Tb(III) complexes with 1-phenyl-3-methyl-4-stearoyl-pyrazol-5-one as a material for luminescence Langmuir–Blodgett films

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ABSTRACT

Synthesis and properties of new luminescent amphiphilic Tb(III) complexes [TbL$_3$·2H$_2$O]·3H$_2$O, TbL$_3$·bipy, [H$_3$O][TbL$_4$]·6H$_2$O and [H$_3$O][TbL'$_3$L]·H$_2$O, where HL is 1-phenyl-3-methyl-4-stearoylpyrazolone-5 and HL' is 1-phenyl-3-methyl-4-formylpyrazolone-5, are reported. The complexes have been characterized by elemental and thermal analysis, FTIR and luminescence spectroscopy methods. Formation and properties of Langmuir–Blodgett films of the complexes are described.

Luminescent Langmuir–Blodgett Film
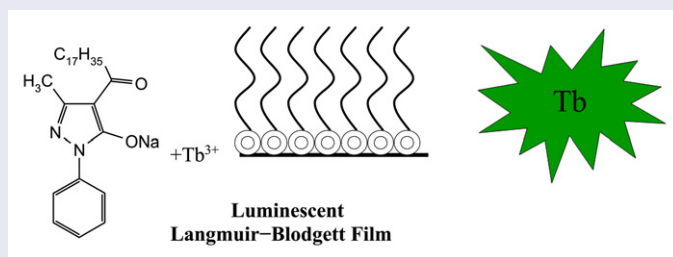
1. Introduction

The miniaturization of components is an important goal in the electronic industry [1]. Toward the purpose of producing reliable components, chemists must produce materials showing predictable properties in the bulk and also demonstrate the ability of these materials to be organized on surfaces. When designing any functional supramolecular construct, careful consideration must be given to the components of the system. In the case of metal complex systems, this refers to both the ligand and the metal center [2].
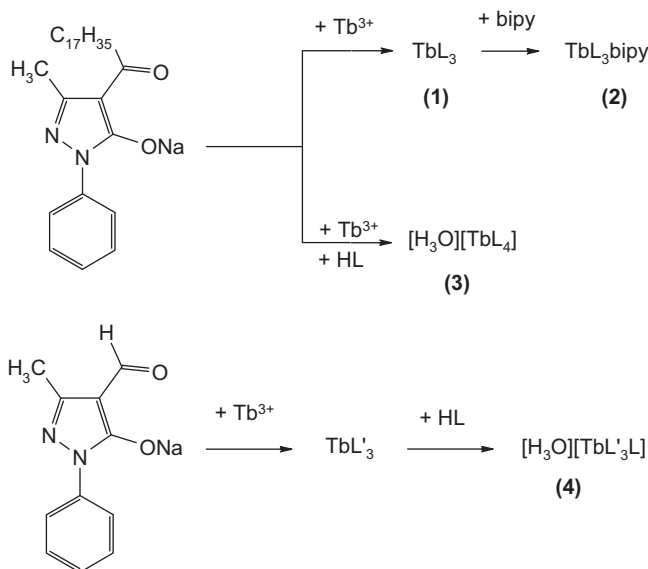
Scheme 1 Synthesis of target complexes.

Organic electronic components have already been incorporated into products such as organic light-emitting diodes (OLEDs), displays, thin film transistors (TFTs) or flexible electronic paper. Many molecule-based materials which exhibit useful properties, usually associated to inorganic materials, such as magnetism and luminescence, have been constructed. The development of metal-supramolecular architectures is an active and diverse research field, rich in fascinating chemistry with many potential applications [3]. While historically this field has been heavily skewed towards transition metal-based systems, there is a subsection made up of lanthanide-based assemblies that have been the focal point for some research groups, owing to their well-known optical and magnetic properties. Moreover, with the current drive to develop more complex luminescent and magnetically interesting materials (e.g. luminescent cellular imaging systems, luminescent sensors, MRI contrast agents, Light Emitting Devices, Single Molecule Magnets) the use of Ln^{3+} ions in the assembly of complex and functional architectures have gained attention. The hard Lewis acid nature and large coordination spheres of the lanthanides suggests ligands which are rich in oxygen and nitrogen donors, providing good building blocks for supramolecular systems [4].

