

# Anhydrous Praseodymium Salts in the Ionic Liquid [bmpyr][Tf<sub>2</sub>N]: Structural and Optical Properties of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] and [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>]

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Purposely designed ionic liquids can be excellent solvents for spectroscopic studies of rare earth compounds. Absorption and emission spectra of anhydrous PrI<sub>3</sub> and Pr(Tf<sub>2</sub>N)<sub>3</sub> in the ionic liquid 1,1-*n*-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide, [bmpyr][Tf<sub>2</sub>N], at room temperature are presented together with the emission spectra of solid [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] and [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N]. After excitation into the <sup>3</sup>P<sub>1</sub> level, remarkable luminescence not only from the <sup>1</sup>D<sub>2</sub> level but also from the <sup>3</sup>P<sub>0</sub> and even from the <sup>3</sup>P<sub>1</sub> level is observed. Amazingly in the case of the solid compounds and even more astonishing for a solution of Pr(Tf<sub>2</sub>N)<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N] the strongest luminescence transitions start from the <sup>3</sup>P<sub>0</sub> level. From a solution of PrI<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N] single crystals of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] were grown. The compound crystallizes in the space group *P*4<sub>3</sub>2<sub>1</sub>2 with *a* = *b* = 1464.8(2) pm and *c* = 2846.9(5) pm at 298(2) K and *a* = *b* = 1454.52(7) pm and *c* = 2852.4(2) pm at 170(2) K, respectively. The structure is characterized by [PrI<sub>6</sub>] octahedra winding along the 4<sub>3</sub> screw parallel to the crystallographic *c* axis. Above each octahedral face one 1-butyl-1-methyl-pyrrolidinium cation is tangentially located. The bis(trifluoromethylsulfonyl)amide anions fill the remaining space. From a solution of Pr(Tf<sub>2</sub>N)<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N] the compound [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] is obtained which crystallizes triclinic, space group *P*1̄, with *a* = 12.3217(13) pm, *b* = 12.4275(14) pm, *c* = 22.6422(24) pm, α = 94.440(9)°, β = 102.630(8)°, and γ = 105.791(9)°. Here the main structural feature is the separation of the hydrophobic [Pr(Tf<sub>2</sub>N)<sub>5</sub>]<sup>2-</sup> and hydrophilic bmpyr<sup>+</sup> parts in the structure.

## 1. Introduction

Lanthanide compounds have gained wide attention as materials for light-emitting diodes<sup>1</sup> and medical<sup>2</sup> and biological applications<sup>3</sup> because trivalent lanthanide cations (Ln<sup>3+</sup>) generally display intense luminescence in the visible and near-IR regions. Properties such as narrow emission bands, a reasonably long decay time, and typically a large difference between the excitation and emission wavelength are favorable. Unfortunately, luminescence lifetimes and quantum yields for Ln<sup>3+</sup> in conventional solvents are usually low as coordination of these solvent molecules to the lanthanide ions leads to efficient nonradiative depopulation of the excited

state via vibronic coupling with the vibrational states of X–H oscillators (X = C, N, O).<sup>4</sup> Recently, we were able to show that the replacement of conventional solvents by carefully designed *ionic liquids* such as 1-dodecyl-3-imidazolium bis(trifluoromethanesulfonyl)amide leads to a dramatic increase of lifetimes of the excited state and quantum yields of emission.<sup>5</sup> Furthermore, it has been observed that not only energy transfer from certain ionic liquids can substantially increase the luminescence of Eu<sup>3+</sup> but also the emission color can be tuned by the choice of the anion.<sup>6</sup>

*Ionic liquids* typically are built up by a large organic cation such as imidazolium, pyridinium, or quaternary ammonium ions and anionic counterions such as halides or BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, or CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. By a common definition, the melting point of ionic liquids is below 100 °C. Many ionic liquids are even liquid at room temperature (*room-temperature ionic liquids*) and below.<sup>7</sup> The appropriate choice of the anion/cation

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combination allows tuning of many physical and chemical properties of ionic liquids such as miscibility with water and other solvents, dissolving ability, polarity, viscosity, and density.

The solvent properties of ionic liquids can be designed in such a way that good solubility of inorganic lanthanide compounds such as LnI<sub>3</sub> is obtained and that, at the same time, no C–H, N–H, and O–H oscillators get introduced into the inner coordination sphere of the lanthanide ion that could quench the luminescence due to vibronic coupling. This can be achieved by choosing weakly coordinating anions (WCAs) that bear no such bonds, like, for example, the bis-(trifluoromethanesulfonyl)amide anion. In this respect, ionic liquids become interesting solvents to investigate the spectroscopic behavior of lanthanide complexes in solution, especially of complexes with weakly binding ligands, which otherwise would be unable to compete with the solvent molecules for a binding site at the lanthanide ion.<sup>8</sup> A prerequisite is certainly that the ionic liquid itself is optically transparent in the region under study.

Here we report on the absorption and emission spectra of PrI<sub>3</sub> and Pr(Tf<sub>2</sub>N)<sub>3</sub> in the ionic liquid [bmpyr][Tf<sub>2</sub>N] (1-*n*-butyl-methylpyrrolidinium bis(trifluoromethanesulfonyl)-amide). Furthermore, we were able to crystallize and structurally characterize the compounds [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] and [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] from these solutions.

## 2. Experimental Section

**Synthesis.** All preparations were carried out under an argon atmosphere using a glovebox or standard Schlenk techniques. Special attention has to be paid to strictly anhydrous conditions as any water present leads to a dramatic reduction up to total quenching of the luminescent properties of the samples.<sup>9</sup>

To synthesize PrI<sub>3</sub>, the respective amounts of the elements were placed in a silica tube which was sealed off under vacuum and subsequently heated for 30 h at 200 °C. The crude product was purified by sublimation under high vacuum at 800 °C.<sup>10</sup>

Pr(Tf<sub>2</sub>N)<sub>3</sub> was synthesized by dissolving praseodymium metal (99.9%, Chempur), in an aqueous solution of HTf<sub>2</sub>N (95%, Fluka) and removing the solvent. The crude, greenish product was sublimated at 280 °C under reduced pressure (10<sup>-3</sup> mbar) to yield colorless Pr(Tf<sub>2</sub>N)<sub>3</sub>.

