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Dysprosium-Based Ionic Liquid Crystals: Thermal, Structural, Photo- and Magnetophysical Properties

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ABSTRACT: [C12mim][DyBr6] (C12mim = 1-dodecyl-3-methylimidazolium) represents a new material with interesting luminescent behavior as well as mesomorphic and magnetic properties. The compound was found to show thermotropic liquid crystalline behavior and forms smectic mesophases which were investigated by hot-stage polarizing optical microscopy and differential scanning calorimetry. The emission color of [C12mim][DyBr6] can be tuned from white to orange-yellow by the choice of the excitation wavelength. Sample excitation with λex = 366 nm leads to the blue-whitish luminescence from the imidazolium cation itself. With λex = 254 nm the common Dy(III) emission is observed which mainly arises from the 4F9/2 → 4H13/2 transition and, in consequence, the sample appears orange. Magnetic measurements show for Dy(III) in [C12mim][DyBr6] an effective magnetic moment of μeff = 9.6 μB at room temperature. The sample shows superparamagnetism and can be manipulated by an external magnetic field. In addition, the crystal structure of the corresponding acetonitrile solvate [C12mim][DyBr6]-2CH3CN (orthorhombic, Pbca, No. 62, Z = 8, Pearson code oP1328, a = 14.888(4) Å, b = 18.240(7) Å, c = 49.411(13) Å, 5596 unique reflections with I > 2σ(I), R1 = 0.1047, wR2 = 0.2442, GOF = 1.167, T = 298(2) K) has been elucidated. It is characterized by alternating double layers of [C12mim]+ cations of opposite orientation and nearly ideal [DyBr6]3− octahedra with hydrogen bonded acetonitrile. The structure of [C12mim][DyBr6]-2CH3CN serves as a structure model for the solvate free [C12mim][DyBr6].

Introduction

Ionic liquid crystal (ILC) research is located at the boundary of two fields of research: ionic liquids (ILs) and liquid crystals (LCs) which attract particular attention of scientists both in industry and academia.1,2 Ionic liquids have received substantial interest in recent years. Their inherent properties such as in most cases negligible vapor pressures, wide liquidus ranges, good thermal stabilities, considerable electric conductivities, and wide electrochemical windows have been shown to be advantageous for a large number of applications.3 Today they are predominately used in separation, various electrochemical applications, in organic synthesis and catalysis.3 As salts, ionic liquids are composed of distinct cations and anions which make them widely tunable. The variety of cation/anion-combinations leads to the description of ILs as “designer solvents”.2 Indeed, they may be designed for specific applications by choosing the appropriate cation and anion combination.

At the same time the interdisciplinary and intensive development of liquid crystals is based on the variety of mesogenic phases and their diverse properties based on the anisotropic nature of this state of matter.4 Ionic compounds which contain one or two anisotropically shaped ions (rod-like or disk-like) are likely able to form mesophases. Such compounds can be addressed as ionic liquid crystals. ILCs feature some specific properties untypical for “traditional” LCs consisting of neutral molecules. Here, for example, ionic conductivity and uncommon ordering of the liquid-crystalline states (tetragonal smectic and nematic columnar phases) can be named as examples.5 At the present time derivatized N-methyl-imidazolium cations are by far the most popular ILCs used for both ILs and ILCs.6 It is known that certain 1-alkyl-3-methylimidazolium salts with 12 and more carbon atoms in the side chain can form lamellar mesophases whose (mesophase) stability increases with increasing length of the alkyl chain.6c Obviously the research field of ILCs includes a multitude of conceivable compounds whose mesomorphic behavior is based on the amphiphilic nature one of the ions (either cation or anion). The unlimited capacities in ILC research correspond to the variety of ionic liquids as recent works show.7 Moreover, in the last few decades, metal-containing liquid crystals (metalomogesones) have been studied as a special class of ILCs. By choosing a suitable metal ion as the ILC constituent additional functionalities can be introduced to the material. Thus, multifunctional materials can be received by the combination of the mesomorphic behavior with unique properties of metal ions (such as redox-activity, magnetism, or luminescence). Several reviews survey the intensive studies on metalomesogens.8a–b,8d In contrast to neutral, uncharged mesomorphic metal complexes their ionic analogues have been studied far less. Some recent reviews give an overview of the research activities in the field of d-,8c,8d and f-element mesogens.10 The majority of investigated metallomesogens (including ILCs) comprises the metal ion in the anisotropic part of the compound. In contrast, fewer works report on ILCs where an anisotropically shaped cation is coupled with a complex metal anion of high symmetry such as tetrahedral or octahedral. So far, in this field most work has been undertaken on tetrahalometalates of d-elements. However, similar compounds with f-element cations are of potential interest because of their photoluminescent and magnetic properties. There is an immense interest in light emitting liquid crystals.11 By the variation of the emitting lanthanide center compounds emitting in the three basic colors (Tm3+ for blue, Eu3+ for red, and Tb3+ for green) can be made. Indeed, by doping ionic liquid crystals with lanthanide complexes highly luminescent
Dysprosium Tribromide, DyBr₃. DyBr₃ was synthesized according to a modified literature procedure. 6

