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ARTICLE TYPE

Phosphonium-based tetrakis dibenzoylmethane Eu(III) and Sm(III) complexes: synthesis, crystal structure and photoluminescence properties in a weakly coordinating phosphonium ionic liquid

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Highly luminescent anionic Ln(III) β-diketonate complexes of formula $[P_{8,8,8,1}][Ln(dbm)_4]$, with Ln = Eu^{3+} and Sm^{3+}, $[P_{8,8,8,1}]$ = trioctylmethylphosphionium and dbm = 1,3-diphenylpropane-1,3-dione were synthesized. The single crystal X-ray structure of the samarium and europium complexes showed that the metal ion was surrounded by four ligands and that no water or solvent molecules were coordinated. The solid complexes showed good thermal stability up to 250 °C. The complexes easily dissolved in the ionic liquid trioctylmethylphosphionium bis(trifluoromethylsulfonyl)imide $[P_{8,8,8,1}][Tf_2N]$, due to the presence of a common phosphonium countercation in the ionic liquid and in the Eu(III) and Sm(III) complexes. The photoluminescence of the complexes was studied in the solid state and in ionic liquid as well as in acetonitrile (MeCN) as solvent.

The past three decades have witnessed continuing interest in the field of lanthanide based materials research. Lanthanide (III) β-diketonate complexes have been widely studied either as tris (LnL_3 type) or tetrakis (β-diketonate) complexes $[C]^+[Ln(L)_4]^-$ type.[1,2] Because of the lower coordination number of tris complexes (generally six), they usually contain water or other solvent molecules in the first coordination sphere, which is detrimental for obtaining high luminescence intensities. In the latter case, all the coordination positions are filled up by four β-diketonate ligand donor atoms and the charge neutrality is provided by an organic cation. An additional ligand in the tetrakis complexes provides better shielding of the Ln^{3+} ion which can lead to significant enhancement of the luminescence properties of the complex by avoiding the coordination of strongly quenching solvent molecules.[3,4] Even though, tetrakis complexes usually show much higher luminescence intensities than the corresponding hydrated tris complexes[2,5,6,7] there are few reports on the lanthanides complexes of the $[C]^+[Ln(L)_4]^-$ type as compared to the tris complexes of the LnL_3 type and the number of crystal structures available for tetrakis β-diketonate complexes is limited as compared to the tris complexes.[1] However, these ligands exhibit lower photostability for the corresponding complexes in conventional organic solvents.

Recent studies have successfully demonstrated the use of room-temperature ionic liquids (RTILs) in photochemistry and spectroscopy.[8,9,10,11,12,13,14,15,16,17] Lanthanide metal containing ionic liquids are being viewed as new types of promising soft materials which can combine the advantageous properties of the ionic liquids with additional intrinsic magnetic, optical and catalytic properties of the incorporated metal complex anion.[13] Therefore, it is attractive and desirable to develop ionic liquids containing high concentrations of lanthanides. Most of the studies on the lanthanide compounds in ionic liquids have been performed with ionic liquids based on imidazolium cations and on the emission of Eu^{3+} due to high-luminescence intensity combined with relatively easy-to-interpret emission spectra of the Eu^{3+} ion.[3,10,11,14,15,16]

For example, a high quantum yield and an enhanced photostability have been reported for a Eu(III) tetrakis complex after dissolving in a weakly coordinating imidazolium ionic liquid (IIL).[3] The improvement of the photophysical properties of tetrakis complex in ionic liquid $[HMIM][Tf_2N]$ were explained based on hydrogen bonding between the cation and ligands.

Even though Sm^{3+} has, intrinsically, lower optical performances than Eu as reported in a few papers,[17,18,19] it is an interesting lanthanide emitter. In fact, in addition to visible luminescence, it also shows a large luminescence contribution in the near-infrared region (NIR). Due to the poor absorbing abilities (molar extinction coefficients (ε) less than 3 L mol^{-1} cm^{-1}) and smaller energy gap between the emitting level and the next lower energy level (7500 cm^{-1}) of Sm^{3+}, it shows weaker luminescence intensity compared to other lanthanide ions,[17] that can be enhanced by using efficient sensitizing ligands such as β-diketonates.

Phosphonium ionic liquids (PILs) have been available in large scale for about two decades and their use has gained great interest as reaction media.[20,21] They were found to have a wider electrochemical window than the imidazolium salts. Unlike imidazolium ionic liquids, PILs will not be reduced by the electropositive f-elements and therefore these are suitable for study of the electrochemical properties and electrodeposition of f-elements. Moreover, PILs are found to be thermally more stable and often easier to obtain colourless than nitrogen-based analogues.[22] Recently we have also reported the synthesis and optical properties of metal-free dansyl-based luminescent ILs.[23] When the lanthanide complexes are dissolved in imidazolium ILs, the acidic hydrogen atom on the imidazolium ring forms hydrogen bonds with the diketonate anion oxygens.[17] Even though in our case, the α-protons on the phosphonium cation are poorly acidic and poorly hydrogen bonding towards the dibenzoylmethane ligand, nonetheless previous reports indicate strong ion pairing with the anion.[24]

The aim of this paper was to prepare new phosphonium lanthanide complexes with: (1) a good shielding of the lanthanide ion accomplished by an efficient light harvesting antenna such as 1,3-diphenylpropane-1,3-dione, (2) good solubility in the weakly coordinating ionic liquid, trioctylmethylphosphionium bis(trifluoromethanesulfonyl)imide) $[P_{8,8,8,1}][Tf_2N]$.

We here report a straightforward and efficient synthesis of trioctylmethylphosphionium tetrakis (dibenzoylmethane) europate(III) $[P_{8,8,8,1}][Eu(dbm)_4]$ (**I**) and trioctylmethylphosphionium tetrakis (dibenzoylmethane) samarate(III) $[P_{8,8,8,1}][Sm(dbm)_4]$ (**II**) complexes and their photoluminescence properties in the $[P_{8,8,8,1}][Tf_2N]$ phosphonium ionic liquid. The introduction of the trioctylmethylphosphionium countercation $[P_{8,8,8,1}]$ in the Eu(III) and Sm(III) complexes ensured their solubility in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$. The photophysical properties of solutions of tetrakis europium and samarium complexes in $[P_{8,8,8,1}][Tf_2N]$ were investigated systematically. The visible luminescence of (**I**) and (**II**) in solid state and in $[P_{8,8,8,1}][Tf_2N]$ has been studied along with the near infrared emission (NIR) of (**II**). $[P_{8,8,8,1}][Tf_2N]$ IL was used in this study, since the $[Tf_2N]$ anions are known to coordinate very weakly to the lanthanide ions.