The ionic liquid [bmpyr][Tf<sub>2</sub>N] was synthesized following a literature procedure.<sup>11</sup> First, [bmpyr]Br was obtained by solvent-free alkylation of *N*-methylpyrrolidine with 1-bromobutane at 80 °C. The crude product was recrystallized from acetonitrile/toluene, dissolved in water, and heated to 70 °C. One equivalent of lithium bis(trifluoromethanesulfonyl)amide in water was added dropwise, and the mixture was stirred for 24 h at room temperature. The

**Table 1. Crystal Data and Structure Refinement Parameters for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N]**

empirical formula	PrI <sub>6</sub> S <sub>2</sub> F <sub>6</sub> O <sub>4</sub> N <sub>5</sub> C <sub>36</sub> H <sub>80</sub>	
molecular mass	1751.50 g/mol	
temperature	298(2) K	170(2) K
wavelength	0.710 73 Å	
crystal system	tetragonal	
space group	P4 <sub>3</sub> 2 <sub>1</sub> 2 (no. 96)	
unit cell dimensions	$a = b = 1464.8(2)$ pm	$a = b = 1454.52(7)$ pm
	$c = 2846.9(5)$ pm	$c = 2852.4(2)$ pm
	$\alpha = \beta = \gamma = 90^\circ$	
volume	$6108(2) \times 10^6$ pm <sup>3</sup>	$6034.6(6) \times 10^6$ pm <sup>3</sup>
Z	4	
density (calculated)	1.905 mg/m <sup>3</sup>	1.839 mg/m <sup>3</sup>
absorption coefficient $\mu$	3.953 mm <sup>-1</sup>	3.998 mm <sup>-1</sup>
$F(000)$	3352	
crystal size	0.1 × 0.2 × 0.3 mm <sup>3</sup>	0.1 × 0.2 × 0.3 mm <sup>3</sup>
$\theta$ range for data collection	1.56–27.39°	1.57–27.31°
index ranges	$-18 \leq h \leq 18$ $-18 \leq k \leq 18$ $-36 \leq l \leq 36$	$-18 \leq h \leq 18$ $-18 \leq k \leq 18$ $-36 \leq l \leq 36$
reflections collected	60 693	55 865
independent reflections	6870 [R(int) = 0.1494]	6731 [R(int) = 0.1524]
completeness to $\theta = 29.61^\circ$	99.4%	99.2%
refinement method	full-matrix least squares on $F^2$	
data/restraints/parameters	6870/15/338	6731/15/348
goodness of fit on $F^2$	0.794	1.027
final R indices [I > 2σ(I)]	$R_1 = 0.0418,$ $wR_2 = 0.0635$	$R_1 = 0.0582,$ $wR_2 = 0.1116$
R indices (all data)	$R_1 = 0.1316,$ $wR_2 = 0.0827$	$R_1 = 0.0924,$ $wR_2 = 0.1223$
absolute structure parameter	-0.04(6)	0.01(6)
CCDC no.	273 376	272 863

product, which formed a second phase to water, was purified by addition of activated charcoal and filtration through aluminum oxide. It was washed with small aliquots of water until no halide residues could be detected in the extract (AgNO<sub>3</sub> test). The ionic liquid was dried for 120 h in a Schlenk tube at 150 °C under reduced pressure and rigorous stirring.

For a solution of PrI<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N], PrI<sub>3</sub> (~26 mg, 0.05 mmol) was put in a silica tube (11 mm in diameter), and then [bmpyr][Tf<sub>2</sub>N] (~0.5 mL, 0.75 g, 1.8 mmol) was added. The tube was sealed off under dynamic vacuum and heated to 120 °C until the rare-earth salts were completely dissolved. To obtain [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N], the amount of PrI<sub>3</sub> was increased (~52 mg, 0.1 mmol) to achieve super-saturation. By heating the reaction mixture to 393 K and subsequent cooling to room temperature (2 K/min), crystals of the composition [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] precipitated from the solution.

[bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] was synthesized from Pr(Tf<sub>2</sub>N)<sub>3</sub> (123 mg, 0.125 mmol) and [bmpyr][Tf<sub>2</sub>N] (355 mg, 0.25 mL, 0.8 mmol). The educts were placed in a silica tube that was sealed under vacuum. The reaction was carried out at 120 °C for 36 h. Single crystals form as an insoluble product after cooling the reaction mixture to room temperature (5 K/min). The product was separated by cannula filtration from the ionic liquid.

**X-ray Crystal Structure Determination.** All data were collected on a Stoe IPDS-II single-crystal X-ray diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710 73$  Å) at 298(2) and 170(2) K, respectively. Analysis of the reflection conditions for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] led to the two possible space groups P4<sub>3</sub>2<sub>1</sub>2 and P4<sub>3</sub>2<sub>1</sub>2. Structure solution<sup>12</sup> and refinement<sup>13</sup> succeeded in the

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**Table 2. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters [ $U(\text{eq})$ ,  $\text{\AA}^2 \times 10^3$ ]<sup>a</sup> for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] at 298(2) and 170(2) K**

	298(2) K				170(2) K			
	x	y	z	$U(\text{eq})$	x	y	z	$U(\text{eq})$
Pr	7639(1)	7639(1)	5000	48(1)	7635(1)	7635(1)	5000	30(1)
I(1)	7726(1)	9739(1)	5236(1)	62(1)	7719(1)	9755(1)	5236(1)	43(1)
I(2)	7311(1)	8028(1)	3936(1)	59(1)	7290(1)	8045(1)	3942(1)	41(1)
I(3)	7665(1)	5529(1)	4873(1)	64(1)	7658(1)	5508(1)	4868(1)	49(1)
S(1)	11 496(7)	7644(10)	2116(5)	141(4)	11 436(5)	7579(7)	2057(3)	70(2)
S(2)	12 045(9)	7035(10)	2341(5)	131(4)	12 021(7)	7114(6)	2364(4)	75(3)
O(1)	11 370(30)	6710(20)	2260(20)	320(50)	11 330(20)	6686(18)	2281(15)	79(12)
O(2)	10 720(20)	7920(30)	1850(20)	210(20)	10 569(17)	7920(30)	1907(15)	87(12)
O(4)	12 954(16)	7110(30)	2199(12)	240(20)	12 939(14)	6910(20)	2276(13)	142(17)
O(5)	11 400(20)	6335(17)	2360(12)	148(14)	11 400(20)	6361(16)	2424(14)	71(9)
N(10)	9513(8)	5776(7)	3366(3)	59(3)	9539(8)	5781(8)	3378(4)	43(2)
C(10)	9823(11)	5002(10)	3079(5)	100(5)	9828(11)	5008(10)	3068(7)	64(4)
C(11)	9120(20)	5452(15)	3781(9)	230(15)	9227(13)	5388(16)	3837(7)	90(7)
C(12)	9970(20)	4820(20)	4008(10)	239(18)	10 098(15)	5080(30)	4044(9)	162(16)
C(13)	10 630(30)	5540(30)	3865(9)	300(20)	10 853(14)	5736(15)	3879(7)	86(6)
C(14)	10 318(13)	6275(14)	3522(8)	132(7)	10 346(13)	6309(12)	3508(8)	78(5)
C(15)	8930(20)	6414(19)	3136(7)	206(14)	8807(12)	6333(15)	3153(8)	84(6)
C(16)	9022(11)	6796(11)	2686(5)	97(5)	9002(12)	6824(12)	2704(6)	68(4)
C(17)	8367(18)	7480(20)	2517(9)	242(17)	8300(20)	7450(20)	2536(7)	169(16)
C(18)	8446(16)	7870(16)	2083(8)	192(12)	8384(18)	7914(18)	2114(11)	141(12)
N(20)	14 324(12)	4596(9)	1443(6)	113(5)	14 285(11)	4597(9)	1479(6)	76(5)
C(20)	14 783(18)	5391(18)	1674(9)	192(12)	14 640(20)	5440(20)	1747(11)	168(15)
N(21)	12 190(30)	8293(19)	2319(9)	114(10)	12 013(19)	8228(18)	2303(9)	62(7)
C(21)	8869(19)	10 070(20)	3844(9)	198(18)	8820(20)	10 110(20)	3861(7)	154(16)
C(22)	10 644(18)	10 450(30)	1495(18)	300(30)	10 564(16)	10 510(20)	1489(18)	230(30)
C(23)	9820(30)	10 130(16)	1830(8)	200(15)	9709(16)	10 139(12)	1810(8)	92(7)
C(24)	8935(16)	10 107(13)	1509(6)	135(8)	8872(12)	10 141(12)	1471(5)	65(5)
C(25)	5795(16)	6398(19)	3167(9)	146(9)	5764(18)	6459(13)	3125(8)	98(8)
C(26)	12 920(20)	4684(15)	1984(9)	194(14)	12 743(17)	4685(14)	1949(9)	106(8)
C(27)	12 170(20)	4260(20)	2334(9)	220(15)	12 060(15)	4240(20)	2331(8)	127(10)
C(28)	12 420(20)	4324(17)	2754(8)	189(10)	12 420(20)	4349(19)	2769(8)	128(9)
C(100)	12 170(20)	7460(20)	1571(9)	220(50)	12 072(15)	7342(17)	1513(7)	100(20)
F(101)	13 020(20)	7180(30)	1642(12)	208(16)	12 915(13)	7116(15)	1602(8)	88(6)
F(102)	11 991(18)	8120(20)	1270(9)	169(12)	12 026(16)	8053(15)	1237(7)	89(7)
F(103)	11 750(40)	6720(30)	1404(10)	184(18)	11 600(20)	6712(18)	1290(11)	125(13)
C(200)	11 900(30)	7510(20)	1745(9)	125(15)	11 786(18)	7605(17)	1781(7)	310(70)
F(201)	12 130(50)	6910(30)	1440(20)	390(50)	11 940(20)	6940(20)	1491(8)	200(30)
F(202)	12 260(40)	8290(20)	1654(17)	390(40)	12 210(20)	8340(20)	1656(10)	161(15)
F(203)	11 020(30)	7630(40)	1714(15)	320(40)	10 898(17)	7790(30)	1762(12)	150(20)

