



# Green-light emitting norbornene based terbium-containing copolymers. Synthesis, photo- and electroluminescent properties



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## ARTICLE INFO

### Article history:

Received 25 December 2013  
Received in revised form 3 February 2014  
Accepted 5 February 2014

### Keywords:

Terbium  
Copolymer  
ROMP  
Electroluminescence  
Photoluminescence

## ABSTRACT

New terbium-containing copolymers were prepared by ring-opening metathesis copolymerization (ROMP) of norbornene substituted terbium complex  $Tb(L1)_2(L2)(TPPO)_2$  ( $L1$  = 1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonato,  $L2$  = 1-phenyl-3-methyl-4-(5-bicyclo[2.2.1]hept-5-en-2-yl)-5-pyrazolonato, TPPO = triphenylphosphine oxide) and carbazole-containing norbornene derivatives. The photoluminescence (PL) spectra of the copolymers contained strong narrow bands of terbium ion at 492 ( $^5D_4 \rightarrow ^7F_6$ ), 550 ( $^5D_4 \rightarrow ^7F_6$ ), 586 ( $^5D_4 \rightarrow ^7F_4$ ), 624 ( $^5D_4 \rightarrow ^7F_3$ ) nm and emission in the region of 350–450 nm assigned to copolymer matrixes. The electroluminescence (EL) spectrum of the tree-layer device of configuration of ITO/Tb-copolymer(40 nm)/BATH(30 nm)/Alq<sub>3</sub>(30 nm)/Yb revealed intense emission bands of Tb(III) ions and a broad band at ca. 520 nm of low intensity attributed to emission from triplet level of carbazole groups. The maximum luminance of 70 cd/m<sup>2</sup> at 17.5 V, the maximum current efficiency of 0.56 cd/A at 11 V and the maximum power efficiency of 0.16 lm/w at 11 V were achieved. The CIE coordinates (0.28, 0.47) were corresponded to green color and independent on driving voltage.

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## 1. Introduction

In the last decade an increased attention was focused on the preparation of the luminescent lanthanide complexes and their application as emitting materials in organic light emitting diodes (OLEDs) [1–4]. This is explained by the unique ability of lanthanide ions to emit extremely narrow emission bands in the visible and near-infrared spectral region. The efficiency of luminescence originating from f–f transitions in great extent depends on the type of organic ligands surrounding the lanthanide center [5,6]. The most suitable ligands were found to be O,O- and O,N-chelate groups with extended  $\pi$ -conjugated systems. Among lanthanide derivatives, the highest EL characteristics exhibited terbium complexes with pyrazolonate ligands [7,8]. For preparation of emissive layers in OLED devices lanthanide complexes are usually vacuum deposited or spin-coated after doping into the charge-transporting polymer matrix. In both cases the materials formed have significant drawback. Vacuum deposited films are prone to crystallization during operation of OLEDs which causes a decrease in the performance

of devices. The emissive layers prepared by doping phosphorescent emitters into polymeric host exhibit tendency to phase separation, i.e., aggregation of phosphorescent emitters, which also results in significant reduction of operating characteristics of device. To overcome this drawback the copolymers with pendant groups containing covalently linked lanthanide complexes were synthesized [9–19]. Copolymers of this type can be prepared by the copolymerization of the lanthanide-containing monomers and the monomers containing charge-transporting groups [9,12–14]. Another synthetic approach envisages the linking of lanthanide complexes to polymer chain by anchor groups in side chains of the previously prepared organic copolymers [10,11,15–18,20]. The anionic anchor groups such as carboxylate groups [9,11–15] and neutral chelating ligands such as 2,2'-bipyridine, terpyridine and 1,10-phenanthroline [10,16–18,20] were used to link the lanthanide complexes to copolymer chain. The neutral anchor ligands serve also as energy transfer fragments [18]. The most of lanthanide-containing EL polymers have been prepared by free radical polymerization [9,12–15,18], the Suzuki coupling polymerization [10,11,16,17] or ring-opening metathesis polymerization [20,21]. ROMP as a method for polymer synthesis is especially attractive because the polymerization proceeds usually in a controllable fashion, in mild conditions and allows to obtain polymers

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with narrow polydispersity and predictable molecular-mass characteristics [22–24].

In this work, we report the synthesis, PL and EL properties of new terbium-containing copolymers. For preparation of polymeric materials ROMP reactions of norbornene based terbium- and carbazole-containing comonomers were used. The isolated copolymers revealed good film forming properties, high decomposition and glass-transition temperatures. The intense metal-centered emission was observed in their PL and EL spectra.

