

Spectral and Electroluminescent Properties of Coordination Compounds of Terbium (III) with Ibuprofen (in Solid Form, Chloroform Solutions, and Polyvinylcarbazole Films)

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Received February 16, 2015; in final form, March 6, 2015

Abstract—Spectral properties of terbium (III) complexes with composition of TbL₃DL, where L is an anion of d,l-2-(4-isobutylphenyl)propanoic acid (ibuprofen) and DL is 2,2'-dipyridyl (Dipy), 1,10-phenanthroline (Phen), or triphenylphosphine oxide (TPPO), have been studied in a solid form, chloroform solutions, and polyvinylcarbazole (PVC) films. It has been demonstrated that, in PVC films, occupation of the emitting level of terbium (III) involves the participation of polymer. The emission decay lifetimes of terbium in the chloroform solutions and PVC films have been measured. The possibility of the appearance of electroluminescence of complexes in PVC films has been studied.

DOI: 10.1134/S0030400X15080196

INTRODUCTION

Due to the unique characteristics of luminescent radiation of coordination compounds of lanthanides, they are widely used as luminescent materials for various applications [1], components of organic light-emitting diodes (OLEDs) [2, 3], solar concentrators [4], and molecular reporters in biomedical studies [5].

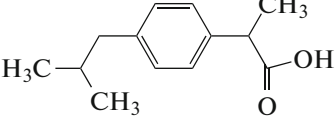
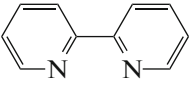
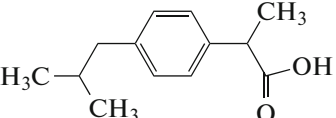
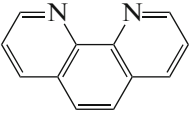
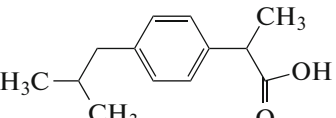
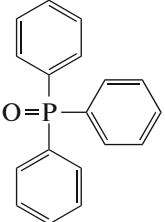
In this regard, the most attractive complexes are those with europium (III) and terbium (III) ions, which, with well-chosen ligands, emit with a rather high efficiency in the red (613 nm) and green (546 nm) regions of the spectrum, respectively. Although there is a wide set of already existing complexes, only a few of them satisfy the parameters necessary for obtaining highly efficient and stably functioning OLEDs. Many problems appear already in the beginning of manufacturing of a multilayer sample. First, these complexes are sufficiently rather to subject to vacuum deposition due to, as a rule, high molecular mass. Often (for forming a layer by centrifugation), complexes have limited solubility in solvents desired. Moreover, to create excitons, the recombination of which leads to the light emission, they should possess electron affinity and have a low ionization potential. In [6–9], OLEDs based on terbium (III) complexes with very high luminance (up to 9000 cd/m²) were described, which were obtained by thermal vacuum deposition. Upon making an emitting layer using PVC, results as a rule are more modest. Thus, the highest luminance

characteristics (500 and 200 cd/m²) were demonstrated in [10, 11], which were obtained, however, at a rather high voltage (~20 V).

The present study investigates spectral characteristics and photo- and electroluminescence of terbium (III) mixed ligand complexes based on d,l-2-(4-isobutylphenyl)propanoic acid (HL), which represents the substance of ibuprofen, a nonsteroidal anti-inflammatory drug [12]. It is produced by the pharmaceutical industry in large amounts; thus, coordination compounds on its basis may be of interest not only for materials science, but also in the future to solve the problem of utilization of drugs that have expired or been phased out for particular reasons. We note that attempts to construct OLEDs based on lanthanide complexes with drugs have been already undertaken, in particular, using aspirin [13, 14].

