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Coordination compounds of rare-earth metals with organic ligands for electroluminescent diodes

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Abstract. Data on lanthanide coordination compounds with organic ligands used in the design of electroluminescent diodes are summarised and systematically represented. The molecular and electronic structures and spectroscopic characteristics of these compounds are considered. A comparative analysis of the properties of organic electroluminescent diodes with different compositions of emitting and conductive layers is presented. The bibliography includes 147 references.

I. Introduction

The design of organic electroluminescent diodes (or organic light-emitting diodes, OLEDs) for the construction of planar multicolour information displays and high-value-in-use multicolour indicators, as well as of low-cost and efficient light sources, is a new field of investigation in molecular electronics and applied synthetic chemistry. Organic electroluminescent diodes are multilayer sandwich structures capable of converting electrical energy into light energy. There is good reason to expect that, in the near future, this unique property of OLEDs will make it possible to construct planar lightweight and very cheap displays and display panels, which will be superior to liquid-crystal analogues in the main parameters, and produce unconventional light sources for different purposes. The following two most important aspects of this area of scientific research should be mentioned: the development and construction of radically new superthin flexible polychromic displays and a gradual change from luminescent bulbs and incandescent lamps to organic and hybrid light-emitting diodes as illuminants. Nowadays, the power efficiency of laboratory light sources based on organic materials is already better than the light output of incandescent lamps (15 – 20 lm W^{-1}) and is in excess of 50 lm W^{-1}, the theoretically possible efficiency being higher than 300 lm W^{-1}. The service lifetime of these lamps (10 000 hours) is more than 50 times longer than that of modern incandescent lamps. The light efficiency of gas luminescent tubes is slightly higher than that of modern OLED sources. However, these tubes are essentially inferior to OLED devices in many respects (explosion hazard, toxicity, inadequacy of perception of light by human eye, *etc.*).

Lanthanide complexes with organic ligands (hereinafter referred to as lanthanide complexes) belong to one of the most promising classes of compounds for the design of electroluminescent devices owing to specific electronic structures of these metals. Although these complexes have found application in the design of OLEDs about 10 years ago, this aspect has been already considered in several exhaustive reviews published in leading journals.[1–4] Investigations in this field are progressing so rapidly that, although a short period of time has passed since the latest review publication,[4] a need has arisen to generalise and analyse the available data once again. The present review summarises data on the molecular structures and spectroscopic characteristics of luminescent-active rare-earth complexes. The principles of selection and combination of such complexes in the design of OLED devices are considered. Problems in the design of light-emitting diodes on the basis of these compounds, which are associated with optimisation of their compositions by introducing additional luminescent and transport layers, are discussed. The review covers all data published in this area up to the present day. The data are classified and represented according to the nature of the ligand. In some cases, the photoluminescent properties of complexes are used as the key feature.

II. Main characteristics of electroluminescent devices based on organic compounds

Electroluminescence was discovered by Losev (Nizhny Novgorod Radiolaboratory),[5] who found electrically induced light emission in silicon carbide crystals. However, during the period of vigorous development of semiconductor physics, light-emitting recombination in semiconductors seemed to be unlikely, at least from practical point of view. The situation changed radically after the discovery of intense light emission in p – n transitions in gallium arsenide. In the early 1960s, the General Electric Company produced a commercial light-emitting device (LED) based on the inorganic semiconductor GaAsP.

Electroluminescence of organic compounds was described for the first time for anthracene in 1963.[6] However, the efficiency of these devices was too low for practical applications, and this discovery did not stimulate research on light-emitting devices. Only in the late 1980s, after the construction of a new type of light-

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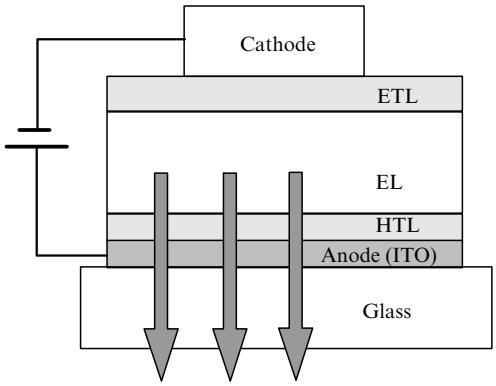


Figure 1. Scheme of an organic light-emitting diode (see the text).

emitting diode based on aluminium hydroxyquinolinate (Alq_3)[7] and poly(*p*-phenylenevinylene) (PPV),[8] was a new line of investigation aimed at designing and studying organic light-emitting diodes opened.

Typical OLED devices have single-layer or multilayer sandwich structures ~100 nm thick (Fig. 1).

Cells consist of the following sequence of components: a glass support coated with a transparent conducting layer of indium tin oxide (ITO) serving as the anode; an organic hole-transport layer (HTL), an emitting layer (EL), an electron-transport layer (ETL) and a metallic cathode as an aluminium film.

Below are given the formulas of organic and complex compounds, which are most often used in lanthanide-containing OLED devices (these abbreviations are used hereinafter).

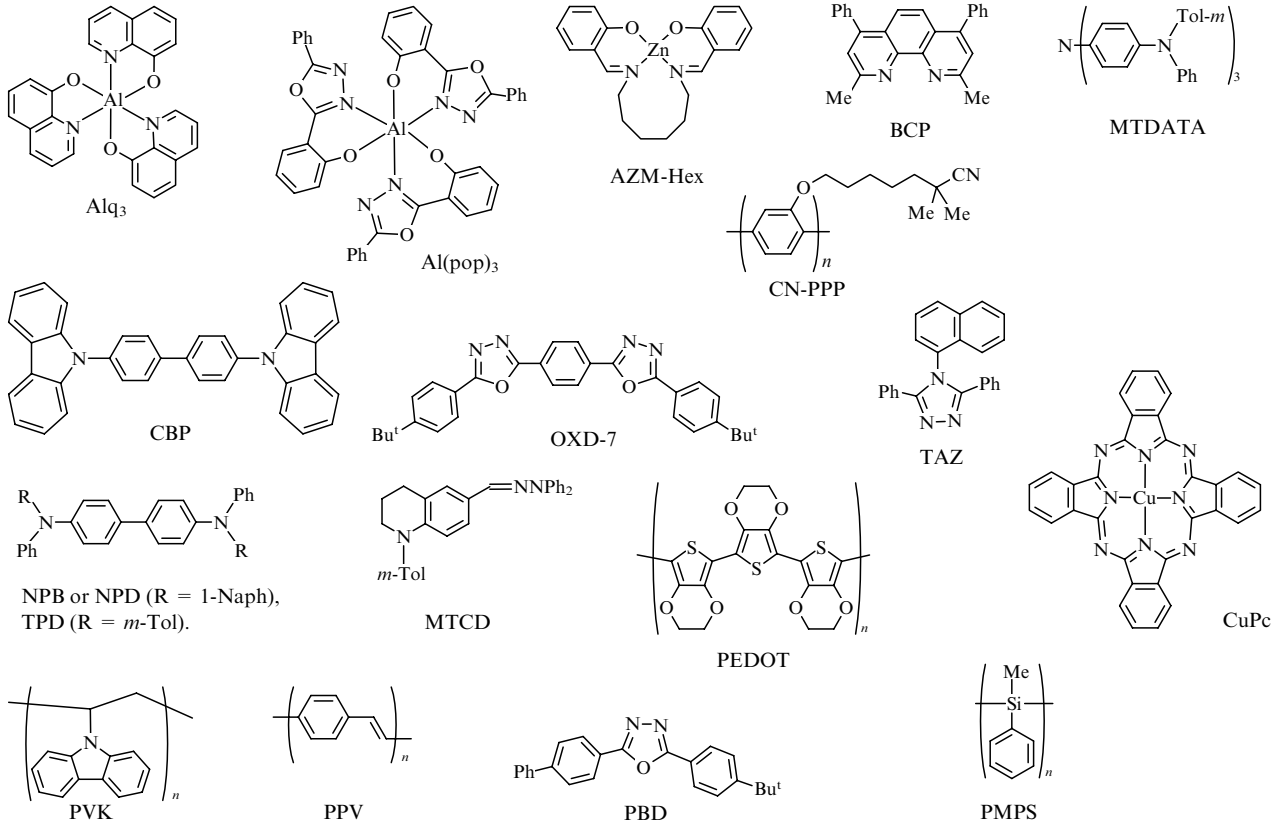
Theoretical models of charge transport in these compounds were considered in detail.[9–11]

Lanthanide complexes studied as emitters, OLED devices constructed on the basis of these compounds, and the maximum brightnesses of the latter are presented in Table 1.

The efficiency of conversion of absorbed energy into light emission is characterised mainly by the luminescence quantum yield, *e.g.*, the number of photons per absorbed light quantum (in the case of photoluminescence) or per injected electron–hole pair (in the case of electroluminescence). The quantum yield, which ignores the possibility of absorption of this emission in the device, is called the internal quantum yield, whereas the external quantum yield is associated with directly measured light emission from the device. The external quantum efficiency of a light-emitting diode is determined as a ratio of the number of quantums emitted from the material to the number of charge carriers passing through the light-emitting diode during the same period of time.[72]

Nowadays, cells based on the organic compound rubrene (5,6,11,12-tetraphenyltetracene) exhibit the highest electroluminescence efficiency of all the known OLED devices. In these cells, the maximum brightness exceeds 200 000 cd m^{-2} and the light emission efficiency is ~8 lm W^{-1}.[73] Of complex compounds, tris(2-phenylpyridine)iridium has the best characteristics in cells: the maximum brightness is 100 000 cd m^{-2}, the light emission efficiency being the same (~8 lm W^{-1}).[74] The maximum brightness of the best lanthanide-containing device based on terbium pyrazolone complex **51**(**Tb**) is 20 000 cd m^{-2}, and the efficiency of this device is 3.24 lm W^{-1}.[66]

However, in spite of the fact that rare-earth complexes are considerably less efficient than organic compounds, they have attracted great attention because of specific features of the mechanism of luminescence providing monochromatic radiation. Electronic spectra of lanthanide ions are associated with f–f transitions in the 4f layer shielded from external fields by the closed 5s and 5p shells. This provides narrowing of the emission line to 10 nm, which is inaccessible for other luminophores. At the same time, the fact that transitions within the same electronic configuration are parity-forbidden results in low absorptivity of f–f transitions ($\varepsilon \leqslant 10$ mol^{-1} litre cm^{-1}) and, as a consequence, in low luminescence efficiency of free ions.[75] Interactions of 4f electrons with the crystal field lead to a change in the radius of the f



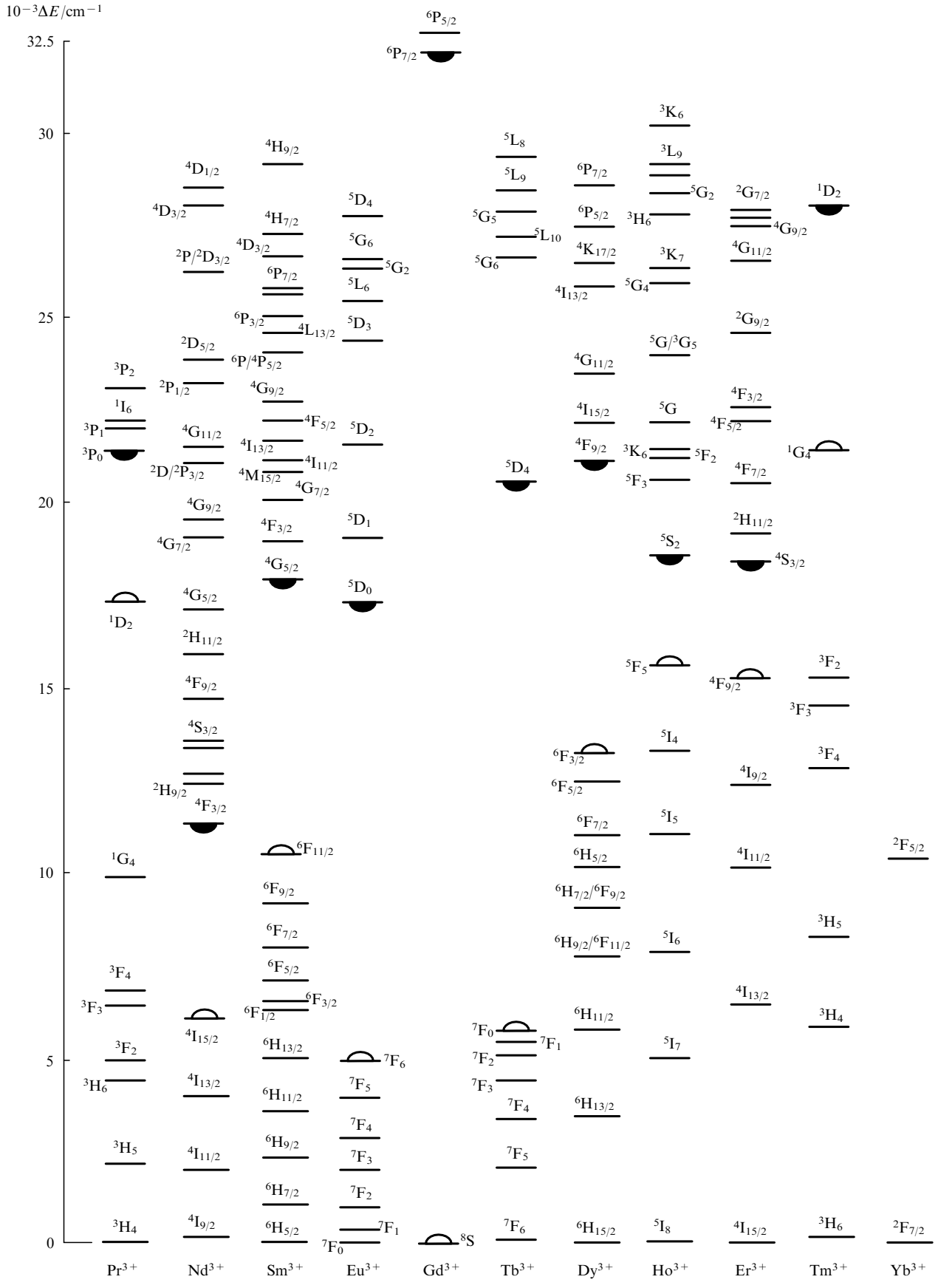


Figure 2. Diagram of the terms of rare-earth ions in solutions.[76]

Table 1. Emitting lanthanide complexes with organic ligands.