Rare earth compounds are of importance because they provide intense fluorescence emission with high quantum efficiency, as well as sharp emission peaks with a narrow peak width at half-height, excellent fluorescence monochromaticity and long lifetimes. Rare earth β-diketone complexes with intense light emission have been used as laser materials and probes in fluorescence immunoassays. Their high fluorescence quantum yield is due to the high absorption coefficient of the ligand they bind and its efficient intramolecular energy transfer [5]. Besides classical β-diketones, an interesting functionalization has been the fusion of a pyrazole ring to the chelating arm, affording an interesting family of enolizable ligands. 4-Acylpyrazol-5-ones as ligands have been used for a long time as convenient metal extractants or chelating reagents in the spectroscopic

Table 1. Characteristics of the prepared complexes.

	Complex	Property, melting point	FTIR (KBr, cm^{-1})	Element Anal. CalC. (%)	Found (%)	m/z
1	[TbL$_3$·2H$_2$O]·3H$_2$O C$_{84}$H$_{139}$N$_6$O$_{11}$Tb	White solid, 85 °C	2920, 2851, 1623, 15,95, 1506, 1490, 1384, 1079, 983, 846, 755, 690	C, 64.34; H, 8.93; N, 5.36	C, 64.12; H, 8.63; N, 5.21	MALDI 1479 (TbL$_3$+H$^+$)
2	[TbL$_3$·bipy] C$_{94}$H$_{137}$N$_8$O$_6$Tb	Light brown solid, 70 °C	2922, 2852, 1652, 1617, 1593, 1500, 1457, 1449, 1368, 1077, 1001, 757, 692	C, 69.09; H, 8.45; N, 6.86	C, 68.93; H, 8.29; N, 6.99	MALDI 1634 (TbL$_3$Dipy + H$^+$)
3	[H$_3$O][TbL$_4$]·6H$_2$O C$_{112}$H$_{187}$N$_8$O$_{15}$Tb	Beige solid, 77 °C	2922, 2852, 1616, 1582, 1506, 1370, 1079, 1002, 984, 906, 845, 755, 690	C, 65.79; H, 8.53; N, 5.48	C, 65.64; H, 8.75; N, 5.74	MALDI 1937 (H$_3$OTbL$_4$+H$^+$) FAB 1479 (TbL$_3$+H$^+$) 441 (HL + H$^+$)
4	[H$_3$O][TbL'$_3$L]·H$_2$O C$_{61}$H$_{75}$N$_8$O$_{10}$Tb	Light yellow solid, 126 °C	2922, 2851, 1635, 1594, 1533, 1500, 1441, 1395, 1370, 1165, 1078, 1062, 1031, 902, 806, 757, 691, 594, 510	C, 59.12; H, 5.78; N, 9.04	C, 59.31; H, 6.02; N, 9.01	MALDI 1223 (H$_3$OTbL'$_3$L + H$^+$) FAB 763 (TbL'$_3$+H$^+$) 441 (HL + H$^+$)

determination of metals in traces [6]. In order to explore the potential of the Ln complexes for photonic applications it is advantageous to incorporate them in an inert host matrix due to dissolution or dispersion of discrete lanthanide complexes in a polymer matrix or attachment of the lanthanide complexes to the polymer matrix through covalent bonds [7]. Recent attempts have been reported to find a route by forming thin films using Langmuir–Blodgett (LB) techniques [8, 9]. Here, we present the syntheses, characterization and luminescent properties of Langmuir–Blodgett (LB) films based on homo- and heteroleptic terbium(III) complexes with 1-phenyl-3-methyl-4-stearoylpyrazolone-5 (HL) and 1-phenyl-3-methyl-4-formylpyrazolone-5 (HL').

2. Experimental

2.1. Materials and methods

Elemental analyses of C, H, and N were performed with a Euro EA3000 Elemental Analyzer. IR spectra were measured with a FSM 2202 spectrometer with KBr pellets from 4000–400 cm^{-1}. Thermogravimetric experiments were performed on a Paulik–Paulik–Erdey Q-derivatograph under static air. Mass spectra were obtained on VG Autospec EBE (FAB$^+$) and MICROFLEX Bruker (MALDI$^+$) spectrometers.

