Supplementary Material (ESI) for CrystEngComm
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Supporting informations

Structural and spectroscopic elucidation of imidazolium and pyridinium based hexachloridophosphates and niobates

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NMR spectra

[EMIm][PCl_6] (1)

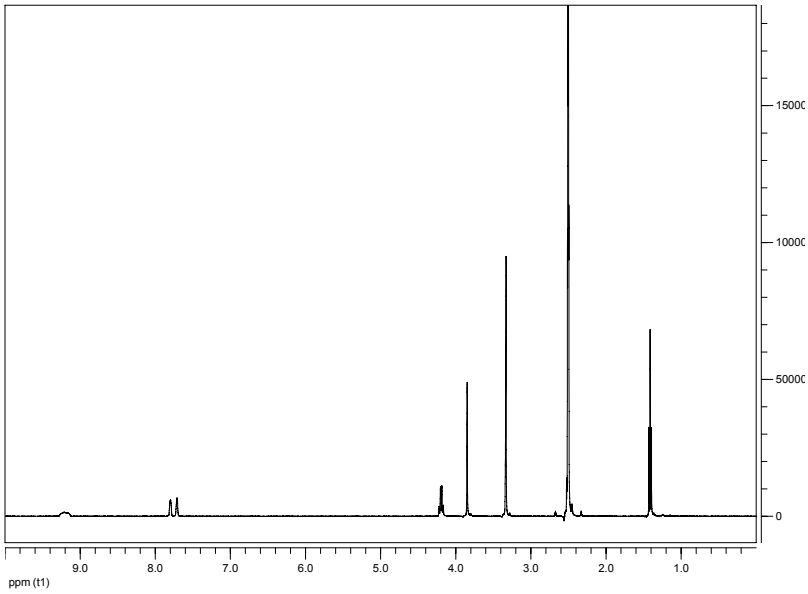

Fig. S1 ^{1}H NMR spectrum of [EMIm] [PCl_6] (**1**) (DMSO, 400 MHz, 25 °C).

[EMIm] [$NbCl_6$] (2)

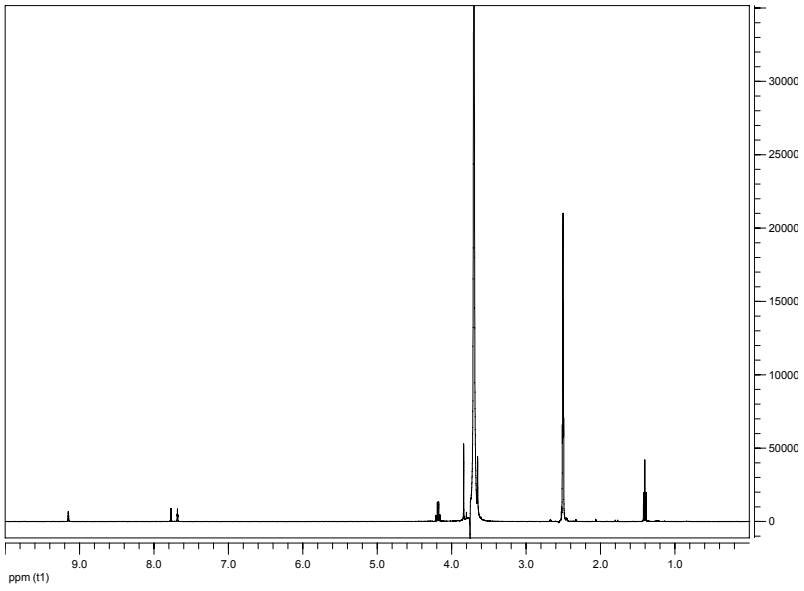

Fig. S2 ^{1}H NMR spectrum of [EMIm] [$NbCl_6$] (**2**) (DMSO, 400 MHz, 25 °C).

