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Terbium β-Diketonate Based Highly Luminescent Soft Materials

Si-Fu Tang[a] and Anja-Verena Mudring*[a]

Dedicated to Prof. Dr. Gerd Meyer on the occasion of his 60th birthday

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[C_4mim][Tb(hfacac)$_4$] (**1**) and [C_4mpyr][Tb(hfacac)$_4$] (**2**) (C_4mim = 1-butyl-3-methylimidazolium, C_4mpyr = *N*-butyl-*N*-methylpyrrolidinium) were obtained by reacting [C_4mim]Cl (for **1**) or [C_4mpyr]Br (for **2**) with (hexafluoroacetyl)acetone and terbium(III) chloride in a basic ethanol/water solution. Single-crystal X-ray structure analysis reveals Tb^{III} to be chelated by four (hexafluoroacetyl)acetonate anions. Differential scanning calorimeter (DSC) investigations show both compounds to melt below 120 °C. For [C_4mpyr][Tb(hfacac)$_4$] (**2**) the DSC traces indicate an organic plastic crystal behavior (OPCB). Both compounds show very strong emission in the visible region of light which are characteristic for the terbium(III) ion.

Introduction

In recent years ionic liquids (ILs) have attracted considerable attention from both academic and industrial researchers for their unique chemical and physical properties.[1] Commonly, ionic liquids show many merits,[2] such as negligible vapour pressures, wide liquidus ranges, good thermal stabilities, considerable electric conductivities, wide electrochemical windows. Many of the properties such as a negligible vapor pressure and flash point have been related to aspects of "green" chemistry.[3] In addition, ionic liquids are widely tunable. They can be decorated either on cations or anions by introducing functional organic groups or metal ions. Metal-containing ionic liquids can exhibit both the properties of ionic liquids and those of metal ions which can include magnetic, photophysical/optical or catalytic properties. In consequence, ionic liquids can be designed to meet special applications and therefore can be regarded as one kind of "soft" materials.[4] Recent examples of highly luminescent and magnetic ionic liquids are [$C_x$mim][Eu(Tf$_2$N)$_4$] [x = 3 and 4; Tf$_2$N = bis(trifluoromethylsulfonyl)amide], [C_4mpyr]$_2$[Eu(Tf$_2$N)$_5$] (C_4mpyr = *N*-methyl-*N*-propylpyrrolidinium) and [C_6mim]$_{5-x}$[Dy(SCN)$_{8-x}$(H$_2$O)$_x$] (x = 0–2, C_6mim = 1-hexyl-3-methylimidazolium).[5]

1,3-Diketone based ligands are characterised by their special structural features and their delocalized electronic structures. It has been well established that they can form stabile lanthanide complexes and display intense absorption transitions. In the past decades, such compounds were extensively studied as luminescent lanthanide materials.[6] However, in the field of ionic liquids, only a very few attempts have been made to introduce 1,3-diketones into ionic liquids for the reason that usually the 1,3-diketonates can decompose in water. But deprotonated 1,3-diketones such as 2-thenoyltrifluoroacetonate (tta) are stable in ethanol/water mixtures. The europium β-diketonate complex 1-hexyl-3-methylimidazolium tetrakis(2-thenoyltrifluoroacetonato)europate(III), [C_6mim][Eu(tta)$_4$][4] (C_6mim = 1-hexyl-3-methylimidazolium) was found to be photochemically stabile in the ionic liquid [C_6mim][Tf$_2$N] and exhibited excellent photophysical properties such as a high quantum yield. By coupling one or two mesogenic units (cholesterol or cyanobiphenyl) to an imidazolium cation, ionic liquid crystals were obtained with tetrakis(2-thenoyltrifluoroacetonato)europate(III) as the anion.[7] In order to obtain a highly luminescent ionic liquid, we selected (hexafluoroacetyl)acetone (Hhfacac). Reaction of Hhfacac with [C_4mim]Cl or [C_4mpyr]Br and terbium(III) chloride in basic ethanol/water solutions yielded the new compounds [C_4mim][Tb(hfacac)$_4$] (**1**) and [C_4mpyr][Tb(hfacac)$_4$] (**2**).

Results and Discussion

Compounds **1** and **2** have been prepared by reacting (hexafluoroacetyl)acetonate, [C_4mim]Cl (for **1**) or [C_4mpyr]Br (for **2**) with TbCl$_3$·6H$_2$O in ethanol/H$_2$O. By recrystallizing from ethanol, crystals suitable for X-ray diffraction can be obtained.

