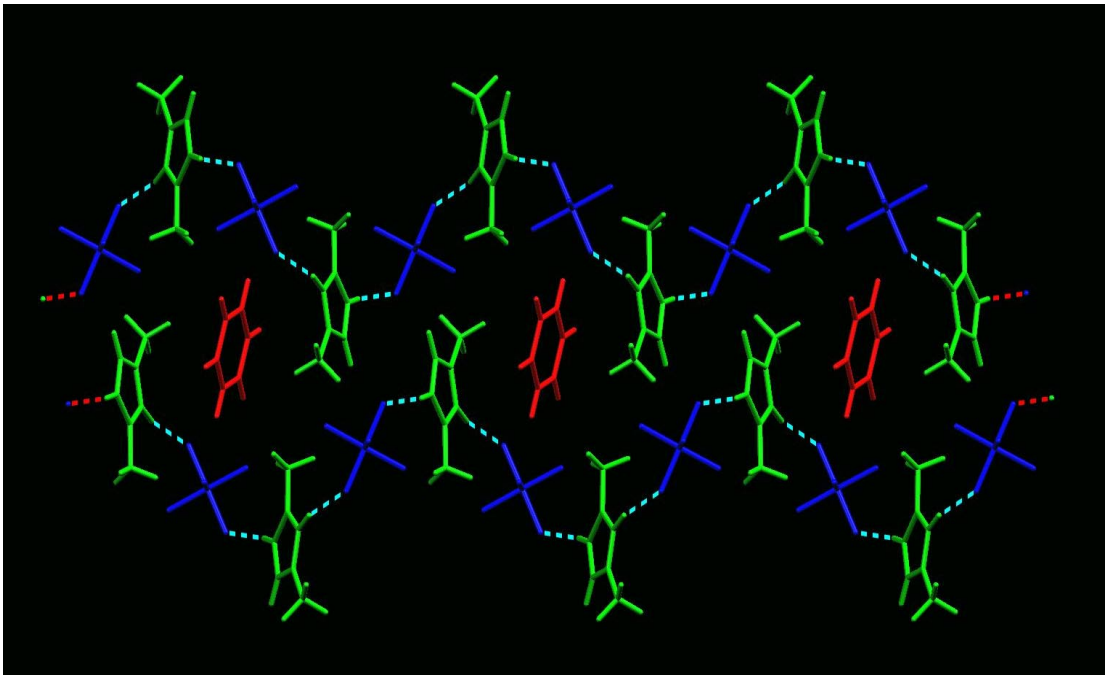
Supplementary Data

Compound	1,3-dimethylimidazolium hexafluorophosphate (173 K)	1,3-dimethylimidazolium hexafluorophosphate (293 K)	1,3-dimethylimidazolium hexafluorophosphate-0.5benzene clathrate
Color / Shape	colorless / platelet	colorless block	colorless block
Empirical formula	$C_5H_9N_2F_6P$	$C_5H_9N_2F_6P$	$C_8H_{12}F_6N_2P$
Formula weight	242.11	242.11	281.17
Temperature	173(2) K	293(2) K	150(2) K
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Pbca	Pbca	$P2_1/c$
Number of Reflections	939	1934	3315
Unit cell dimensions	a = 11.302(8) Å b = 9.337(6) Å c = 17.947(12) Å	a = 11.254(2) Å b = 9.3606(19) Å c = 17.986(4) Å	a = 6.3616(8) Å b = 11.7383(14) Å c = 15.9061(19) Å β = 98.002(2)
Volume	1894(2) Å^3	1894.7(7) Å^3	1176.2(2) Å^3
Z	8	8	4
Density (calculated)	1.698 mg/m^3	1.698 mg/m^3	1.588 mg/m^3
Absorption coefficient	0.347 mm^{-1}	0.347 mm^{-1}	0.292 mm^{-1}
Diffractometer / scan	Siemens SMART / CCD area detector	Siemens SMART / CCD area detector	Station 9.8 Daresbury[a] laboratory, Bruker SMART / CCD area detector
Radiation	MoKα (graphite monochrom.)	MoKα (graphite monochrom.)	Silicon 111 monochrom.
Wavelength	0.71073 Å	0.71073 Å	0.68670 Å
F(000)	976	976	572
Crystal size	0.50 x 0.30 x 0.02 mm	0.38 x 0.30 x 0.26 mm	0.10 x 0.10 x 0.20 mm
θ range for data collection	2.27 to 23.37	2.26 to 26.37	2.09 to 29.33
Index ranges	$-12 \le h \le 10$, $-10 \le k \le 10$, $-19 \le l \le 19$	$-14 \le h \le 11$, $-11 \le k \le 10$, $-16 \le l \le 22$	$-8 \le h \le 8$, $-8 \le k \le 16$, $-21 \le l \le 22$
Reflections collected	7832	10979	8378
Independent / observed refls.	1372(R_{int} = 0.0331) / 1143([I>2σ(I)])	1934(R_{int} = 0.0689) / 1377([I>2σ(I)])	3315(R_{int} = 0.0593) / 2992([I>2σ(I)])
Absorption correction	SADABS[b]	SADABS[b]	SADABS[b]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Computing	SHELXTL, Ver. 5[c]	SHELXTL, Ver. 5[c]	SHELXTL, Ver. 5[c]
Data / restraints / parameters	1372 / 0 / 163	1934 / 0 / 127	3315 / 0 / 156
Goodness-of-fit on F^2	1.050	1.024	1.096
SHELX-93 weight parameters	0.0461, 1.3707	0.0954, 0.0000	0.0546, 0.2601
Final R indices [I>2σ(I)]	R1 = 0.0335, wR2 = 0.0860	R1 = 0.0529, wR2 = 0.1408	R1 = 0.0474, wR2 = 0.1158
R indices (all data)	R1 = 0.0413, wR2 = 0.0892	R1 = 0.0708, wR2 = 0.1528	R1 = 0.0506, wR2 = 0.1195
Largest diff. peak and hole	0.361 and -0.259 eÅ^{-3}	0.428 and -0.462 eÅ^{-3}	0.773 and -0.340 eÅ^{-3}

[a] Cernik, R. J.; Clegg, W.; Catlow, C. R. A.; Bushnell-Wye, G.; Flaherty, J. V.; Greaves, G. N.; Hamichi, M.; Burrows, I.; Taylor, D. J.; Teat S. J. *J. Synchrotron Rad.* **1997**, *4*, 279; Clegg W.; Elsegood M. R. J.; Teat S. J.; Redshaw C.; Gibson V. C. *J. Chem. Soc., Dalton Trans.* **1998**, 3037.
[b] Sheldrick, G. M. *SADABS*, University of Göttingen, Germany, 1997.
[c] Sheldrick, G. M. *SHELXL97* and *SHELXS97*, University of Göttingen, Germany, 1997.



Packing in the crystal structure of the inclusion complex $[C_1mim][PF_6]\cdot 0.5C_6H_6$ color coded by symmetry, 1,3-dimethylimidazolium cations (*green*), hexafluorophosphate anions (*blue*) and benzene molecules (*red*), showing C(4)-H···F(13) and C(2)-H···F(14) interactions forming cation-anion helical chains and the cavity bounded by four methyl groups in which the benzene molecules are held in a staggered π-stacked sandwich.