carbaldehyde **E** can be prepared as described early [13]. In the second approach the reaction of 2-bromoacetophenone **G** with two equivalents of hydrazide of 6-methoxycarbonylpyridine-2-carboxylic acid **F** [14] can be used according to a procedure described by Saraswathi and Srinivasan in 1971 [15]. Obviously, the first approach seems to be more efficient, since it does not involve the significant consumption of less synthetically accessible mono-hydrazide **F**.

For the synthesis of 1,2,4-triazines **C** we have followed our previously reported method for the preparation of 3-(6-methoxycarbonylpyridin-2-yl)-6-(3-nitrophenyl)-1,2,4-triazine [11]. Thus, according to the described procedure 1,2,4-triazine precursors **2a**, **b,d,e** (Scheme 2) have been obtained starting from hydrazones



Scheme 1. Retrosynthetic analysis for the synthesis of necessary ligands.



Scheme 2. Synthesis of neutral lanthanide complexes of ligands 6 and 7. Reagents and conditions: (*i*) 6-methoxycarbonylpyridin-2-carbaldehyde, 10 h, 20 °C, then AcOH, 118 °C, 5 min; (*ii*) 6-methoxycarbonylpyridin-2-carboxylic acid hydrazide (2 equiv.), AcONa, ethanol–AcOH (4:1), 50 °C, 15 h; (*iii*) 2,5-norbornadiene, *o*-xylene, 143 °C, 19 h; (*iv*) 1-morpholinocyclopentene, *o*-xylene, 143 °C, 3 h; (*v*) NaOH, ethanol, 78 °C, 1 h, then HCl, 20 °C; (*vi*) NaOH (1 equiv.), methanol, 65 °C, 5 min, then EuCl₃*6H₂O (0.33 equiv.), 20 °C.

1a,b,d,e. The resulting 1,2,4-triazines were pure enough and they were immediately subjected to an aza-Diels–Alder reaction with 1-morpholinocyclopentene or 2,5-norbornadiene. The resulted 2,2'-bipyridines **3** and **4** can be isolated very easily in pure form by column chromatography. It is noteworthy to mention that in case of 1,2,4-triazine **2c** this approach failed. Therefore, for the synthesis of 1,2,4-triazine **2c** the second approach was successfully used [11] starting from 2-bromo-4'-methoxyacetophenone **5c**. Subsequent alkaline hydrolysis of esters **3** and **4** afforded the free acids **6** and **7**.

As a final step 2,2'-bipyridine carboxylic acids **6** and **7** were subjected to react with $LnCl_3*6H_2O$ in the presence of a base to afford **Eu**·**6** and **Ln*7** complexes, whose metal-to-ligand ratio is the same as in the complexes published earlier by us [8]. According to the analytical data each complex contains one lanthanide cation coordinated to three ligand molecules (in a carboxylate form), i.e. the resulting complexes are neutral.

Table 1 contains a photophysical data for the complexes **Eu**·**6** and **Ln*7**. Compared to the earlier published complexes [8] the absorption maxima for these complexes are shifted towards longer wavelengths (313–330 nm), thus indicating the lower values of the energy of π - π *-transitions. The reducing of energy of π - π *-transitions is a consequence of the improved conjugation between the

aromatic substituent and the bipyridine core since the carboxyl group does not impede the coplanar arrangement of the aromatic substituent towards bipyridine moiety. However, in the case of complexes of cyclopentene-annelated bipyridine acids **Ln*7** values of the bathochromic shift of the absorption maxima are smaller. Europium cation luminescence spectra of complexes **Eu-6** and **Eu*7** contain narrow emission lines at 592, 616 and 695 nm, which are common for the europium complexes (Figs. 2 and 3).