Experimental section

All reagents used were ACS grade and were used as received without any further purification. $[P_{8,8,8,1}][CH_3OCO_2]$ and $[P_{8,8,8,1}][Tf_2N]$ ionic liquids were synthesized and purified according to previously reported procedures.[25] ^{1}H-NMR, ^{13}C-NMR and hmqc spectra were collected on a Varian Unity spectrometer operating at 400 MHz for ^{1}H and at 100 MHz for ^{13}C in $CDCl_3$ solution at 25 °C with TMS as internal standard. The ^{1}H-NMR spectrum of $[P_{8,8,8,1}][dbm]$ was acquired at 60 °C as a neat compound, *i.e.* without dissolving in a deuterated solvent. A calibrated coaxial glass capillary inserted into the NMR tube filled with $[D_6]$-DMSO was used to lock the magnetic field.

Photoluminescence excitation, emission and time-resolved analysis were carried out using a Horiba–Jobin Yvon Fluorolog 3–21 spectrofluorimeter. A Xenon arc lamp was used as a continuous-spectrum source selecting the excitation wavelength by a double Czerny–Turner monochromator. The detection system was constituted by a iHR300 single grating monochromator coupled to an R928 PMT (range 185 – 900 nm) or to an R5509-73 PMT (range 300 – 1700 nm). The excitation spectra were recorded with 1 nm band pass resolution, dividing the PMT signal by the intensity of the lamp, measured by using a calibrated photodetector. The emission spectra were recorded with 1 nm band-pass resolution and corrected for the response of the instrument, keeping into account the wavelength dependent efficiencies of the optical elements and detectors.

Time-resolved analyses were performed in multi-channel scaling modality (MCS) by using a tunable pulsed Nd:YAG laser system as excitation source (wavelength selection from 210 nm to 2300 nm, 10 Hz repetition rate, 6 ns pulse duration). The decay profiles were fitted with the least squares method, by using a single exponential equation. External quantum efficiency Φ_{ext} values were obtained according to Eq. (1) by using an integrating sphere coupled to the same Fluorolog-3 system and by measuring the rate between the number of emitted photons and the number of absorbed photons. The internal quantum efficiency Φ_{int} of the lanthanide ion can be estimated on the basis of Eq. (2), where τ is the measured luminescence lifetime and τ_{rad} is the radiative lifetime. For europium τ_{rad} can be estimated from the emission spectrum by using Eq. (3), where n indicates the refractive index of the sample and $I(^5D_0\rightarrow{}^7F_J)/I(^5D_0\rightarrow{}^7F_1)$ is the ratio between the total integrated emission from the Eu $^5D_0$ level to the ^7F_J manifold (J=0–4) and the integrated intensity of the transition $^5D_0\rightarrow{}^7F_1$.[26]

Other research groups have investigated theoretically the radiative transition probability for samarium and a general conclusion seems to be in the order of 3 ms, which was here taken for comparison.[27,28]

$$\Phi_{ext} = \frac{N_{em}}{N_{abs}} \tag{1}$$

$$\Phi_{int} = \frac{\tau}{\tau_{rad}} \tag{2}$$

$$\left(\frac{1}{\tau_{rad}}\right)_{Eu} = 14.65\, n^3\, \frac{I(^5D_0 \rightarrow {}^7F_J)}{I(^5D_0 \rightarrow {}^7F_1)} \tag{3}$$

TGA-DTG thermogravimetric analyses were performed in air from 30 °C to 900 °C with a heating rate of 20 °C/min with a Netzsch STA 409 thermobalance.

All the details of the XRD measurements are reported in the supporting information.

$[P_{8,8,8,1}][CH_3OCO_2]$

Trioctylphosphine (TOP, 25 mL, 20.8 g, 56 mmol), DMC (30 mL, 32.1 g, 356 mmol) and methanol (30 mL) were combined (two phases) in a sealed 200 mL steel autoclave fitted with a pressure gauge and a thermocouple for temperature control. Three freeze-pump-thaw cycles were carried out to ensure complete degassing of the mixture. The empty volume was then filled with nitrogen. The autoclave was heated for 20 h at 140 °C with magnetic stirring, after which time it was cooled and vented. Methanol and residual DMC were removed from the mixture by rotary evaporation, to give $[P_{8,8,8,1}][CH_3OCO_2]$ (27.5 g, 100%) as a viscous clear colourless liquid. ^{1}H NMR (neat, 60 °C, 400 MHz, DMSO-d$_6$): δ = 3.15 (s, 3H; CH_3OCO$_2$), 2.33 (br t, 6H; P-CH_2), 1.88 (d, J(P,H) = 14 Hz, 3H; P-CH_3), 1.42 (br, 6H), 1.27 (br, 6H), 1.11 (br, 24H), 0.70 ppm (br t, 9H); ^{13}C{^{1}H} NMR (neat, 60 °C, 100 MHz, DMSO-d$_6$), CH$_2$ assigned by 2D INADEQUATE): δ = 155.8 (1 C; C=O), 50.0 (1 C; CH$_3$ O), 30.9 (3 C; C$_6$), 29.9 (d, J(P,C) = 15 Hz, 3 C; C$_3$), 28.2 (3 C; C$_5$), 28.0 (3 C; C$_4$), 21.6 (3 C; C$_7$), 20.7 (d, J(P,C) = 4 Hz, 3 C; C$_2$), 19.0 (d, J(P,C) = 48 Hz, 3 C; C$_1$), 12.8 (3 C; C$_8$), 2.6 ppm (d, J(P,C)

= 53 Hz, 3 C; P-*C*H_3); FTIR (neat): 2900, 2856, 1669 cm^{-1}.

$[P_{8,8,8,1}][Tf_2N]$

The $[P_{8,8,8,1}][Tf_2N]$ ionic liquid was prepared by a metathesis reaction between $[P_{8,8,8,1}][CH_3OCO_2]$ (8.0 g, 16.26 mmol) and bis(trifluoromethane)sulfonimide lithium salt $[LiNTf_2]$ (4.66 g, 16.26 mmol) in water. The mixture was stirred at 70 °C for 2 h. The product was extracted with 3 aliquots (50 mL) of CH_2Cl_2, dried over Na_2SO_4, and the solvent was removed under reduced pressure to afford pure, and dry $[P_{8,8,8,1}][Tf_2N]$ as a clear liquid. (6.10 g, 60%) ^{1}H NMR (neat, 60 °C, 400 MHz, DMSO-d_6): δ = 1.96 (br, 6H; P-CH_2), 1.55 (d, *J*(P,H) = 13 Hz, 3H; P-CH_3), 1.34 (br, 6 H), 1.24 (br, 6 H), 1.09 (br, 24H), 0.68 ppm (br t, 9H); $^{13}C\{^1H\}$ NMR (neat, 60 °C, 100 MHz, DMSO-d_6): d = 119.1 (q, *J*(F,C) = 321 Hz, 2C; *C*F_3), 30.6 (3C; C_6), 29.3 (d, *J*(P,C) = 15 Hz, 3C; C_3), 27.8 (3C; C_5), 27.5 (3C; C_4), 21.4 (3C; C_7), 20.2 (d, *J*(P,C) = 5 Hz, 3C; C_2), 19.0 (d, *J*(P,C) = 48 Hz, 3C; C_1), 12.6 (3C; C_8), 2.3 ppm (d, *J*(P,C) = 52 Hz, 3C; P-*C*H_3); FTIR (neat): = 2930, 2859, 1468, 1352 cm^{-1}.

