Mixed-ligand terbium terephthalates: Synthesis, photophysical and thermal properties and use for luminescent terbium terephthalate thin film deposition

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ABSTRACT

Addition of potassium terephthalate K_2tph to an aqueous solution of a mixture of terbium nitrate and ancillary ligands L resulted in the formation of mixed-ligand terbium terephthalates Tb_2tph$_3$(TPPO)$_8$(H$_2$O)$_4$ (II), Tb_2tph$_3$(TOPO)$_2$(H$_2$O)$_4$ (III), Tb_2tph$_3$(diglyme)$_2$(H$_2$O) (IV), Tb_2tph$_3$(tetraglyme)$_4$(H$_2$O)$_3$ (V), Tb_2tph$_3$(Phen)$_2$(H$_2$O)$_2$ (VI). The composition of the mixed-ligand complexes (MLCs) was confirmed by elemental analysis, Raman spectroscopy, thermal analysis, and luminescent spectroscopy. According to the thermal analysis data, II–V exhibit lower thermal stability in comparison with the terephthalate hydrate Tb_2tph$_3$(H$_2$O)$_4$ (I). MLCs II, IV, and V are able to eliminate ancillary ligands, followed by formation of anhydrous Tb_2tph$_3$, while in case of III and IV ligand elimination is accompanied by partial thermal decomposition of Tb_2tph$_3$. Solubility tests showed that MLC II exhibits sufficient solubility in acetonitrile for thin film deposition. Thus thin films of II were deposited by spin-coating, and luminescent thin films of Tb_2tph$_3$ were obtained for the first time by thermal treatment of II films.

1. Introduction

Unique luminescent properties of lanthanide coordination compounds, such as their ability to exhibit quantum yields up to 100% and quasi-monochromatic emission, makes them useful as luminescent materials. However compounds, which are among the most widely used today, namely β-diketonates and pyrazolonates, exhibit rather low UV stabilities [1–3]. At the same time a number of lanthanide aromatic carboxylates Ln(R_xC$_6$H$_{5−x}$COO)$_3$ ("benzoates") with unique photophysical properties [4–6] and intriguing structural features [7–9] have been disclosed recently. Substituted benzoic acid anions are attractive as ligands as they are efficient sensitizers of lanthanide luminescence [4,5], their carboxylate groups interact strongly with the oxophilic lanthanides, the delocalized π−electron system provides a strongly absorbing chromophore [4,5,10]. These advantages result in the appearance of highly efficient and very stable lanthanide benzoate luminescence [11,12]. However the low volatility and solubility, caused by their polymeric structure [3,13–15], prevents their deposition as films, which is a prerequisite for the use in optoelectronic devices, such as, e.g. OLEDs [16–18]. This difficulty of thin film deposition

with appropriate morphology is the most probable explanation for the poor brightness of Tb-carboxylate based OLEDs. The present maximum brightness of 350 cd/m^2 is still ∼35% lower than that observed for Tb-diketonate containing OLEDs [19–22], and is the most probable explanation for the lack of an active research in the field of OLEDs based on aromatic carboxylates since 2002 [23–27].
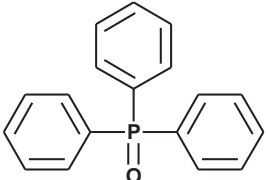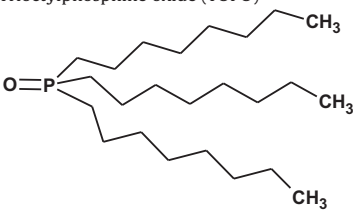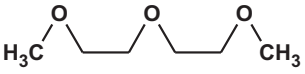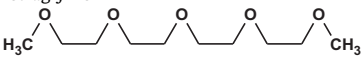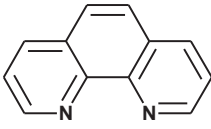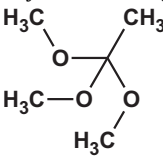
Lately, great efforts has devoted to the design of lanthanide complexes with rigid aromatic polycarboxylate ligands: dicarboxylates (terephthalates, phthalates, isophthalates, imidazole-4,5-dicarboxylates, 3,5-pyrazoledicarboxylates) and tricarboxylates (1,2,3-benzenetricarboxylates, 1,3,5-benzenetricarboxylates) [28]. Dicarboxylic terephthalic acid (1,4-benzenedicarboxylic acid, H_2tph) is known not only as a rigid building block, but also as an excellent light-harvester for lanthanide luminescence for both europium and terbium [3,29,30,32]; recently white light emitting materials based on heterometallic terephthalate of Ce^{3+}, Eu^{3+} and Tb^{3+} have been reported [31].

The formation of mixed-ligand complexes (MLCs) with ancillary neutral ligands is a well-known modification of lanthanide carboxylate structures, solubilities, and both luminescent and thermal properties [5,29]. Little attention, however, has been paid to mixed-ligand complexes (MLCs) of the lanthanide terephthalates. The difficulties encountered in the preparation of MLCs are most likely due to the rigidity of the 3D networks formed by lanthanides with dicarboxylate ligands (Ln$_2$(Carb)$_3$) [33,34]. To the best of our

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Table 1
Neutral ligands L, reagent ratios, and elemental analysis results for MLC synthesis.