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[a] Anorganische Chemie I – Festkörperchemie und Materialien,
Ruhr-Universität Bochum,
44801 Bochum, Germany
Fax: +49-234-32-14591
E-mail: anja.mudring@rub.de

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Compound **1** crystallizes in *P*bca with eight formula units in the unit cell. There are overall two Tb^{III} ions, eight hfacac anions and two [C$_4$mim]$^+$ cations in the asymmetric unit which equals to two [C$_4$mim][Tb(hfacac)$_4$] molecules (see Figure 1). Each Tb^{III} ion is eight-coordinated by oxygen atoms from four chelating (hexafluoroacetyl)acetonate anions. The coordination polyhedron around Tb^{III} can be best described as a square antiprism. The Tb–O distances range from 2.34(2) to 2.42(2) Å (see Table 1) which are comparable to those reported for other terbium(III) acetylacetonates.[8]

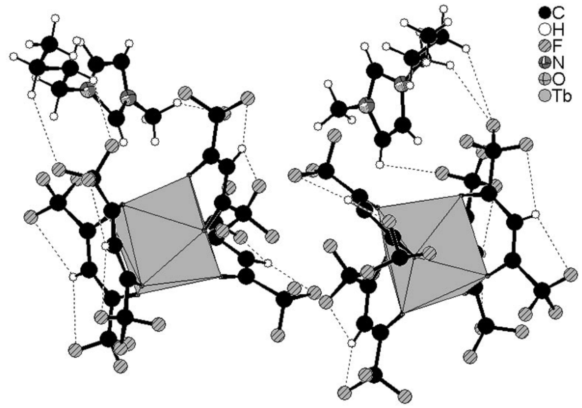

Figure 1. Asymmetric unit of [C$_4$mim][Tb(hfacac)$_4$] (**1**). C–H···F hydrogen bonds are presented by dotted grey lines. Tb, C, H, N, O and F atoms are drawn as light grey, black, open circles, medium grey with octand, medium grey with hatching, and, light grey with cross, respectively.

Table 1. Selected bond lengths [Å] for compounds **1** and **2**.

1			
Tb(1)–O(1)	2.40(2)	Tb(2)–O(9)	2.39(2)
Tb(1)–O(2)	2.42(2)	Tb(2)–O(10)	2.37(2)
Tb(1)–O(3)	2.35(2)	Tb(2)–O(11)	2.38(2)
Tb(1)–O(4)	2.35(2)	Tb(2)–O(12)	2.38(2)
Tb(1)–O(5)	2.38(2)	Tb(2)–O(13)	2.35(2)
Tb(1)–O(6)	2.38(2)	Tb(2)–O(14)	2.34(2)
Tb(1)–O(7)	2.34(2)	Tb(2)–O(15)	2.40(2)
Tb(1)–O(8)	2.36(2)	Tb(2)–O(16)	2.39(2)
2			
Tb(1)–O(6)	2.331(6)	Tb(1)–O(2)	2.352(6)
Tb(1)–O(4)	2.343(7)	Tb(1)–O(7)	2.364(7)
Tb(1)–O(3)	2.346(6)	Tb(1)–O(5)	2.360(6)
Tb(1)–O(8)	2.347(7)	Tb(1)–O(1)	2.370(7)

A large amount of C–H···F hydrogen bonds can be found within the [Tb(hfacac)$_4$] anion as well as between the [C$_4$mim]$^+$ cations and [Tb(hfacac)$_4$]$^-$ anions (see Table 2). They play a very important role in assembling the structure. The acidic hydrogen atom in each (hexafluoroacetyl)acetonate anion forms two C–H···F hydrogen bonds with two respective fluorine atoms of the two adjacent CF$_3$ groups at a proper angle. Meanwhile the fluorine atoms can also form intramolecular hydrogen bonds with the [C$_4$mim]$^+$ cation or intermolecular ones with [C$_4$mim]$^+$ cation of neighboring molecules. Through the linkage of intra- and intermolecular C–H···F interactions, a 2D layer is formed in the *bc* plane (see Figure 2, a). These layers are further linked into a supramolecular 3D structure. The CF$_3$ groups are oriented at the interspace of layers (see Figure 2, b). Such a fluorine segregation seems to be typical of this type of compounds. We have observed this for many complex metal bis(trifluoromethyl)sulfonates.[9] As can be concluded from the distances given in Table 2 the strength of these hydrogen bonds decrease at the following order: intraanion (2.65–2.81 Å) > intercation–anion (3.15–3.68 Å) > intermolecular (3.05–3.86 Å) interactions judged from the C···F distances.

