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# Eu<sup>3+</sup> as a dual probe for the determination of IL anion donor power: A combined luminescence spectroscopic and electrochemical approach



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# ABSTRACT

This work is aimed at giving proof that  $Eu(Tf_2N)_3$  ( $Tf_2N = bis(trifluoromethanesulfonyl)amide$ ) can act as both an optical and electrochemical probe for the determination of the Lewis acidity of an ionic liquid anion. For that reason the luminescence spectra and cyclic voltammograms of dilute solutions of  $Eu(Tf_2N)_3$  in various ionic liquids were investigated. The  $Eu^{2+/3+}$  redox potential in the investigated ILs can be related to the Lewis basicity of the IL anion. The IL cation had little influence. The lower the determined halfwave potential, the higher the IL anion basicity. The obtained ranking can be confirmed by luminescence spectroscopy where a bathochromic shift of the  ${}^5D_0 \rightarrow {}^7F_4$  transition indicates a stronger Lewis basicity of the IL anion.

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# 1. Introduction

lonic liquids (ILs) are receiving growing attention as solvent replacements for conventional organic solvents [1]. Often they are considered to be environmentally more benign and chemically safe because many ILs have low flammabilities and flash points. However, the most important advantage that ionic liquids offer over conventional organic solvents (and water) is the tuneability of their solvent properties through the choice of the respective cation/anion combination. It is estimated that roughly 10<sup>18</sup> ionic liquids are accessible [2]. Each ionic liquid with a specific cation–anion combination offers a new set of chemical and physical properties. In consequence, ILs can be truly designed for a certain application. However, to do so, it is important to be able to know and predict fundamental solvent properties such as polarity and acidity.

Solvent polarity and acidity will determine the solubility of substances and are able to influence the outcome of chemical reactions, the position of chemical equilibria as well as reaction rates [3]. It is not an easy task to determine the acidity of non-aqueous media, but several methods have been used to describe the solvent power of ionic liquids addressing their polarity. A common approach for determining the solvent polarity is to evaluate the UV–Vis spectra of optical probes such as

\* Corresponding author. *E-mail address:* anja.mudring@rub.de (A.-V. Mudring). solvatochromic dyes or transition metal complexes in the solvents under investigation. The absorption or emission bands of the probe show a strong shift in their optical spectra (solvatochromic shift) which can be related to the polarity of the solvent in which they are dissolved [4,5]. However, it has been realized that it is difficult to analyze and separate specific interactions in the liquid which becomes even more important in non-classical, highly structured solvents such as ionic liquids.

For ionic liquids Kamlet–Taft parameters derived from solvatochromic studies of organic dyes have been associated with different solvent properties, such as  $\pi^*$  with dipolarity and polarizability,  $\alpha$  with the hydrogen bond acceptor capability and  $\beta$  with the hydrogen bond acceptor capability and  $\beta$  with the hydrogen bond acceptor capability. Although it was noticed that  $\alpha$  is largely dependent on the IL anion and  $\beta$  on the IL cation, an analysis of separate influences of cation and anion that would ultimately allow for a designed choice of the cation–anion combination was not possible. But the unique power of ionic liquids is that through a smart choice of the cation and anion a solvent with designed properties can be created. For that reason it would be interesting to have probes that allow testing specifically for certain solvent properties.

Solvent polarity as such is rather complex. IUPAC defines solvent polarity as being "the overall solvation capability (or solvation power) for (i) starting materials and products, which influences chemical equilibrium; (ii) reactants and activated complexes ("transition states"), which determines reaction rates; and (iii) ions or molecules in their ground and first excited state, which is responsible for light absorptions in the various wavelength regions. This overall solvation capability depends on the action of all, non-specific and specific, intermolecular solute-solvent interactions, excluding such interactions leading to definite chemical alterations of the ions or molecules of the solute" [6].

According to Reichardt solvent-solute interactions can be divided into specific and non-specific interactions [7]. Non-specific interactions are instantaneous/induced dipole forces (dispersion or London forces), dipole/induced-dipole forces (induction or Debye forces), dipole/dipole forces (orientation or Keesom forces) and ion/dipole forces (Coulomb forces) which might quite well get addressed through measurements of continuum properties such as dielectric constants. Specific interactions include hydrogen bond donor and/or hydrogen bond acceptor interactions, electron pair donor/electron pair acceptor or charge-transfer interactions, solvophobic interactions (which can become important only in highly structured solvents). As ionic liquids contain, in contrast to conventional molecular solvents, charged ions it is expected that electron-donor-acceptor interactions have a rather high influence. In consequence, an important property of ionic liquids as solvents is their Lewis acidity and basicity or, in other words, their electron acceptor and donor capability. It is anticipated that the electron acceptor properties of an IL depend largely on the cation whereas the IL anion governs the IL electron donor properties.

We could confirm this hypothesis through evaluation of spectroscopic properties of certain transition metal compounds in different ionic liquids. They made it possible to separate the anionic influence, hence Lewis basicity. We were able to rank various IL anions with respect to their Lewis basicity by evaluating the absorption spectra of the indicator complex (Ni(tmen)(acac)][B(Ph)<sub>4</sub>] (tmen = tetramethylethylendiamine, acac = acetylacetonate) [8]. In a second step we transferred Duffy's concept of the *optical basicity* [9] to ILs by using Mn(Tf<sub>2</sub>N)<sub>2</sub> as a spectroscopic probe [10].