L	$[Tb^{3+}]:[tph^{2-}]:[L]$	Composition
Triphenylphosphine oxide (TPPO)	2:3:8	$Tb_2tph_3(TPPO)_8(H_2O)_4$ (II) calcd. for $Tb_2C_{168}H_{140}O_{24}P_8$: C, 66.46; H, 4.21; found: C, 65.63; H, 4.27;
	4:3:8 2:3:12	
Trioctylphosphine oxide (TOPO)	2:3:8	$Tb_2tph_3(TOPO)_2(H_2O)_4$ (III) calcd. for $Tb_2C_{49}H_{73}O_{17}P$: C, 53.95; H, 7.46; found: C, 53.39; H, 7.75;
	4:3:1 2:3:10	
Diglyme	2:3:ᵃ	$Tb_2tph_3(diglyme)_2(H_2O)$ (IV) calcd. for $Tb_2C_{36}H_{42}O_{19}$: C, 39.43; H, 3.86; found: C, 39.65; H, 3.33;
Tetraglyme	2:3:ᵃ	$Tb_2tph_3(tetraglyme)_4(H_2O)_3$ (V) calcd. for $Tb_2C_{64}H_{106}O_{35}$: C, 43.84; H, 6.09; found: C, 44.26; H, 6.41;
o-Phenanthroline (Phen)	2:3:8	$Tb_2tph_3(Phen)_2(H_2O)_2$ (VI) calcd. for $Tb_2C_{48}H_{32}N_4O_{14}$: C, 47.78; H, 2.67%; N, 4.64; found: C, 47.18; H, 2.66; N, 4.11
Dibutyl ether diethylene glycol (dbdg)	2:3:ᵃ	$Tb_2tph_3(H_2O)_4$ (I) calcd. for $Tb_2C_{24}H_{20}O_{16}$: C, 32.67; H, 2.28; found: C, 32.43; H, 2.21;
Ethyl orthoformate (etof)	2:3:ᵃ	$Tb_2tph_3(H_2O)_4$ (I) calcd. for $Tb_2C_{24}H_{20}O_{16}$ C, 32.67; H, 2.28; found: C, 32.28; H, 2.32;

ᵃ L was used as a solvent. Otherwise ethanol was used as a solvent.

knowledge, information on mixed-ligand terephtalates is limited to one example of a europium MLC, $[Eu_2tph_3(Phen)_2(H_2O)_2]_n$ [35,36]. Thus, this work is devoted to the synthesis and characterization of lanthanide mixed-ligand terephthalates on example of terbium compounds and to the evaluation of benzene dicarboxylates as the luminescent materials. Ancillary ligands of different classes (aromatic diimine, phosphine oxides, and polyesters) were selected for corresponding MLC syntheses (Table 1).

2. Experimental

The following commercially available chemicals were used without further purification: terbium(III) nitrate pentahydrate 99.9%, potassium hydroxide, triphenylphosphine oxide, trioctylphosphine oxide, o-phenanthroline, and ethylene glycol dimethyl ether (diglyme) were purchased from Aldrich, and diethylene glycol dibutyl ether was purchased from Acros. All other solvents used were of analytical reagent grade and purchased from Aldrich. Ethylene glycol tetramethyl ether (tetraglyme) was purchased from Aldrich and purified by vacuum distillation.

Elemental analyses were performed with a Vario EL III Heraeus instrument. *Raman spectra* were recorded using a Renishaw InVia spectrometer. *UV–vis spectra* were recorded with a Shimadzu UV-3100 spectrophotometer; *corrected luminescence spectra* and luminescence decays were recorded with a Fluorolog 3 spectrofluorimeter. *XRD analyses* were performed on a Rigaku D/MAX 2500

(CuK_{α}). *Thermal analyses* were carried out in nitrogen atmosphere at a heating rate of 10°/min within 20–720 °C on a TG-DSC111 thermoanalyser, SETARAM, France CALVET type, with samples in platinum vessels, 75 μL volume.

2.1. Syntheses

Terbium terephthalate $Tb_2tph_3(H_2O)_4$ (I) was synthesized by the reaction of stoichiometric amounts of $Tb(NO_3)_3 \cdot 5H_2O$ and K_2tph (from H_2tph and KOH). The products were dried in air at room temperature.

I calcd. for $Tb_2C_{24}H_{20}O_{16}$: C, 32.67; H, 2.28; found: C, 32.22; H, 2.20;

2.2. Mixed ligand complex syntheses

Method 1. Suspensions of I and solutions of L were mixed in corresponding solvents and refluxed during 24 h. When L = TPPO, TOPO, Phen, ethanol was used as solvent, the ration of reagents being $[Tb^{3+}]:[L] < 1:5$, while diglyme, tetraglyme, dbdg, and etof served both as ligands and solvents. Precipitates were filtered off, thoroughly washed with ethanol and dried in vacuum at 60 °C. According to elemental analysis, all the precipitates corresponded to the starting material I.

Method 2. Aqueous solutions of K_2tph (from KOH and H_2tph) were added dropwise to the solutions of the MLCs, in situ prepared from $Tb(NO_3)_3 \cdot 5H_2O$ and L. After K_2tph addition, a white precipitate was immediately formed, filtered off, thoroughly washed with water and ethanol successively and dried in vacuum at 60 °C. Neutral ligands L, reagent ratios, and elemental analysis results for the compounds are given in Table 1.

MLC solubility tests. Solubility of I–VI in acetonitrile and ethanol:benzene mixtures was estimated only roughly (Table 2). A suspension of each compound was refluxed during several hours. After cooling and precipitation, 5 ml of clear solution were placed in a vessel with known mass, and solvent was evaporated to dryness. The mass change of the vessel yielded the corresponding quantity of the dissolved product.