The sensitized luminescence of terbium (III) ions in complexes with HL was found in aqueous solutions and was applied for analytic determination of ibuprofen [15–17]. In the presence of donor-active ligands (DLs), such as 2,2'-dipyridyl (Dipy), 1,10-phenanthroline (Phen), or triphenylphosphine oxide (TPPO), mixed ligand complexes are formed, owing to which the luminous intensity of terbium (III) significantly increases. We isolated these complexes in a solid form for the first time. They have the composition TbL₃DL, with ibuprofen entering into the coordination sphere of the complex in the form of an anion, while DL

Table 1. Composition and some characteristic of terbium mixed ligand complexes

Complex	HL	DL	Yield, %	Content Tb (III), % Found/calculated	Temperature of beginning of decomposition, °C
TbL ₃ Dipy			45.7	17.80/17.04	250
TbL ₃ Phen			69.0	16.44/16.61	260
TbL ₃ TPPO			68.8	13.24/13.57	180

enters as a neutral ligand. According to the data of thermogravimetric analysis, the compounds isolated are anhydrous and do not decompose upon heating up to temperature of 180–250°C (Table. 1).

EXPERIMENTAL

To synthesize complexes, ibuprofen (Sigma-Aldrich; purity, 99.4%) was used. To an ethanol solution of 50 mL containing 0.5 mmol of the corresponding DL, 309 mg of HL (1.5 mmol) and an aqueous solution containing 0.5 mmol terbium (III) perchlorate were added. Then, during stirring with a magnetic stirrer, an ammonia solution (1 : 1) was added to the reaction mixture before beginning of the precipitation. The next day, the precipitate was filtered, washed with some portions of ethanol, and dried. The terbium (III) content in the complexes isolated was determined by complexometric titration.

Absorption spectra were recorded using an SM2203 spectrophotometer (Belarus), and fluorescence and phosphorescence spectra were measured on a Carry Eclipse spectrofluorimeter (Intertech Corp.), which can be used to study long-lived states. Phosphorescence lifetimes were assessed by the kinetics of a luminescence decay, which represented in the general case a superposition of exponents

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + \dots + A_n \exp(-t/\tau_n).$$

In the case of a monoexponential decay of the emission, semilogarithmic transformation of a curve takes the form of a straight line, the slope coefficient of which characterizes the emission decay constant

and the reciprocal of which is the triplet lifetime. For the case of a superposition of exponents, semilogarithmic transformation of a curve represents a broken line. The decay coefficient and lifetimes are found upon analyzing every straight region of the curve obtained.

The values of triplet levels of the ligands are obtained based on the spectra of phosphorescence of gadolinium complexes at 77 K. The spectra were recorded by a Fluolog FL3-22 fluorimeter (Horiba Jobin Yvon, France).

The spectral properties of the complexes were studied in solutions of chloroform, PVC films (Aldrich), and in a powdered state.

The electroluminescent properties of the compounds were studied in samples obtained by centrifugation of a PVC solution in chlorobenzene with terbium complexes. The PVC content in the initial solution was 5 mg/mL, while that of TbL₃Dipy was 4×10^{-3} M and that of TbL₃Phen and TbL₃TPPO was about 2×10^{-3} M (near the solubility limit).

The samples were prepared on glass substrates with a deposited ITO layer, which served as an anode. A standard procedure of substrate washing in an aqueous solution of ammonia with further ultrasonic washing in acetone and isopropanol was used. At the final stage, the substrates were treated with oxygen plasma on an ATTO setup (Diener, Germany). In addition, all the procedures were carried out in a DELLIX glove box (China) under dry nitrogen with water and oxygen content of a few ppm. Thin films from the solutions were deposited using a KW-4A centrifuge (Chemat Technology) with further drying in a vacuum drying

