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Mendeleev Commun., 2014, **24**, 91–93
Mendeleev Communications

Mixed-ligand terbium hydroxyaromatic carboxylates with *o*-phenanthroline: luminescence quenching at 300 and 77 K

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DOI: 10.1016/j.mencom.2014.03.008

A luminescence quenching mechanism of mixed-ligand terbium aromatic carboxylates with *o*-phenanthroline, leading to a high temperature sensitivity of luminescence, was suggested.

At a temperature decrease from 350 to 50 K, the luminescence intensity of organic compounds increases because of the phonon vibration freezing.[1] At the same time, the luminescence intensity of compounds known as 'luminescent thermometers' grows so drastically with decreasing temperature that it cannot be explained only by an increase in structural rigidity upon cooling.[2–5] For example, the mixed-ligand complex of terbium tris-salicylate with *o*-phenanthroline, $Tb(carb^2)_3(Phen)$ (Figure 1), was described[6] to exhibit a very high luminescence intensity ratio at 77 and 300 K (I_{77}/I_{300}), which can be caused by a change of the impact of several intramolecular energy transfer processes at a temperature change. Indeed, it is known that benzoic acid derivative anions $carb^-$ can efficiently sensitize Tb^{III} luminescence,[7] whereas the presence of OH substituents[8] and Phen ligands[9] in the coordination sphere of terbium promotes luminescence quenching.

We suggested that absorption and subsequent energy transfer to the emitting level of terbium in $Tb(carb^2)_3(Phen)$ occurs through the carboxylate anion, while terbium luminescence competes with non-radiative energy transfer to the Phen triplet level and non-radiative relaxation *via* the salicylate anion OH vibrations. Quenching processes are considerably slowed down as the temperature decreases, which leads to an increase in the terbium ion luminescence intensity. To confirm this statement, we have selected mixed-ligand terbium complexes $Tb(carb)_3(Phen)$ **1**–**5** with Phen and aromatic carboxylic acid anions differing in the number and positions of OH substituents (Figure 1). The analysis of temperature-sensitive alterations of the luminescent properties of **1**–**5** reveals the preferable quenching mechanism: either *via* the triplet state of the Phen ligand or *via* the OH vibrations.

Mixed-ligand complexes (MLCs) $Tb(carb)_3(Phen)$ **1**–**5** (where Hcarb = $Hcarb^1$–$Hcarb^5$, respectively) were synthesized according to a procedure described elsewhere.[10,†] Their composition was confirmed by elemental analysis, IR spectroscopy (Figure S1, see Online Supplementary Materials) and TGA (Figure S2). IR spectra revealed the characteristic vibrations of both $carb^-$ and Phen, and an intense broad band of water OH vibrations was absent from the range of 3200–3600 cm^{-1}, while a low-intensity broad band of carboxylate anion OH groups was observed in the spectra of **2**–**5** (Figure S1).

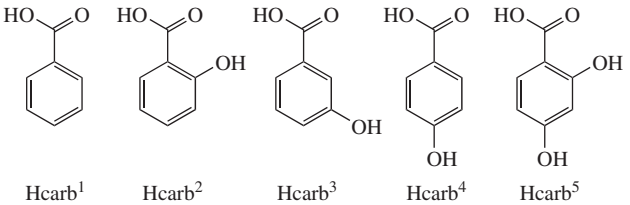

Figure 1 Aromatic acids Hcarb.

The triplet energies of carboxylate anions were determined from the position of 0–0 phonon transition of the phosphorescence band in the 77 K luminescence spectra of the corresponding gadolinium carboxylates $Gd(carb)_3$ synthesized by a conventional approach.[7] To distinguish phosphorescence and fluorescence bands, the luminescence spectra were also measured at 300 K, at which phosphorescence does not appear. The position of the 0–0 phonon transition was determined by the Gaussian deconvolution of the phosphorescence band (Figure S4). The triplet state values were in a range of ~21 700–23 500 cm^{-1} in good agreement with published data for these carboxylates (Table 1).