Film deposition. Films were deposited from the saturated solution in acetonitrile on a glass/ITO substrate by the spin-coating technique.

Thermal treatment. Thermal treatments of II powder samples and thin films were carried out via isothermal heating at 300 °C in vacuum (0.01 mmHg) for 3 h.

3. Results and discussion

3.1. Synthesis

There are two well-known approaches widely used for syntheses of lanthanide carboxylate MLCs with the general formula $Ln(Carb)_3(L)_n(H_2O)_m$ – monocarboxylate derivatives [39]:
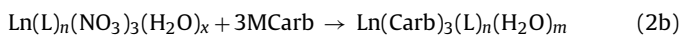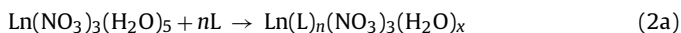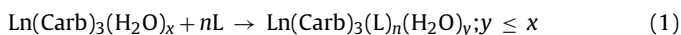
$$Ln(Carb)_3(H_2O)_x + nL \rightarrow Ln(Carb)_3(L)_n(H_2O)_y; y \leq x \quad (1)$$

$$Ln(NO_3)_3(H_2O)_5 + nL \rightarrow Ln(L)_n(NO_3)_3(H_2O)_x \quad (2a)$$

$$Ln(L)_n(NO_3)_3(H_2O)_x + 3MCarb \rightarrow Ln(Carb)_3(L)_n(H_2O)_m \quad (2b)$$

The first one is based on the introduction of the ancillary ligand L into the structure of carboxylate hydrates, accompanied by partial or complete substitution of coordinated water molecules. The second route includes consecutive steps: terbium chloride or nitrate transformation into soluble mixed-ligand compound followed by a ligand exchange reaction with soluble carboxylate salts.

It is obvious that in case of terbium terephalate hydrate the branched system of intermolecular binding and, as consequence, extremely low solubility prevents MLC formation according to first method (1). Even the second route bears the risk of precipitation of insoluble I instead of MLC formation via reaction (2b).

To check the suitability of these approaches to the synthesis of MLCs of terbium terephthalate, we selected a set of ancillary ligands of different classes, which, on one hand, possess a high donor activity and, on the other hand, have quite bulky structures to support the transformation of the branched 3D polymeric structure of terephthalates into a soluble form of the MLCs. The ancillary ligands chosen were aromatic and aliphatic phosphine oxides (TPPO and TOPO), polyethers of different structure (diglyme, tetraglyme, dbdg, and etof), and aromatic diimine (Phen) (see Table 1), the MLC of europium terephthalate with Phen is already being known [34,36]. The selected ligands have previously been demonstrated to readily penetrate the lanthanide coordination sphere in inorganic nitrates or chlorides as well as with organic carboxylates, thus forming MLCs [5,40–42].

The first route proved to be inefficient for all the ancillary ligands studied: MLCs were neither formed in solution nor in the precipitates, the precipitates still containing I only.

In syntheses via the second route (Eqs. (2a)–(2b)), on mixing of the reagents, the products were formed as precipitates, which were thoroughly washed with ethanol and water and completely dried in vacuum at 60 °C during several hours to avoid ligand and solvent impurities. According to elemental analytical data, products II–VI, corresponding to MLCs, contained both water and ancillary ligands (Table 1), and, as exemplified by II, III syntheses, the composition of the MLCs formed did not depend on the reagents' stoichiometry. For the case of two ligands (dbdg and etof), formation of MLCs did not occur, and products were identified as terbium terephthalate hydrate (I).

However, the data of elemental analysis alone do not suffice to confirm the true mixed-ligand nature of compound II–VI. Indirect proof of MLC formation is provided in solubilities in comparison to I (Table 2). Furthermore we complemented the elemental analysis by following combination of methods: (1) thermal analysis, which showed a stepwise loss of mass according to the ligand elimination, followed by the terephatalate full decomposition into oxide; (2) Raman spectroscopy, which is more informative than IR [16,18,43,44] for analysis of spectra with aromatic and carboxylic vibrations; (3) luminescence spectroscopy, which can show changes in the emission via band splitting, excitation spectra and lifetimes of the excited state, caused by MLC formation.