<sup>a</sup>  $U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

space group  $P4_32_12$  (no. 96) for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] and for [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] in the space group  $P1$  (no. 2). Crystal structure solution by direct methods using SHELXS-97 yielded the heavy atom positions. Subsequent difference Fourier analyses and least squares refinement allowed the localization of the remaining atom positions. In the final step of the crystal structure refinement hydrogen atoms of idealized  $-\text{CH}_2$  and  $-\text{CH}_3$  groups were added and treated with the riding atom model; their isotropic displacement factor was chosen as 1.2 times the preceding carbon atom. Crystal data and structural refinement parameters of the two structures are summarized in Tables 1 and 2 for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] and Tables 3 and 4 for [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>]. Data reduction was carried out with the program package X-Red,<sup>14</sup> and numerical absorption correction was carried out with the program X-Shape.<sup>15</sup> For crystal structure drawings the program Diamond was used.<sup>16</sup> Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB2 1EZ, fax (+44)1223-336-033; e-mail deposit@ccdc.cam.ac.uk), on quoting the depository numbers CCDC-272863 and CCDC-273376 for [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] and CCDC-283069 for [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] the authors and the journal citation.

**Spectroscopic Investigations.** Absorption spectra were recorded with a Cary 5 E (Varian, Palo Alto, U.S.A.) with a quartz–iodine

radiation source (visible) and a deuterium lamp (UV). Excitation and emission spectra were recorded at room temperature with a SPEX-Fluorolog DM3000F (Jobin Yvon GmbH, München, Germany) with a xenon lamp as the excitation source and a photomultiplier tube for detection. Electronic transitions were assigned according to the energy level diagrams of trivalent rare earth ions.<sup>17</sup>

### 3. Results and Discussion

**Structural Investigations.** By reaction of the ionic liquid with anhydrous PrI<sub>3</sub> pale yellow greenish crystals of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] (Figure 1) were obtained. The compound crystallizes with the axial space group  $P4_32_12$  (no. 96) with four formula units in the unit cell; see Tables 1 and 2 and Figures 1–4. Formally, the compound can be viewed as a solvent adduct with [bmpyr][Tf<sub>2</sub>N] being the solvent according to the formulation [bmpyr]<sub>3</sub>[PrI<sub>6</sub>]·[bmpyr][Tf<sub>2</sub>N].

The asymmetric unit, corresponding to one formula unit of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N], is formed by four cations of the ionic liquid, bmpyr, one (slightly distorted) [PrI<sub>6</sub>] octahedron,

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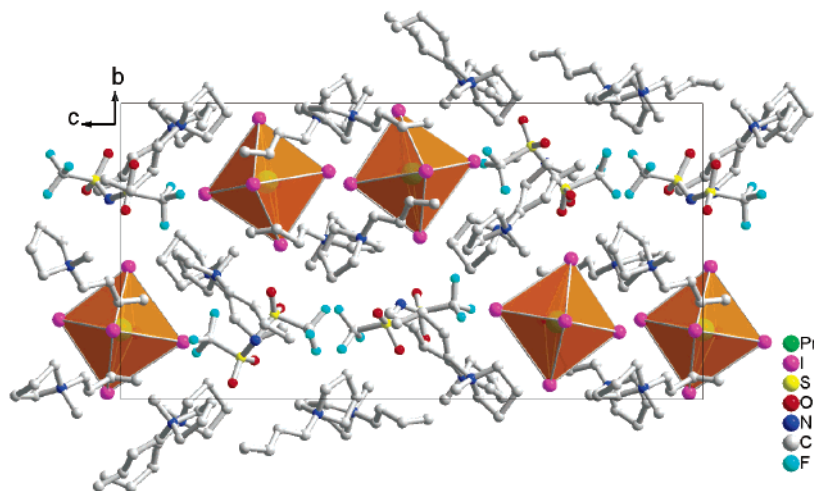


Figure 1. Crystal structure of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N], viewed along [100]. Hydrogen atoms are omitted for clarity.