Excitation and luminescence spectra were recorded on a FluoroMax-4 spectrofluorimeter. Solid sample quantum yields were determined using absolute method and integrating sphere. The lifetime was measured on a Panorama-2 spectrofluorimeter. The luminescence spectra of films were obtained in the wavelength from 430–700 nm using an "AvaSpec-ULS2048L-TEC-USB2" wave spectrometer

("Avantes", Holland) with a vacuum optical cryostat. The luminescence was excited by a module of an "AvaLight-LED" spectrometer equipped with a UV-LED (wavelength maximum of 355 nm). Luminescence spectra measurements were carried out from 80 K to 293 K using a "Janis VPF-100" optical vacuum cryostat (Janis, USA) with a temperature controller "Lakeshore Model 335" ("Lakeshore Cryotronics", USA).

Surface pressure–surface area ($\pi - A$) isotherm measurements and LB film deposition to solid substrates (glass plates with gold plating) were carried out using a KSV MINITROUGH 2 LB. To record the $\pi - A$ isotherms of monolayers at the air–water interface, the subphase of the Langmuir trough was filled with ultrapure water subphase at 24 °C and then 40 ml of chloroform solution of HL (1.5×10^{-3} M) or complex (5×10^{-4} M) was spread on the aqueous subphase of the Langmuir trough by using a micro-syringe. The complete system was controlled via a computer. After waiting 15 min to allow solvent evaporation, the $\pi - A$ isotherms were recorded at a rate of 10 mm/min.

The complex monolayer at the air water interface was transferred onto solid substrates by a vertical transfer method at 1 mm/min to form monolayer LB films. During the depositions, the transfer surface pressure was fixed at 34 mN/m for **1** and 43 mN/m for **2**. The monolayer was transferred along the Y-type.

2.2. Preparation of the complexes

All starting reagents and chemicals were purchased from Aldrich or Merck and used without purification. 4-Acylpyrazolones were synthesized by literature methods [10, 11]. Stearoyl chloride was synthesized from stearyl acid and $SOCl_2$. Complexes **1** and **2** were synthesized by known methods [10, 12].

The homoleptic **3** was synthesized according to the following procedure. Sodium hydroxide (1.5 mmol) was dissolved in 10 mL of ethanol and 2 mmol of HL was added. The mixture was stirred under heating for 20–30 min and a solution of 0.5 mmol $Tb(NO_3)_3$ in 10 mL of ethanol was added. The resulting mixture was stirred again for 30 min under careful heating. The reaction mixture was filtered and kept overnight. The beige precipitate was collected by filtration, washed with ethanol and finally dried in air and over P_2O_5 in desiccator.

The heteroleptic **4** was synthesized according to the following procedure. Into a solution of 0.825 g $[TbL'_3(H_2O)_2]$ [13] in 20 mL of ethanol 0.455 g of HL was added and stirred for 30 min with weak heating. The reaction mixture was filtered and left overnight. The light-yellow precipitate was collected by filtration, washed with ethanol and finally dried in air and over P_2O_5.

Complexes **1**–**4** were purified by column chromatography using a mixture of chloroform and hexane (v/v, 1/1) as eluent. Evaporation of the solvents afforded a solid product.