\[\text{DyBr}_3\] and the structure of the related acetonitrile solvate \([\text{C}_{12}\text{mim}]_2\text{DyBr}_3\) and the structure of the related acetonitrile solvate \([\text{C}_{12}\text{mim}]_2\text{DyBr}_3\) - 2CH₃CN.

Experimental Details

Synthesis and sample handling were carried out under standard Schlenk and Argon-glovebox techniques. All solvents were dried using standard procedures. Cylindrical Karl Fischer titration shows no measurable water content in the samples under investigation. 6

1-Methyl-3-dodecylimidazolium Bromide, \([\text{C}_{12}\text{mim}]\text{Br}\). 3.4 mL of 1-methylimidazole (3.50 g, 0.043 mol) (99%, Acros organics, Geel, B) is dissolved in 100 mL of dry acetonitrile. Then 10.0 mL (10.38 g, 0.042 mol) of dodecylbromide (99% Acros organics, Geel, B) are added dropwise and the reaction mixture is heated under reflux for 18 h. After the mixture is cooled to room temperature about 50 mL of the solvent is removed under vacuum. Upon adding the concentrated acetonitrile solution dropwise to cold (−30 °C) dry tolulene \([\text{C}_{12}\text{mim}]\text{Br}\) precipitates as a white powder. The reaction product is filtered off and recrystallized two times from dry acetonitrile/toluene. Before use the product is dried from any remaining solvent for 48 h under dynamic vacuum at 100 °C.

Elemental analysis (%) calcd for \([\text{C}_{12}\text{mim}]\text{Br}\): C 57.63, H 9.74, N 6.02; found: C 41.41, H 6.51, N 6.02.

H NMR. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-300 spectrometer (operating at 300 MHz for H) (Bruker Germany GmbH, D). 6

Vibrational Spectroscopy. MIR (KBr pellet). \[\text{v} \text{[cm}^{-1}] = 3262.5 \text{ (w), 3149.4 (m), 3083.8 (s), 3062.6 (s), 2950.7 (s), 2916.0 (s), 2869.7 (s), 2852.4 (s), 1772.4 (w), 1668.2 (w), 1629.7 (m), 1711.8 (m), 1473.4 (m), 1437.2 (m), 1384.7 (w), 1344.2 (w), 1317.2 (w), 1292.2 (w), 1178.4 (w), 1126.3 (w), 1088.7 (w), 1054.9 (w), 1042.4 (w), 1022.2 (w), 1004.8 (w), 943.1 (w), 887.2 (w), 862.1 (m), 792.6 (m), 763.7 (w), 742.5 (w), 729.0 (w), 715.5 (m), 661.5 (m), 622.9 (m).