$[P_{8,8,8,1}][dbm]$

In a 50 mL round bottomed flask were combined equimolar amounts of 1,3-diphenyl-1,3-propanedione (dbm) (2.27 g. 10.14 mmol) and $[P_{8,8,8,1}][CH_3OCO_2]$ (5 g. 10.14 mmol). The mixture was stirred at RT for 2 h, and then stirred under vacuum to eliminate co-products MeOH and CO_2. The resulting viscous red ionic liquid was obtained in quantitative yield (6.134 g, 99.5%). ^{1}H NMR (neat, 60 °C, 400 MHz, DMSO-d_6) δ (ppm): 8.48 (m, 4H), 8.03–7.83 (m, 4H), 7.83–7.75 (m, 2H), 7.09 (s, 1H), 2.73 (m, 6H), 2.42 (d, *J* = 13.9 Hz, 3H, CH_3-P), 2.03–1.59 (m, 36H), 1.42 (t, *J* = 6.8, 5.6 Hz, 9H); $^{13}C\{^1H\}$ NMR (neat, 60 °C, 400 MHz, DMSO-d_6) δ (ppm): 180.49 (C=O), 126.64, 126.18, 89.55 (C^-), 31.08, 29.99, 28.35,21.87, 20.95, 19.20 (CH_2-P, *J*=48.5MHz), 3.21, 2.90 (CH_3-P, *J*= 51.3 MHz) FTIR: 3055, 3028, 2955, 2925, 2854, 2731, 1608, 1565, 1493, 1465, 1431, 722.

$[P_{8,8,8,1}][Eu(dbm)_4]$ (I)

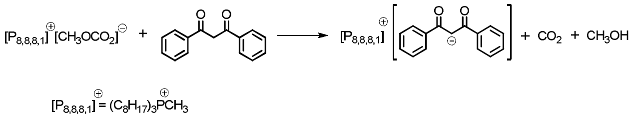
An aqueous solution (6 mL) of $EuCl_3•6H_2O$ (0.57 g. 1.58 mmol) was added dropwise to $[P_{8,8,8,1}][dbm]$ (3.88 g. 6.32 mmol) in ethanol (10 mL). The reaction mixture was stirred for 2 h during which time the complex precipitated, it was then was filtered and dried under high vacuum (10^{-1} mbar/1 h). The crystals of $[P_{8,8,8,1}][Eu(dbm)_4]$ (I) were suitable for single-crystal X-ray structure determination ($C_{85}H_{98}EuO_8P$: Mr: 1430.62) Yield (1.56g, 69%), m.p.: 194.7-198.5. ^{1}H NMR (400 MHz, CDCl3-d_1) δ (ppm): 16.89 (s, 1H), 8.02-8.00 (m, 16H), 7.65- 7.44 (m, 24H) 2.60-2.45 (m, 6H), 2.2 (d, *J* = 13.3 Hz, 3H, CH_3-P), 1.64-1.21 (m, 36H) 0.89 (m, 9H), °C FTIR: 3060 (νs(C-H)ar, 3029, 2954, 2925, 2856 (νs(C-H); 1957, 1896; 1600, 1552, 1515 (νs(C-O); 1470, 1425, 1310 νs(C-O···M); 1280, 1220; 1180 (νs(C-P); 1066 (νs(C-O); 1030 ν(Ring deformation), 940, 780, 720 cm^{-C}, Raman: 1595 (ν(C=C)ar; 1556; 1488, 1443 w (ν(C=C)ar; 1309 s (ν(C-H)ar; 1274, 1178; 1059, 1000 (Ring deformation); 940, 788, 682 (Ring deformation); 617, 460 m (ν(Eu-O); 240, 190 ν(Eu-O chelate ring deformation); 133, Anal. Calcd: C, 71.2%; H, 6.85%. Found: C, 69.94%; H, 6.70%.

$[P_{8,8,8,1}][Sm(dbm)_4]$ (II)

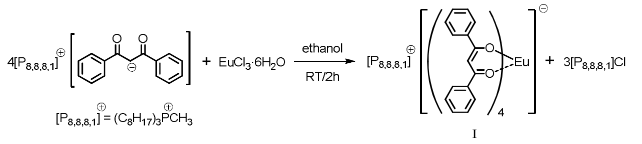
An aqueous solution (6 mL) of $Sm(NO_3)_3•6H_2O$ (0.96 g. 2.16 mmol) was added dropwise to $[P_{8,8,8,1}][dbm]$ (5.263 g. 8.64 mmol) in ethanol (6 mL). The reaction mixture was stirred for 2 h during which time the complex precipitated, it was then was filtered and dried under high vacuum (10^{-1} mbar/4h). It was purified by recrystallization from ethanol (2.59 g, 84%) . The complex showed red/orange luminescence under the UV lamp (366 nm). ($C_{85}H_{98}SmO_8P$: Mr: 1429.016) m.p.: 232.4-240.7 °C; ^{1}H NMR (400 MHz, CDCl3-d_1) δ (ppm): 17.03 (s, 1H), 8.35-8.24 (m,16H), 7.51-7.42 (m, 8H), 7.41, 7.34 (m, 16H), 1.34-1.25 (m, 6H), 1.11-1.035 (m, 6H), 1.01-0.97 (m, 6H), 0.90-0.81 (m, 6H), 0.58-0.49 (m, 6H), 0.41-0.29 (m, 6H), 0.06- -0.2 (m, 6H), -0.48 (d, *J* = 12.5Hz, 3H, CH_3-P) FTIR (KBr): = 3062, 2927, 2854 (C-H), 1760 (C=O), 1616, 1596, 1554, 1515, 1465, 1423, 1307, 1276, 1218, 1176, 1068 (C-P), 1025, 941, 717, 690 cm^{-1}; Raman: 1595, 1488, 1443, 1312, 1274, 1179, 1060, 997, 938, 785, 670, 617, 402, 241, 196, 127. Anal. Calcd: C, 71.37%; H, 6.85%. Found: C, 71.35%; H, 6.80%.

