

A Luminescent Ionic Liquid Crystal: $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ Anna Getsis,^[a] Sifu Tang,^[a] and Anja-Verena Mudring*^[a]**Keywords:** Europium / Ionic liquids / Ionic liquid crystals / Lanthanides / Luminescence / Thermobehavior

$[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}\cdot\text{CH}_3\text{CN}$ (**2**) was obtained at -15°C by reacting europium bromide with $[\text{C}_{12}\text{mim}]\text{Br}$ (1-dodecyl-3-methylimidazolium bromide) in acetonitrile. **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The structure is characterized by double layers of $[\text{C}_{12}\text{mim}]$ cations with interdigitated alkyl chains which are separated by anion layers formed by $[\text{EuBr}_6]$ octahedra and $\text{Br}\cdots\text{CH}_3\text{CN}$ units. Upon warming to room temperature **2**

looses acetonitrile to form the room temperature ionic liquid crystal $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ (**1**). The temperature dependent structural behavior has been characterized by differential scanning calorimetry and hot-stage polarizing optical microscopy. In the temperature range of -3 to 98°C **1** adopts a smectic liquid crystal phase. At 77 K **1** shows a strong red emission with a lifetime of 2.6 ms. Analysis of the emission spectrum yields a quantum efficiency of 0.45.

Introduction

Ionic liquids (*ILs*) are currently receiving considerable attention from both academic and industrial researchers for their unique chemical and physical properties and property combinations.^[1] Ionic liquids can show many features which are advantageous for a number of applications,^[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 “green” chemistry.^[3] Indeed, ionic liquids are a widely tunable class of compounds. They can be decorated either on the cation or anion by introducing functional organic groups or metal ions. Metal-containing ionic liquids can combine the properties of ionic liquids with those of metal ions such as specific magnetic, photophysical/optical or catalytic properties. Recent examples of highly luminescent and magnetic metal-based ionic liquids are $[\text{C}_x\text{mim}][\text{Eu}(\text{Tf}_2\text{N})_4]$ [$x = 3$ and 4 ; $\text{Tf}_2\text{N} = \text{bis}(\text{trifluoromethylsulfonyl})\text{amide}$], $[\text{C}_4\text{mpyr}]_2[\text{Eu}(\text{Tf}_2\text{N})_5]$ ($\text{C}_4\text{mpyr} = 1\text{-butyl-1-methylpyrrolidinium}$) and $[\text{C}_6\text{mim}]_{5-x}[\text{Dy}(\text{SCN})_{8-x}(\text{H}_2\text{O})_x]$ ($x = 0\text{--}2$, $\text{C}_6\text{mim} = 1\text{-hexyl-3-methylimidazolium}$).^[4] In summary, ionic liquids can be designed to meet special applications and thus can be regarded as one kind of “soft” materials.

So far derivatized *N*-methyl-imidazolium cations are by far the most popular cations used for *ILs*.^[1] It is known that certain 1-alkyl-3-methylimidazolium salts with ten to

twelve and more carbon atoms in the side chain can become liquid crystals and form lamellar mesophases. Generally the mesophase stability increases with increasing length of the alkyl chain.^[5] Such compounds which can adopt the liquid crystalline state of matter can be addressed as ionic liquid crystals (*ILCs*).^[6] They combine the properties of typical ionic liquids with those of liquid crystals. Generally, ionic liquids which contain one or two anisotropically shaped ions (rod-like or disk-like) are likely able to form mesophases. However, *ILCs* feature some properties not encountered in “traditional” *LCs* consisting of neutral molecules such as ionic conductivity and uncommon ordering of the liquid-crystalline states (tetragonal smectic and nematic columnar phases).^[7] Recently, it was shown that double alkyl-substituted imidazolium *ILCs* show strong non-Newtonian fluidic behavior in the *LC* state while they are Newtonian liquids in the liquid *IL* state.^[5g] However, aside from changing the substituents at the imidazolium rings or coupling imidazolium rings via different spacers the charged head group can be changed. A special interest in the field of metal-containing liquid crystals focuses on light emitting liquid crystals for potential applications in emissive *LC* displays.^[8] By incorporating 4f-element cations *ILCs* emitting in the three basic colors (Tm^{3+} for blue, Eu^{3+} for red and Tb^{3+} for green) can be obtained.^[9] In addition, aligned luminescent *LCs* can emit polarized light.^[10] A high magnetic anisotropy of the lanthanide ion as found for Tb^{3+} , Dy^{3+} and Tm^{3+} makes the alignment of the mesophase in an external magnetic field possible.^[11] Thus, such compounds might be of interest for the use of electric and magnetic switchable devices.^[12]

