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β-Diketonate Heteroligand Complex of Terbium and Polymer Material on Its Basis. Synthesis, Photo-, and Electroluminescent Properties

L. N. Bochkarev, A. V. Safronova, and G. V. Basova

Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, Nizhnii Novgorod, 603950 Russia
e-mail: lnb@iomc.ras.ru

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Abstract—New β-diketonate heteroligand complex of terbium is synthesized. On its basis, using the method of metathesis polymerization, a terbium-containing polymer has been prepared. The synthesized polymer material forms nanodimensional films possessing photo- and electroluminescent properties.

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Functional derivatives of norbornene are widely used as monomers in metathesis polymerization with the ring opening (ROMP), that allows to prepare various functionalized polymer materials [1–3] including those containing chemically bound atoms of transition [1, 4] and non-transition [1] metals in the side chains. As a rule, the ROMP of cycloolefins and their functional derivatives proceeds at room temperature in a controlled regime and results in formation of polymers with specified molecular mass characteristics [1–3], which is an advantage of this method over conventional radical polymerization. Recently, the ROMP method was employed for the synthesis of the Pt- and Ir-containing polymers, successfully used as emission materials in organic light-emitting diodes (OLEDs) [5, 6]. In the last decade, the research on application of the monomer coordination compounds of lanthanides as electroluminescent materials was intensively developed [7, 8]. Much less information is available on the synthesis and application as emitting layers in OLEDs of the lanthanide-containing polymers. Recently, Zeng et al. reported on the preparation of Tb- and Eu-containing polymers with electroluminescent properties using the method of radical polymerization [9, 10]. The ROMP method was applied to the synthesis of the Yb-containing polymer with metal-centered photoluminescence in the near IR region, but the electroluminescent properties of the polymer material were not investigated [11].

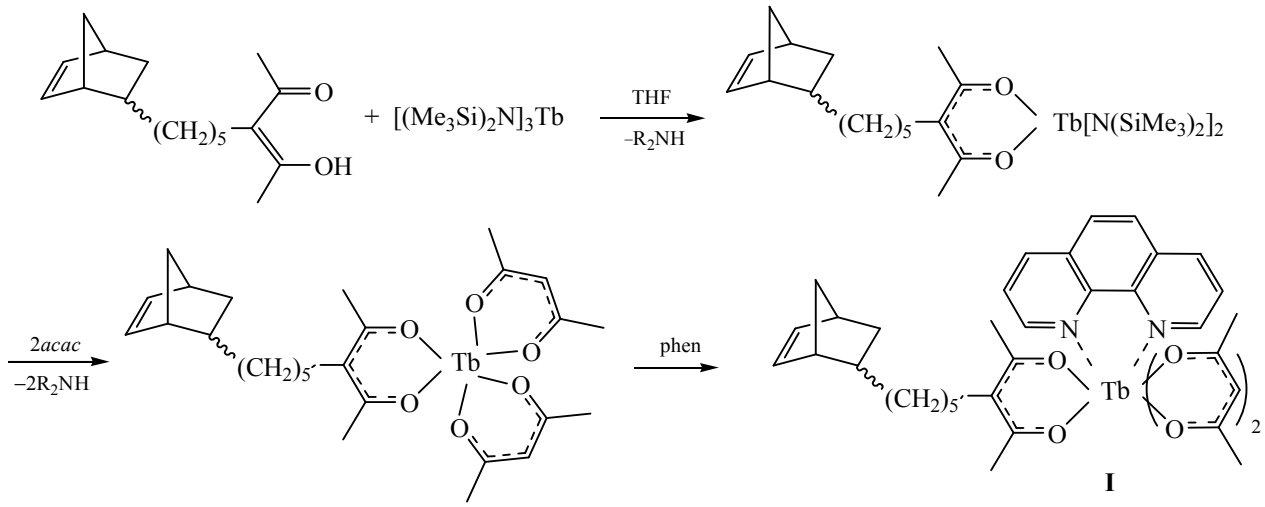
In the present work we have synthesized a new heteroligand β-diketonate derivative of terbium, {3-(5-bicyclo[2.2.1]hept-5-en-2-ylpentyl)pentane-2,4-dionato-*O,O*}bis(pentane-2,4-dionato-*O,O*)-(1,10-phenanthrolinato-*N,N*)terbium (**I**). Compound **I** was obtained by successive substitution of the amide groups in $[(Me_3Si)_2N]_3Tb$ by the norbornene-containing acetylacetonate ligand and the unsubstituted acetylacetonate ligands. In the final stage, 1,10-phenanthroline was introduced in the coordination sphere of terbium as a neutral ligand. The general scheme of the synthesis is represented in Scheme 1.