[1,4-BMPy][PCl_6] (3)

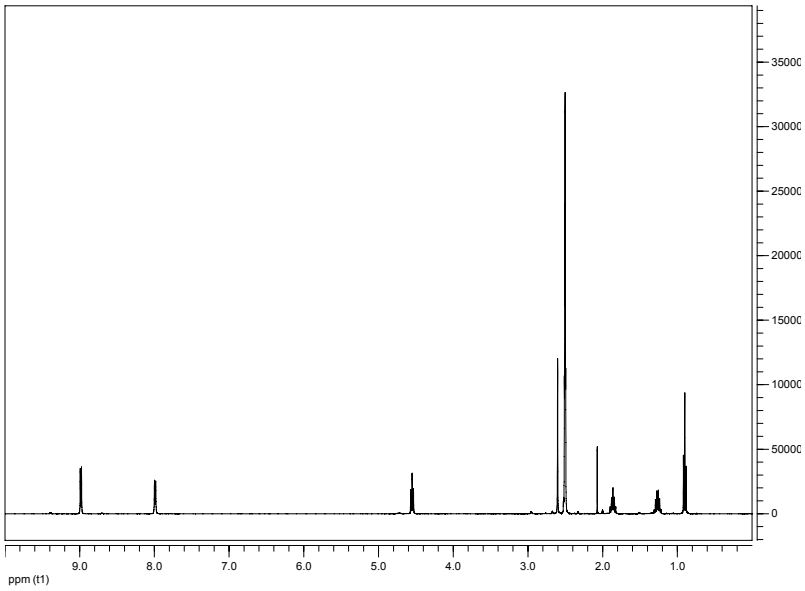

Fig. S3 ^{1}H NMR spectrum of [1,4-BMPy] [PCl_6] (**3**) (DMSO, 400 MHz, 25 °C).

[1,4-BMPy][$NbCl_6$] (4)

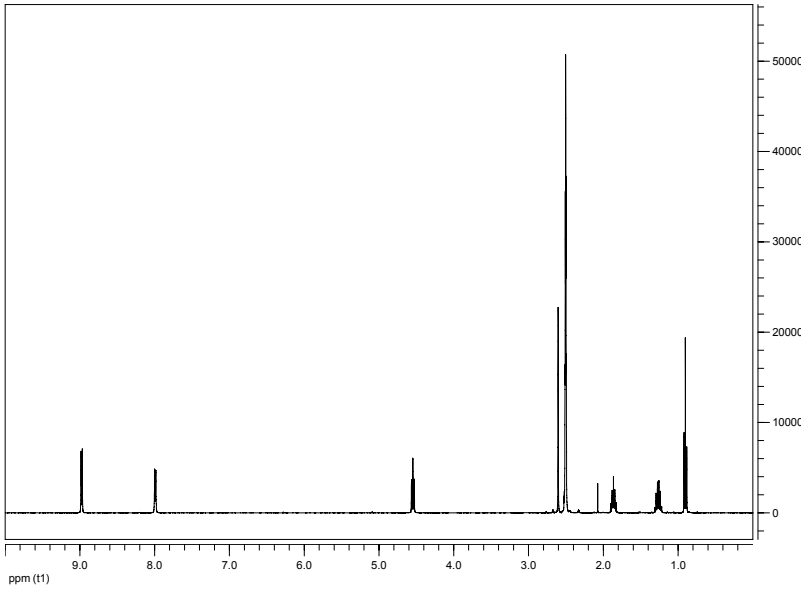

Fig. S4 ^{1}H NMR spectrum of [1,4-BMPy] [$NbCl_6$] (**4**) (DMSO, 400 MHz, 25 °C).

[1,3-BMPy][$NbCl_6$] (5)