MIR (KBr pellet). \[\text{v} \text{[cm}^{-1}] = 1571.1 \text{ (s), 1521.0 (s), 1016.3 (s), 976.8 (w), 943.8 (w), 877.8 (w), 814.3 (s), 780.8 (w), 752.6 (w), 692.6 (s), 658.9 (s), 651.8 (s), 622.9 (s).

IR (PE pellet). \[\text{v} \text{[cm}^{-1}] = 1016.3 (s), 976.8 (s), 877.8 (s), 814.3 (s), 780.8 (s), 752.6 (s), 692.6 (s), 658.9 (s), 651.8 (s), 622.9 (s).

Elemental Analysis. Elemental analyses were obtained for \([\text{C}_{12}\text{mim}]\text{Br}\) on a Euro Vektor elemental analyzer EuroEA 3000 (HEKAttech GmbH, Wegberg, D) and for the title compound on Vario EL (Elementar Analysensysteme GmbH, Hanau, D.). 6

Thermal Measurements. Differential scanning calorimetry (DSC) was performed with a controlled rate 7.5 °C min⁻¹ in a PE pellet matrix for the far IR range (50–600 cm⁻¹) and in KBr matrix for the middle IR (MIR) range (600–4000 cm⁻¹). Raman spectra were recorded with a FRA 106-S Fourier Transform Raman spectrometer (Bruker Optik GmbH, Ettlingen, D) at 150 mW. Raman samples were measured in glass capillaries with an inner diameter of 0.1 cm and 0.15 mm wall thickness.

UV-visible. UV-visible absorption spectra were measured at room temperature on a Cary 30 spectrometer (Varian, Palo Alto, USA). The sample was ground into fine powder sealed under argon in a silica sample holder.

Luminescence Spectroscopy. Excitation and emission spectra and also luminescence decays were recorded on a Jobin Yvon Horiba Fluorolog FL3 with a xenon lamp as the excitation source and a photomultiplier tube for detection.

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A1 microscope (Carl Zeiss MicroImaging GmbH, Göttingen, D) equipped with a hot stage, THMS600 (Linkam Scientific Instruments Ltd., Surrey, UK), and temperature controller Linkam TMS 94 (Linkam Scientific Instruments Ltd., Surrey, UK). The images were recorded as movies with a digital camera after initial heating during then cooling stage.

Magnetic Measurements. The magnetic properties have been investigated by a super conducting quantum interference device (SQUID, Quantum Design MPMS-XL-5). 38 mg of [C12mim]-[DyBr6] were sealed in a silica glass tube under argon atmosphere.

Crystal Structure. Single crystals of 2 suitable for X-ray diffraction precipitated from an acetonitrile solution of 1 upon cooling to 5 °C as colorless needles. Single crystal X-ray structure analysis reveals that 2 crystallizes in the orthorhombic space group Pbca (No. 61) (α = 14.888(4) Å, β = 18.240(7) Å, γ = 49.411(13) Å, Z = 8, V = 13417(7) Å3) (Table 1 in Supporting Information). The asymmetric unit contains three crystallographically independent [C12mim] cations, one unique [DyBr6] octahedron and two acetonitrile molecules. Dy is 6-fold coordinated by bromide ions in the form of a nearly ideal octahedron. The Dy−Br interatomic distances range from 2.771 to 2.815 Å (Supporting Information), which are slightly longer compared to common inorganic salts as for example LiRb2[DyBr6] where values of 2.730−2.759 Å are found.22 This finding is in agreement with the vibrational spectra of the solvent free compound 1 where the Dy−Br vibrations are shifted to lower values (see below) due to the larger Dy−Br distances. Bonding distances and angles for the 1-dodecyl-3-methylimidazolium cations in

Table 1. Transition Temperatures and Enthalpies for [C12mim][DyBr6] after Recrystallization from Acetonitrile