All stages proceed at room temperature practically instantly after mixing the reagents. Complex **I** was isolated in 96% yield as an air-stable pale-brown fine crystalline compound moderately soluble in tetrahydrofuran (THF) and practically insoluble in aliphatic hydrocarbons. The data of elemental analysis and IR spectroscopy correspond to the given formula.

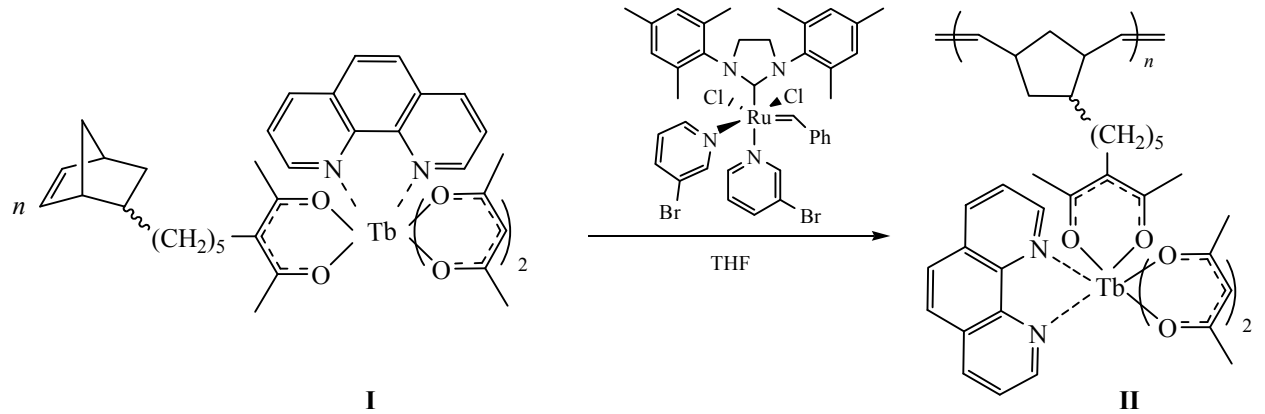
The obtained terbium-containing monomer **I** enters the ROMP reaction when using the Grubbs 3rd generation catalyst (Scheme 2).

The reaction proceeds at room temperature in 30 min and results in the formation of the polymer compound **II**, which unlike the starting monomer **I** is practically insoluble in THF, chloroform, aliphatic and aromatic hydrocarbons, but readily soluble in acetylacetone. Polymer **II** isolated in 56% yield is an air-stable pale-

Scheme 1.



Scheme 2.



brown powder. Unfortunately, due to low solubility in THF, the obtained polymer could not be characterized by the gel permeation chromatography (GPC). The spectrum of photoluminescence (Fig. 1, *1*) of the polymer as a film (40 nm) prepared by the spin-coating method from the solution in acetylacetone contains a band of the ligand-centered emission (372 nm) and weak bands with maxima at 492 and 547 nm belonging to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions of ion Tb^{3+}.