When investigating in a different context the solvation and ligand exchange processes of ytterbium(III) salts in ionic liquids such as  $(C_4mpyr)(Tf_2N)$   $(C_4mpyr = N-butyl-N-methylpyrrolidinium)$ or (C<sub>4</sub>mpyr)(TfO) we made an interesting observation: We found that the Yb<sup>2+</sup>/Yb<sup>3+</sup> redox potential strongly depends on the local chemical environment and coordination of Yb3+ by the IL anion. It was found that the more coordinating the IL anion is, the less negative the redox potentials (vs. Fc/Fc<sup>+</sup>) [11]. Thus, it also should be possible to electrochemically determine the Lewis basicity of an IL with a given anion by investigating the redox potential of a dissolved lanthanide bis(trifluoromethanesulfonyl)amide, Ln(Tf<sub>2</sub>N)<sub>3</sub>. An additional advantage of using lanthanide salts as a probe is, that many of the trivalent lanthanides show distinct photoluminescence. As Yb<sup>3+</sup> is spectroscopically inactive in the visible range of the electromagnetic spectrum, we choose for this study Eu<sup>3+</sup> which is commonly used as a structural probe. To date several  $Eu^{3+}$  containing ionic liquids and liquid crystals are known [12]. In case of  $Eu^{3+}$  it is possible to monitor the electron donation power of the anion via the shift of (hyper-) sensitive transitions in the luminescence spectra. Thus, by using the same probe, Eu(Tf<sub>2</sub>N)<sub>3</sub>, but different analytical tools, namely cyclic voltammetry and luminescence spectroscopy, it should be possible to access the electron donor power of an IL anion. To check whether Eu(Tf<sub>2</sub>N)<sub>3</sub> can work as both, an optical and electrochemical probe for the anion Lewis basicity we have investigated solutions of  $Eu(Tf_2N)_3$  in a set of ionic liquids with anions of weak (e.g.  $Tf_2N^-$ ), middle (e.g.  $TfO^-$ ) and strong (e.g. DCA<sup>-</sup>) Lewis basicity and recorded the respective luminescence spectra and cyclic voltammograms.

#### 2. Experimental section

#### 2.1. Chemicals and synthesis

LiTfO (98%), Eu(TfO)<sub>3</sub> (98%) and Eu<sub>2</sub>O<sub>3</sub> (99.9%) were purchased from Sigma-Aldrich, Schnelldorf, D. LiTf<sub>2</sub>N, (N<sub>4441</sub>)(Tf<sub>2</sub>N), (C<sub>2</sub>mim)(MeSO<sub>3</sub>), (C<sub>2</sub>mim)(TfO) and (C<sub>4</sub>pyr)(Tf<sub>2</sub>N) (all 99%) were purchased from IoLiTec, Heilbronn, D. (P<sub>666 14</sub>)Cl (95%) was provided by Cytec, Stamford, USA. All commercial ILs were purified prior to the experiments.

Methylimidazole (98%), *N*-methylpyrrolidine (98%), the respective halogen alkanes (>98%) were purchased from Acros, Geel, B and distilled prior to use.

# 2.2. General purification procedure for ILs

The respective IL was diluted with  $CH_2CI_2$  or  $CHCI_3$  and washed several times with deionized water to remove any excess of halides or alkali metal salts (AgNO<sub>3</sub> test) as well as unreacted starting material. After filtration of the solution over a column with neutral  $AI_2O_3$  and active charcoal the solvent was removed under high vacuum and the ILs dried under dynamic vacuum for 1–2 days at 80–90 °C.

# 2.3. Synthesis of HTf<sub>2</sub>N

 $HTf_2N$  was obtained by sublimation at 70 °C from a solution of LiTf\_2N in concentrated sulfuric acid under reduced pressure ( $10^{-3}$  mbar). The crude product was resublimed for further purification. Yield: 90%.

$$^{1}$$
H-NMR(D<sub>2</sub>O) :  $\delta$ (ppm) = 4.77(s, 1H)

<sup>19</sup> F-NMR(D<sub>2</sub>O) : 
$$\delta$$
(ppm) = -79.16(s, 6F)

$$^{13}C{19F}-NMR(D_2O):\delta(ppm) = 19.27(s, 2C)$$

# 2.4. Synthesis of $Eu(Tf_2N)_3$

 $Eu_2O_3$  was suspended in deionized water and five-fold molar excess of an aqueous  $HTf_2N$  solution was added dropwise. After complete dissolution of  $Eu_2O_3$  the water was boiled off until a slurry solid appeared. This slurry was transferred to a Schlenk tube and dried at 140–160 °C under high vacuum. The residual solid was sublimed for purification under reduced pressure at 270 °C.

Elemental analysis : Eu(Tf<sub>2</sub>N)<sub>3</sub>

calc.N 4.23%.C 7.26%, H 0.00%, S 19.39 %

found N 4.19%.C 7.25%, H 0.10%, S 20.34%

#### 2.5. Synthesis of 1-alkyl-3-methylimidazolium bromides

 $(C_n mimBr)$  bromides (n = 2, 3, 4 and 6) were obtained by alkylation of 1-methylimidazole with the respective halogen alkane [13]. All bromides except  $C_6 mimBr$ , which is liquid, were obtained as crystalline white powders.

 $(C_2 \text{mim})Br:^1H - NMR (CDCl_3) : \delta (ppm)$ 

$$= 1.23 \ (t, 3H, J = 7.4 \ Hz); 3.75 \ (s, 3H); 4.06 \ (q, 2H, J = 7.2 \ Hz);$$
 7.39  $(s, 2H); 9.82 \ (s, 1H)$ 

 $(C_3 \text{mim})Br:^1H - NMR (CDCl_3) : \delta (ppm)$ 

$$= 0.44 \ (t, 3H, J = 7.4 \ Hz); 1.45 \ (hex, 2H, J = 7.2 \ Hz); 3.61 \ (s, 3H);$$

$$3.82 (t, 2H, J = 7.2 Hz); 7.82 (d, 2H, J = 1.7 Hz); 9.67 (s, 1H)$$

$$\begin{split} & C_4 mim) Br: {}^1H-NMR \; (CDCl_3): \delta \; (ppm) = 0.85 \; (t, 3H, J = 7.4 \; Hz); \\ & 1.27 \; (hex, 2H, J = 7.1, 7.4 \; Hz); 1.81 \; (pen, 2H, J = 7.1, 7.4 \; Hz); \\ & 4.02 \; (s, 3H); 4.24 \; (t, 2H, J = 7.1 \; Hz); 7.56 \; (d, 2H, J = 1.7 \; Hz); 10.19 \; (s, 1H) \end{split}$$

$$(C_6 \text{mim})Br:^1H - \text{NMR} (\text{CDCl}_3) : \delta (\text{ppm}) = 0.75 (t, 3H, J = 7.4 \text{ Hz});$$

