Ionic Liquids (2)

DOI: 10.1002/anie.200802390

Dysprosium Room-Temperature Ionic Liquids with Strong Luminescence and Response to Magnetic Fields**

*Bert Mallick, Benjamin Balke, Claudia Felser, and Anja-Verena Mudring**

Ionic liquids have inherent properties, such as negligible vapor pressures in most cases, wide liquid ranges, good thermal stabilities, considerable electric conductivities, wide electrochemical windows, which have been shown to be advantageous for a large number of applications.[1] As salts, ionic liquids are composed of distinct cations and anions, which makes them widely tuneable. They may be designed for specific applications through the choice of the respective cation and anion and the ion combination.

Metal-containing ionic liquids are auspicious new materials which can favorably combine the properties of ionic liquids with magnetic, photophysical/optical or catalytic properties that originate from the metal incorporated in the complex anion. Recently, it has been shown that solutions of lanthanide compounds in ionic liquids are promising soft luminescent materials for use in photochemistry and spectroscopy.[2] However, trivalent lanthanides are not only of interest as luminescent materials, but also as magnetic metal centers. The ions Gd–Tm in particular have high local magnetic moments ranging from 8 μ_B to 11 μ_B. The challenge we took is to synthesize room temperature liquids that combine the properties of a soft luminescent material with a ferrofluid.

The term ferrofluid traditionally applies to fluids in which colloidal or nanoparticles of magnetic materials, for example iron oxides, are embedded in a carrier liquid.[3] Usually these liquids are water or long chain hydrocarbons. However, recently we were able to show that ionic liquids also offer advantages as the liquid nanoparticle support.[4]

Recently a novel class of magnetic ionic liquids was discovered. In these single-component materials, the magnetic ion is no longer introduced as small particles, but through complex ions of metals which have a high magnetic moment. The first example is $[C_4mim][FeCl_4]$ (C_4mim = 1-butyl-1-methylimidazolium). Although the compound has been known for a while,[5] its magnetic properties and potential application have only recently been evaluated.[6] For $[C_4mim][FeCl_4]$, a magnetic mass susceptibility χ_g of 40.6×10^{-6} emu g^{-1} corresponding to a molar susceptibility χ_{mol} of 0.0137(7) emu mol^{-1} was reported. The effective magnetic moment of $\mu_{eff} = 5.8\,\mu_B$ is in accordance with a high-spin $S = 5/2$ state. Similar values are found for other iron(III)-based liquids.[7]

Owing to the high single-ion magnetic moments, these ionic liquids show a strong response to external magnetic fields. It has been shown that not only the liquid itself can be manipulated by a magnetic field, but also that nonmagnetic (diamagnetic) materials can be transported and separated according to their density and magnetic susceptibility in these liquids.[8] In this context, purely organic magnetic ionic liquids based on radical ions, such as 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate (TEMPO-OSO_3), have recently become available.[9] With respect to metal-based magnetic ionic liquids, to date only transition-metal-based liquids, mostly based on high-spin d^5 iron(III) in the form of tetrachloro- and tetrabromoferrate(III) with various counter cations have been explored.[10] Recently, other magnetic ionic liquids with other transition metal ions and gadolinium(III) were synthesized.[11] The incorporation of lanthanide ions into ionic liquids offers the advantage of a metal ion that has a considerably higher effective magnetic moment than any known transition metal, and thus would give the best response to an external magnetic field. The effective magnetic moment of dysprosium(III) has been calculated to be $\mu_{eff} = 10.48\,\mu_B$, which is roughly twice the value of iron(III).[12] Furthermore, the photophysical properties of dysprosium(III) would also make it possible to have a luminescent fluid.