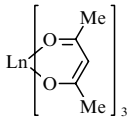
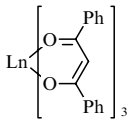
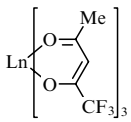
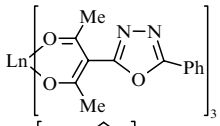
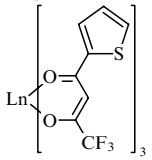
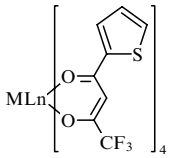
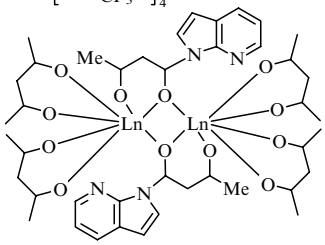
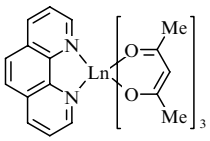
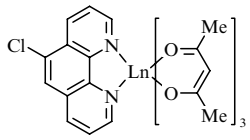
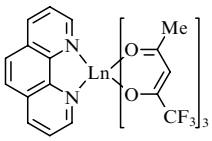
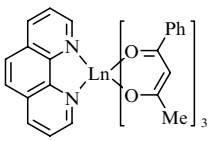
Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
1(Ln)	$Ln(acac)_3$		ITO/TPD/**1**(**Tb**)/Al ITO/PVK/PVK:**1**(**Tb**):PBD/PBD/Al	7 (at 0.4 mA cm^{-2}) 17 (at 13 V)	12 13
2(Ln)	$Ln(dbm)_3$		ITO/TPD/**2**(**Eu**)/Al	–	14
3(Ln)	$Ln(tfac)_3$		ITO/PVK/PVK:**3**(**Tb**):PBD/PBD/Al	25 (at 11 V)	13
4(Ln)	$Ln(acac\text{-}OXD)_3$		ITO/PVK:PBD:**4**(**Tb**)/$Al(pop)_3$/CsF/Al	550 (at 20 V)	15
5(Ln)	$Ln(tta)_3$		ITO/PMPS:**5**(**Eu**)/PBD/Mg/Ag	0.3 (at 18 V)	16
6(Ln)	$MLn(tta)_4$		ITO/PVK:**6**(**NaEu**)/OXD-7/Alq_3/Al	36.7 (at 26 V)	17
7(Ln) [a]	$[Ln(acac\text{-}azin)_3]_2$		ITO/PVK:**7**(**Tb**)/PBD/LiF/Al	0.65 (at 13 V)	18
8(Ln)	$Ln(acac)_3(phen)$		ITO/PVK/**8**(**Tb**)/Al ITO/PVK/PVK:**8**(**Tb**):PBD/PBD/Al ITO/PVK/**8**(**Tm**)/Al ITO/PVK/**8**(**Dy**)/Al ITO/PVK:**8**(**Er**)/Al:Li/Ag	210 36 (at 10 V) 6 (at 16 V) 20 –	19 13 20 21 22
9(Ln)	$Ln(acac)_3$-(Cl-phen)		ITO/TPD/**9**(**Tb**)/Alq_3/Li:Al	95 (at 0.65 A m^{-2})	23, 24
10(Ln)	$Ln(tfac)_3(phen)$		ITO/PVK/PVK:**10**(**Tb**):PBD/PBD/Al	58 (at 8 V)	13
11(Ln)	$Ln(mppd)_3(phen)$		ITO/PVK/**11**(**Eu**)/Al	–	25

Table 1 (continued).

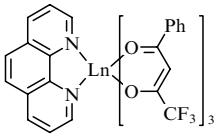
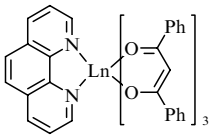
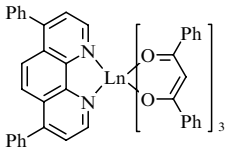
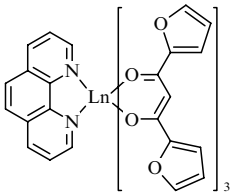
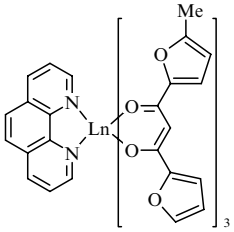
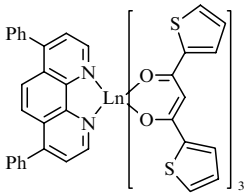
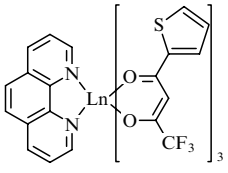
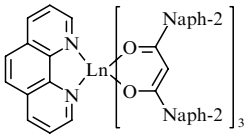
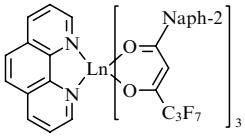
Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
12(Ln)	$Ln(bfa)_3(phen)$		ITO/PVK/PVK:**12(Sm)**:PBD/Al	135 (at 10 V)	26
13(Ln)	$Ln(dbm)_3(phen)$		ITO/TPD/**13(Eu)**:PBD/Alq_3/Mg:Ag	460 (at 16 V)	27
			ITO/**13(Eu)**/Alq_3/**8(Gd)**/Alq_3/Al	–	28
			ITO/TPD/**13(Eu)**/Mg:Ag/Ag	3.7 (at 17 V)	29
			ITO/TPD/**13(Eu)**/BCP/Alq_3/Mg:Ag/Ag	42 (at 16 V)	29
			ITO/TPD/**13(Tm)**/Mg:Ag	–	30
			ITO/TPD/**13(Er)**/Mg:Ag	–	30
14(Ln)	$Ln(dbm)_3(bath)$		ITO/TPD/**14(Eu)**/Mg:Ag	150 (at 18 V)	31
			ITO/TPD/TPD:**14(Eu)**/**14(Eu)**/Mg:Ag	820 (at 18 V)	31
			ITO/PVK/**14(Eu)**/Mg:Ag	400 (at 15 V)	32
			ITO/**14(Gd)**/**14(Eu)**/**14(Gd)**/Ag:Mg	100 (at 0.01 mA cm^{-2})	31
			ITO/TPD/**14(Ho)**/Mg:Ag	–	33
			ITO/TPD/**14(Tm)**/Mg:Ag	–	30
			ITO/TPD/**14(Er)**/Mg:Ag	–	30
15(Ln)	$Ln(dfp)_3(phen)$		ITO/TPD/**15(Eu)**/AlLi	34 (at 12 V)	34
16(Ln)	$Ln(mdfp)_3(phen)$		ITO/TPD/**16(Eu)**/AlLi	32.0 (at 9 V)	35
17(Ln)	$Ln(dtp)_3(bath)$		ITO/TPD/**17(Eu)**/Alq_3/AlLi	450 (at 15 V)	36
18(Ln)	$Ln(tta)_3(phen)$		ITO/TPD/**18(Eu)**/BCP/Alq_3/Mg:Ag	32	37
			ITO/TPD/**18(Eu)**:CBP/BCP/Alq_3/MgAg	500 (at 100 mA cm^{-2})	37
			ITO/TPD/**18(Eu)**:PBD/PBD/Mg	320	38
			ITO/TPD/**18(YEu)**/Alq_3/Mg:Ag	99 (at 11 V)	39
19(Ln)	$Ln(dnm)_3(phen)$		ITO/PVK/**19(Eu)**/Al	–	25
20(Ln)	$Ln(hfnh)_3(phen)$		ITO/TPD/**20(Eu)**:CBP/BCP/Alq_3/LiF/Al	967	40
			ITO/TPD/**20(Sm)**:CBP/BCP/Alq_3/LiF/Al	42	40

Table 1 (continued).

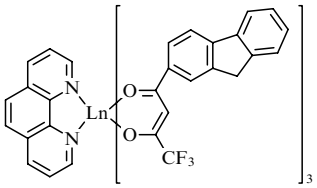
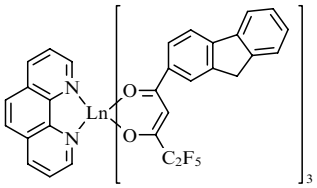
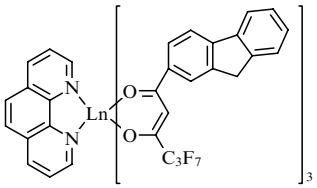
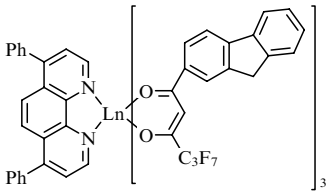
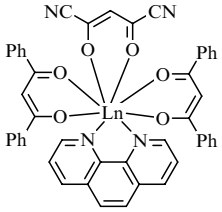
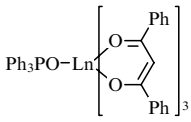
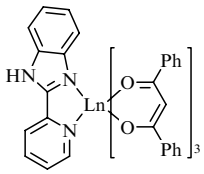
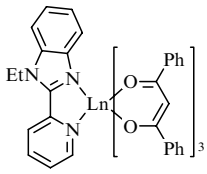
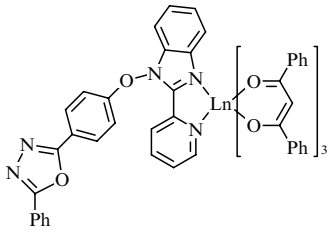
Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
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22(Ln)	$Ln(flpa)_3(phen)$		ITO/TPD/**22(Eu)**:AZM-Hex/Mg	–	14
23(Ln)	$Ln(flha)_3(phen)$		ITO/TPD/**23(Eu)**:AZM-Hex/Mg	–	14
24(Ln)	$Ln(flha)_3(bath)$		ITO/TPD/**24(Eu)**:AZM-Hex/Mg	10	14
25(Ln)	$Ln(dbm)_2$-(danac)(phen)		ITO/TPD/**25(Eu)**/Al	924 (at 380 mA cm^{-2})	41
26(Ln)	$Ln(dbm)_3(TPPO)$		ITO/TPD/**26(Eu)**/BCP/Alq_3/Mg:Ag	320 (at 14.5 V)	42
27(Ln)	$Ln(dbm)_3(hpbm)$		ITO/TPD/**27(Eu)**/Al	1.14 (at 23 V)	43
28(Ln)	$Ln(dbm)_3(epbm)$		ITO/TPD/**28(Eu)**/Al ITO/TPD/**28(Eu)**/Alq_3/Al	29 (at 11 V) 180 (at 18 V)	43 43
29(Ln)	$Ln(dbm)_3$-(pybm-OXD)		ITO/TPD/**29(Eu)**/LiF/Al	322 (at 21 V)	44

Table 1 (continued).

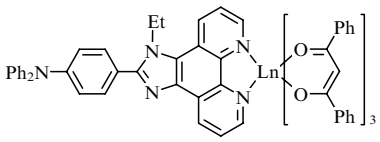
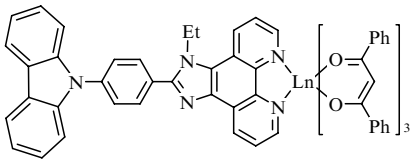
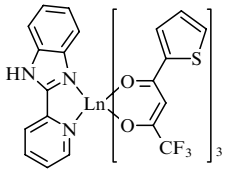
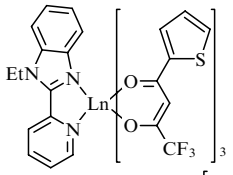
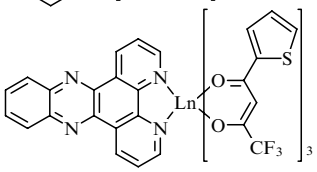
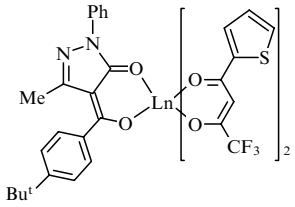
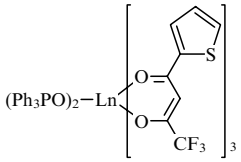
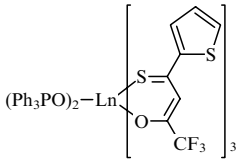
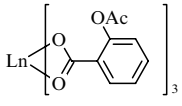
Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
30(Ln)	$Ln(dbm)_3(tpip)$		ITO/**30(Eu)**/MgAg/Ag ITO/TPD/**30(Eu)**/BCP/Alq_3/MgAg/Ag	19 (at 13.5 V) 1305 (at 16 V)	43 45
31(Ln)	$Ln(dbm)_3(cpip)$		ITO/TPD/**31(Eu)**/MgAg/Ag ITO/TPD/**31(Eu)**/**14(Eu)**/MgAg/Ag ITO/TPD/**31(Eu)**/BCP/Alq_3/MgA/Ag	537 (at 13 V) 1050 (at 16 V) 1460 (at 14 V)	46 46 46
32(Ln)	$Ln(tta)_3(hpbm)$		ITO/TPD/**32(Eu)**/Alq_3/Al	< 7 (at 16 V)	47
33(Ln)	$Ln(tta)_3(epbm)$		ITO/TPD/**33(Eu)**/Alq_3/Al	36.6 (at 21 V)	47
34(Ln)	$Ln(tta)_3(dppz)$		ITO/TPD/**34(Eu)**:CBP/BCP/Alq_3	1670 (at 13.6 V)	48
35(Ln) [b]	$Ln(tta)_2(pmbbp)$-(phen)		ITO/TPD/**35(Eu)**/Alq_3/Mg:Al	16 (at 12.5 V)	49
36(Ln)	$Ln(tta)_3(TPPO)_2$		ITO/MTCD/**36(Sm)**/Alq_3/Al ITO/MTCD/**36(Sm)**/Al ITO/TPD/**36(Eu)**/Alq_3/Al	0.5 – 10 (at 18 V)	50 50 51
37(Ln)	$Ln(stta)_3(TPPO)_2$		–	-	52
38(Ln)	$Ln(as)_3$		ITO/PVK/PVK:PBD:**38(Tb)**/PBD/Alq_3/Al ITO/PVK/PVK:PBD:**38(Tb)**/PBD/Al	– 4.0 (at 22 V)	53 53

Table 1 (continued).