3.2. Thermal analysis

A thermal analysis of I–VI was run in inert atmosphere. TGA data of II–VI were compared with I (Fig. 1, Fig. S1). After complete dehydration of I in the temperature range of 20–150 °C anhydrous Tb_2tph_3 was formed, that was thermally stable until ∼400 °C
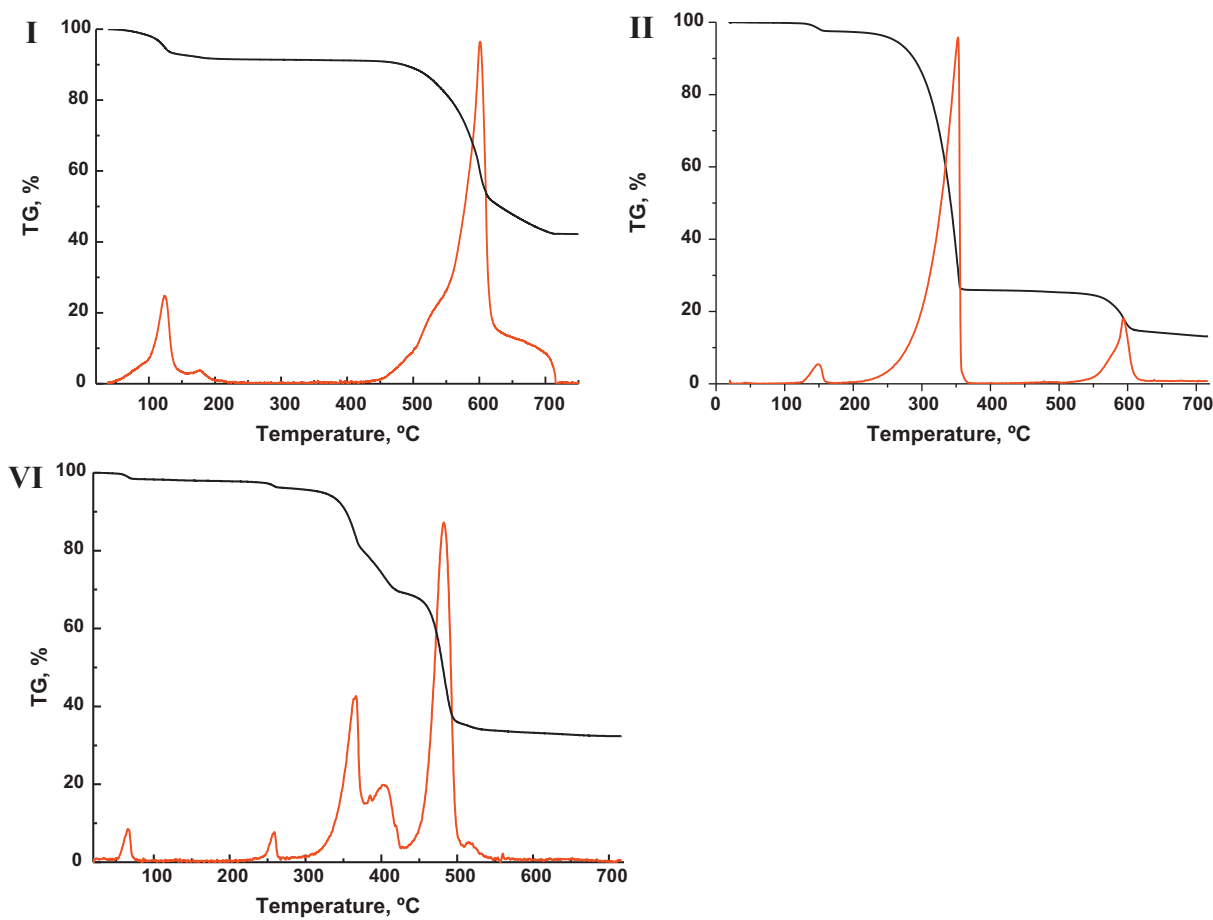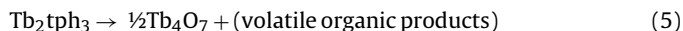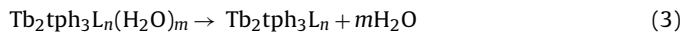
Table 2
Solubilities of the compounds I–VI in acetonitrile and benzene:ethanole mixture, g l^{-1}/mmol l^{-1}.

	I	II	III	IV	V	VI
Acetonitrile	$0.05/5.7 \times 10^{-2}$	6.8/2.2	$0.30/1.8 \times 10^{-2}$	2.1/1.9	2.3/1.7	$0.05/4.2 \times 10^{-2}$
Ethanol:benzene	$0.02/2.3 \times 10^{-2}$	$0.5/1.6 \times 10^{-1}$	$0.1/6.1 \times 10^{-2}$	$0.1/9.1 \times 10^{-2}$	$1.0/5.7 \times 10^{-1}$	$0.1/8.5 \times 10^{-2}$
Molar mass	882	3106	1647	1096	1752	1182

Fig. 1. TG and DTG data of complexes $Tb_2tph_3(H_2O)_4$ (I), $Tb_2tph_3TPPO_8(H_2O)_4$ (II), and $Tb_2tph_3Phen_2(H_2O)_2$ (VI).

(Fig. 1a), after which it completely decomposed into terbium oxide Tb_4O_7 in the temperature range between 450 and 700 °C according to reaction (5).

In TG curves of MLCs, the stages of both dehydration and ancillary ligand elimination appear at temperatures below 400 °C, thus weight loss steps can be described by Eqs. (3)–(5):

$$Tb_2tph_3L_n(H_2O)_m \rightarrow Tb_2tph_3L_n + mH_2O \qquad (3)$$

$$Tb_2tph_3L_n \rightarrow Tb_2tph_3 + nL \qquad (4)$$

$$Tb_2tph_3 \rightarrow \tfrac{1}{2}Tb_4O_7 + (\text{volatile organic products}) \qquad (5)$$

The TG-DTG curves of II illustrate this stepwise weight loss process: in the range of 100–150 °C elimination of four water molecules occurs, while in the range of 200–350 °C a loss of eight molecules of TPPO and formation of Tb_2tph_3 is observed, which is thermally stable until at least 400 °C.

Similar thermal behavior was found for IV and V (Fig. S1). In case of III and VI the stages of the elimination of ancillary ligands (4) and complete decomposition (5) are very close to each other in TG curves and can be separated only in DTG curves, as illustrated in Fig. 1 for VI. Two DTG peaks at 80 °C and 270 °C correspond to the loss of water molecules, while peaks at 365 °C and 405 °C are ascribed to the elimination of coordinated o-phenanthroline ligands.

3.3. XRD studies

X-ray powder diffraction was used to compare the phases of the synthesized MLC and I. Powder XRD patterns of II–VI differ from that of I. The XRD pattern of VI coincides with the data recalculated from a single crystal structure analysis of $Eu_2tph_3Phen_2(H_2O)_2$ [34] (Fig. 2), except for the shifts of reflexes due to the different ionic radii of Eu^{3+} and Tb^{3+}, thus confirming their isostructurality.