Table 2. C–H···F hydrogen bonds in **1**.[a]

C–H···F	D–H	H···A	D···A	∠ (DHA)
Intraanion				
C3–H3···F2	0.93	2.38	2.74(3)	102.3
C3–H3···F4	0.93	2.44	2.78(3)	101.9
C8–H8···F8	0.93	2.46	2.75(4)	98.0
C8–H8···F10	0.93	2.28	2.65(4)	103.5
C13–H13···F15	0.93	2.40	2.71(4)	99.1
C13–H13···F16	0.93	2.52	2.80(5)	97.4
C18–H18···F20	0.93	2.46	2.71(6)	95.4
C18–H18···F23	0.93	2.52	2.80(4)	98.0
C23–H23···F26	0.93	2.41	2.75(4)	101.2
C23–H23···F28	0.93	2.32	2.67(3)	101.7
C28–H28···F32	0.93	2.49	2.80(4)	99.9
C28–H28···F34	0.93	2.54	2.81(4)	96.7
C33–H33···F39	0.93	2.46	2.76(4)	98.8
C33–H33···F40	0.93	2.41	2.76(4)	102.8
C38–H38···F44	0.93	2.46	2.75(3)	98.6
C38–H38···F46	0.93	2.38	2.73(4)	101.9
Interanion–cation				
C44–H44···F14	0.93	2.95	3.31(6)	104.5
C45–H45B···F5	0.97	2.92	3.60(6)	128.2
C47–H47A···F5	0.97	2.95	3.68(6)	133.2
C49–H49B···F30	0.96	2.52	3.15(8)	123.0
C54–H54B···F48	0.97	2.79	3.57(4)	138.3
C55–H55B···F47	0.97	2.73	3.58(5)	146.6
Intermolecular				
C8–H8···F17_$2	0.93	2.92	3.43(4)	116.1
C13–H13···F10_$3	0.93	2.76	3.25(3)	114.0
C28–H28···F13_$4	0.93	3.00	3.86(4)	155.4
C38–H38···F20_$5	0.93	2.87	3.60(5)	136.1
C41–H41A···F1_$6	0.96	2.70	3.16(6)	110.0
C42–H42···F3_$6	0.93	2.76	3.05(5)	99.2
C45–H45A···F12_$6	0.97	2.76	3.18(5)	107.2
C45–H45B···F31_$1	0.97	2.71	3.61(5)	153.9
C45–H45B···F32_$1	0.97	2.86	3.73(5)	149.1
C47–H47B···F21_$6	0.97	2.86	3.76(7)	153.8
C49–H49B···F2_$6	0.96	2.93	3.86(6)	164.1
C51–H51···F41_$7	0.93	2.97	3.51(6)	118.7
C52–H52···F35_$7	0.93	2.96	3.77(8)	146.4
C55–H55B···F28_$5	0.97	3.00	3.67(4)	127.5
C55–H55A···F44_$8	0.97	2.70	3.52(4)	141.9

[a] Operators for generating equivalent atoms: $1 *x* + 1, *y*, *z*; $2 *x* – 1/2, –*y* + 1/2, –*z*; $3 *x* + 1/2, –*y* + 1/2, –*z*; $4 *x* – 1, *y*, *z*; $5 *x* – 1/2, *y*, –*z* + 1/2; $6 –*x* + 3/2, *y* + 1/2, *z*; $7 –*x* + 1/2, *y* + 1/2, *z*; $8 –*x*, *y* + 1/2, –*z* + 1/2.

The structure of compound **2** is very similar to that of compound **1** but the asymmetric unit only contains one cation [C$_4$mpyr]$^+$ and one anion [Tb(hfacac)$_4$]$^-$. The Tb^{III} ion

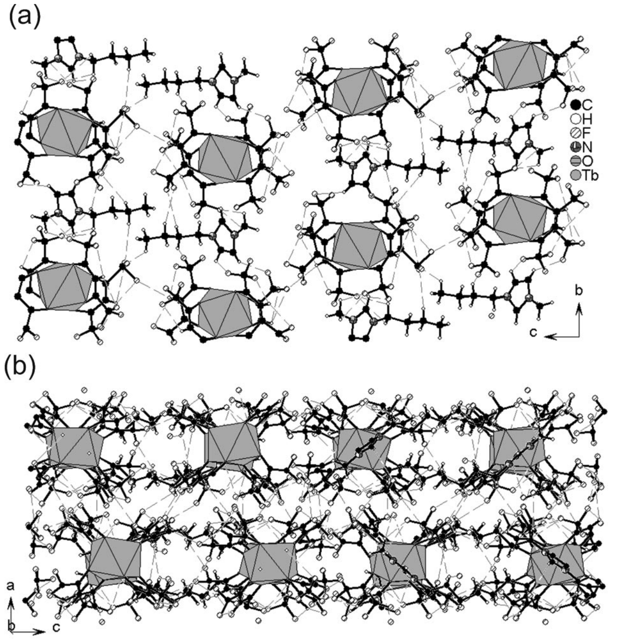

Figure 2. (a) 2D layer of $[C_4mim][Tb(hfacac)_4]$ (**1**) in *bc* plane; (b) 3D supramolecular structure of **1** down the *b*-axis. C–H···F hydrogen bonds are presented in dotted grey lines. The TbO_8 antiprisms are shaded in light grey. Tb, C, N, F and O atoms are drawn as light grey, black, medium grey with octand, open and light grey with hatched circles, respectively.

is also chelated by four (hexafluoroacetyl)acetonate anions in the form of an (slightly distorted) square antiprism. The Tb–O distances range from 2.331(6) to 2.370(7) Å (see Figure 3 and Table 1).

