

**Electronic Supplementary Information**

**Three novel anions based on pentafluorophenyl amine combined with two new synthetic strategies for the synthesis of highly lipophilic ionic liquids**

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**Materials and General Methods.** All reactions and manipulations were carried out under an atmosphere of purified argon using Schlenk techniques and an inert atmosphere glove box (MBraun MB 150 BG-I). All solvents were dried using standard procedures<sup>[1]</sup> stored and high-end dried by passing a stream via absorption columns filled with alumina/molecular sieve (3 Å)/R3-11G-catalyst (BASF AG).

NMR spectra were recorded at the following spectrometers:

- BRUKER ARX 200: <sup>1</sup>H(200.1 MHz), <sup>13</sup>C(50.3 MHz), <sup>19</sup>F(188.3 MHz), <sup>31</sup>P(81.0 MHz).
- BRUKER AC 300: <sup>1</sup>H(300.1 MHz), <sup>13</sup>C(75.5 MHz).
- BRUKER ARX 300: <sup>1</sup>H(300.1 MHz), <sup>13</sup>C(75.5 MHz), <sup>19</sup>F(282.4 MHz), <sup>31</sup>P(121.5 MHz).

Chemical shifts are referenced to the  $\delta$ -scale and spectra were recorded at 298 K. For the calibration residual proton respectively the carbon signals from the deuterated solvents were used:

<sup>1</sup>H-NMR: C<sub>6</sub>D<sub>6</sub> (7.15 ppm); D<sub>3</sub>CCN (1.94 ppm); d<sup>6</sup>-DMSO (2.50 ppm).

<sup>13</sup>C-NMR: C<sub>6</sub>D<sub>6</sub> (128.0 ppm); D<sub>3</sub>CCN (1.3 ppm); d<sup>6</sup>-DMSO (39.5 ppm).

Fluorine and phosphorous spectra were calibrated externally: <sup>19</sup>F: CFCl<sub>3</sub> (0 ppm); <sup>31</sup>P: 85% aqueous H<sub>3</sub>PO<sub>4</sub>-solution (0 ppm).

All non-proton nmr spectra were recorded broadband-<sup>1</sup>H-decoupled.

Coupling constants of the F-F-coupling in the C<sub>6</sub>F<sub>5</sub>-moieties are not listed since all signals are pseudo-multiplets originating from higher-order coupling. All *ortho*-F-atoms appear as pseudo duplets, the *meta*-F and *para*-F-atoms as pseudo triplets. All observed pseudo-coupling constants are in the range between 18 and 22 Hz.

Infrared spectra were recorded as KBr pellets with a BRUKER IFS 88 spectrometer or as nujol mulls between KBr plates using a NICOLET 510 M spectrometer.

EI mass spectra were recorded with a FINNIGAN MAT CH7-spectrometer with an electron energy of 70 eV.

ESI mass spectra were recorded on a FINNIGAN TSQ 700 spectrometer using acetonitrile as transport medium.

Elemental analyses were performed with a CHN-Rapid-Analyzer (Heraeus)

UV/Vis-spectra were recorded using a SHIMADZU UV-1601 PC spectrometer using 1 mm quartz-glass cuvettes.

Optical melting points were recorded with a BÜCHI MP-B-540 apparatus in sealed glass capillaries.

Thermogravimetric analyses were carried out with a METTLER Toledo TGA/SDTA 851<sup>e</sup> under a constant stream of nitrogen in alumina crucibles. Dynamic scanning calorimetry measurements were carried out with a METTLER Toledo DSC 821<sup>e</sup> under a constant stream of nitrogen in open aluminium crucibles.

All chemicals were purchased from the companies SIGMA-ALDRICH, ACROS or MERCK and purified according to standard procedures. The following substances were prepared according to literature procedures: BFPFA-H<sup>[iii]</sup>, 1,3-Diisopropylimidazoliumyliden<sup>[iii]</sup>, Bu<sub>3</sub>PCH<sub>2</sub><sup>[iv]</sup>

**X-ray crystal structure analyses:**

X-ray diffraction intensities were collected on a STOE IPDS-I and IPDS-III diffractometer systems using Mo-K<sub>α</sub>-radiations (0.71073 Å). The structures were solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full matrix least squares procedures on  $F_0^2$ . All non-hydrogen atoms were refined with anisotropic displacement coefficients. The H atoms were located from the difference map and refined isotropically. The following program packages were used: WinGX<sup>[v]</sup>, SIR-97<sup>[vi]</sup>, SHELXL-97<sup>[vii]</sup>.

**Synthesis of  $\text{HN}(\text{C}_6\text{F}_5)\text{SO}_2\text{CF}_3$  (PFTFSI-H):** A solution of 17.75 g (96.80 mmol) Sodium bistrimethylsilylamide in 100 ml of diethylether was cooled to  $-78\text{ }^\circ\text{C}$ . Then a solution of 8.86 g (48.34 mmol) 2,3,4,5,6-pentafluoroaniline in 20 ml diethylether was added. The resulting solution was brought to  $0\text{ }^\circ\text{C}$  and stirred at this temperature for 2 h. The reaction mixture was cooled again to  $-78\text{ }^\circ\text{C}$  and a precooled solution of 8.14 ml (48.34 mmol) triflic acid anhydride in 50 ml diethylether was added slowly to the reaction mixture via a cannula. The reaction mixture was slowly brought to room temperature and stirred for 12 hours. All volatiles were removed under reduced pressure at  $50\text{ }^\circ\text{C}$ . The colourless residue was suspended in 100 ml  $\text{CFCl}_3$  and the suspension is cooled to  $0\text{ }^\circ\text{C}$ . Then 15 ml of concentrated sulphuric acid is added and the mixture is refluxed for two additional hours. The phases were separated by decantation and the fluorous phase was stored at  $-30\text{ }^\circ\text{C}$  which leads to the formation of colourless crystals. The precipitate was separated from the solution, dried *in vacuo* and finally sublimed ( $90\text{ }^\circ\text{C}/10^{-2}\text{ mbar}$ ). This leads to a yield of 10.45 g PFTFSI-H (69%) as a white solid which melts at  $56\text{ }^\circ\text{C}$ .

**CHN-Analysis:** found (calculated): C: 26.21% (26.68%), H: 0.57% (0.32%), N: 4.37% (4.44%).

**IR:** (nujol):  $\tilde{\nu}/\text{cm}^{-1}$ : 631(m), 681(w), 895(s), 986(s), 1047(s), 1119(s), 1140 (w), 1159(w), 1180(s), 1205(s), 1287(s), 1317(m), 1502(m), 1520(m), 1649(w), 3219(br, N-H).

**EI-MS:**  $m/z = 315$  ( $\text{M}^+$ , 8%), 182 ( $\text{HNC}_6\text{F}_5^+$ , 92%), 155 ( $\text{C}_3\text{F}_5^+$ , 51%), 69 ( $\text{CF}_3^+$ , 100%)

**$^1\text{H-NMR}$**  ( $\text{d}^6$ -DMSO, 300 MHz):  $\delta = 12.33$  ppm (s, 1H, NH).

**$^{19}\text{F-NMR}$**  ( $\text{d}^6$ -DMSO, 282 MHz):  $\delta = -77.41$  ppm (s, 3H,  $\text{CF}_3$ ),  $-149.13$  ppm (d, 2H, *o*-F),  $-163.95$  ppm (t, 1H, *p*-F),  $-165.40$  ppm (t, 1H, *m*-F).