Here we report on the synthesis as well as on the structural, thermal and photophysical properties of $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ (**1**) and its acetonitrile solvate $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}\cdot\text{CH}_3\text{CN}$ (**2**).

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Results and Discussion

Compounds **1** and **2** have been obtained by reacting 1-dodecylimidazolium bromide, $[\text{C}_{12}\text{mim}]\text{Br}$ and europium bromide in acetonitrile. At low temperatures $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} \cdot \text{CH}_3\text{CN}$ (**2**) crystallizes from this solution which loses acetonitrile upon heating to room temperature and forms $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ (**1**).

Structural Analysis

$[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} \cdot \text{CH}_3\text{CN}$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell. The asymmetric unit is equal to the formula unit and contains four crystallographically distinct $[\text{C}_{12}\text{mim}]^+$ cations, one complex $[\text{EuBr}_6]^{3-}$ anion and one molecule of acetonitrile (Figure 1, top). As found for the similar compounds $[\text{C}_{12}\text{mim}]_3[\text{LnBr}_6] \cdot 2\text{CH}_3\text{CN}$ ($\text{Ln} = \text{Dy}, \text{Tb}$)^[13] the Ln^{3+} cation is coordinated by six Br^- anions in the form of an almost ideal octahedron. The Eu–Br interatomic dis-

