Electronic Supplementary Material for CrystEngComm

In situ crystallization of ionic liquids with melting points below -25 ^{o}C

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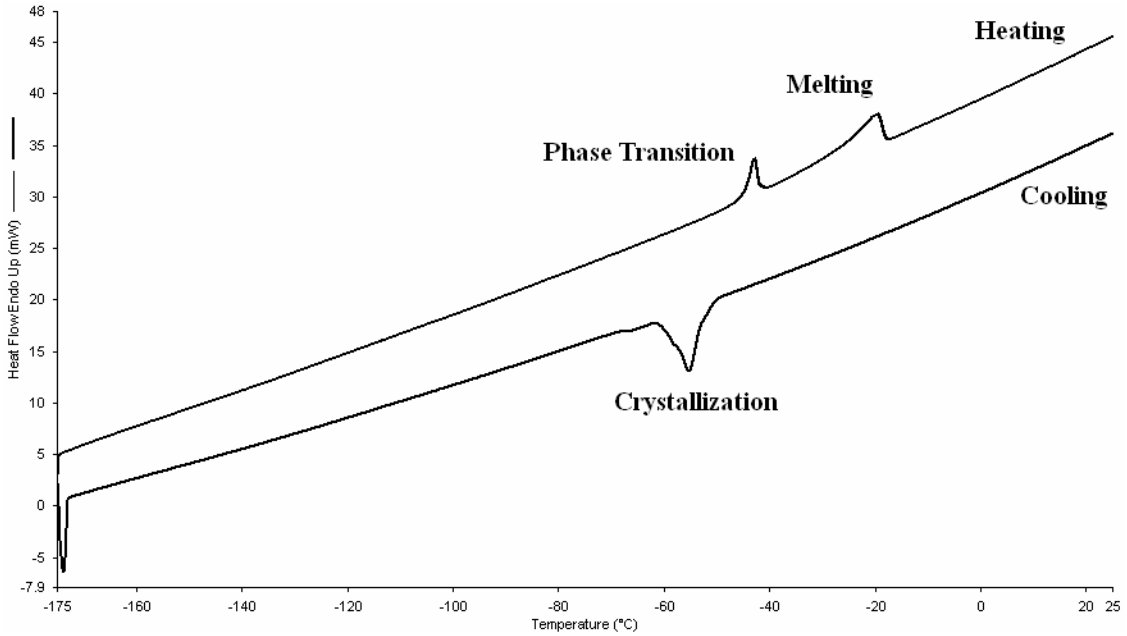
Supplementary Information

DSC Measurements

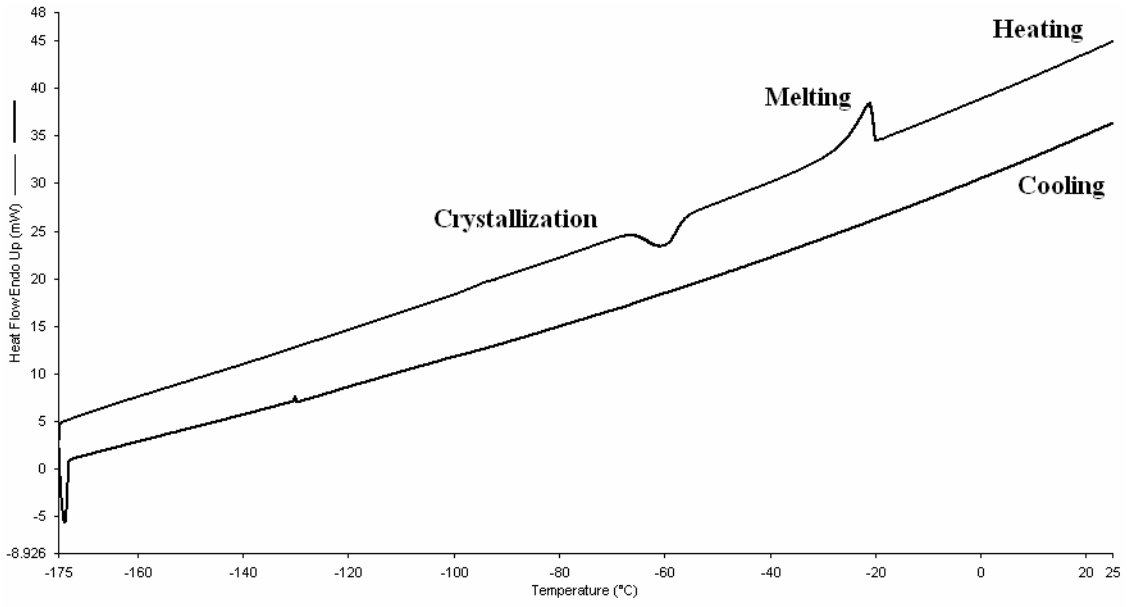
DSC measurements were carried out on a Perkin Elmer Diamond HyperDSC®, calibrated using an indium primary standard, with solid-solid transitions for cyclohexane and ethylbenzene as supplementary low temperature standards.