It is known that the use of polyvinylcarbazole (PVC) as a hole-conducting material substantially increases the working characteristics of the OLED devices [7]. In the case of the lanthanide-containing luminophores the increase of efficiency of OLEDs in the presence of a layer of matrix of PVC is explained by more effective transfer of the excitation energy to the lanthanide ion [12]. As a result, in the photoluminescence spectrum of the two-layer composition (Fig. 1, *2*) consisting of the PVC film (60 nm) and the coating of polymer **II** (40 nm) the emission bands of the terbium ion (492 and 547 nm) are substantially stronger.

To investigate the electroluminescent properties of the terbium-containing polymer the model OLED device of the ITO/PVC/**II**/Alq_3/Yb configuration was prepared. The layer of indium-tin oxide (ITO) played a role of the anode, PVC was a hole-conducting layer, compound **II** was an emitting layer, aluminum 8-oxyquinolinate was an electron-conducting layer, and the layer of ytterbium metal was used as the cathode. The electroluminescence spectrum was registered (Fig. 2), which was a superposition of emission of Alq_3 (wide band with the maximum at 525 nm) and the emission bands of ion Tb^{3+}: 492, 547, 589, and 624 nm,

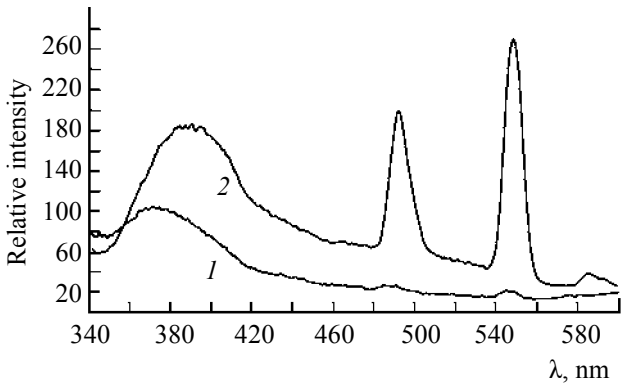


Fig. 1. Photoluminescence spectra: (*1*) polymer **II** as a film and (*2*) compositions PVK/(II); λ_{exc} 320 nm.

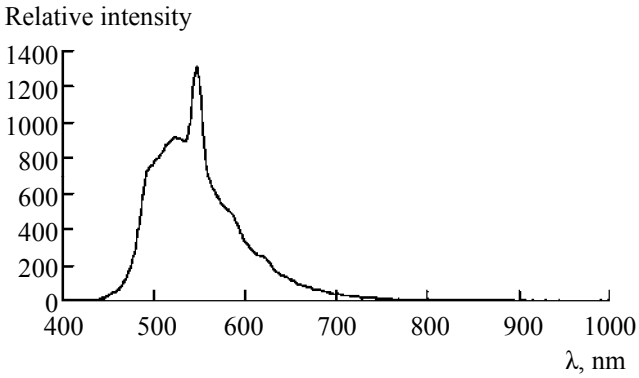


Fig. 2. Electroluminescence spectrum of the OLED device of the ITO/PVK/**II**/Alq_3/Yb configuration.

corresponding to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions. The maximum brightness of luminescence was 10 cd m^{-2} at 18 V.

Thus, a new norbornene-containing β-diketonate terbium derivative is synthesized, which enters the ROMP reaction to form the terbium-containing polymer **II**. The prepared polymer is shown to form the nanodimensional coatings having the properties of the ligand- and metal-centered photoluminescence and the metal-centered electroluminescence. The brightness of the nonoptimized OLED device with the terbium-containing polymer **II** as the emitting layer was 10 cd m^{-2} at 18 V. The studies on optimization of the OLED aimed at improving its working characteristics are in progress.

EXPERIMENTAL

All operations were performed in evacuated tubes using the standard Schlenk technique. The solvents used were thoroughly purified and degassed. The Grubbs 3rd generation catalyst [13, 14], $[(Me_3Si)_2N]_3Tb$ [15], 3-(5-bicyclo[2.2.1]hept-5-en-2-ylpentyl)pentane-2,4-dione [5] were synthesized as described in the literature. PVC (Aldrich), 1,10-phenanthroline (Aldrich) were used without further purification.