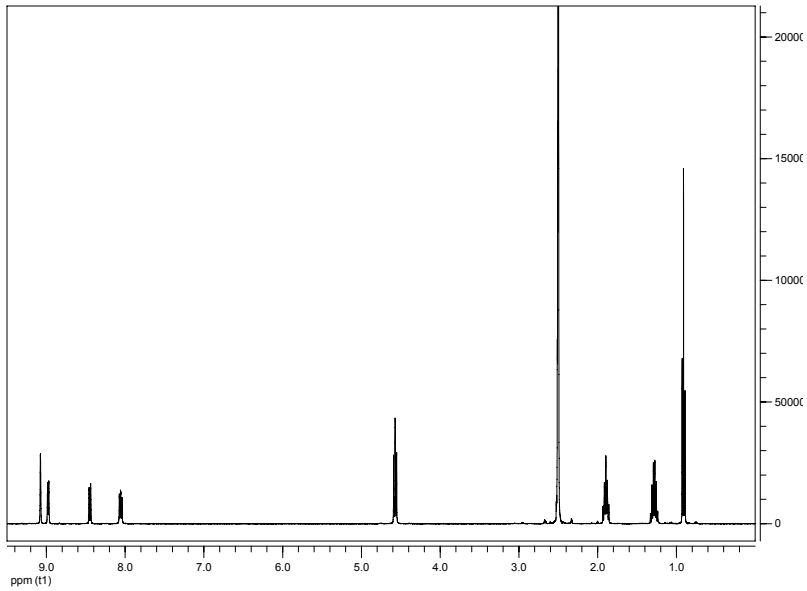

Fig. S5 ^{1}H NMR spectrum of [1,3-BMPy] [$NbCl_6$] (**5**) (DMSO, 400 MHz, 25 °C).

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Raman spectra

[EMIm][PCl_6] (1)

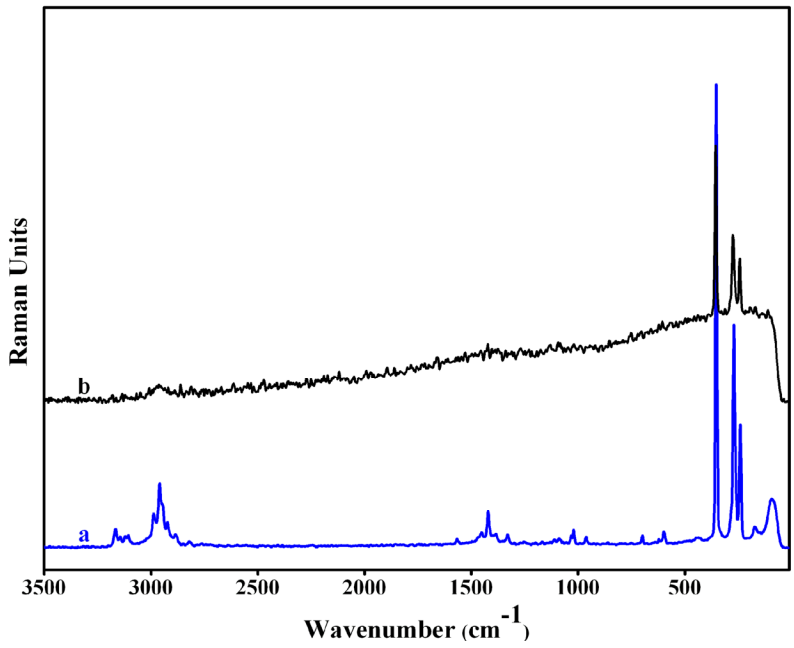

Fig. S6 FT-Raman spectra (Nd:YAG laser, $\lambda_{exc.}$ = 1064 nm) of crystalline (RT) (a) and liquid (175 °C) (b) [EMIm][PCl_6] (**1**). (Raman intensity in arbitrary units).

[EMIm][$NbCl_6$] (2)