[emim]OTf and [emim]NTf_2 were obtained from Merck GgaA, and A. G. Degussa, Germany to a HP (high purity) specification that included a water level of < 100 ppm. Ionic liquids were manipulated only in a nitrogen filled glove box.

Ionic liquid samples were sealed in Al pans in a nitrogen-filled glove box, with an empty Al pan was used as reference. DSC measurements were carried out in a helium atmosphere on samples of different sizes and the samples initially examined using different rates of heating and cooling. All of the DSC data discussed in the manuscript were measured on 7-12mg samples (weighed to 5 decimal places using a digital analytical balance). Each sample was cooled and heated at 5 °C/min in the range +40 °C to -170 °C.



DSC Plot of [emim]OTf



DSC Plot of [emim]NTf_2

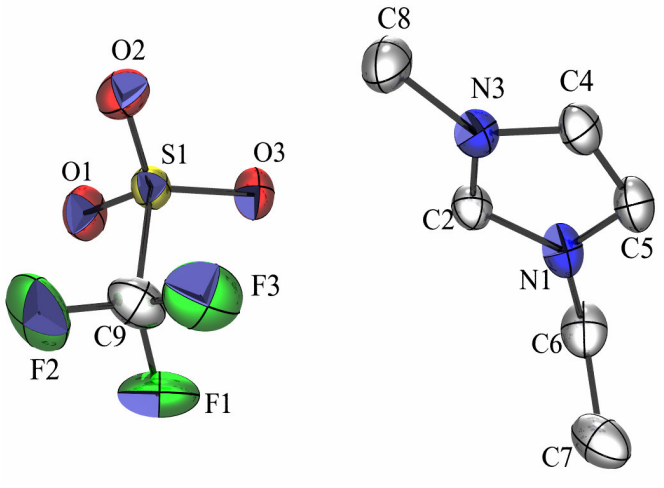
In situ crystallization experiments

Prior knowledge of the thermal behavior of the materials studied enabled conditions for the *in situ* crystallization experiments using the 'Challenge' Optical Heating and Crystallization Device (Bruker AXS) to be defined. Differences in heating and cooling conditions in the DSC and OHCD experiments, and the possible formation of polymorphs, lead us, at present, to be cautious about correlating definitively the structure revealed by crystallography with the dominant transition in the DSC. Low temperature X-ray diffraction studies will examine polymorph formation and associated phase changes, both known to be affected by thermal history and the presence of impurities. In the zone-melting experiments, laser intensity is increased over 1-2 minutes from 0 just to melt the polycrystalline material (a value that is different from ionic liquid to ionic liquid). The molten zone is moved along the capillary at about 3 cm/hour. Intensity was reduced to 0 within 2-5 minutes after each scan. The ionic liquid sample was monitored visually using a NTSC-Digital Video Camera (Model LCL-211H, Watec America Corp., USA), with a magnification of 1x-3x.