Results and discussion

Both complexes **I** and **II** were prepared starting from the parent colourless ionic liquid $[P_{8,8,8,1}][CH_3OCO_2]$, by exchanging the methylcarbonate anion with dibenzoylmethane to yield the corresponding pure phosphonium dibenzoylmethanate $[P_{8,8,8,1}][dbm]$ (Scheme 1), accompanied by only methanol and CO_2 as by-products. Addition of $EuCl_3•6H_2O$ or $Sm(NO_3)_3•6H_2O$ according to the procedure reported by Melby et al yielded the desired lanthanide complexes.[29] Complex **I** was prepared by dissolving 4 molar equivalents of the ionic liquid $[P_{8,8,8,1}][dbm]$ in ethanol, followed by the dropwise addition of 1 equiv. of the $EuCl_3•6H_2O$ in water. (Scheme 2)

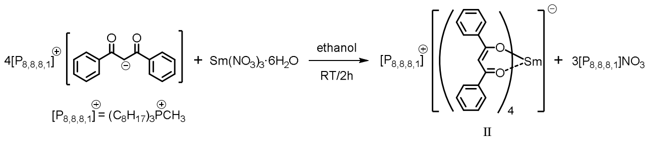


Scheme 1 Synthesis of $[P_{8,8,8,1}][dbm]$



Scheme 2 Synthesis of complex (**I**)

Complex **II** was prepared by dissolving 4 molar equivalents of the ionic liquid $[P_{8,8,8,1}][dbm]$ in ethanol, followed by the dropwise addition of 1 equiv. of the $Sm(NO_3)_3•6H_2O$ in water. (Scheme 3)



Scheme 3 Synthesis of complex (**II**)

Previous reports on the synthesis of lanthanide ionic liquid complexes involved deprotonating a diketone with a base, adding a halide ionic liquid, and a lanthanide salt, followed by isolation of the product.[17] In the present instance, the diketonate ionic liquid [$P_{8,8,8,1}$][dbm] was formed spontaneously by mixing the parent [$P_{,8,8,8,1}$][CH_3OCO_2] with dibenzoylmethane. Then the ionic liquid-lanthanide complexes were generated directly from [$P_{8,8,8,1}$][dbm] by the addition of the lanthanide salt.

Crystal structures of (I) and (II)

Attempts to determine the crystal structure of the newly synthesized compounds were done starting from crystals obtained from slow evaporation of ethanol solutions. Important disorder contribution have been encountered in all the Eu crystals. The crystallographic data and refinement details are summarized in the supporting information. [$P_{8,8,8,1}$][Eu(dbm)$_4$] and [$P_{8,8,8,1}$][Sm(dbm)$_4$] complexes show monoclinic cells, containing two crystallographically independent molecules for the Europium complex (Figure 1) and one for Samarium one. (Figure 2) No crystallization solvent molecules have been found trapped in the crystal packing.

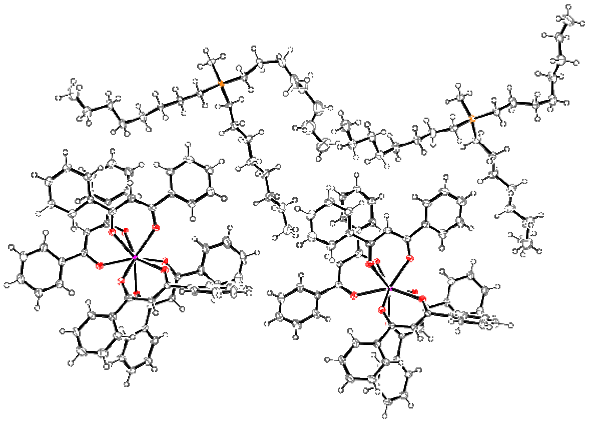


Fig. 1 Preponderant conformation found in the asymmetric unit of [$P_{8,8,8,1}$][Eu(dbm)$_4$] crystal (50% probability ellipsoids)

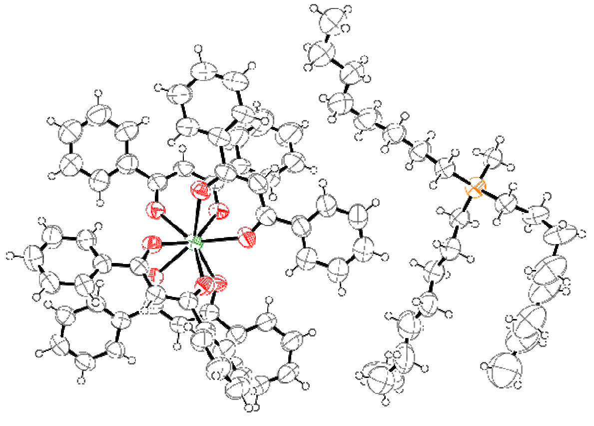


Fig. 2 X-ray structure (50% probability ellipsoids) of [$P_{8,8,8,1}$][Sm(dbm)$_4$].

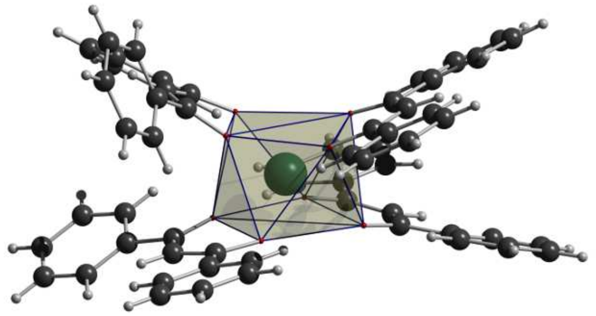


Fig. 3 Ball and stick representation of metal coordination sphere. Both [$P_{8,8,8,1}$][Ln(dbm)$_4$] (Ln = Eu, Sm) show a distorted square antiprism coordination geometry

Both the complexes show a mean bond length of 2.40(4) Å around the metal atom and mean bond angles of 75(5)°. The overall coordination geometry (Figure 3) resembles a distorted square antiprism as previously reported in literature for similar tetrakis complexes.[30]

Thermal analyses

Thermal analyses of the complexes **I** and **II** were carried out under pure nitrogen and in a 2:1 N_2/air atmosphere in the temperature range from 40 to 900 °C, at a heating rate 10 °C/min.