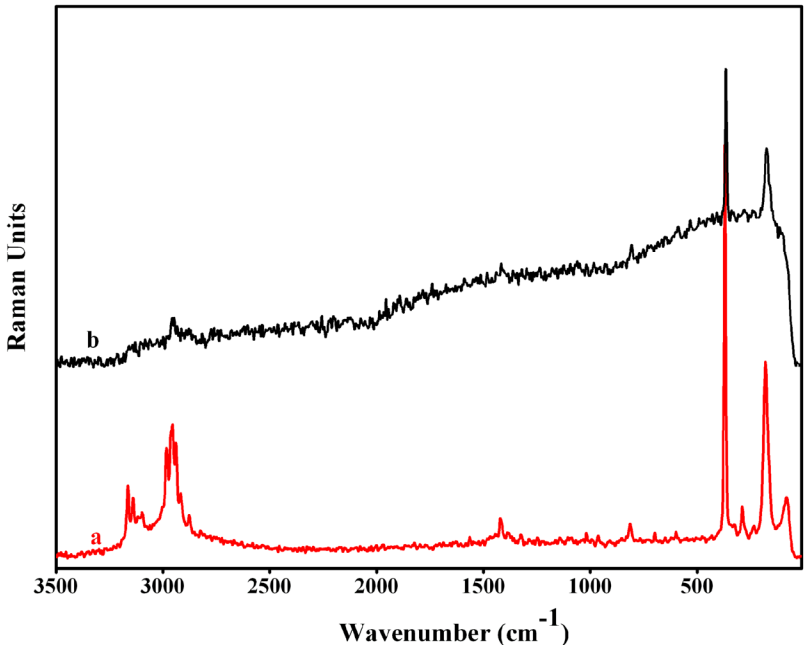

Fig. S7 FT-Raman spectra (Nd:YAG laser, $\lambda_{exc.}$ = 1064 nm) of crystalline (RT) (a) and liquid (150 °C) (b) [EMIm][$NbCl_6$] (**2**). (Raman intensity in arbitrary units).

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[1,4-BMPy][PCl_6] (3)

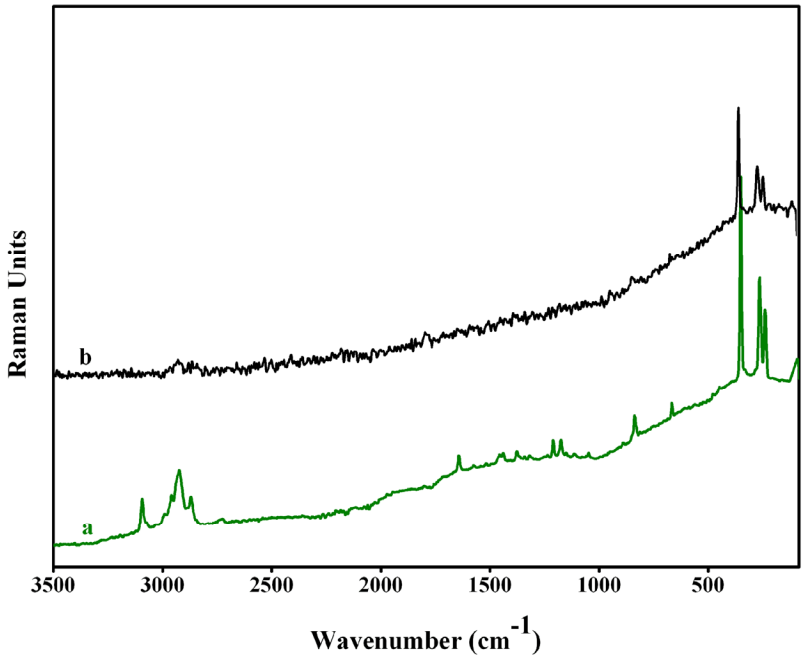

Fig. S8 FT-Raman spectra (Nd:YAG laser, $\lambda_{exc.}$ = 1064 nm) of crystalline (RT) (a) and liquid (100 °C) (b) [1,4-BMPy][PCl_6] (**3**). (Raman intensity in arbitrary units).

[1,4-BMPy][$NbCl_6$] (4)