GC analysis of the volatile compounds was performed on a Tsvet-500 chromatograph (steel column 0.3×200 cm filled with SE-30 (5%) on Inerton AW). Detector catharometer, carrier gas helium.

FT–IR spectra were taken on a FSM 1201 instrument for samples prepared as suspensions in mineral oil. The films of the polymer materials were prepared on a "Spincoat G3-8" centrifuge. The thickness of the films was determined on a "Meta-900" ellipsometer. The photoluminescence spectra were recorded on a "Perkin Elmer LS 55" fluorescence spectrometer. The electroluminescence spectrum was obtained on an "Ocean Optics USB 2000" spectrofluorimeter.

[3-(5-Bicyclo[2.2.1]hept-5-en-2-ylpentyl)pentane-2,4-dionato-*O,O*]bis(pentane-2,4-dionato-*O,O*)(1,10-phenanthrolinato-*N,N*)terbium (II). To the solution of $[(Me_3Si)_2N]_3Tb$ (1.05 g) in 8 ml of THF the solution of NBE-$(CH_2)_5$-*acac* (0.43 g) in 5 ml of THF was added, then the solutions of acetylacetone (0.32 g) in 5 ml of THF and of phenanthroline (0.29 g) in 5 ml of THF were added. The mixture was stirred with a magnetic stirrer for 10 min, the solvent and volatile products were evaporated in a vacuum. In the volatile products 0.67 g (85%) of $(Me_3Si)_2NH$ was found by the GC method. The pale-brown solid residue was washed with hexane and dried in a vacuum to obtain 1.26 g (96%) of complex **I**. IR spectrum, ν, cm^{-1}: 3058 w, 758 m (C_{arom}–H); 1602 s, 919 m, 1517 s, 1456 s (C=C–C=O); 1399 s, 1345, 1260 w (CH_2, Me, C_{arom}–C_{arom}); 1190 w, 852 m, 734 m, 722 m (C–H); 656 w (Tb–O). No changes were observed in the sample exposed to air for a month. Found, %: C 58.58; H 5.86; Tb 19.64. $C_{39}H_{49}N_2O_6Tb$. Calculated, %: C 58.65; H 5.93; Tb 19.90.

Polymerization of complex I. To the solution of **I** (0.24 g) in 5 ml of THF the Grubbs 3rd generation catalyst (0.01 g, 4 mol%) in 2 ml of THF was added. The reaction mixture was stirred at room temperature with a magnetic stirrer. After 2–3 min a pale-brown precipitate was formed. After stirring the mixture for 30 min 0.1 ml of ethyl vinyl ether was added to deactivate the catalyst. The precipitate was separated

by centrifugation, washed with THF (2×5 ml), and dried in a vacuum at room temperature to constant weight. The terbium-containing polymer **II,** 0.13 g (56%) was obtained as a pale-brown powder. IR spectrum, ν, cm^{-1}: 3055 sh, (C_{arom}–H); 1714; 1590 s, 1520 s, 1462 s (C=C–C=O), 1380 s, 1348 sh, 1294 w (CH_2, C_{arom}–C_{arom}), 1260, 1150 w (Me), 1145 w, 846 m, 732 m, 722 m (C–H), 675 w (Tb–O). No changes were observed in the sample exposed to air for a month.

Preparation of the OLED device. On the glass support of the 1.4×3.4 cm size precoated with the ITO layer (100 nm, 100 Ω cm^{-2}) a layer of PVC (60 nm) from the chloroform solution (10 mg ml^{-1}) was deposited by the spin-coating method (2000 cpm, 1 min), then on the layer of PVC insoluble in acetylacetone a layer of polymer **II** (40 nm) was coated from the solution in acetylacetone (5 mg ml^{-1}, 2500 cpm, 30 s). The sample was dried in the air at room temperature for 1 day. Finally, a layers of Alq_3 (30 nm) and ytterbium metal (150 nm) were deposited on the layer of the polymer by the vacuum deposition technique (10^{-6} mm Hg).

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