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# Substituted naphtholates of rare earth metals as emissive materials

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## Abstract

The synthesis, characterization, photoluminescent (PL) and electroluminescent (EL) behavior of trivalent Sc, Nd, Gd, Er, Tm and Yb complexes with 3-(5-methylbenzoxazol-2-yl)naphthol (L-5Me) and 3-(6-methylbenzoxazol-2-yl)naphthol (L-6Me) ligands are reported. An X-ray analysis of Sc(L-5Me)<sub>3</sub>, Sc(L-6Me)<sub>3</sub> as well as non-methylated analogue Sc(L)<sub>3</sub> has shown monomeric structure of the complexes whereas the lanthanide naphtholates according to LDI-TOF data are dimers Ln<sub>2</sub>(L-5Me)<sub>6</sub> and Ln<sub>2</sub>(L-6Me)<sub>6</sub>. The scandium complexes under photo- and electro-excitation revealed intensive ligand-centered luminescence peaked at 522 nm.

The PL and EL spectra of Nd, Tm and Yb compounds displayed moderate ligand-centered emission along with narrow bands of corresponding *f-f* transitions.

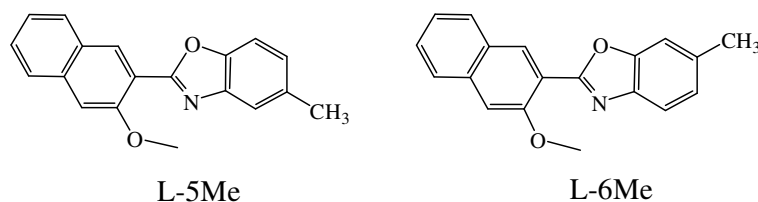
## Introduction

Among the potential applications of rare earth compounds one of the most attractive is the area of luminescent materials because of their unique ability to generate narrowband emission of *f-f* transitions.<sup>1</sup> Both organic<sup>2</sup> and inorganic<sup>3</sup> derivatives possess useful luminescent properties. The wavelengths of this emission can vary from near UV to near IR range depending on the nature of the lanthanide. Scandium, yttrium and lanthanum having no f-electrons as well as lutetium with completely filled f-shell do not give metal-centered luminescence but their derivatives are of considerable interest as model compounds and potential ligand-luminescent phosphores. Since the luminescence spectra of rare earth metal complexes and their intensity depends greatly on the nature of ligands, the choice of lanthanide coordination environment is very important.<sup>4</sup>

Previously, we have found that scandium complexes  $\text{Sc}(\text{L})_3$  and most of lanthanide compounds of  $(\text{L})_2\text{Ln}(\mu\text{-L})_2\text{Ln}(\text{L})_2$  type with 3-(2-benzoxazol-2-yl)-2-naphtholate and 3-(2-benzothiazol-2-yl)-2-naphtholate ligands display efficient PL and EL properties.<sup>5,6</sup> EL intensity of scandium (benzoxazolyl)naphtholate in visible region was found much higher than that of standard electroluminophore aluminum 8-oxyquinolate and higher than luminance of all OLED devices based on rare earth metal complexes.<sup>5</sup> In the luminescence spectra of Pr, Nd, Ho, Er, Tm and Yb complexes the bands of metal-centered emission were observed as well. The EL efficiency of ytterbium (benzothiazolyl)naphtholate in near IR region turned out ten times higher than that of other organolanthanide electroluminophores.<sup>6</sup> To explain the observed phenomenon an excitation circuit comprising the formation of an intermediate system with the divalent ytterbium has been proposed.<sup>6</sup> In an attempt to find evidence of the proposed excitation mechanism, we synthesized and studied the structure and luminescent properties of Sc, Nd, Gd, Er, Tm and Yb naphtholates which are similar to listed above, but contain methyl substituents in the position 5 or 6 of the benzoxazole fragments. For preparation of the mentioned complexes we used the reactions of silylamides  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  with respective naphthole. Earlier this method was successfully applied for the synthesis of other water-free lanthanide phenolates and naphtholates.<sup>5,6</sup>