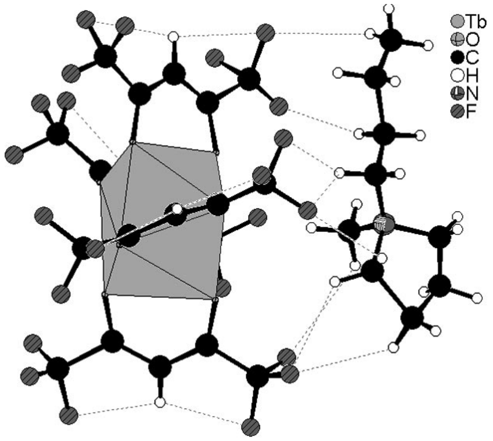

Figure 3. Asymmetric unit of $[C_4mpyr][Tb(hfacac)_4]$ (**2**). C–H···F hydrogen bonds are presented by dotted grey lines. Bonds are presented by dotted grey lines. Tb, C, H, N, O and F atoms are drawn as light grey, black, open circles, medium grey with octand, medium grey with hatching, and, light grey with cross, respectively.

Extensive intra and intermolecular hydrogen bonding is also found (see Table 3) in this compound. For hydrogen bonds within the $[Tb(hfacac)_4]^-$ anion the C···F distances range from 2.68 to 2.82 Å. Hydrogen bonds between fluorine atoms of the $[Tb(hfacac)_4]^-$ anions and hydrogen atoms of the $[C_4mpyr]^+$ cations are obvious weaker and the interatomic lengths are found between 3.36 and 3.58 Å. The intermolecular hydrogen bonds are the weakest with interatomic distances of 3.65–3.82 Å. Figure 4 illustrates the ion packing.

Table 3. C–H···F hydrogen bonds in **2**.[a]

C–H···F	D–H	H···A	D···A	∠ (DHA)
Intraanion				
C3–H3A···F1	0.93	2.37	2.72(2)	102.3
C3–H3A···F4	0.93	2.38	2.73(2)	102.1
C8–H8A···F9	0.93	2.50	2.79(1)	98.8
C8–H8A···F11	0.93	2.40	2.73(1)	100.7
C13–H13A···F13	0.93	2.32	2.68(1)	102.2
C13–H13A···F17	0.93	2.37	2.70(1)	100.5
C18–H18A···F19	0.93	2.52	2.77(2)	95.8
C18–H18A···F22	0.93	2.57	2.82(2)	95.7
Interanion–cation				
C30–H30B···F22	0.96	2.78	3.58(4)	141.2
C32–H32A···F23	0.97	2.63	3.55(3)	159.3
C33–H33A···F14	0.97	2.94	3.55(3)	121.8
C33–H33A···F15	0.97	2.86	3.63(3)	137.0
C34–H34C···F5	0.96	2.86	3.54(2)	128.8
C37–H37B···F6	0.97	2.74	3.40(3)	126.4
C38–H38B···F6	0.97	2.61	3.36(3)	133.9
C38–H38A···F14	0.97	2.77	3.39(2)	122.9
Intermolecular				
C8–H8A···F3_\$1	0.93	2.78	3.67(2)	161.2
C13–H13A···F5_\$2	0.93	2.97	3.77(1)	145.1
C18–H18A···F6_\$3	0.93	2.77	3.65(1)	158.2
C34–H34C···F11_\$4	0.96	2.94	3.75(3)	141.9
C35–H35A···F7_\$5	0.97	2.86	3.82(4)	176.6

[a] Operators for generating equivalent atoms: \$1 $-x + 1$, $-y$, $-z + 2$; \$2 $x - 1/2$, $-y + 1/2$, $z - 1/2$; \$3 $-x + 3/2$, $y - 1/2$, $-z + 3/2$; \$4 $-x + 2$, $-y$, $-z + 2$; \$5 $x + 1$, y, z.