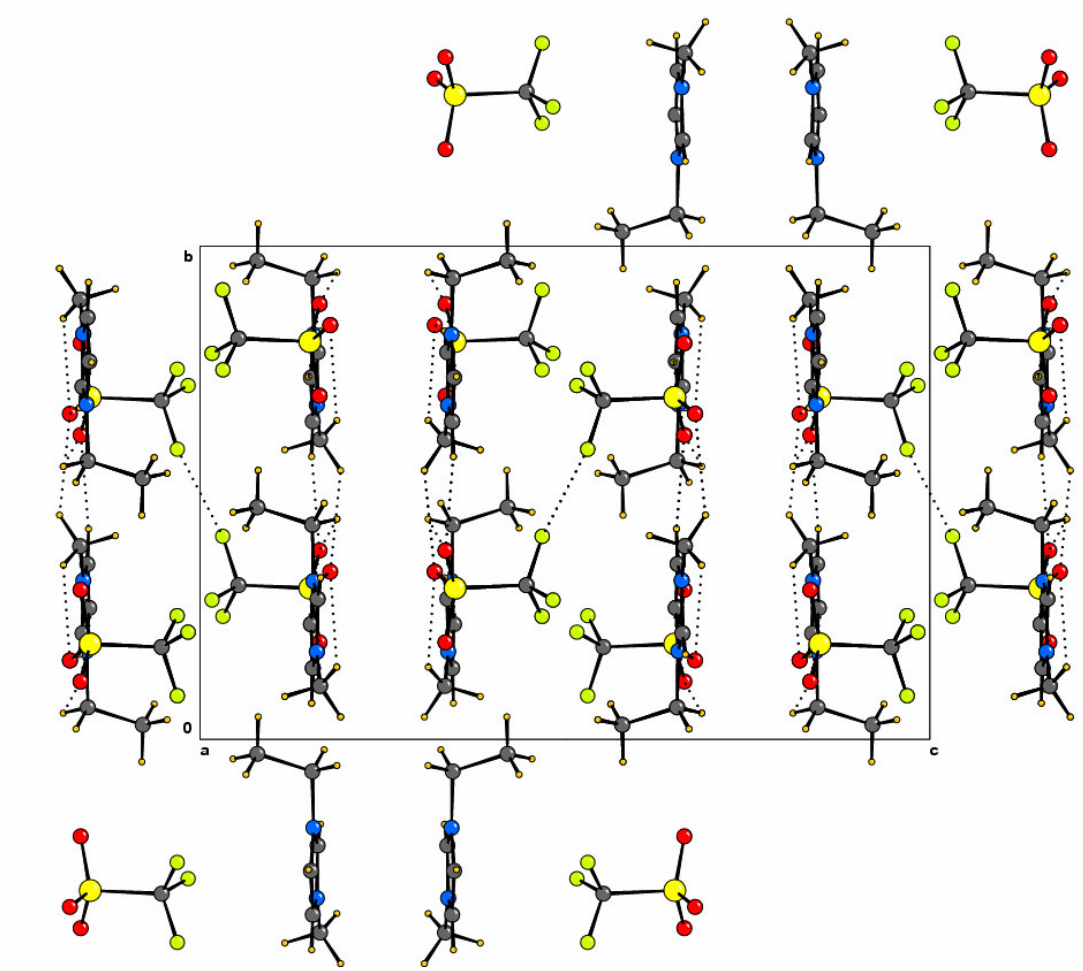
As the capillary containing the liquid was mounted vertically in the diffractometer (fitted with an Oxford Cryosystem cooling device) it was not possible to collect data with ϕ = 90° and 180°. Only a single ω scan, with ϕ = 0°, was recorded and used for structure solution and refinement. As a result, the completeness of data is in the range 70-80%, less than usual for single crystal data.

