# SPECTRAL AND LUMINESCENT PROPERTIES OF THIN FILMS BASED ON DIALKOXY-SUBSTITUTED TERBIUM(III) BENZOATE DERIVATIVES

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*Thin films (~100 nm) of mixed-ligand complexes of terbium(III) with 3,5-diethoxybenzoic, 2,5-dimethoxybenzoic, and 3,4-diethoxybenzoic acids and phenanthroline and the Tb complex with only 3,4-diethoxybenzoic acid have been obtained. Electron and optical microscopy found that the complex crystallized during formation of the films. The complexes were doped into a poly-N-vinylcarbazole matrix in weight ratios from 1:1 to 10:1 to improve the quality of the film surface. It was assumed that the polymer participated in excitation of luminescence of the complexes in the film based on the dependence of the integral intensity of the film luminescence on the weight ratio of components in it and on the kinetics of film luminescence.*

**Introduction.** Lanthanide (Ln) compounds are currently widely used in many scientific areas because of their luminescent properties [1, 2], i.e., narrow luminescence bands and high quantum yields of electroluminescence, and the ability to change the physical properties of compounds without degrading the quality of the luminescence characteristics [3]. The production of LED devices characterized by uniform emission and high image contrast is one thrust for the use of these compounds [4–6].

Carboxylic acids can be used as ligands to produce luminescent coordination complexes with high thermal and photostability. Few studies have focused on the fabrication and study of materials based on Ln complexes of benzoic acids [7–9] despite the above advantages of such compounds.

The aim of the present work was to study the photoluminescence of thin films based on mixed-ligand complexes of terbium(III) [Tb(III)] with 3,5-diethoxybenzoic (H3,5DEBz), 3,4-diethoxybenzoic (H3,4DEBz), and 2,5-dimethoxybenzoic acids (H2,5DMBz).

**Experimental.** Thin films of both pure complexes and those doped in poly-*N*-vinylcarbazole (PVC) were prepared by spin-coating from $CHCl_3$ solutions. The process included several steps. First, substrates for direct deposition of the solutions were prepared. The surface was cleaned in three media, i.e., soap solution, deionized $H_2O$, and *i*-PrOH with sonication. Solutions of the luminophores were prepared by dissolving a weighed portion of the compounds in a calculated amount of solvent ($CHCl_3$). A series of PVC–complex solutions were prepared by mixing solutions of the pure compounds with a solution of the polymer in $CHCl_3$ in various proportions. The deposition used a micropipette. The tested mixtures had to be deposited before spinning to avoid breaks and pileups. Eventually, excesses of the solution were ejected from the substrate by centrifugal force. The solvent was evaporated to leave a thin layer of the substance on the substrate. The thickness of the obtained films was determined using a MII-4M microinterferometer (LOMO, Russia). In all instances, samples of the same thickness (90 nm) were produced. The error of the measurement was ±5 nm. The film microstructure was studied using an optical microscope in reflected and transmitted light at 80× magnification. Spectra were excited and recorded and luminescence of the thin films was recorded on a Fluorat-02 Panorama spectrofluorimeter (Lumex, Russia) at room temperature.