## Results and discussion

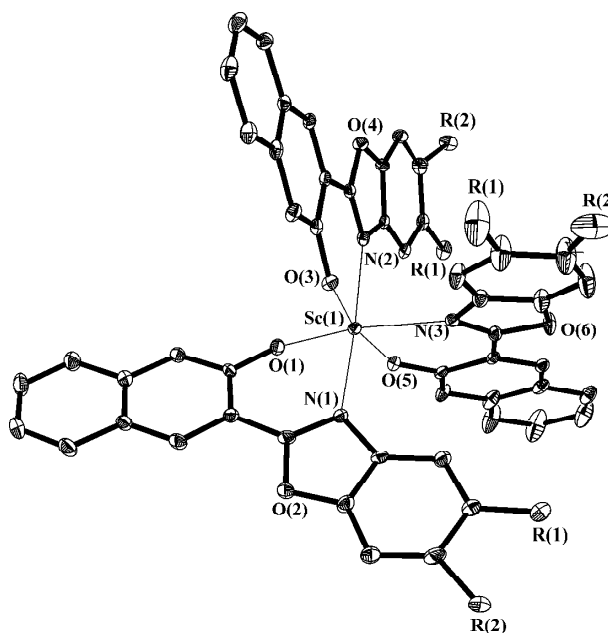
The reactions of  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  with substituted naphthols H(L-5Me) or H(L-6Me) in 1:3 ratio easily proceed at room temperature and afford the desired products in 75-87% yield. In the case of scandium the isolated complexes  $\text{Sc}(\text{L-5Me})_3$  (**1**),  $\text{Sc}(\text{L-6Me})_3$  (**2**) are monomeric whereas Nd, Gd, Er, Tm and Yb naphtholates form the dimeric molecules  $\text{Ln}_2(\text{L-5Me})_6$  ( $\text{Ln} = \text{Nd}$  (**3**), Gd (**4**), Er (**5**), Tm (**6**), Yb (**7**)) and  $\text{Ln}_2(\text{L-6Me})_6$  ( $\text{Ln} = \text{Nd}$  (**8**), Gd (**9**), Er (**10**), Tm (**11**), Yb (**12**)).



The molecular structure of the scandium complexes **1**, **2** was confirmed by X-ray analysis. The monomeric arrangement was found also for non-methylated analogue  $\text{Sc}(\text{L})_3$  synthesized previously.<sup>5</sup> In contrast, the lanthanide complexes are dimeric, as it has been proved by the LDI-TOF mass-spectrometry of erbium derivative **5** (Fig. S4) and previously obtained X-ray data for non-methylated neodymium complex  $\text{Nd}_2(\text{L})_6$ .<sup>6</sup>

Crystals of the scandium complexes suitable for structure investigation (obtained by slow cooling of their solutions in DME or ether) contained crystallized molecules of the solvents.

According to X-ray analysis data complexes  $\text{Sc}(\text{L})_3$ ,  $\text{Sc}(\text{L-5Me})_3$  (**1**) and  $\text{Sc}(\text{L-6Me})_3$  (**2**) adopt a monomeric structure where scandium atom is bounded by three bidentate substituted (benzoxazol-2-yl)naphtholate ligands (Fig.1, Table 1). The Sc atoms have a distorted octahedral environment. In general, complexes  $\text{Sc}(\text{L})_3$ , **1** and **2** have similar structure which practically does not differ from that of previously published (benzoxazol-2-yl)phenolates of scandium<sup>7</sup> and indium.<sup>8</sup> The Sc-O and Sc-N distances in  $\text{Sc}(\text{L})_3$ , **1** and **2** are in the ranges of 1.974(1)÷2.013(1) Å and 2.292(2)÷2.394(1) Å, respectively, what is close to the lengths of analogous bonds in the scandium tris[2-(2-benzoxazol-2-yl)phenolate] (1.992(2) ÷2.004(2) Å and 2.275(2) ÷2.348(2) Å). (Benzoxazol-2-yl)naphtholate ligands in  $\text{Sc}(\text{L})_3$ , **1** and **2** are practically planar. The dihedral angles between benzoxazol and naphthol fragments are 2.2÷13.0° in  $\text{Sc}(\text{L})_3$ , 2.5÷11.9° in **1** and 6.1÷13.2° in **2**, which is close to the values of corresponding angles in scandium (benzoxazol-2-yl)phenolate complex. Thus, the introduction of methyl substituents in position 5 or 6 of the benzoxazolyl cycle does not cause a significant change in the molecular geometry of scandium benzoxazolyl-naphtholate.



**Fig. 1.** Molecular structures of  $\text{Sc}(\text{L})_3$  ( $\text{R}(1)=\text{R}(2)=\text{H}$ ), **1** ( $\text{R}(1)=\text{Me}$ ,  $\text{R}(2)=\text{H}$ ) and **2** ( $\text{R}(1)=\text{H}$ ,  $\text{R}(2)=\text{Me}$ ). Thermal ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity.