<table>
<thead>
<tr>
<th></th>
<th>first cooling</th>
<th></th>
<th>second heating</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>T/°C</td>
<td>ΔH/(kJ/mol)</td>
<td>ΔS/(J/molK)</td>
</tr>
<tr>
<td>L-iso ** P 1</td>
<td>113.5</td>
<td>−2.0</td>
<td>−5.2</td>
</tr>
<tr>
<td>P 1 ** P 2</td>
<td>112.5</td>
<td>−2.9</td>
<td>−7.5</td>
</tr>
<tr>
<td>P 2 ** P 3</td>
<td>86.3</td>
<td>−0.09</td>
<td>−0.26</td>
</tr>
<tr>
<td>P 3 ** P 4</td>
<td>25.7</td>
<td>−4.5a</td>
<td>−15.2a</td>
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<td>P 4 ** P 5</td>
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<tr>
<td>P 5 ** glass</td>
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a Because of the baseline drift, the values of ΔH and ΔS are less precise.

Figure 1. Crystal structure of [C12mim][DyBr6]-2CH3CN, view along the crystallographic a axis (top) and along the crystallographic b axis (bottom).

Figure 2. Constituents of the asymmetric unit in the crystal structure of [C12mim][DyBr6]-2CH3CN: three unique [C12mim] cations (top); [DyBr6] octahedron with hydrogen bonded acetonitrile molecules, viewed along the b axis (bottom).

Results and Discussion

Crystal Structure. Single crystals of 2 suitable for X-ray diffraction precipitated from an acetonitrile solution of 1 upon cooling to 5 °C as colorless needles. Single crystal X-ray structure analysis reveals that 2 crystallizes in the orthorhombic space group Pbca (No. 61) (α = 14.888(4) Å, β = 18.240(7) Å, γ = 49.411(13) Å, Z = 8, V = 13417(7) Å3) (Table 1 in Supporting Information). The asymmetric unit contains three crystallographically independent [C12mim] cations, one unique [DyBr6] octahedron and two acetonitrile molecules. Dy is 6-fold coordinated by bromide ions in the form of a nearly ideal octahedron. The Dy−Br interatomic distances range from 2.771 to 2.815 Å (Supporting Information), which are slightly longer compared to common inorganic salts as for example LiRb2[DyBr6] where values of 2.730−2.759 Å are found.22 This finding is in agreement with the vibrational spectra of the solvent free compound 1 where the Dy−Br vibrations are shifted to lower values (see below) due to the larger Dy−Br distances. Bonding distances and angles for the 1-dodecyl-3-methylimidazolium cations in

I are widely in the expected range and can be compared to the ones in short chain N-alkyl-N-methylimidazolium compounds investigated by us previously.23 Two of the dodecyl chains (cations 1 and 2) adopt all-trans conformations (Figure 2), while the third (cation 3) reveals a gauche conformation around the C7−C8 bond with a torsion angle of 54°. Such “crank-handle”-like arrangements have been previously observed in analogous hexafluorophosphatolime salts.
In I, the cations themselves form rows which are stacked along the unique axis \(a\). The alignment of the cations in a row can be seen by viewing along the crystallographic \(b\) axis. (Figure 1) The cations stack in such a way that their alkyl tails alternate in orientation in neighboring layers. By this a double layer structure is formed.