3.4. Raman spectroscopy

The Raman spectroscopic analyses are based on the direct comparison between I, the respective MLCs and the ligands, the spectral
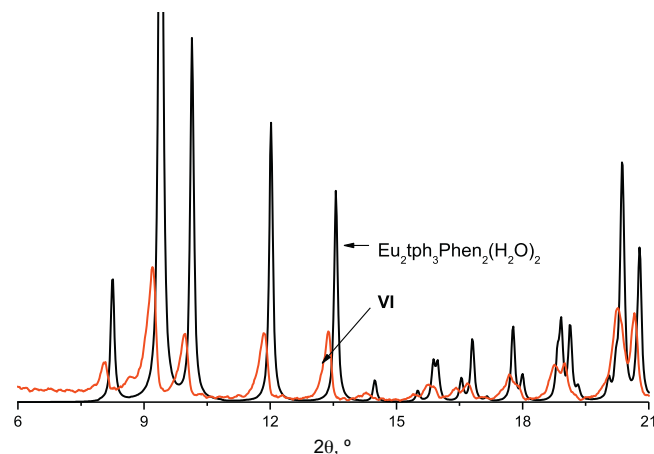

Fig. 2. Comparison of the calculated powder XRD pattern of $Eu_2tph_3Phen_2(H_2O)_2$ [16] and measured XRD of $Tb_2tph_3Phen_2(H_2O)_2$ (VI).
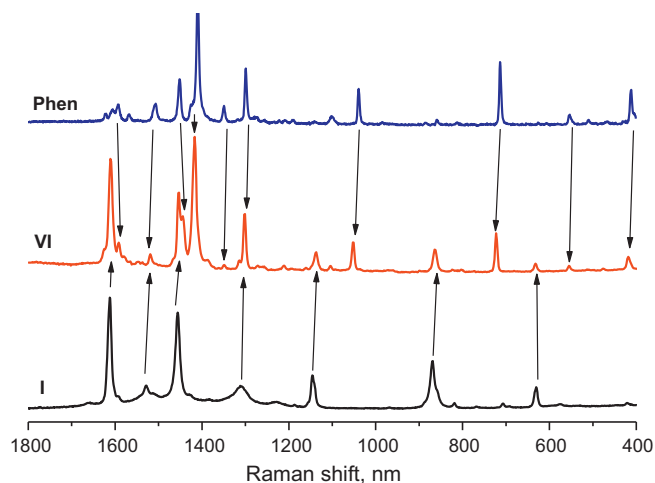
Fig. 3. Raman spectra of $Tb_2tph_3(H_2O)_4$ (I), $Tb_2tph_3Phen_2(H_2O)_2$ (VI), and Phen.

ranges reproduced covering the most characteristic vibrations. The formation of the MLC is thus indicated by the appearance or disappearance, respectively, of ancillary ligand bands. For I-TOPO-III and I-tetrglyme-V the spectral range of 2800–3200 cm^{-1} served this purpose, where the appearance of the aliphatic C—H vibrations of ligand in addition to the aromatic C—H vibrations of tph^{2-} ions could be traced. As opposed to that, it is difficult to select characteristic bands of the Phen ligand, do not overlap with aromatic bands of tph^{2-}. Therefore, for I, Phen and VI, the comparison

of the spectra only confirms that spectrum of VI is a superposition of both I and Phen with slightly shifted bands (Fig. 3).

In the comparison of I, II and TPPO (Fig. 4a) the Raman intensities of TPPO appeared to be so intense that tph^{2-} vibrations could be detected only at a high zoom of the spectrum (Fig. 4b). After thermal treatment of II, leading to the TPPO elimination with formation of anhydrous Tb_2tph_3 (Ia), the tph^{2-} bands become visible in the Raman spectrum (Fig. 4d).

$$Tb_2tph_3(TPPO)_8(H_2O)_4(II) \rightarrow 4H_2O + 8TPPO + Tb_2tph_3(Ia) \quad (6)$$
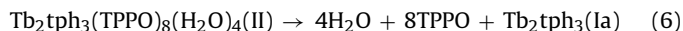
In the TPPO spectrum bands at 1026 and 999 cm^{-1} can be attributed to P=O vibrations, and bands at 617 and 684 cm^{-1} – to P–C$_6$H$_5$ vibrations. In the spectrum of II, the P=O bands are split and slightly shifted to higher frequencies with regard to free TPPO (1029 and 997, 1003 cm^{-1}) (Fig. 4c). Bands of P–C$_6$H$_5$ groups, which do not take part in the complexation, do not change their positions.