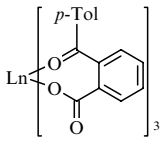
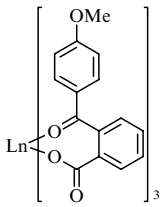
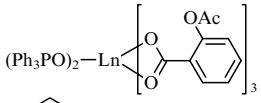
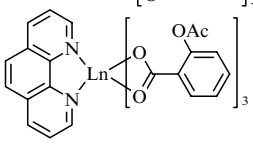
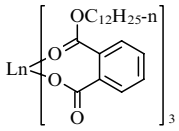
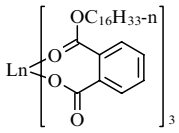
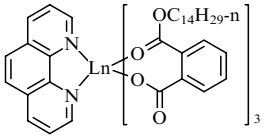
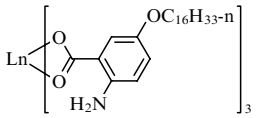
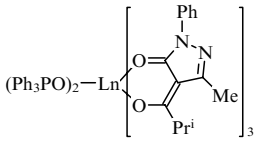
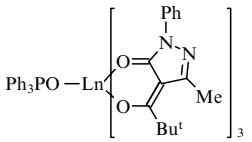
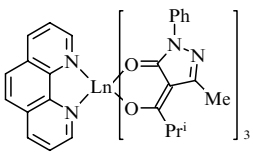
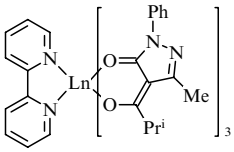
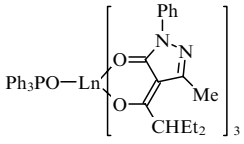
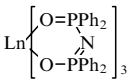
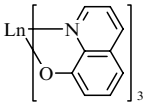
Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
39(Ln)	$Ln(mebb)_3$		ITO/PVK:PBD:**39(Tb)**/CaAl	0.7	54
40(Ln)	$Ln(meobb)_3$		ITO/PVK:PBD:**40(Tb)**/CaAl	7	54
41(Ln)	$Ln(as)_3(TPPO)_2$		ITO/PEDOT/PVK/**41(Tb)**/Al	–	55
42(Ln)	$Ln(as)_3(phen)$		ITO/PVK:**42(Tb)**/Al	–	56
43(Ln)	$Ln(mdp)_3$		ITO/PVK/PVK:PBD:**43(Tb)**/Alq_3/Al	16 (at 24 V)	57
44(Ln)	$Ln(mhp)_3$		ITO/PPV/PVK:**44(Tb)**:PBD/Alq_3/Al	74 (at 18 V)	58
45(Ln)	$Ln(mtp)_3(phen)$		ITO/PPV/PVK:**45(Tb)**:PBD/Alq_3/Al	152 (at 24 V)	59
46(Ln)	$Ln(ahb)_3$		ITO/PPV/PVK:**46(Tb)**:PBD/Alq_3/Al ITO/PVK:**46(Tb)**:PBD/Al	35 (at 20 V) 18 (at 14 V)	60 60
47(Ln)	$Ln(pmip)_3$-$(TPPO)_2$		ITO/TPD/**47(Tb)**/Alq_3/Al ITO/TPD/**47(Lu)**/BCP/Alq_3/Mg:Ag/Ag	920 (at 18 V) 119 (at 19 V)	61 62
48(Ln)	$Ln(tbpmp)_3$-$(TPPO)$		ITO/MTDATA/TPD/**48(Tb)**/TAZ/Al ITO/**48(Tb)**/Al ITO/**48(Tb)**/Ca	2200 (at 14 V) 6 (at 23 V) 226	63 63 64
49(Ln)	$Ln(pmip)_3(phen)$		ITO/TPD/**49(Gd)**/BCP/Mg:Ag/Ag ITO/TPD/**49(Lu)**/BCP/Alq_3/Mg:Ag/Ag	230 (at 17 V) 776 (at 17 V)	65 62

Table 1 (continued).

Type of complex	Formula	Structure	OLED Device	Maximum brightness /cd m^{-2}	Ref.
50(Ln)	Ln(pmip)$_3$(bipy)		ITO/TPD/**50(Lu)**/BCP/Alq$_3$/Mg:Ag/Ag	1010 (at 16 V)	62
51(Ln)	Ln(ebpmp)$_3$-(TPPO)		ITO/TPD/**51(Tb)**/Alq$_3$/Mg:Ag/Ag ITO/NPB/**51(Tb)**/BCP/Alq$_3$/Mg:Ag/Ag	20000 (at 20 V) 12000 (at 18 V)	66 66
52(Ln)	Ln(pip)$_3$		ITO/TPD/**52(Tb)**/Alq$_3$/Mg:Al	20 (at 25 V)	67
53(Ln)	Lnq$_3$		ITO/TPD/**53(Er)**/Al ITO/TPD/**53(Nd)**/Al ITO/TPD/**53(Yb)**/Al	–	68–71

[a] In this case, only two of six identical ligands are shown; [b] in the structural formula, the phen ligand is omitted for simplicity.

shell and partial or complete removal of degeneracy resulting in splitting of the energy levels (Fig. 2).[76]

It should be noted that emission can occur only from particular excited levels, which are indicated in the diagram presented in Fig. 2 by black semicircles. The schemes of electron transitions for selected lanthanide ions are shown in Fig. 3.

Some transitions can be made parity-allowed by admixing states of excited electron levels of the ligand to the states of the 4f^n-electronic configuration.[77] As a consequence, the luminescence intensity of lanthanide ions sharply increases upon complexation with certain organic ligands. In these compounds, the light energy is absorbed primarily by the organic moiety of the complex, *i.e.*, the ligand serves as an 'antenna' (Fig. 4).[78]

The mechanism of electroluminescence of lanthanide compounds includes three steps. The first step involves electron – hole recombination, resulting in exciton generation and excitation of the ligand to the singlet (S_1) and triplet (T_1) levels. In the second step, the energy of the excited ligand is transferred (from the triplet level) to the emitting level of the metal ion. The latter step involves emission from the corresponding level of the metal atom. Therefore, photoluminescence differs from electroluminescence only in the nature of excitation energy. It should be noted that, in the case of electroluminescence, the excitation of the T level of the ligand is not forbidden by quantum-mechanics. Since it is this level from which the energy transfer to metal occurs, the emitting level of the metal atom can be efficiently filled in the presence of an appropriate ligand. It is quite evident that the efficiency of energy transfer to the emitting levels of a lanthanide ion depends primarily on the nature of the ligand coordinated to this ion.[4] Of the rare-earth derivatives, β-diketonate, carboxylate, pyrazolonate and hydroxyquinolinate complexes are presently the most efficient electroluminescent materials for OLED devices.

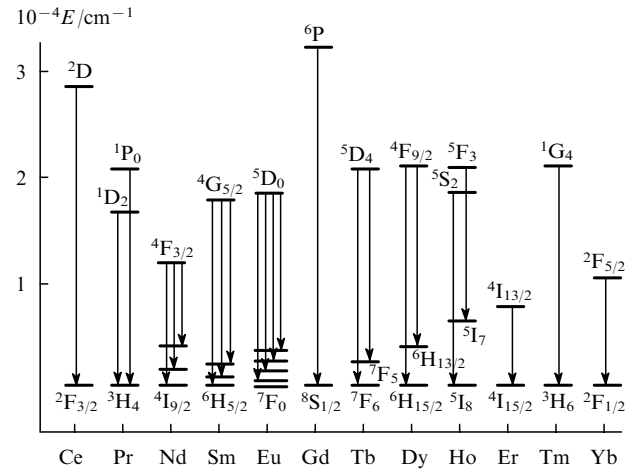


Figure 3. Diagrams of emission transitions in lanthanide ions.

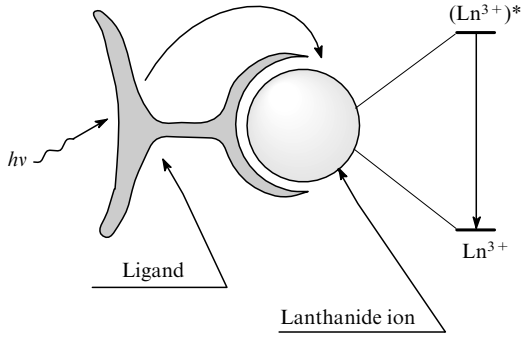


Figure 4. Scheme of energy transfers in lanthanide complexes.

III. Light-emitting diodes based on lanthanide coordination compounds

1. Light-emitting diodes based on rare-earth β-diketonates

The use of lanthanide complexes in the design of electroluminescent cells was documented for the first time in 1990.[12] Kido *et al.*[16] described a two-layer OLED with a structure of ITO/TPD/**1(Tb)**/Al based on terbium acetylacetonate [**1(Tb)**] with a maximum brightness of 7 cd m^{-2} at a current density of 0.4 mA cm^{-2}. In this case, the electroluminescence spectrum was found to be identical to the photoluminescence spectrum. The maximum emission was observed at 544 nm, which cor-

responds to the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb^{3+} ion. Shortly thereafter, the first europium OLED was constructed based on trifluoroacetylacetonate complex **5(Eu)**, which was molecularly dispersed in polymethylphenylsilane (PMPS) serving as a hole-transport layer.[16] The ITO/PMPS-**5(Eu)**/PBD/Mg/Ag device exhibited red emission characteristic of europium compounds with a maximum brightness of 0.3 cd m^{-2} at 18 V. Campos *et al.*[79] improved the luminescence characteristics of an analogous device based on complex **5(Eu)** with the use of a diamine hole-transport layer instead of polysilane, and a maximum brightness of $\sim$10 cd m^{-2} was achieved.

It should be noted that europium complexes proved to be the most promising luminescent materials for red emitters, because they generate monochromatic light with a wavelength of 614 nm, whereas known organic materials serving as emitters for the red spectral region give a broad band ($\sim$100 nm) resulting in colour distortion. At the same time, the theoretically predicted high luminescence efficiency of lanthanide complexes remains so far unachievable under real conditions. Some authors relate this problem to poor transport properties of lanthanide complexes and believe that this problem can be solved by choosing organic ligands, which improve this property of materials.

Nakaya and co-workers[34] used compound **15(Eu)** for the construction of the two-layer device ITO/TPD/**15(Eu)**/AlLi with a maximum brightness of 34 cd m^{-2} at 12 V. A comparison of these data with the properties of complex **18(Eu)** (7 cd m^{-2}), which has been used earlier for this purpose, led these authors to conclude that compound **15(Eu)** has good charge-transport properties in the solid state. More recently, this research group[35] used complex **16(Eu)** as an emitting and electron-transport layer in a two-layer OLED device. The characteristics of this device (32.0 cd m^{-2} at 9 V) were also attributed to the improved electron-transport properties due to the presence of the furyl fragment. Okada *et al.*[36] used 1,3-di(2-thionyl)propane-1,3-dione (dtp) as the β-diketonate ligand and 4,7-diphenyl-1,10-phenanthroline (bath) as the neutral ligand to prepare complex **17(Eu)**, and the latter was used for the construction of a three-layer OLED. The researchers observed bright red emission with a maximum brightness of 450 cd m^{-2} at 15 V. In the study,[41] the external efficiency of 3.5% and the maximum brightness of 924 cd m^{-2} at 380 mA cm^{-2} were achieved with the use of complex **25(Eu)** with mixed ligands.

Taking into account the good luminescent properties of azaindole, Wang *et al.*[18] synthesised terbium and yttrium complexes with the modified acetylacetonate ligands $[Ln(acac\text{-}azin)_3]_2$ [**7(Ln)**] and established their molecular structures by X-ray diffraction. The photoluminescence quantum yield of complex **7(Tb)** (11%) is lower than that of complex **1(Tb)** (19%). The low quantum yield is apparently associated with the fact that the triplet level of the ligand (22 220 cm^{-1}) is only 1720 cm^{-1} higher than the $^5D_4$ level of Tb^{3+} (20 500 cm^{-1}) and it does not provide essential excitation of the metal cation. However, the authors of the cited study succeeded in achieving the efficiency of 0.65 cd A^{-1} at 13 V by choosing an appropriate composition of PVK and PBD.

Wang *et al.*[15] focussed their attention on the synthesis of β-diketonate ligands containing oxadiazole fragments. These fragments were chosen because oxadiazole derivatives are widely used as electron-transport and hole-blocking materials. The external efficiency of the OLED device ITO/PVK : PBD : **4(Tb)**/$Al(pop)_3$/CsF/Al was $\sim$1.1% and 0.6% and the brightness was 100 and 550 cd m^{-2} at 15 and 20 V, respectively.

In the study,[44] the oxadiazole substituent was introduced into 2-(2-pyridyl)benzimidazole and the resulting compound was used as the neutral ligand in the europium complex $Eu(dbm)_3$(pybm-OXD) [**29(Eu)**]. A two-layer OLED device containing this compound [ITO/TPD/**29(Eu)**/LiF/Al] had an external quantum efficiency of 1.7% at 612 nm and a maximum brightness of 322 cd m^{-2} at 21 V. This study demonstrated that the introduction of the oxadiazole fragment into the lanthanide complex improves the charge-transport properties of the complex and simplifies the structure of an electroluminescent cell.