3. Results and discussion

3.1. General characterizations

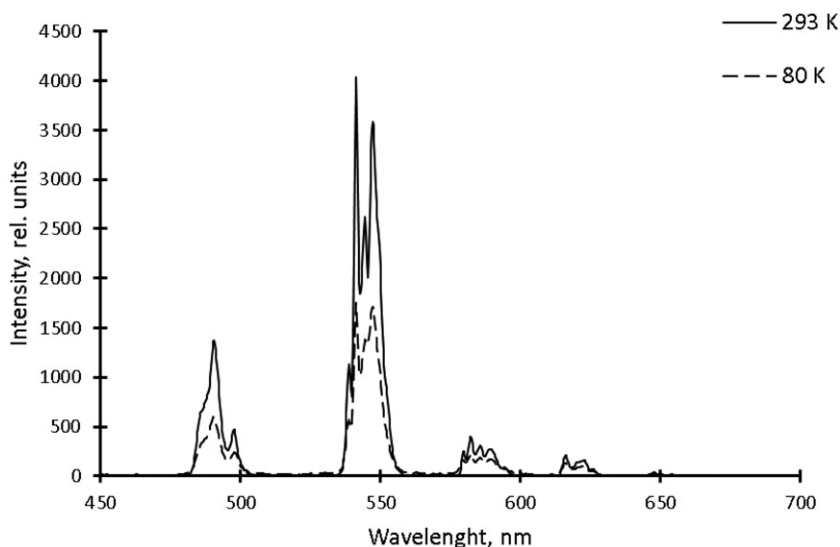Complexes **1**–**4** were synthesized by the following sequential preparation routes.

Figure 1. Luminescence spectrum of $[TbL_3 \cdot 2H_2O] \cdot 3H_2O$ (**1**) at 293 and 80 K ($\lambda_{exc} = 355$ nm, $t_{ac} = 1$ s).

Preparation of **3** was achieved by treating $Tb(NO_3)_3$ by 1-phenyl-3-methyl-4-stearoylpyrazolone-5 in a 1:4 stoichiometric M/HL ratio in the presence of NaOH. Complex **4** was prepared by treatment of $[Tb(L')_3]$ by HL. All complexes were isolated from the reaction media as white solids or light-yellow greasy materials at room temperature. The CHN microanalyses (Table 1) of the complexes are consistent with the proposed formulas. The MALDY-mass spectra of the compounds matched well with their formula weights also.

Complexes were initially characterized by IR spectra. A broad band in the complex at 3400 cm^{-1} (νOH) is due to the water molecules in the chelate. The ligand band at 1590 cm^{-1} shifts to $1635–1616$ cm^{-1} in the metal complexes, indicating involvement of the $C=O$ group in chelation. The complexes show additional bands at $1383–1368$ cm^{-1} assigned to $C–O$, indicating coordination of ligand at enol deprotonated form. Remarkably, the characteristic stretching vibrations of CH_2 are located at $2922–2920$ and $2852–2851$ cm^{-1}.

The thermal stabilities of **1–4** have been studied by thermogravimetric analysis (TG and DTA). Weight loss and endothermic effects at $50–250\,°C$ are associated with loss of water molecules and sample melting. The complexes are thermally stable up to $250–270\,°C$. Further increase of temperature leads to thermal oxidative degradation, with decomposition of the organic part of the complex in the temperature range $270–700\,°C$ with strong exothermal effects near $500\,°C$.

The crystal structures of $[YL_3 \cdot 2H_2O]$ and $[TbL_3 \cdot C_2H_5OH \cdot H_2O]$, similar to **1**, were determined by X-ray diffraction analysis earlier [7, 10]. According to X-ray studies, three aliphatic fragments n-$C_{17}H_{35}$ are codirected, which results in the formation of layers following the fastener-sticker principle. The coordination polyhedron of the central atom can be described as a strongly distorted square antiprism. The structure of **2** coordination polyhedron may be similar $TbL'_3 \cdot phen$ which was determined by X-ray diffraction and is a distorted square antiprism made up of six O atoms of three 4-formylpyrazol-5-one anions and two N atoms of 1,10-phenanthroline [13].
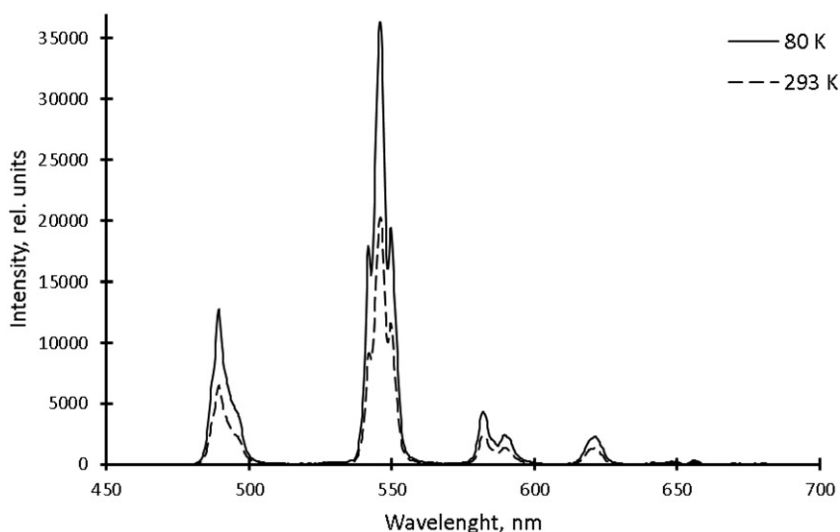
Figure 2. Luminescence spectrum of TbL$_3$·bipy (**2**) at 293 and 80 K (λ_{exc}=355 nm, t_{ac}=1 s).