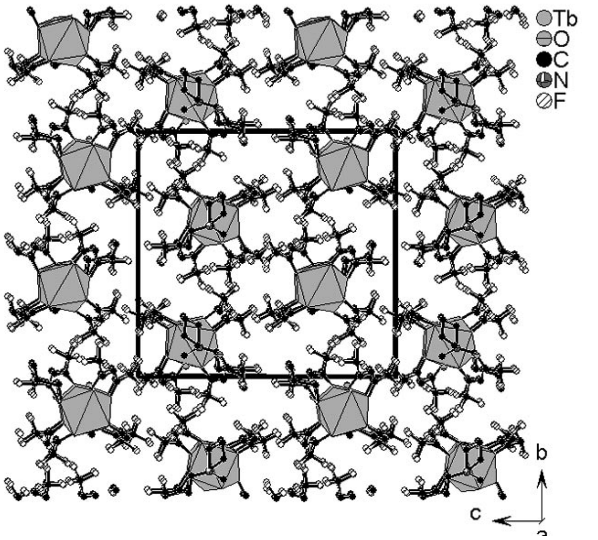

Figure 4. View of the structure of **2** down the *a*-axis. Hydrogen atoms are omitted for clarity. The TbO_8 antiprisms are shaded in light grey. Tb, C, N, F and O atoms are drawn as light grey, black, medium grey with octand, open and light grey with hatched circles, respectively.

Thermal Investigations

From the DSC traces of **1** and **2** (Figures 5 and 6), it is obvious that they have entirely different thermal behaviors. For compound **1**, the thermobehavior is very simple. It melts at 116.2 °C (the onset of the thermal event) and crystallizes at 102.3 °C upon cooling. For compound **2** the thermobehavior is more complicated. In the range of 20 to 150 °C, there are overall four distinct endothermic solid-solid phase transitions which are observed at 38.0, 57.7, 85.8 and 98.4 °C before finally melting occurs at 111.4 °C. The magnitude of the thermal changes of the solid-solid phase transitions can be associated with the rotation of the pyrrolidinium cation about the molecular axis during the heating process and points to a progressive transformations from a fully ordered crystalline state to an increasingly disordered phases.[10] The final entropies of fusion (ΔS_f = 20.6 $\mathrm{J\,mol^{-1}\,K^{-1}}$) match the Timmerman's criterion ($\Delta S_f \approx$ 20 $\mathrm{J\,mol^{-1}\,K^{-1}}$) for molecular plastic crystals very well.[11] This kind of organic plastic crystal behaviour (OPCB) is very rarely observed in the field of IL materials.[11–12]

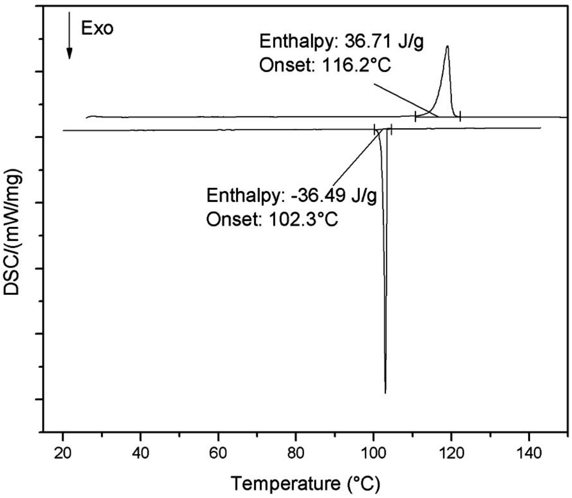

Figure 5. Thermogram of [C$_4$mim][Tb(hfacac)$_4$] (**1**).

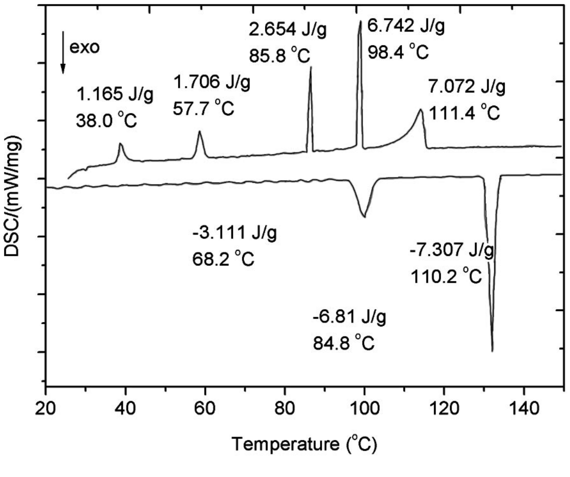

Figure 6. Thermogram of [C$_4$mpyr][Tb(hfacac)$_4$] (**2**).

The TGA curves of compounds **1** and **2** were shown in Figure 7. In the temperature range of 25 to 600 °C, they all show one-step weight losses. Both of them are thermally stable up to about 220 °C. At higher temperature decomposition occurs rapidly. The total weight losses at 600 °C for compounds **1** and **2** are about 68.4 and 76.9%, respectively, the final residues could not be identified. However, from the slopes of TGA curves, it is obvious that the decomposition of the two compounds is incomplete even at 600 °C.