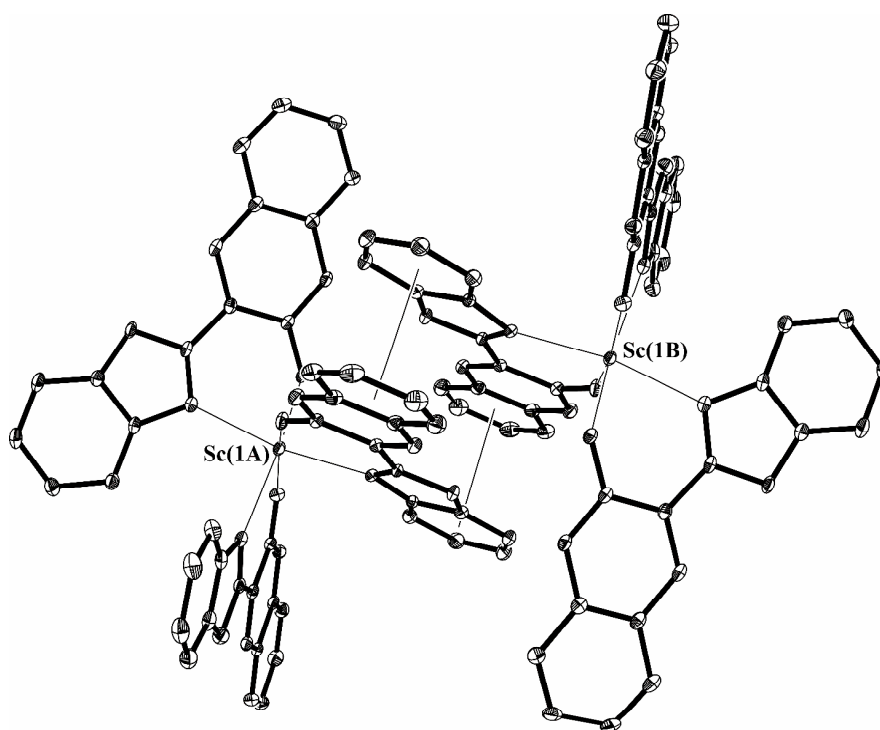
**Table 1.** Selected distances (Å) and angles (deg.) for scandium complexes.

	Sc(L) <sub>3</sub>	<b>1</b>	<b>2</b>
Distance			
Sc(1)-O(3)	1.9959(10)	2.0024(16)	2.0132(12)
Sc(1)-O(5)	1.9969(9)	1.9837(16)	1.9862(12)
Sc(1)-O(1)	2.0049(9)	1.9810(19)	1.9741(14)
Sc(1)-N(1)	2.2964(12)	2.292(2)	2.3198(15)
Sc(1)-N(2)	2.3084(12)	2.299(2)	2.2969(15)
Sc(1)-N(3)	2.3943(13)	2.339(2)	2.3600(16)
Angle			
O(3)-Sc(1)-O(5)	96.87(4)	166.90(8)	160.07(6)
O(3)-Sc(1)-O(1)	97.96(4)	96.67(7)	99.92(5)
O(5)-Sc(1)-O(1)	164.43(4)	96.00(7)	97.64(5)
O(3)-Sc(1)-N(1)	94.13(4)	O(1)-Sc(1)-N(1) 80.79(8)	O(1)-Sc(1)-N(2) 91.75(5)

It is interesting to note that the mentioned above (benzoxazol-2-yl)phenolates and (benzoxazol-2-yl)naphtholates of scandium and indium are monomeric units in a crystal whereas related neodymium (benzoxazol-2-yl)naphtholate<sup>6</sup> and praseodymium (benzoxazol-2-yl)phenolate<sup>9</sup> are dimeric compounds. In order to gain more insight into the causes of the large difference in the structures between related complexes, we calculated the shielding of central metal atom by ligand solid angle approach (G-parameter).<sup>10</sup> According to the calculations the G parameters in the complexes Sc(L)<sub>3</sub>, **1** and **2** are 86.9(2), 87.7(2) and 87.0(2) %, respectively. These data indicate that steric situation in all three complexes is substantially identical and does not depend on the presence of the Me substituents in the (benzoxazolyl)naphtholate ligands. The G parameters in the Sc<sup>7</sup> and In<sup>8</sup> (benzoxazolyl)phenolates are 86.6(2) and 88.1(2) % which is consistent with the same parameters in Sc(L)<sub>3</sub>, **1** and **2**. It follows that (benzoxazolyl)naphtholate and (benzoxazolyl)phenolate ligands have the similar steric characteristics. Really, the G parameters of (benzoxazolyl)naphtholate ligands in Sc(L)<sub>3</sub>, **1** and **2** vary in the range from 29.3(2) to 31.0(2) % whereas the same values of (benzoxazolyl)phenolate ligands are from 29.8(2) to 30.9(2) %. Calculation of G parameters for monomeric Nd and Pr complexes yielded a values of 69.7(2) and 70.2(2) %, respectively, which are close to each other and significantly less than those of monomeric Sc and In complexes. Consequently, the Nd and Pr atoms in the monomeric units are insufficiently shielding from intermolecular Ln...ligand interactions as compared to monomeric complexes of Sc and In. The realization of such interactions causes formation of dimeric molecules of the Nd and Pr complexes in a crystal. The G parameters in