3.2. Photophysical studies

Luminescent properties for thin films and solid samples are similar. Since the title complexes are candidates for luminescent materials for LB films they have been studied to evaluate photo-physical characteristics of solid samples of the complexes. Diffuse reflectance spectra and excitation spectra in **1**–**4** consist of a broad band at 340–355 nm (Figures S1–S3, in the supplementary material) assigned to π–π* transition of ligand. This region was used to excite photoluminescence.

An important condition for intense luminescence is an optimal energy gap between the ligand triplet levels and the lanthanide resonance levels. Obviously, for each element and each ligand type some optimal energy gap exists. Indeed, for effective energy transfer in terbium(III) carboxylates, the difference between the triplet energy of the organic ligand and the resonance e($^5D_4$) level difference should be 2500–4000 cm^{-1} [14]. Triplet level energy of 1-phenyl-3-methyl-4-stearoylpyrazol-5-one (21980 cm^{-1}) was determined from phosphorescent spectra of the samarium(III) complex in CHCl$_3$ at 77 K. The resonance level energy of Tb^{3+} is 20430 cm^{-1} and the magnitude of the energy gap (1550 cm^{-1}) is outside the optimal range. However, all complexes show a distinctive Tb(III) luminescence at 480–675 nm consisting of five emission bands, assigned to transitions from $^5D_4$ excited state to ^7F_J (J=6–2) ground states (Figures 1 and 2). Excitation spectra for **1**–**4** monitored at 542 nm ($^5D_4$–$^7F_5$) are similar to their absorption spectra. The most intense bands at 489 nm and 542 nm correspond to $^5D_4\rightarrow{}^7F_6$ and $^5D_4\rightarrow{}^7F_5$ transitions. Less intense bands at 585 and 625 nm correspond to $^5D_4\rightarrow{}^7F_4$ and $^5D_4\rightarrow{}^7F_3$ transitions. The splitting of the hypersensitive band at 542 nm provides evidence for a low symmetry of the coordination polyhedron in **1** and higher symmetry in **2**.