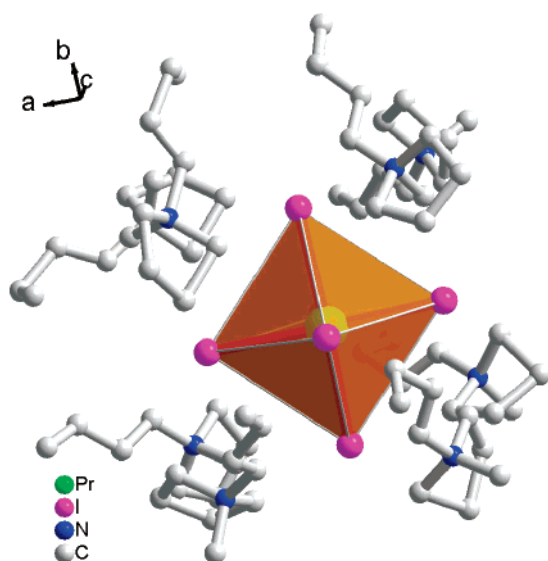


Figure 2. Local surrounding of the [PrI<sub>6</sub>] octahedra by eight [bmpyr]<sup>+</sup> cations in [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N].

and one anion of the ionic liquid, Tf<sub>2</sub>N<sup>-</sup>. Four bmpyr cations are situated above the faces of the [PrI<sub>6</sub>] octahedron in such a way that the pyrrolidinium rings are almost parallel to the four faces of the [PrI<sub>6</sub>] octahedron (Figure 2). For interatomic distances see Supporting Information.

Note the two different conformations of the butyl alkyl side chains of the bmpyr cation. Molecular dynamic simulations predict a similar local surrounding of [LnCl<sub>6</sub>]<sup>3-</sup> units (Ln = La, Eu) in the ionic liquids [bmim][PF<sub>6</sub>] and [bmim]-[tetrachloroaluminate] (bmim = 1-butyl-3-methyl-imidazolium).<sup>18</sup>

The [PrI<sub>6</sub>] octahedra wind themselves along the 4<sub>3</sub> screw axis parallel to the crystallographic *c* axis. The octahedra are tilted against the crystallographic *c* axis as can be seen from Figure 3.

The Tf<sub>2</sub>N<sup>-</sup> anions fill the gaps of the {[PrI<sub>6</sub>]@8[bmpyr]} units winding also along the 4<sub>3</sub> screw axis parallel to the crystallographic *c* axis. The anions are displaced against the cationic fragment. The Tf<sub>2</sub>N<sup>-</sup> anions themselves are strongly disordered (Figure 4). High conformational flexibility and a

Table 3. Crystal Data and Structure Refinement Parameters for [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>]

empirical formula	PrI <sub>6</sub> S <sub>2</sub> F <sub>6</sub> O <sub>4</sub> N <sub>5</sub> C <sub>36</sub> H <sub>80</sub>
molecular mass	1802.16 g/mol
temperature	198(2) K
wavelength	0.710 73 Å
crystal system	triclinic
space group	<i>P</i> $\bar{1}$ (no. 2)
unit cell dimensions	<i>a</i> = 1232.04(12) pm <i>b</i> = 124 261(14) pm <i>c</i> = 2264.0(2) pm $\alpha$ = 94.440(9)° $\beta$ = 102.632(8)° $\gamma$ = 105.792(8)°
volume	3219.8(6) × 10 <sup>6</sup> pm <sup>3</sup>
<i>Z</i>	2
density (calculated)	1.859 mg/m <sup>3</sup>
absorption coefficient $\mu$	1.235 mm <sup>-1</sup>
<i>F</i> (000)	1788
crystal size	0.1 × 0.2 × 0.3 mm <sup>3</sup>
$\theta$ range for data collection	1.72–25.00°
index ranges	−14 ≤ <i>h</i> ≤ 14 −14 ≤ <i>k</i> ≤ 14 −26 ≤ <i>l</i> ≤ 26
reflections collected	40 163
independent reflections	11 337 [ <i>R</i> (int) = 0.1106]
completeness to $\theta$ = 29.61°	100%
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>
data/restraints/parameters	11 337/4/894
goodness of fit on <i>F</i> <sup>2</sup>	0.954
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0743, <i>wR</i> <sub>2</sub> = 0.1742
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1316, <i>wR</i> <sub>2</sub> = 0.0827
CCDC no.	283 069

strong tendency to packing frustrations of both the cation and the anion are believed to be the key to low melting salts and, thus, to (room temperature) ionic liquids. This is obvious in our case as it was difficult to obtain a crystal of sufficient quality for single-crystal X-ray structure analysis. Many specimens showed an extreme disorder of the cation and anion belonging to the included “solvent”. The crystal structure refinement of the best specimen that is reported here exhibits even at 170(2) K large displacement factors for the [bmpyr] cations and the [Tf<sub>2</sub>N] anion.

The bis(trifluoromethanesulfonyl)amide anion, Tf<sub>2</sub>N<sup>-</sup>, belongs to the class of WCAs. Indeed, in the present case the Tf<sub>2</sub>N<sup>-</sup> anion is incorporated in the crystal structure of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] in a noncoordinating mode. The adopted trans conformation has been shown by theoretical calcula-