The new ionic liquids $[C_6mim]_{5-x}[Dy(SCN)_{8-x}(H_2O)_x]$ (x = 0–2, C_6mim = 1-hexyl-3-methylimidazolium) were synthesized from $[C_6mim]SCN$, KSCN, and $Dy(ClO_4)_3 \cdot 6\,H_2O$ according to a literature procedure for similar lanthanide-based ionic liquids.[13] All the liquids show a strong response to conventional neodymium magnets (Figure 1). The compounds $[C_6mim]_3[Dy(SCN)_6(H_2O)_2]$ (**1**), $[C_6mim]_4[Dy(SCN)_7(H_2O)]$ (**2**), and $[C_6mim]_5[Dy(SCN)_8]$ (**3**) all contain dysprosium(III) as the magnetically active ion with a $4f^9$ electron configuration. The effective magnetic moments at

Figure 1. Response of the orange-colored ionic liquid **1** to a neodymium magnet.

---

[*] Dipl.-Chem. B. Mallick, Prof. Dr. A.-V. Mudring
Anorganische Chemie I – Festkörperchemie und Materialien
Ruhr-Universität Bochum, 44780 Bochum (Germany)
Fax: (+49) 234-32-14951
E-mail: anja.mudring@rub.de
Homepage: http://www.anjamudring.de

Dipl.-Chem. B. Balke, Prof. Dr. C. Felser
Anorganische Chemie, Gutenberg Universität Mainz
Staudinger Weg 9, 55128 Mainz (Germany)

[**] Support by the DFG priority program SPP 1166 "Lanthanoid Specific Functionalities" and the Fonds der Chemischen Industrie through a Dozentenstipendium for AVM is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802390.

298 K are given in Table 1, and fit very well to the expected value for dysprosium(III). Compounds **1**–**3** are (super)paramagnetic liquids at room temperature as can be seen from the field dependency of the magnetic moment. Figure 2a gives the respective plot for **2** as an example (for **1** and **3**, see the Supporting Information). No interaction between the

Table 1: Effective magnetic moments, and gram and molar susceptibilities for **1**–**3** at 298 K.

	μ_{eff} [μ_B]	χ_g [emu g^{-1}]	χ_{mol} [emu mol^{-1}]
1	10.4	43×10^{-6}	0.045
2	10.6	38×10^{-6}	0.047
3	10.4	32×10^{-6}	0.047