The europium cation luminescence quantum yields of complexes **Eu**·**6** and **Eu*****7** (up to 28%) and europium luminescence lifetime (up to 1.5 ms) are generally higher of those for earlier published complexes [8] (Table 1). As it was expected based on the previously obtained data, the complexes **Eu**·**6** showed very low solubility in non-polar solvents, and this makes them less preferred from the viewpoint of practical use. With regards to the complexes **Eu*****7**, the annulation of cyclopentene fragment resulted in the significant increase in their solubility (up to 10 g/L in CH₂Cl₂). However, the annulation of aliphatic cycle resulted in a lowering of europium cation luminescence quantum yield for the complexes **Eu*****7** compared to **Eu**·**6** while maintaining the same characteristics of the emission spectra (Table 1, Fig. 3). Apart from, the luminescence lifetime and quantum yield for the complexes **Eu**·**7** are lower than that of the same properties

Table 1 Photophysical properties of lanthanide complexes of ligands 6 and 7.

Ligand structure	Ar	Complex	Absorption, λ_{max} , nm (ϵ , 10 ⁻³ M ⁻¹ cm ⁻¹) ^a	${\it \Phi}^{{\sf b}}$	τ ^c , ms
Ar N COOH	Ph	Eu*7a	313 (50.7)	0.095	1.5
	Tol	Eu*7b	322 (40.4)	0.013	1.5
	4-MeOC ₆ H ₄	Eu*7c	321 (44.4)	0.12	1.3
	4-BrC ₆ H ₄	Eu*7e	320 (32.7)	0.28	1.1
	$4-FC_6H_4$	Eu*7d	275 (28.9), 318 (45.6)	0.15	1.5
	$4-FC_6H_4$	Tb*7d	257 (18.4), 279 (19.3), 321 (34.7)	-	
Ar N COOH	Ph	Eu 6a	280, 328 [*]	0.26	0.9
	Tol	Eu 6b	282, 330 [*]	0.15	1.1
	$4-FC_6H_4$	Eu 6d	280, 324 [*]	0.23	1.2

^a In a solution of CH₂Cl₂ at room temperature.

^b Europium cation luminescence quantum yield in CH₂Cl₂ solution were determined using optically matching solutions of [Ru(bpy)₃]Cl₂ [16].

^c Europium cation luminescence lifetime.

* Due to the low solubility the extinction coefficient could not be measured.



Fig. 2. The absorption (a) and europium cation luminescence (b) spectra of europium complexes Eu·6 (Eu·6a – black lines; Eu·6b – red lines; Eu·6d – blue lines) in CH₂Cl₂ solution at room temperature. (Color online).



Fig. 3. The absorption (a) and europium cation luminescence (b) spectra of europium complexes Eu*7 (Eu*7a – black lines; Eu*7b – red lines; Eu*7c – blue lines; Eu*7d – green lines; Eu*7e – dark yellow lines) in CH₂Cl₂ solution at room temperature. (Color online.)

previously reported for some of known lanthanide complexes, for instance reported in a source [6] luminescence lifetime up to 2.81 ms and the quantum yield of up to 85%.

In addition, for a number of complexes **Eu***7 besides the europium cation luminescence (lifetime up to 1.5 ms) the own

fluorescence of aryl-2,2'-bipyridine moiety with a much more shorter wavelength emission maximum (350–450 nm) is observed. The comparison of the intensity of fluorescence (due to the emission from S1 state localized on the ligand) and europium cation emission demonstrates the influence of the nature of aryl substituents on the efficiency of the ligand-to-metal energy transfer. The maximum share of the fluorescence in the total luminescence quantum yield was observed for the complex **Eu***7c bearing 4-methoxyphenyl-2,2'-bipyridine moiety. Thus, introduction of the electron-donating substituents into the ligand core complicates the energy transfer. Apparently, this is due to the significant reduction of the energies of S1 and T1 levels of the ligand in respect to the 5D_0 state of the chelated europium cation, which makes energy transition between T1 and 5D_0 states to be less favorable. The introducing of halogen atoms (fluorine or bromine, complexes **Eu*7d** and **Eu*7e**) into the aromatic substituent of the 2,2'-bipyridine ligand resulted in the most effective energy transfer: the almost complete quenching of fluorescence with the increasing of the europium cation luminescence quantum yield were observed.