**Table 4. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters [ $U(\text{eq}), \text{\AA}^2 \times 10^3$ ]<sup>a</sup> for [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] at 198(2) K**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Pr	7838(1)	9025(1)	7343(1)	29(1)	O(62)	6828(9)	9221(9)	9304(4)	75(3)
N(3)	5758(7)	6405(7)	8316(4)	39(2)	O(63)	6642(5)	10311(6)	7512(3)	37(2)
S(31)	6176(2)	6148(2)	7736(1)	38(1)	O(64)	5571(7)	11573(6)	7839(5)	61(2)
S(32)	4716(2)	5546(2)	8507(1)	37(1)	F(61)	8189(7)	11577(8)	9744(3)	78(2)
O(31)	6873(6)	7220(6)	7614(4)	45(2)	F(62)	8952(7)	11708(8)	8980(4)	86(3)
O(32)	5352(7)	5409(7)	7231(4)	62(2)	F(63)	9313(7)	10584(9)	9614(4)	92(3)
O(33)	4341(6)	4416(6)	8198(3)	43(2)	F(64)	3887(5)	9457(6)	8014(3)	58(2)
O(34)	4934(7)	5724(7)	9164(3)	51(2)	F(65)	4889(5)	8431(5)	7723(3)	52(2)
C(31)	7277(12)	5416(11)	7985(7)	62(4)	F(66)	4091(5)	9386(6)	7088(3)	54(2)
C(32)	3485(9)	6090(10)	8238(6)	50(3)	O(70)	5842(6)	8301(7)	6633(3)	48(2)
F(31)	7795(9)	5299(9)	7540(5)	95(3)	F(70)	3667(9)	7374(14)	5127(4)	140(5)
F(32)	6786(8)	4429(6)	8118(5)	95(3)	N(72)	5877(18)	7130(30)	5686(10)	249(19)
F(33)	8070(7)	6021(8)	8463(4)	80(3)	S(72)	5051(4)	7411(4)	6148(2)	91(1)
F(34)	3252(6)	6098(6)	7647(3)	64(2)	C(72)	4361(16)	100(30)	5631(8)	157(13)
F(35)	3712(7)	7147(7)	8515(4)	69(2)	F(76)	3714(11)	8597(18)	5884(5)	176(8)
F(36)	2559(6)	5454(8)	8389(5)	85(3)	F(74)	5221(9)	9073(10)	5513(5)	111(4)
N(4)	1376(7)	9202(8)	7917(4)	41(2)	S(73)	7118(3)	7156(3)	5854(1)	63(1)
S(41)	577(2)	8908(2)	8371(1)	39(1)	O(73)	7722(6)	7602(6)	6487(3)	38(2)
S(42)	939(2)	9247(2)	7216(1)	38(1)	O(72)	7744(19)	7546(10)	5414(5)	149(8)
O(41)	9332(5)	8452(6)	8068(3)	38(2)	C(76)	6995(13)	5693(11)	5780(6)	66(4)
O(42)	915(6)	9742(7)	8882(4)	52(2)	F(71)	6395(8)	5157(8)	5241(4)	95(3)
O(43)	9762(5)	9324(6)	7041(3)	36(2)	F(77)	8014(11)	5550(9)	5880(6)	124(5)
O(44)	1812(6)	25(6)	7019(4)	52(2)	F(75)	6511(17)	5230(9)	6190(6)	190(9)
C(41)	949(10)	7692(10)	8668(6)	50(3)	O(74)	4137(9)	6472(10)	6149(7)	140(7)
C(42)	830(10)	7855(10)	6835(6)	48(3)	N(1)	3925(7)	2129(7)	9225(4)	40(2)
F(41)	334(6)	7341(6)	9062(3)	58(2)	C(1)	5781(10)	8936(9)	602(6)	48(3)
F(42)	2080(5)	8017(7)	8959(3)	65(2)	C(2)	4693(10)	8514(9)	74(5)	47(3)
F(43)	734(7)	6842(6)	8222(3)	64(2)	C(3)	4088(10)	7333(10)	177(6)	52(3)
F(44)	4(5)	7057(5)	6975(3)	51(2)	C(4)	5069(11)	2983(11)	9335(7)	64(4)
F(45)	1829(6)	7618(6)	7009(4)	63(2)	C(5)	6825(12)	7614(12)	10358(6)	62(3)
F(46)	563(8)	7839(7)	6239(3)	73(2)	C(6)	7328(12)	6662(13)	10458(7)	66(4)
N(5)	9488(9)	1880(7)	6732(4)	47(2)	C(7)	8019(11)	6555(15)	9987(7)	73(4)
S(51)	9834(2)	1956(2)	7448(1)	36(1)	C(8)	8479(19)	5563(15)	10055(10)	103(6)
S(52)	8282(4)	1160(3)	6295(2)	95(2)	C(9)	3243(10)	1932(9)	8567(5)	44(3)
O(51)	9148(5)	1017(5)	7685(3)	32(1)	N(2)	3232(8)	2637(7)	6319(4)	42(2)
O(52)	1056(6)	2258(7)	7669(4)	54(2)	C(14)	4400(20)	1462(17)	6047(12)	67(6)
O(53)	7790(6)	91(6)	6477(3)	44(2)	C(15)	4900(30)	2080(30)	6643(18)	67(6)
O(54)	7406(8)	1911(8)	6163(5)	94(4)	C(10)	4970(20)	2663(15)	6125(10)	117(8)
C(51)	9420(12)	3179(11)	7717(6)	59(3)	C(11)	4196(14)	3290(17)	6089(9)	91(5)
C(52)	8670(18)	865(15)	5634(7)	85(5)	C(12)	3474(16)	2580(16)	6991(8)	35(3)
F(51)	9873(8)	4067(6)	7480(4)	80(2)	C(13)	2320(20)	1610(20)	5914(11)	35(3)
F(52)	8269(7)	2938(7)	7577(5)	79(2)	C(16)	3980(40)	2450(40)	6890(20)	103(11)
F(53)	9801(9)	3404(7)	8322(4)	89(3)	C(17)	3180(20)	1464(16)	6027(11)	103(11)
F(54)	9338(9)	324(11)	5728(5)	101(3)	C(18)	2140(20)	2800(20)	6089(16)	97(9)
F(552)	7641(11)	287(12)	5197(5)	139(5)	C(19)	2790(40)	3660(40)	6270(30)	97(9)
F(562)	9031(12)	1854(12)	5412(5)	159(7)	C(20)	1990(70)	3800(50)	6220(50)	110(20)
N(6)	6399(8)	541(9)	8600(4)	50(2)	C(21)	1910(110)	4030(100)	6420(80)	110(20)
S(61)	5940(2)	590(2)	7905(1)	43(1)	C(22)	270(60)	4700(70)	6260(20)	123(13)
S(62)	7253(2)	9877(3)	8872(1)	46(1)	C(23)	1260(60)	4440(70)	5960(20)	123(13)
C(62)	4598(9)	382(10)	7668(5)	44(3)	C(24)	710(60)	5100(60)	6130(40)	134(15)
C(61)	8500(10)	1014(12)	9327(5)	54(3)	C(25)	860(40)	4990(40)	5650(20)	134(15)
O(61)	7720(7)	9376(7)	8426(3)	46(2)					

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

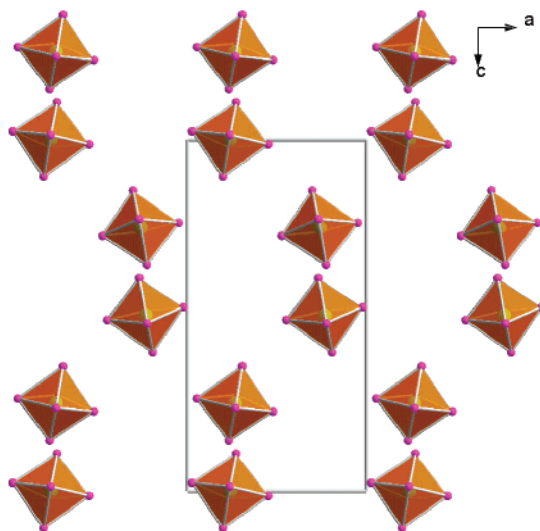
tions to be the more stable one for the “free” anion.<sup>24</sup> Only recently the first two lanthanide compounds with bis(trifluoromethanesulfonyl)amide ligands were discovered and

structurally characterized, La(Tf<sub>2</sub>N)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub><sup>19</sup> with a trivalent lanthanide and [mppyr]<sub>2</sub>[Yb(Tf<sub>2</sub>N)<sub>4</sub>] with a divalent lanthanide cation.<sup>8</sup>

To force the bis(trifluoromethanesulfonyl)amide to coordinate to a lanthanide cation we reacted Pr(Tf<sub>2</sub>N)<sub>3</sub> with the ionic liquid [bmpyr][Tf<sub>2</sub>N] and obtained a compound of the composition [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>]. The compound crystallizes in the triclinic centro-symmetric space group  $P\bar{1}$  with two formula units in the unit cell (Tables 3 and 4).

The structure of [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] is built up by [Pr(Tf<sub>2</sub>N)<sub>5</sub>]<sup>2-</sup> complex anions which are forming sheets parallel to the crystallographic *a*–*b* plane and are separated in the *c* direction by [bmpyr] cations (Figure 5). By this, as often observed in the case of Tf<sub>2</sub>N<sup>-</sup> complex compounds, separate hydrophobic (Tf<sub>2</sub>N<sup>-</sup>) and hydrophilic (bmpyr) regions are formed in the structure.