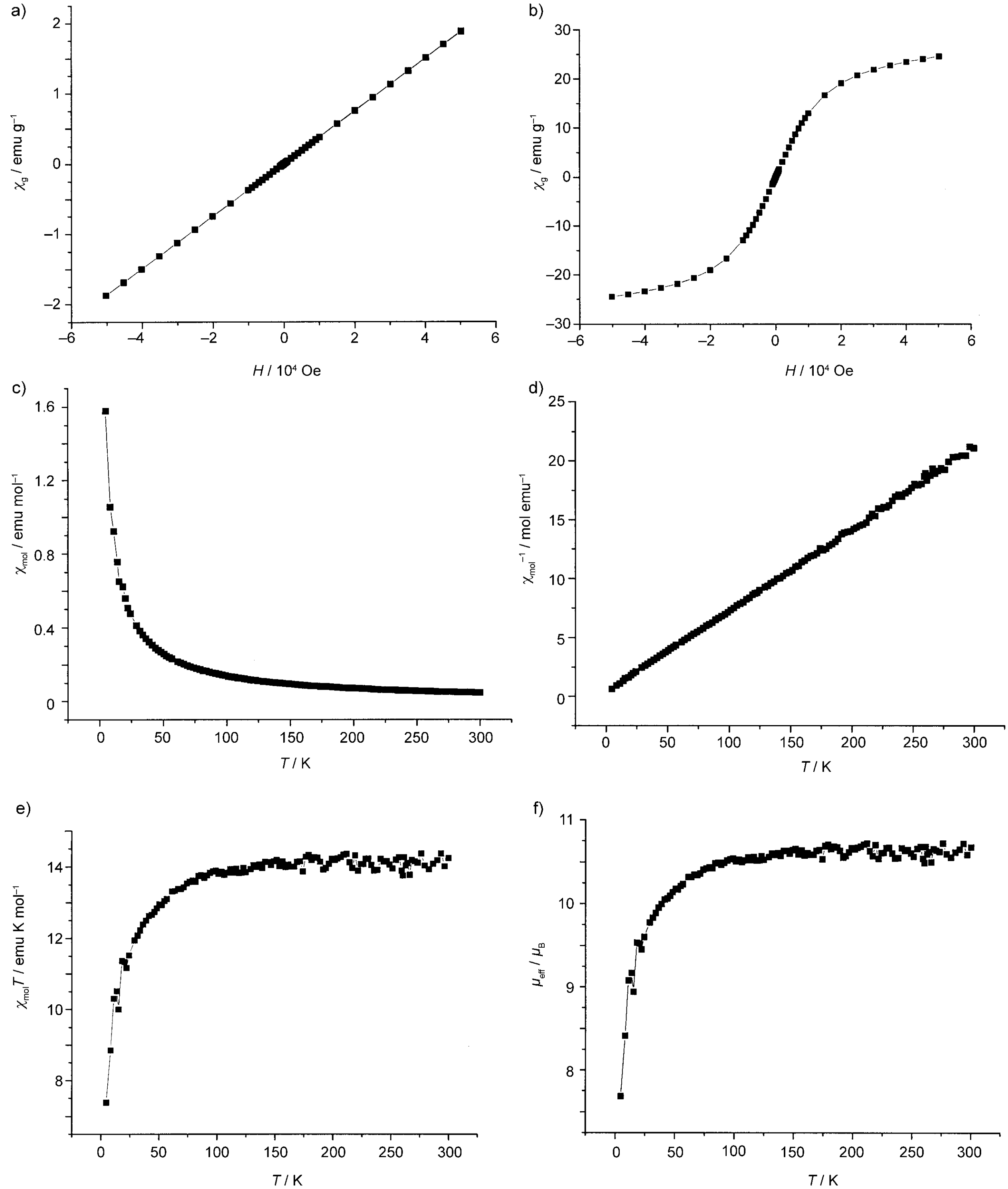

Figure 2. Field dependence of the mass susceptibility χ_g at a) 300 K and b) 5 K. Temperature dependence of c) the static molar susceptibility and d) the reciprocal molar susceptibility at a field of 10000 Oe. Temperature dependence of e) the product of the temperature and the static molar susceptibility and f) the effective magnetic moment at a field of 10000 Oe for **2**.

magnetic moments can be observed at this temperature. The product of the static molar susceptibility and the temperature ($\chi_{mol}T$) and the effective magnetic moment (μ_{eff}) are independent, from room temperature down to about 150 K (Figure 2 e,f)) at which **1**–**3** are still liquids. Below 150 K, the values start to drop, presumably owing to weak antiferromagnetic interaction in the solid state.

The room-temperature ionic liquids **1**–**3** all have an intense yellow emission, which is characteristic for dysprosium(III). The excitation spectra (see the Supporting Information) and the emission spectra of **1**–**3** show the characteristic Dy^{III} transitions (Figure 3).[14] As expected, the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is the most intense for all the samples, and its lineshape is extremely sharp, indicating high color purity. For all the samples, a monoexponential intensity decay was detected, indicating that only one dysprosium(III) species is present. The $Dy(^4F_{9/2})$ lifetime of **1** at room temperature is 23.8 μs. For **2** and **3**, the respective lifetimes are 40.34 μs and 48.4 μs. In aqueous solutions, in which the luminescence of the photoexcited state is quenched predominantly by O−H vibrations of water molecules in the inner sphere of Ln^{III}, decay times between 9 μs and 11 μs are typically found; in D_2O, 43 μs to 139 μs.[15] In anhydrous ionic liquids, lifetimes up to 63 μs have been observed.[16] In this context the observed lifetimes of **1**–**3** are quite high. As expected, the highest decay time is found for anhydrous **1**, for which the thiocyanate ligands are not prone to take up the energy of the excited state for ligand vibrations, and thus seem to provide a fairly rigid ligand environment. The compounds with water as co-ligand have lower lifetimes, also as expected. However, in **2**, for which only one water molecule is present in the dysprosium(III) ligand sphere compared to **3** with two H_2O ligands, excitation of O−H vibrations is by far less likely, leading to a rather high luminescence decay time for **2**.