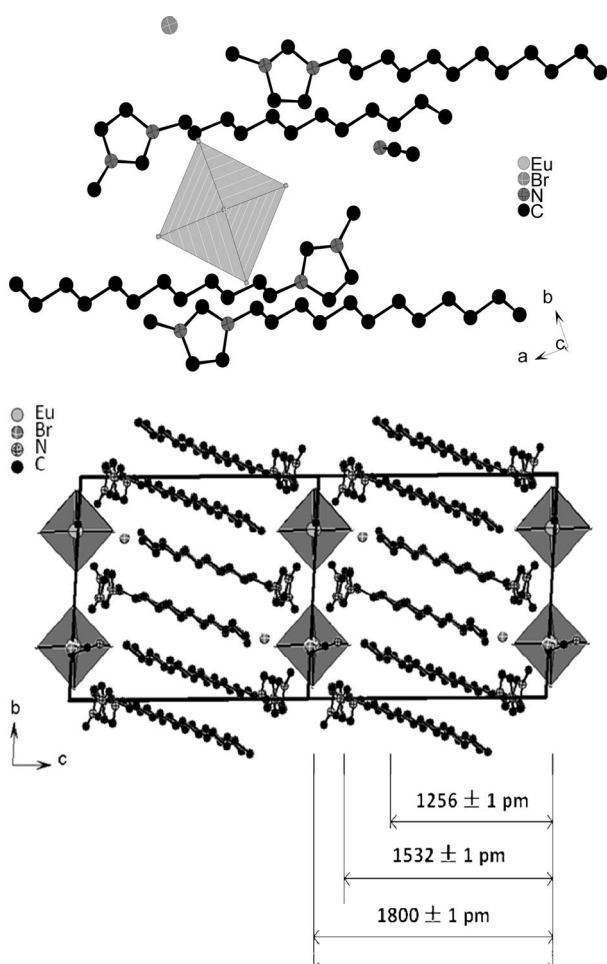


Figure 1. Asymmetric unit of $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} \cdot \text{CH}_3\text{CN}$ (**2**) (top); view along the crystallographic a axis of the unit cell of **2**, hydrogen atoms omitted for clarity (bottom). Eu, Br, N, C atoms are drawn as light gray, middle gray (front ellipse dashed), dark gray (principal ellipses and back dotted) and dark circles, respectively. $[\text{EuBr}_6]^{3-}$ octahedra are shaded in gray.

tances vary between 281.4 and 284.0 pm. With a mean value of 283.9 pm they are slightly larger than that of other salts with Eu^{3+} in octahedral coordination like $[\text{EuBr}_2(\text{thf})_5][\text{EuBr}_4(\text{thf})_2]$ with $d(\text{Eu}-\text{Br}) = 278.8\text{--}282.6$ pm, $[\text{EuBr}_3(\text{dme})_2]$ with $d(\text{Eu}-\text{Br}) = 279.9\text{--}282.6$ pm or $[\text{EuBr}_2(\text{diglyme})_2][\text{EuBr}_4(\text{diglyme})]$ with $d(\text{Eu}-\text{Br}) = 279.5\text{--}285.4$ pm.^[14] A similar observation was made for $[\text{C}_{12}\text{mim}]_3[\text{LnBr}_6] \cdot 2\text{CH}_3\text{CN}$ ($\text{Ln} = \text{Dy}, \text{Tb}$) where the mean Ln–Br distance is also larger than commonly found.^[13]

The bonding distances and angles of the $[\text{C}_{12}\text{mim}]^+$ cations are in the expected range and can be compared to values found in the similar compounds $[\text{C}_{12}\text{mim}]_3[\text{LnBr}_6] \cdot 2\text{CH}_3\text{CN}$ ($\text{Ln} = \text{Dy}, \text{Tb}$).^[13]

All cations show an *all-trans* conformation of the dodecyl-chain. The $[\text{C}_{12}\text{mim}]^+$ cations form rows parallel to the crystallographic a -axis (Figure 2, bottom). Two cation rows stack with opposite orientation so that the alkyl chains