**Synthesis of  $\text{HN}(\text{C}_6\text{F}_5)\text{SO}_2\text{C}_4\text{F}_9$  (PFNFSI-H):** A solution of 17.15 g (93.53 mmol) sodium bistrimethylsilylamide in 100 ml of diethylether was cooled to  $-78\text{ }^\circ\text{C}$ . Then a solution of 8.56 g (46.77 mmol) 2,3,4,5,6-pentafluoroaniline in 20 ml diethylether was added. The resulting solution was brought to  $0\text{ }^\circ\text{C}$  and stirred at this temperature for 2 h. The reaction mixture was cooled again to  $-78\text{ }^\circ\text{C}$  and a precooled solution of 8.40 ml (46.77 mmol) nonafluorobutylsulfonylfluoride in 50 ml diethylether was added slowly to the reaction mixture via a cannula. The reaction mixture was slowly brought to room temperature and stirred for 12 hours. All volatiles were removed under reduced pressure at  $50\text{ }^\circ\text{C}$ . The colourless residue was suspended in 100 ml  $\text{CFCl}_3$  and the suspension is cooled to  $0\text{ }^\circ\text{C}$ . Then 15 ml of concentrated sulphuric acid is added and the mixture is refluxed for two additional

hours. The phases were separated by decantation and the fluorous phase was evaporated *in vacuo* to dryness and finally sublimed (100 °C/ 10<sup>-2</sup> mbar). This leads to a yield of 18.18 g PFNFSI-H (84%) as a white solid which melts at 73 °C.

**CHN-Analysis:** found (calculated): C: 25.00% (25.82%), H: 0.83% (0.22%), N: 4.69% (3.01%).

**IR:** cm<sup>-1</sup>: (nujol):  $\tilde{\nu}$ /cm<sup>-1</sup>: 625(m), 650(m), 681(w), 700(w), 735(m), 833(w), 893(s), 991(s), 1053(m), 1136(s), 1209(s), 1518(m), 1629(w), 3270(br, N-H).

**EI-MS:** m/z = 465(M<sup>+</sup>, 8%), 232(M<sup>2+</sup>, 8%), 182 (HNC<sub>6</sub>F<sub>5</sub><sup>+</sup>, 100%), 155 (C<sub>5</sub>F<sub>5</sub><sup>+</sup>, 30%), 69 (CF<sub>3</sub><sup>+</sup>, 52%).

**<sup>1</sup>H-NMR** (d<sup>6</sup>-DMSO, 300 MHz):  $\delta$  = 13.24 ppm (s, 1H, NH).

**<sup>19</sup>F-NMR** (d<sup>6</sup>-DMSO, 282 MHz):  $\delta$  = -80.53 ppm (t, 3F, CF<sub>3</sub>), -113.90 ppm (s, 2F, -CF<sub>2</sub>-CF<sub>3</sub>), -120.88 ppm (s, 2H, -CF<sub>2</sub>-), -125.88 ppm (t, 2F, -SO<sub>2</sub>-CF<sub>2</sub>), -148.80 ppm (d, 2F, *o*-F), -164.89 ppm (t, 1F, *m*-F), -165.83 ppm (*m*, 1F, *p*-F).

**Synthesis of 1-methyl-3-butylimidazoliumylidene:** In a 500 ml flask were placed 18.55 g (0.11 mol) 1-methyl-3-butylimidazolium chloride, 2.81 g (0.12 mol) potassium hydride and 0.60 g (5.31 mmol) potassium *tert*-butanolate. Subsequently 250 ml THF were added, and a gas evolution was observed immediately. The resulting slurry was stirred for 2 days at ambient temperature. Then the THF was removed *in vacuo* at room temperature. The resulting residue was heated to 120 °C and the product was condensed in a nitrogen cooled Schlenk tube at 10<sup>-2</sup> mbar. The product was collected as a colourless oil (yield 60-80%), that decomposes slowly at room temperature under inert gas. The substance was therefore stored at -80 °C as a solid.

**<sup>1</sup>H-NMR** (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta$  = 0.72 ppm (*t*, 3H, -CH<sub>3</sub>), 1.14 ppm (*sx*, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.58 ppm (*q*, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.44 ppm (*s*, 3H, N-CH<sub>3</sub>), 3.82 ppm (*t*, 2H, N-CH<sub>2</sub>), 6.64 ppm (*pd*, 2H, NCHCHN), 6.71 ppm (*s*, 1H, N<sub>2</sub>C-H).

**<sup>13</sup>C-NMR** (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta$  = 13.7 ppm (CH<sub>3</sub>), 19.9 ppm (N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 34.0 (N-CH<sub>2</sub>-CH<sub>2</sub>-), 37.5 ppm (N-CH<sub>3</sub>), 50.4 ppm (N-CH<sub>2</sub>-), 119.1 ppm (NCH), 119.8 ppm (NCH), 215.1 ppm (NCN).

**Synthesis of 1-methyl-3-butyl-2-methylenimidazoline:** In a 250 ml flask were placed 9.43 g (50.0 mmol) 1,2-dimethyl-3-butylimidazolium chloride, 2.20 g (55.0 mmol) potassium

hydride and 0.28 g (2.5 mmol) potassium *tert*-butanolate. Subsequently 100 ml THF were added, and a gas evolution was observed immediately. The resulting slurry was stirred for 2 days at ambient temperature. Then THF was removed *in vacuo* at room temperature. The resulting residue was heated to 120 °C and the product was condensed in a nitrogen cooled Schlenk tube at 10<sup>-2</sup> mbar. The product was collected as a colourless oil (yield 60-80%), that decomposes slowly at room temperature under inert gas. The substance was therefore stored at -80 °C as a solid.

**<sup>1</sup>H-NMR** (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta$  = 0.92 ppm (*t*, 3H, -CH<sub>3</sub>), 1.30 ppm (*sx*, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.60 ppm (*q*, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 2.74 ppm (*s*, 3H, N-CH<sub>3</sub>), 2.83 ppm (*s*, 2H, CCH<sub>2</sub>), 3.22 ppm (*t*, 2H, N-CH<sub>2</sub>), 5.77 ppm (*pd*, 2 H, NCHCHN).

**<sup>13</sup>C-NMR** (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta$  = 13.9 ppm (CH<sub>3</sub>), 20.2 ppm (N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 29.7 (N-CH<sub>2</sub>-CH<sub>2</sub>-), 32.5 ppm (N-CH<sub>3</sub>), 39.8 (CCH<sub>2</sub>), 45.8 ppm (N-CH<sub>2</sub>-), 112.1 ppm (NCH), 113.1 ppm (NCH), 152.0 ppm (NCN).

**Synthesis of [iPiPIM][BPFPA]:** A solution of 0.52 g (1.49 mmol) BPFPA-H in 20 ml diethylether was cooled to -78 °C. Then 0.25 ml (1.49 mmol) 1,3-diisopropylimidazoliumylidene was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resultant solution was evaporated to dryness and washed twice with 20 ml of hexane. The resultant white solid was dried *in vacuo* yielding a white solid which melts at 109 °C. X-ray quality crystals were obtained by recrystallisation from diethylether at -30 °C.

**CHN-Analysis:** found (calculated): C: 50.14% (50.31%), H: 3.43% (3.42%), N: 8.72% (8.38%).

**IR:** (nujol):  $\tilde{\nu}$  /cm<sup>-1</sup>: 556(w), 812(w), 883(w), 935(w), 967(m), 1017(m), 1263(w), 1303(m), 1596(w), 1636(w).