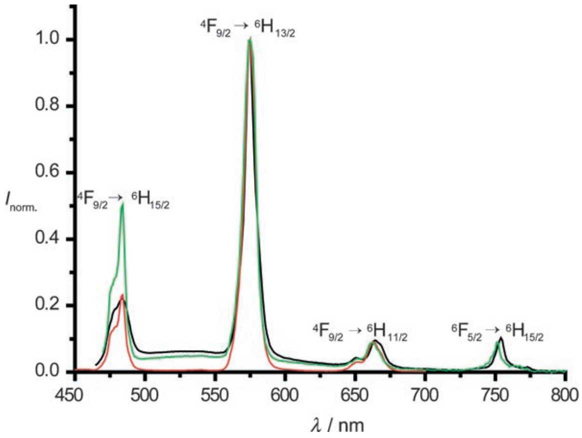

Figure 3. Emission spectra with transition assignment of **1** (green), **2** (red), and **3** (black) at room temperature under excitation at $\lambda_{ex} = 453$ nm.

Compounds **1**–**3** are the first examples of room temperature ionic liquids that combine magnetic and luminescent properties. All three compounds show strong response to the magnetic field and are far superior to the known transition-metal ionic liquids because of the extremely high effective moment of dysprosium(III). Furthermore, **1**–**3** have excellent photophysical properties: namely, long luminescence decay times and high color purity. Thus, the compounds are not only of great interest from an academic viewpoint, but they might also be extremely valuable materials for various applications as an ionic liquid that can be manipulated by external magnetic fields and at the same time can be monitored by its luminescence.

Experimental Section

$[C_6mim]SCN$ was synthesized by reacting 35.5 g (0.144 mol) C_6mimBr with 27.9 g (0.287 mol) KSCN in acetone (300 mL).[17] Yield: 97 %. Elemental analysis (%) calcd for $[C_6mim]SCN$: C 58.63, H 8.50, N 18.65, S 14.23; found: C 58.60, H 8.89, N 18.70, S 13.70.

$Dy(ClO_4)_3 \cdot 6H_2O$ was obtained by dissolving Dy_2O_3 (4.0 g, 10.72 mmol; 99.9 %, ChemPur) in 60 % aqueous $HClO_4$ (10.75 g, 7.02 mL, 64.2 mmol; Riedel-de Haën) in water (40 mL) and subsequent removal of the excess water under vacuum (72 h, 3 mbar). Special caution should be taken when handling perchlorates. However, for the hydrates (!) the risk of explosion is minor.

$[C_6mim]_{5-x}[Dy(SCN)_{8-x}(H_2O)_x]$; $x = 0$–2: Molar fractions of $[C_6mim]SCN$ and KSCN (> 99 %, AppliChem) and $Dy(ClO_4)_3 \cdot 6H_2O$ to give about 1 mmol of product were stirred in 20 mL dry ethanol for 24 h. During this time, the majority of $KClO_4$ formed precipitates. To remove the remaining $KClO_4$ after filtration, ethanol was removed under vacuum from the reaction mixture and the liquid residue was dissolved in dry dichloromethane (20 mL), left for 24 h at 4 °C, and then filtered to remove the remaining $KClO_4$. The products are then dried for 48 h under vacuum. Finally, light orange liquids are obtained. Elemental analysis (%) calcd for $[C_6mim]_3[Dy(SCN)_6(H_2O)_2]$ (**1**): C 47.60, H 17.23, N 6.54; found: C 47.08, H 17.09, N 6.42; for $[C_6mim]_4[Dy(SCN)_7(H_2O)]$ (**2**): C 44.94, H 16.73, N 6.26; found: C 44.63, H 16.69, N 6.20; for $[C_6mim]_5[Dy(SCN)_8]$ (**3**): C 41.23, H 5.86, N 16.03, found: C 40.07, H 5.44, N 15.52.