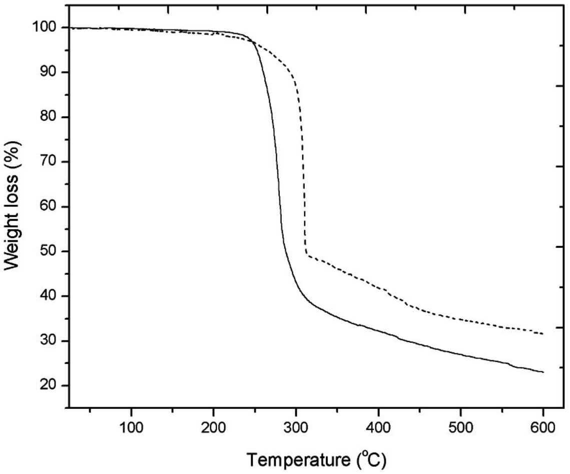

Figure 7. TGA curves for compounds **1** (dashed line) and **2** (solid line).

Optical Investigations

The solid-state luminescence properties of compounds **1** and **2** were investigated at room temperature and 77 K (in liquid nitrogen) (see Figures 8 and 9). From the spectra, it is obvious that compounds **1** and **2** have similar luminescent properties at room temperature and low temperature. For compound **1** at room temperature, when monitored at 546 nm, no f–f transitions could be observed in the excitation spectrum since these are too weak compared to the transitions which are due to light absorption by the β-diketonate ligands. The emission spectrum was measured with 360 nm as the excitation wavelength. A series of sharp lines assigned to transitions from the $^5D_4$ excited state to the different *J* levels of the ground term ^7F (^7F_J, J = 6–2) are found in the luminescence spectrum. These emission bands are 485, 489 ($^5D_4 \rightarrow {}^7F_6$), 541.5, 545.5, 549 ($^5D_4 \rightarrow {}^7F_5$), 582, 587 ($^5D_4 \rightarrow {}^7F_4$), 620.5 ($^5D_4 \rightarrow {}^7F_3$), 638, 649, 650, 657.5 ($^5D_4 \rightarrow {}^7F_2$). The Tb ($^5D_4$) lifetime of **1** for $\lambda_{\mathrm{ex,em}}$ = 360, 546 nm is about 0.3 ms. For compound **2** at room temperature, these emission bands can be found at 484.5, 490, 497.5, 541.5, 544.5, 549, 555, 579, 584, 590.5, 616.5, 619.5, 622.5, 626.5, 638.5, 649, 657.5, and 670 nm. The Tb ($^5D_4$) lifetime of **2** is about 0.06 ms ($\lambda_{\mathrm{ex,em}}$ = 363, 542 nm), obviously shorter than that of **1**, but still not unusal for compounds which contain [Tb(hfacac)$_4$]$^-$ anions.[13] The shorter lifetime for **2** most probably is caused by the motion of the pyrrolidinium cation which leads to an enhanced radiationless decay.

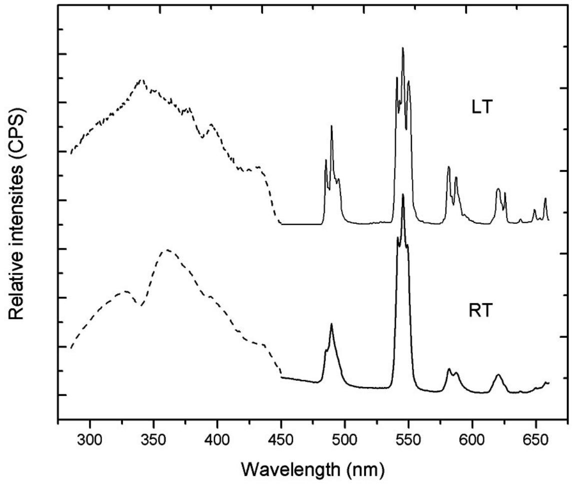

Figure 8. Solid state excitation (dashed line) and emission (solid line) spectra of compound **1** at room temperature (RT) and 77 K (LT).