 $1.20\ (m, 6H); 1.81\ (pen, 2H); 2.05\ (s, 2H); 4.03\ (s, 3H);$ 

$$4.22 \ (t, 2H, J = 7.4 \ \text{Hz}); 7.55 \ (d, 2H, J = 1.6 \ \text{Hz}); 10.24 \ (s, 1H)$$

#### 2.6. Synthesis of 1-propyl-1-methylpyrrolidinium bromide

*n*-Propyl bromide was dropwise added to a solution of 1methylpyrrolidin and dichloromethane. The mixture was stirred for 24 h, washed with ethyl acetate and concentrated. The crude product was dropwise added to cold ethyl acetate and the white crystalline product was filtered off. The product was dried under dynamic vacuum for 1–2 days. Yield: 50.8%.

$$\begin{split} (C_3mpyr)Br: ^1H-NMR \ (CDCl_3): \delta(ppm) &= 1,05 \ (t,3H,J=7.3 \ Hz); \\ 1,84 \ (m,2H); 2,28 \ (s,4H); 3,27 \ (s,3H); 3,59 \ (m,2); 3,80 \ (s,4H) \end{split}$$

# 2.7. Synthesis of 1-alkyl-3-methylimidazolium, ammonium and phosphonium bis(trifluoromethane)sulfonylamides

The respective halide IL was dissolved in deionized water (pH = 6) and after an equimolar amount of LiNTf<sub>2</sub> in water had been added dropwise, the reaction mixture was stirred for 1 day at 70 °C. Then CH<sub>2</sub>Cl<sub>2</sub> was added and the aqueous phase was removed. The organic phase was washed halide-free with deionized water (AgNO<sub>3</sub> test). The solution was filtered over a column filled with neutral Al<sub>2</sub>O<sub>3</sub> and activated charcoal. The organic solvent was removed under reduced pressure and the reaction product finally dried under dynamic vacuum for 1–2 days at 80–90 °C.

 $(C_{2}mim)(Tf_{2}N):^{1}H-NMR (CDCl_{3}): \delta(ppm) = 1.58 (t, 3H, J = 9.0 Hz);$ 

$$4.06 \; (pen, 2H, J = 9.0 \; Hz); 7.73 \; (d, 2H, J = 2.2 \; Hz); 9.00 \; (s, 1H)$$

<sup>19</sup> F-NMR (, CDCl<sub>3</sub>) :  $\delta$ (ppm) = -79.96 (s, 6H)

$$\begin{split} (C_3mim)(Tf_2N):^1H-NMR~(CDCl_3): \delta(ppm) &= 0.87~(t, 3H, J=7.4~Hz);\\ 1.82~(hex, 2H, J=7.2~Hz); 3.84~(s, 3H); 4.05~(t, 2H, J=7.2~Hz);\\ 7.29~(d, 2H, J=1.9~Hz); 8.53~(s, 1H) \end{split}$$

<sup>19</sup> F-NMR (CDCl<sub>3</sub>) :  $\delta$ (ppm) = -79.43 (s, 6H)

 $(C_4 mim)(Tf_2N]:^1H-NMR (CDCl_3): \delta(ppm) = 0.89 (t, 3H, J = 7.1 Hz);$ 

$$\begin{split} &1.31~(hex,2H,J=7.1,7.4~\text{Hz});1.80~(pen,2H,J=7.2,7.4~\text{Hz});3.87~(s,3H);\\ &4.11~(t,2H,J=7.2~\text{Hz});7.30~(d,2H);8.59~(s,1H) \end{split}$$

<sup>19</sup> F-NMR (CDCl<sub>3</sub>) : 
$$\delta$$
(ppm) = -79.32 (s, 6H)

$$\begin{split} (C_6 mim)(Tf_2 N): {}^{1}H-NMR \ (, CDCl_3): \delta(ppm) &= 0.83 \ (t, 3H, J = 7.4 \ Hz); \\ 1.26 \ (m, 6H); 1.81 \ (pen, 2H); 3.87 \ (s, 3H); 4.11 \ (t, 2H, J = 7.4 \ Hz); \\ 7.30 \ (d, 2H, J = 1.7 \ Hz); 8.61 \ (s, 1H) \end{split}$$

<sup>19</sup> F-NMR (CDCl<sub>3</sub>) :  $\delta$ (ppm) = -79.27 (s, 6H)

$$(C_3 mpyr)(Tf_2N)^1H$$
-NMR (, CDCl<sub>3</sub>) :  $\delta$ (ppm) = 0, 91 (t, 3H, J = 7.3 Hz);  
1.68 (m, 2H); 2.08 (m, 4H); 2.97 (s, 3H); 3.25 (m, 2H); 3.34 (m, 4H)

<sup>19</sup> F-NMR (CDCl<sub>3</sub>) :  $\delta$ (ppm) = -79, 43 (s, 6H)

 $(P_{666\ 14}](Tf_2N)^1H-NMR\ (,CDCl_3): \delta(ppm)=0.83-0.95\ (m,12H),$ 

 $1.22\text{--}1.60\ (m,48\text{H}), 2.01\text{--}2.19\ (m,8\text{H})$ 

<sup>19</sup> F-NMR (CDCl<sub>3</sub>) :  $\delta$ (ppm) = -78.93 (s, 6F)