3.5. Luminescent characteristics

Despite their low solubility in common solvents (Table 2), acetonitrile solutions of complexes I–VI displaying luminescence at micromolar concentrations were obtained. In the excitation spectrum of I two bands are observed (~270 and ~320 nm) (Fig. 5a). In case of III, IV, and VI the intensity of the band at ~320 nm significantly decreases and even disappears for VI (Fig. 5a). Such changes of the character of solution excitation spectra indicate the additional energy transfer processes, brought about by MLC formation. Fig. 6
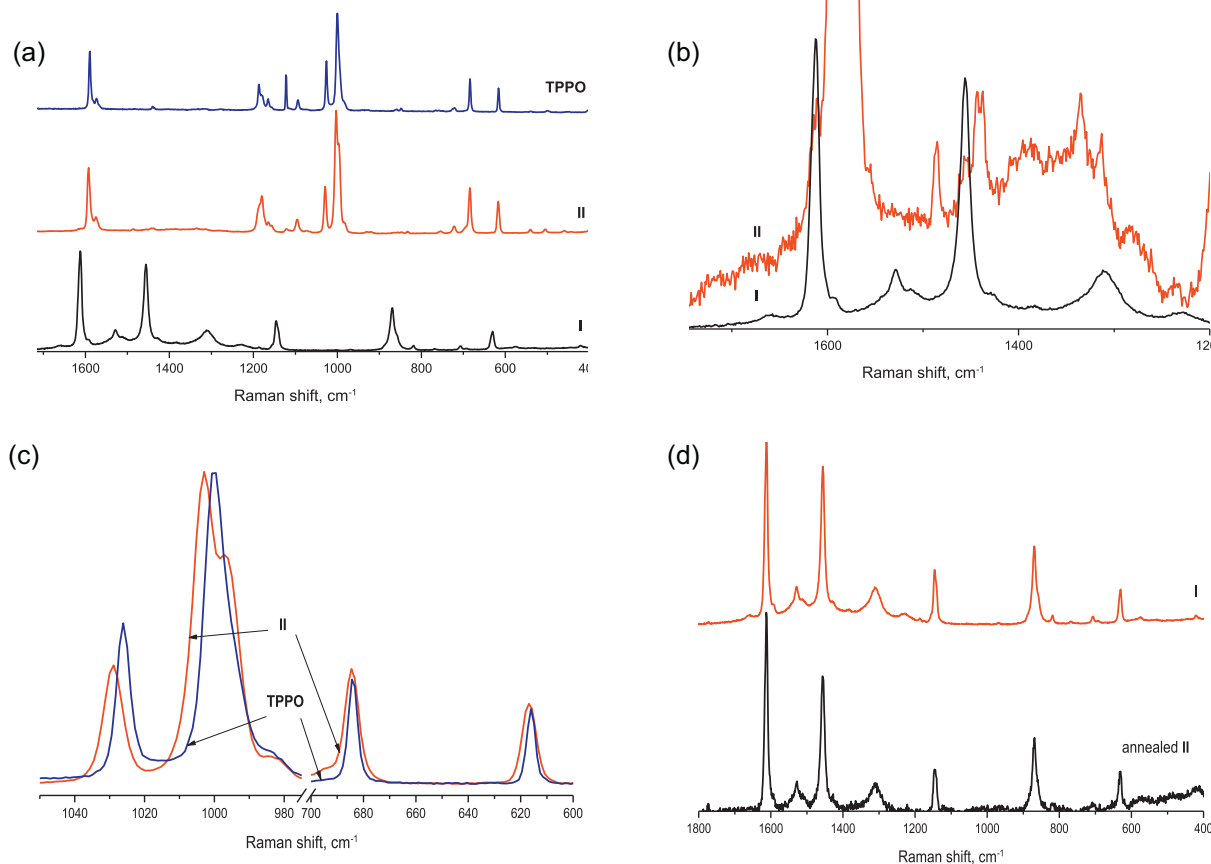

Fig. 4. Raman spectra of $Tb_2tph_3(H_2O)_4$ (I), $Tb_2tph_3TPPO_8(H_2O)_4$ (II), and annealed I (Ia).
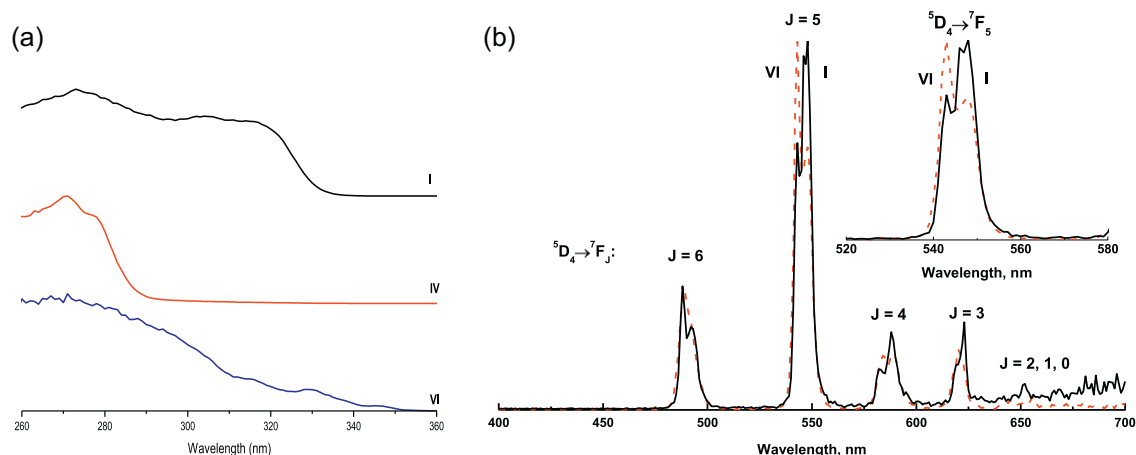
Fig. 5. Normalized (a) excitation spectra of $Tb_2tph_3(H_2O)_4$ (I), $Tb_2tph_3(diglyme)_2(H_2O)$ (IV), and $Tb_2tph_3Phen_2(H_2O)_2$ (VI) in acetonitrile, λ_{em} = 545 nm, and (b) emission spectra of $Tb_2tph_3(H_2O)_4$ (I) and $Tb_2tph_3Phen_2(H_2O)_2$ (VI) in acetonitrile, λ_{ex} = 280 nm.