Table 2. Spectral characteristics of complexes

Compound	C, M ⁻¹	λ_{ab} , nm	ϵ , M ⁻¹ cm ⁻¹	λ_{ex} , nm	λ_{em} , nm (ligand)
TbL ₃ Dipy	10 ⁻⁵	282		—	375
	10 ⁻³	282	9400	260 + 310	*
	Powder			328 + 270 (sh)	*
TbL ₃ Phen	10 ⁻⁵	266	24500	—	375
	10 ⁻³	272	23000	275–294	*
	Powder			300–320	*
TbL ₃ TPPO	10 ⁻⁵	266	3900	—	375
	10 ⁻³	266	2750	268	*

* Emission of ligand is almost absent.

cabinet. PEDOT:PSS (AI 4083 Heraeus Clevios) was deposited at a rate of 4000 rpm for 30 s and was dried at a temperature of 120°C. The films from the PVC solutions were deposited at a rate of 2000 rpm and were dried at a temperature of 80°C. The thicknesses of the PEDOT films and of emitting layers were 30 and 80 nm, respectively. Deposition of organic compounds and cathodes was performed using an AUTO-306 evaporation setup. The thickness of the films was monitored during deposition using a quartz sensor and was measured on control substrates by a KLA TEN-COR Micro Xam-100 profilometer.

The electroluminescent properties were measured using a bench consisting of a KEITHLEY237 voltage source and analyzer and an AvaSpec 2048 optic spectrometer. At the same time, the current–voltage and voltage–luminance dependences and spectral composition of the emission were measured.

RESULTS AND DISCUSSION

Spectral Properties in Solutions and Powders

Table 2 gives spectral characteristics for solutions of high and low concentrations in chloroform and solid form. The absorption spectra of the organic part of the molecule are within 260–280 nm, and, upon an increase in the concentration from 10⁻⁵ to 10⁻³ M, they almost do not change. The luminescent excitation spectra (monitoring at a wavelength of 546 nm) noticeably differ from the absorption spectra. Thus, for the concentrated solution of TbL₃Dipy, two bands with maxima at 260 and 310 nm appear instead of the band at $\lambda = 282$ nm (Fig. 1a). This fact may indicate that the terbium (III) excited states are occupied mainly by one of the ligands, the contribution of which to the absorption spectrum is minimal. The excitation spectrum of the powder of this complex has a shoulder in the region of the absorption band and maximum in a redder region at 328 nm.

The excitation spectrum of the solution of the complex TbL₃Phen broadens, when compared to the

absorption spectrum, almost by a factor of two with a maximum in a redder region (Fig. 1b). Based on the excitation spectrum, it maybe suggested that the population of the ⁵D₄ level of terbium (III) occurs with the two ligands being involved. The excitation spectrum of the powder of this complex additionally broadens and shifts to a red region.

In contrast to the two compounds mentioned above, the excitation spectrum of the concentrated solution of TbL₃TPPO reproduces its absorption spectrum (Fig. 1c). It appears that, in this complex, the absorption regions of the both ligands are close, and, in connection with this, it is difficult to suggest, which of them prevails in the occupation of the ⁵D₄ level of terbium (III). In the excitation spectrum of the powder, a new band in a region of 320 nm appears together with a band in the absorption region.

Thus, the excitation spectra give evidence of different roles played by ligands in the occupation of the emitting level of terbium (III) and possibly of a more complex structure of the molecules in the solid form.

The luminescence of the complexes was recorded in the “fluorescence” and “phosphorescence” modes of operation of the fluorimeter. At concentrations of 10⁻⁵ M, in the fluorescence mode of operation, the emission of ligands with a maximum at ~375 nm was observed for all the compounds. The similarity of the emission bands suggests that the emission is caused by one and the same center, which in the structures studied is represented by the ligand L. At low concentrations, the terbium emission is insignificant, which may be due to dissociation of the complexes under these conditions. At a concentration of 10⁻³ M, in contrast, the emission consisting of two narrow bands with maxima at $\lambda = 490, 546, 586,$ and 622 nm belongs almost only to terbium (III), and the ligand emission is insignificant. It should be noted that the intensity of the emission of the TbL₃Phen complex is five times higher, when compared to that of the complexes with TbL₃Dipy and TbL₃TPPO. Occupation of the ⁵D₄