<sup>31</sup>P-NMR (CDCl<sub>3</sub>) :  $\delta$  = 32.89 (s, 1P)

2.8. Synthesis of 1-butyl-3-methylpyrrolidinium dicyanamide

1-Butyl-3-methylimidazolium bromide was dissolved in deionized water and a slight molar excess of silver dicyanamide suspended in deionized water was added. The mixture was stirred for 2 h at 60 °C, then filtered and dried. The crude product was dissolved in  $CH_2Cl_2$ , upon cooling to 5 °C most of the silver bromide precipitated. After separation from silver halide by filtration, the remaining solution was filtered over a column filled with neutral  $Al_2O_3$  and activated charcoal. The solvent was removed under reduced pressure and the IL dried under dynamic vacuum for 1–2 days at 80–90 °C.

$$\begin{split} (C_4mim)(\text{DCA}): ^1H-\text{NMR} \ (\text{CDCI}_3): \delta(\text{ppm}) &= 0.85 \ (t, 3H, J=7.2 \ \text{Hz}); \\ 1.27 \ (\text{hex}, 2H, J=7.6 \ \text{Hz}); 1.81 \ (\text{pen}, 2H, J=7.6 \ \text{Hz}); 4.02 \ (s, 3H); \\ 4.24 \ (t, 2H, J=7.4 \ \text{Hz}); 7.56 \ (d, 2H); 10.19 \ (s, 1H) \end{split}$$

#### 2.9. Synthesis of 1-butyl-1-methylimidazolium triflate

1-Butyl-3-methylimidazolium bromide was dissolved in acetone/ acetonitrile (50:50) and an equimolar amount of LiTfO in acetone was added. The mixture was stirred for 1 day at 60 °C and then filtered. The solvent was removed under reduced pressure and the crude product dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Upon cooling to 5 °C most of the Li halide precipitated and the precipitate was filtered off. The remaining solution was washed halide-free with deionized water (AgNO<sub>3</sub> test) and filtered over a column filled with neutral Al<sub>2</sub>O<sub>3</sub> and activated charcoal. The residual organic phase was freed from solvent under reduced pressure and dried under dynamic vacuum for 1–2 days at 80–90 °C.

 $(C_4 \text{mim})(\text{TfO})^1 \text{H}-\text{NMR} (\text{acetone}-d_6) : \delta(\text{ppm}) = 0.96 (t, 3\text{H}, J = 7.4 \text{ Hz});$ 

 $1.40\ (hex, 2H); 1.84\ (m, 2H); 2.25\ (s, 4H); 3.20\ (t, 3H, J = 7.3\ Hz);$ 

3.55 (m, 2H); 3.70 (m, 4H)



Fig. 1. Electrochemical cell used for cyclic voltammetry measurements under inert conditions.

<sup>19</sup> F–NMR (.Acetone– $d_6$ ) :  $\delta = -78.88 (s, 3F)$ 

#### 2.10. Synthesis of 1-butyl-3-methylimidazolium perchlorate

1-Butyl-3-methylimidazolium bromide was dissolved in  $CH_2Cl_2$  in a flask and an equimolar amount of  $NaClO_4$ · $H_2O$  suspended in  $CH_2Cl_2$  was added.  $Na_2SO_4$  was added to remove the crystal water of the sodium salt. The resulting mixture was stirred for 3 days at RT. The precipitated alkali halide was filtered off and the remaining reaction mixture then washed halide free (AgNO\_3 test). After filtration of the solution over a column filled with neutral or acidic  $Al_2O_3$  and active charcoal the residual organic phase was freed from solvent and dried under dynamic vacuum for 1–2 days at 80–90 °C. General caution should be taken as perchlorates are know to violently decompose when dry or heated to elevated temperatures.

$$\begin{split} (C_4 mim)(\text{ClO}_4):^1 \text{H-NMR} \ (\text{DMSO}-d_6): \delta(\text{ppm}) &= 0.86 \ (\text{t}, 3\text{H}, \text{J} = 7.4 \ \text{Hz}); \\ 1.24 \ (\text{hex}, 2\text{H}, \text{J} = 7.4 \ \text{Hz}); 1.76 \ (\text{pen}, 2\text{H}, \text{J} = 7.2 \ \text{Hz}); 3.84 \ (\text{s}, 3\text{H}); \\ 4.14 \ (\text{t}, 2\text{H}, \text{J} = 7.2 \ \text{Hz}); 7.61 \ (\text{d}, 2\text{H}, \text{J} = 2.0 \ \text{Hz}); 8.99 \ (\text{s}, 1\text{H}) \end{split}$$

 ${}^{13}\text{C}-\text{NMR} \ (\text{DMSO}-d_6): \delta = 12.5 \ (\text{s}); 18.1 \ (\text{s}); 30.6 \ (\text{s}); 35.0 \ (\text{s}); 47.9 \ (\text{s});$ 

 $121.5\;(s);122.8\;(s);135.7\;(s)$ 

# 2.11. Synthesis of 1-ethyl-3-methylimidazolium ethylsulfate

Et<sub>2</sub>SO<sub>4</sub> was added dropwise to an equimolar amount of dry methylimidazole. After complete addition of the starting materials the

resulting mixture was stirred for 1 day at 60 °C. After cooling to room temperature the mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and filtered over a column filled with neutral or acidic Al<sub>2</sub>O<sub>3</sub> and active charcoal. The solvent was removed under vacuum and the residual dried under high vacuum for 1–2 days at 80–90 °C. Caution: Although we have never observed any sudden decomposition, organic perchlorates are known



Fig. 2. From top to bottom: Emission spectra of  $Eu(Tf_2N)_3$  in  $(C_4mim)(Tf_2N)$ ,  $(C_4mpyr)(Tf_2N)$  and in  $(C_4mpyr)(DCA)$ .

#### Table 1

 $^5D_0 \to ^7F_J$  (J = 0-4) transition maxima in nm for 0.025 M solutions of Eu(Tf\_2N)\_3 in various ionic liquids.