Unfortunately, no terbium cation luminescence was observed for the complex **Tb*****7d**. Apparently, an increase of the degree of conjugation of the ligand reduces its energy of the excited states, which greatly complicates the energy transfer to the higher energetic ⁵D₄ level of terbium cation, and, thus, the sensitisation of its luminescence. In the europium complexes the ligand-to-metal energy transfer takes place on the ⁵D₀ level, which is much lower in energy, therefore the sensitisation of europium cation luminescence is observed.

It should be noted that in case of using 5-aryl-2,2'-bipyridine-6carboxylic acid as a ligand, we observed a very faint luminescence



Fig. 4. Europium cation luminescence emission spectrum of the Eu*7d complex recorded in a frozen glass of MTHF-DCM at 77 K.

of terbium cation [8] which is probably due to the less pronounced conjugation between 2,2'-bipyridine moiety and the aromatic substituent and, consequently, higher excited state energy of the ligand.

Besides the europium cation luminescence in solutions the similar emission in crystalline form of the Eu^{III} complexes is possible. Except the absence of short-wavelength bands of fluorescence these spectra do not differ from the ones recorded in a solution. In a temperature range of 77–300 K no temperature dependence of phosphorescence spectra is also observed. In particular, highly resolved europium cation luminescence spectra were recorded in organic solvents glasses, i.e. a mixture of dichloromethane and methyltetrahydrofuran (MTHF-DCM) at the temperature of 77 K. Fig. 4 shows one of such europium cation emission spectra recorded for the complex **Eu*7d**.

The structures of the complexes were confirmed by elemental analysis, mass spectrometry (ES-MS), and IR spectroscopy. The obtaining data correlate with ones for the previously described by us complexes of 5-aryl-2,2'-bipyridine-6-carboxylic acids [8]. For the more detailed study the X-ray analysis has been performed for the complexes **Eu*7b** and **Eu*7d**.

According to the X-ray data (Figs. 5 and 6), in both cases the central metal atom coordinates with three anions of bipyridine carboxylic acid, i.e. Eu^{III} coordination number in these complexes is 9. These data clearly confirm the absence of solvent molecules in the coordination sphere of the Eu cation.

In both cases the aromatic substituent is significantly twisted out of the plane of the associated pyridine ring (the values of torsion angles are in the range of 36.29–47.95°). The bond lengths between the europium atom and the pyridine nitrogen atom are in the range of 2.52–2.72 Å, with oxygen atoms in the range of 2.3–2.4 Å.

The neutral complex Eu*7d is crystallized as solvate with methanol (1:3). The molecules of the MeOH are fixed in the crystal packing by intermolecular H-bonds with O-atoms of the carboxylic moiety of the ligands (distances are in the range 1.97-2.07 Å, see Fig. S1, Supporting information). In the crystal packing there are the hydrogen bonds between fluorine atoms and hydrogens of cyclopentene moiety, distances between them are 2.5 Å (Fig. S2. Supporting information). Ligand molecules are packed in stacks (Fig. 5b), which is explained by the presence of intra- and intermolecular π - π -interactions. This is supported by an almost coplanar arrangement of the pyridine rings of the interacting ligands of complex (Fig. 5a, the value of the angle between the planes of rings is 26°), and the short distance between these rings, i.e. 2.9–4.0 Å. Moderate intermolecular π - π -interactions are supported in the same way: in this case the distance is 3.7 Å. As a result, there is a significant deviation from the coplanar arrangement of two out





Fig. 6. (a) The molecular structure of the complex Eu*7b and (b) the arrangement of the molecules of the complex Eu*7b in the crystal according to X-ray data (solvent molecules and hydrogen atoms are omitted for clarity).



Fig. 7. The coordination polyhedra of the complexes Eu*7d (a) and Eu*7b (b) according to the X-ray data.

of three of bipyridine fragments of europium complex (the values of torsion angles are 12° and 27°), which is non-typical for the bipyridine chelates. It is worthy to mention that the similar effect has been described previously for neutral lanthanide complexes of ligands bearing the extended aromatic system such as 6-benzimi-dazolylpyridine-2-carboxylic acids [17] or 2-benzimidazolyl-8-hydroxyquinolines [18].