The cations are oriented such that angles of 32.8°, 25.6°, and 30.8° (for cations 1, 2, and 3 respectively; cf. Figure 2) between the alkyl chains and the bilayer plane normal are adopted. The layers are 15.7745 ± 0.0025 Å thick, and the length of a C\(_{12}\)mim cation in an all trans conformation amounts to 17.46 ± 0.04 Å. The bilayer thickness is 23.1959 ± 0.0025 Å and the bilayer distance reaches 24.6704 ± 0.0025 Å, leaving an empty space of 1.475 Å in between. Within the layers a structural segregation into hydrophilic and hydrophobic domains can be observed. The hydrophobic parts are formed by the interdigitated \(n\)-alkyl tails of the imidazolium cation, whereas the charged imidazolium head groups together with the hexabromodysprosate octahedra form the hydrophilic structure part. Within a layer each [DyBr\(_6\)]\(^{3-}\) anion is surrounded by six [C\(_{12}\)mim]\(^+\) cations and two acetonitrile molecules. Nonclassical hydrogen bonds between cations and anions can be discussed. (NN)Csp\(_2\)333 Br and (NC)Csp\(_2\)333 Br interactions that are shorter than the commonly accepted limiting values of 3.72 Å and 3.75 Å exist not only within the hydrophilic parts of each layers but also between them (Figure 3). The formation of separate hydrophilic and hydrophobic structure parts already makes the formation of liquid crystalline phases possible. However, the compound loses acetonitrile before such a phase transition takes place. Judging from optical polarizing microscopy the layered-like structure seems to be preserved and the formation of smectic phases can be observed (see below).

**Infrared and Raman Spectroscopy.** The far-IR and Raman spectra of [C\(_{12}\)mim]Br and [C\(_{12}\)mim]\(_3\) [DyBr\(_6\)] deviate significantly (Figure 6). The recorded far-IR and Raman spectra show the expected vibrations for a [DyBr\(_6\)]\(^{3-}\) octahedron. Typically, the unsymmetrical stretching vibration (\(F_{1u}\)) can be detected in the far-IR spectrum and the symmetrical stretching vibration (\(A_{1g}\)) in Raman spectrum. The observed values of 157 cm\(^{-1}\) for the \(F_{1u}\) and 155 cm\(^{-1}\) for the \(A_{1g}\) modes correspond are slightly lower than the values found for tris(pyridinium) hexabromodysprosate(III), [pyH]\(_3\) [Dy-Br\(_6\)] (\(F_{1u}=161\) cm\(^{-1}\); \(A_{1g}=159\) cm\(^{-1}\))\(^{26}\) and tris(triphenyl- phosphonium) hexabromodysprosate(III), [Ph\(_3\)PH]\(_3\) [DyBr\(_6\)] (\(F_{1u}=160\) cm\(^{-1}\); \(A_{1g}=158\) cm\(^{-1}\)).\(^{27}\) This is in agreement with the enlarged Dy–Br distance found in 2 when compared to other DyBr\(_6\) compounds. No C≡N vibrations can be observed in the range between 2100 and 2250 cm\(^{-1}\)\(^{28}\) (Supporting Information) which clearly shows that samples of I do not contain acetonitrile.
Thermal Analysis. The thermal properties of 1 were examined by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The DSC traces of 1 are shown in Figure 4. Table 1 gives the respective transition temperatures, enthalpies, and entropies. Upon cooling from the isotropic melt, five thermal events can be resolved occurring at 113.5 °C, 112.5 °C, 83.6 °C, 25.7 °C and at about −20 °C (temperatures of the onset of the thermal effect are given). In the second heating cycle, six thermal effects can be detected, taking place at ∼−20 °C, 27.8 °C, 49.9 °C, 87.3 °C, 112.3 °C and ∼115.5 °C. By reducing the heating and cooling ramp from 10 to 1 °C/min, it becomes clear that the effects taking place upon heating with 10 °C/min at 49.9 and 27.8 °C fall together in the cooling cycle at the thermal event at 25.7 °C (Supporting Information). It has to be mentioned that all further heating and cooling cycles are reproducible and are similar to the first cooling and second heating. To elucidate the thermal behavior of 1 POM investigations where carried out. As commonly observed, it is quite difficult to observe unambiguous defect textures for mesophases of imidazolium based ILCs by polarizing optical microscopy as the compounds show a strong tendency to form spontaneously single homeotropic monodomains which gives a dark field between crossed polarizers of the microscope.
and it is quite difficult to disturb this alignment in order to evoke more meaningful textures.\textsuperscript{1,29} The dilemma is further enhanced by the fact that compound 1 is sensitive to atmosphere and the sample for POM measurements has to be handled under strictly inert conditions between two hermetically sealed cover slides which can stand just a certain degree of external pressure. However, POM investigations show that always the highest thermal event corresponds to the clearing point and the coolest thermal event to a glass transition — apparently the samples show no tendency for homogeneous crystallization. All other observed transitions are associated with LC—LC transitions. The optical textures observed on cooling from the isotropic melt showed the emergence of b\textsuperscript{2}atonnetes (Figure 5, left), which can coalesce to give rise to a focal conic texture (Figure 5, right). Both b\textsuperscript{2}atonnetes and fan-shape textures are characteristic for smectic phases. The focal conic fan textures originates when a layered structure forms conical domains. The dark homeotropic areas where no birefringence is observed when the long axis of the imidazolium cations is aligned parallel to the incident polarized light so that the light wave vector cannot be rotated. Upon further cooling, the dark homeotropic areas vanish (Figure 5(2)) and even in the glassy state the material looks anisotropic and not crystalline (Figure 5(1)). Judging from the crystal structure of 2 it seems quite likely that 1 forms smectic mesophases. This assumption is supported by the fact that smectic A phases have been reported for several 1-\textit{n}-alkyl-imidazolium ILCs.\textsuperscript{6c} For transition metal tetrachlorometallate SmA-SmA polymorphism has been observed.\textsuperscript{30} This behavior is possibly because the layer structure originates not only from the hydrophobic van-der-Waals interactions between the long cation-alkyl tails but is strongly stabilized by the Coulombic interactions in the hydrophilic part. In consequence, the alkyl-tails can melt independently from the layers and several smectic phases can be adopted due to the different space requirements of the alkyl tails with rising freedom as well as their orientation toward the layer normal. Unfortunately, we are not able to further investigate the structure of the formed phases as we have no means to carry out temperature-dependent SAXS measurements under strictly anhydrous conditions.