**<sup>1</sup>H-NMR** (D<sub>3</sub>CCN, 300 MHz):  $\delta$  = 0.83 ppm (*d*, 12 H, NCH(CH<sub>3</sub>)<sub>2</sub>), 3.90 ppm (*m*, 2 H, NCH), 5.85 ppm (*s*, 2 H, NCHCHN), 9.40 (*s*, 1 H, NCHN).

**<sup>13</sup>C-NMR** (D<sub>3</sub>CCN, 50 MHz):  $\delta$  = 21.9 ppm (NCH(CH<sub>3</sub>)<sub>2</sub>), 52.8 ppm (NCH(CH<sub>3</sub>)<sub>2</sub>), 118.4 ppm (NCHCHN), 138.0 ppm (NCN).

**<sup>19</sup>F-NMR** (D<sub>3</sub>CCN, 282 MHz):  $\delta$  = -183.35 ppm (*t*, 1 F, *p*-F), -169.80 ppm (2 F, *m*-F), -160.94 ppm (*d*, 2 F, *o*-F).

**Synthesis of [BMIM][BPFPA]:** A solution of 0.45 g (3.23 mmol) 1-methyl-3-butylimidazoliumylidene in 20 ml diethylether was cooled to -78 °C. Then 1.13 g (3.23 mmol) decafluorodiphenylamine dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was recrystallized from diethylether yielding 1.26 g (80%) of a bright yellow solid which melts at 77 °C.

**CHN-Analysis:** found (calculated): C: 49.08% (49.29%), H: 3.24% (3.10%), N: 8.72% (8.62%)

**IR:**  $\text{cm}^{-1}$ : (nujol):  $\tilde{\nu}/\text{cm}^{-1}$ : 413 (m), 430 (w), 448 (w), 465 (w), 561 (w), 623 (w), 644 (w), 723 (w), 741 (w), 889 (w), 970 (m), 1018 (m), 1096 (w), 1167 (w), 1200 (w), 1308 (w), 1464 (s), 1491 (m), 1508 (m), 1520 (m), 1570 (w), 1638 (w), 1655 (w), 2853 (w), 2959 (w).

**ESI-MS:** cation: 139.1 (100%) anion: 347.9 (100%).

**<sup>1</sup>H-NMR** (CD<sub>3</sub>CN, 300 MHz):  $\delta$  = 0.92 ppm (*t*, 3H, -CH<sub>3</sub>), 1.30 ppm (*sx*, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.78 ppm (*q*, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.80 ppm (*s*, 3H, N-CH<sub>3</sub>), 4.10 ppm (*t*, 2H, <sup>3</sup>*J* = 7.3 Hz, N-CH<sub>2</sub>), 7.34 ppm (*pd*, 2 H, NCHCHN), 8.51 ppm (*s*, 1H, N<sub>2</sub>C-H).

**<sup>13</sup>C-NMR** (CD<sub>3</sub>CN, 75 MHz):  $\delta$  = 13.6 ppm (CH<sub>3</sub>), 19.9 ppm (N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 32.6 ppm (N-CH<sub>2</sub>-CH<sub>2</sub>-), 36.7 ppm (N-CH<sub>3</sub>), 50.3 ppm (N-CH<sub>2</sub>-), 123.2 ppm (NCH), 124.6 ppm (NCH), 136.9 ppm (NCN)

**<sup>19</sup>F-NMR** (CD<sub>3</sub>CN, 282 MHz):  $\delta$  = -187.18 ppm (*m*, 1H, *p*-F), -171.95 ppm (*t*, 2H, *m*-F), -162.62 ppm (*dd*, 2H, *o*-F).

**Synthesis of [BMIM][PFTFSI]:** A solution of 0.27 g (1.93 mmol) 1-methyl-3-butylimidazoliumylidene in 15 ml diethylether was cooled to -78 °C. Then 0.61 g (1.93 mmol) PFTFSI-H dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was dissolved in acetonitrile. The solution was filtered over activated charcoal dried in vacuum and washed with hexane yielding 0.54 g (61%) of a colourless liquid.

**CHN-Analysis:** found (calculated): C: 39.81% (39.74%), H: 3.46% (3.33%), N: 9.46% (9.27%).

**ESI-MS:** cation: 139.1 (100%) anion: 314.0 (100%).

**IR** (substance):  $\tilde{\nu}$  /cm<sup>-1</sup>: 603(m), 625(m), 892(m), 987(s), 1040(s), 1125(m), 1168(s), 1203(s), 1297(s), 1460(w), 1511(s), 1573(w), 2879(w), 2966(w), 3153(w).

**<sup>1</sup>H-NMR** (CD<sub>3</sub>CN, 300 MHz):  $\delta$  = 0.92 ppm (*t*, 3H, -CH<sub>3</sub>), 1.31 ppm (*sx*, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.79 ppm (*q*, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.82 ppm (*s*, 3H, N-CH<sub>3</sub>), 4.12 ppm (*t*, 2H, <sup>3</sup>*J* = 7.3 Hz, N-CH<sub>2</sub>), 7.36 ppm (*pd*, 2 H, NCHCHN), 8.51 ppm (*s*, 1H, N<sub>2</sub>C-H).

**<sup>13</sup>C-NMR** (CD<sub>3</sub>CN, 75 MHz):  $\delta$  = 13.6 ppm (CH<sub>3</sub>), 19.9 ppm (N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 32.6 ppm (N-CH<sub>2</sub>-CH<sub>2</sub>-), 36.8 ppm (N-CH<sub>3</sub>), 50.3 ppm (N-CH<sub>2</sub>-), 123.3 ppm (NCH), 124.6 ppm (NCH), 137.0 ppm (NCN).

**<sup>19</sup>F-NMR** (CD<sub>3</sub>CN, 188 MHz):  $\delta$  = -78.93 ppm (*s*, 3H, CF<sub>3</sub>), -152.15 ppm (*d*, 2H, *o*-F), -168.51 ppm (*t*, 1H, *m*-F), -170.00 ppm (*t*, 1H, *p*-F).

**Synthesis of [BMIM][PFNFSI]:** A solution of 0.74 g (5.36 mmol) 1-methyl-3-butyylimidazoliumylidene in 15 ml diethylether was cooled to -78 °C. Then 2.50 g (5.36 mmol) PFNFSI-H dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was dissolved in acetonitrile. The solution was filtered over activated charcoal dried in vacuum and washed with hexane yielding 0.50 g (29%) of a colourless liquid.

**CHN-Analysis:** found (calculated): C: 35.78% (35.81%), H: 2.49% (2.59%), N: 7.15% (6.97%).

**IR** (substance):  $\tilde{\nu}$  /cm<sup>-1</sup>: 446 (w), 467 (w), 490 (m), 525 (s), 586 (s), 619 (s), 646 (m), 683 (w), 698 (m), 731 (s), 748 (s), 781 (s), 797 (m), 828 (m), 862 (m), 895 (s), 986 (s), 1007 (s), 1024 (s), 1047 (s), 1134 (s), 1152 (s), 1171 (w), 1206 (s), 1302 (s), 1350 (s), 1385 (m), 1433 (m), 1460 (s), 1510 (s), 1574 (m), 1626 (m), 2882 (m), 2942 (m), 2969 (s), 3117 (m), 3154 (m).