The complex **Eu***7**b** is crystallized as (aqueous) solvated with methanol, in which, as well as for compound **Eu***7**d**, MeOH is fixed in the crystal packing by intermolecular H-bonds with O-atoms of the carboxylic moiety of the ligands. The molecules of the complex **Eu***7**b** are ordered in a crystal in one-dimensional structure due to intermolecular π - π -interactions between the aromatic substituents (this is confirmed by their coplanar arrangement, as well as the closest distance between them of 3.36 Å), and the pyridine rings of the ligands (the distance between them is 3.4–4.0 Å) (Fig. 6b). In this case the intramolecular π - π -interactions were not observed.

For the both complexes the europium cation with three bipyridyl ligands forms 6 five-membered chelated cycles (Fig. 7), with formation of the distorted trigonal antiprismatic coordination polyhedron.

Thus, according to the obtained XRD results, the introduction of the aromatic substituents in the 5'-position of 2,2'-bipyridine-6-carboxylic acids increases the intra- and intermolecular π - π -interactions between the ligand molecules and thereby controls the

self-organization of europium complexes molecules in the crystalline phase. It should be noted that the presence of more efficient intermolecular π - π -interaction can facilitate energy transfer from the conjugated polymer to dye, which is important for creating a device based [19].

4. Conclusions

In summary, based on previously published results [8] we optimized the synthetic approach to 5-aryl-2,2'-bipyridine-6(6')-carboxylic acids as ligands for lanthanide cations. In general, the proposed synthetic approach allows to vary the structure of the ligand and, therefore, to tune the desired properties of the complex by the variation of three factors: the nature of the aromatic substituent, the position of the carboxyl group and the presence of annulated aliphatic carbocycle.

It was found that the novel ligands are not suitable for sensitisation of terbium cation luminescence in contrast to europium. The europium complexes based on the ligands having a fused cyclopentene fragment, are more promising in view of their better solubility in non-polar solvents (up to 10 g/L in CH₂Cl₂). Europium complexes of 6-(4-aryl-6,7-dihydro-5*H*-cyclopenta[*c*]pyridin-1-yl) picolinic acids, reported in a current manuscript, are more interesting in comparison with chelates of 4-aryl-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenta[*c*]pyridine-3-carboxylic acids reported earlier by us [8] due to their longer absorption wavelengths maxima, i.e. more less energy for their excitation, as well as their higher europium cation luminescence efficiency. It should be mentioned that introducing of halogen atoms, such as fluorine or bromine, in the aromatic substituent of the 2,2'-bipyridine core resulted in the almost complete quenching of the ligand fluorescence. Despite of the lower efficiency of europium cation luminescence of new complexes (quantum yield up to 28% and luminescence lifetime up to 1.5 ms) compare to the described earlier chelates, the substantially higher solubility in non-polar solvents of first ones will determine the practical interest to them.

The XRD studies of two complexes exhibited the presence of intra- and intermolecular π - π -interaction, enhanced by the introduction of aromatic substituents in the ligand. This observation could be important from the viewpoint of practical use of such chelates.

Acknowledgment

This work was supported by the Russian Scientific Fund (Grant # 15-13-10033).

Appendix A. Supplementary data

CCDC 1454214 and 1454215 contains the supplementary crystallographic data for complexes **Eu*7d** and **Eu*7b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data (the experimental data for all new compounds and complexes, the detailed description of ¹H, ¹³C and ¹⁹F NMR spectra for all new compounds, the pictures of ¹H, ¹³C and ¹⁹F NMR spectra for all new compounds, the IR data for the new complexes and additional figures) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. poly.2016.07.025.