Table 1: Crystallographic date for [emim]OTf and [emim]NTf_2

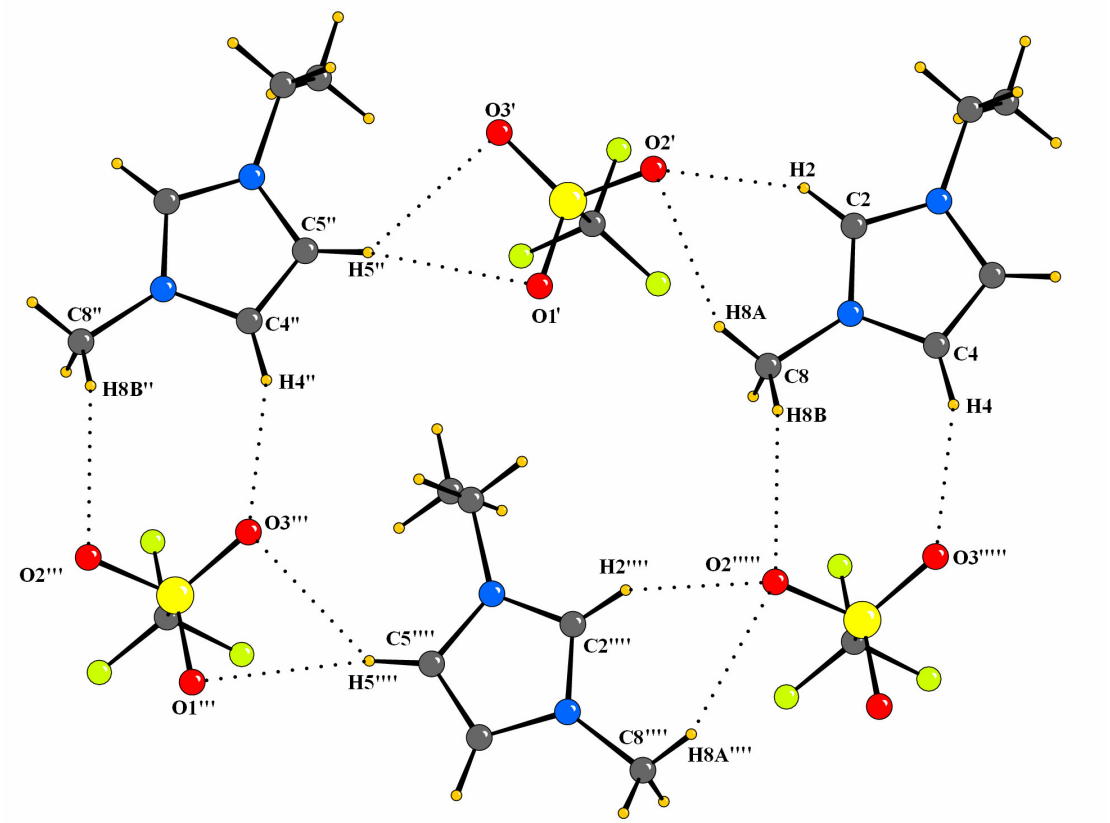
	(1) [emim]OTf	**(2) [emim]NTf_2**
Formula	$C_7H_{11}N_2O_3F_3S$	$C_8H_{11}N_3O_4F_6S_2$
FW	260.2	391.3
Colour	Colourless	Colourless
Crystal System	Orthorhombic	Orthorhombic
Space Group	*Pbca*	$Pca2_1$
Z	8	8
a/Å	10.183(5)	18.499(9)
b/Å	12.384(7)	8.626(8)
c/Å	18.294(8)	19.255(9)
Volume/Å^3	2307.0(2)	3072.6(4)
Temp/K	150	230
D_{calc}/gcm^{-3}	1.50	1.69
μ/mm^{-1}	0.316	0.432
Measured	10196	25029
Unique	2028	2947
$\theta_{min, max}$/°	2.2, 25.3	2.1, 25.4
Parameters	147	413
R_obs	0.052	0.082
***wR*2_obs**	0.130	0.194
$\delta\rho_{min, max}$/eÅ^{-3}	-0.281, 0.353	-0.352, 0.411
GooF	1.149	0.948



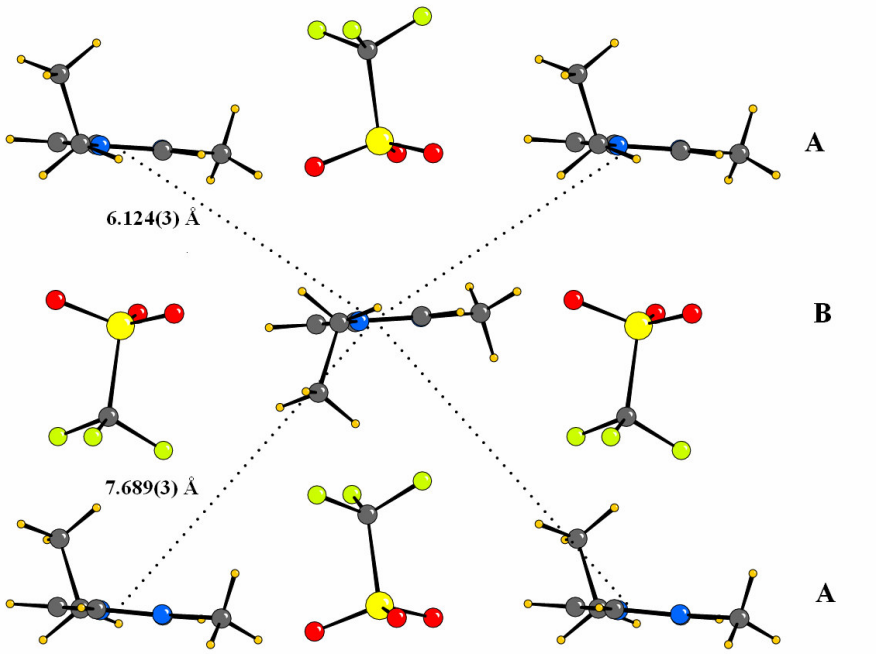
ORTEP of [emim]OTf, ellipsoids are drawn with 50% ellipsoidal probability.