**ESI-MS:** cation: 139.0 (100%) anion: 464.0 (100%).

**<sup>1</sup>H-NMR** (CD<sub>3</sub>CN, 300 MHz):  $\delta$  = 0.93 ppm (*t*, 3H, -CH<sub>3</sub>), 1.31 ppm (*sx*, 2H, CH<sub>2</sub>-CH<sub>3</sub>), 1.79 ppm (*q*, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.81 ppm (*s*, 3H, N-CH<sub>3</sub>), 4.11 ppm (*t*, 2H, N-CH<sub>2</sub>), 7.35 ppm (*pd*, 2 H, NCHCHN), 8.44 ppm (*s*, 1H, N<sub>2</sub>C-H).

**<sup>13</sup>C-NMR** (CD<sub>3</sub>CN, 75 MHz):  $\delta$  = 13.6 ppm (CH<sub>3</sub>), 19.9 ppm (N-(CH<sub>2</sub>)<sub>2</sub>-CH<sub>2</sub>-), 32.6 ppm (N-CH<sub>2</sub>-CH<sub>2</sub>-), 36.8 ppm (N-CH<sub>3</sub>), 50.3 ppm (N-CH<sub>2</sub>-), 123.3 ppm (NCH), 124.6 ppm (NCH), 137.0 ppm (NCN).



**<sup>19</sup>F-NMR** (CD<sub>3</sub>CN, 282 MHz):  $\delta$  = 81.70 ppm (t, 3H, CF<sub>3</sub>), -114.81 ppm (s, 2H, -CF<sub>2</sub>-CF<sub>3</sub>), -121.56 ppm (s, 2H, -CF<sub>2</sub>-), -126.62 ppm (t, 2F, -SO<sub>2</sub>-CF<sub>2</sub>), -151.51 ppm (d, 2F, *o*-F), -168.79 ppm (t, 2F, *m*-F), -170.19 ppm (*m*, 1F, *p*-F).

**Synthesis of [BMMIM][BPFPA]:** A solution of 2.32 g (15.27 mmol) 1-methyl-3-butyl-2-methylenimidazoline in 15 ml diethylether was cooled to -78 °C. Then 5.33 g (15.27 mmol) decafluorodiphenylamine dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was crystallized from diethylether yielding 4.44 g (58%) of a colourless solid which melts at 46 °C. X-ray quality crystals were obtained by recrystallisation from diethylether at -30 °C.

**CHN-Analysis:** found (calculated): C: 50.80% (50.31%), H: 3.84% (3.42%), N: 8.48% (8.38%)

**IR:** cm<sup>-1</sup>: (nujol):  $\tilde{\nu}$ /cm<sup>-1</sup>: 561(m), 642(w), 706(m), 723(m), 758(m), 774(m), 816(m), 970(s), 997(s), 1109(w), 1138(m), 1196(m), 1275(s), 1346(m), 1508(m), 1561(m), 1636(m) 1780(w)

**ESI-MS:** cation: 153.1 (100%) anion: 348.0 (100%).

**<sup>1</sup>H-NMR** (D<sub>3</sub>CCN, 300 MHz):  $\delta$  = 0.83 ppm (t, 3 H, CH<sub>2</sub>CH<sub>3</sub>), 1.22 ppm (sext, 2 H, CH<sub>2</sub>CH<sub>3</sub>), 1.62 ppm (quin, 2 H, NCH<sub>2</sub>CH<sub>2</sub>), 2.39 ppm (s, 3 H, NCH<sub>3</sub>), 3.59 ppm (s, 3 H, CCH<sub>3</sub>), 3.92 ppm (t, 2H, NCH<sub>2</sub>), 7.18 ppm (pd, 2 H, NCHCHN).

**<sup>13</sup>C-NMR** (D<sub>3</sub>CCN, 75 MHz):  $\delta$ /ppm = 7.9 ppm (CCH<sub>3</sub>), 13.1 ppm (CH<sub>2</sub>CH<sub>3</sub>), 19.5 ppm (CH<sub>2</sub>CH<sub>3</sub>), 31.3 ppm (NCH<sub>2</sub>CH<sub>2</sub>), 33.9 ppm (NCH<sub>3</sub>), 48.0 ppm (NCH<sub>2</sub>), 120.6 ppm (NCH), 122.3 ppm (NCH), 142.8 ppm (NCN).

**<sup>19</sup>F-NMR** (D<sub>3</sub>CCN, 282 MHz):  $\delta$  = -187.32 ppm (m, 1 F, *p*-F), -171.96 ppm (m, 2 F, *m*-F), -162.68 ppm (m, 2 F, *o*-F).

**Synthesis of [BMMIM][PFTFSI]:** A solution of 0.41 g (2.71 mmol) 1-methyl-3-butyl-2-methylenimidazoline in 15 ml diethylether was cooled to -78 °C. Then 0.85 g (2.71 mmol) PFTFSI-H dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was dissolved was washed with pentane yielding 0.85 g (67%) bright yellow liquid.

**CHN-Analysis:** found (calculated): C: 40.93% (41.12%), H: 3.70% (3.67%), N: 9.28% (8.99%).

**IR:**  $\text{cm}^{-1}$ : (substance):  $\tilde{\nu}/\text{cm}^{-1}$ : 603(w), 625(w), 891(m), 986(m), 1039(s), 1125(m), 1155(m), 1202(s), 1296(s), 1459(w), 1499(s), 1510(s), 1590(w), 2966(w)

**ESI-MS:** cation: 153.0 (100%) anion: 314.0 (100%).

**$^1\text{H-NMR}$**  ( $\text{D}_3\text{CCN}$ , 200 MHz):  $\delta$  = 0.93 ppm (t, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.33 ppm (sext, 2 H,  $\text{CH}_2\text{CH}_3$ ), 1.73 ppm (q, 2 H,  $\text{NCH}_2\text{CH}_2$ ), 2.49 ppm (s, 3 H,  $\text{NCH}_3$ ), 3.69 ppm (s, 3 H,  $\text{CCH}_3$ ), 4.02 ppm (t, 2H,  $\text{NCH}_2$ ), 7.25 ppm (pd, 2 H,  $\text{NCHCHN}$ ).

**$^{13}\text{C-NMR}$**  ( $\text{D}_3\text{CCN}$ , 75 MHz):  $\delta/\text{ppm}$  = 10.0 ppm ( $\text{CCH}_3$ ), 13.6 ppm ( $\text{CH}_2\text{CH}_3$ ), 20.0 ppm ( $\text{CH}_2\text{CH}_3$ ), 32.2 ppm ( $\text{NCH}_2\text{CH}_2$ ), 35.6 ppm ( $\text{NCH}_3$ ), 48.9 ppm ( $\text{NCH}_2$ ), 121.7 ppm ( $\text{NCH}$ ), 123.2 ppm ( $\text{NCH}$ ).

**$^{19}\text{F-NMR}$**  ( $\text{D}_3\text{CCN}$ , 188 MHz):  $\delta$  = -171.92 ppm (t, 1 F, *p*-F), -170.41 ppm (2 F, *m*-F), -153.92 ppm (d, 2 F, *o*-F), -80.71 ppm (s, 3 F,  $\text{CF}_3$ ).