\textbf{Luminescence Spectroscopy}. The photoluminescence of 1 was studied. Trivalent dysprosium, Dy\textsuperscript{3+} with a 4\textit{f}\textsuperscript{9} electron configuration, is known for its intensive luminescent transitions, $^4\text{F}_9/2 \rightarrow ^4\text{H}_{15/2}$ in the blue region of light and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ in the yellow-orange spectral region.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Dependence of light emission of 1 on the excitation wavelength. (Left: 3D spectrum; right: top view of the 3d spectrum; Rayleigh bands are omitted).}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure10.png}
\caption{Comparison of the luminescence spectra of 1 and [C\textsubscript{12}mim]Br.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure11.png}
\caption{Phosphorescence spectra of 1.}
\end{figure}
Figure 7 shows the excitation spectrum of \( \lambda_{\text{em}} = 575 \) nm together with the emission spectra recorded for the excitation wavelengths \( \lambda_{\text{ex}} = 352, 366, \) and 254 nm at room temperature. Spectra recorded at 70 °C showed no significant changes. The excitation spectrum of \( \lambda_{\text{ex}} = 254 \) nm shows the \( f-f \) transitions characteristic for Dy(III). As well the emission spectrum of \( \lambda_{\text{ex}} = 254 \) nm shows the typical emission originating from emission from the \( 4F_{9/2} \) level. The \( 4F_{9/2} \rightarrow 6H_{13/2} \) as a hypersensitive transition (\( \Delta L = 2, \Delta J = 2 \)) is comparatively strongly influenced by the local environment of the trivalent lanthanide cation. Its intensity strongly determines the visible appearance of the luminescent dysprosium compound; depending on the intensity ratios of the \( 4F_{9/2} \rightarrow 6H_{15/2} \) and \( 4F_{9/2} \rightarrow 6H_{13/2} \) transition the emission has either a whitish or yellowish color. The \( 4F_{9/2} \rightarrow 6H_{13/2} \) transition at 575 nm is the most intense for \( \lambda_{\text{ex}} = 254 \) nm of an UV lamp (Figure 8). Excitation with a longer wavelength of \( \lambda_{\text{ex}} = 366 \) nm results in a white-blueish emission of the sample.