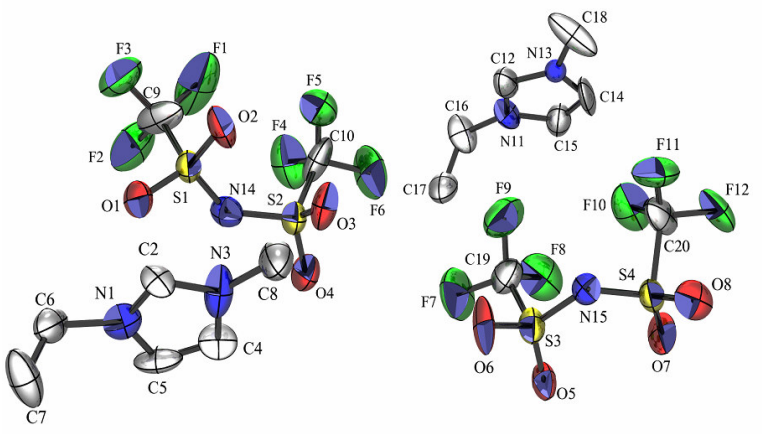
Packing of [emim]OTf viewed down *a* axis; intermolecular interactions are marked as dotted lines.



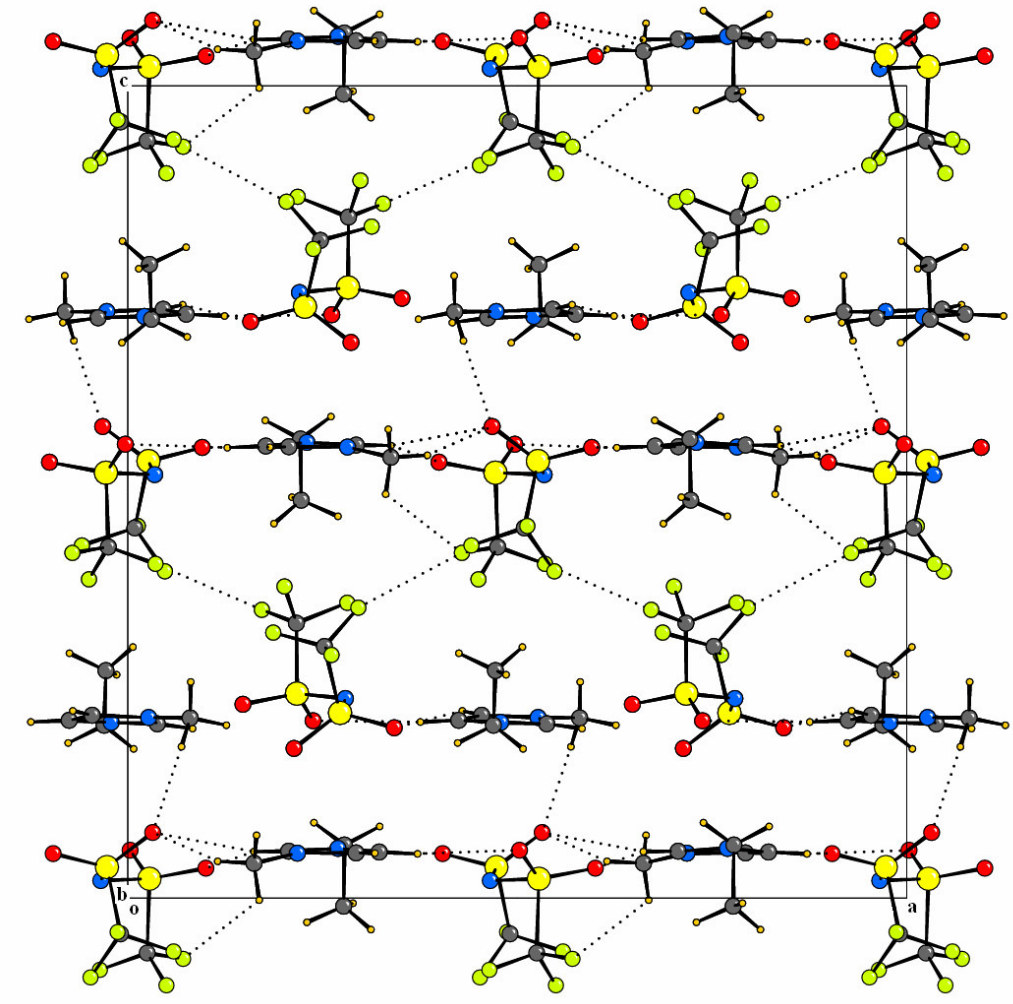
C-H···O Hydrogen bonded network of cations and anions in [emim]OTf.