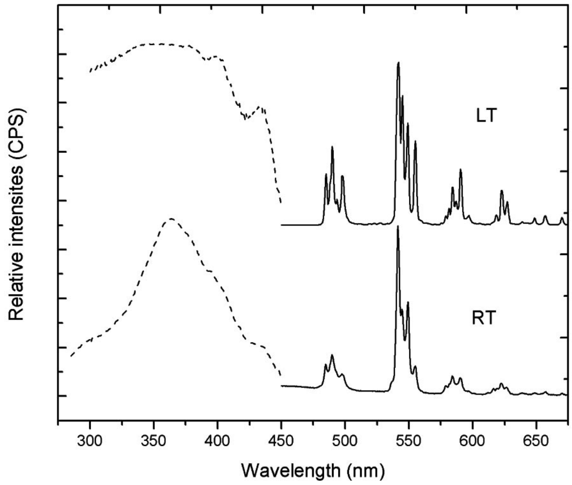

Figure 9. Solid state excitation (dashed line) and emission (solid line) spectra of compound **2** at room temperature (RT) and 77 K (LT).

Once the compounds are frozen in liquid nitrogen, the f–f transitions for Tb^{III} became sharper and finer. For compound **1** at 77 K, it is obvious that $^5D_4 \rightarrow ^7F_6$ transition splits into three peaks (485, 489.5 and 495 nm), $^5D_4 \rightarrow ^7F_5$ splits into four peaks (540.5, 543, 545.5 and 550 nm), $^5D_4 \rightarrow ^7F_4$ turns into four peaks (581.5, 584, 587, and 593.5 nm), $^5D_4 \rightarrow ^7F_3$ (620, 625.5 nm). The peak intensities of $^5D_4 \rightarrow ^7F_2$ are also obviously enhanced. The most remarkable change is the life time. It is found to be strongly temperature-dependent, at 77 K it is prolonged to 1.27 ms. Similar results are also found for compound **2**, at 77 K its life time extended to 1.30 ms which is even slight larger than that of compound **1**. The temperature-dependence of lifetime can be ascribed to the dependence of vibrational excitation and energy back transfer on temperature.

Conclusions

In summary, two terbium β-diketonate containing ionic liquids were synthesized. It turns out that they have very similar structures. Both compounds show characteristic terbium luminescent properties in the green region which are strongly enhanced upon cooling. Interestingly, both compounds show different thermobehaviors since they contain different cations, compound **2** shows rarely observed organic plastic crystal behaviour. This is also mirrored by the lifetimes of the photoexcited Tb ($^5D_4$) state. We are going to further explore the crystal chemistry of pyrroldinium (hexafluoroacetyl)acetonates in order to investigate the existence of plastic crystalline phases more deeply.

Experimental Section

Materials and Instrumentation: All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Phase transition temperatures were determined on differential scanning calorimeter (NETZSCH DSC 240 F1). Measurements were carried out at a heating rate of 5 °C/min in sealed aluminum pans with an argon flow rate of 20 mL/min. The reference sample was an empty Al container. Thermogravimetric analyses were carried out on a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} using dried N_2 as the purging gas (10 mL min^{-1}). IR spectra were recorded on a Bruker Alpha-P FT-IR spectrometer in the range of 4000–400 cm^{-1}. Raman spectra were obtained from the bulk solids recorded at 150 mW on a Bruker IFS-FRA-106/s. For the measurement, the respective samples were sealed under an argon atmosphere in glass capillaries. The data were recorded at room temperature. Solid state excitation and emission spectra were recorded using a Fluorolog 3 (Jobin Yvon Gmbh, München, Germany) with a xenon lamp as the excitation source and a photomultiplier tube for detection. Bulk samples were sealed in quartz tubes. Electronic transitions were assigned according to the energy level diagrams of trivalent rare earth ions.[14]

Compounds **1** and **2** were synthesized according to a modified literature procedure.[4] For **1** [bmim]Cl (0.1747 g, 1.0 mmol), (hexafluoroacetyl)acetone (Hhfacac, 0.8322 g, 4 mmol) and 4 mL (4 mmol) of 1 M NaOH aqueous solution were added to 6 mL ethanol in a 25 mL beaker. The reaction mixture was stirred and heated up to 50 °C. When a clear solution was formed an aqueous solution of terbium(III) chloride (0.2489 g, 2/3 mmol $TbCl_3 \cdot 6H_2O$ in 2 mL of water) was added dropwise using a syringe. The reaction solution was stirred for another 30 min at 50 °C and then cooled to room temperature. A white precipitate was formed which was collected by filtration and carefully washed with ice-cooled water. Bulk samples were dried under vacuum at room temperature for 2 d. Suitable single-crystals for X-ray crystal structure analysis were obtained by recrystalisation from ethanol.