**Synthesis of [BMMIM][PFNFSI]:** A solution of 1.13 g (7.42 mmol) 1-methyl-3-butyl-2-methylenimidazoline in 15 ml diethylether was cooled to  $-78^\circ\text{C}$ . Then 3.45 g (7.42 mmol) PFNFSI-H dissolved in 10 ml diethylether was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was evaporated to dryness and the residue was dissolved was washed with pentane yielding 2.79 g (61%) of a yellow solid which melts at  $46^\circ\text{C}$ .

**CHN-Analysis:** found (calculated): C: 36.62% (36.96%), H: 2.88% (2.78%), N: 6.88% (6.81%).

**IR:**  $\text{cm}^{-1}$ : (substance):  $\tilde{\nu}/\text{cm}^{-1}$ : 586 (m), 733(m), 863(m), 891(m), 982(s), 1023(w), 1054(m), 1132(m), 1149(m), 1224(m), 1299(m), 1350(w), 1459(w), 1498(m), 1513(m), 2968(w).

**ESI-MS:** 2\*cation+anion: 770.2 (100%) anion: 463.9 (100%).

**$^1\text{H-NMR}$**  ( $\text{D}_3\text{CCN}$ , 300 MHz):  $\delta$  = 0.93 ppm (t, 3 H,  $\text{CH}_2\text{CH}_3$ ), 1.33 ppm (sext, 2 H,  $\text{CH}_2\text{CH}_3$ ), 1.72 ppm (q, 2 H,  $\text{NCH}_2\text{CH}_2$ ), 2.49 ppm (s, 3 H,  $\text{NCH}_3$ ), 3.68 ppm (s, 3 H,  $\text{CCH}_3$ ), 4.02 ppm (t, 2H,  $\text{NCH}_2$ ), 7.24 ppm (pd, 2 H,  $\text{NCHCHN}$ ).

**$^{13}\text{C-NMR}$**  ( $\text{D}_3\text{CCN}$ , 75 MHz):  $\delta/\text{ppm}$  = 10.0 ( $\text{CCH}_3$ ), 13.6 ( $\text{CH}_2\text{CH}_3$ ), 20.0 ( $\text{CH}_2\text{CH}_3$ ), 32.2 ( $\text{NCH}_2\text{CH}_2$ ), 35.6 ( $\text{NCH}_3$ ), 48.9 ( $\text{NCH}_2$ ), 121.7 ( $\text{NCH}$ ), 123.1 ( $\text{NCH}$ ).

**$^{19}\text{F-NMR}$**  ( $\text{D}_3\text{CCN}$ , 282 MHz):  $\delta$  = -170.28 ppm (t, 1 F, *p*-F), -168.76 ppm (2 F, *m*-F), -151.52 ppm (d, 2 F, *o*-F), -126.63 (t, 2 F,  $\text{SO}_2\text{CF}_2$ ), -121.58 (t, 2 F,  $\text{SO}_2\text{CF}_2\text{CF}_2$ ), -114.82 (t, 2 F,  $\text{F}_3\text{CCF}_2$ ), -81.71 (t, 3 F,  $\text{CF}_3$ ).

**Synthesis of [Bu<sub>3</sub>PMe][BPFPA]:** A solution of 1.25 g (3.58 mmol) BPFPA-H in 20 ml Diethylether was cooled to -78 °C. Then 0.77 g (3.58 mmol) tri-n-butylmethylidenphosphorane was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. The resulting solution was brought to dryness and the residue was recrystallized from diethylether yielding 1.06 g (52%) of a colourless solid which melts at 66 °C.

**CHN-Analysis:** found (calculated): C: 52.73% (53.10%), H: 5.10% (5.35%), N: 2.43% (2.48%).

**IR:** cm<sup>-1</sup>: (nujol):  $\tilde{\nu}$ /cm<sup>-1</sup>: 559(w), 644(w), 706(m), 815(m), 937(m), 1000(m), 1018(m), 1099(w), 1200(w), 1307(m), 1493(s), 1636(w), 2965(m).

**ESI-MS:** cation: 217.2 (100%) anion: 347.9 (100%).

**<sup>1</sup>H-NMR** (D<sub>3</sub>CCN, 300 MHz):  $\delta$  = 0.93 ppm (t, 9 H, CH<sub>3</sub>), 1.35 - 1.55 ppm (br m, 12 H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.67 ppm (d, <sup>2</sup>J<sub>P-H</sub> = 13.41 Hz, 3 H, PCH<sub>3</sub>), 2.04 (br m, 6 H, PCH<sub>2</sub>).

**<sup>13</sup>C-NMR** (D<sub>3</sub>CCN, 75 MHz) :  $\delta$  = 4.4 ppm (d, <sup>1</sup>J<sub>C-P</sub> = 52.27 Hz, 1 C, PCH<sub>3</sub>), 13.5 ppm (s, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 20.5 ppm (d, <sup>2</sup>J<sub>C-P</sub> = 49.52 Hz, 3 C, PCH<sub>2</sub>), 23.9 ppm (d, <sup>4</sup>J<sub>C-P</sub> = 4.40 Hz, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 24.5 ppm (d, <sup>3</sup>J<sub>C-P</sub> = 15.96 Hz, 3 C, PCH<sub>2</sub>CH<sub>2</sub>).

**<sup>19</sup>F-NMR** (D<sub>3</sub>CCN, 282 MHz):  $\delta$  = -186.60 ppm (t, 1 F, *p*-F), -171.81 ppm (2 F, *m*-F), -162.35 ppm (d, 2 F, *o*-F).

**<sup>31</sup>P-NMR** (D<sub>3</sub>CCN, 121 MHz):  $\delta$  = 31.90 ppm.

**Synthesis of [Bu<sub>3</sub>PMe][PFTFSI]:** A solution of 0.87 g (2.77 mmol) PFTFSI-H in 20 ml diethylether was cooled to -78 °C. Then 0.60 ml (2.77 mmol) tri-n-butylmethylidenphosphorane was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. All volatiles were removed in vacuo and the residue was washed with hexane. After drying 1.07 g (77%) of a colourless oil which solidifies at 21 °C was obtained.

**CHN-Analysis:** found (calculated): C: 45.03% (45.20%), H: 5.38% (5.69%), N: 2.63% (2.64%)

**IR:** cm<sup>-1</sup>: (nujol):  $\tilde{\nu}$ /cm<sup>-1</sup>: 603(m), 625(m), 890(m), 987(m), 1039(s), 1125(m), 1161(m), 1202(s), 1297(s), 1384(w), 1460(m), 1509(s), 2877(w), 2938(m), 2965(m).

**ESI-MS:** cation: 217.2 (100%) anion: 314.0 (100%).

**<sup>1</sup>H-NMR** (D<sub>3</sub>CCN, 300 MHz):  $\delta$  = 0.95 ppm (t, 9 H, CH<sub>3</sub>), 1.35 - 1.59 ppm (br m, 12 H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.71 ppm (d, <sup>2</sup>J<sub>P-H</sub> = 13.22 Hz, 3 H, PCH<sub>3</sub>), 2.09 (br m, 6 H, PCH<sub>2</sub>).

**<sup>13</sup>C-NMR** (D<sub>3</sub>CCN, 75 MHz) :  $\delta$  = 4.4 ppm (d, <sup>1</sup>J<sub>C-P</sub> = 52.82 Hz, 1 C, PCH<sub>3</sub>), 13.5 ppm (s, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 20.5 ppm (d, <sup>2</sup>J<sub>C-P</sub> = 49.52 Hz, 3 C, PCH<sub>2</sub>), 23.9 ppm (d, <sup>4</sup>J<sub>C-P</sub> = 4.40 Hz, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 24.4 ppm (d, <sup>3</sup>J<sub>C-P</sub> = 15.96 Hz, 3 C, PCH<sub>2</sub>CH<sub>2</sub>).