The magnetic properties were investigated by a superconducting quantum interference device (SQUID, Quantum Design MPMS-XL-5) using approximately 40 mg to 60 mg of the sample. Vibrational Spectroscopy (MIR), thermal investigations, and further magnetic measurements are given in the Supporting Information.

Received: May 22, 2008

Keywords: dysprosium · ionic liquids · lanthanides · luminescence · magnetic properties

---

[1] For a recent review on the topic see: N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123.

[2] a) K. Driesen, P. Nockemann, K. Binnemans, *Chem. Phys. Lett.* **2004**, *395*, 306; b) E. Guillet, D. Imbert, R. Scopelliti, J.-C. Bünzli, *Chem. Mater.* **2004**, *16*, 4063; c) A. Babai, A.-V. Mudring, *Chem. Mater.* **2005**, *17*, 6230; d) S. Arenz, A. Babai, K. Binnemans, K. Driesen, R. Giernoth, A.-V. Mudring, P. Nockemann, *Chem. Phys. Lett.* **2005**, *402*, 75; e) P. Nockemann, E. Beurer, K. Driesen, R. Van Deun, K Van Hecke, L. Van Meervelt, K. Binnemans, *Chem. Commun.* **2005**, 4345; f) S. F. Tang, A. Babai, A.-V. Mudring, *Angew. Chem.* **2008**, *120*, 7743; *Angew. Chem. Int. Ed.* **2008**, *47*, 7631.

[3] a) S. Odenbach, *Phys. Unserer Zeit* **2001**, *32*, 122; S. Odenbach, *Magnetovicous Effects in Ferrofluids*, Springer, Berlin, **2002**.

[4] A.-V. Mudring, B. Mallick, B. Balke, G. Fecher, C. Felser, *J. Mater. Chem.*, submitted.

[5] M. S. Sitze, E. R. Schreiter, E. V. Patterson, R. G. Freeman, *Inorg. Chem.* **2001**, *40*, 2298.

[6] S. Hayashi, H. Hamaguchi, *Chem. Lett.* **2004**, *33*, 1590.

[7] S. Hayashi, H. Hamaguchi, *IEEE Trans. Magn.* **2006**, *42*, 12.

[8] M. Okuno, H. Hamaguchi, *Appl. Phys. Lett.* **2006**, *89*, 132506.

[9] Y. Yoshida, H. Tanaka, G. Saito, *Chem. Lett.* **2007**, *36*, 1096.

[10] Y. Yoshida, G. Saito, *J. Mater. Chem.* **2006**, *16*, 1254.

[11] R. E. Del Sesto, M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes, P. Williams, *Chem. Commun.* **2008**, 447.

[12] A. Weiss, H. Witte, *Magnetochemie*, Verlag Chemie, Weinheim, **1973**.

[13] P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt, K. Binnemans, *J. Am. Chem. Soc.* **2006**, *128*, 13658.

[14] a) G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Interscience Publishers, New York, **1968**; b) W. T. Carnall, H. M. Crosswhite, H. Crosswhite, Energy Level Structure and Transition Probabilities in the Spectra of Trivalent Lanthanides in LaF_3. Special Report **1977** (Argonne, IL: Chemistry Division, Argonne National Laboratory).

[15] a) *Systematics and the Properties of the Lanthanides* (Ed.: S. P. Shina), D. Reidel, Dordrecht, **1983**, chap. 10, pp. 451–499; b) T. Berthoud, P. Decambox, B. Kirsch, P. Mauchien, C. Moulin, *Anal. Chim. Acta* **1989**, *220*, 235; c) T. Kimura, R. Nagaishi, Y. Kato, T. Yoshida, *Radiochim. Acta* **2001**, *89*, 125; d) R. Nagaishi, T. Kimura, S. P. Sinha, *Mol. Phys.* **2003**, *101*, 1007.

[16] A.-V. Mudring, A. Babai, S. Arenz, R. Giernoth, K. Binnemans, K. Driesen, P. Nockemann, *J. Alloys Compd.* **2006**, *418*, 204.

[17] A. Kamal, G. Chouhan, *Tetrahedron Lett.* **2005**, *46*, 1489.