Thermal analysis of (I)

The TG/DTG curves for the Europium complex are shown in Figure 4. It showed excellent thermal stability up to 250 °C. Two significant weight losses are evident: the first (47%) in the temperature range of 250–425 °C; and the second one (34%) in the temperature range of 425–600 °C. From the derivative curve it was apparent that the maximum weight loss occurred at 325 °C. No weight loss was observed in the region (30–115 °C) due to the absence of any moisture or coordinated water molecules in the complex. Since the curves were identical under pure N_2, we can hypothesize a two-step decomposition.

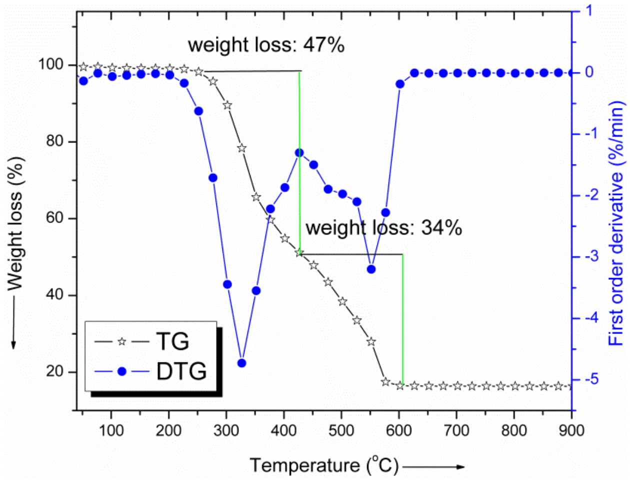


Fig. 4 TG–DTG curve of the complex **(I)** in a 2:1 N_2/air atmosphere

Thermal analysis of (II)

The TG/DTG curves for the Sm complex are shown in Figure 5. High thermal stability is an essential requirement for most applications. The complex shows an excellent thermal stability up to 285 °C, which is high enough for most luminescence applications. The weight loss can be divided into two stages similar to the europium complex discussed above. The first weight loss (49.6%) was observed in the temperature range of 285–410 °C and the second one (32.1%) in the temperature range of 410–610 °C. From the derivative curve it was apparent that the maximum/highest weight loss occurred at 385.3 °C. No weight loss was observed in the region (30–115 °C) due to the absence of any moisture or coordinated water molecules in the complex. Since the curves were identical under pure N_2, we can hypothesize a two-step decomposition in this case also.

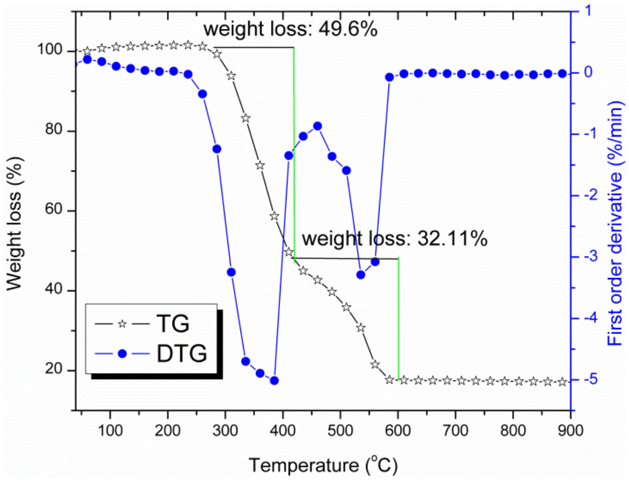


Fig. 5 TG–DTG curve of the complex (**II**) in a 2:1 N_2/air atmosphere

Photoluminescence properties

Photoluminescence properties of Eu complex (I)

The room temperature photoluminescence excitation spectra of complex (**I**) in solid state or dissolved in acetonitrile (MeCN) and in the clear and colourless ionic liquid $[P_{8,8,8,1}][Tf_2N]$ are shown in Figure 6. The excitation spectra were obtained by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} at 611 nm or 614 nm. The solid state excitation spectrum showed broad band absorption up to 500 nm, with maximum absorption around 415 nm due to the efficient $\pi \rightarrow \pi^*$ transition of the dbm ligands.[31,32,33] The narrow band at 464 nm was assigned to the $^7F_0 \rightarrow {}^5D_2$ transition. The excitation spectra of the complex (**I**) dissolved in acetonitrile (MeCN) and in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ were shifted to shorter wavelengths, with a broad maximum around 330 nm and a narrow peak around 390 nm respectively.

The emission spectra of the (**I**) in solid state, dissolved in acetonitrile (MeCN) and dissolved in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ obtained by excitation at 415, 350 and 390 nm respectively, are presented in Figure 7. Dissolving complex (**I**) in MeCN and in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ was found to affect differently the spectroscopic fine structure of the emission spectrum of the compound compared to the solid state.

The excitation energy was absorbed by the ligands and transferred to the Eu^{3+} emitting centre in a subsequent step (antenna effect). The emission spectrum for the solid state consisted of several transitions $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) related to the radiative de-excitation from the $^5D_0$ emitting level of Eu^{3+} [579 ($^5D_0 \rightarrow {}^7F_0$), 591 ($^5D_0 \rightarrow {}^7F_1$), 611, 613 ($^5D_0 \rightarrow {}^7F_2$), 651 ($^5D_0 \rightarrow {}^7F_3$) and 691, 702 nm ($^5D_0 \rightarrow {}^7F_4$)]. The spectrum was dominated by the so-called “europium red” $^5D_0 \rightarrow {}^7F_2$ emission as the dominant band (hypersensitive transition) peaking at 611 nm, giving an intense red luminescence output for the complex (**I**). The intensity ratio R ($^5D_0 \rightarrow {}^7F_2$)/I($^5D_0 \rightarrow {}^7F_1$) was 18.9. Such a high ratio is typical of the Eu^{3+} ion without inversion symmetry.[34]

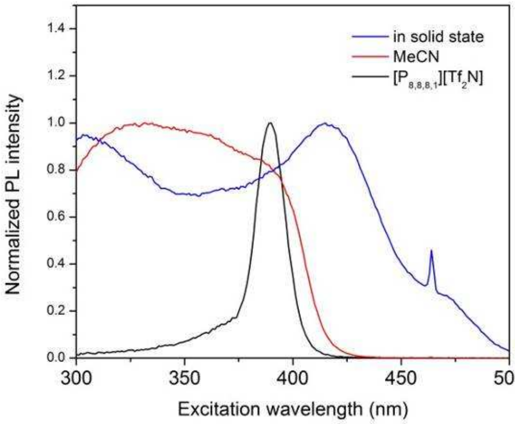


Fig. 6 Room temperature excitation spectra of complex (**I**) in solid state (λ_{em} = 611 nm), in ionic liquid $[P_{8,8,8,1}][Tf_2N]$ (λ_{em} = 614 nm) and in MeCN (λ_{em} = 611 nm)