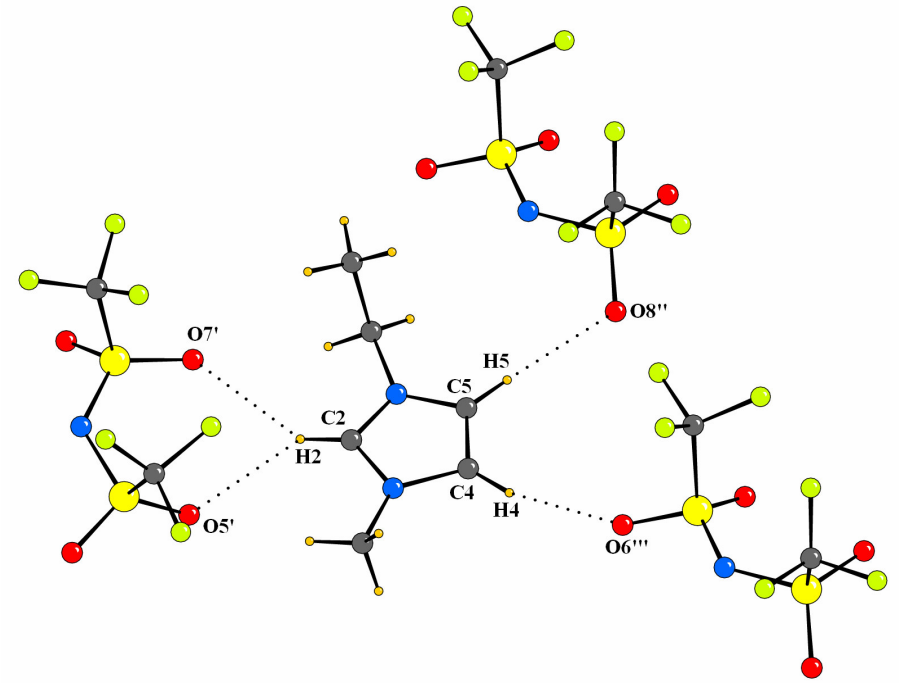
Stacking of imidazolium rings in [emim]OTf