**<sup>19</sup>F-NMR** (CD<sub>3</sub>CN, 188 MHz):  $\delta$  = -78.87 ppm (s, 3H, CF<sub>3</sub>), -152.00 ppm (d, 2H, *o*-F), -168.63 ppm (t, 1H, *m*-F), -170.14 ppm (t, 1H, *p*-F).

**<sup>31</sup>P-NMR** (D<sub>3</sub>CCN, 121 MHz):  $\delta$  = 31.92 ppm.

**Synthesis of [Bu<sub>3</sub>PMe][PFNFSI]:** A solution of 1.29 g (2.77 mmol) PFNFSI-H in 20 ml Diethylether was cooled to -78 °C. Then 0.60 ml (2.77 mmol) tri-n-butylmethylidenphosphorane was added via a syringe. The resulting mixture was slowly brought to room temperature and stirred overnight. All volatiles were removed in vacuo and the residue was washed with hexane. After drying 1.46 g (77%) of a colourless oil.

**CHN-Analysis:** found (calculated): C: 37.89% (40.54%), H: 4.50% (4.44%), N: 2.09% (2.06%)

**IR:** cm<sup>-1</sup>: (nujol):  $\tilde{\nu}$ /cm<sup>-1</sup>: 587(m), 618(w), 893(m), 985(s), 1047(s), 1134(m), 1151(s), 1212(s), 1299(s), 1350(m), 1460(m), 1510(s), 2878(w), 2939(m), 2967(m).

**ESI-MS:** cation: 217.2 (100%) anion: 464.1 (100%).

**<sup>1</sup>H-NMR** (D<sub>3</sub>CCN, 300 MHz):  $\delta$  = 0.94 ppm (t, 9 H, CH<sub>3</sub>), 1.30 - 1.60 ppm (br m, 12 H, PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.69 ppm (d, <sup>2</sup>J<sub>P-H</sub> = 13.40 Hz, 3 H, PCH<sub>3</sub>), 1.97-2.20 ppm (br m, 6 H, PCH<sub>2</sub>).

**<sup>13</sup>C-NMR** (D<sub>3</sub>CCN, 75 MHz) :  $\delta$  = 4.4 ppm (d, <sup>1</sup>J<sub>C-P</sub> = 52.82 Hz, 1 C, PCH<sub>3</sub>), 13.5 ppm (s, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 20.5 ppm (d, <sup>2</sup>J<sub>C-P</sub> = 49.52 Hz, 3 C, PCH<sub>2</sub>), 23.8 ppm (d, <sup>4</sup>J<sub>C-P</sub> = 4.40 Hz, 3 C, CH<sub>2</sub>CH<sub>3</sub>), 24.4 ppm (d, <sup>3</sup>J<sub>C-P</sub> = 15.96 Hz, 3 C, PCH<sub>2</sub>CH<sub>2</sub>).

**<sup>19</sup>F-NMR** (CD<sub>3</sub>CN, 282 MHz):  $\delta$  = 81.70 ppm (t, 3H, CF<sub>3</sub>), -114.72 ppm (s, 2H, -CF<sub>2</sub>-CF<sub>3</sub>), -121.53 ppm (s, 2H, -CF<sub>2</sub>-), -126.60 ppm (t, 2F, -SO<sub>2</sub>-CF<sub>2</sub>), -151.30 ppm (d, 2F, *o*-F), -168.65 ppm (t, 2F, *m*-F), -169.90 ppm (*m*, 1F, *p*-F).

**<sup>31</sup>P-NMR** (D<sub>3</sub>CCN, 121 MHz):  $\delta$  = 31.93 ppm.

**Crystal data for [iPiPIM][BPFPA]**

Habitus, colour	prism, colourless	
Crystal size	0.42 x 0.15 x 0.12 mm <sup>3</sup>	
Crystal system	Monoclinic	
Space group	C 2/c	Z = 4
Unit cell dimensions	a = 14.1670(16) Å	α = 90°.
	b = 11.0290(10) Å	β = 91.0680(10)°.
	c = 13.6160(14) Å	γ = 90°.
Volume	2127.1(4) Å <sup>3</sup>	
Cell determination	8436 peaks with Theta 1.5 to 27.1°.	
Empirical formula	C <sub>21</sub> H <sub>17</sub> F <sub>10</sub> N <sub>3</sub>	
Formula weight	501.38	
Density (calculated)	1.566 mg/m <sup>3</sup>	
Absorption coefficient	0.155 mm <sup>-1</sup>	
F(000)	1016	

## Data collection:

Diffractometer type	IPDS2
Wavelength	0.71069 Å
Temperature	293(2) K
Theta range for data collection	2.34 to 26.76°.
Index ranges	-17<=h<=17, -13<=k<=13, -17<=l<=17
Data collection software	STOE WinXpose (X-Area)
Cell refinement software	STOE WinCell (X-Area)
Data reduction software	STOE WinIntegrate (X-Area)

## Solution and refinement:

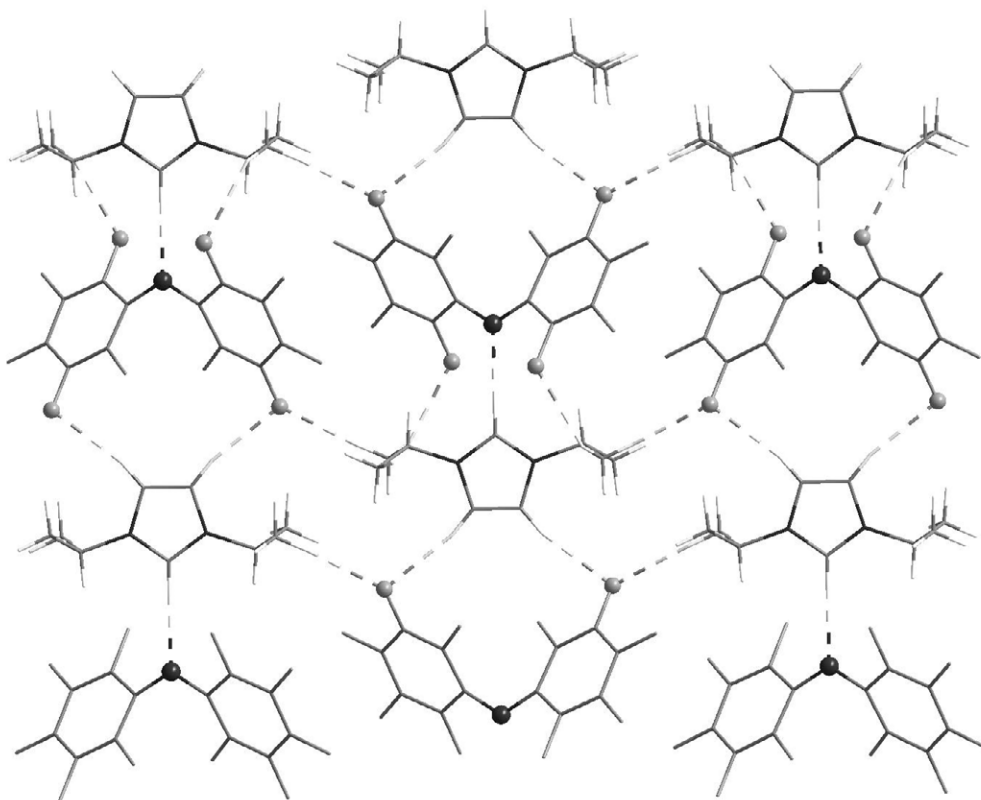
Reflections collected	10551
Independent reflections	2269 [R(int) = 0.0338]
Completeness to theta = 25.00°	100.0 %
Observed reflections	1627 [I > 2sigma(I)]
Reflections used for refinement	2269
Extinction coefficient	X = 0.0051(8)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9961 and 0.9401
Largest diff. peak and hole	0.208 and -0.231 e·Å <sup>-3</sup>
Solution	direct/ difmap
Refinement	Full-matrix least-squares on F <sup>2</sup>
Treatment of hydrogen atoms	geom, mixed
Programs used	SIR97 ( <i>Giacovazzo et al.</i> , 1997)
	SHELXL-97 ( <i>Sheldrick</i> , 1997)
	Diamond 3.1, STOE IPDS2 software
Data / restraints / parameters	2269 / 0 / 190
Goodness-of-fit on F <sup>2</sup>	1.032
R index (all data)	wR2 = 0.1020
R index conventional [I > 2sigma(I)]	R1 = 0.0355