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**Figure 3.** Arrangement of the [PrI<sub>6</sub>] octahedra in [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N].

The praseodymium cation itself is coordinated by five bis-(trifluoromethylsulfonyl)amide ligands in the form of a (distorted) monocapped square antiprism (coordination number 9, the preferred coordination number for larger trivalent lanthanide cations). Four Tf<sub>2</sub>N<sup>-</sup> ligands coordinate bidentately, one just monodentately (Figure 6) with an average Pr–O distance of 249 pm. Three of the bidentate ligands adopt a trans conformation while one exhibits a cis conformation (with respect to the –CF<sub>3</sub> groups). The monodentate ligand shows trans conformation. Coordination of oxygen atoms influences the S–O bonding distance. For S–O bonds involving a coordinating oxygen atom, a mean interatomic S–O distance of 145 pm is found while for “free” oxygen atoms a shorter mean S–O distance of 143 pm is observed (cf. Supporting Information, Table 2).

**Optical Investigations.** By dissolving PrI<sub>3</sub> and Pr(Tf<sub>2</sub>N)<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N], in both cases transparent, pale yellow

green solutions are obtained. The absorption spectrum of the solutions shows the expected transitions from the <sup>3</sup>H<sub>4</sub> ground level to <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>2</sub>, and <sup>1</sup>D<sub>2</sub> levels according to the well-known energy level diagram of trivalent rare earth elements<sup>20</sup> (Supporting Information). The strong absorption above 400 nm can be assigned to ligand → metal charge-transfer absorptions which are stronger in the case of the iodide containing solution. Above 245 nm, absorptions of the ionic liquid itself are observed.

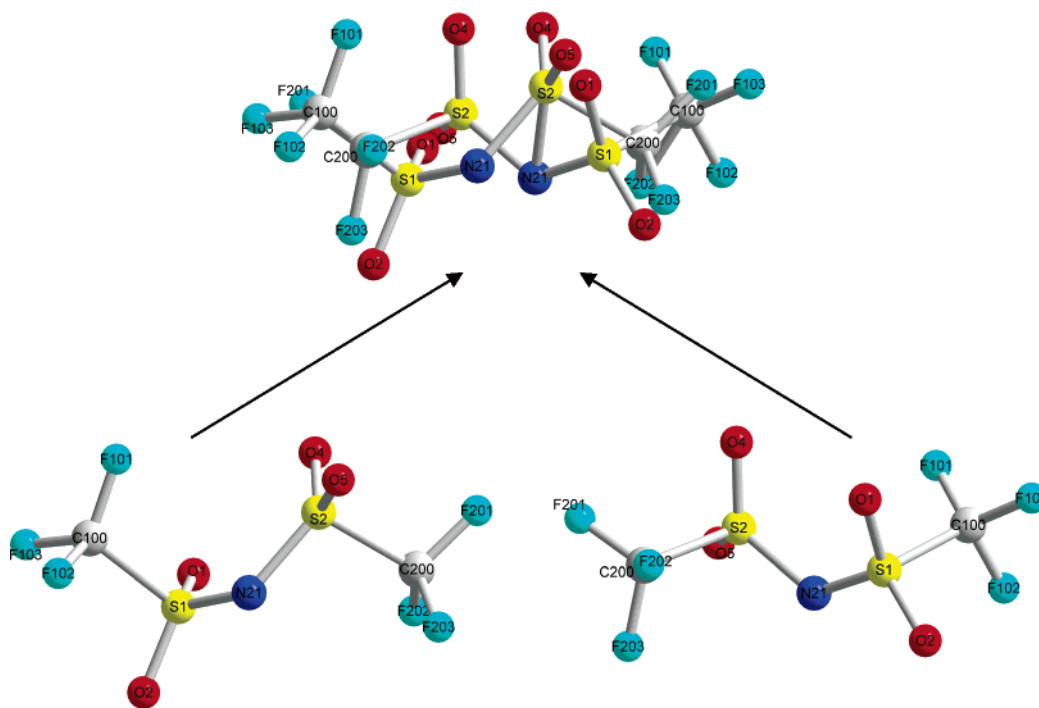
In principle, transitions from the <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub>, and <sup>1</sup>D<sub>2</sub> levels can be observed for Pr<sup>3+</sup> in the visible region of light. Figure 7 illustrates the relevant part of the schematic energy diagram of trivalent praseodymium.

The luminescence spectra of PrI<sub>3</sub> (Figure 8) and Pr(Tf<sub>2</sub>N)<sub>3</sub> (Figure 9) dissolved in [bmpyr][Tf<sub>2</sub>N] as well as those of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] (Figure 10) and [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>3</sub>] (Figure 11) were recorded at room temperature under excitation into the <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> level (corresponding to a wavelength of 443 nm).

The transition at 670 nm can originate from both the <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>3</sub> and the <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>5</sub> transitions as both states are populated under the chosen conditions.

The emission spectra of both a solution of PrI<sub>3</sub> (Figure 8) and Pr(Tf<sub>2</sub>N)<sub>3</sub> (Figure 9) dissolved in [bmpyr][Tf<sub>2</sub>N] show similar features. This is not astonishing taking into consideration that both solutions must contain Pr<sup>3+</sup> solvated by Tf<sub>2</sub>N<sup>-</sup>. Most probably the complex is [Pr(Tf<sub>2</sub>N)<sub>5</sub>]<sup>2-</sup> as can be concluded from the single-crystal X-ray structure analysis (see above). In addition the solution of PrI<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N] should contain Pr<sup>3+</sup> in the form of [PrI<sub>6</sub>]<sup>3-</sup>, as can again be deduced from the single-crystal X-ray structure analysis.

As previously reported, for Pr<sup>3+</sup> the <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> transition generally yields the most intense emission.<sup>21</sup> Radiative transitions from the <sup>1</sup>D<sub>2</sub> level are more probable than transitions from the <sup>3</sup>P<sub>j</sub> levels as radiative transitions are more



**Figure 4.** Disorder of the Tf<sub>2</sub>N<sup>-</sup> anion in [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N].