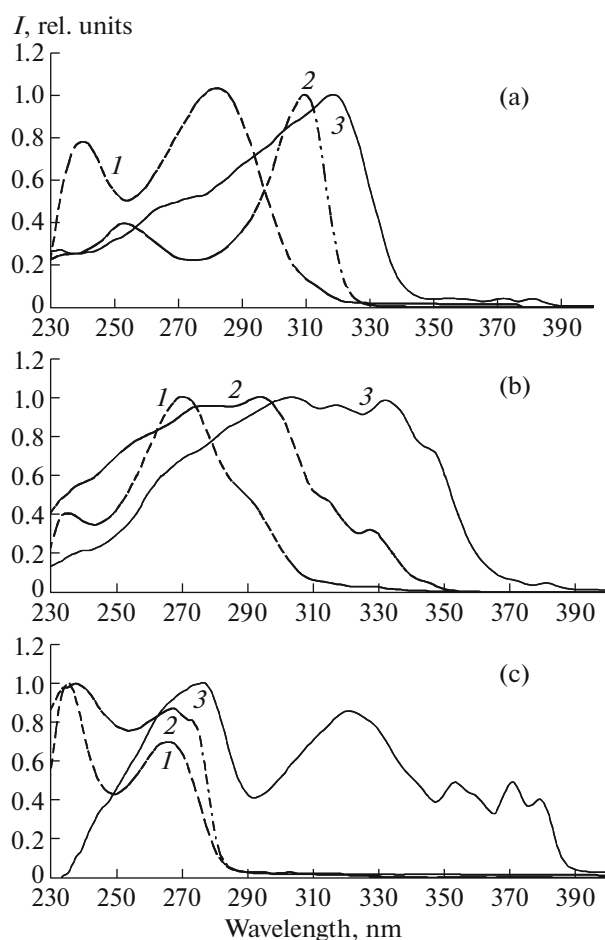


Fig. 1. (1) Absorption and (2, 3) fluorescence excitation spectra for (a) TbL_3Dipy , (b) TbL_3Phen , and (c) TbL_3TPPO complexes in a chloroform solution at $C = (1, 2) 10^{-3}$ M and (3) powder.

level of terbium (III) in this complex occurs more efficiently than that in the other two. This seems to be caused by the fact that the extinction of this complex is significantly higher (Table 2); though the luminescence has been recorded at a frontal mode of excitation of the solution in a cell with a layer thickness of 1 mm, where the effect of inhomogeneity of the volume excited should be minimal and the reabsorption of these compounds is simply absent.

Upon recording of the emission in the phosphorescence mode, a significant increase in the intensity of luminescence of the terbium (III) ion was observed. The decay curves of the emission were single exponential; the decay lifetime for TbL_3Dipy was 1.53 ms; for TbL_3TPPO it was 1.57 ms, and for TbL_3Phen it was significantly smaller, 0.69 ms. The decay lifetime did not depend on which of the emission bands was monitored.

Spectral Properties of Complexes in PVC Films

The spectral properties of the complexes in PVC films are studied, because this polymer is often used in OLED either independently as a hole transport or as a matrix for emitting substances.