$C_{28}H_{19}F_{24}N_2O_8Tb$ (1126.37): calcd. C 29.86, H 1.70, N 2.49; found C 29.71, H 1.44, N 2.47. IR: $\tilde{\nu}$ = 3175 (w), 3158 (w), 3105 (w), 2973 (w), 2945 (w), 2887 (w), 2360 (w), 2343 (w), 2329 (w), 1647 (vs), 1604 (w), 1558 (s), 1534 (s), 1507 (s), 1488 (s), 1255 (s), 1193 (s), 1170 (vs), 1136 (vs), 1098 (vs), 952 (w), 845 (w), 800 (s), 768 (w), 751 (m), 741 (m), 660 (s), 585 (s), 528 (m), 465 (m), 418 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 3176 (w), 3144 (w), 3105 (w), 2972 (m), 2939 (m), 2918 (m), 2881 (w), 1672 (w), 1649 (w), 1570 (w), 1483 (w), 1452 (m), 1431 (w), 1418 (m), 1393 (w), 1350 (vs), 1254 (m), 1150 (w), 1103 (m), 1055 (w), 1024 (w), 951 (s), 908 (w), 743 (s), 660 (w), 623 (w), 581 (w), 515 (w), 465 (w), 363 (w), 320 (w), 249 (vs), 197 (w), 149 (s), 95 (s) cm^{-1}.

Compound **2** was synthesized in a similar way except [C$_4$mim]Cl was replaced by [C$_4$mpyr]Br. $C_{29}H_{24}F_{24}NO_8Tb$ (1129.41): calcd. C 30.84, H 2.14, N 1.24; found C 30.03, H 1.57, N 1.22. IR: $\tilde{\nu}$ = 3150 (w), 2979 (w), 2945 (w), 2887 (w), 2353 (w), 2326 (w), 2096 (w), 2041 (w), 1647 (s), 1610 (w), 1557 (m), 1530 (m), 1507 (s), 1490 (m), 1480 (m), 1430 (w), 1347 (w), 1250 (s), 1194 (s), 1133 (vs), 1095 (s), 1003 (w), 949 (w), 926 (w), 797 (s), 767 (w), 739 (m), 658 (s), 582 (s), 527 (m), 465 (w), 419 (w) cm^{-1}. Raman: $\tilde{\nu}$ = 3144 (w), 2976 (m), 2951 (m), 2908 (m), 2885 (w), 1674 (w), 1651 (w), 1483 (w), 1454 (m), 1394 (w), 1350 (vs), 1256 (m), 1150 (w), 1107 (m), 1059 (w), 949 (s), 907 (w), 743 (s), 581 (w), 513 (w), 480 (w), 465 (w), 369 (w), 297 (w), 249 (vs), 197 (w), 147 (s), 108 (m), 93 (m), 85 (s) cm^{-1}.

X-ray Crystal Structure Determination: Intensity data of compound **1** were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 153(2) K. Data reduction was carried out with the program package X-red[15] and numerical absorption corrections were carried out with the program X-Shape[16] Data for **2** were collected on a Bruker smart 1000 single-crystal X-ray diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 273(2) K. Data reduction was carried out with the program package SAINT[17] and a numerical absorption correction with the program SADABS[18] Crystal structure solution by direct methods using SIR92[19] yielded the heavy atom positions. Subsequent difference Fourier analyses and least-squares refinement with SHELXL-97[20] allowed for the location of the remaining atom positions. In the final step of the crystal structure refinement hydrogen atoms of idealized CH_2 and CH_3 groups were added and treated with the riding atom mode; their isotropic displacement factor were chosen as 1.2 and 1.5 times the preceding carbon atom, respectively.

Crystal Data for 1: $C_{28}H_{19}F_{24}N_2O_8Tb$, Mr = 1126.37 g mol^{-1}, orthorhombic, $Pbca$, a = 17.155(3), b = 22.416(5), c = 42.753(9) Å, V = 16440(6) Å^3, Z = 8, λ = 0.71073 Å, T = 153(2) K, ρ = 1.820 g cm^{-3}, μ = 1.875 mm^{-1}, F(000) = 8736. 89232 reflections were collected, of which 14424 were unique (R_{int} = 0.2938). GOF = 1.095. R_1/R_2 = 0.1032/0.2355 [$I > 2\sigma(I)$].

Crystal Data for 2: $C_{29}H_{24}F_{24}NO_8Tb$, Mr = 1129.41 g mol^{-1}, monoclinic, $P2_1/n$, a = 11.758(2), b = 18.521(4), c = 21.021(7) Å, β = 112.35°, V = 4234(2) Å^3, Z = 4, λ = 0.71073 Å, T = 273(2) K, ρ = 1.772 g cm^{-3}, μ = 1.820 mm^{-1}, F(000) = 2200. 40461 reflections were collected, of which 9852 were unique (R_{int} = 0.1677). GOF = 0.689. R_1/R_2 = 0.0476/0.0778 [$I > 2\sigma(I)$].

CCDC-727038 (for **1**) and CCDC-727039 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): IR, Raman spectra, and XRD patterns.

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