The luminescence spectrum and excited state lifetime measurements were carried out for compounds **1**–**5** and **3**·2H_2O–**5**·2H_2O at 77 and 300 K. The luminescence intensity and excited state lifetimes of **3**–**5** coincided with those of their hydrates; thus, water molecules in the hydrates are hydrogen-bonded to the

Table 1 Photophysical characteristics of complexes **1**–**5** at 77 and 300 K and triplet state energies (E_T) of the carboxylate ligands.

Compound	τ_{77}/ms	τ_{300}/ms	τ_{77}/τ_{300}	I_{77}/I_{300}	E_T/cm^{-1}
1	1.05(1)	0.093(2)	10	8	21 700 (23 200[7])
2	0.68(2)	0.0128(3)	50	23	23 300 (23 800[11])
3	0.630(2)	0.0119(4)	50	23	22 200 (22 500[12])
4	0.750(2)	0.0464(16)	60	30	22 700 (23 530[13])
5	0.56(1)	0.0043(2)	130	80	23 500 (24 000[14])

† By the addition of an aqueous solution of 3 equiv. of Kcarb to an ethanol solution of an equimolar mixture of $TbCl_3·6H_2O$ and Phen·H_2O, the MLC $Tb(carb)_3(Phen)(H_2O)_x$ [x = 0, Hcarb = $Hcarb^{1,2}$ (**1**, **2**); x = 2, Hcarb = = $Hcarb^{3–5}$ (**3**·2H_2O–**5**·2H_2O)] were obtained as precipitates. The water content of air-dried products was determined from TG curves (Figure S1). Anhydrous **3**–**5** were obtained by the thermal treatment of **3**·2H_2O–**5**·2H_2O at low pressure at 150–200 °C for 1h.

Elemental analysis was performed on a Vario Micro Cube analyzer.

$Tb(carb^1)_3(Phen)$ **1**. Found (%): C, 56.35; H, 3.20; N, 3.89. Calc. for $TbC_{33}H_{23}N_2O_6$ (M = 702) (%): C, 56.42; H, 3.30; N, 3.99.

$Tb(carb^2)_3(Phen)$ **2**. Found (%): C, 52.78; H, 3.24; N, 4.03. Calc. for $TbC_{33}H_{23}N_2O_9$ (M = 750) (%): C, 52.81; H, 3.09; N, 3.73.

$Tb(carb^3)_3(Phen)$ **3**. Found (%): C, 52.74; H, 3.31; N, 3.78. Calc. for $TbC_{33}H_{23}N_2O_9$ (M = 750) (%): C, 52.81; H, 3.09; N, 3.73.

$Tb(carb^4)_3(Phen)$ **4**. Found (%): C, 52.69; H, 3.17; N, 3.80. Calc. for $TbC_{33}H_{23}N_2O_9$ (M = 750) (%): C, 52.81; H, 3.09; N, 3.73.

$Tb(carb^5)_3(Phen)$ **5**. Found (%): C, 49.36; H, 3.04; N, 3.69. Calc. for $TbC_{33}H_{23}N_2O_{12}$ (M = 798) (%): C, 49.64; H, 2.90; N, 3.51.