this case are increased up to 91.2(2) and 87.7(2) %, respectively. It should be noted that the average value of G parameter in monomeric (85(3) %) and dimeric (88(1) %) lanthanide guanidinate complexes<sup>11,12</sup> is close to those in Sc(L)<sub>3</sub>, **1** and **2**, (benzoxazolyl)phenolates of Sc,<sup>7</sup> In<sup>7</sup> and dimeric complexes of Nd and Pr.<sup>6,9</sup> The conclusion based on the G values well agrees with the results of direct DFT calculations: dimerization is unfavorable for Sc(L)<sub>3</sub> complexes (the energy costs are 18 kcal/mol) and is favorable for lanthanide Ln(L)<sub>3</sub> complexes (the energy release is 21 and 11 kcal/mol for Ln = Nd and Yb, respectively).

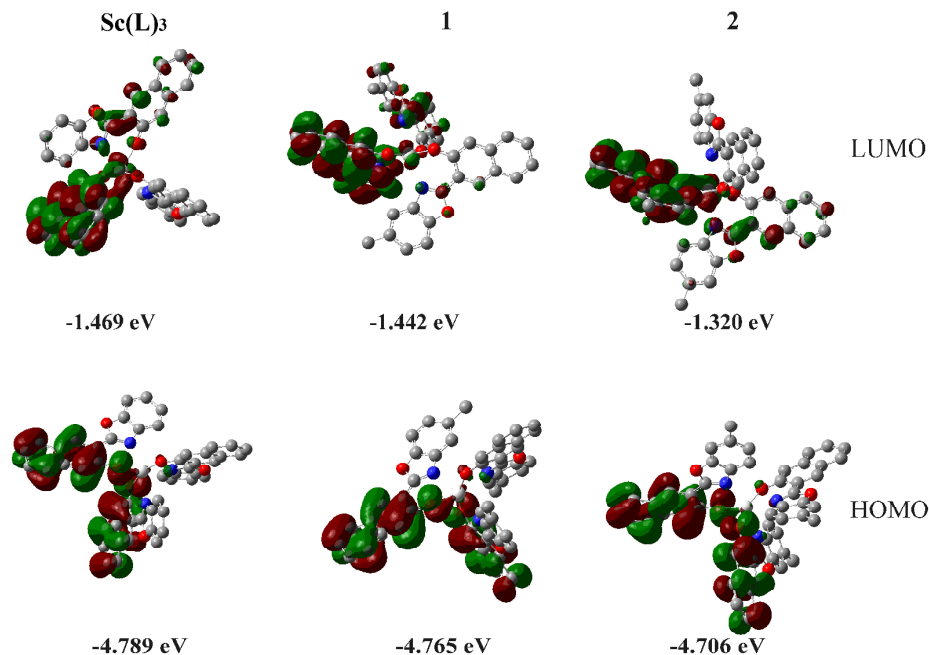
In the crystals of Sc(L)<sub>3</sub>, **1** and **2** the intermolecular  $\pi \dots \pi$  interactions<sup>13</sup> between naphtholate ligands of adjacent molecules are realized (Fig. 2). The distances between average planes of these ligands are 3.342 Å in Sc(L)<sub>3</sub>, 3.349 Å in **1** and 3.358 Å in **2**.



**Fig. 2.** Fragment of crystal packing of Sc(L)<sub>3</sub>. The similar motifs take place in complexes **1** and **2**.

In order to evaluate the influence of methyl groups and their position on the electronic structure, we carried out DFT calculations of isolated molecules of complexes Sc(L)<sub>3</sub>, **1** and **2** using different approaches: B3LYP functional with DZVP basis set and PBE functional with extended basis set H: (6s2p)/[2s1p], C,N,O: (10s7p3d)/[3s2p1d], Sc: (19s,15p,11d,5f)/[6s,5p,3d,1f]. The results obtained are quite similar. It should be noted that selected levels of calculations adequately reproduce the geometric parameters of these molecules in a crystal. The difference in bond lengths does not exceed 0,03 Å. The HOMO of Sc(L)<sub>3</sub>, **1** and **2** represent an

almost pure ligand orbitals which are localized on naphtholate fragments of (benzoxazolyl)naphtholate ligands. The metal contribution is only 5 % in  $\text{Sc}(\text{L})_3$ , 4 % in **1** and 2 % in **2**. On going to LUMO, the contribution of the metal wave functions remains virtually unchanged as compared to the HOMO and is equal to 7, 2, and 3 % for  $\text{Sc}(\text{L})_3$ , **1** and **2**, respectively. Thus, the HOMO-LUMO electronic transition can be considered as an interligand charge transfer with a minimal contribution of LMCT. Interesting to note that in related scandium (benzoxazolyl)phenolate<sup>7</sup> the metal contribution in HOMO is less than 1 % whereas its contribution in LUMO (14-26 %) significantly exceeds analogous value in  $\text{Sc}(\text{L})_3$ , **1** and **2**.