	$^5D_0 \rightarrow  ^7F_1$	$^5D_0 \rightarrow  ^7F_2$	$^5D_0 \rightarrow \ ^7F_4$
(C <sub>2</sub> mim)(Tf <sub>2</sub> N)	592	615	688/695
$(C_3 mim)(Tf_2N)$	592	614	689/695
$(C_4 mim)(Tf_2N)$	593	615	690/695
$(C_6 mim) (Tf_2 N)$	592	614	690/695
$(C_3mpyr)(Tf_2N)$	592	615	689/695
$(C_4 mpyr)(Tf_2N)$	591	614	689/695
(N <sub>444 1</sub> )(Tf <sub>2</sub> N)	592	615	690/695
(P <sub>666 14</sub> )(Tf <sub>2</sub> N)	588/596	612.5/615/619.5	690/695/699.5*
$(C_2 mim)(ClO_4)$	591	614/618	689/697
(C <sub>2</sub> mim)(MeSO <sub>3</sub> )	591/594	612	688/698
(C <sub>4</sub> mim)(TfO)	591	611/616	699
(C <sub>4</sub> mpyr)(DCA)	592.5	614/618.5 (616)	692.5/700
(C <sub>2</sub> mim)(EtSO <sub>4</sub> )	592	612/615/619	697/702

to decompose violently especially at elevated temperatures. Cautious handling of the substance is highly recommended.

 $(C_2 mim)(EtSO_4)$ :<sup>1</sup>H-NMR (, CDCl<sub>3</sub>) :  $\delta(ppm) = 0.85 (t, 3H, J = 7.2 Hz);$ 

 $1.27 \; (hex, 2H, J = 7.2 \; Hz); 1.81 \; (pen, 2H); 4.02 \; (s, 3H);$ 

 $4.24 \; (t, 2H, J = 7.5 \; Hz); 7.56 \; (s, 2H); 10.19 \; (s, 1H)$ 

2.12. Sample preparation for luminescence measurements and cylic voltammetry studies

 $Eu(Tf_2N)_3$  and  $Eu(TfO)_3$  were dissolved in the respective IL under inert conditions to obtain 0.025 M solutions in a glovebox. The dissolution process was facilitated by ultrasound and heating to 70 °C.

#### 3. Instrumentation

# 3.1. Elemental Analyses

Elemental analyses were performed using a Euro Vektor CHNS-O Euro EA3000 analyzer. The samples were sealed in small tin tubes in the glove box.

#### 3.2. NMR

All NMR spectra were recorded on a Bruker DPX AC 300 spectrometer with an automatic sample changer.

#### 3.3. Photoluminescence

Excitation and emission photoluminescence spectra were recorded at room temperature on a Fluorolog 3 (Horiba Jobin Yvon GmbH, München, D) with a 450 W xenon lamp as a steady state excitation



Fig. 3. Cyclic voltammograms of  $Eu(Tf_2N)_3$  in  $(C_4mim)(Tf_2N)$  vs.  $Fc/Fc^+$  at scan rates of a) 10 mV/s, b) 50 mV/s, c) 100 mV/s and d) 200 mV/s.

source, a double excitation monochromator, an emission monochromator and a photomultiplier for detection. For excitation spectra the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition of Eu<sup>3+</sup> was monitored, to obtain the emission spectra the level of Eu<sup>3+</sup> was excited into the most intense absorption which is the  ${}^{7}F_{0} \rightarrow {}^{7}L_{6}$  transition. All spectra were recorded at room temperature. Electronic transitions were assigned according to the Dieke energy level diagram for trivalent 4f-elements. [14]

#### 3.4. Cyclic voltammetry

The measurements carried out under  $N_2$  as a protection gas in a custom-made electrochemical cell (Fig. 1) with a three electrode alignment. An Ag rod reference electrode (Metrohm AG, Filderstadt, D), a 1 mm Pt wire counter electrode (VWR) and a 2 mm diameter Pt disk working electrode (Metrohm AG, Filderstadt, D) were used.

All cyclic voltammograms were referenced against the ferrocene/ ferrocenium redox couple. The redox potential of this redox couple was determined in the IL under investigation and the respective correction applied to the collected data. The solutions of  $Eu^{3+}$  in ferrocene as well as the solutions of  $Eu(Tf_2N)_3$  in the ILs were equilibrated 5 s prior to measurement and the third cycle scan was used for data analysis. Between two measurements the built Helmholtz electrical double layer was destroyed by stirring and gently heating the sample above room temperature and checked for a steady state potential as an indicator for the thermodynamic equilibrium after cooling to room temperature. The steady state potential was used as the starting potential.

#### 4. Results and discussion

For a proof of concept that  $Eu(Tf_2N)_3$  can act as both, a spectroscopic and electrochemical probe for the Lewis basicity of the ionic liquid anion three prominent IL anions of different Lewis acidity were chosen. Previous investigations indicate that bis(trifluoromethanesulfonyl)amide,  $(Tf_2N)^-$ , is an anion of weak Lewis basicity, trifluorosulfonate,  $(TfO)^-$ , an anion of medium Lewis basicity and dicyanamide,  $(DCA)^-$  an anion of strong Lewis basicity. As counter cations typical IL cations such as 1-alkyl-3-methylimidzolium, quarternary ammonium and phosphonium cations with different alkyl chain lengths were chosen. A prerequisite for the study was that the chosen ILs had to have a low viscosity to ensure that the thermodynamic equilibrium can be reached fast and to come as close as possible to a reversible electrochemical reaction.