Unlike the solid state, the emission bands related to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions for the complex (**I**) dissolved in acetonitrile (MeCN) and in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ were broadened. It is well known that rare earths luminescence is sensitive to the local environment and can experience a line broadening passing from an ordered state to a more disordered or dynamic system.[35] The broadening of the photoluminescence emission peaks passing from the pure complex in solid state to the complex in liquid (either in molecular solvent or ionic liquid) is thus commonly observed for rare earth complexes in solution, due to the electrostatic interactions and collisions with the surrounding molecules. The emission band at 611 nm due to the $^5D_0 \rightarrow {}^7F_2$ transition was shifted to 614 nm in the ionic liquid. This band broadening is particularly evident for complex (**I**) dissolved in the ionic liquid as well as its shift to 614 nm. This effect could perhaps be attributed to the interactions existing between the phosphonium cation and the ligand.[24] In our case, these interactions are revealed by the change of the ^1H-NMR chemical shifts of the P-CH_3 protons in the presence of different anions. This effect may be analogous to the one observed for encapsulated lanthanide complexes,[36] as previously suggested by others.[3] It should be noted that the emission spectrum for all the samples showed only one peak due to $^5D_0 \rightarrow {}^7F_0$ transition (579 nm), which implies that all the Eu^{3+} ions occupy a site of the same symmetry.[37,38] The hypersensitive transition ($^5D_0 \rightarrow {}^7F_2$) for the emission at 614 nm revealed changes of the coordination sphere of the Eu^{3+} ion. The symmetry and strength of the ligand field around Eu^{3+} could be determined from the ratio of the relative intensities between the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ transitions (Table 1). In contrast to the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition, the intensity of the electric dipole $^5D_0 \rightarrow {}^7F_2$ transition changed with the variation of the ligand field strength. The R value for the complex (**I**) dissolved in MeCN and $[P_{8,8,8,1}][Tf_2N]$ was 19.2 and 9.2 respectively.

By using Eq.(3) the radiative lifetime of Eu^{3+} in the three different environments was estimated. The refractive index for

MeCN is 1.344, for $[P_{8,8,8,1}][Tf_2N]$ it was estimated based on the reported value of $[P_{6,6,6,14}][Tf_2N]$ at 20 °C as 1.45[39] and for the solid state was assumed to be 1.5 for comparison purposes. The obtained radiative lifetime values are reported in Table 1.

The luminescence decay curves of Eu^{3+} related to the $^5D_0 \rightarrow {}^7F_2$ emission in the pure europium complex (**I**) in solid state, dissolved in acetonitrile (MeCN) and dissolved in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ are shown in Figure 8. The lifetime measurements were performed at room temperature at 611 nm (solid state and MeCN) or 614 nm (ionic liquid $[P_{8,8,8,1}][Tf_2N]$) emission wavelength under pulsed laser excitation at 390 nm. The decay curves were fitted by a single exponential and the lifetime values for all the samples are listed in Table 1. The lifetime of the $^5D_0$ excited state of the pure complex was 0.58 ms. This value was, as expected, higher than lifetimes of several tris complexes with dibenzoylmethane ligands[40] and tetrakis europium complexes.[41]

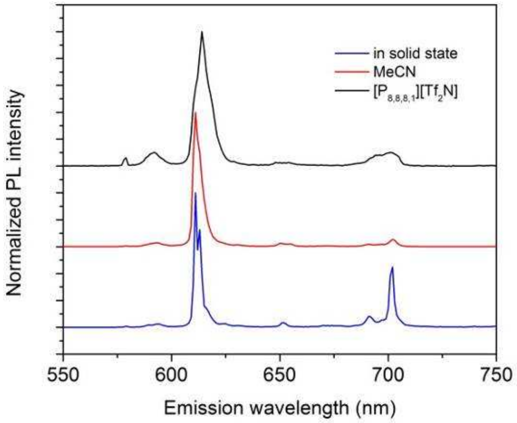


Fig. 7 Room temperature emission spectra of complex (**I**) in solid state ($\lambda_{exc.}$ = 415 nm), in MeCN ($\lambda_{exc.}$ = 350 nm) and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$ ($\lambda_{exc.}$ = 390 nm)

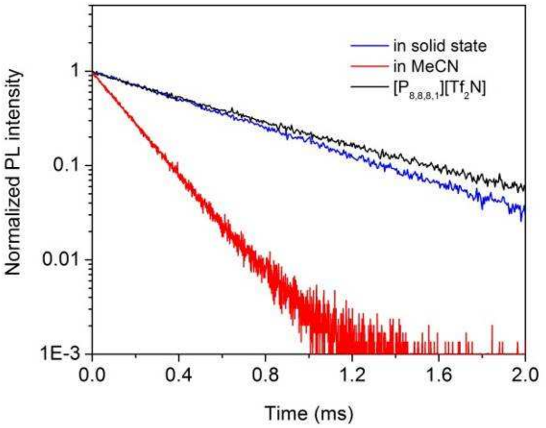


Fig. 8 Photoluminescence decay curves for complex (**I**) in solid state, in the MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$

When dissolved in ionic liquid the complex (**I**) showed higher lifetime as compared to the lifetime value of the complex in solid state and the one dissolved in MeCN solvent.

The internal quantum efficiency calculated from Eq. (2) is reported in Table 1. Φ_{int} reached a value as high as 92% for the pure complex in solid state while it was 12% and 33% in MeCN and $[P_{8,8,8,1}][Tf_2N]$, respectively, an indication of significant nonradiative recombination pathways. The measurements of the external quantum efficiency corresponding to the rate between absorbed and emitted photons followed a similar trend. It is worth observing that the rate between Φ_{ext} and Φ_{int} was an indication of the transfer efficiency between the antenna ligand and the rare earth. For complex (**I**) this value was estimated at about 60%. The longer lifetime in ionic liquid compared to the solid state is not commonly observed and can be rationalized based on the following two considerations. The first concerns the radiative lifetime of each system which in the case of Eu complex was evaluated directly from the experimental spectrum and resulted much higher in the ionic liquid than in the solid state. The other concerns the non-radiative recombinations which are related to the vibrational energy losses and other quenching mechanisms. In this case, as expected, the liquid environment results more dissipative than the solid state and this is reflected in the internal Φ_{int} (33% vs 92%). Globally, in our system the balance resulted in favour of the ionic liquid, as verified by the direct lifetime measurement.

Table 1. Optical data for the Eu complex (**I**) in solid state, dissolved in MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$.