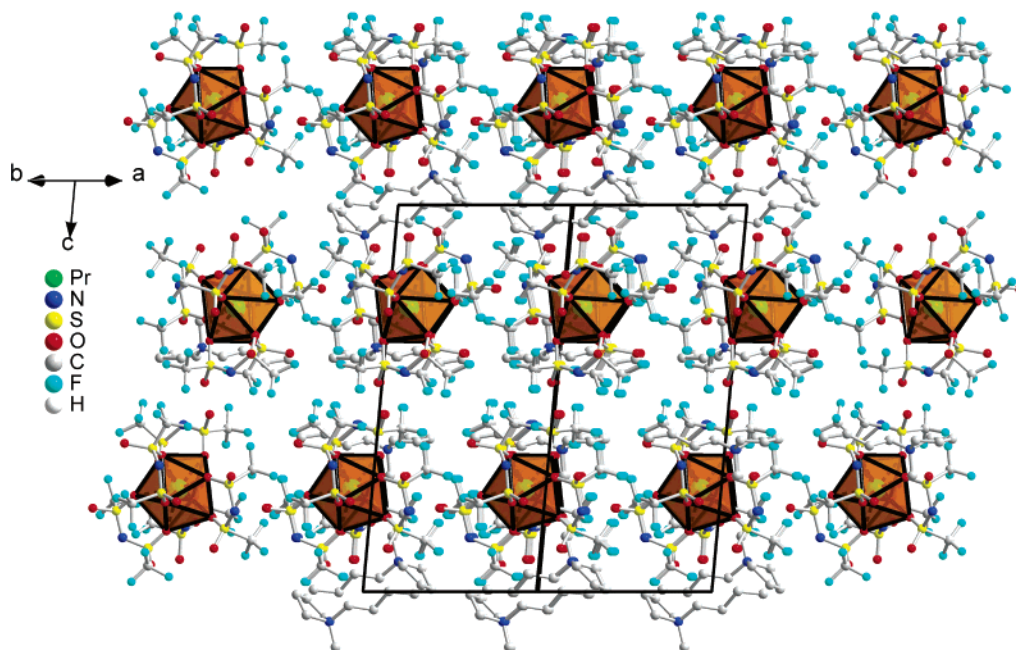


Figure 5. Crystal structure of  $[\text{bmpyr}]_2[\text{Pr}(\text{Tf}_2\text{N})_5]$ . Hydrogen atoms are omitted for clarity.

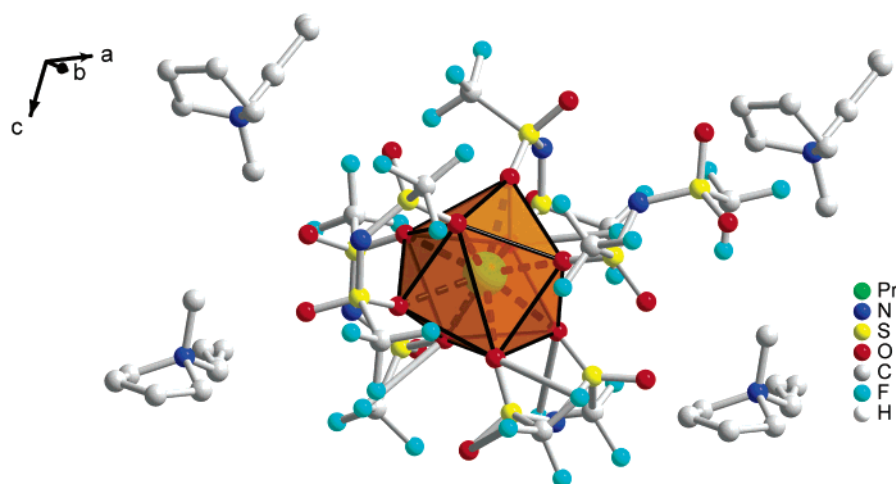


Figure 6. Local surrounding of  $\text{Pr}^{3+}$  in solid  $[\text{bmpyr}]_2[\text{Pr}(\text{Tf}_2\text{N})_5]$ .

likely to occur when energy gaps are larger. The  $^1\text{D}_2$  level exhibits the largest energy gap ( $\sim 6500\text{ cm}^{-1}$ , compared to  $3500\text{ cm}^{-1}$  for  $^3\text{P}_0 \rightarrow ^1\text{D}_2$ ) to the next lower lying level in the region under investigation.<sup>22</sup> Especially for solutions of trivalent praseodymium compounds, the emission from the  $^1\text{D}_2$  level is expected to be far more intense compared to the emission from the level  $^3\text{P}_0$  as multiphonon relaxations due to the presence of high frequency oscillators present in or of the solvent lead readily to a depopulation of the  $^3\text{P}_0$  level. For example, anhydrous  $\text{Pr}(\text{di-tert-butyl-1,3-diketone})_3$  shows in absolute dimethylsulfoxide the  $^3\text{H}_4 \leftarrow ^1\text{D}_2$  as well as the  $^3\text{H}_6 \leftarrow ^3\text{P}_0$  transitions whereas in the presence of water only the  $^3\text{H}_4 \leftarrow ^1\text{D}_2$  transition is observed.<sup>23</sup> It is especially noteworthy that both the solutions of  $\text{PrI}_3$  and of  $\text{Pr}(\text{Tf}_2\text{N})_3$  in  $[\text{bmpyr}][\text{Tf}_2\text{N}]$  show emissions from the  $^3\text{P}_1$  levels with unusual high intensities, even at room temperature. Usually the radiationless population of the  $^1\text{D}_2$  level from the excited  $^3\text{P}_1$  states is preferred at this temperature. The luminescence from the  $^3\text{P}_0$  level is more intense compared to luminescence from the  $^1\text{P}_1$  level as its population takes place via the  $^3\text{P}_1$

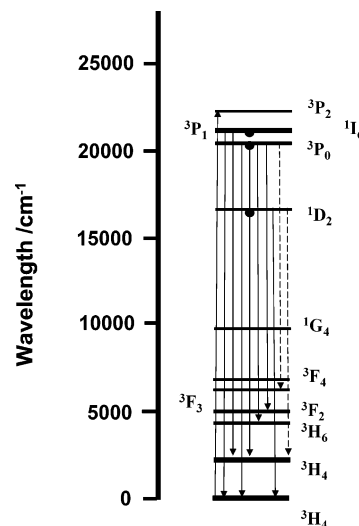
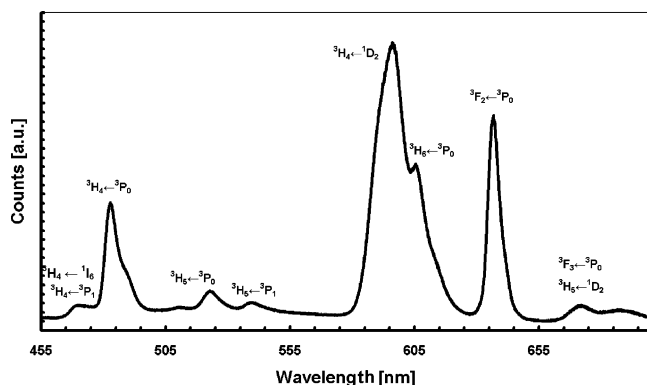
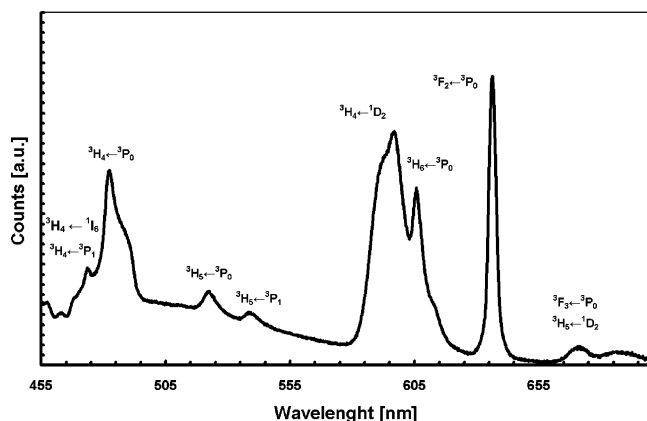