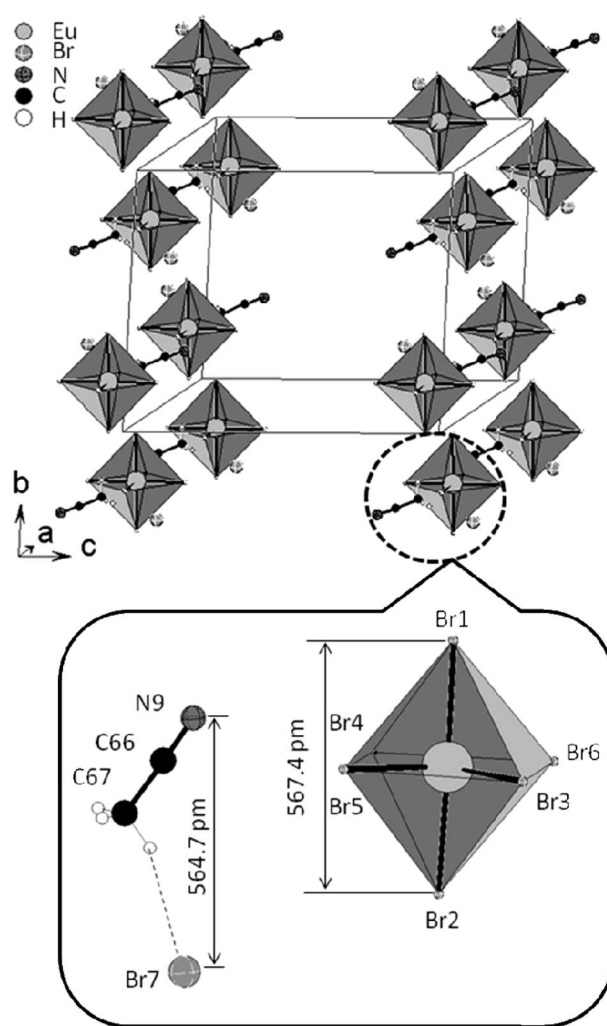


Figure 2. Anion packing in the unit cell of $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} \cdot \text{CH}_3\text{CN}$ (**2**) (top) and comparison of the space requirements of a $\text{Br} \cdots \text{CH}_3\text{CN}$ moiety and a $[\text{EuBr}_6]$ octahedron (bottom). Eu, Br, N, C atoms are drawn as light gray, middle gray (front ellipse dashed), dark gray (principal ellipses and back dotted) and dark circles, respectively. $[\text{EuBr}_6]^{3-}$ octahedra are shaded in gray with front faces open.

interdigitate. The amphiphilic character of the cations favors the formation of a bilayered structure as typically found for imidazolium or pyrrolidinium ionic liquid crystals.^{[5], [15]} The hydrophobic structure parts formed by the alkyl-chains are separated by the charged cationic head groups which interact with an anion layer formed by $[\text{EuBr}_6]^{3-}$ octahedra and $\{\text{Br}\cdots\text{CH}_3\text{CN}\}$ moieties. Interestingly, the space requirement of a $[\text{EuBr}_6]^{3-}$ octahedron and a $\{\text{Br}\cdots\text{CH}_3\text{CN}\}$ unit are roughly the same (Figure 2) which explains why the two moieties can pack efficiently with each other. As can be grasped from Table 1 not only between the single Br^- anion and acetonitrile non-classical hydrogen bonds^[16] are formed.

Table 1. Hydrogen bonds in $[\text{C}_4\text{mim}]_4[\text{EuBr}_6]\text{Br}\cdot\text{CH}_3\text{CN}$ (**2**).

	$d(\text{C}\cdots\text{Br})$ [pm]		$d(\text{H}\cdots\text{Br})$ [pm]
C2 \cdots Br7	373.6	H2A \cdots Br7	282.7
C102 \cdots Br1	385.1	H102 \cdots Br1	304.7
C103 \cdots Br7	372.4	H103 \cdots Br7	295.1
C104 \cdots Br5	388.3	H104 \cdots Br5	324.2
C202 \cdots Br1	368.9	H202 \cdots Br1	284.2
C203 \cdots Br7	360.1	H203 \cdots Br7	281.0
C204 \cdots Br5	374.3	H204 \cdots Br5	304.9
C302 \cdots Br2	391.7	H302 \cdots Br2	311.9
C303 \cdots Br6	383.2	H303 \cdots Br6	342.8
C304 \cdots Br3	386.7	H304 \cdots Br3	306.7
C402 \cdots Br6	372.6	H402 \cdots Br6	290.0
C403 \cdots Br4	378.2	H403 \cdots Br4	298.4
C404 \cdots Br6	378.2	H404 \cdots Br6	339.5
$\angle(\text{C}-\text{H}-\text{Br})$ [°]			
C2-H2A \cdots Br	158.4		
C102-H102 \cdots Br1	145.7		
C103-H103 \cdots Br7	141.4		
C104-H104 \cdots Br5	128.0		
C202-H202 \cdots Br1	152.0		
C203-H203 \cdots Br7	143.6		
C204-H204 \cdots Br5	132.7		
C302-H302 \cdots Br2	144.9		
C303-H303 \cdots Br6	108.9		
C304-H304 \cdots Br3	145.2		
C402-H402 \cdots Br6	148.7		
C403-H403 \cdots Br4	144.8		
C404-H404 \cdots Br6	107.6		