The obtained solution emission spectra of all the compounds I–VI are typical for terbium compounds, showing luminescent bands, originated from transitions of the terbium ion, and no emission in the blue region was observed (Fig. 5b). The Stark splitting of the terbium emission bands is observed in the spectrum of I, and the relative intensity ratios between the split bands changes in going to the spectra of MLCs, as exemplified in Fig. 5b for VI. This change can be taken as yet another indirect proof for MLC formation (Fig. 5b, inset).

The lifetime of the excited state is a very sensitive characteristic of the coordination environment of the central ion, so its dramatic change for MLCs III, IV, and VI in comparison to I (Table 3) proves the participation of the ancillary ligands in the energy transfer processes.

It is noteworthy that in case of II and V no significant changes in the excitation spectra and lifetimes of the excited state were observed, which shows that their ancillary ligands do practically not participate in energy transfer processes.

3.6. Terbium tetephthalate MLCs evaluation as luminescent materials

An evaluation of the potential of MLCs as luminescent materials was carried out in comparison with homoligand terbium terephthalate, taking into account the following properties: (a)
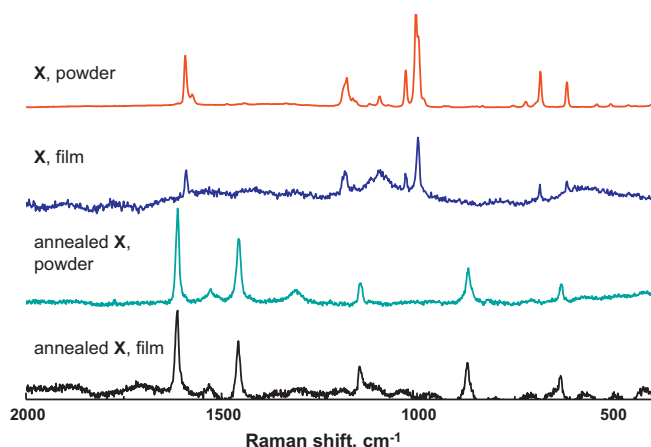

Fig. 6. Raman spectra of $Tb_2tph_3TPPO_8(H_2O)_4$ (II) and Ia powder and thin film.

luminescence efficiency, (b) stability and (c) solubility, the latter being mandatory for thin film formation, if the complexes volatility is too low for vapor deposition.

In case of VI, the luminescence is quenched significantly, that is related to the well-known effect of terbium luminescence quenching by coordinated o-phenantroline [40]. In case of compounds II–V, there is no dramatic change of luminescence intensities. The thermal stability of compounds II–V decreases in comparison to I, because of ancillary ligand elimination, which occurs in the temperature range from 80 to 230 °C (Table S1).

This deterioration of photophysical properties or thermal stability of MLCs in comparison to the homo-ligand terbium terephthalate discourages their use as luminescent thin-film materials. However, at the same time, compounds II and V demonstrate a significant increase of solubility (up to two orders of magnitude), which enables their thin film deposition by convenient the spin-coating technique.

Thus we decided to use these soluble, but unstable MLCs not as luminescent materials, but as precursors for the highly stable homoligand terbium terephthalate. The procedure follows a method of thin film deposition of non-volatile, insoluble homoligand aromatic carboxylates $Ln(Carb)_3$, which was proposed recently [37,38] and consists of two steps:

(1) Synthesis of soluble aromatic carboxylate MLC with neutral donor ligands L of general formula $Ln(Carb)_3L_n(H_2O)_x$
(2) MLC thin film deposition and annealing and formation of the parent carboxylate according to reaction $Ln(Carb)_3L_n(H_2O)_x$ (film) $\rightarrow Ln(Carb)_3$ (film) $+ nL\uparrow + nH_2O\uparrow$

A major requirement of a successful use of this method, a co-ligand L should be chosen that reversibly forms soluble MLC and evaporates after decomposition of the MLC according to reaction (4).

The analysis of the resulting MLC characteristics shows that compound II satisfies all these requirements, and has thus been selected as the precursor for thin films deposition of Tb_2tph_3 (Ia).

Powder and thin films of Ia were obtained on isothermal heating of both bulk sample and thin films (300 °C, 0.01 mmHg). According to the elemental and thermal analyses, the Ia powder composition corresponds to Tb_2tph_3. In the range of 400–2000 cm^{-1} Raman spectra of I and Ia are identical (Fig. 6), and lifetimes of the excited state of I and Ia also coincide (Table 3).

Table 3
Lifetimes of the $^5D_4$ excited state (ms, ±0.01) of compounds I–VI and Ia, measured for the relaxation to the $^7F_5$ state.