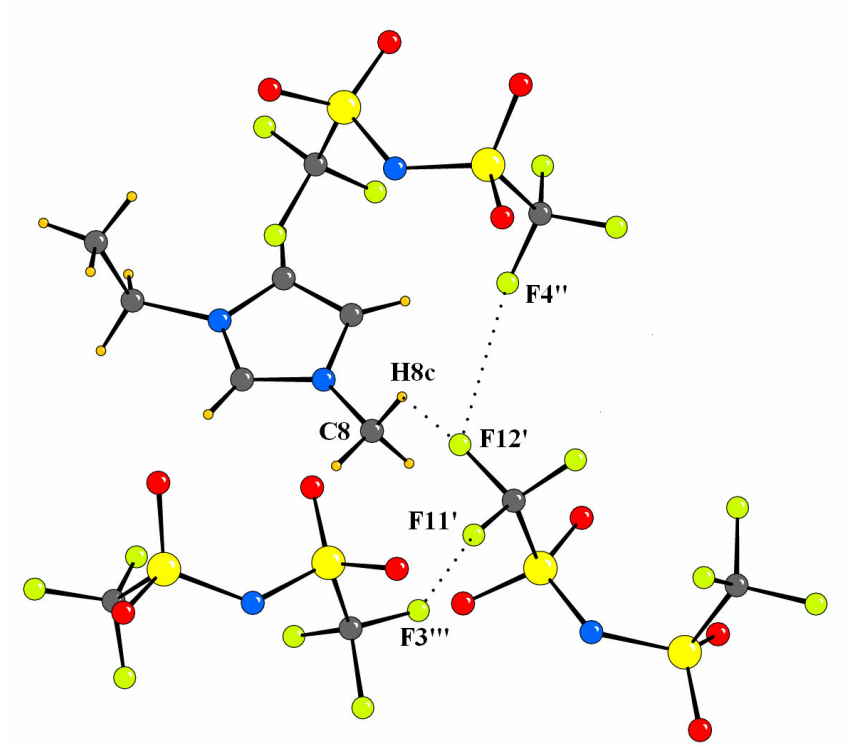
ORTEP of [emim]NTf_2, ellipsoids are drawn with 50% ellipsoidal probability



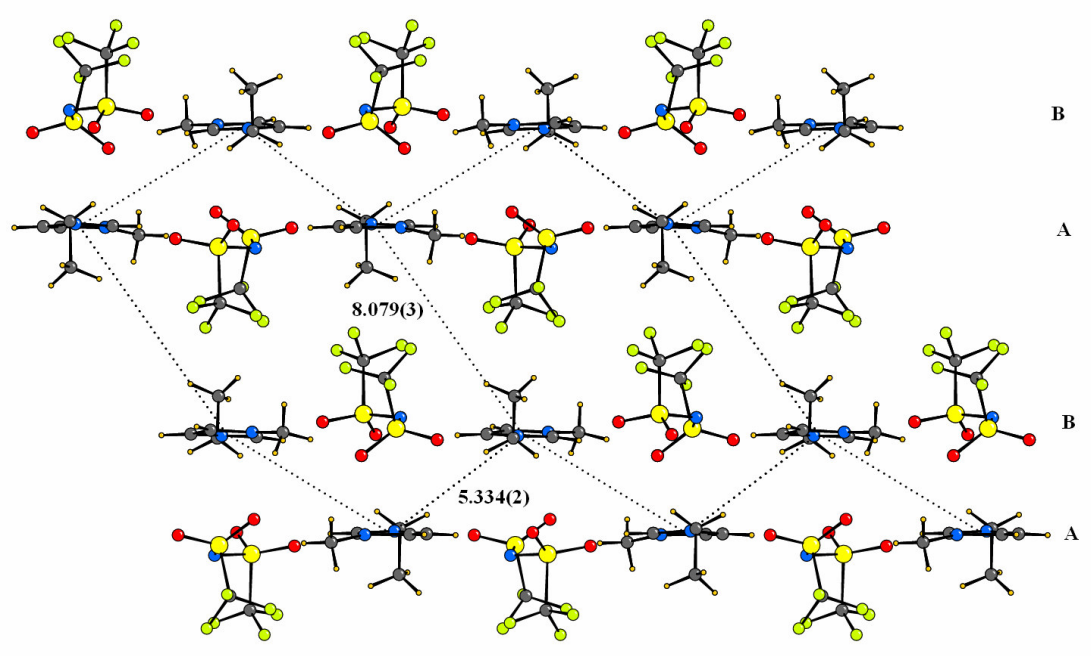
Packing of [emim]NTf_2 viewed down *b* axis; intermolecular interactions are marked as dotted lines.



C-H···O Hydrogen bonded network of cations and anions in [emim]NTf_2



C-F···F and C-H···F interactions in [emim]NTf_2.