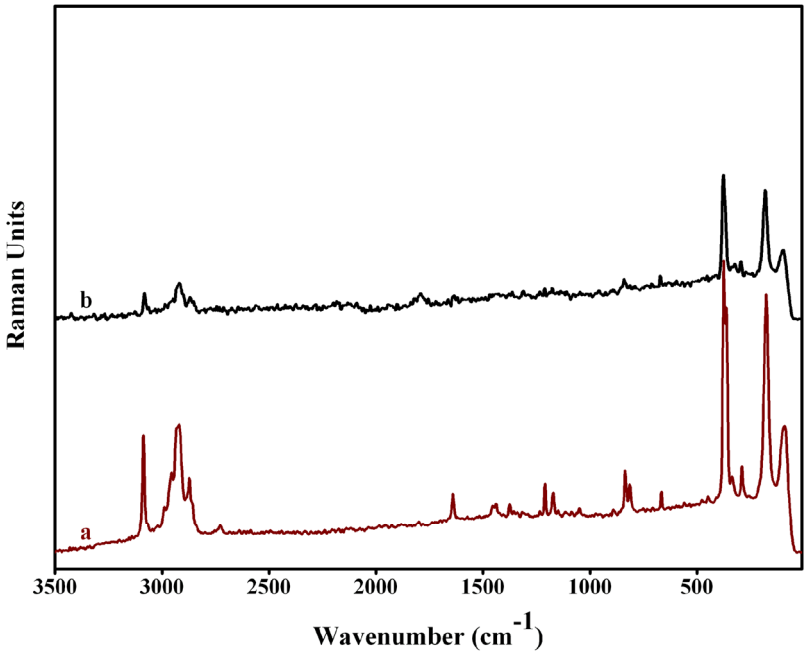

Fig. S9 FT-Raman spectra (Nd:YAG laser, $\lambda_{exc.}$ = 1064 nm) of crystalline (RT) (a) and liquid (100 °C) (b) [1,4-BMPy][$NbCl_6$] (**4**). (Raman intensity in arbitrary units).

[1,3-BMPy][$NbCl_6$] (5)

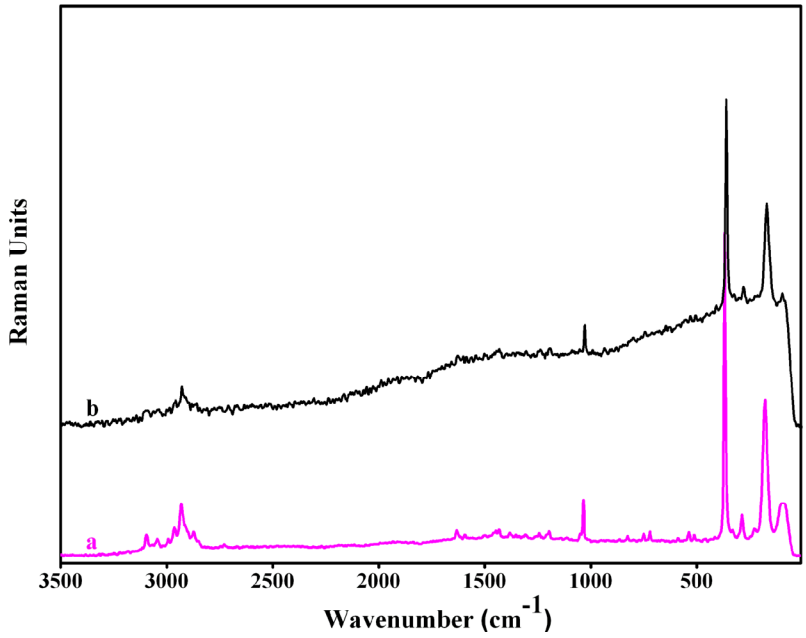

Fig. S10 FT-Raman spectra (Nd:YAG laser, $\lambda_{exc.}$ = 1064 nm) of crystalline (RT) (a) and liquid (100 °C) (b) [1,3-BMPy][$NbCl_6$] (**5**). (Raman intensity in arbitrary units).

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DSC traces

[1,4-BMPy][PCl_6] (3)