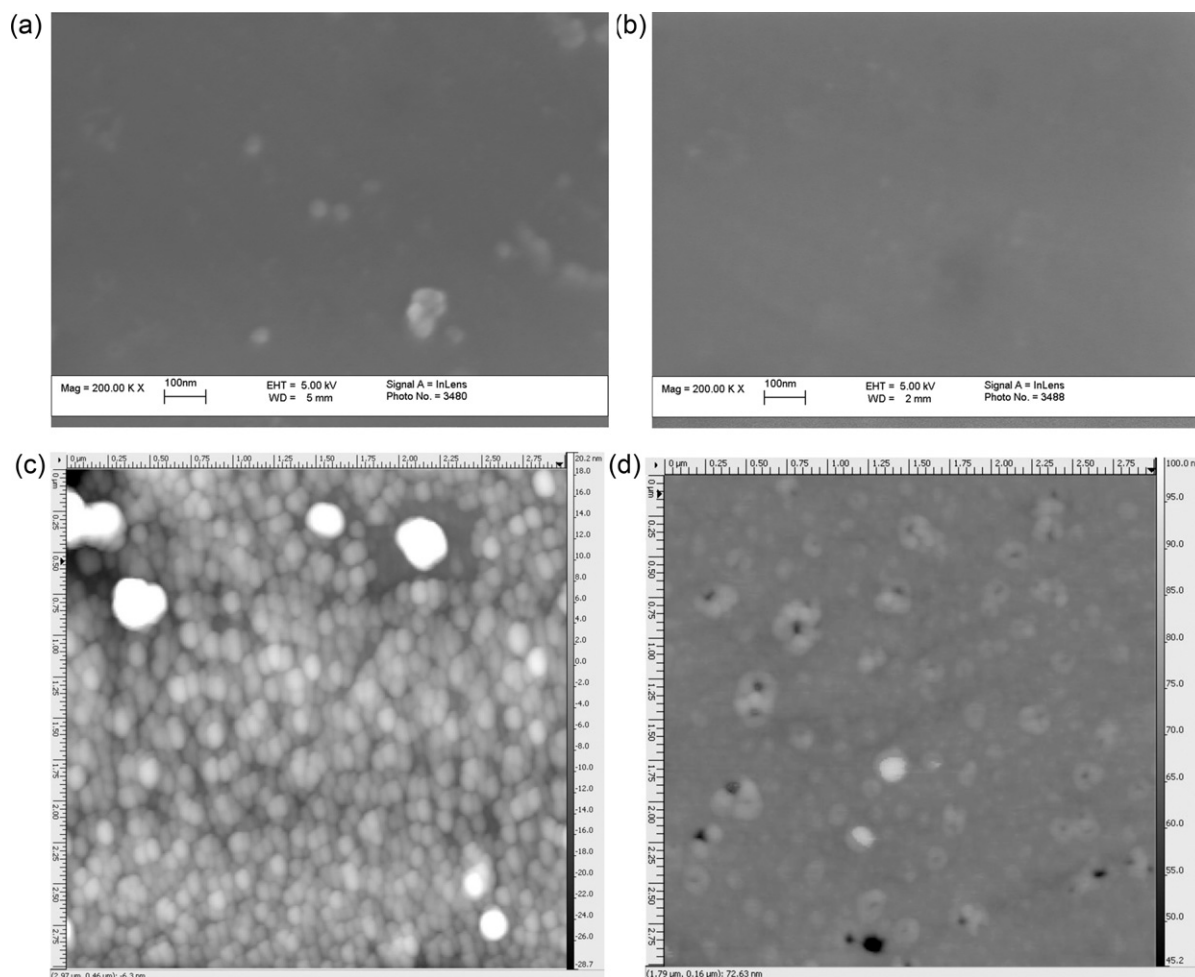| I	II	III	IV	V	VI	Ia
0.72	0.77 (powder) 0.78 (film)	1.32	1.48	0.74	0.25	0.73 (powder) 0.72 (film)

Fig. 7. SEM (a, b) and AFM (c, d) images of $Tb_2tph_3TPPO_8(H_2O)_4$ (II) and Ia films.

The most important aspect is that the luminescent characteristics, including the lifetimes of the excited states, are the same for film of Ia and for I and Ia powders (Table 3), respectively, as well.

The surface of the films deposited was investigated by atomic force and scanning electron microscopy (Fig. 7).

One can see the presence of areas with high surface roughness of the initial II films, giving a root-mean square roughness of Sq = 8.0 nm and average roughness of Sa = 4.8 nm according to a 3 μm × 3 μm scan. These areas, however, disappear on the surface of the annealed Ia film, and its roughness for the same size scan is only Sq = 1.98 nm and Sa = 1.00 nm. Thus, thermal treatment does not only lead to TPPO elimination, but also to a smoothing of the film surface. This seems to be a common feature of coordination compound thin films, as was demonstrated for thin films deposited both from vapor phase and from solution [1,18,45,46].

The combination of the spectroscopic methods applied lets us conclude that we have received a thin film of MLC compound II and subsequently transformed it (Eq. (6)) into a thin film of I, which was shown to be of rather good quality.

4. Conclusion

Using a series of ancillary ligands, it was shown that mixed-ligand terbium terephthalates can be synthesized via ligand exchange reaction between soluble terbium mixed-ligand nitrate and soluble carboxylate salts. The formation of MLCs with TPPO, TOPO, diglyme, tetraglyme, and Phen was confirmed by elemental and thermal analyses, Raman spectroscopy, and by their luminescence characteristics. TPPO and tetraglyme ligands did not participate in energy transfer processes, which was confirmed by the invariability of the excited state lifetimes and excitation spectra after complexation. According to the thermal analysis data, MLCs with TPPO, TOPO, diglyme, and tetraglyme exhibit lower thermal stabilities as compared to the homoligand terephthalate. At the same time, at elevated temperatures, MLCs with TPPO, diglyme,

and tetraglyme can eliminate ancillary ligands under formation of terbium terephthalate. Solubility tests showed that the complex $Tb_2tph_3TPPO_8(H_2O)_4$ exhibits the highest solubility in acetonitrile among the MLCs studied, which allowed its to use in the fabrication of terbium terephthalate thin films via the decomposition of mixed-ligand complexes. Terbium terephthaslate films were deposited for the first time and were of high quality (Sq = 1.98 nm and Sa = 1.00 nm).

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.12.021.

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