N1-C1	1.363(2)	C13-N11	1.328(2)
N1-C13	3.122(3)	C14-N11	1.373(2)
C13-H1	0.92(2)	F2'-H2	2.48(2)
N1-H1	2.20(2)	F2''-H6	2.58(2)
		F5-H5	2.63(2)

Selected bond lengths of [*i*PiPIM][BPFPA] in Å.

C1-N1-C1	121.7(2)	N11-C13-N11'	108.7(2)
C13-N11-C14	108.3(1)	C14-C14-N11	107.3(1)
C13-H1-N1	180.0	C14-H2-F2'	167.2(15)
C10-H6-F2''	164.6(17)	C10-H5-F5	125.2(14)

Selected bond angles of [*i*PiPIM][BPFPA] in °.



Depiction of a layer of [*i*PiPIM][BPFPA]. Hydrogen-bridge-bonds are shown as dashed lines, heteroatoms incorporated in hydrogen-bridge-bonds are highlighted as solid balls.

**Crystal data for [BMMIM][BPFPA]**

Habitus, colour	block, colourless
Crystal size	0.39 x 0.36 x 0.15 mm <sup>3</sup>
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	Z = 2
	a = 9.8625(11) Å
	α = 81.843(13)°
	b = 10.3192(12) Å
	β = 80.651(13)°
	c = 10.8965(12) Å
	γ = 75.228(13)°
Volume	1052.2(2) Å <sup>3</sup>
Cell determination	8000 peaks with Theta 2.1 to 26°.
Empirical formula	C <sub>21</sub> H <sub>17</sub> F <sub>10</sub> N <sub>3</sub>
Formula weight	501.38
Density (calculated)	1.583 mg/m <sup>3</sup>
Absorption coefficient	0.157 mm <sup>-1</sup>
F(000)	508

## Data collection:

Diffractometer type	IPDS1
Wavelength	0.71073 Å
Temperature	466(2) K
Theta range for data collection	2.05 to 26.01°.
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12
Data collection software	STOE Expose
Cell refinement software	STOE Cell
Data reduction software	STOE Integrate

## Solution and refinement:

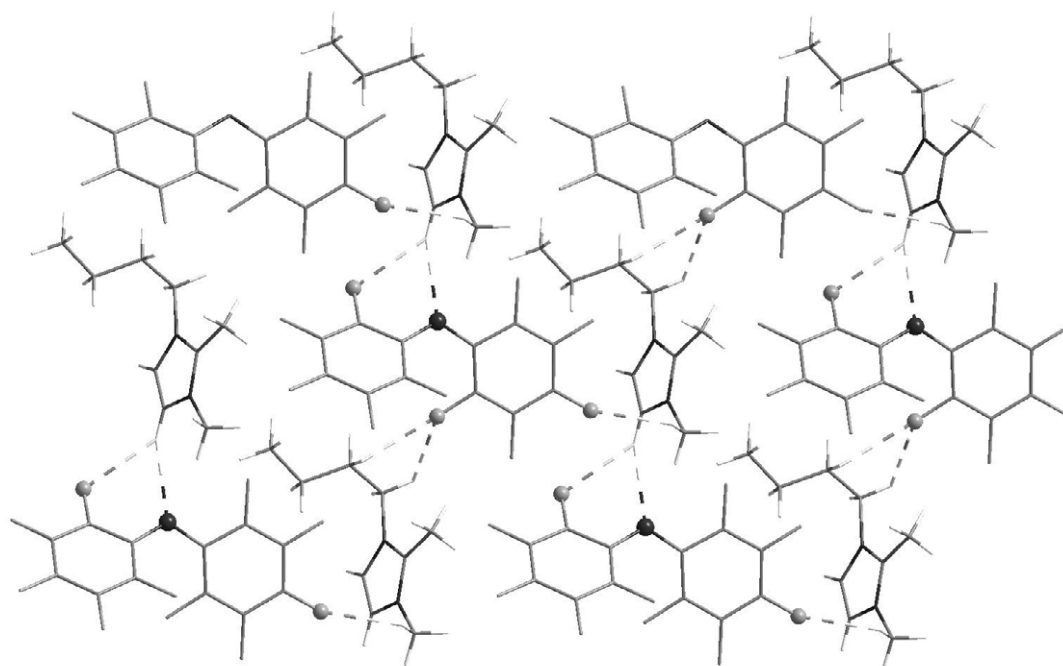
Reflections collected	10424
Independent reflections	3839 [R(int) = 0.0573]
Completeness to theta = 25.00°	93.5 %
Observed reflections	3077 [I > 2σ(I)]
Reflections used for refinement	3839
Absorption correction	Semi-empirical from equivalent
Max. and min. transmission	0.9768 and 0.9413
Largest diff. peak and hole	0.196 and -0.163 e·Å <sup>-3</sup>
Solution	direct/ difmap
Refinement	Full-matrix least-squares on F <sup>2</sup>
Treatment of hydrogen atoms	geom, mixed
Programs used	SIR97 ( <i>Giacovazzo et al.</i> , 1997) SHELXL-97 ( <i>Sheldrick</i> , 1997) Diamond 3.1, STOE IPDS1 software
Data / restraints / parameters	3839 / 0 / 375
Goodness-of-fit on F <sup>2</sup>	1.037
R index (all data)	wR2 = 0.0984
R index conventional [I > 2σ(I)]	R1 = 0.0345

C1-N1	1.377(2)	C7-N1	1.359(2)
C13-N2	1.337(2)	C13-N3	1.332(2)
C14-H2	0.94(2)	C16-H6	0.99(2)
C18-H9	0.99(2)	C19-H11	1.04(2)
N1-H2	2.48(2)	F1-H2	2.64(2)
F8'-H6	2.47(2)	F10''-H9	2.65(2)
F10''-H11	2.59(2)		

Selected bond lengths of [BMMIM][BPFPA] in Å.