Chinese researchers[43,45] combined the phenanthroline fragment possessing the electron-transport properties and the triphenylamine fragment with the hole-transport properties in a neutral ligand. The resulting europium complex **30(Eu)** was used for the construction of the single-layer OLED ITO/**30(Eu)**/MgAg/Ag with a maximum brightness of 19 cd m^{-2} at 13.5 V and the four-layer device ITO/TPD/**30(Eu)**/BCP/Alq_3/MgAg/Ag with an external quantum efficiency of 0.85%, a light efficiency of 1.44 lm W^{-1} and a maximum brightness of 1305 cd m^{-2} at 16 V. With the aim of synthesising new highly efficient luminescent compounds, these authors[46] introduced the carbazole fragment into the neutral phenanthroline ligand. Devices based on compound **31(Eu)** exhibited excellent luminescent properties and had good stability. For example, the two-layer OLED ITO/TPD/**31(Eu)**/MgAg/Ag exhibited a maximum brightness of 537 cd m^{-2} at 13 V and an efficiency of 0.089 lm W^{-1}, the three-layer device ITO/TPD/**31(Eu)**/**14(Eu)**/MgAg/Ag exhibited a maximum brightness of 1050 cd m^{-2} at 16 V and an efficiency of 0.50 lm W^{-1}, and the four-layer device ITO/TPD/**31(Eu)**/BCP/Alq_3/MgAg/Ag had the highest brightness of 1460 cd m^{-2} at 14 V and an efficiency of 0.54 lm W^{-1}.

In the study,[43] two new ligands, *viz.*, 2-(2-pyridyl)benzimidazole (hpbm) and 2-(2-pyridyl)-1-ethylbenzimidazole (epbm), were used instead of phenanthroline. Europium complexes with these ligands, **27(Eu)** and **28(Eu)**, were used for the design of the OLED devices ITO/TPD/**27(Eu)**/Al, ITO/TPD/**28(Eu)**/Al and ITO/TPD/**28(Eu)**/Alq_3/Al. The brightness of ITO/TPD/**27(Eu)**/Al (29 cd m^{-2} at 11 V) is much higher than that of ITO/TPD/**28(Eu)**/Al (1.14 cd m^{-2} at 23 V). The authors believed that compound **27(Eu)**, like most europium complexes, has poor transport properties. More recently, these authors used thenoyl trifluoroacetonate (tta) as the central ligand[47] and found that the brightness of the OLED based on $Eu(tta)_3$(epbm) [**33(Eu)**] (36.6 cd m^{-2}) is much higher than that of the OLED based on $Eu(tta)_3$(hpbm) [**32(Eu)**] (< 7 cd m^{-2}).

In the study,[48] complex **34(Eu)** was synthesised with the use of substituted phenanthroline (dppz) as the central ligand, and the OLED ITO/TPD/**34(Eu)** : CBP/BCP/Alq_3 was constructed based on this complex; the external quantum efficiency of this device was 2.1% and the brightness was 1670 cd m^{-2}.

Presently, it is believed that ligands in complexes destined for the design of OLED devices should satisfy the following main requirements: (1) the triplet level of the ligand should match the emission level of metal; (2) the ligands should have the electron- and hole-transport properties to promote charge injection and exciton generation in the complex; (3) the complex should be easily deposited onto a support without the formation of aggregates and crystals and should be compatible with other components of the device.[26] It is evident that the position of the triplet level of the ligand relative to the corresponding level of metal is of considerable importance. However, in spite of numerous experimental and theoretical studies devoted to this problem, a theoretical model allowing the synthesis of the desired highly luminescent lanthanide complexes is lacking.

To simplify the task, comparative studies of related complexes are carried out with the aim of developing theoretical models. For example, Zheng *et al.*[13] investigated the photo- and electroluminescent properties of four terbium complexes, **1(Tb)**, **3(Tb)**, **8(Tb)** and **10(Tb)**. The comparative characteristics of OLED devices based on these complexes are given in Table 2.

It can be seen from this table that the introduction of fluorine atoms into the acetylacetonate ligand and additional coordination of the metal ion by the neutral phenanthroline ligand lead to an increase in the electroluminescence intensity. The emission bands of the ligand in the spectra of the complexes were not observed, which confirms high efficiency of excitation transfer from the levels of the ligand to the terbium ion in all four complexes. This led the authors to conclude[13] that the electroluminescence inten-

Table 2. Characteristics of the OLED devices ITO/PVK/PVK:Tb-complex:PBD/PBD/Al.[13]

Tb complex	Luminescence yield η (%)	Voltage /V	Maximum brightness /cd m^{-2}
10(Tb)	0.25	8	58
8(Tb)	0.16	10	36
3(Tb)	0.11	11	25
1(Tb)	0.08	13	17

sity of lanthanide complexes is determined primarily by the ratio of the energy of the triplet level of the ligand to the energy of the emission level of lanthanide. Theoretical and experimental studies demonstrated that for the ligand-to-metal energy transfer to occur, the emission level of the metal must be somewhat lower than the triplet level T_1 of the ligand, and the optimal difference $\Delta E(T_1 - {}^5D_4)$ for terbium complexes should be 2400±300 cm^{-1}. The triplet level of the fluorine-containing acetylacetonate ligand (22 720 cm^{-1}) is lower than that of the acetylacetonate ligand (25 310 cm^{-1}). Hence, the electroluminescence efficiency of complex **3(Tb)** with the Tb^{3+} ion ($^5D_4$ = 20 500 cm^{-1}) is higher than that of **1(Tb)** with the same ion.[80–84] The fact that the introduction of phenanthroline also increases luminescence was attributed to the intramolecular energy transfer from the β-diketonate ligand to phenanthroline (the triplet level of the β-diketonate ligand is much higher than that of phenanthroline), with the result that $\Delta E(T_1 - {}^5D_4)$ approaches the optimal value.[13]

The intramolecular ligand-to-ligand energy transfer providing the necessary height of the triplet level of the ligand was observed also in samarium complex **12(Sm)**.[26] Lowering of the energy of the triplet level of the bfa ligands (T_1 = 21 480 cm^{-1}) to 21 277 cm^{-1} (in the complex) due to the introduction of the phen ligand (T_1 = 21 400 cm^{-1}) is accompanied by a decrease in the distance between the triplet level and the emission level of the metal ($^4G_{5/2}$ = 18 000 cm^{-1}) and provides bright emission of the samarium ion. It should be noted that the luminescence spectrum of samarium consists of three main peaks at 563, 598 and 643 nm corresponding to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions, respectively, which is responsible for the orange colour of emission.[50] The two- and three-layer OLED devices ITO/MTCD/**36(Sm)**/Alq_3/Al and ITO/MTCD/**36(Sm)**/Al were constructed on the basis of complex **36(Sm)**; however, the luminescence intensity of both devices appeared to be low (~0.5 cd m^{-2}).[2,50]

The spectrum of thulium shows a narrow blue line at 480 nm assigned to the electron transition $^1G_4 \rightarrow {}^3H_6$.[85] This is presently the most desired colour of luminescence. However, data on the use of thulium compounds for the design of OLED devices are so far very scarce, probably because of the high price of this lanthanide. Li and co-workers[20] used complex **8(Tm)** for the construction of an OLED, but its characteristics unexpectedly appeared to be noticeably worse than those of the terbium analogue (the maximum brightness was as low as 6 cd m^{-2} at 16 V). The authors of the cited study believed that this is associated with large $\Delta E(T_1 - {}^1G_4)$ for the thulium complex (the triplet level of the acetylacetonate ligand is 25 500 cm^{-1}, the $^1G_4$ level of the Tm^{3+} ion is 21 196 cm^{-1}). In the study,[86] the $^1D_2$ level was considered as the emission level of the Tm^{3+} ion, and the absence of luminescence in complexes with the terphenyl ligands (the energy of the T_1 level in these ligands is ~23 500 cm^{-1}) was attributed to the high energy of the $^1D_2$ level (~27 800 cm^{-1}). However, an investigation of the photoluminescent properties of thulium β-diketonate complexes[85] confirmed emission in thulium from the $^1G_4$ (21 275 cm^{-1}) and $^3H_4$ (12 500 cm^{-1}) levels: $^1G_4 \rightarrow {}^3H_6$ (475 nm) (this transition has the maximum intensity), $^1G_4 \rightarrow {}^3F_4$ (650 nm), $^1G_4 \rightarrow {}^3H_5$ (780 nm) and $^3H_4 \rightarrow {}^3H_6$ (795 nm) (Fig. 5).

It was found[30] that the replacement of the acac ligand with the dbm ligand gives rise to electroluminescence in the ITO/TPD/**13(Tm)**/Mg:Ag and ITO/TPD/**14(Tm)**/Mg:Ag devices in the near-IR region. However, the emission intensity appeared to be much lower than that in analogous erbium complexes **13(Er)** and **14(Er)**.

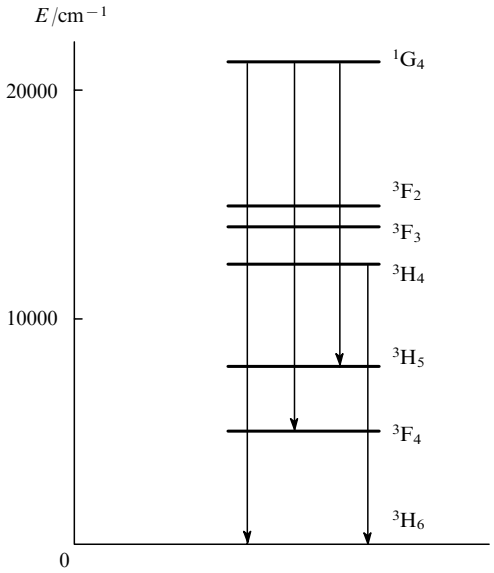


Figure 5. Diagrams of emission transitions in the Tm^{3+} ion.[85]

Holmium complex **14(Ho)** in an analogous OLED device with a structure of ITO/TPD/**14(Ho)**/Mg:Ag shows photo- and electroluminescence in the visible and near-IR regions.[33] Due to the presence of an intense band at a wavelength of 1500 nm, these complexes hold promise as materials for optical communications devices, for which the 1.3–1.5 μm region (a frequency window of modern light pipes) is of great importance.

Dysprosium tris(acetylacetonate) complex **8(Dy)** was used as an emitter for the construction of a white-emitting OLED cell.[21] The Dy^{3+} cation has two intense emission bands in the visible region, blue (~480 nm) and yellow (~580 nm), corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions. However, the drawbacks of this device are low resistance of the complex to voltage and weak luminescence (lower than 20 cd m^{-2}) associated, apparently, with inefficient energy transfer from the triplet level of the ligands to the dysprosium ion.

However, analysis of the spectra of numerous substituted europium β-diketonate complexes showed that the change in the luminescence intensity cannot be attributed solely to the difference in the energy of the triplet levels of the ligands.[87] In the cited study, the electron system of the β-diketonate ligand was changed by introducing substituents possessing different donor–acceptor properties and steric characteristics, the relative arrangement of the substituents in the ligands being varied and particular linking groups, which block energy transfer within the ligands, being constructed. These experiments demonstrated that an increase in the donating ability of the β-diketonate ligand, weakening of the Eu–N bonds, strengthening of the Eu–O bonds and the introduction of the methylene or oxymethylene bridges separating the π-electron system of the ligand from the Eu^{3+} ion lead to a decrease in the efficiency of the ligand-to-metal excitation energy transfer and, as a consequence, to a decrease in the luminescence intensity of europium.[87,88]

Bazan and co-workers[25] found that, in spite of the different nature of the substituents, the triplet levels of the tta, dbm, flta, flpa and flha ligands present in complexes **5(Eu)**, **2(Eu)**, **21(Eu)**, **22(Eu)** and **23(Eu)** are located in close proximity (in the region of 20 500 cm^{-1}). Hence, the corresponding β-diketonates should have similar efficiency of energy transfer from these ligands to the europium ion. However, the luminescence intensities of these complexes and cells constructed on their basis appeared to be

different. The best result was obtained for the ITO/TPD/**24(Eu)**:AZM-Hex/Mg device with a maximum brightness of 10 cd m^{-2}. It is expected that an increase in the purity of the starting compounds and optimisation of the structure of the device would allow an increase in the luminescence brightness.

Recently, Chinese researchers have achieved remarkable results by replacing the flha ligand in complexes **23(Eu)** and **23(Sm)** with the hfnh ligand.[40] New complexes **20(Eu)** and **20(Sm)** exhibited electroluminescence in the OLED devices ITO/TPD/**20(Eu)**:CBP/BCP/Alq_3/LiF/Al and ITO/TPD/**20(Sm)**:CBP/BCP/Alq_3/LiF/Al with maximum brightnesses of 967 and 42 cd m^{-2}, respectively.

It should be noted that a search for new organic ligands for lanthanide complexes destined for the construction of OLED devices was traditionally limited to oxygen- and nitrogen-containing compounds. However, the synthesis of terbium complex **52(Tb)** with the imidodiphosphinate ligands has been recently documented.[67] This compound showed photoluminescence with a quantum yield of 14%, the maximum brightness of electroluminescence in the OLED device based on this compound (ITO/TPD/**52(Tb)**/Alq_3/Mg:Al) was 20 cd m^{-2} at 25 V, and the external efficiency was 0.7 cd A^{-1}.