The basis for the detection of the ionic liquid anions' Lewis basicity through  $Eu(Tf_2N)_3$  is that the  $Tf_2N$  anion is an extremely weakly coordinating anion (WCA) [15]. Any stronger coordinating IL anion will expel  $Tf_2N^-$  from the coordination sphere of  $Eu^{3+}$  upon dissolution of  $Eu(Tf_2N)_3$ . Such ligand exchange reactions for  $Ln(Tf_2N)_3$  (Ln = lanthanide) have been evidenced in several ILs by multiple techniques. It was observed that upon dissolution of ytterbium(III) bis(trifluoromethanesulfonyl)amides in  $(C_4mpyr)(TfO)$  the  $TfO^-$  anion, as the stronger Lewis base, replaces the  $Tf_2N^-$  anions completely in the coordination sphere of Yb(III) [16]. The respective complex anions  $[Yb(TfO_6)]^{3-}$  and  $[Yb(Tf_2N)_5]^{2-}$  could be characterized unambiguously by X-ray crystal structure analysis.



Fig. 4. Cyclic voltammograms of Eu(Tf<sub>2</sub>N)<sub>3</sub> in (C<sub>4</sub>mim)(DCA) vs. Fc/Fc<sup>+</sup> at different scan rates of a) 10 mV/s, b) 50 mV/s, c) 100 mV/s, and d) 200 mV/s.

Gradual exchange of  $Tf_2N^-$  in the ligand sphere of transition metals by stronger coordinating ligands has also been investigated by molecular dynamic simulations [17]. EXAFS studies on ligand exchange processes confirm that ligand exchange of the weakly coordinating  $Tf_2N^-$  by stronger coordinating anions takes place for  $Eu(Tf_2N)_3$ [18]. It is assumed that  $Eu(Tf_2N)_3$  will show a behavior similar to that of Yb(Tf\_2N)\_3 and that e.g.  $[Eu(Tf_2N)_5]^{2-}$  as found in (C<sub>4</sub>mpyr)<sub>2</sub>  $[Eu(Tf_2N)_5]$  [19] will form when  $Eu(Tf_2N)_3$  is dissolved in a Tf\_2N-IL and  $[Eu(TfO)_6]^{3-}$  forms when  $Eu(Tf_2N)_3$  is dissolved in a TfO-IL. Similarly, ligand exchange will occur when  $Eu(Tf_2N)_3$  is dissolved in a DCA-IL like (C<sub>4</sub>mim)(DCA).

# 5. Luminescence spectroscopic studies

Thus, we have started investigating some ionic liquids by dissolving  $Eu(Tf_2N)_3$  and recording the luminescence spectra upon excitation into the most intense  ${}^7F_0 \rightarrow {}^7L_6$  transition (see Fig. 2 for representative luminescence spectra and Table 1 for the compiled data).

For Eu<sup>3+</sup> there exist two transitions that are guite sensitive towards changes in the coordination sphere. These are the hypersensitive  ${}^{5}D_{0} \rightarrow$  $^{7}F_{2}$  transition (usually found around 610–625 nm) and the sensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition (typically found around 680–710 nm). Amongst those two the second one shows larger wavelength shifts depending on the local surrounding of the emitting ion. A bathochromic shift of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition is observed in the presence of strongly electron donating ligands [20]. Consequently a hypsochromic shift points to weak donor properties of the ligand. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition corresponds to a magnetic dipole interaction and is typically quite unaffected by the chemical surrounding of Eu<sup>3+</sup>. Both the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ transitions correspond to generally forbidden electric dipole transitions. However, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$  transition might gain some intensity through spin–orbit contributions. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition cannot be observed for  $Eu^{3+}$  at a site with  $C_n$ ,  $C_{nv}$  and  $C_s$  symmetry. Mixing with other configurations may lead to an appreciable intensity of this transition.

First we wanted to the check the cation influence and looked at various Tf<sub>2</sub>N-based ILs with different cations (Table 1). Indeed, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition seems to be quite unaffected by the respective IL cation, regardless whether it is a 1-alkyl-3-methylimidzolium, a quarternary ammonium or a phosphonium cation. However, a shift of the maximum of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition is noticeable when the anion is exchanged (Table 1 and Fig. 2) and, as expected, the DCA anion leads to a significant bathochromic shift of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition compared to Tf<sub>2</sub>N<sup>-</sup> which points to its higher Lewis basicity.

Based on the maxima of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$  transition the investigated IL anions can be ranked according to increasing Lewis basicity as follows  $Tf_{2}N^{-} < CIO_{4}^{-} < MeSO_{3}^{-} < TfO^{-} < DCA^{-} < EtSO_{4}^{-}$ .

#### 6. Electrochemical studies

Initial cyclic voltammetry revealed for  $Yb(Tf_2N)_3$  that the more Lewis basic and stronger coordinating the anion present in the ligand sphere of  $Ln^{3+}$  was the more negative the redox potential became. This suggests that it might be possible to establish a Lewis basicity scale for IL anions by electrochemical means. To check whether such an electrochemically determined redox potential of  $Eu^{2+/3+}$  in the respective IL can be used as a measure of its anion's electron donor power we dissolved  $Eu(Tf_2N)_3$  in various ILs and determined the redox half-wave potentials by means of cyclic voltammetry at different scan rates (see Figs. 3–4 for representative data and Table 2 for a compilation of data).