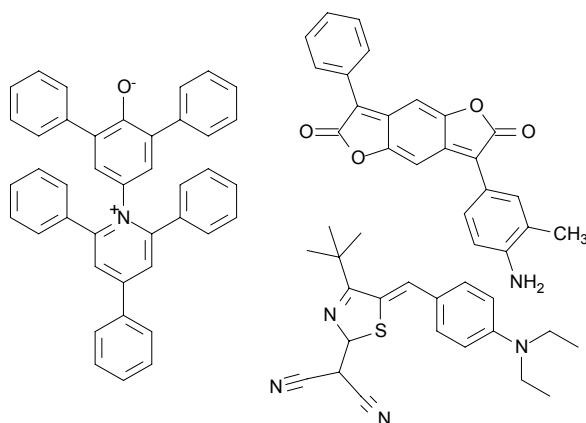
N1-C1-C2	118.6(1)	C11-C12-C7	124.3(1)
C13-N2-C14	109.5(1)	C14-H2-N1	157.0(14)
C14-H2-F1	137.8(13)	C16-H6-F8	111.4(12)
C18-H9-F10	123.5(12)	C19-H11-F10	110.5(12)

Selected bond angles of [BMMIM][BPFPA] in °.

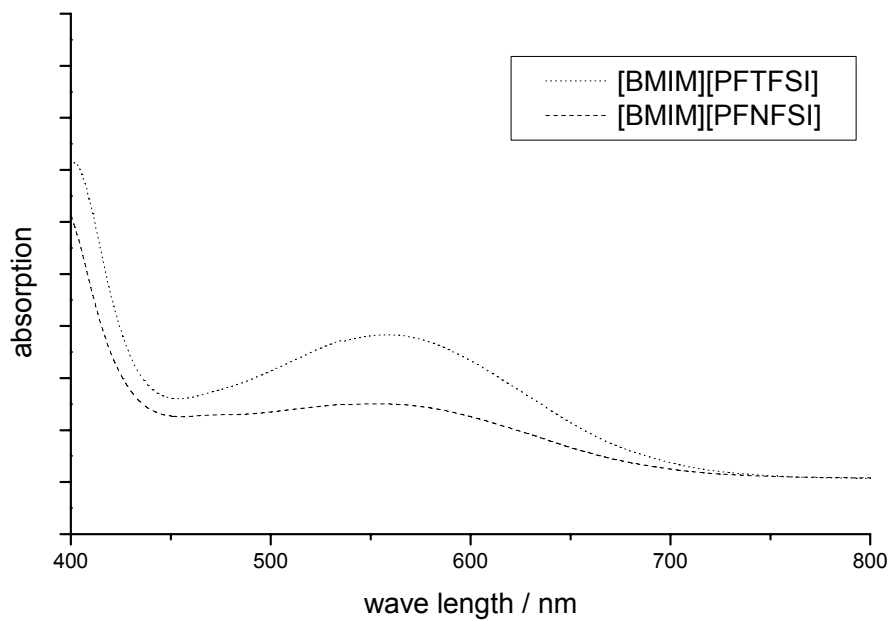


Depiction of a layer of [BMMIM][BPFPA]. Hydrogen-bridge-bonds are shown as dashed lines, heteroatoms incorporated in hydrogen-bridge-bonds are highlighted as solid balls.

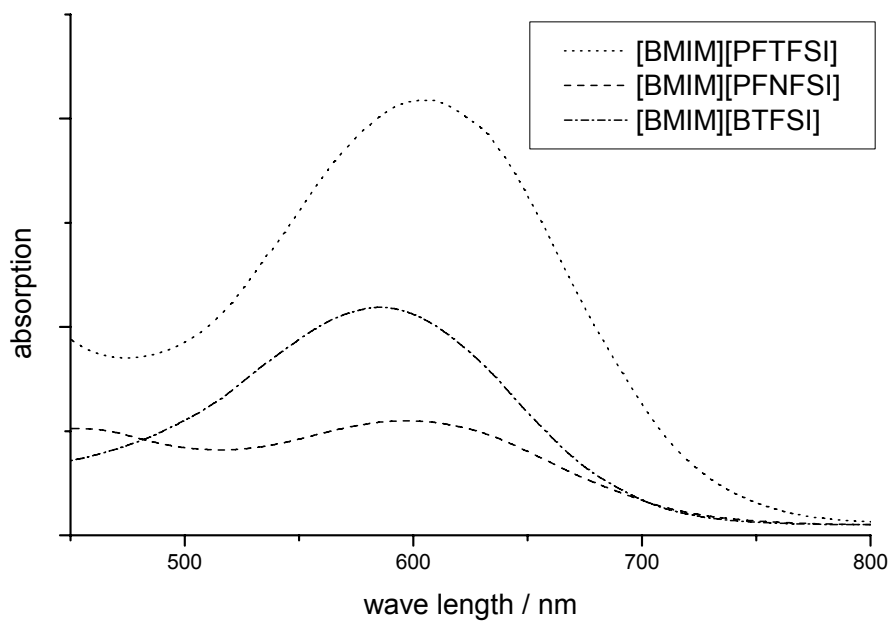




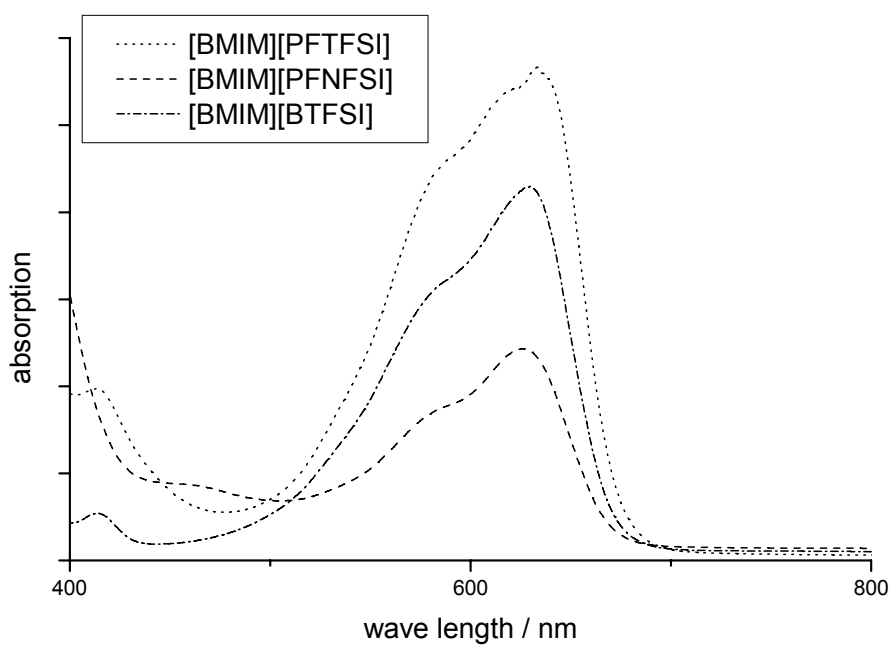
Solvatochromic dyes: Reichardt's dye (left), Spange's dyes for the determination of  $\beta$  (upper right, dye 1) and  $\pi^*$  (lower right, dye 2).



UV/VIS-spectra of [BMIM][PFTFSI] and [BMIM][PFNFSI] with *Reichardt's* dye.



UV/VIS spectra of [BMIM][PFTFSI], [BMIM][PFNFSI] und [BMIM][BTFSI] with *Spanges dye 1*.



UV/VIS spectra of [BMIM][PFTFSI], [BMIM][PFNFSI] und [BMIM][BTFSI] with *Spanges dye 2*.

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- [<sup>v</sup>] WinGX - Ver. 1.70.01, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data, L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837-838.
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