The Yb^{3+}, Nd^{3+}, Pr^{3+} and Er^{3+} ions are known to have emission bands in the near-IR region, *i.e.*, in the region of communications frequencies. However, complexes of these metals are of limited use as materials for OLED devices because of a low luminescence intensity. For example, the maximum quantum yield of neodymium, praseodymium and erbium acetylacetonate complexes is as low as 2.8×10^{-2}%.[89]

In attempting to find new luminescent materials, Voloshin *et al.*[52] synthesised neodymium and ytterbium thiodiketonate complexes **37(Nd)** and **37(Yb)**. However, the luminescent properties of these complexes appeared to be substantially worse than those of oxygen-containing analogues **36(Nd)** and **36(Yb)**, which was attributed to a substantially lower position of the triplet level of the sulfur-containing ligand (slightly higher than 12 000 cm^{-1}). These authors studied also Pr^{3+} β-diketonates and carboxylates[90] and demonstrated that emission in praseodymium complexes occurs not only in the IR region but also in the visible region depending on the energy of the triplet level of the ligand. However, the quantum yield is also very low (at most 0.2%).

The most efficient energy transfer from the triplet level of the ligand to the metal ion in fluorinated neodymium β-diketonates was observed in a compound containing the pentafluorophenyl substituents, which is characterised by the lowest triplet level of the ligand ($\Delta E \approx 1400$ cm^{-1}) and the largest overlap between the phosphorescence spectrum of the ligand and the absorption spectrum of Nd^{3+} in the 400–650 nm region.[91] An increase in the luminescence intensity was observed in neodymium complexes with asymmetric β-diketonate ligands, in which all C–H bonds are replaced with C–F or C–D bonds.[92] However, this increase is more likely to be attributable to weakening of luminescence quenching rather than to a change in the position of the triplet level.

In actuality, quenching processes play an essential role not only for lanthanides exhibiting luminescence in the near-IR region but also for all rare-earth metals. Hence, when searching for highly luminescent complexes for OLED devices, it is necessary to take into account the possibility of such processes occurring. For example, OH oscillators in coordinated water molecules were found to be the most efficient quenchers both in the solid state and in solution.[93–95] Other oscillators (NH, CH and C=O) are less active. The degree of quenching by water molecules is inversely proportional to the energy gap between the emission level and the ground state, and each oscillator independently quenches the excited state. The energy gaps for Yb^{3+}, Eu^{3+}, Tb^{3+}, Sm^{3+} and Dy^{3+} are approximately equal to 10 200, 12 300, 14 200, 7400 and 7850 cm^{-1} respectively.[86,96] Consequently, the emitting states of ytterbium and europium correspond to the third vibrational overtone of an OH oscillator ($\nu_{OH} \approx 3300-3500$ cm^{-1}), whereas the emitting state for terbium corresponds to the fourth harmonics. Hence, the efficiency of quenching by coordinated water molecules is much lower for the terbium ion. It is necessary to take into account the distance to the europium and terbium ions in the case of CH oscillators ($\nu_{CH} \approx 3050$ cm^{-1} for aromatic and $\nu_{CH} \approx 2950$ cm^{-1} for aliphatic). For example, quenching does not occur in complexes in which this distance is shorter than 3.4 Å.[86] Luminescence is not observed in Ho^{3+} complexes containing C–H bonds, because the energy transition $^5S_2 \rightarrow {}^5F_5$ [$\Delta E(Ho^{3+}) \approx 3000$ cm^{-1}] resonates with the CH vibrational mode ($\nu_{CH} \approx 2900-3100$ cm^{-1}). Deuteration of the ligand is inefficient in the case of Pr^{3+} [$\Delta E(Pr^{3+}) \approx 4100$ cm^{-1}] and Nd^{3+} [$\Delta E(Nd^{3+}) \approx 5300$ cm^{-1}], because the energy gaps in neodymium and praseodymium correspond to the first CD vibrational overtone.[86] The inductive resonance mechanism of radiationless transitions between the electronic levels of lanthanide ions in the condensed phase has been considered in detail in publications by Ermolaev and co-workers.[97–99]

2. Light-emitting diodes based on mixed β-diketonate complexes

In recent years, along with a selection of neutral ligands in complex compounds, a new line of research on the introduction of the second metal ion into complex molecules has assumed increasing importance.[19,100]

Li and co-workers[101] were the first to use the mixed $Eu_xTb_{1-x}(acac)_3(phen)$ complexes [**8(Eu,Tb)**] as an emitting layer. However, no data in support of the composition of this compound were presented. The device was reported to generate white emission resulting from mixing of the green emission of Tb^{3+} (550 nm), red emission of Eu^{3+} (616 nm) and blue emission of the NPB compound (450 nm). It was noted that the device is simple, but the luminescence characteristics were not published. More recently, these authors[19] considered the emission mechanism of complex **8(Eu,Tb)**. Interestingly, the maximum brightness of the composite ITO/PVK/**8(Tb)**/Al is 210 cd m^{-2}, whereas the maximum brightness of an analogous device with a europium complex, ITO/PVK/**8(Eu)**/Al, is as low as a few units of cd m^{-2}. In the luminescence spectrum of a device containing complex **8(Eu,Tb)** as the emitting layer, the red peak (615 nm) belonging to Eu^{3+} is much stronger than the green peak (545 nm) belonging to Tb^{3+}. The intensity of red emission in the mixed complex is 10 times higher than that of the mononuclear europium complex. The probable energy transfer process is shown in Fig. 6.

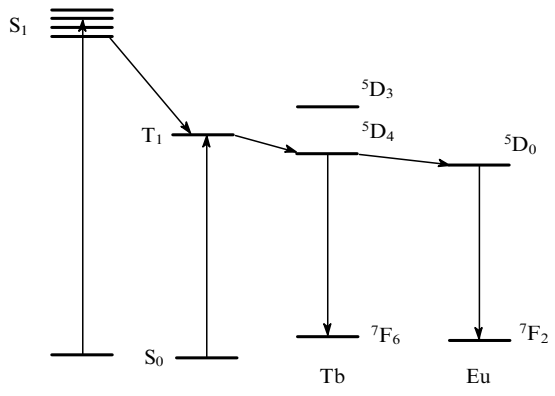


Figure 6. Energy diagram of dinuclear europium – terbium complexes.[19]

As can be seen from Fig. 6, several radiationless $S_1 \rightarrow T_1$ ($Tb^{3+} \rightarrow Eu^{3+}$) transitions are possible. As a result, the energy can be predominantly released through the $^5D_0 \rightarrow {}^7F_2$ emission of the Eu^{3+} ion. Hence, the red emission in the mixed compound is an order of magnitude more bright than that in the compound containing only europium.

An increase in the emission brightness from 32 to 99 cd m^{-2} on going from a mononuclear to dinuclear emitter was observed also for the OLED devices ITO/TPD/**18**(**Eu**)/Alq_3/Mg : Ag and ITO/TPD/**18**(**Eu**,**Y**)/Alq_3/Mg : Ag. It was hypothesised that the presence of the Y^{3+} ion promotes energy transfer from the triplet level of the ligand to the europium ion, resulting in an increase in the emission intensity.[39]

An alternative approach, which is also based on the use of several lanthanides in one OLED device, was described in the study.[23] With the aim of designing a white-emitting diode, a multilayer cell containing complex **9**(**Tb**) as the green (548 nm) emitting layer, complex **18**(**Eu**) as the red emitting layer (612 nm), the compound TPD as simultaneously the hole-transport and emitting (blue, 405 nm) layer and Alq_3 as the electron-transport layer was constructed. Actually, the device exhibited white emission, the emission brightness being 95 cd m^{-2}.

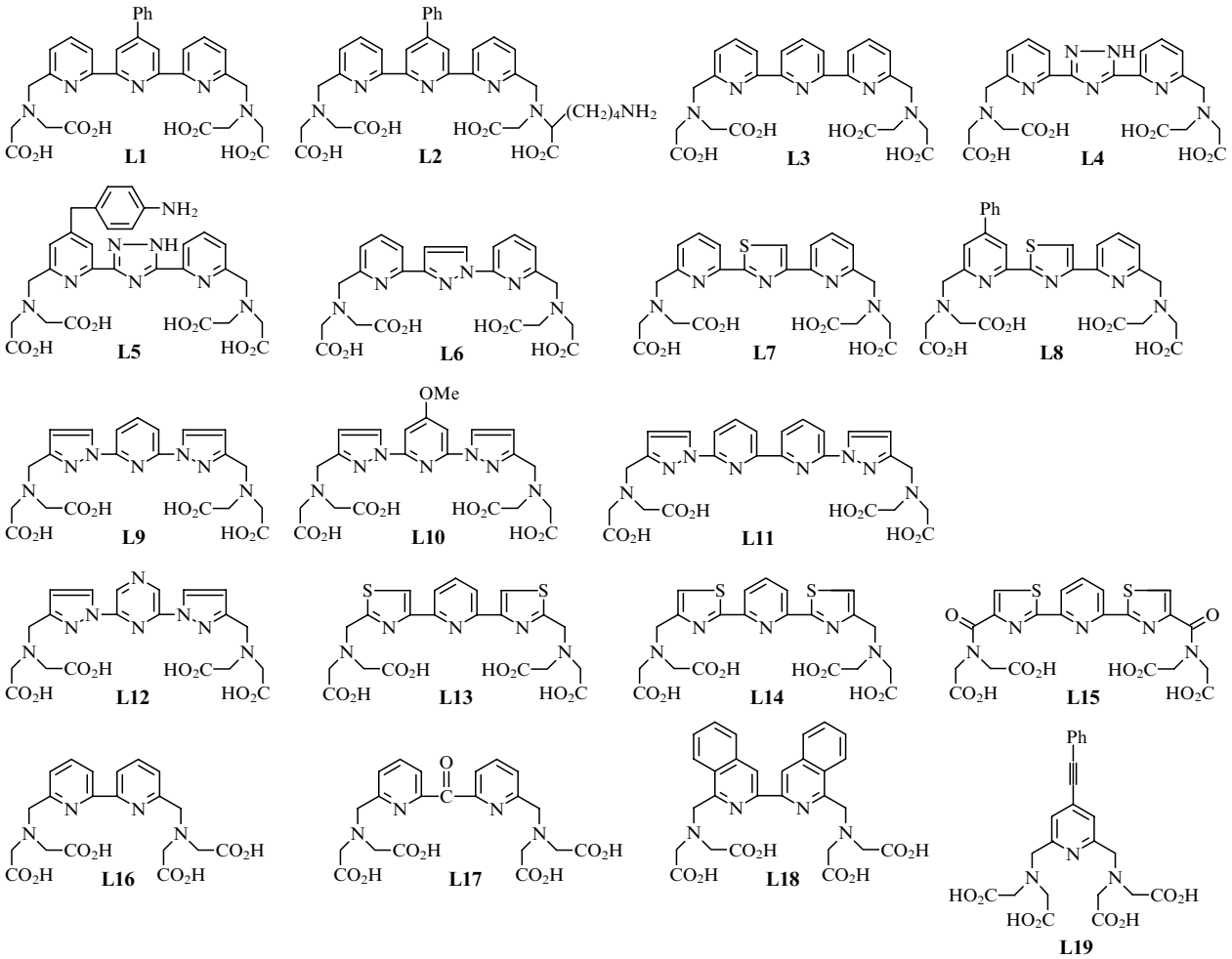
3. Light-emitting diodes based on rare-earth carboxylates

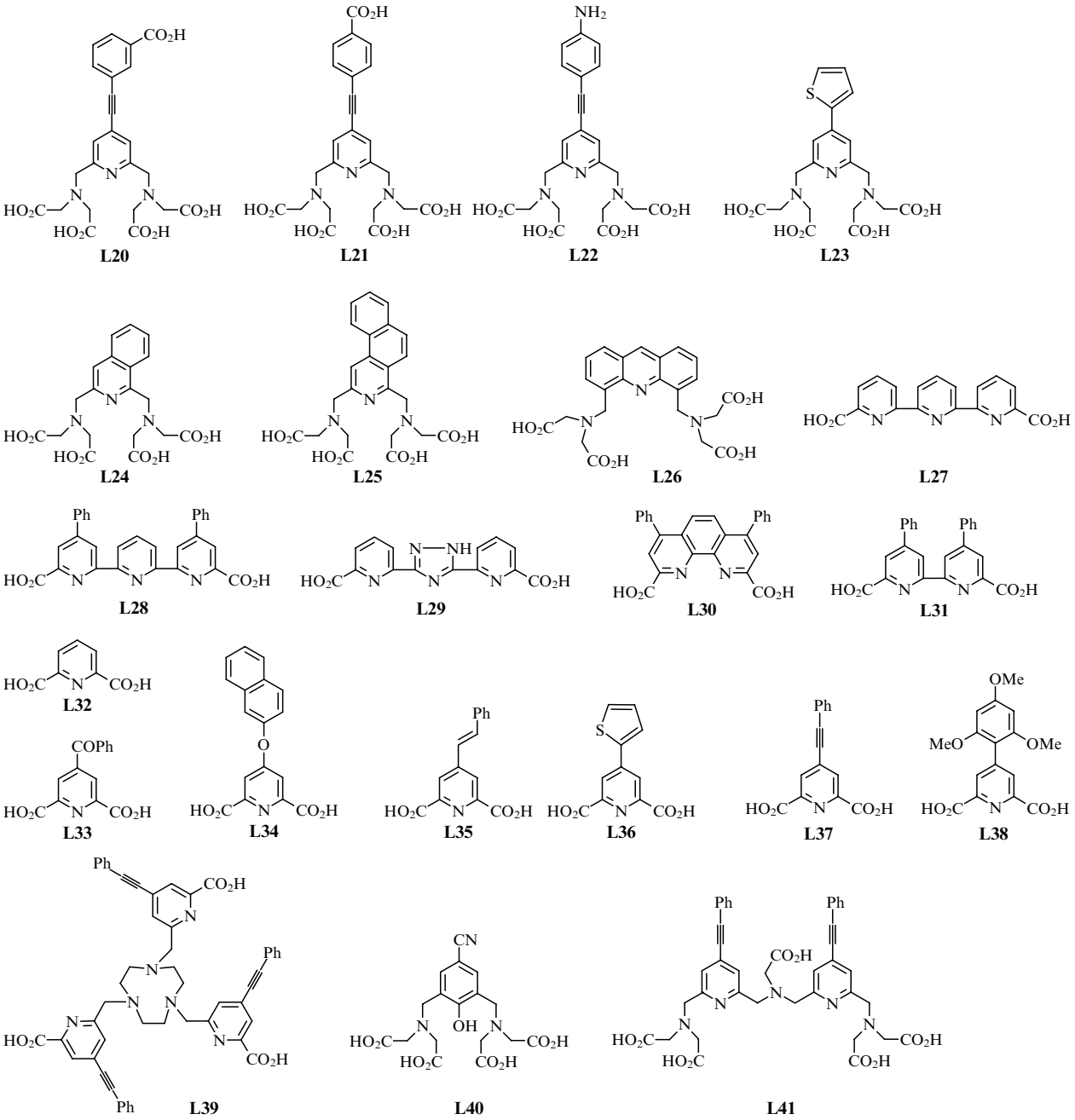
As mentioned above, most studies on luminescent lanthanide complexes with organic ligands dealt with β-diketonate complexes because they are readily accessible, stable in air and show rather high emission activity. However, a considerable drawback of these compounds is their low photo and thermal stability.[53] In this respect, another class of rare-earth complexes, *viz*., lanthanide carboxylates, have advantages. The latter not only have good ultraviolet absorption properties but also possess luminescence and thermal stability, which is better compared to the corresponding characteristics of β-diketonates.