## 2. Experimental

### 2.1. Measurement and characterization

Fourier transform infrared (FTIR) spectra of the monomers in KBr pellets and the polymers as thin films between KBr plates were recorded using IR Fourier spectrometer FSM 1201. GPC analysis was conducted with a Knauer liquid chromatography system equipped with two Phenomenex columns (Phenogel, pore size of  $10^5$  and  $10^4$  Å), an internal differential refractive detector Smartline RID 2300 using HPLC grade tetrahydrofuran as mobile phase at 40 °C (2 ml/min flow rate). The columns were calibrated with polystyrene standards. The molecular weight was quantified by universal calibration using 13 polystyrene standards. Differential scanning calorimetry (DSC) was performed on a DSC 204 F1 “Phoenix” (“Nttsch”) under dry argon atmosphere at a flow rate of 20 cm<sup>3</sup>/min and a heating rate of 5 °C/min. Thermogravimetric analysis (TGA) was performed by Perkin Elmer PYRIS 6 TGA thermogravimeter under a dry nitrogen gas flow at a heating rate of 5 °C/min. Ultraviolet-visible (UV-vis) absorption spectra were recorded using a Perkin Elmer Lambda 25 UV/VIS spectrometer. The PL spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrometer. Relative PL quantum yields of the synthesized terbium-containing monomers and copolymers in CH<sub>2</sub>Cl<sub>2</sub> were measured at ambient conditions with an excitation wavelength of 290 nm, and the values were calculated using Rhodamine 6G in ethanol ( $\Phi = 0.95$ ) as standard [25] according to the known procedure [26]. For the calculations of PL quantum yields only Tb<sup>3+</sup> emission bands were considered. The EL spectra and current-voltage-luminescence characteristics were measured with an Ocean Optics USB 2000 fluorimeter and a computer controlled TEC-23 power supply under ambient conditions.

### 2.2. Materials and reagents

Na(L1)(DME) [27], 1-phenyl-3-methyl-4-(5-bicyclo[2.2.1]hept-5-en-2-yl)-5-pyrazolone (HL2) as a mixture of *endo* and *exo* isomers with the ratio of 75:25 [28], bicyclo[2.2.1]hept-5-en-2-yl(9H-carbazol-9-yl)methanone as a mixture of *endo* and *exo* isomers with the ratio of 75:25 [20], 9-(bicyclo[2.2.1]hept-5-en-2-yl-methyl)-9H-carbazole as a mixture of *endo* and *exo* isomers with the ratio of 75:25 [29], 9-(5-(bicyclo[2.2.1]hept-5-en-2-yl)-pentyl)9H-carbazole as a mixture of *endo* and *exo* isomers with the ratio of 75:25 [30] and (H<sub>2</sub>IMes)(3-Br-py)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (Grubbs' third-generation ruthenium catalyst) [31,32] were prepared according to the literature procedures. Aluminum tris(8-quinolate)(Alq<sub>3</sub>), terbium trichloride, 4,7-diphenyl-1,10-phenanthroline (BATH), TPPO, Yb metal (Aldrich) were used as received. All experiments with air- and moisture sensitive intermediates and compounds were carried out under an inert atmosphere of dry argon using standard Schlenk techniques. The solvents were purified and dried by conventional methods.

### 2.3. Syntheses of monomers

#### 2.3.1. Synthesis of bis(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonato)[1-phenyl-3-methyl-4-(5-bicyclo[2.2.1]hept-5-en-2-yl)-5-pyrazolonato]terbium (1)

Na(L1)(DME) (0.64 g, 1.84 mmol) in THF (10 ml) was added to suspension of TbCl<sub>3</sub> (0.24 g, 0.92 mmol) in THF (7 ml) and stirred at 40 °C for 5 h. The formed precipitate of NaCl (0.11 g, 1.80 mmol) was separated by centrifugation. The solution of the formed (PMIP)<sub>2</sub>TbCl was treated with Na(L2) (prepared from HL2 (0.28 g, 0.92 mmol) and NaH (0.02 g, 0.92 mmol)) in 10 ml THF and the mixture was stirred at 40 °C for 5 h. The precipitate of NaCl (0.05 g, 0.85 mmol) was separated and solvent was removed under reduced pressure. The residue was washed with hexane and dried in vacuum at 60 °C for 1 h to yield monomer 1 (0.72 g, 84%) as pale yellow microcrystalline solid. FTIR (KBr, cm<sup>-1</sup>): 3060, 2968, 2929, 2870 (C<sub>Ar</sub>-H), 1618 (C=O), 1596, 1582, 1528, 1491 (C<sub>Ar</sub>-C<sub>Ar</sub>), 1438, 1399, 1370, 1317, 987, 931, 907, 880, 834, 785, 756, 739 (C-H). Elemental analysis for C<sub>46</sub>H<sub>47</sub>N<sub>6</sub>O<sub>6</sub>Tb: % Calc.: C, 58.85; H, 5.05; Tb, 16.93. Found: C, 58.79; H, 5.06; Tb, 16.89.