Despite nonoptimal values of the ligand's triplet energy level, **1**–**4** demonstrate good efficiency of excitation energy transfer to resonance level of terbium(III) ions. The luminescence quantum yields of **1**–**4** in the solid state were 31, 12, 43, and 25%, respectively, which are similar to that of the corresponding ligand.
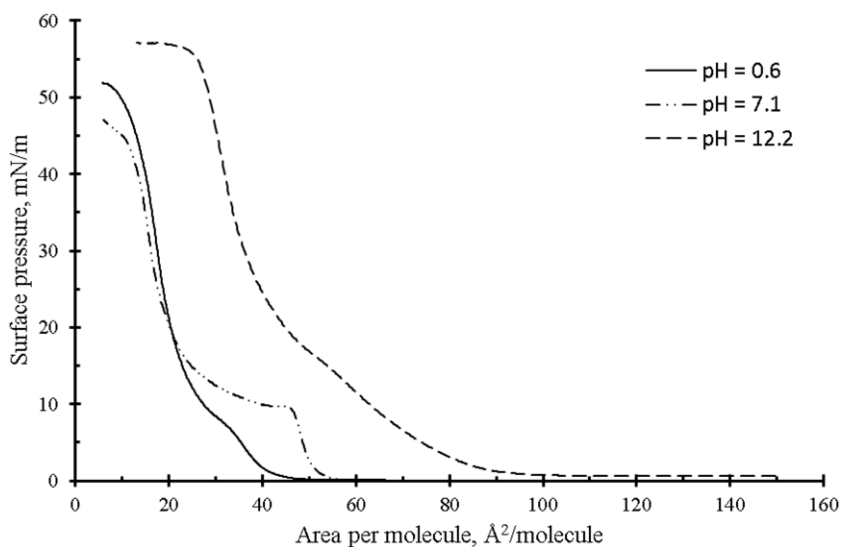
Figure 3. The $\pi-A$ isotherms of 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazolone monolayer on aqueous subphases at different pH.
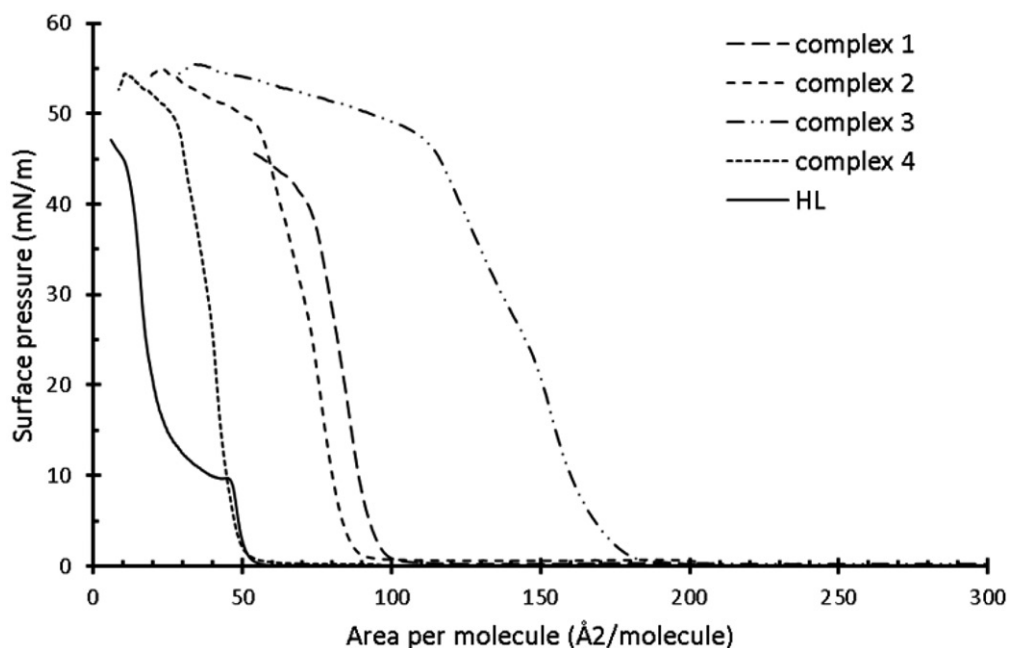

Figure 4. The $\pi-A$ isotherms of terbium complex monolayers formed on aqueous subphase at pH 6.

The excited state lifetimes for **1**–**4** were recorded for solid samples at an excitation wavelength of 355 nm at room temperature and monitoring of the $^5D_4{\rightarrow}^7F_5$ transition. Corresponding decay curves are shown in Figures S4–S7 in the supplementary material. The decay curves of both homoleptic Tb^{3+} compounds **1** and **3** can be fitted by single exponential function. The corresponding lifetimes are 626 (**1**) and 513 (**3**) µs.