It should be noted that lanthanide carboxylates are traditionally extensively studied by spectroscopic methods.[102, 103] In the review by Vicentini *et al*.,[104] the relationship between the molecular structure and emission spectra of metal ions was demonstrated with the use of numerous europium complexes (primarily, with carboxylates). The emission spectra were found to depend on the coordination number and symmetry. For example, the presence of two peaks belonging to the $^5D_0 \rightarrow {}^7F_0$ transition and a large number of peaks belonging to the $^5D_0 \rightarrow {}^7F_{1,2}$ transition are indicative of two different states of the europium ion. It was hypothesised that compounds characterised by broadened and poorly resolved $^5D_0 \rightarrow {}^7F_{1,2}$ transition bands have a polymeric nature. However, it was noted that a deep insight into the relationship between the structure and the luminescent properties requires that the structural data for complexes studied by spectroscopic methods be substantially extended.

Lanthanide carboxylates were used for the development of the concept of modeling of highly luminescent lanthanide systems. Latva *et al*.[105] studied more than 40 compounds with various carboxylate ligands **L1**–**L41** and confirmed the already known principle that the synthesis of luminescent europium and terbium compounds should be performed with the use of ligands having a high absorption coefficient and an efficient intrasystem transition from the singlet to triplet level. The efficiency of ligand-to-metal energy transfer and the luminescence quantum yield of Ln^{3+} depend on numerous factors, among which are the energy of the lower triplet level of the ligand (which plays the major role), the distance between the donor and acceptor in the luminophore molecule, quenching mechanisms, *etc*.

A range of compounds under study was chosen in such a way that the distance between the donor and acceptor remained virtually constant, the energy of the triplet level of the ligand being varied from 18 600 to 27 000 cm^{-1}. It was found for the first time that the triplet level of the ligand in the complex should be not only somewhat higher than the resonance level of the ion but also somewhat different, each lanthanide being characterised by its





own optimum ΔE. In the publication,[105] it was concluded that the difference between the triplet level of the ligand and the resonance level of terbium in terbium compounds should be no smaller than 1850 cm^{-1}. However, the exact energy gap for europium compounds remains unknown. The dependence of the quantum yield of terbium and europium compounds on the position of the triplet level of the ligand is shown in Fig. 7.

The following dependence (the so-called Latva rule) was revealed: the optimum gap widths for Eu^{3+} and Tb^{3+} are $2500 < \Delta E(^3\pi\pi^* - {}^5D_0) < 3500$ and $2500 < \Delta E(^3\pi\pi^* - {}^5D_4) < 4000$ cm^{-1}, respectively.[105]

In addition, investigation of carboxylate complexes[106] demonstrated that the intrasystem transfer is efficient when the difference between the singlet and triplet levels of the ligand $\Delta E(^1\pi\pi^* - {}^3\pi\pi^*)$ is ~ 5000 cm^{-1}. For example, the luminescence quantum yields for europium and terbium complexes with the 5′-methyl-2,2′-bipyridyl ligands containing the carboxyl or phosphonium substituent at position 6 do not satisfy the Latva rule. The ratio of the quantum yields opposite to the above rule was attributed to the fact that $\Delta E(^1\pi\pi^* - {}^3\pi\pi^*)$ for a phosphonium-containing ligand (6750 cm^{-1}) is closer to the ideal value (5000 cm^{-1}) compared to the carboxyl-containing analogue (7100 cm^{-1}).

The introduction of the neutral coordinated phenanthroline ligand into lanthanide carboxylates was found[107,108] to increase luminescence. Presumably, a new ligand-to-ligand transition occurs if the level of the neutral ligand is lower than the triplet level of the main ligand and, as a consequence, the energy transfer from phenanthroline to the lanthanide ion increases. Tsaryuk *et al.*[109] studied photoluminescence of europium acetates $Eu(OAc)_3$(phen-R), where phen-R is 3,4,7,8-tetramethyl-, 5-methyl-, 5-phenyl-, 4,7-diphenyl- or 5-nitrophenanthroline, and found that the nature of phenanthroline has no effect on the luminescent properties of the complexes.

An alternative approach to the design of highly luminescent lanthanide carboxylates was developed by Selvin and co-workers.[110–114] This method is based on the use of well-known organic laser dyes, which enhance emission in complexes, as substituents

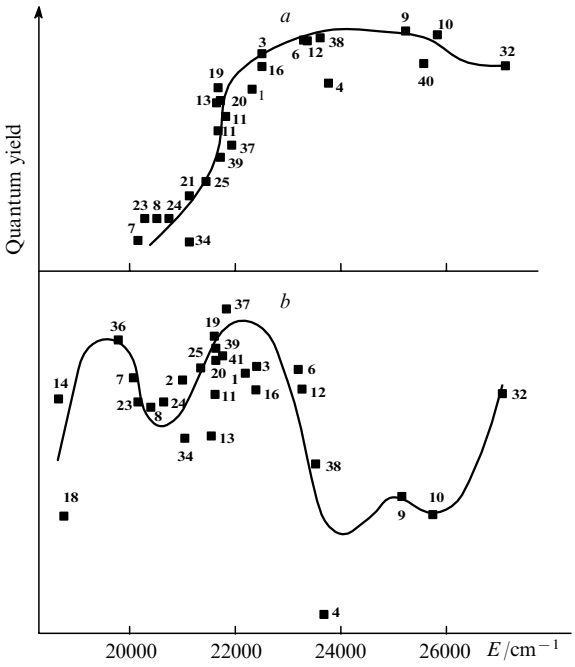


Figure 7. Plots of the quantum yields of terbium (*a*) and europium (*b*) carboxylate complexes *vs.* the energy of the triplet level of the ligand.[105] (The letter L in the notations of the ligands is omitted for simplicity.)

in the carboxylate ligand. However, this modification of the carboxylate ligand appeared to be inefficient.

In spite of considerable progress in theoretical studies concerned with luminescence of lanthanide carboxylates, publications on the use of these compounds in electroluminescent devices are few in number.

Edwards *et al.*[54] synthesised europium and terbium benzoylbenzoate complexes, which gave rather high photoluminescence quantum yields: **39(Tb)**, 4%; **40(Eu)**, 16%; and **40(Tb)**, 27%. However, electroluminescence was not observed in compound **40(Eu)**, and the maximum brightnesses of OLED devices based on compounds **39(Tb)** and **40(Tb)** are as low as 7 and 0.7 cd m^{-2}, respectively.

The OLED devices with structures of ITO/PVK/PVB : PBD : **38(Tb)**/PBD/Alq_3/Al and ITO/PVK/PVB : PBD : **38(Tb)**/PBD/Al were designed on the basis of terbium acetylsalicylate **38(Tb)**.[53] The electroluminescence spectrum of the terbium ion was not observed for the former device, whereas the latter showed strong green emission characteristic of Tb^{3+} with a maximum brightness of 4.0 cd m^{-2} at 22 V.

Electroluminescence typical of the terbium ion (545 nm) was observed in the OLED cell ITO/PEDOT/PVK/**41(Tb)**/Al based on terbium acetylsalicylate containing neutral triphenylphosphine oxide.[55] Bright green electroluminescence of terbium at 547.5 nm was observed also in the three-layer OLED device ITO/PVK : **42(Tb)**/Al.[56]

A drawback of carboxylate derivatives of lanthanides as luminophores for OLED devices is their low solubility. To increase solubility, oligomeric hydrocarbon substituents are introduced into the organic moiety of complexes. For example, Chinese researchers[58] synthesised readily soluble terbium hexadecylphthalate complex **44(Tb)** and designed the OLED device ITO/PPV/PVK : **44(Tb)** : PBD/Alq_3/Al on the basis of this complex with a maximum brightness of 74 cd m^{-2} at 18 V. In the discussion, these authors noted that, according to the Latva rule, luminescence of the Tb^{3+} ion was observed at the difference T_1(22 951 cm^{-1}) − $^5D_4$(20 500 cm^{-1}) = 2331 cm^{-1}. The position of the triplet level of the ligand was determined using an analogous gadolinium complex.

More recently, terbium monododecylphthalate complex **43(Tb)** containing a shorter alkyl chain was synthesised.[57] The OLED device ITO/PVK/PVK : PBD : **43(Tb)**/Alq_3/Al also showed green emission with a maximum brightness of 16 cd m^{-2} at 24 V.

In the study,[59] terbium monotetradecylphthalate phenanthroline complex **45(Tb)** was used to design the OLED device ITO/PPV/PVK : **45(Tb)** : PBD/Alq_3/Al with a maximum brightness of 152 cd m^{-2} at 24 V and an external quantum efficiency of 0.017%. The electroluminescence spectrum of the cell was identical to the photoluminescence spectrum in which the most efficient transition is observed from $^5D_4$ to $^7F_5$ at 545 nm with a linewidth of at least 10 nm.

Zheng *et al.*[60] synthesised a new carboxylate ligand, *o*-amino-4-cetylbenzoate, and used it to prepare terbium complex **46(Tb)**. The OLED device ITO/PPV/PVK : **46(Tb)** : PBD/Alq_3/Al showed characteristic emission of the terbium ion with a maximum brightness of 35 cd m^{-2} at 20 V, the characteristics of the device ITO/PVK : **46(Tb)** : PBD/Al being worse (the maximum brightness was only 18 cd m^{-2}).

4. Light-emitting diodes based on rare-earth complexes containing pyrazolone ligands

In recent years, a new class of compounds, *viz.*, lanthanide complexes with pyrazolone ligands coordinated to the metal ion through the chelate β-diketonate group (Table 1, compounds **47**–**51**), has attracted the attention of researchers concerned with the design of materials for image converters.[63] The heteroligand complex $Eu(tta)_2$(pmbbp)(phen) [**35(Eu)**] synthesised by Tsutsui and co-workers[49] is one of the first compounds belonging to this class. The light-emitting diode ITO/TPD/**35(Eu)**/Alq_3/Mg : Al prepared on the basis of the above complex generated emission at a wavelength of 613 nm with a brightness of 16 cd m^{-2} at 12.5 V, which is twice as good as for compound **18(Eu)**. By contrast, the $Eu(pmbbp)_3$(phen) complex does not show luminescence at all because of the low position of the triplet level of the ligand. It was expected that luminescence in mixed-ligand complex **35(Eu)** would be low due to energy transfer from the thiophenediketonate ligand to the pyrazolonediketonate one. The observed increase in luminescence was attributed to the improvement of the charge-transport properties of the complex.

Huang and co-workers[61] found that compound **47(Tb)** also possesses good electron-transport properties. The diode ITO/TPD/**47(Tb)**/Alq_3/Al designed on the basis of this complex has a maximum brightness up to 920 cd m^{-2} at 18 V and a luminescence efficiency of 0.51 lm W^{-1} at a current density of 0.70 mA cm^{-2}.

In the study,[63] a brightness of 2200 cd m^{-2} at 14 V was achieved in the OLED device ITO/MTDATA/TPD/**48(Tb)**/TAZ/Al designed with the use of new terbium pyrazolone complex **48(Tb)**. The maximum efficiency of the device was 2.6 lm W^{-1} at a brightness of 25 cd m^{-2}. Interestingly, the maximum brightness of the single-layer cell ITO/**48(Tb)**/Al was only 6 cd m^{-2} at 23 V. The use of a potassium cathode made it possible to increase the maximum brightness and the efficiency to 226 cd m^{-2} and 0.67 cd A^{-1}, respectively.[64] However, the maximum brightness of 2200 cd m^{-2} was achieved with the use of an appropriate combination of electron- and hole-transport layers. This result shows once again that the efficiency of devices substantially depends on their composition.