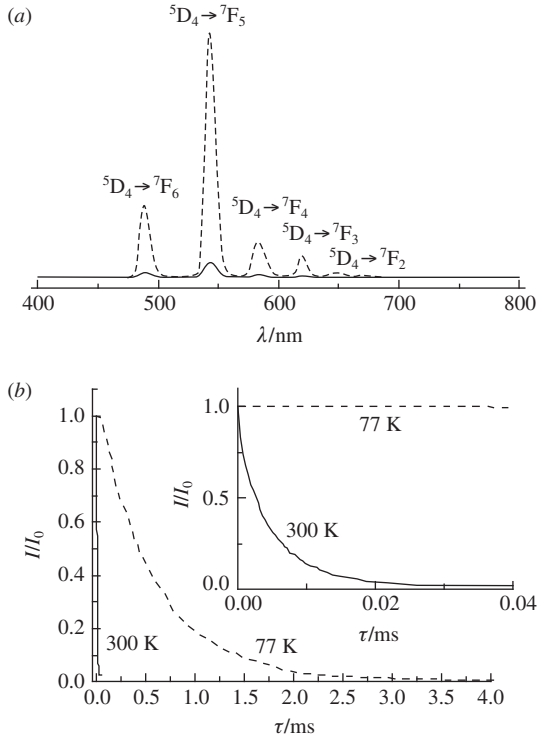

Figure 2 (*a*) Normalized luminescence spectra and (*b*) relaxation kinetics of the $^5D_4$ excited state to the $^7F_6$ ground state of Tb(carb^5)$_3$(Phen) at 77 and 300 K.

peripheral ligand OH groups and are not coordinated by the central terbium ion.

The luminescence intensity I and the excited state lifetime τ of compounds **1**–**5** increase with lowering temperature (Figure S3). Luminescence intensity ratio (I_{77}/I_{300}) and the lifetime of the excited state ratio (τ_{77}/τ_{300}) were selected as parameters characterizing the temperature dependence of the luminescence properties (Figure 2, Table 1).

These data show that a change in the I_{77}/I_{300} and τ_{77}/τ_{300} values for compounds **1**–**5** has a similar character, as expected[7] (Figure 3). The lowest values of I_{77}/I_{300} and τ_{77}/τ_{300} are observed for complex **1**, unsubstituted benzoic acid (Hcarb^1) derivative. These values for monohydroxybenzoic acid derivatives **2**–**4** are almost independent of the hydroxyl substituent position, but they are higher than those of **1**. Maximum I_{77}/I_{300} and τ_{77}/τ_{300} values were recorded for dihydroxybenzoic acid derivative **5**.

At the same time, no dependence of the I_{77}/I_{300} and τ_{77}/τ_{300} ratios on the carboxylate anion triplet state energy E_T was observed (Figure 3), *i.e.* they are affected by only the number of hydroxyl substituents of the carb$^-$ benzene ring. This suggests that both

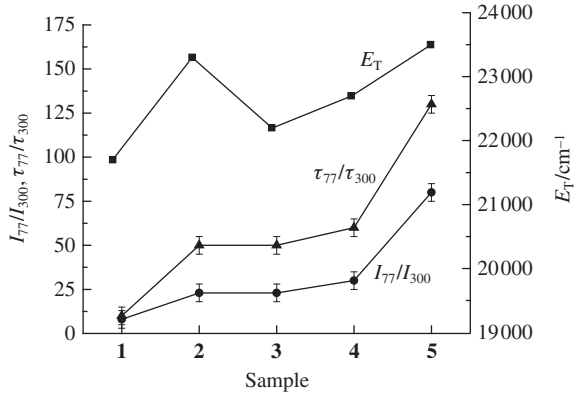

Figure 3 Luminescence intensity ratios I_{77}/I_{300}, excited state lifetime ratios τ_{77}/τ_{300} and carboxylate triplet state energies E_T for compounds **1**–**5**.

Table 2 Photophysical characteristics of Tb(carb^1)$_3$, **1**, Tb(carb^4)$_3$, and **4**.