	Solid	MeCN	$[P_{8,8,8,1}][Tf_2N]$
$I(^5D_0\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$	18.9	19.2	9.2
τ_{rad} (ms)	0.63	1.29	2.09
τ_{meas} (ms)	0.58	0.16	0.69
Φ_{int} (%)	92	12	33
Φ_{ext} (%)	58	7	20

Photoluminescence properties of Sm complex (II)

The room temperature excitation spectrum of the complex (**II**) in solid state, dissolved in acetonitrile (MeCN) and in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ are shown in Figure 9. The excitation spectra were recorded by monitoring the emission at 650 nm. The PLE of the complex (**II**) in solid state was similar to the one observed for complex (**I**) because the antenna ligand is the same: a broad band absorption up to 500 nm with a maximum at about 418 nm. The excitation spectra of the complex (**II**) dissolved in acetonitrile (MeCN) and in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ were shifted to shorter wavelengths, with a broad absorption band under 400 nm or a narrow peak around 390 nm, respectively.

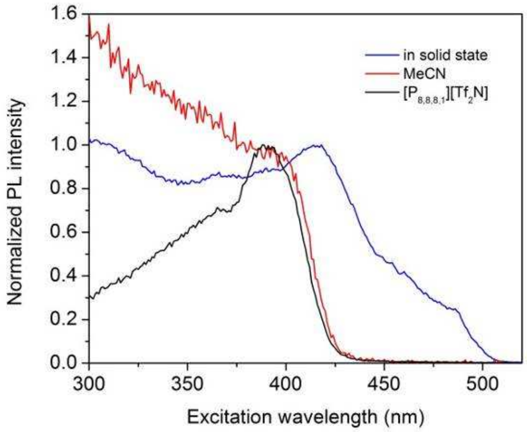


Fig. 9 Room temperature excitation spectrum (λ_{em} = 650 nm) of the (**II**) complex in solid state (black line), in MeCN (red line), and in ionic liquid (blue line)

The emission spectra of the complex (**II**) in solid state, dissolved in acetonitrile (MeCN) and dissolved in the ionic liquid $[P_{8,8,8,1}][Tf_2N]$ obtained by excitation at 418, 350 and 390 nm respectively, are presented in Figure 10 for the visible range and in Figure 11 for the NIR range. The emission properties of complex **II** are different from those of **I** as they are related to the different rare earth (Sm *vs* Eu). The assignments of lines are given in Table 2. The dibenzoyl methane ligands (dbm) absorbed the excitation energy and transferred it to the Sm^{3+} emitting centre. The emitting level for all the samarium emissions was the $^4G_{5/2}$ level. The emission spectrum exhibited four emission transitions in the visible at 563, 608, 650 and 709 nm due to $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ transitions. The $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition was the hypersensitive transition and responsible for the most intense line (c) in the visible region (650 nm). The complex showed the characteristic orange colour of the Sm^{3+} ion. A peak located at 563 nm, due to $^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition, had predominant magnetic dipolar character. For the Sm^{3+} ion, the ratio between the integrated areas of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ and $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (R) transitions, in the emission spectrum, was used as a measure for the polarizability of its chemical environment. The intensity ratio R calculated for the complex (**II**) in solid state was 13.3. This value was quite high for a Sm^{3+} complex[17] and was similar to Eu(III) β-diketonate complexes.

In addition to visible emission, complex (**II**) also displayed emission in the NIR region of the electromagnetic spectrum (Figure 11). The main line in the NIR area was at 950 nm due to $^4G_{5/2} \rightarrow {}^6F_{5/2}$ transition.

The emission spectrum of the Sm complex (**II**) dissolved in MeCN or in ionic liquid $[P_{8,8,8,1}][Tf_2N]$ was similar to the one in the solid state. Nevertheless, as previously observed also for complex (**I**), transitions were broadened with respect to the solid state as typically observed in solution, due to the electrostatic interactions and collisions with the surrounding molecules.[35]

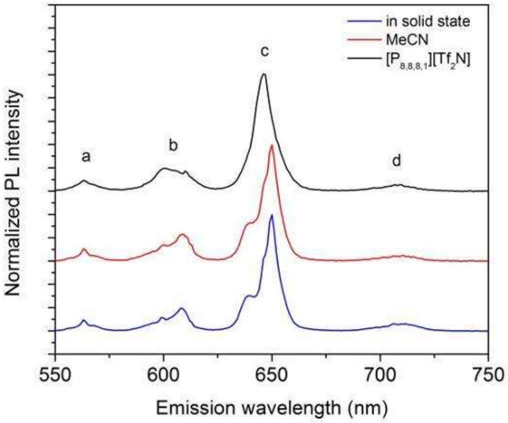


Fig. 10 Emission spectra of complex (**II**) in solid state (λ_{exc} = 418nm), dissolved in MeCN (λ_{exc} = 350nm) and ionic liquid Tf_2N (λ_{exc} = 390nm)

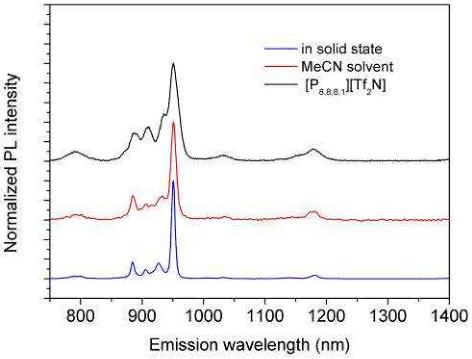


Fig. 11 NIR luminescence of complex (**II**) in solid state (λ_{exc} = 418 nm), dissolved in MeCN (λ_{exc} = 350 nm) and ionic liquid $[P_{8,8,8,1}][Tf_2N]$ (λ_{exc} = 390 nm)

Table 2 Peak assignment for the observed Sm^{3+} transitions.[42]

line	Line assignment	Wavenumber (cm^{-1})	Wavelength (nm)
a	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	17762	563
b	$^4G_{5/2} \rightarrow {}^6H_{7/2}$	16447	608
c	$^4G_{5/2} \rightarrow {}^6H_{9/2}$	15384	650
d	$^4G_{5/2} \rightarrow {}^6H_{11/2}$	14104	709
e	$^4G_{5/2} \rightarrow {}^6H_{13/2}$	12579	795
f	$^4G_{5/2} \rightarrow {}^6F_{1/2}$	11325	883
g	$^4G_{5/2} \rightarrow {}^6H_{15/2}$	11061	904
h	$^4G_{5/2} \rightarrow {}^6F_{3/2}$	10810	925
i	$^4G_{5/2} \rightarrow {}^6F_{5/2}$	10526	950
j	$^4G_{5/2} \rightarrow {}^6F_{7/2}$	9652	1036
k	$^4G_{5/2} \rightarrow {}^6F_{9/2}$	8475	1180

The luminescence decay curves for the complex (**II**) in solid state, in MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$ are shown in Figure 12. The lifetime measurements were performed at 650 nm under pulsed laser excitation at 390 nm. The decay curves were fitted by a single exponential and the lifetime values are reported in Table 3. The lifetime values for the complex (**II**) in solid state, in MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$ were respectively 63.5 µs, 3.1 µs and 19.1 µs. The complex (**II**) in ionic liquid showed a higher lifetime as compared to the complex in MeCN solvent, in agreement with what observed for complex (**I**). However, in this case the longest lifetime was observed in the solid state.