In principle, it should not be possible to excite Dy(III) with a conventional UV lamp (\( \lambda_{\text{ex}} = 254 \) nm) as the CT absorption band of Dy(III) lies around 200 nm. However, it is known that through sensitation via the host matrix or via impurities luminescence of Dy(III) under an UV lamp can be achieved. Indeed, \( \lambda_{\text{ex}} = 254 \) nm shows a yellowish emission under excitation with \( \lambda_{\text{ex}} = 254 \) nm of an UV lamp (Figure 8).
Apparently, the [C12mim]+ cation works as a sensitizer and is able to activate Dy(III) in I via energy transfer. Indeed, [C12mim]Br shows absorptions in the range from 200 to 300 nm (Supporting Information). Excitation with longer wavelengths leads to an additional strong and broad emission in the blue region of light (Figure 9) stemming from the imidazolium cation which conceals the \(^{4}F_{9/2} \rightarrow ^{6}H_{15/2}\) emission of Dy(III) at 480 nm in the sample.

From comparison with the luminescence spectra of pure [C12mim]Br, it becomes clear that the bluish white appearance of I comes from a combination of the luminescence of the imidazolium cations and a smaller contribution from the transition of Dy(III) (Figure 10).

Even small changes in the excitation wavelength crucially determine the intensity distributions of the [C12mim]+ to Dy(III) luminescence. If the sample is excited with \(\lambda_{ex} = 366\) nm the luminescence from the imidazolium cation overweights the \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) luminescence of Dy(III) by far. However, under excitation with \(\lambda_{ex} = 352\) nm the intensity of the Dy(III) \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) is strongly increased. Consequently, the luminescence color of I can be tuned by the choice of the excitation wavelength. Such a behavior has previously been noted for the ionic liquid crystal compound [C12mim]Cl when doped with Eu\(^{3+}\).

Phosphorescence spectra of I show just the typical Dy(III) transitions regardless of the excitation wavelength as the luminescence of the [C12mim]+ cations is too short-lived (Figure 11). The luminescence decay time of the \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) transition of Dy\(^{3+}\) is 47 \(\mu s\) at room temperature and still 46 \(\mu s\) at 70 °C (Supporting Information).

Magnetism. \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) (I) contains the magnetic active ion Dy\(^{III}\) with an 4\(d^6\) electron configuration. The effective magnetic moment of Dy\(^{III}\) has been calculated to \(\mu_{\text{eff}} = 10.48\mu_B\). The measured value for I at room temperature is slightly less with \(\mu_{\text{eff}} = 9.6\mu_B\). Because of the high magnetic anisotropy of the Dy\(^{III}\) ion the liquid crystalline phases of [C12mim][DyBr6] could potentially be aligned in an external magnetic field.

In particular, the low viscous modifications that exist right below the clearing point should be aligned by an external applied magnetic field. Figure 12 summarizes the magnetic measurements performed on I. Figure 12b shows the temperature dependence of the reciprocal molar susceptibility measured in an external applied magnetic field of 10,000 Oe. As expected from the Curie–Weiss law for a paramagnet the fit of the data results in \(\theta = 0\). The field dependency of the magnetic moment of I is shown for 300 K and 5 K in Figure 12, panels e and f, respectively. The compound exhibits (super)paramagnetic behavior at room temperature. No interaction between the magnetic moments can be observed at this temperature. The field dependent behavior of the sample changes at 5 K. The magnetic moment increases about an order of magnitude while decreasing the temperature from 300 K to 5 K. The shape of the 5 K hysteresis loop is somehow similar to that of a soft-magnetic ferromagnetic one which is quite normal for superparamagnetic compounds. The paramagnetic contribution is still that dominant that even an external field of 50,000 Oe is not sufficient to saturate the magnetic moments at 5 K. The values of the coercive field \(H_C\) and the remanence \(B_r\) are exactly zero.