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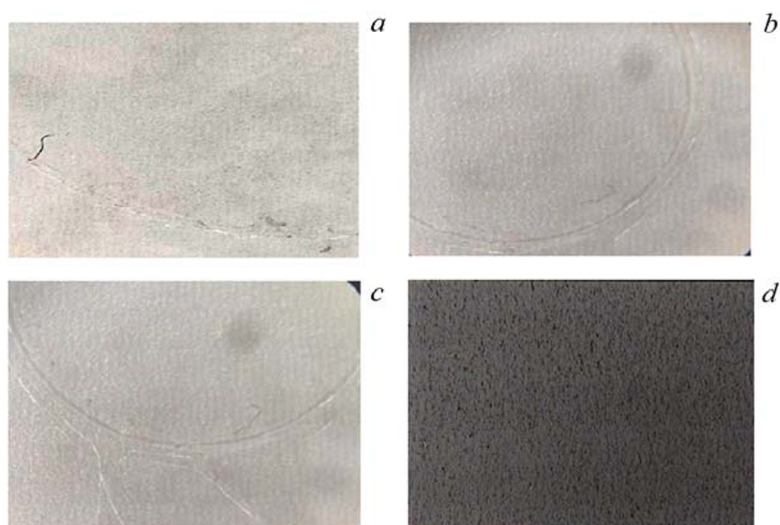
Fig. 1. Photomicrographs of film surfaces of mixed-ligand complexes with phenanthroline and 3,4-diethoxybenzoic (a), 3,5-diethoxybenzoic (b), and 2,5-dimethoxybenzoic acids (c) and the complex with only 3,4-diethoxybenzoic acid (d); magnification 80×.
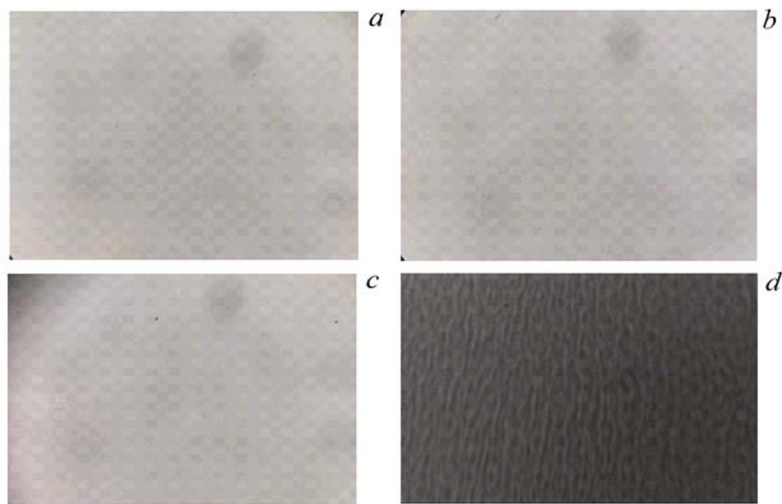


Fig. 2. Photomicrographs of film surfaces of PVC:CC; CC are terbium complexes with phenanthroline and 3,4-diethoxybenzoic (a), 3,5-diethoxybenzoic (b), and 2,5-dimethoxybenzoic acids (c) and the complex with only 3,4-diethoxybenzoic acid (d); magnification 80×.

**Results and Discussion.** Figure 1 shows photomicrographs of the surface of the obtained thin films of pure Tb(III) complexes. The substances were observed to crystallize during formation of the films so that many defects appeared. The presence of defects in the film could cause electrical breakdown in the OLED during use and shorten the service lifetime of the device. Doping of the crystallized compounds (CC) into a polymer matrix could improve the quality of the obtained films [10]. PVC was chosen as this matrix in the present work because of its broad use as a hole-conducting material in organic LEDs.