The absorption spectra of the PVC films doped with the complexes repeat the spectrum of PVC itself. This is not surprising, since its mass composition significantly exceeds that of the complexes. Moreover, the main absorption bands of the complexes are located within a region of the intense PVC band with a maximum at 296 nm. It is of the greatest interest that the excitation spectra of luminescence upon recording at a terbium emission wavelength of 546 nm also reproduce the absorption spectrum of PVC. This fact indicates that the emitting state of terbium (III) is well populated with the polymer participation being involved. It is of interest that this also takes place in an excitation region of 330–340 nm (the long-wavelength absorption band of PVC), where the complex ligands are manifested not only in the absorption, but also in the excitation spectra. Förster energy transfer in this composition of the compounds is impossible, since for this it is necessary that the singlet states of the acceptor (in our case, complex ligands) lie slightly lower (or coincide) with the fluorescing state of the donor (in our case, PVC). PVC emits in a region of ~ 410 nm, and the ligand absorbs in a region of 270–280 nm. Two variants of the involvement of PVC in the population of the 5D_4 level of terbium (III) may be suggested. First, energy transfer from the triplet state of PVC to the triplet state of the ligands and further, intramolecularly, to the 5D_4 level of terbium (III). Second, the direct energy transfer from the triplet level of the polymer to the 5D_4 level of terbium (III) may be suggested. In the first case, it is necessary that the triplet level of PVC be higher than the triplet level of one of the ligands, and, in the second case, it is sufficient that it be resonant (equal in regards to the energy or slightly higher) with the emitting level of terbium (III).

The PVC emission at room temperature at 400–420 nm is excimer fluorescence of a sandwich structure of a dimer of carbazole chromophores [18, 19]. The PVC phosphorescence was studied in details in a number of studies both in solutions [20, 21] and in the form of films [22–24] mainly at low temperatures. The unstructured emission band of PVC with a maximum at ~ 500 nm at temperatures higher 55 K is attributed to excimer phosphorescence [24] having two main components during decay with lifetimes of 7.7 and 1.7 s [25]. In the present study, weak emission of the PVC film was recorded without dopants at room temperature in a region of 500 nm with a delay of 0.1 ms after the excitation pulse (insert in Fig. 2). There are reasons to believe that this is phosphorescence.

Figure 3 gives a scheme of the triplet states of all the ligands, PVC, and 5D_4 level of terbium (III). It may be

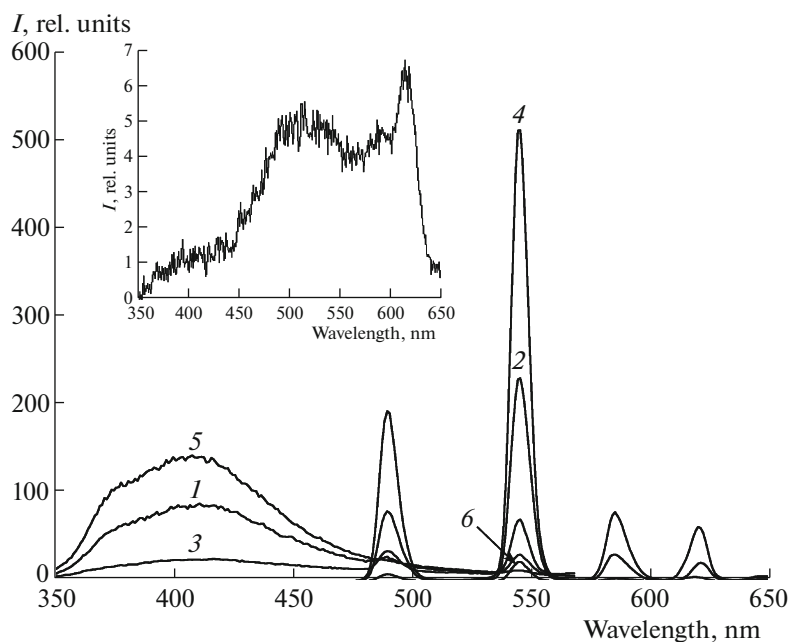


Fig. 2. Luminescence spectra of PVC films doped by (1, 2) TbL_3Dipy , (3, 4) TbL_3Phen , and (5, 6) TbL_3TPPO recorded in the fluorescence (1, 3, 5) and phosphorescence (2, 4, 6) modes. The inset gives luminescence of the PVC film without dopants.

seen from the scheme that the triplet state of PVC is resonant with the levels of TPPO and ibuprofen. Thus, the involvement of PVC in the population of the emitting level of terbium takes place via the main ligand of the complexes, ibuprofen.