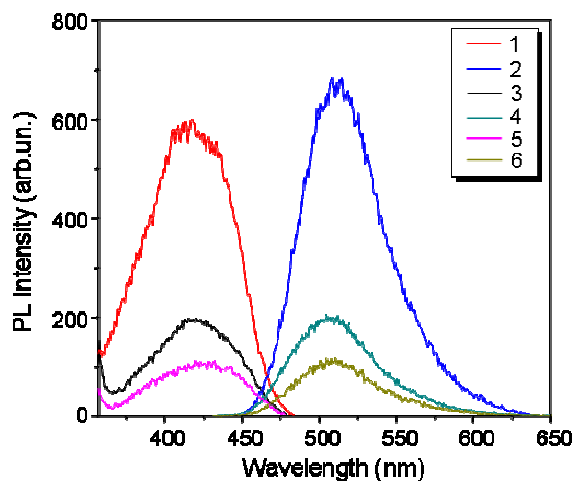


**Fig. 3.** The B3LYP/DZVP HOMO and LUMO isosurfaces (the electron density of 0.02 a.u.) for complexes  $\text{Sc}(\text{L})_3$ , **1** and **2**.

The HOMO and LUMO energies (Fig. 3) in the complexes **1** and **2** differ from each other less than in **2** and **3**. Thus, the methyl substituents in position 6 have greater influence on the energy values of HOMO-LUMO than in position 5. Charges on Sc cations in **1-3** do not depend on the position of the methyl groups and are equal to +1.37 e.

Physical and luminescent properties of complexes obtained also undergo minor changes with the insertion of the methyl substituents into the benzoxazole fragments of the ligands. The absorption (Fig. S5), excitation and PL (Fig. 4) spectra of scandium complexes **1** and **2** in THF solutions actually do not differ from those of non-methylated analogue  $\text{Sc}(\text{L})_3$ <sup>5</sup> but the quantum yields are noticeably lower: about 9 % for **1**, **2** and 58 % for  $\text{Sc}(\text{L})_3$ .





**Fig. 4.** Excitation ( $\lambda_{\text{mon}}$  508 nm) and PL ( $\lambda_{\text{ex}}$  420 nm) spectra of  $\text{Sc}(\text{L})_3$  (1, 2), **1** (3, 4) and **2** (5, 6) in THF solution.

The presence of three naphtholate ligands in the coordination sphere of the complexes leads to 3-fold splitting of their  $\pi$  and  $\pi^*$  levels. Calculated HOMO and LUMO energies in the free LH ligand are -5.15 and -2.77 eV in DFT/PBE approach, which well agree with the spectral properties. Corresponding one-electron energies of the occupied and unoccupied states for  $\text{Sc}(\text{L})_3$  are -4.98, -4.91, -4.73 and -2.79, -2.69, -2.66 eV, respectively, i.e. instead of one  $\pi - \pi^*$  transition between frontier orbitals in the free ligand nine possible  $\pi - \pi^*$  and ILCT transitions appear in the complex. Most of intersections of the excited states are located in the vicinity of the ground state which causes fast radiationless  $\text{S}_1$  transitions up to the lowest excited states (Fig. S1). Apparently, this leads to high PL quantum yield of  $\text{ScL}_3$ . The picture of terms for the complexes with methylated ligands is quite similar. The observed decrease of PL yield in this case is caused probably by increasing of number of C-H groups which are well known quenchers. The calculated energy of excited terms at various geometry of the complex gives a ground to expect the red shift of the band maximum in the PL spectra by  $\sim 0.5$  eV with respect to the band in the excitation spectrum, which agrees well with the experimental data (Fig. 4).