Nevertheless, the compound can be manipulated by an external magnetic field due to the large anisotropic magnetic moment of the Dy\(^{3+}\) ion like the similar ionic liquids \([\text{C4mim}][\text{Dy(SCN)}_6](\text{H}_2\text{O})_{3}]^{38}\). No interaction between the magnetic moments can be observed at this temperature. The field dependent behavior of the sample changes at 5 K. The magnetic moment increases about an order of magnitude while decreasing the temperature from 300 K to 5 K. The shape of the 5 K hysteresis loop is somehow similar to that of a soft-magnetic ferromagnetic one which is quite normal for superparamagnetic compounds. The paramagnetic contribution is still that dominant that even an external field of 50,000 Oe is not sufficient to saturate the magnetic moments at 5 K. The values of the coercive field \(H_C\) and the remanence \(B_r\) are exactly zero.

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Conclusions

\([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) represents an interesting new material that is highly luminescent and at the same time strongly responds to external applied fields. Furthermore, the compound shows the formation of liquid crystalline mesophases over a wide temperature range from 115 °C down to −20 °C including room temperature. The mesophases formed by \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) were identified to be of lamellar structures by hot-stage polarizing optical microscopy. As already observed for the parent [C12mim]Br ionic interactions tend to stabilize such smectic mesophases. A structure model for the smectic phases of [C12mim][DyBr6] can be obtained from the single crystal structure of its acetonitrile solvate [C12mim][DyBr6]·2CH3CN as unfortunately crystallization of \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) failed. \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\)·2CH3CN forms a layered structure where double layers of hydrophilic and hydrophobic structure regions alternate. The hydrophilic structure parts are formed by interdigitated dodecyl tails of imidazolium cations with different orientation. The hydrophilic structure regions are built up by the charged imidazolium head groups and octahedral hexabromodysprosiate(III) complex anions together with hydrogen bonded acetonitrile. It is anticipated that the ion arrangement is largely retained when the solvate acetonitrile molecules are lost.

\([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) shows either a bright white or orange-yellow emission upon irradiation with UV light. Apparently the imidazolium cation works as a sensitizer for the Dy(III). Excitation with a wavelength of \(\lambda_{ex} = 366\) nm leads to the characteristic blue-whitish luminescence from the imidazolium cation itself. When using the shorter wavelength \(\lambda_{ex} = 254\) nm the sample appears orange due to emission from Dy(III). The lifetime of the \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) emission, the most intense transition, is quite unaffected by the temperature and state of matter. The luminescence decay time of the \(^{4}F_{9/2} \rightarrow ^{6}H_{13/2}\) transition of Dy\(^{3+}\) is 47 \(\mu s\) at room temperature and still 46 \(\mu s\) at 70 °C. Also the spectra look alike indicating that no significant changes occur in the first coordination sphere of Dy\(^{3+}\). Magnetic measurements show for Dy(III) in \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\) an effective magnetic moment of \(\mu_{\text{eff}} = 9.6\mu_B\) at room temperature. The sample shows superparamagnetism and can be manipulated by an external magnetic field. As Dy\(^{3+}\) has a large anisotropic magnetic moment is should be principally possible to align the liquid crystal phases in an external magnetic field. In particular, the comparatively low viscous phases that are formed right below room temperature should respond easily to a magnetic field. However, this has to be subjected to further investigations.

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Supporting Information Available: Graphical representation of the vibrational spectra (MIR, FIR, and Raman) of compound I, UV–vis and luminescence spectra of C12mimBr, lifetime measurements of I, as well as information on the crystal structure solution and refinement of \([\text{C12mim}]^{+}\)\([\text{DyBr}_6]^{-}\)·2CH3CN is available. This information is available free of charge via the Internet at http://pubs.acs.org.
(3) For a recent review on the topic, see Plechkova, N. V.; Seddon, K. R. Chem. Soc. Rev. 2008, 37, 123.