Though the mutual energy position of the PVC triplet and emitting state of the terbium (III) ion allows the excitation energy transfer directly from PVC, this transfer is of low-probability. The terbium (III) ion is solvated with the ligands and, thus, spatially distant from PVC, and the triplet-triplet energy transfer is exchange-resonance in regards to its origin and implemented at very small distances.

The emission spectra of the complexes in the PVC films recorded in the fluorescence and phosphorescence modes are given in Fig. 2. The excitation was implemented at the short-wave band of PVC at $\lambda = 296$ nm. The hardware options of the fluorimeter (slits, photomultiplier voltage) were the same for all the samples and modes of recording the emission spectra. The emission spectra of the complexes in PVC recorded in the mode "fluorescence" are represented by emission of PVC with a maximum at 400 nm and by a set of narrow bands belonging to emission of the terbium (III) ion: 490, 546, 586, and 622 nm. All the samples have in common the PVC emission prevailing in the fluorescence mode. The TbL_3TPPO compound noticeably differs by significantly lower intensity of its emission (the intensity of the emission of PVC being several times higher), when compared to the films with TbL_3Dipy and TbL_3Phen . Analyzing this fact, it may be suggested that the energy transfer

from PVC to TbL_3TPPO is less efficient than that in the films with TbL_3Dipy and TbL_3Phen .

Upon recording of the emission in the phosphorescence mode with a delay of 0.1 ms after the pulse, only emission of the terbium (III) ion was observed, with the PVC emission being absent in all the samples. The intensity of the terbium emission recorded in the "phosphorescence" mode is about seven times higher than that in the mode "fluorescence." Upon comparison of the compounds with each other, the greatest intensity of the emission is found in TbL_3Phen , it

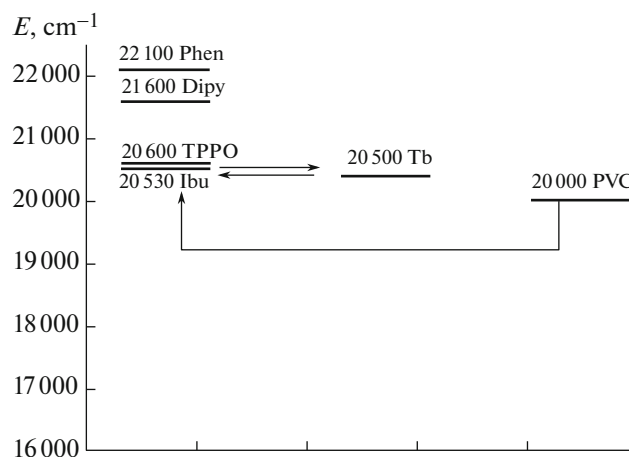


Fig. 3. Position of triplet levels of PVC, ligands, and Tb(III) .

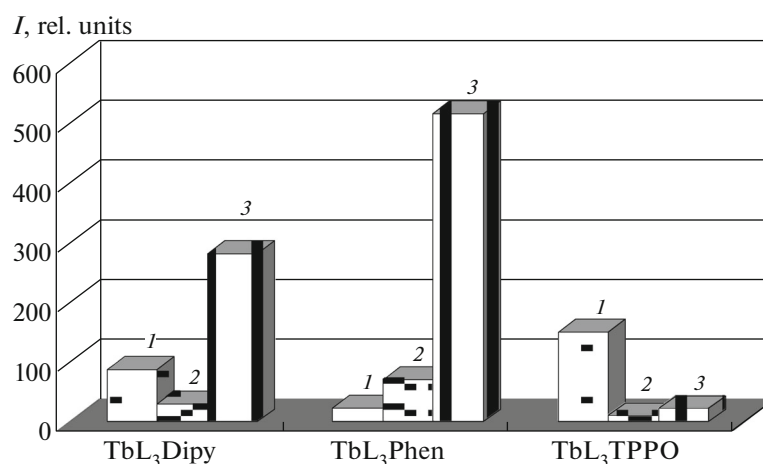


Fig. 4. Intensity of emission of PVC films doped with complexes. 1 corresponds to PVC emission ($\lambda = 410$ nm) and 2 corresponds to emission of a terbium (III) ion ($\lambda = 546$ nm) recorded in a mode “fluorescence”; 3 corresponds to emission of a terbium (III) ion ($\lambda = 546$ nm) recorded in a mode “phosphorescence.”