Compound	τ_{77}/ms	τ_{300}/ms	τ_{77}/τ_{300}
Tb(carb^1)$_3$	2.15(2)	2.50(2)	0.9
1	1.05(1)	0.093(2)	10
Tb(carb^4)$_3$	1.79(2)	0.532(4)	3
4	0.75(2)	0.046(2)	60

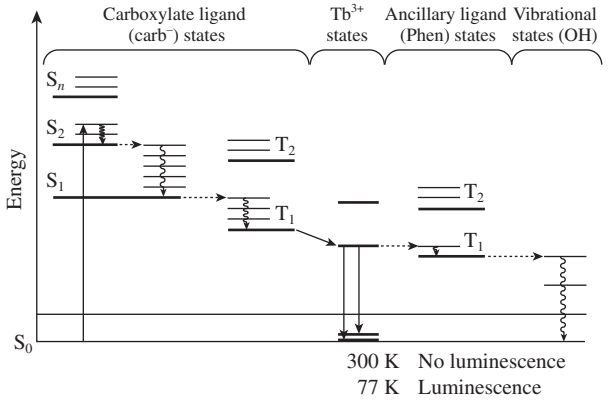

Figure 4 MLC luminescence at 77 and 300 K.

Phen and OH groups participate in the energy transfer, which causes luminescence quenching at 300 K (Figure 4).

The luminescence quenching at room temperature is due to excitation energy transfer to the triplet level of Phen followed by rapid non-radiative relaxation *via* the OH vibrations. At lower temperatures, the non-radiative relaxation processes are significantly slowed down, corresponding to a great reduce of the non-radiative relaxation constant, leading to an increase in luminescence intensity. When the number of benzene ring hydroxyl substituents increases from 0 to 2, MLC luminescence intensity at room temperature decreases, and the I_{77}/I_{300} ratio grows. Thus, the maximum $I_{77}/I_{300} = 80$ and $\tau_{77}/\tau_{300} = 130$ were obtained for the MLC of complex **5** (Figure 4). Meantime, further increasing of the number of hydroxyl substituents is useless since the absolute value of the luminescence intensity decreases as the ratio I_{77}/I_{300} rises.

To confirm that the quenching process involves both OH groups and Phen, τ_{77}/τ_{300} values were measured for the tris-carboxylates Tb(carb^1)$_3$ and Tb(carb^4)$_3$[‡] and compared with those for compounds **1** and **4** (Table 2).

The comparison of the lifetimes of the excited state of Tb(carb)$_3$ and Tb(carb)$_3$(Phen) shows that, in both cases, the introduction of the Phen ligand in the MLCs reduces the excited state lifetime at both 300 and 77 K, *i.e.* luminescence quenching *via* Phen triplet level takes place even at 77 K, although being much weaker.

The τ_{77}/τ_{300} value for Tb(carb^1)$_3$ that contains neither OH nor Phen is less than 1; that is, in the absence of both quenchers, the luminescence intensity does not increase on cooling. Luminescence lifetime is a highly structure-sensitive characteristic, so its slight decrease is probably due to a change in the terbium coordination environment geometry at low temperature.

Complex Tb(carb^4)$_3$ contains only OH groups, and its τ_{77}/τ_{300} value is 3. In the presence of only a Phen quencher in the MLC [Tb(carb^1)$_3$(Phen) **1**] the τ_{77}/τ_{300} ratio is 10, and after introduction of both quenchers (complex **4**) the τ_{77}/τ_{300} value reaches 60. Such a non-additive behaviour suggests a synergistic effect of OH and Phen quenchers and confirms the proposed scheme of luminescence quenching (Figure 4).

Thus, the luminescence quenching of Tb(carb)$_3$(Phen) at 300 K is due to energy transfer to the triplet level of Phen followed by non-radiative relaxation *via* the vibrations of OH groups. There-

‡ Synthesized according to a published procedure.[7]

fore, to achieve a high thermal sensitivity of luminescence, it is necessary to introduce simultaneously OH substituents into the carboxylate anion and *o*-phenanthroline into the terbium MLC, whose mutual influence increases the thermal sensitivity of luminescence. This allowed us to suggest compound **5** as a new material with a high thermal sensitivity of luminescence intensity (I_{77}/I_{300} = 80).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2014.02.008.

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Received: 5th August 2013; Com. 13/4176