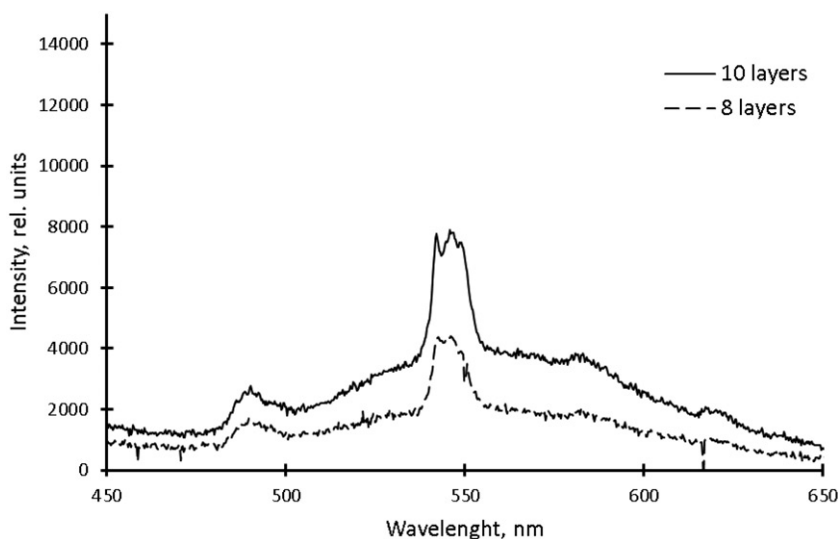The decay curves for **2** and **4** were satisfied very well by the bi-exponential equation (Equation 1):

Figure 5. Luminescence spectrum of eight and ten layers of LB films based on $TbL_3 \cdot bipy$ (**2**) at 293 K ($\lambda_{exc} = 355$ nm, $t_{ac} = 300$ s).

$$I(t) = B_1 \cdot e^{\left(-t/\tau_1\right) + \ B_2 \cdot e^{\left(-t/\tau_2\right)}} \tag{1}$$

The average lifetime is then calculated as:

$$\tau_{av} = \left(B_1\tau_1^2 + B_2\tau_2^2\right)/\left(B_1\tau_1 + B_2\tau_2\right) \tag{2}$$

The best fits give averaged lifetime of 857 and 651 µs for **2** and **4**, typical for Tb^{3+} complexes [15].

3.3. Surface pressure–area isotherms and LB films

Figure 3 shows the $\pi - A$ isotherms of 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazolone at different pH values of the aqueous solution. These $\pi - A$ isotherms indicate the realization of keto-enol tautomeric equilibria.

As can be seen from Figure 4, the $\pi - A$ isotherms of complexes differ from the HL isotherm on pure water with other conditions being equal (pH, temperature, etc.). Compression isotherms have a typical form. The area per molecule in the monolayer for complex compounds exceeds by ∼4 or more times the area of the original HL molecule. This is related to the geometry of the complex polyhedron coordination. At the same time, Langmuir films possess good compressibility and high collapse pressure.

As can be seen from Figure 4, the area per molecule of **4** monolayer is about 50 Å², which corresponds to the area per ionizable HL molecule in the monolayer at pH larger than 12. We can also assume that HL monolayer at near-neutral pH is partially ionized as evidenced by the presence of a sharp bend on the $\pi - A$ isotherm of HL monolayer at the area per molecule of ≍50 Å² at pH ≥6. The areas per molecule of monolayers of **1** and **2** are larger than those for **4** and lie in the range 90–100 Å²/molecule. The largest molecular area in the monolayer corresponds to **3**.

The luminescence spectra of LB films of **1** and **2**, obtained at room temperature, display broad emission bands at 490 nm and 541 nm, which correspond to the characteristic $^5D_4{\rightarrow}^7F_6$ and $^5D_4{\rightarrow}^7F_5$ transitions for Tb^{3+}. The $^5D_4{\rightarrow}^7F_6$ and $^5D_4{\rightarrow}^7F_5$ transition bands are also visible for the $TbL_3{\cdot}bipy$ complex at an accumulation time of 300 s. The intensity of the emission bands in the spectra depends on the number of layers, as shown in Figure 5.

4. Conclusion

Homo- and heteroleptic complexes of Tb(III) with 1-phenyl-3-methyl-4-stearoylpyrazol-5-one and 1-phenyl-3-methyl-4-formylpyrazol-5-one have been assembled and characterized. The results presented herein indicate that the complexes demonstrate high luminescence in solid state and LB films and can be used as emitting materials in probes and sensors.

Acknowledgements

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