Vibrational Spectroscopy

Upon heating to room temperature $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}\cdot\text{CH}_3\text{CN}$ (**2**) loses acetonitrile and forms the solvent free compound $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ (**1**). The complete loss of acetonitrile can be proven by vibrational spectroscopy. No vibrational modes can be detected between 2100–2300 cm^{-1} where the characteristic $\text{C}\equiv\text{N}$ vibrations should be observed. Through Raman spectroscopy it is also possible to distinguish crystalline, mesomorphous and amorphous ordering. Indeed, the Raman spectrum of **1** confirms the low degree of ordering in the alkyl chains in the liquid crystalline state through the large linewidth of vibrations that can be assigned to the alkyl-chains. In addition, it is possible to elucidate the conformation of the alkyl side chains. Combined experimental and theoretical Raman investigation of

various 1-butyl-3-methylimidazolium salts have shown that *all-trans* conformers should give a broad signal at about 625 cm^{-1} while the *gauche* conformer should show a band at about 603 cm^{-1} .^[17] Both features can be detected in the Raman spectrum of liquid crystalline $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ pointing to a loss of ordering compared to the solid state (cf. Figure 1). The recorded far-infrared (FIR) and Raman spectra show the expected vibrations for the $[\text{C}_{12}\text{mim}]^+$ cation and $[\text{EuBr}_6]^{3-}$ anion (Figure 3). The unsymmetrical stretching vibration (F_{1u}) of the $[\text{EuBr}_6]$ octahedron can be detected in the far infrared spectrum (FIR) at 160 cm^{-1} . The symmetrical stretching vibration (A_{1g}) appears in the Raman (Ra) spectrum at 156 cm^{-1} . In comparable compounds the A_{1g} vibration is typically found around 155/156 cm^{-1} , the F_{1u} vibration between 158–164 cm^{-1} .^[18]

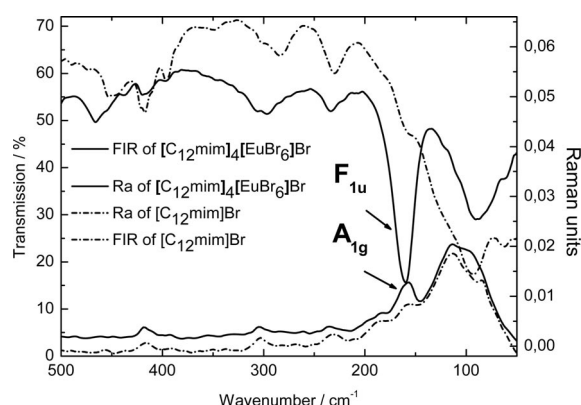


Figure 3. FIR (top two lines) and Raman (bottom two lines) spectra of **1** (solid lines) and $\text{C}_{12}\text{mimBr}$ (dash and dot lines) for comparison.

Thermal Investigations

$[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ forms at room temperature a smectic liquid crystal from DSC (differential scanning calorimetric) investigations and POM (polarizing optical microscopy) measuring (Figure 4). The DSC traces show two endothermic phase transitions upon heating at -3.2 and 98.2 °C with transition enthalpies of 38.1 kJ/mol and 2.3 kJ/mol, respectively. Temperature dependent POM confirms the first transition to be the flow point ($\text{S} \rightarrow \text{LC}$), the second one belongs to the clearing point ($\text{LC} \rightarrow \text{L}_{\text{ISO}}$). Upon cooling the transitions reappear with similar transition enthalpies. The $\text{L}_{\text{ISO}} \rightarrow \text{LC}$ transition occurs at 97.6 °C which corresponds well to the temperature found in the heating cycle. But the $\text{LC} \rightarrow \text{S}$ transition is found with a phase transition temperature of -16.6 °C at substantially lower temperatures. This indicates a good stabilization of the liquid crystalline state leading to a suppressing of the crystallization. POM shows for **1** textures which are indicative of a SmA phases like fan-shaped textures. Samples of **1** also have a strong tendency to form homeotropic areas which is quite characteristic for smectic *ILC*.^{[5], [15]}