References

- (a) Highly Efficient OLEDs with Phosphorescent Materials, in: H. Yersin (Ed.), Progress in Electroluminescence Based on Lanthanide Complexes, Wiley-VCH, 2008, p. 391. Ch. 12;
- (b) H. Xu, R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang, X. Liu, Chem. Soc. Rev. 43 (2014) 3259.
- [2] L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, Coord. Chem. Rev. 254 (2010) 487.
- [3] (a) N. Thejo-Kalyani, S.J. Dhoble, Renew. Sustain. Energy Rev. 16 (2012) 2696;
 (b) J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357;
 (c) A de Bettencourt-Dias Dalton Trans (2007) 2229
- [4] (a) K. Binnemans, in: Handbook on the Physics and Chemistry of Rare Earths, 35, Elsevier, Amsterdam, 2005, p. 107;
- (b) K. Binnemans, Chem. Rev. 109 (2009) 4283.
- [5] (a) S. Comby, D. Imbert, A.-S. Chauvin, J.-C.G. Bünzli, L.J. Charbonnière, R.F. Ziessel, Inorg. Chem. 43 (2004) 7369;
 (b) G.S. Kottas, M. Mehlstäubl, R. Fröhlich, L. De Cola, Eur. J. Inorg. Chem. (2007) 3465
- [6] M.B.S. Botelho, M.D. Gálvez-López, L. De Cola, R.Q. Albuquerque, A.S.S. de Camarro, Eur. L. Loorg, Chem. (2013) 5064.
- Camargo, Eur. J. Inorg. Chem. (2013) 5064. [7] (a) N.M. Shavaleev, S.V. Eliseeva, R. Scopelliti, J.-C.G. Bünzli, Inorg. Chem. 49 (2010) 3927;
- (b) N.M. Shavaleev, S.V. Eliseeva, R. Scopelliti, J.-C.G. Bünzli, Inorg. Chem. 54 (2015) 9166.
- [8] A.P. Krinochkin, D.S. Kopchuk, D.N. Kozhevnikov, Polyhedron 102 (2015) 556.
 [9] (a) R.A.A. Foster, M.C. Willis, Chem. Soc. Rev. 42 (2013) 63;
 - (b) A. Rykowski, D. Branowska, J. Kielak, Tetrahedron Lett. 41 (2000) 3657; (c) D.L. Boger, Tetrahedron 39 (1983) 2869;
 - (d) D.S. Kopchuk, G.V. Zyryanov, I.S. Kovalev, A.F. Khasanov, A.S. Medvedevskikh, V.L. Rusinov, O.N. Chupakhin, Chem. Heterocycl. Compds. 49 (2013) 500.
- [10] V.N. Kozhevnikov, D.N. Kozhevnikov, O.V. Shabunina, V.L. Rusinov, O.N. Chupakhin, Tetrahedron Lett. 46 (2005) 1791.
- [11] A.M. Prokhorov, V.N. Kozhevnikov, D.S. Kopchuk, H. Bernard, N. Le Bris, R. Tripier, H. Handel, B. Kőenig, D.N. Kozhevnikov, Tetrahedron 67 (2011) 597.
- [12] B.B. Dey, J. Chem. Soc. 105 (1914) 1039.
 [13] C. Platas-Iglesias, M. Mato-Iglesias, K. Djanashvili, R.N. Muller, L. Vander Elst, J.
- A. Peters, A. De Blas, T. Rodriguez-Blas, Chem. Eur. J. 10 (2004) 3579.
 [14] Z. Xu, L.K. Thompson, D.O. Miller, J. Chem. Soc., Dalton Trans. (2002) 2462.
- [15] T.V. Saraswathi, V.R. Srinivasan, Tetrahedron Lett. 12 (1971) 2315.
- [16] K. Nakamaru, Bull. Chem. Soc. Jpn. 55 (1982) 2697.
- [17] N.M. Shavaleev, F. Gumy, R. Scopelliti, J.G. Bűnzli, Inorg. Chem. 48 (2009) 5611.
- [18] N.M. Shavaleev, R. Scopelliti, F. Gumy, J.G. Bűnzli, Inorg. Chem. 47 (2008) 9055.
- [19] H. Xu, Q. Sun, Z. An, Y. Wei, X. Liu, Coord. Chem. Rev. 293-294 (2015) 228.