being twice as high as TbL₃Dipy and 20 times as high as TbL₃TPPO. A diagram of the comparative emission of the samples is given in Fig. 4.

The decay lifetimes of the complexes placed into the polymer film are given in Table 3. The decay lifetimes in the matrix, when compared to the concentrated solutions, are unexpectedly slightly lower. Here, whereas in the solutions the decay curve was monoexponential, in PVC, it was rather biexponential with close decay lifetimes.

Electroluminescence

The possibility of the complexes to emit in a field of the voltage applied has been studied. Two main methods for manufacturing light-emitting layers in OLED cells are known: a thermal vacuum deposition method of substance onto a substrate and centrifugation of a solution. In our case, the both methods were used. It has been found that the complexes studied are badly susceptible to thermal vacuum deposition, that’s why OLED cells using this method have not been manufactured. Upon forma-

tion of the cells by the second method of deposition of the emitting layer, samples with composition ITO/PEDOT:PSS/PVC+K/BCP/Ca/Al have been made, where K is one of the complexes and BCP (2,9-dimethyl-4,7-diphenyl-phenanthroline) is often used as an electron transport and blocking layer for holes. The cathode and BCP were deposited by thermal vacuum deposition.

The emission spectra of the samples in a field of the voltage applied are given in Fig. 5.

For the samples with the complexes TbL₃Dipy and TbL₃Phen, emission of the terbium (III) ion is observed, which is presented by a set of narrow bands with maxima at $\lambda = 490, 546, 590,$ and 620 nm and small admixture of PVC emission at a region of 400 nm. As for the sample containing TbL₃TPPO, its spectrum belongs to the PVC emission. The emission of the terbium (III) ion is given by a peak of low intensity located at a wavelength of 546 nm. For the same sample, an additional broad emission band of unknown origin is observed in a region of 615 nm.

It may be noted that the nature of the emission of the complexes in PVC upon photo- and electroexcitation is preserved. Occupation of the emitting state of the terbium (III) ion upon electroexcitation as during photoexcitation seems to occur mainly via the excited state of PVC. For example, the samples with PVC + TbL₃TPPO both upon photo- and electroexcitation are represented mainly by PVC emission. The intensity of the electroluminescence of all the samples is weak and constitutes several cd/m^2 at electrode voltage of 12 V.

Table 3. Decay lifetimes of luminescence of terbium complexes

Compound	τ_{em} , ms (in chloroform)	τ_{em} , ms (in PVC)
TbL ₃ Dipy	1.53	0.69; 1.0
TbL ₃ Phen	0.69	0.42; 0.58
TbL ₃ TPPO	1.57	0.5; 0.82

Concentration of compounds in chloroform is 2×10^{-3} M. Recording at $\lambda = 546$ nm.