When looking at the cyclic voltammograms of  $Eu(Tf_2N)_3$  in the various ionic liquids at different scan rates it becomes obvious that reduction and oxidation peaks are in all cases far apart, indicating a poor reversibility of the redox reaction. At lower scan rates the separation of both peaks becomes less but never gets so low that reversibility is achieved. It seems that IL viscosity and, hence, also IL conductivity, are

the main origin of this behavior. In the more viscous ionic liquids like (P<sub>666 14</sub>](Tf<sub>2</sub>N) (η@20 °C = 165 cP [21]) and (C<sub>4</sub>mpyr)(TfO)(η@20 °C = 158 cP [22]) as well as (C<sub>4</sub>mim)(TfO)(η@20 °C = 90 cP [23]) the oxidation and reduction peaks are farther apart than in less viscous ILs like (C<sub>4</sub>pyr)(Tf<sub>2</sub>N) (η@20 °C = 77 cP [24]), (C<sub>4</sub>mim)(Tf<sub>2</sub>N) (η@20 °C = 63.5 cP<sup>17</sup>), (C<sub>2</sub>mim)(TfO)(η@20 °C = 42.7 cP [25]) and (C<sub>4</sub>mim)(DCA) (η@20 °C = 33.2) [26]. Furthermore, the dependency of the half-wave potential with the scan rate is less in the latter ILs. Comparing the halfwave potential of Eu<sup>2+/3+</sup> at low scan rates (which allows for the best approximation of a reversible chemical reaction) in Tf<sub>2</sub>N ionic liquids with different cations, it becomes obvious that E<sub>1/2</sub> is found for all ILs roughly at -0.4 V and can be seen as independent from the IL cation. If Eu(Tf<sub>2</sub>N)<sub>3</sub> is added to a TfO IL E<sub>1/2</sub> gets more negative and assumes

Table 2

Half-wave potentials, of the Eu<sup>3+/2+</sup>, reduction and oxidation potential in various ILs at different scan rates. Data referenced against Fc/Fc<sup>+</sup>.

IL scan rate/ mV s <sup>-1</sup>	$E_{\frac{V_2}{V}}$ (Eu <sup>3+/2+</sup> )	Reduction potential/ V vs. Fc/Fc <sup>+</sup>	Oxidation potential/ V vs. Fc/Fc <sup>+</sup>
	E (EC.N.)		
$(P_{666 \ 14})(II_2N)$	$Eu(If_2N)_3$		
200	-0.62	-1.19	-0.04
100	-0.52	-0.97	-0.07
50	-0.44	-0.79	-0.08
10	-0.39	-0.65	-0.13
(C <sub>4</sub> pyr)(Tf <sub>2</sub> N)	Eu(Tf <sub>2</sub> N) <sub>2</sub>		
200	-0.43	-091	-0.05
100	-0.46	-0.84	-0.08
50	-0.45	-0.80	-010
10	-0.44	-0.72	-0.17
$(C_4 mim)(Tt_2N)$	$Eu(II_2N)_3$	1.00	0.10
200	-0.57	-1.08	0.13
100	-0.53	-0.90	-0.05
50	-0.46	-0.83	-0.16
10	-0.39	-0.77	-0.10
$(C_2 mim)(ClO_4)$	Eu(Tf <sub>2</sub> N) <sub>3</sub>		
200	-0.57	-0.98	-0.15
100	-0.53	-0.90	-017
50	-0.53	-0.86	-0.21
10	-0.48	-0.71	-0.25
10	0110	0071	0120
(C <sub>4</sub> mim)(TfO)	Eu(Tf <sub>2</sub> N) <sub>3</sub>		
200	-0.51	-1.32	0.31
100	-0.52	-1.21	0.18
50	-0.52	-1.19	0.16
10	-0.52	-1.09	0.05
(C-mim)(TfO)	$F_{11}(Tf_N)_{-}$		
200	0.62	1 11	0.14
100	-0.62	0	-0.14
50	-0.67	-0.97	-0.25
10	-0.71	-0.97	-0.57
10	0.71	0.05	0.52
(C <sub>4</sub> mpyr)(TfO)	Eu(TfO)3		
200	-0.63	-1.42	0.17
100	-0.70	-1.36	-0.04
50	-0.72	-1.29	-0.15
10	-0.73	-1.14	-0.32
(C₄mim)(EtSO₄)	$Eu(Tf_2N)_2$		
200	-0.96	-1.55	-0.37
100	-0.98	-1.45	-0.52
50	-0.97	-140	-0.53
10	-1.00	-1.34	-0.66
(C <sub>4</sub> mim)(DCA)	$Eu(Tf_2N)_3$		
200	-1.08	-1.58	-0.57
100	-1.09	-1.54	-0.63
50	-1.07	-1.44	-0.70
10	-1.08	-1.37	-0.79

values of about -0.7 V which is similar to that found for Eu(TfO)<sub>3</sub> in TfO-ILs. The Eu^{2+/3+} redox potential is observed to be the most negative in (C4mim)(DCA). From this it can be concluded that the redox potentials are mainly affected by the IL anion. The larger the Lewis basicity of the anion the more negative the Eu^2+/Eu^3 redox potential becomes. The spectroscopic results can be basically confirmed.

# 7. Conclusions

Irreversible one-electron transfer processes corresponding to the Eu<sup>2+/3+</sup> redox couple were found for solutions of Eu(Tf<sub>2</sub>N)<sub>3</sub> in various ionic liquids. The irreversibility of the electron transfer could be related to the high viscosity of the investigated ILs. At lower scan rates the separation between oxidation and reduction process becomes less indicating the approximation of a quasi-reversible electrochemical reaction. The redox potentials at low scan rates depend also strongly on the IL anion. The cation's influence appears to be small. For the DCA ionic liquid the most negative redox potential was found, followed by the TfO and Tf<sub>2</sub>N ionic liquids. Thus, the redox potential can be related to the Lewis basicity of the IL anion. From cyclovoltammetric investigation the IL anions can be ordered with respect to rising Lewis basicity as follows: Tf<sub>2</sub>N<sup>-</sup> > TfO<sup>-</sup> > EtSO<sub>4</sub><sup>-</sup> > DCA<sup>-</sup>.

Luminescence spectroscopy confirms these results. The used luminescent Eu<sup>3+</sup> ion doped in several ILs showed to be a very sensitive probe to its coordination sphere and hence to its surrounding ligands with different donation properties.

In summary, the determination of the Lewis basicity of IL anions by investigation of the optical and electrochemical properties of  $Eu^{3+}$  appears to be promising and a proof of concept for this method could be given. At this point a larger set of ionic liquids with different cation and anion combinations needs to be investigated to be able to compare the methods with other established techniques for the determination of ionic liquids' acidity and basicity.