The PL spectra of solid gadolinium complexes **4** and **9** at 295 K also consist of single broad bands peaked at about 522 nm. At 77 K the bands are shifted to the red region and located respectively at 595 and 590 nm, which allowed determining the triplet levels of the ligands as 16800 and 16950  $\text{cm}^{-1}$  for **4** and **9**, accordingly. Low position of the triplet levels gave grounds to expect that the ligands would be suitable sensitizers for Nd, Er, Tm and Yb, whose resonant levels are below 16850  $\text{cm}^{-1}$ .<sup>14</sup> Really, it was found that the complexes **3**, **7**, **8**, **12** exhibit the emission bands in near IR region characteristic for respective metals along with the ligand-centered emission at 522 nm (Fig. 5). Intensity of the bands was insensitive to the



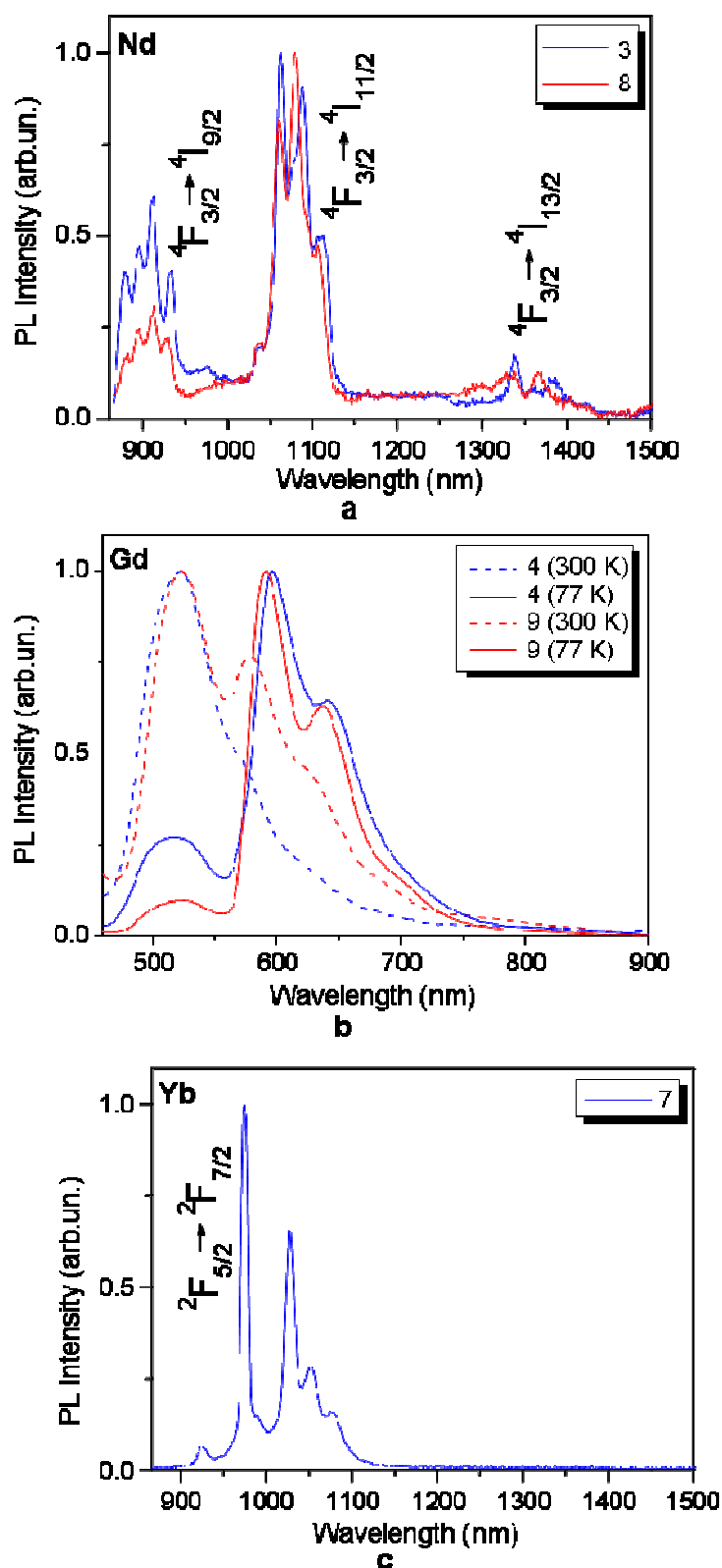


Fig. 5. PL spectra of solid 3, 4, 7, 8, 9 ( $\lambda_{\text{ex}}$  405 nm).

position of the methyl substituents in the ligands. In the spectra of thulium complexes **6**, **11** the  $f$ - $f$  transitions ( $^3H_4 \rightarrow ^3H_6$ ) have been observed as a weak narrow band at 795 nm.

To study EL properties of the synthesized complexes the three-layer devices consisting of ITO glass as the anode, N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) as the hole-transporting layer, the lanthanide heterocyclic complex as a neat emission layer, 4,7-diphenyl-1,10-phenanthroline (BATH) as an electron-transport and hole-blocking layer and Yb as the cathode were fabricated. Comparison of the data obtained for (L-5Me), (L-6Me) and non-methylated derivatives (L)<sup>5</sup> revealed that the insertion of Me groups into the ligands causes insignificant changes in the shape of EL spectra which, like PL spectra, contain of the ligand-centered emission at about 520-530 nm and a set of bands of *f-f* transitions of respective metals (Fig. 6).