Complex **49(Gd)** was used[65] as the electron-transport and emission layer. The observed green emission at 535 nm characterises the pyrazolone complex as ligand-emitting. The maximum brightness of an OLED device designed on the basis of this complex is 230 cd m^{-2} at 17 V. Another example of the use of lanthanide complexes as ligand-emitting rather than traditional metal-emitting compounds was given in the study,[62] where the synthesis of three lutetium pyrazolone complexes, **47(Lu)**, **49(Lu)** and **50(Lu)**, was documented. Complex **47(Lu)** was studied by X-ray diffraction. The results of this study confirmed the fact that

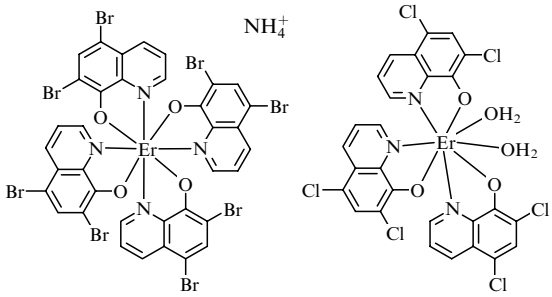
the nature of the neutral ligand may strongly affect the luminescence intensity. The photoluminescence spectra of all complexes are similar. However, the intensity for complex **47(Lu)** appeared to be 100 times higher. At the same time, the brightness of electroluminescence of the OLED device ITO/TPD/**47(Lu)**/BCP/Alq_3/Mg : Ag/Ag constructed with the use of this complex was at most 119 cd m^{-2} at 19 V, whereas a brightness of 1010 cd m^{-2} at 16 V was achieved in the ITO/TPD/**50(Lu)**/BCP/Alq_3/Mg : Ag/Ag device designed on the basis of a bipyridyl complex, whose photoluminescence characteristics are worse, and the brightness of the ITO/TPD/**49(Lu)**/BCP/Alq_3/Mg : Ag/Ag device designed with the use of a phenanthroline complex was 776 cd m^{-2} at 17 V. Triphenylphosphine oxide complex **47(Lu)** was found to have good transport properties, whereas the bipyridyl [**50(Lu)**] and phenanthroline [**49(Lu)**] complexes easily form exciplexes with TPD having high emission brightness. These data show that not only highly photoluminescent complexes but also compounds, which are weakly photoluminescent but form exciplexes with high electroluminescence efficiency, can be used as emitters for OLEDs. The authors believed that the function of a neutral ligand is to provide energy exchange between the neutral and valence-bound ligands. In the bipyridyl [**50(Lu)**, 280 nm] and phenanthroline [**49(Lu)**, 265 nm] complexes, the luminescence decreases as a result of energy transfer from the pyrazolone ligand to the neutral ligand, whereas this transfer does not occur in TPPO-containing complex **47(Lu)**.[115] It should be noted that the ITO/TPD/**47(Tb)**/Alq_3/Al device has the better luminescent properties with a maximum brightness of 2680 cd m^{-2}. These data suggest that the main role of the neutral ligands is to change the transport properties of materials. More recently, Huang *et al.*[116] successfully used compound **47(Tb)** as an electron-transport layer instead of Alq_3, which also confirmed the excellent electron-transport properties of this compound.[66] In complex **51(Tb)**, the number of coordinated triphenylphosphine oxide groups was decreased due to the steric effect of the new pyrazolone ligand, which provides a balance between the hole- and electron-transport properties of the complex. However, the brightness of a single-layer device based on this compound is as low as 46 cd m^{-2}. The use of additional hole- (TPD) and electron-transport (Alq_3) layers made it possible to increase the emission brightness of the diode ITO/TPD/**51(Tb)**/Alq_3/Mg : Ag/Ag to 20 000 cd m^{-2} at 20 V, and the efficiency was increased to 3.24 lm W^{-1}. A further optimisation of the device [ITO/NPB/**51(Tb)**/BCP/Alq_3/Mg:Ag/Ag] resulted in an increase in the efficiency to 11.4 lm W^{-1} at 7 V and the maximum brightness to 12 000 cd m^{-2} at 18 V.

5. Light-emitting diodes based on rare-earth complexes containing quinoline derivatives as ligands

In spite of the fact that the first brief communication [117] on the design of a single-layer light-emitting diode with the use of neodymium 8-hydroxyquinolinate was published almost 10 years ago, 8-hydroxyquinoline derivatives of lanthanides have attracted considerable attention only in 1999 after a series of publications on infrared emission in an erbium 8-hydroxyquinolinate-based OLED device, in which the erbium compound was used as the emission and electron-transport material.[2,3] The electroluminescence at a wavelength of 1.53 μm associated with the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was observed in the ITO/TPD/**53(Er)**/Al device containing erbium 8-hydroxyquinolinate.[68,69] Analogous diodes based on Nd^{3+} complexes show electroluminescence at 0.9, 1.06 and 1.32 μm (Nd^{3+}),[70] whose highest peak (1.06 μm) corresponds to the $^4F_{3/2} \rightarrow {}^4F_{11/2}$ transition. The luminescence of a diode containing ytterbium 8-hydroxyquinolinate at 0.98 nm is associated with the interatomic $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.[71] Investigation of the kinetics of electroluminescence of the Erq_3 complex revealed two different times (0.23 and 2.2 ms). In the study,[118] this was attributed to the occurrence of different intraatomic transitions in the erbium ion.

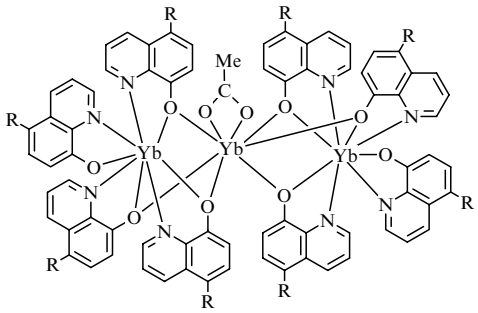
It was noted that the electroluminescence in devices based on hydroxyquinoline derivatives of lanthanides is substantially weaker than the photoluminescence of the same complexes. Additional studies by time-resolved photoluminescence [119] demonstrated that the luminescence intensity is substantially influenced by deactivation processes, which depend on the nature of the solvent and ligands. It was estimated [119] that the luminescence efficiency of erbium 8-hydroxyquinolinate can vary in the range of 0.002% – 0.03%.

It should be noted that rare-earth 8-hydroxyquinolinates, which were used for the construction of the above-mentioned OLED devices, were not structurally investigated. It was believed that all these compounds are structurally similar to the well-known aluminium analogue Alq_3. This assumption was indirectly confirmed by investigation of thin films of erbium and ytterbium 8-hydroxyquinolinates by X-ray photoemission spectroscopy.[120] However, recent X-ray diffraction studies demonstrated that rare-earth 8-hydroxyquinolinates have various structures, which are sharply different from that of the aluminium compound. It was found that none of lanthanide complexes corresponds to the formula Lnq_3.[121] Compound **A**, which is most compositionally similar to Lnq_3, contains, in addition to the metal atom and three 8-hydroxyquinolinate ligands, an ammonium cation. In complex **B**, the metal ion is coordinated by two water molecules.

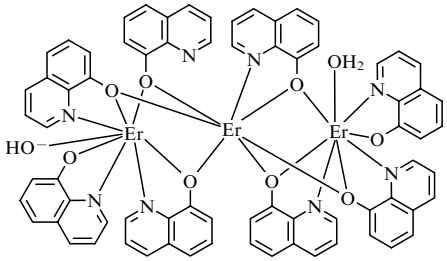


A **B**

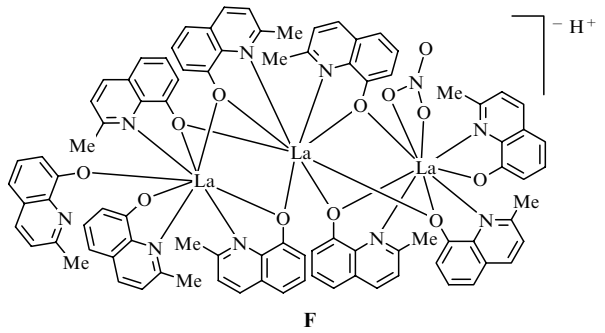
All other known lanthanide quinolinates are trinuclear clusters containing Ln^{3+} cations coordinated by the 8-hydroxyquinolinate anions.



C (R = H),
D (R = Cl).



E



F

In complexes **C** and **D**, the central atom in the Ln – Ln – Ln group is coordinated by the acetate anion, whereas one of the terminal erbium atoms in compound **E** is coordinated by both the quinolinate ligands and the hydroxy group. Compound **F** [122] studied by X-ray diffraction and ^{1}H NMR spectroscopy is of particular interest. In the molecules of the latter, one of the 8-hydroxyquinolinate ligands is coordinated in a monodentate fashion, which is unusual for such complexes, and contains the N – H group.

Electroluminescence of the above-mentioned complexes, as well as of the recently prepared quinolinates containing no water and acidic residues, was not studied.[122] However, their photoluminescence spectra confirm the above-mentioned quenching with coordinated water molecules, organic solvent molecules or acidic residues.

IV. Optimisation of lanthanide-containing light-emitting diodes

In the design of highly efficient lanthanide-based OLED devices, not only a high luminescence intensity of these complexes but also optimisation of the construction of a light-emitting element, *i.e.*, the use of an optimal combination of materials of electrodes and electron-transport, hole-transport and emitter layers, is of great importance. For example, the maximum brightness of compound **13(Eu)** in a single-layer OLED device is as low as 0.3 cd m^{-2}, whereas the maximum brightness of the ITO/TPD/**13(Eu)** : PBD/Alq_3/Mg : Ag device, which was prepared [27] by introducing this compound into a layer of 1,3,4-oxadiazole (PBD) possessing good electron-transport properties, is 460 cd m^{-2}. Presumably, a substantial increase in the maximum brightness is associated with primary excitation of oxadiazole due to charge recombination. The excitation energy is transferred to the ligand and then to lanthanide. Li *et al.*[123] noted that an OLED device, which was constructed with the use of PVK as the hole-transport layer and complex **8(Tb)** as the emission layer, showed bright luminescence with a maximum brightness of 210 cd m^{-2}, whereas pure green emission of the Tb^{3+} cation at 545 nm was not observed in a device constructed with the use of TPD as the hole-transport layer.

Doping of the TPD layer with complex **14(Eu)** led to an increase in the brightness of the two-layer device ITO/TPD/**14(Eu)**/Mg : Ag from 150 to 820 cd m^{-2}; the external quantum efficiency was 1%.[31] Simultaneously, the emission time was increased from 18 to 200 h and the colour purity was considerably improved. The authors believed that compound **14(Eu)** possesses excellent electron-transport properties.

Study of the electroluminescent properties of europium complex **13(Eu)** showed [29] that the two-layer device ITO/TPD/**13(Eu)**/Mg : Ag/Ag based on this complex has a narrow emission peak at 613 nm; however, the maximum brightness is low (3.7 cd m^{-2} at 17 V). The poor performance was attributed to the insufficiently good electron-transport properties of the complex. The introduction of Alq_3 as an additional electron-transport layer into a device resulted in yellow emission due to simultaneous emission of Alq_3 and **13(Eu)**. With the aim of improving the electroluminescent device, a BCP layer was added as a hole-blocking layer. The resulting ITO/TPD/**13(Eu)**/BCP/Alq_3/Mg : Ag/Ag diode showed pure red emission (615 nm) with a maximum brightness of 42 cd m^{-2} at 16 V. Luminescence of Alq_3 was found to be absent in this device due to the presence of the BCP layer, which blocks hole injection, with the result that electron – hole recombination occurs only within the layer composed of the europium compound.

Forrest and co-workers [37] studied electroluminescence of complex **18(Eu)** doped into a CBP layer with a wide energy gap, which is responsible for bipolar charge transfer. In the cited study, a maximum external quantum efficiency of 1.4% was achieved for a 'guest – host' system at a low current density. An increase in the density from 1 to 100 mA cm^{-2} led to a substantial decrease in the efficiency due to triplet – triplet annihilation. The OLED devices ITO/TPD/**18(Eu)** : CBP/BCP/Alq_3/MgAg, which differ in the concentration of **18(Eu)** (1%, 2% and 100%), possess different characteristics. The device containing 100% of the europium complex as an emitter exhibited the poorest performance (the maximum brightness was 32 cd m^{-2}), whereas the device containing 1% of the europium complex had the best performance (the maximum brightness was 500 cd m^{-2} at 100 mA cm^{-2}).

The light-emitting diode based on compound **26(Eu)**, ITO/TPD/**26(Eu)**/BCP/Alq_3/(Mg : Ag or Al : Li), exhibited pure red emission with a maximum brightness of 320 cd m^{-2} at 14.5 V, whereas the OLED device ITO/TPD/**26(Eu)**/Alq_3/Mg : Ag, which does not include a BCP layer serving as a hole-blocking material, showed only yellow emission with a brightness of 420 cd m^{-2} (see Refs 42, 124).

The introduction of complex **13(Eu)** (20%) into a matrix possessing the hole-transport properties led to an increase in the brightness of the OLED device ITO/CuPc/**13(Eu)** : NPD/BCP/Alq_3/LiF/Al to 200 cd m^{-2} (see Ref. 125).

In the study,[126] it was demonstrated that doping of complex **13(Eu)** into phosphorescent layers of dimethoxybenzophenone or triphenylacetophenone also led to a slight increase in electroluminescence.

According to the results of the investigation,[32] compound **14(Eu)**, unlike phenanthroline complex **13(Eu)**, possesses excellent electron-injection, transport and luminescent properties. This compound combined with PVK in the ITO/PVK/**14(Eu)**/Mg : Ag diode exhibits pure monochromatic red emission with a brightness 400 cd m^{-2} at 15 V. The replacement of PVK with NPB (ITO/NPB/**14(Eu)**/Mg : Ag) leads to a substantial change in the emission colour: a broad band at 483 nm appears in addition to the narrow emission band of Eu^{3+} at 615 nm with the result that the colour of the device becomes white with a maximum brightness of 550 cd m^{-2} at 9 V. The authors of the study [32] believed that the presence of electroluminescence at a low operating voltage ($\sim$2 V) is proof of the excellent electron-injection and electron-transport properties of complex **14(Eu)**. Since the broad band at 483 nm cannot be assigned to the NPB compound, which has its own luminescence band at 440 nm, this band is, apparently, caused by emission of an exciplex, that appears between the layers of NPB and compound **14(Eu)**.