Stacking of imidazolium rings in [emim]NTf_2

Additional references

1. List of publications reporting ionic liquid structures containing $[emim]^+$

No	Authors	Reference	Compound
1	A. Elaiwi et. al	J. Chem. Soc. Dalton Trans. **1995**, 3467-3472.	[emim]Br [emim]I $[emim]AlBr_4$
2	A. S. Larsen et. al	J. Am. Chem. Soc. *122*, **2000**, 7264-7272.	$[emim]CB_{11}H_{12}$ $[emim]CB_{11}H_6Cl_6$ $[emim]CB_{11}H_6Br_6$ $[emim]MeCB_{11}H_{11}$ $[emim]EtCB_{11}H_{11}$ $[emim]MPrCB_{11}H_{11}$ $[emim]BuCB_{11}H_{11}$
3	J. Fuller et. al	Chem. Commun. **1994**, 299-300.	$[emim]PF_6$
4	C. J. Dymek Jr et. al	J. Mol. Struct. *213*, **1989**, 25-34.	[emim]Cl
5	J. S. Wilkes et. al	Chem. Commun. **1992**, 965-967.	$[emim]NO_2$ $[emim]NO_3$ $[emim]_2SO_4$
6	M. Hasan et. al	Inorg. Chem. *38*, **1999**, 5637-5641	$[emim]AuCl_4$
7	P. B. Hithcoock et. al	Acta Crystallogr. Sect. C54, **1998**, 1594-1596.	$[emim]_2PdCl_4$
8	Y. Yoshida et. al	Inorg. Chem. *43*, **2004**, 1458-1462.	$[emim]Ag(CN)_2$
9	F. Liu et. al	J. Sol. State Chem. *169*, **2002**, 199-207.	$[emim]_2[Cd(SCN)_6]$
10	A. K. Abdul-Sada et. al	Chem. Commun. **1986**, 1753-1754.	[emim]I
11	J. A. Boon et. al	J. Chem. Cryst. *25*, **1995**, 57-62.	$[emim][Na][AlCl_4]_2$
12	P. B. Hithcoock et. al	Inorg. Chim. Acta. *113*, **1986**, L25-L26.	$[emim]_2UCl_6$ $[emim]_2UO_2Cl_4$
13	D. Appleby et. al	J. Chem. Soc. Dalton Trans. **1990**, 1879-1887.	$[emim]_3Ru_2Br_9$
14	K. Matsumoto et. al	Sol. State Sci. *4*, **2002**, 23-26.	$[emim]HF_2$
15	Y. Yoshida et. al	Bull. Chem. Soc. Jpn. *78*, **2005**, 1921-1928.	$[emim]_2FeCl_4$

2. List of publications reporting ionic liquid structures containing $[CF_3SO_3]^-$

No	Authors	Reference	Compound
1	J. S. Wilkes et. al	Supramol. Chem. *1*, **1993**, 191-193	[mim]OTf
2	E. Rijnberg et. al	Inorg. Chem. *37*, **1998**, 56-63	$[But_2im]OTf$
3	O. Stenzel et. al	J. Chem Soc. Dalton Trans. **2002**, 1132-1138.	[2-Memmim]OTf [2-Meemim]OTf
4	R. E. Banks et. al	Acta Crystallogr. Sect. C59, **2003**, m141-m143.	[pyF]OTf
5	A. R. Choudhury *et al*	J. Am Chem. Soc. 127, **2005**, 16792.	[bmim]OTf

3. List of publications reporting ionic liquid structures containing $[(CF_3SO_2)_2N]^-$

No	Authors	Reference	Compound
1	J. J. Golding *et al*	Chem. Commun. **1998**, 1593-1594.	$[EtBz(2\text{-}Me)im]NTf_2$
2	J. J. Jordy *et al*	Tet. Lett. *45*, **2004**, 4429-4431.	$[mimCMeCO_2Et]NTf_2$
3	J. D. Holbrey *et al*	J. Chem. Soc. Dalton Trans. **2004**, 2267-2271.	[dmim] NTf_2 $[1,2,3\text{-}teim]NTf_2$
4	C. M. Forsyth *et al*	Chem. Mat. *14*, **2002**, 2103-2108	[NMe1Mepyrr] NTf_2 $[Me_2pyrr]NTf_2$ $[Me_3NH]NTf_2$ $[NPr_4]NTf_2$
5	P. A. Fox *et al*	*Chem. Commun.,* **2005**, 3679.	$[[Me_3NBH_2mim]NTf_2$
6	C. M. Forsyth *et al*	*Chem. Mater.*, 14, **2002**, 2103.	$[Me_3NH]NTf_2$
7	A. R. Choudhury *et al*	J. Am Chem. Soc. 127, **2005**, 16792.	$[bmpyr]NTf_2$ $[nhexpy]NTf_2$