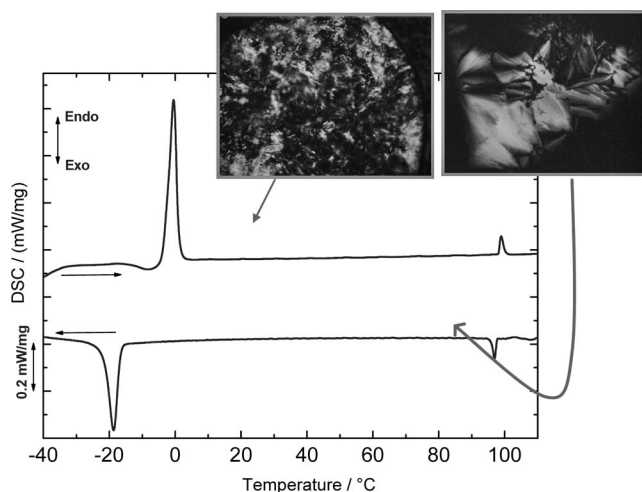


Figure 4. DSC-thermogram of **1** with corresponding POM micrographs.

Photophysical Investigations

Eu³⁺ is well known for its intense and efficient red luminescence which originates from interconfigurational f–f transitions (⁵D₀ → ⁷F_J).^[19] Indeed, **1** shows a strong red emission at 77 K (liquid nitrogen). In the excitation as well as the emission spectrum of **1** the characteristic ⁵D₀ → ⁷F_J (*J* = 0, 1, 2, 3, 4) transitions of Eu³⁺ are observed.^[20] Whilst the intensity of the magnetic dipole transitions ($\Delta J = 1, 3, 5$) is little disturbed by the ligand field, the intensity of the electronic dipole transitions ($\Delta J = 2, 4$) shows a high sensitivity to the local surrounding and the chemical nature of the ligand.^[21] The intensity ratio of the first electric and the magnetic dipole transition, the asymmetry parameter, gives valuable information on the coordination environment of Eu³⁺ in the respective compound.^[22] I(⁵D₀ → ⁷F₂)/I(⁵D₀ → ⁷F₁)-ratio of **1** is found to be about 1.26 which is comparable to the value of 1.4 found in the distorted elpasolite Cs₂NaEuCl₆ where Eu³⁺ is coordinated by an distorted octahedron of chloride neighbors.^[23] Similar values have been found for [pyH]₃[EuX₃] (pyH = pyridinium, X = Cl, Br) and are generally taken as characteristic for a distorted octahedral coordination environment of Eu³⁺.^[24] This finding agrees well with the crystal structure analysis of **2** where at low temperature a slightly distorted [EuBr₆]³⁻ octahedron is found and the vibrational spectra of **1** where the respective characteristic vibrations can be detected. The distortion from ideal O_h symmetry is also confirmed by the observation of a weak ⁷F₀ → ⁵D₀ transition in the excitation spectrum of **1**. As both, the excited ⁵D₀ as well as the ⁷F₀ ground states are singly degenerate and only one symmetric ⁷F₀ → ⁵D₀ transition is observed, indicating only one Eu³⁺ species can be present in **1**.^[25] To investigate the lifetime of the excited state the most intense emission from ⁵D₀ → ⁷F₂ was investigated. The decay time was found to be 2.6 ms at 77 K. This value is similar to the ones found for typical europium(III) containing ionic liquids.^[4a] In order to check for the quantum yield of **1**, we tried to estimate the ⁵D₀ quantum efficiency (*q*) from the emission spectrum and life-

time of the ⁵D₀ state by assuming that only nonradiative (*k_{nr}*) and radiative (*k_r*) processes lead to the depopulation of the ⁵D₀ state.^[26] Then the quantum efficiency *q* can be defined as Equation (1).