#### 2.3.2. Synthesis of bis(1-phenyl-3-methyl-4-isobutyryl-5-pyrazolonato)[1-phenyl-3-methyl-4-(5-bicyclo[2.2.1]hept-5-en-2-yl)-5-pyrazolonato]bis(triphenylphosphine oxide)terbium (2)

The mixture of 1 (0.60 g, 0.64 mmol) and TPPO (0.32 g, 1.28 mmol) in 15 ml THF was stirred at room temperature for 5 h. The course of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction (5 h) the solvent was removed and the residue was washed with hexane and dried in vacuum at 60 °C for 3 h. The monomer 2 was isolated as pale yellow microcrystalline solid (0.83 g, 91%). FTIR (KBr, cm<sup>-1</sup>): 3073, 3055, 2965, 2955, 2869 (C<sub>Ar</sub>-H), 1618 (C=O), 1593, 1582, 1534, 1495 (C<sub>Ar</sub>-C<sub>Ar</sub>), 1456, 1437 (C-P), 1399, 1367 (C-H), 1316, 1259, 1177 (P=O), 1120, 988, 929, 907, 880, 834, 786, 756, 739 (C-H). Elemental analysis for C<sub>82</sub>H<sub>77</sub>N<sub>6</sub>O<sub>8</sub>P<sub>2</sub>Tb: % Calc.: C, 65.86; H, 5.19; Tb, 10.63. Found: C, 65.80; H, 5.14; Tb, 10.60.

### 2.4. Synthesis of copolymers P1–P3

To a solution of monomer 2 (0.11 g, 0.07 mmol) and 9-(bicyclo[2.2.1]hept-5-en-2-yl-methyl)-9H-carbazole (0.10 g, 0.36 mmol) in 8 ml of CH<sub>2</sub>Cl<sub>2</sub> third generation Grubbs's catalyst (0.0038 g, 0.0043 mmol) in 1 ml of CH<sub>2</sub>Cl<sub>2</sub> was added. The mixture was stirred at ambient temperature. After complete monomer conversion (6 h by TLC), the polymerization was quenched by the addition of few drops of ethyl vinyl ether and stirred for an additional 20 min. The reaction mixture was poured into hexane. The resulting solid was collected by filtration, redissolved in CH<sub>2</sub>Cl<sub>2</sub>, and reprecipitated into hexane. The solid was dried in vacuum at 70 °C until the weight remained constant. The yield of the copolymer P1 (air stable, colorless powder) was 0.19 g (92%). FTIR (KBr, cm<sup>-1</sup>): 3049, 2974, 2930, 2868 (C<sub>Ar</sub>-H), 1615 (C=O), 1596, 1535, 1482 (C<sub>Ar</sub>-C<sub>Ar</sub>), 1454 (C-P), 1370 (C-H), 1326, 1156, 1070 (P=O), 908, 786, 750, 737, 724 (C-H). Elemental analysis for C<sub>182</sub>H<sub>172</sub>N<sub>11</sub>O<sub>8</sub>P<sub>2</sub>Tb: % Calc.: C, 76.37; H, 6.06; Tb, 5.55. Found: C, 76.34; H, 6.01; Tb, 5.53.

Copolymerization of monomer 2 and 9-(5-(bicyclo[2.2.1]hept-5-en-2-yl)-pentyl)9H-carbazole was carried out in the same way. Time of the reaction – 8 h. The copolymer P2 was isolated as colorless solid. Yield: 0.15 g (83%). FTIR (KBr, cm<sup>-1</sup>): 3049, 2974, 2930, 2868 (C<sub>Ar</sub>-H), 1615 (C=O), 1594, 1531, 1482 (C<sub>Ar</sub>-C<sub>Ar</sub>), 1460 (C-P), 1370 (C-H), 1326, 1155, 1064 (P=O), 908, 786, 750, 737, 724 (C-H). Elemental analysis for C<sub>202</sub>H<sub>212</sub>N<sub>11</sub>O<sub>8</sub>P<sub>2</sub>Tb: % Calc.: C, 77.20; H, 6.80; Tb, 5.06. Found: C, 77.15; H, 6.76; Tb, 5.51.

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