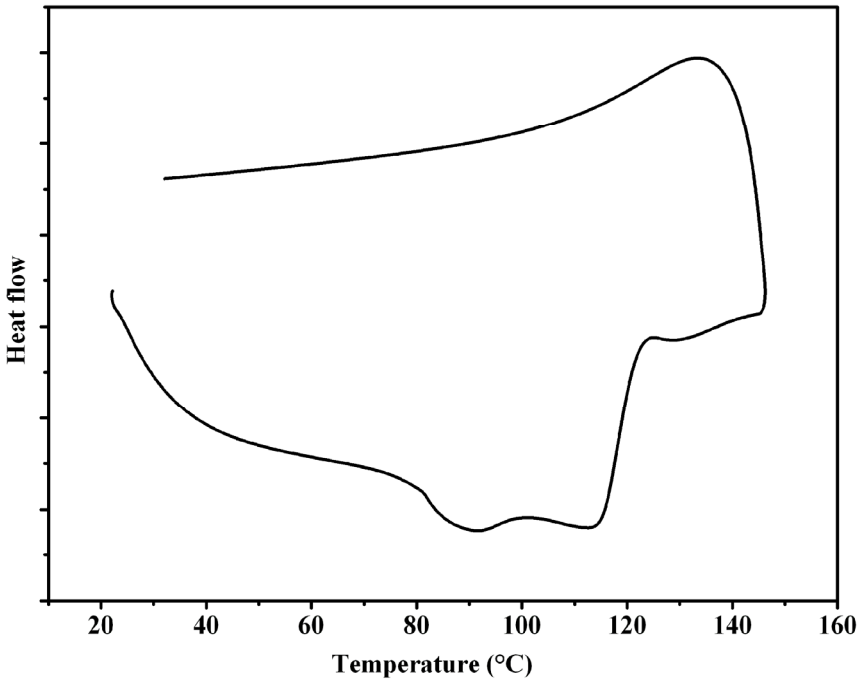

Fig. S11 Differential scanning calorimetry results for compound **(3)**

[1,4-BMPy][$NbCl_6$] (4)

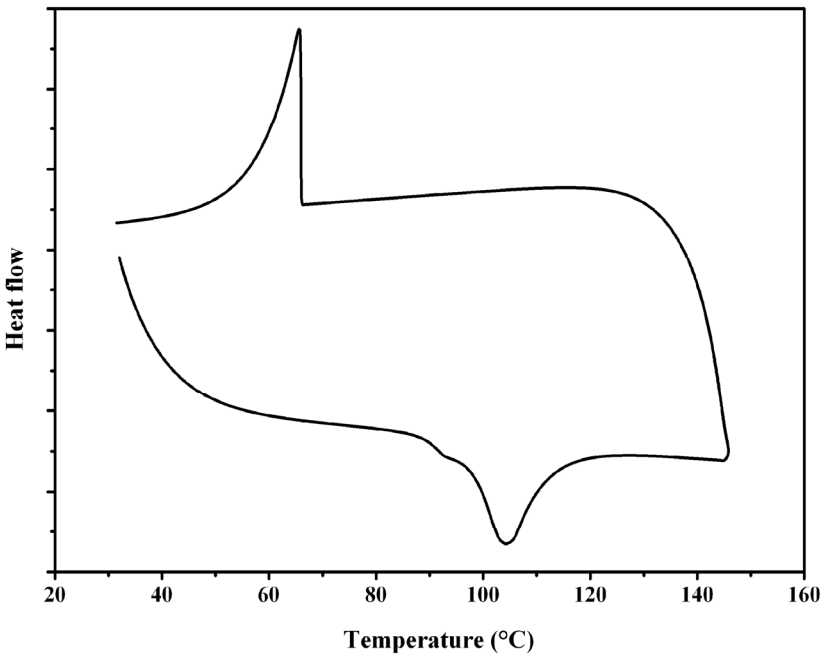

Fig. S12 Differential scanning calorimetry results for compound **(4)**

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[1,3-BMPy][$NbCl_6$] (5)

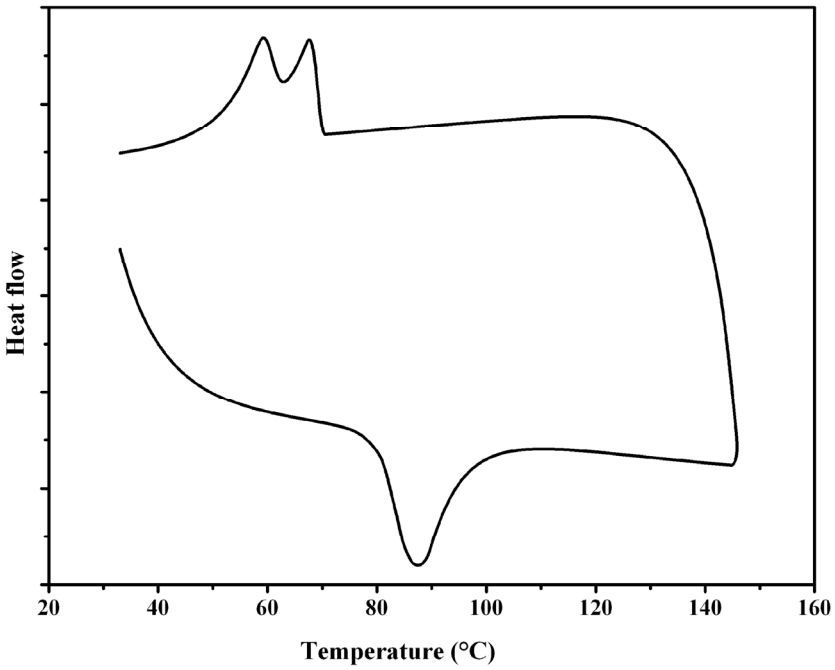

Fig. S13 Differential scanning calorimetry results for compound **(5)**

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Table S1 Selected internuclear distances (Å) and angles (°) for **1 – 5**