$$q = k_r / (k_r + k_{nr}) \quad (1)$$

The influence of the ⁵D₀ → ⁷F_{5,6} transitions on the depopulation of the ⁵D₀ state is ignored as no detectable signal could be obtained, as often encountered. The radiative contribution thus can be calculated from the relative intensities of the ⁵D₀ → ⁷F_{0–4} transitions as Equation (2),

$$k_r = A_{0 \rightarrow 1} \frac{\hbar \omega_{0 \rightarrow 1}}{S_{0 \rightarrow 1}} \sum_{J=0}^4 \frac{S_{0 \rightarrow J}}{\hbar \omega_{0 \rightarrow J}} \quad (2)$$

where *A*_{0–1} is the Einstein coefficient of spontaneous emission between the ⁵D₀ and ⁷F₁ Stark levels, usually considered to be equal to 50 s^{–1}.^[26] The $\hbar \omega_{0 \rightarrow J}$ and *S*_{0–*J*} are the energy and the integrated intensity of the ⁵D₀ → ⁷F_{*J*} transitions, respectively. Appropriate analysis of the emission yields the quantum efficiencies to be 0.45 (Figure 5). This value is somewhat less than found for C₁₂mimCl doped with EuX₃ (X = Cl, NO₃, ClO₄, CF₃SO₃) where values of 0.52–0.61 have been reported.^[27] The CIE color coordinates

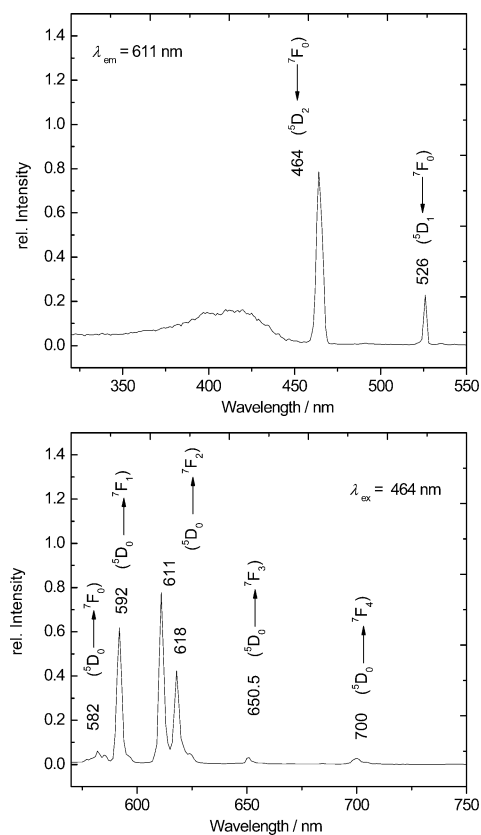


Figure 5. Normalized excitation (top) and emission (bottom) spectra of **1**.

for $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}$ (**1**) are $x = 0.579$, $y = 0.411$ which represent a red luminescence of high color purity and are similar to values found for $[\text{C}_4\text{mim}][\text{DTSA}]\cdot\text{Eu}[\text{DTSA}]$ (DTSA = ditoluenesulfonylamide).^[28]