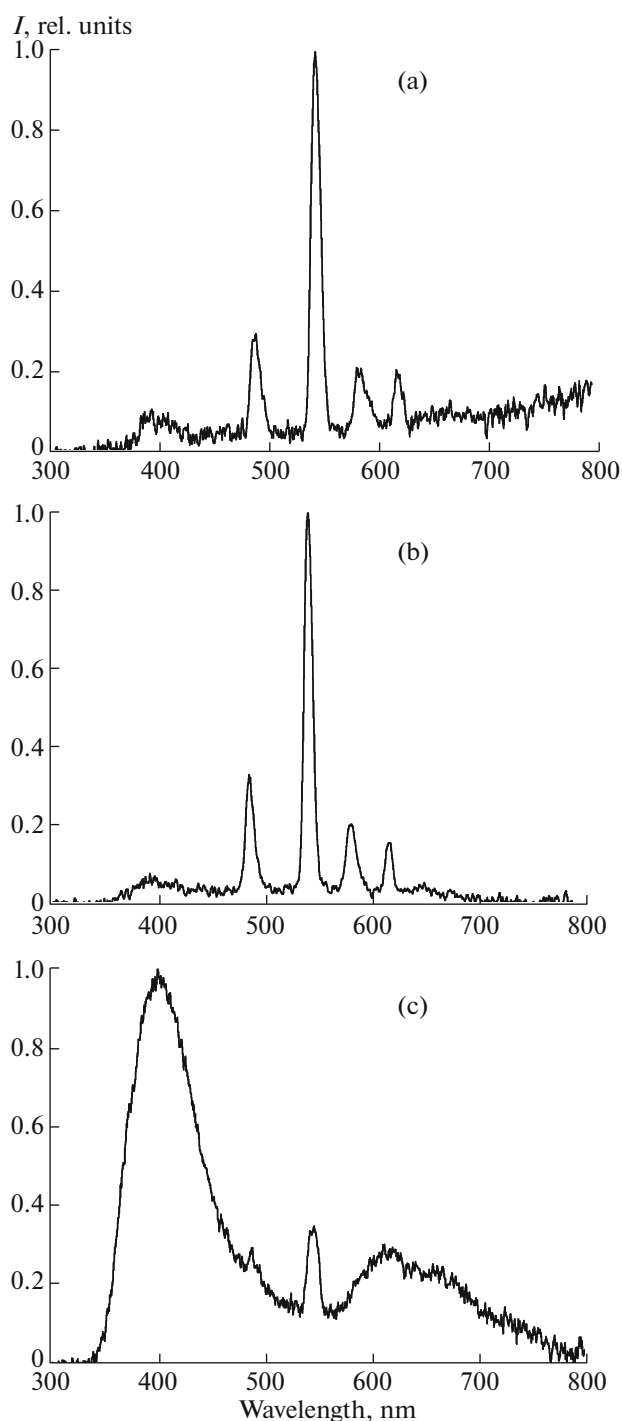


Fig. 5. Electroluminescence spectra of samples with composition ITO/PEDOT:PSS/PVC+K/BCP/Ca/Al, where K = TbL₃Dipy (a), TbL₃Phen (b), and TbL₃TPPO (c).

CONCLUSIONS

The spectral properties of all the three mixed ligand complexes of terbium (differing in the second ligand) have been studied in the solutions of chloroform and PVC films in the fluorescence and phosphorescence

(with a delay of 0.1 ms after the excitation pulse) recording modes. It has been found that the intensity of the emission of the terbium (III) ion in the second case is noticeably higher than that in the first case, which is due to the phosphorescence origin of the emission. The decay lifetimes of the emission vary within 0.5–1.6 ms and depend on the origin of the second ligand and the environment (chloroform solution, PVC film).

It has been demonstrated that, in the PVC films, the emitting level of the terbium (III) ion, ⁵D₄, is efficiently populated, with the triplet state of the polymer being involved both upon photo- and electroexcitation; the efficiency of the energy transfer to TbL₃Phen is higher than that to TbL₃Dipy and TbL₃TPPO.

The capability of the complexes to emit in the PVC films upon electroexcitation has been studied. It has been found that, in the samples of TbL₃Phen and TbL₃Dipy, the electroluminescence is represented by the emission of the terbium (III) ion and in those of TbL₃TPPO, by the PVC emission.

ACKNOWLEDGMENTS

This study was supported by the Ministry of Education and Science of the Russian Federation, assignment no. 16.578.2014/k, for carrying out a project part of a state assignment in the field of science.

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Translated by E. Berezhnaya