[EMIm][PCl_6] (1)

P – Cl(1)	2.121(1)	P – Cl(4)	2.140(1)
P – Cl(2)	2.131(1)	P – Cl(5)	2.149(1)
P – Cl(3)	2.134(1)	P – Cl(6)	2.151(1)
Cl(1) – P – Cl(2)	90.217(4)	Cl(2) – P – Cl(5)	179.42(5)
Cl(1) – P – Cl(3)	90.45(4)	Cl(3) – P – Cl(5)	90.01(3)
Cl(2) – P – Cl(3)	90.51(4)	Cl(4) – P – Cl(5)	89.78(4)
Cl(1) – P – Cl(4)	179.07(5)	Cl(1) – P – Cl(6)	90.45(4)
Cl(2) – P – Cl(4)	90.48(4)	Cl(2) – P – Cl(6)	89.88(4)
Cl(3) – P – Cl(4)	90.21(4)	Cl(3) – P – Cl(6)	179.02(4)
Cl(1) – P – Cl(5)	89.51(4)	Cl(4) – P – Cl(6)	88.89(4)

[EMIm][$NbCl_6$] (2)

Nb(1) – Cl(1)	2.334(1)	Nb(2) – Cl(7)	2.335(1)
Nb(1) – Cl(2)	2.340(1)	Nb(2) – Cl(8)	2.338(1)
Nb(1) – Cl(3)	2.345(1)	Nb(2) – Cl(9)	2.344(1)
Nb(1) – Cl(4)	2.350(1)	Nb(2) – Cl(10)	2.347(1)
Nb(1) – Cl(5)	2.355(1)	Nb(2) – Cl(11)	2.363(1)
Nb(1) – Cl(6)	2.371(1)	Nb(2) – Cl(12)	2.369(1)
Cl(1) – Nb(1) – Cl(2)	90.55(3)	Cl(7) – Nb(2) – Cl(8)	92.14(3)
Cl(1) – Nb(1) – Cl(3)	92.62(3)	Cl(7) – Nb(2) – Cl(9)	90.00(2)
Cl(2) – Nb(1) – Cl(3)	176.82(3)	Cl(8) – Nb(2) – Cl(9)	89.43(3)
Cl(1) – Nb(1) – Cl(4)	89.25(2)	Cl(8) – Nb(2) – Cl(10)	177.19(3)
Cl(2) – Nb(1) – Cl(4)	91.02(3)	Cl(9) – Nb(2) – Cl(10)	90.81(3)
Cl(3) – Nb(1) – Cl(4)	88.71(3)	Cl(7) – Nb(2) – Cl(11)	88.38(2)
Cl(4) – Nb(1) – Cl(5)	176.60(3)	Cl(9) – Nb(2) – Cl(11)	178.20(2)
Cl(1) – Nb(1) – Cl(6)	178.00(3)	Cl(7) – Nb(2) –Cl(12)	177.62(3)
Cl(2) – Nb(1) – Cl(6)	87.61(3)	Cl(8) – Nb(2) – Cl(12)	91.72(3)

[1,4-BMPy][PCl_6] (3)

P – Cl(1)	2.114(1)	P – Cl(4)	2.144(1)
P – Cl(2)	2.138 (1)	P – Cl(5)	2.149(1)
P – Cl(3)	2.142(1)	P – Cl(6)	2.159(1)
Cl(1) – P – Cl(2)	91.13(5)	Cl(2) – P – Cl(5)	178.71(7)
Cl(1) – P – Cl(3)	90.85(6)	Cl(3) – P – Cl(5)	90.32(5)
Cl(2) – P – Cl(3)	89.89(5)	Cl(4) – P – Cl(5)	89.73(5)
Cl(1) – P – Cl(4)	90.08(6)	Cl(1) – P – Cl(6)	179.33(7)