Figure 2 shows photomicrographs of the surface of PVC–complex composite films. The surface was observed to be much more uniform and even so that irregularities would not significantly affect the operation of the OLED.
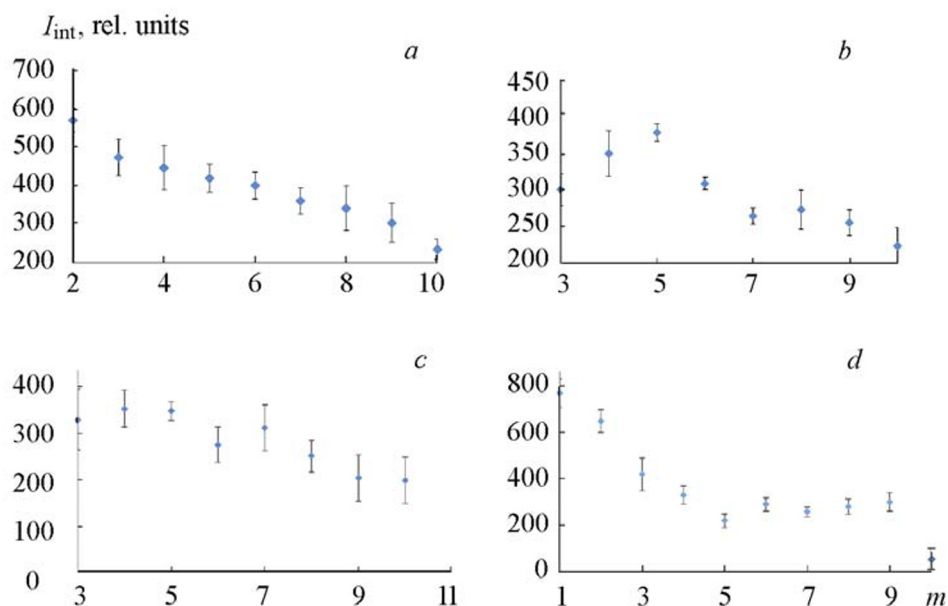
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Fig. 3. Dependences of integrated photoluminescence intensity of terbium(III) complexes on mass ratio $m$ = PVC:CC in film; CC are terbium complexes with phenanthroline and 3,4-diethoxybenzoic (a), 3,5-diethoxybenzoic (b), and 2,5-dimethoxybenzoic acids (c) and the complex with only 3,4-diethoxybenzoic acid (d).
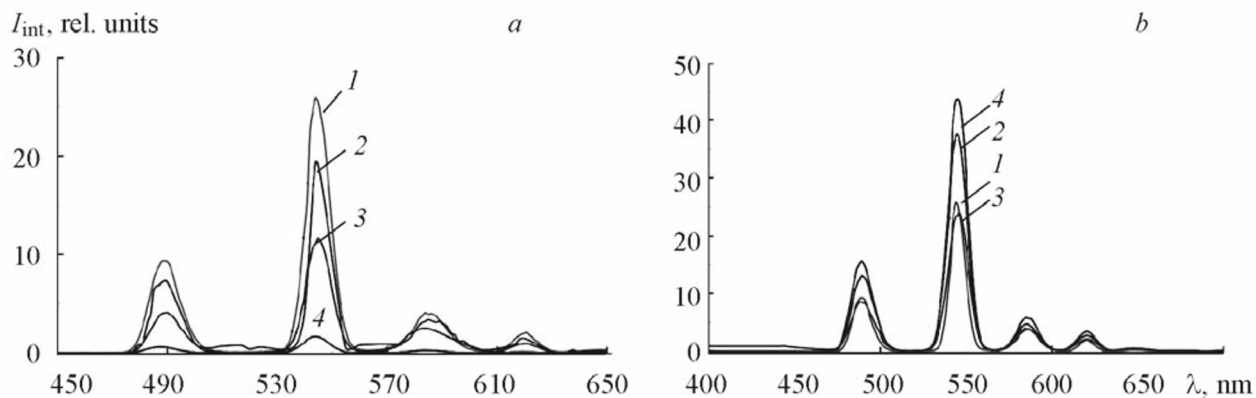


Fig. 4. Luminescence spectra of films in a PVC mixture (a) and pure film (b): terbium with 3,4-diethoxybenzoic acid and phenanthroline (1); terbium with 3,4-diethoxybenzoic acid (2); terbium with 2,5-dimethoxybenzoic acid and phenanthroline (3); terbium with 3,5-diethoxybenzoic acid and phenanthroline (4).

The dependences of the measured integral intensities of the films in the polymer matrix on the mass ratio of the components were obtained (Fig. 3).

Defects were observed in PVC films doped with CC at a PVC:CC ratio < 3:1. The surface became much more uniform and even at higher ratios. The optimal PVC:CC ratio could be determined from the combination of parameters such as the luminescence intensity and the quality of the surface of the obtained materials. A maximum was observed for a 5:1 ratio for a series of samples of a mixed-ligand Tb complex with 3,5-diethylbenzoic acid and phenanthroline. Maxima were not observed in other instances. The integrated intensity decreased as the content of the complex in the film decreased. In summary, it could be concluded that the polymer matrix affected the photoluminescence of the doped complex only if 3,5-diethoxybenzoic acid was used as a ligand.

Photoluminescence of the obtained thin films of pure and doped CC was studied (Fig. 4). The brightest luminescence among the pure complexes was observed for the Tb compound with 3,5-diethoxybenzoic acid and phenanthroline. The luminescence intensities of the complexes dropped sharply upon doping in the polymer matrix. This could be explained by specific charge transfer from the complex to the polymer matrix and involvement of the matrix in fluorescence quenching. This effect was observed for all CC except the complex with 3,4-diethoxybenzoic acid and phenanthroline. The lack of reduction of the luminescence after doping could be explained by involvement of the polymer matrix in charge transfer or a decreased role of re-emission and re-absorption between the complex luminescent centers.

**Conclusions.** Deposition of solutions of pure compounds onto the substrate led to their crystallization, which was prevented by preliminarily doping them into a polymer matrix. This reduced the luminescence of all compounds except the Tb(III) complex with 3,4-diethoxybenzoic acid and phenanthroline. The polymer in the PVC:CC film was involved in luminescence excitation only for the mixed-ligand complex with 3,5-diethoxybenzoic acid and phenanthroline. The optimal PVC:CC ratio was 5:1, for which the film surface remained uniform without crystallization. The optimal ratio could be considered 3:1 for the other studied composites.

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