Conclusions

The structurally characterized compound $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br}\cdot\text{CH}_3\text{CN}$ (**2**) can be grasped as the acetonitrile solvate of the double salt $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} = [\text{C}_{12}\text{mim}]_3[\text{EuBr}_6]\cdot[\text{C}_{12}\text{mim}]\text{Br}$ (**1**). Crystallization of similar double salts containing the “free” halide and a $[\text{LnBr}_6]$ unit has been previously observed, for example in the triphenylphosphonium salt $[(\text{C}_6\text{H}_5)_3\text{PH}]_3[\text{LnBr}_6]\cdot[(\text{C}_6\text{H}_5)_3\text{PH}]\text{Br}$.^[29] From solutions of LnI_3 in the ionic liquid $[\text{C}_4\text{mpyr}][\text{Tf}_2\text{N}]$ (*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl-amide) double salts with a composition of $[\text{C}_4\text{mpyr}]_4[\text{LnI}_6][\text{Tf}_2\text{N}]$ $\text{Ln} = \text{La, Pr, Nd, Sm, Dy, Er}$ crystallize.^[30] They can be structurally understood as in IL $([\text{C}_4\text{mpyr}][\text{Tf}_2\text{N}])$ solvate of $[\text{C}_4\text{mpyr}]_3[\text{LnI}_6]$. Similarly $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} = [\text{C}_{12}\text{mim}]_3[\text{EuBr}_6]\cdot[\text{C}_{12}\text{mim}]\text{Br}$ can be understood as an *ILC* solvate of the *ILC* $[\text{C}_{12}\text{mim}]\text{Br}$ and $[\text{C}_{12}\text{mim}]_3[\text{EuBr}_6]$. The local surrounding of the $[\text{LnX}_6]$ ($\text{X} = \text{Br, I}$) octahedra in these compounds is similar despite the different compositions. The triangular faces of the $[\text{LnX}_6]$ octahedron are capped by the charged cation head groups. Differential scanning calorimetry and hot-stage polarizing optical microscopy show that $[\text{C}_{12}\text{mim}]_4[\text{EuBr}_6]\text{Br} = [\text{C}_{12}\text{mim}]_3[\text{EuBr}_6]\cdot[\text{C}_{12}\text{mim}]\text{Br}$ (**1**) like its parent compound $[\text{C}_{12}\text{mim}]\text{Br}$ is able to form liquid crystalline phases. In the temperature range of -3 to 98°C **1** adopts a smectic liquid crystal phase. At 77 K **1** shows a strong red emission with an appreciable lifetime of 2.6 ms .

Experimental Section

Materials and Instrumentation: $[\text{C}_{12}\text{mim}]\text{Br}$ was synthesized according to a common literature procedure.^[51] All the other 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 $5^\circ\text{C}/\text{min}$ in sealed aluminum pans with an argon flow rate of $20\text{ mL}/\text{min}$. The reference sample was an empty Al container. IR spectra were recorded on a Bruker Alpha-P FT-IR spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. 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 at 77 K 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 silica tubes. Electronic transitions were assigned according to the energy level diagrams of trivalent rare earth ions.^[13]

X-ray Crystal Structure Determination: Intensity data of **2** were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073\text{ \AA}$) at

$170(2)\text{ K}$. Data reduction was carried out with the program package X-red^[31] and numerical absorption corrections were carried out with the program X-Shape^[32]. Crystal structure solution by direct methods using SIR92^[33] yielded the heavy atom positions. Subsequent difference Fourier analyses and least-squares refinement with SHELXL-97^[34] 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 2: $\text{C}_{64}\text{H}_{124}\text{N}_9\text{Br}_6\text{Eu}$, $M_r = 1753.1\text{ g mol}^{-1}$, triclinic, $P\bar{1}$, $a = 1493.1(2)$, $b = 1528.5(2)$, $c = 1833.7(2)\text{ pm}$, $\alpha = 86.38(1)$, $\beta = 79.92(1)$, $\gamma = 87.610(9)^\circ$, $V = 4110.3(9) \times 10^6\text{ pm}^3$, $Z = 2$, $\lambda = 0.71073\text{ \AA}$, $T = 170(2)\text{ K}$, $\rho = 1.421\text{ g cm}^{-3}$, $\mu = 4.205\text{ mm}^{-1}$, 37712 reflections were collected, of which 14182 were unique ($R_{\text{int}} = 0.1379$). $\text{GOF} = 0.935$. $R_1/R_2 = 0.0724/0.1642$ [$I > 2\sigma(I)$].

CCDC-767856 contains 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): Crystallographic information on **2** and further information on the calculation of the quantum efficiency.

Acknowledgments

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