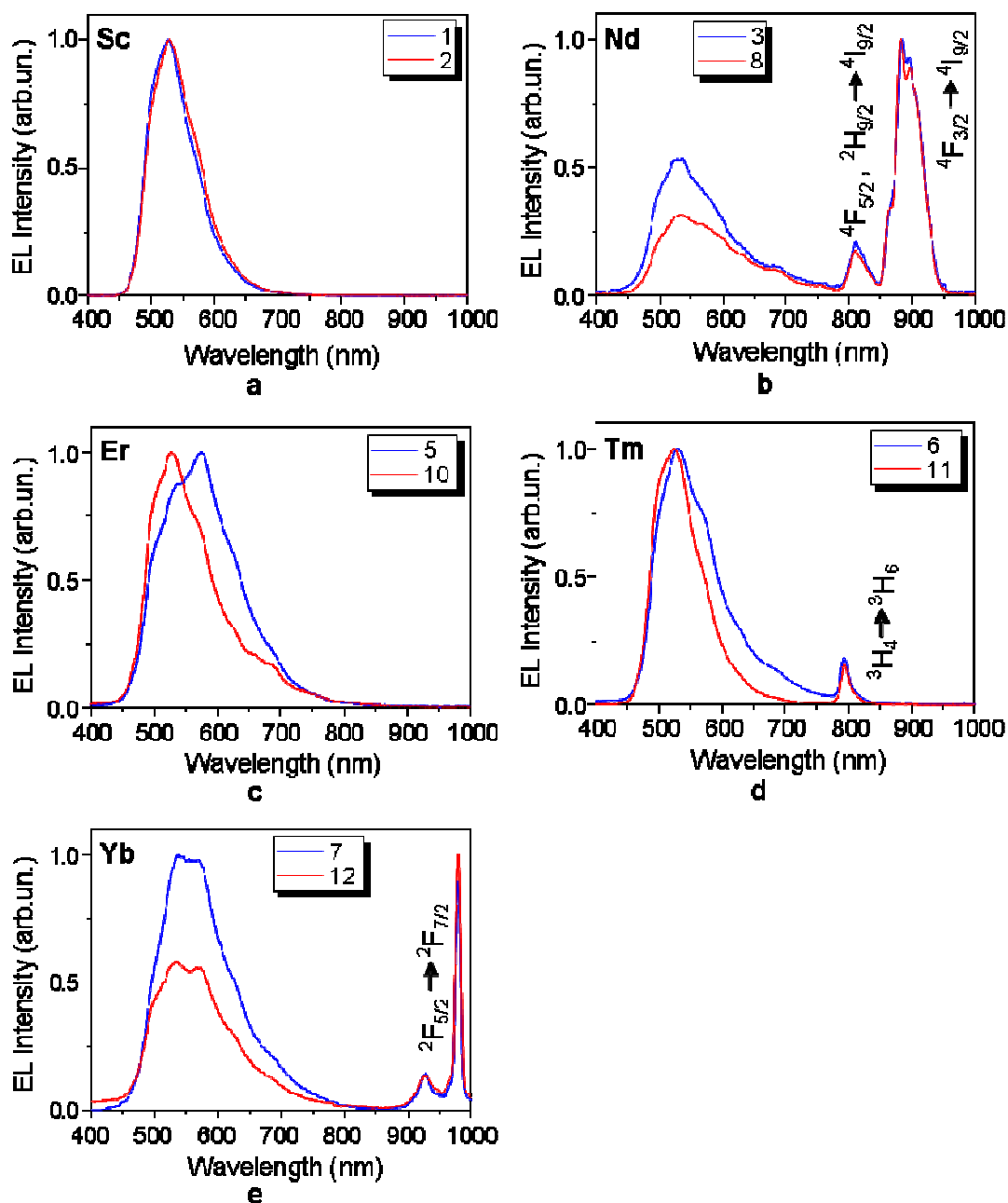


Fig. 6. EL spectra of OLED devices based on complexes 1-3, 5-7, 9-12.