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#### References

- [1] (a) T. Welton, Chem. Rev. 99 (1999) 2071;
  - (b) P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. Engl. 39 (2000) 3772;

- (c) T. Welton, P. Wasserscheid, Ionic liquids in Synthesis, VCH-Wiley, Weinheim, 2002 ·
- (d) K.R. Seddon, Kinet, Katal, 37 (1996) 743:
- C.L. Hussey, Adv. Molten Salt Chem. 5 (1983) 185;
- (f) M.J. Earle, P.B. McCormac, K.R. Seddon, Green Chem. 1 (1) (1999) 23.
- [2] K.R. Seddon, in: S. Boghosian, V. Dracopoulos, C.G. Kontoyannis, G.A. Voyiatzis (Eds.), The International George Papatheodorou Symposium (Proceedings), Institute of Chemical Engineering and High Temperature Chemical Processes, Patras, 1999, p. 131.
- [3] Ch. Reichardt, Pure Appl. Chem. 76 (2004) 1903.
- [4] (a) Ch. Reichardt, Chem. Soc. Rev. 21 (1992) 147;
  - (b) Ch. Reichardt, Chem. Rev. 94 (1994) 2319;
  - (c) E. Buncel, S. Rajagopal, Acc. Chem. Res. 23 (1990) 226;
  - (d) Y. Marcus, Chem. Soc. Rev. 22 (1993) 409;
  - (e) S. Spange, A. Reuter, W. Linert, Langmuir 14 (1998) 3479;
    (f) H. Jin, B. O'Hare, J. Dong, S. Arzhantsev, G.A. Baker, J.F. Wishart, A.J. Benesi, M.
- Maroncelli, J. Phys. Chem. B 112 (2008) 81. [5] A.-V. Mudring, in: B. Kirchner (Ed.). Topics in Current Chemistry, 2010, p. 209.
- 6] P. Müller, Pure Appl. Chem. 66 (1994) 1077.
- [7] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 2nd ed. Wiley-VCH, Weinheim, 1988.
- 8] J. Bartosik, A.-V. Mudring, Phys. Chem. Chem. Phys. 12 (2010) 4005.
- [9] J.A. Duffy, Bonding, Energy levels & Bands in Inorganic Solids, New York, 1990.
- [10] S. Pitula, A.-V. Mudring, Chem. Eur. J. 16 (2010) 3355.
- [11] A. Babai, S. Pitula, A.-V. Mudring, Eur. J. Inorg. Chem. 31 (2010) 4933.
- [12] (a) A. Babai, A.-V. Mudring, Z. Anorg. Allg. Chem. 632 (2006) 1956;
  - S.-F. Tang, J. Cybinska, A.-V. Mudring, Helv. Chim. Acta 92 (2009) 2375;
  - S.-F. Tang, A. Babai, A.-V. Mudring, Angew. Chem. Int. Ed. 47 (2008) 7631;
  - A.-V. Mudring, S.-F. Tang, Eur. J. Inorg. Chem. 18 (2010) 2569;
  - A. Getsis, A.-V. Mudring, Eur. J. Inorg. Chem. 14 (2010) 2172;
  - S.-F. Tang, A.-V. Mudring, Growth Des. 11 (2011) 1437;
  - (g) P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt, K. Binnemans, J. Am. Chem. Soc. 128 (2006) 13658;
  - (h) M. Pellens, B. Thijs, K. Van Hecke, L. Van Meervelt, K. Binnemans, P. Nockemann, Acta Crystallogr. E 64 (2008) m945;
  - (i) P. Nockemann, B. Thijs, K. Lunstroot, T.N. Parac-Vogt, C. Goerller-Walrand, K. Binnemans, K. Van Hecke, L. Van Meervelt, S. Nikitenko, J. Daniels, C. Hennig, R. Van Deun, Chem. Eur. J. 15 (2009) 1449.
- [13] (a) A. Babai, A.-V. Mudring, Chem. Mater. 17 (2005) 6230;
   (b) A. Babai, S. Arenz, R. Giernoth, K. Driesen, P. Nockemann, A.-V. Mudring, J. Alloys Compd. 418 (2005) 204.
- [14] G.H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals, Interscience Publishers, New York, 1968.;

W.T. Carnall, H.M. Crosswhite, H. Crosswhite, Special Report, Chemistry Division, Argonne National Laboratory, Argonne, IL, 1977.

- [15] S.H. Strauss, Chem. Rev. 93 (1993) 927.
- [16] 4 A. Babai, Dissertation, Universität zu Köln, 2006, and ref. 11.
- [17] A. Chaumont, G. Wipff, J. Phys. Chem. B 112 (2008) 12014.
- [18] A. Tomasawa, PhD Thesis, Queen's University, Belfast, 2010; S. Pitula, Dissertation, Universität zu Köln, 2010.
- [19] A. Babai, A.-V. Mudring, Angew. Chem. 44 (2005) 5485.
- [20] S.P. Sinha, J. Inorg. Nucl. Chem. 28 (1966) 189.
- [21] R. Hagiwara, T. Hirashige, T. Tsuda, Y. Tio, Solid State Sci. 4 (2002) 23.
- [22] H. Shirota, A.M. Funstou, J.F. Wishart, E.W. Castner, J. Chem. Phys. 122 (2005) 184512.
- [23] H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. A Chem. 182 (2002) 419.
- [24] R. Bini, M. Malvadi, W.R. Pitner, C. Chiappe, J. Phys. Org. Chem. 21 (2008) 622.
- [25] C. Nanjundiah, F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) 3392.
- [26] L. Galán Sánchez, J.R. Expel, F. Onink, G.W. Meindersma, A.B. de Haan, J. Chem. Eng. Data 54 (2009) 2803.