After introduction of complex **18(Eu)** into hole-transport PVK, the OLED device gives a maximum brightness of 30 cd m^{-2}. The addition of the same complex to electron-transport PBD leads to an increase in the brightness of 417 cd m^{-2}.[127] The maximum luminescence intensity of the single-layer OLED device ITO/**18(Eu)** : PVK/Mg : In was observed at a concentration of 0.12 mol.% of **18(Eu)** in PVK.[128] The use of another electron-transport material (PBD) as a matrix for compound **18(Eu)** made it possible to construct the OLED ITO/TPD/**18(Eu)** : PBD/PBD/Mg with a maximum brightness of 320 cd m^{-2} and an external quantum efficiency of 1%.[38] The maximum brightness of 137 cd m^{-2} was observed,[129] when complex **18(Eu)** was used as a dopant (5%) to the azomethine zinc complex in the emitter layer.

Wong and co-workers [130, 131] studied electroluminescence of europium and samarium complexes **36(Eu)** and **36(Sm)**. The observed luminescence of samarium complexes compared to that of europium complexes was too low. Hence, single-, two and

three-layer OLED devices were constructed with the use of europium complexes. A single-layer device exhibited very low quantum efficiency. A two-layer device was much more efficient due to the presence of TPD as the HTL layer. The introduction of the third ETL layer (Alq_3) did not lead to substantial changes. In another study,[51] a maximum brightness of 10 cd m^{-2} at an operating voltage of 18 V was achieved by constructing an analogous OLED device consisting of compound **36(Eu)**, TPD and Alq_3.

An orange-emitting OLED device with a maximum brightness of 135 cd m^{-2} has been recently constructed [26] with the use of complex **12(Sm)** in combination with PVK and PBD.

Dispersion of compound **8(Er)** into a polymeric PVK matrix afforded the OLED device ITO/PVK: **8(Er)**/Al : Li/Ag with infrared electroluminescence at 1.54 μm.[22] Li and co-workers [132] studied interactions between PVK and various Tb and Eu complexes and found that efficient energy transfer processes occur between PVK and lanthanide complexes.

The above data show that energy transfer processes from a matrix to a compound should be taken into account when rare-earth compounds are used as dopants. It is generally agreed [14] that the energy, which is generated in OLED devices containing lanthanide β-diketonates as dopants upon charge recombination, is transferred from the matrix to the singlet excited state of the ligand, from which it is transferred to the triplet level of the ligand as a result of intersystem crossing, and is finally transferred to the metal ion. In this connection, two main problems should be taken into account in the design of devices: (1) the efficiency of energy transfer from the matrix to lanthanide β-diketonates; (2) the efficiency of energy transfer from the triplet level of the ligand to the metal ion.

In the study,[125] three main mechanisms of excitation of lanthanide complexes in a matrix were proposed.

1. A complex is excited as a result of energy transfer from the matrix to the complex. In this case, the Frenkel exciton should be formed within the emitter layer, in which the resonance transfer of the electronic excitation energy to the complex molecule occurs. If the energy transfer occurs by the Forster mechanism (a dipole mechanism), the spectral overlap between emission bands of the matrix and absorption bands of the complex should take place. If the energy transfer is based on exchange interactions according to the Dexter mechanism (an exchange mechanism), the correspondence between the energy levels and interactions of the involved orbitals are of importance.

2. A complex becomes excited as a result of charge transfer from the matrix, *i.e.*, electrons and holes, which are separately transported to the complex molecule, recombine with the result that the energy is released, and the latter is transferred to the metal ion serving as an emission centre. This requires particular properties of the complex providing simultaneous electron and hole capture.

3. If the emission layer consists only of complex molecules, the latter, as in the previous case, are excited due to recombination of the opposite charges on the complex molecules. Excitation of the complex is most efficient if the charge injection (electron and hole injection) in a layer is balanced and the charges are present at a high concentration and are highly labile. The charge balance can be controlled by introducing an additional charge-blocking layer.

Bazan and co-workers [25] demonstrated that the correspondence between the absorption spectra of the matrix and the dopant is of importance for the design of 'guest–host' systems. For example, the electroluminescence efficiency in a polycyanophenylene (CN-PPP) matrix decreases in a series **19(Eu)** (1.1%) > **13(Eu)** (0.7%) > **11(Eu)** (0.1%) > **8(Eu)** (0.03%), which corresponds to absorption spectra of europium complexes and emission spectra of CN-PPP (Fig. 8).

It was hypothesised [133] that complexes with higher emission energy compared to the absorption energy of the dopant should be used as a matrix for the design of devices with europium-based

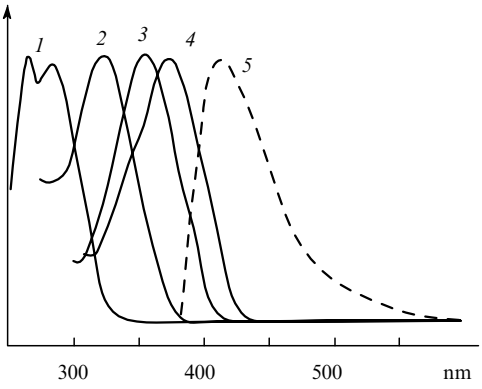


Figure 8. Absorption spectra of the europium β-diketonate complexes EuR_3(phen) (*1–4*) and the emission spectrum of polycyanophenylene (*5*).[25]
R = acac (*1*), mppd (*2*), dbm (*3*), and dnm (*4*).

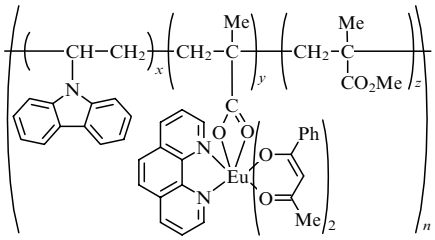
pure red emission. Compound **19(Eu)** was found to be the dopant of choice for TPD used as the matrix.[133]

Li and co-workers [134] found that the hole injection in a layer formed from lanthanide complexes leads to luminescence quenching and is responsible for decomposition of the compound, and these authors suggested an alternative approach to the problem based on interactions between the layers.[31] They constructed several types of OLED devices containing different layers between which europium complex **14(Eu)** was placed. The ITO/TPD/**14(Eu)**/TPD/Alq_3/Ag : Mg device differs from the ITO/**14(Gd)**/**14(Eu)**/**14(Gd)**/Ag : Mg device in that the europium complex is enclosed between the layers of a hole-transport material (TPD) in the former device and between the layers of an electron-transport material [**14(Gd)**] in the latter device. In the ITO/**14(Eu)**/Ag : Mg device containing no separating layers, electroluminescence was not observed due apparently to the fact that hole injection in the europium complex from the ITO anode is hindered. In yet another device, ITO/TPD/**14(Eu)**/Ag : Mg, hole injection occurs from the TPD layer, resulting in red emission. However, the emission time of the latter device is short compared to the other devices. The best results were achieved with the use of the second light-emitting diode with an external quantum efficiency of 4.6% at a current density of 0.01 mA cm^{-2} and a maximum brightness of ~100 cd m^{-2}. Based on these results, the authors concluded that the first device contains an excess of holes, the third device contains an excess of electrons, whereas the concentrations of holes and electrons are balanced in the second device.

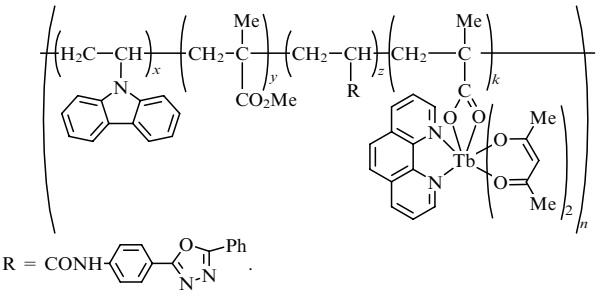
The same authors [28] studied the electron-transport properties of yttrium, lanthanum and gadolinium (their ions show no emission) β-diketonates using complexes **8(Ln)** as an example. These chelates were used as an additional layer in OLED devices. These complexes were found to have good electron-transport properties. The introduction of compound **8(Gd)** as an additional layer into the electroluminescent devices ITO/**13(Eu)**/Alq_3/**8(Gd)**/Alq_3/Al and ITO/TPD/**13(Eu)**/Alq_3/**8(Gd)**/Alq_3/Al increases the quantum efficiency of both devices (for the latter device, the efficiency was increased by a factor of almost two, from 0.6% to 1.0%) and changes the colour of emission from red (characteristic of Eu) to yellow.[135]

Low-molecular-weight lanthanide complexes are widely used for the construction of OLED devices. However, many such complexes are non-technological because film deposition is often accompanied by undesired crystallisation or aggregation. To solve this problem, attempts were made to synthesise high-molecular-weight lanthanide complexes. However, the simplest procedure is apparently based on the introduction of low-molecular-weight europium, terbium and thulium compounds into polymeric matrices, *i.e.*, the design of the above-mentioned 'host–guest' systems with all their drawbacks and advantages.[1, 136–142]

Another solution of this problem is to synthesise polymers containing chemically bound lanthanide ions. An example is a carbon-chain polymer containing europium β-diketonate in side fragments:[143]



The luminescence efficiency of an OLED device constructed on the basis of this polymer is 2.87×10^{-4} lm W^{-1}, and its brightness is 0.228 cd m^{-2} at 29 V. More recently, with the aim of improving the luminescent properties and constructing a single-layer OLED device, oxadiazole fragments were additionally introduced [144] into a copolymer, resulting in the presence of an emission, electron-transport and hole-transport layers in the same layer and, moreover, in the same polymeric matrix.



The resulting single-layer OLED device shows monochromatic green emission at 545 nm. However, the authors mentioned that the brightness of this device is unsatisfactory. A device constructed with the use of a polymeric matrix containing simultaneously europium and terbium shows white emission.[145]

One of the main procedures for the design of OLED devices involves deposition of the corresponding layers of working materials onto an ITO layer. This technological step has a strong effect on the characteristics of light-emitting diodes. The following two main methods are used for layer deposition: sublimation or spraying of a material and the preparation of films from solutions by evaporation of the solvent in a centrifugal field (spin-coating) or under standard conditions. This, as applied to rare-earth compounds, imposes the following additional requirements: rather high thermal stability and good solubility of the compound in an organic solvent suitable for the above operations. The surface quality of thin films of terbium carboxylate complexes prepared from various solvents was studied [146] by scanning atomic force microscopy and optical near-field microscopy. A device prepared from THF was found to have the best performance.

For lanthanide β-diketonate complexes, poor solubility is often a considerable obstacle. Complexes **6**(**NaEu**), **6**(**LiEu**) and **6**(**KEu**) are readily soluble in chloroform, ethanol, acetonitrile and acetone,[17] their photoluminescence spectra are analogous to those of the Eu^{3+} ion, but the fluorescence intensity strongly depends on the nature of the solvent. It was attributed to the fact that high dielectric constants and the coordination ability lead to better solvation of alkali metal ions, which prevents undesired aggregation of europium species. These compounds were used to construct single-, two- and three-layer OLED devices with a maximum brightness of 36.7 cd m^{-2} at 26 V, which is substantially higher than that for the above-described devices based on compound **5**(**Eu**).

V. Conclusion

The data considered in the present review show that there are real prospects for the use of lanthanide complexes in organic light-emitting devices. The most substantial results were achieved in the design of OLED devices based on pyrazolonate complexes (Fig. 9).

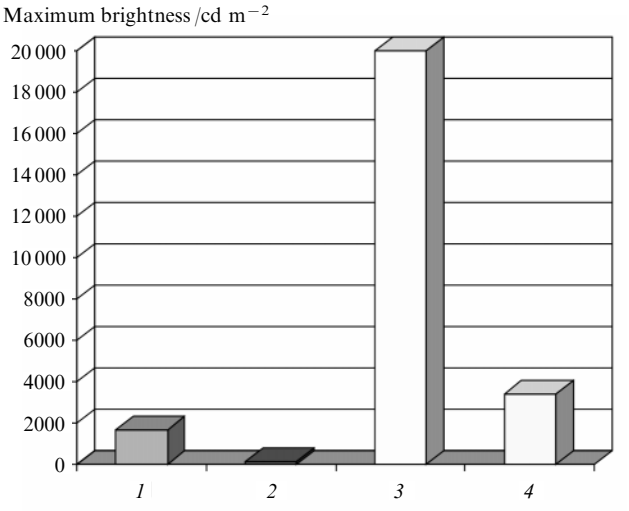


Figure 9. Relative brightnesses of the most efficient OLED based on lanthanide β-diketonates (*1*),[48] carboxylates (*2*)[59] and pyrazolonates (*3*)[66] and Alq_3 (*4*).[147]

As mentioned above, the OLED device constructed with the use of the purely organic compound rubrene still provides record brightness (higher than 200 000 cd m^{-2}).[73] The brightness of a diode constructed with the use of tris(2-phenylpyridine) iridium is somewhat lower (100 000 cd m^{-2}).[74] The characteristics of lanthanide-based OLED devices are noticeably worse. However, the latter devices have the following undeniable advantages: generation of 'pure'-coloured emission and a much lower price compared to the iridium device. In addition, there is good reason to hope that the emission brightness, efficiency, quantum yield and other characteristics of diodes containing organic lanthanide complexes will be sharply improved by choosing an optimum ligand environment.

Analysis of the published data shows that the compositions of lanthanide-containing OLED devices cannot be considered as completely optimised. Elucidation of the factors of interactions between organic matrices and lanthanide compounds is one of the most important problems. A more complete theoretical description of the mechanisms of intramolecular energy transfer is required. An extension of the range of ligands used in these complexes is of considerable significance. This will allow one to synthesise new highly luminescent complexes. Studies of the dependence of the luminescent properties on the nature of the chemical bonds between metals and ligands, the structures of the latter and organisation of the complexes are also of importance. Evidently, a combination of fundamental and applied investigations will provide interesting results and assist in constructing highly efficient OLED devices.

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