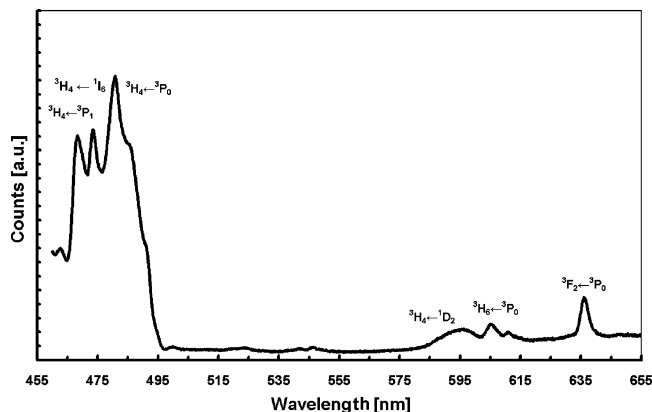
Figure 7. Schematic energy level diagram with the possible electronic transitions of  $4f^2$ -configured  $\text{Pr}^{3+}$ . Observed transitions are marked by arrows.



**Figure 8.** Emission spectrum of PrI<sub>3</sub> dissolved in [bmpyr][Tf<sub>2</sub>N] (recorded at room temperature) under <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> excitation (443 nm).



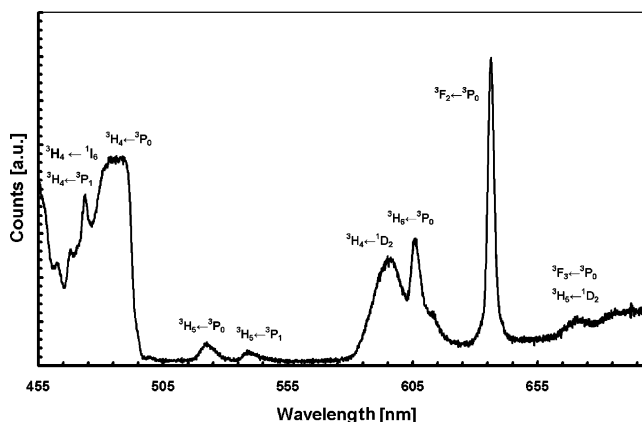
**Figure 9.** Emission spectrum of Pr(Tf<sub>2</sub>N)<sub>3</sub> dissolved in [bmpyr][Tf<sub>2</sub>N] (recorded at room temperature) under <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> excitation (443 nm).



**Figure 10.** Emission spectrum of solid [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] (recorded at room temperature) under <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> excitation (443 nm).

level by a strong radiationless relaxation.<sup>24</sup> This usually leads to total quenching of luminescence from the <sup>3</sup>P<sub>1</sub> level. Even under direct excitation into the <sup>3</sup>P<sub>1</sub> level often only luminescence from the <sup>3</sup>P<sub>0</sub> level is observed.<sup>25</sup> Thus, our system is representative for the comparatively rare case where luminescence from the <sup>3</sup>P<sub>1</sub> state is observed in the liquid state even at room temperature. In the case of Pr(Tf<sub>2</sub>N)<sub>3</sub> in [bmpyr][Tf<sub>2</sub>N] even the <sup>3</sup>H<sub>4</sub> ← <sup>3</sup>P<sub>1</sub> and <sup>3</sup>H<sub>4</sub> ← <sup>1</sup>I<sub>6</sub> transitions can be distinguished.

The emission spectra of the solid compounds [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N] (Figure 10) and [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] (Figure 11)



**Figure 11.** Emission spectrum of solid [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] (recorded at room temperature) under <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> excitation (443 nm).

show, as expected, weaker <sup>3</sup>H<sub>4</sub> ← <sup>1</sup>D<sub>2</sub> transitions than the solution. This is particularly observed in the iodine compound and can be attributed to the pure iodide surrounding of the rare earth cation and, thus, the absence of any low-frequency oscillator bonds in the surroundings of praseodymium. In this compound predominantly high energy transitions (<sup>3</sup>H<sub>4</sub> ← <sup>3</sup>P<sub>1</sub>, <sup>3</sup>H<sub>4</sub> ← <sup>1</sup>I<sub>6</sub>, <sup>3</sup>H<sub>4</sub> ← <sup>3</sup>P<sub>0</sub>) are observed. The emission spectrum of [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] shows broader lines which might be attributed to the lower site symmetry, and a stronger crystal field around Pr<sup>3+</sup> transitions almost exclusively transitions from the <sup>3</sup>P<sub>1</sub> levels. Aside from a reversed intensity distribution of the <sup>3</sup>H<sub>4</sub> ← <sup>3</sup>P<sub>0</sub> and <sup>3</sup>H<sub>4</sub> ← <sup>1</sup>D<sub>2</sub>, the spectrum of [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>] shows a close resemblance to the solution spectra. From this it can be derived that in solution the predominant Pr<sup>3+</sup> species is most probably the complex ion [Pr(Tf<sub>2</sub>N)<sub>5</sub>]<sup>2-</sup>.

#### 4. Conclusions

According to the reaction equation



PrI<sub>3</sub> dissolves in the ionic liquid [bmpyr][Tf<sub>2</sub>N]. Thereby, at least two different praseodymium species are formed. One contains praseodymium octahedrally coordinated by iodine anions, as established by the crystal structure analysis of [bmpyr]<sub>4</sub>[PrI<sub>6</sub>][Tf<sub>2</sub>N]. By reacting Pr(Tf<sub>2</sub>N)<sub>3</sub> with [bmpyr][Tf<sub>2</sub>N] we were able to obtain [bmpyr]<sub>2</sub>[Pr(Tf<sub>2</sub>N)<sub>5</sub>], which was structurally characterized. It shows Pr<sup>3+</sup> coordinated by nine oxygen atoms of five bis(trifluoromethanesulfonyl)-amide ligands in the form of a monocapped square antiprism. In consequence, the remaining praseodymium cations must be solvated by the anion of the ionic liquid.

All systems show strong transitions from the <sup>3</sup>P<sub>1</sub> levels which can be attributed to the absence of any low-frequency oscillators in the immediate neighborhood of the praseodymium cation. As expected for the solid compounds the intensities for the <sup>3</sup>H<sub>4</sub> ← <sup>3</sup>P<sub>0</sub> are enhanced compared to the <sup>3</sup>H<sub>4</sub> ← <sup>1</sup>D<sub>2</sub> transition. Our investigations show that ionic liquids are promising media to study the luminescent properties of rare earth cations in the liquid state as they generally far less quench the optical transition than conven-

(25) Boutinad, P.; Mahiou, R.; Martin, N.; Malinowski, M. *Luminescence* 1997, 72–74, 809–811.



tional solvents. This may open up the way to new liquid luminescent materials.

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**Supporting Information Available:** Further crystallographic information (CIF) and selected bond distances and angles (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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