Intensity of the bands of metal-centered emission in the cases of Tm and Yb derivatives also virtually unchanged but in the case of neodymium complexes **3** and **8** it increased nearly three times (Table 2). This is apparently due to the better match the energy of the triplet levels of (L-5Me) and (L-6Me) the resonant  $^4G_{5/2}$  level of  $Nd^{3+}$  ions ( $16850\text{ cm}^{-1}$ ) than that for non-methylated ligands (L) ( $18600\text{ cm}^{-1}$ ).<sup>5</sup> It is important to note that despite the difference in the energy of triplet levels of methylated and non-methylated ligands intensity of the band of  $^2F_{5/2} - ^2F_{7/2}$  transition is the same in both ytterbium complexes. This is consistent with the assumption about an alternative redox mechanism of  $Yb^{3+}$  excitation in these complexes, which includes the formation of  $Yb^{2+}$  ions on the intermediate stages.<sup>6</sup>

**Table 2.** Performance characteristics for the OLEDs based on complexes **1-3, 5-8, 10-12**.

Complex (№)	Turn-on voltage (V) <sup>a</sup>	Max. luminance		Wall plug efficiency (lm/W <sup>[c]</sup> , mW/W <sup>[d]</sup> )
		Visible (cd/m <sup>2</sup> ) <sup>b</sup>	NIR ( $\mu\text{W}/\text{cm}^2$ ) <sup>[b]</sup>	
Sc(L-5Me) <sub>3</sub> ( <b>1</b> )	3.5	890 (22)	-	1.2 <sup>[c]</sup>
Sc(L-6Me) <sub>3</sub> ( <b>2</b> )	3.5	900 (22)	-	1.2 <sup>[c]</sup>
[Nd(L-5Me) <sub>3</sub> ] <sub>2</sub> ( <b>3</b> )	5	4	80 (22)	0.03 <sup>[d]</sup>
[Nd(L-6Me) <sub>3</sub> ] <sub>2</sub> ( <b>8</b> )	5	6	85 (22)	0.04 <sup>[d]</sup>
[Er(L-5Me) <sub>3</sub> ] <sub>2</sub> ( <b>5</b> )	5	5	-	$5.6 \times 10^{-3}$ <sup>[c]</sup>
[Er(L-6Me) <sub>3</sub> ] <sub>2</sub> ( <b>10</b> )	4.5	7	-	$8.8 \times 10^{-3}$ <sup>[c]</sup>
[Tm(L-5Me) <sub>3</sub> ] <sub>2</sub> ( <b>6</b> )	5	8	5.8 (22)	$3.2 \times 10^{-3}$ <sup>[d]</sup>
[Tm(L-6Me) <sub>3</sub> ] <sub>2</sub> ( <b>11</b> )	4.5	10	7 (22)	$4.3 \times 10^{-3}$ <sup>[d]</sup>
[Yb(L-5Me) <sub>3</sub> ] <sub>2</sub> ( <b>7</b> )	4.5	15	315 (22)	0.82 <sup>[d]</sup>
[Yb(L-6Me) <sub>3</sub> ] <sub>2</sub> ( <b>12</b> )	4.5	16	320 (22)	0.85 <sup>[d]</sup>

<sup>[a]</sup> Voltage at  $0.1\text{ mA}/\text{cm}^2$ . <sup>[b]</sup> Values in parentheses are the voltages at which the luminance was obtained. <sup>[c]</sup><sup>[d]</sup> Value at 12 V.

The current density-voltage and luminance-voltage characteristics of OLEDs based on the complexes with L-5Me and L-6Me ligands virtually are identical (Fig. S7) and similar to characteristics of the devices with the complexes containing non-methylated ligands.<sup>6</sup> This suggests that performed modification of the ligands does not affect on the charge-transport properties of the complexes.

## Conclusions

Thus, Sc, Nd, Gd, Er, Tm and Yb (benzoxazoly)naphtholates containing methyl substituents in the position 5 or 6 of benzoxazoly fragments were synthesized. The X-ray analysis and LDI-TOF spectrometry revealed that the scandium complexes are monomeric  $\text{Sc}(\text{L-Me})_3$  while the lanthanides form dimeric molecules  $\text{Ln}_2(\text{L-Me})_6$ . Investigation of PL and EL properties of the products and comparison them with those of non-methylated analogues revealed that the insertion of methyl groups in the ligands weakly impact on luminescence and charge-transport characteristics of the complexes. The greatest changes were found for neodymium complexes, methylated derivatives of which displayed three times higher the metal-centered emission than that of non-methylated naphtholates. It is assumed that the reason of this effect is better match the triplet level of (L-Me) ligands than that of (L) ligands to the resonance level of neodymium. The same intensity of the bands of  ${}^2\text{F}_{5/2} - {}^2\text{F}_{7/2}$  transition in the PL and EL spectra of ytterbium complexes with methylated and non-methylated ligands speaks in favor of unconventional redox excitation mechanism, which was proposed previously.<sup>5, 15, 16, 17, 18</sup> This, in turn, gives a theoretical premise for finding novel ligands capable to provide the redox path of ytterbium excitation and hence get new efficient NIR emitters.

## Experimental

All procedures for the synthesis, OLED devices fabrication, physical measurements, computations and X-ray measurements are described in the Supplementary Information.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/XXXXXXXXXXXXXXXXXX>.

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