As a general observation, these values were lower than the radiative lifetime reported for this kind of ion in theoretical works, which is about 3 ms, indicating an important role of nonradiative recombinations. Other lifetimes on Sm complexes in different solvents and also in ionic liquids have been reported to range from a few microseconds to hundreds of microseconds.[18,43]

A rough evaluation of the internal quantum efficiency calculated from Eq. (2) by using a radiative lifetime of 3 ms is shown in Table 3. Unfortunately, for the Samarium complex **II** it is not possible to give an evaluation of the radiative lifetime by using a simple formula based on the experimental emission spectra, as was done for Europium using Eq. (3). Therefore, the results obtained based on literature studies on similar complexes are just a rough indication, which can be useful for comparison. Φ_{int} was about 2% for the pure complex in solid state while it was 0.1% and 0.6% in MeCN and $[P_{8,8,8,1}][Tf_2N]$ respectively. The measurements of the external quantum efficiencies were obtained by using an integrating sphere, which in our case is limited to the visible spectral region, and are therefore slightly underestimated However, it is worth observing that they follow the same trend of the internal efficiency values. Significant uncertainty on the internal efficiency related to the unknown radiative lifetime and a 15% uncertainty on the measurement of external efficiency should be kept in mind in comparing these numbers.

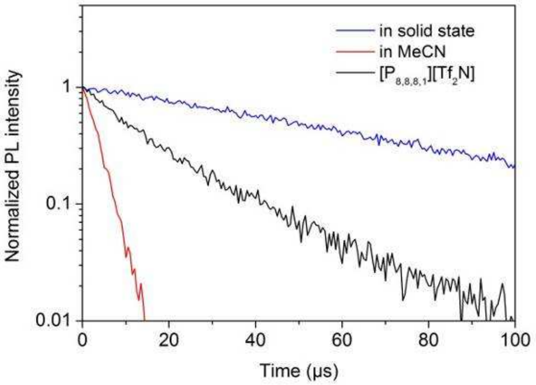


Fig. 12 The decay curve for $^4G_{5/2} \rightarrow {}^6H_{9/2}$ emission in the samarium complex (II) in solid state, in MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$

Table 3. Optical data for the Sm complex **(II)** in solid state, dissolved in MeCN and in ionic liquid $[P_{8,8,8,1}][Tf_2N]$.

	Solid	MeCN	$[P_{8,8,8,1}][Tf_2N]$
$I(^4G_{5/2}\rightarrow{}^6H_{9/2})/I(^4G_{5/2}\rightarrow{}^6H_{5/2})$	13.3	12.2	4.8
τ_{rad} (μs)	3000[27,28]	3000[27,28]	3000[27,28]
τ_{meas} (μs)	63.5	3.1	19.1
Φ_{int} (%)	2.1	0.1	0.6
Φ_{ext} (%)	2.7	< 0.1	0.8

Conclusions

Tetrakis rare earth complexes (Eu^{3+} and Sm^{3+}) with 1,3-diphenylpropane-1,3-dione ligand were synthesized. The crystal structures of complexes (**I**) and (**II**) consists of $[P_{8,8,8,1}]^+$ cations and complex anions. It shows that the Eu^{3+} and Sm^{3+} ions are surrounded by four 1,3-diphenylpropane-1,3-dione ligands. The coordination number of the Eu^{3+} and Sm^{3+} ions is eight. No solvent molecules are coordinated to the central metal ions. Unlike imidazolium cation based lanthanide tetrakis complexes, H-bonding between the $[P_{8,8,8,1}]$ cation and the complex anion is impossible in our case, rather the phosphonium cation is thought to ion-pair with the ligands thus contributing to the stability of the complexes in the present case. Both the Eu and Sm tetrakis complexes showed thermal stability up to 250 and 285 °C, respectively. The photoluminescence of complexes (**I**) and (**II**) in phosphonium ionic liquid $[P_{8,8,8,1}][Tf_2N]$ was studied and the changes in the fine structure of emission spectra were observed. Complex (**I**) showed a lifetime value of 0.58 ms in solid state that increased to 0.69 ms when dissolved in ionic liquid $[P_{8,8,8,1}][Tf_2N]$, while a value of 0.16 ms was observed in acetonitrile solvent. The longer emission lifetime observed for **I** in the IL compared to the solid state is not commonly observed and may indicate that matching the cation of the IL and of the complex might contribute to stabilize the complex. Internal quantum efficiencies as high as 92% in solid state, 33% in ionic liquid but only 12% in acetonitrile were found, indicating an important contribution of nonradiative recombination paths. Moreover, external quantum efficiencies of 58% (solid state), 20% (Ionic liquid) and 7% (acetonitrile) indicate a ligand to emitter transfer efficiency of the order of 60%. The time resolved analysis of complex (**II**) showed a lifetime value of 63.5 μs in solid state which decreased to 19.1 μs when dissolved in ionic liquid and again a much shorter lifetime of 3.1 μs in MeCN. For Sm the internal quantum efficiencies were much lower than Eu. From a value of about 2% in solid state and 1% in ionic liquid, it decreases drastically to 0.1% in acetonitrile, indicating an important contribution of nonradiative recombination paths. These phenomena can justify the difference between our results and previously reported ones.[3] External quantum efficiencies follow the same trend and similar values. The optical properties of the phosphonium ionic liquids synthesized by the procedure here described, along with their ability to dissolve the lanthanide tetrakis β-diketonate complexes open new potential applications for these materials, e.g. for study of the electrochemical properties and electrodeposition of f-elements or for photovoltaic cells. In the case of photovoltaic cells, the emission wavelength of complex **II** at 950 nm would be better compared to the emission of **I** at 612 nm, but the lower efficiency of **II** observed in our case also, still make **I** preferable.

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Notes and references

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†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/ CCDC-1051982 and CCDC-1051983 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

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