Cl(2) – P – Cl(4)	90.04(5)	Cl(2) – P – Cl(6)	89.33(5)
Cl(3) – P – Cl(4)	179.07(7)	Cl(3) – P – Cl(6)	89.63(6)
Cl(1) – P – Cl(5)	90.15(5)	Cl(4) – P – Cl(6)	89.44(5)

[1,4-BMPy][$NbCl_6$] (4)

Nb – Cl(1)	2.324(1)	Nb – Cl(4)	2.346(1)
Nb – Cl(2)	2.340(1)	Nb – Cl(5)	2.348(1)
Nb – Cl(3)	2.341(1)	Nb – Cl(6)	2.381(1)
Cl(1) – Nb – Cl(2)	91.02(5)	Cl(2) – Nb – Cl(5)	89.68(4)
Cl(1) – Nb – Cl(3)	91.53(4)	Cl(3) – Nb – Cl(5)	178.06(4)
Cl(2) – Nb – Cl(3)	89.39(4)	Cl(4) – Nb – Cl(5)	90.64(4)
Cl(1) – Nb – Cl(4)	90.92(6)	Cl(1) – Nb – Cl(6)	179.16(4)
Cl(2) – Nb – Cl(4)	178.04(5)	Cl(2) – Nb – Cl(6)	88.62(4)
Cl(3) – Nb – Cl(4)	90.23(4)	Cl(3) – Nb – Cl(6)	89.22(4)
Cl(1) – Nb – Cl(5)	90.18(4)	Cl(4) – Nb – Cl(6)	89.44(5)

[1,3-BMPy][$NbCl_6$] (5)

Nb(1) – Cl(1)	2.333(1)	Nb(2) – Cl(7)	2.332(1)
Nb(1) – Cl(2)	2.340(1)	Nb(2) – Cl(8)	2.345(1)
Nb(1) – Cl(3)	2.353(1)	Nb(2) – Cl(9)	2.344(1)
Nb(1) – Cl(4)	2.353(1)	Nb(2) – Cl(7)	2.351(1)
Nb(1) – Cl(5)	2.354(1)	Nb(2) – Cl(11)	2.360(1)
Nb(1) – Cl(6)	2.363(1)	Nb(2) – Cl(12)	2.361(1)
Cl(1) – Nb(1) – Cl(2)	89.01(5)	Cl(7) – Nb(1) – Cl(8)	90.10(5)
Cl(1) – Nb(1) – Cl(3)	90.94(5)	Cl(7) – Nb(1) – Cl(9)	90.97(5)
Cl(2) – Nb(1) – Cl(3)	90.48(5)	Cl(8) – Nb(1) – Cl(9)	91.04(5)
Cl(1) – Nb(1) – Cl(4)	177.15(5)	Cl(8) – Nb(1) – Cl(10)	179.47(4)
Cl(2) – Nb(1) – Cl(4)	88.74(5)	Cl(9) – Nb(1) – Cl(10)	88.71(4)
Cl(3) – Nb(1) – Cl(5)	177.48(5)	Cl(7) – Nb(1) – Cl(11)	177.69(5)
Cl(4) – Nb(1) – Cl(5)	88.76(5)	Cl(8) – Nb(1) – Cl(11)	89.23(5)
Cl(1) – Nb(1) – Cl(6)	91.08(5	Cl(9) – Nb(1) – Cl(11)	91.25(5)
Cl(2) – Nb(1) – Cl(6)	178.62(5)	Cl(9) – Nb(1) – Cl(12)	178.23(5)

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Table S2 Raman frequencies (cm^{-1}) of crystalline [EMIm] [PCl_6] (**1**) and of crystalline [1,4-BMPy] [PCl_6] (**3**) in the $[PCl_6]^-$ relevant spectral region along with their estimated intensities and proposed assignment

[EMIm][PCl_6] (**1**)	[1,4-BMPy][PCl_6] (**3**)	$[PCl_6]^-$ [29,30]	Assignment / O_h mode description
440 vw, br [a)]		444	ν_3 / F_{1u} : ν_{as}
353 vvs	351 vvs	360	ν_1 / A_{1g} : ν_s
270 vs	265 vs	283	ν_2 / E_g : ν (+ ν_4 / F_{1u})?
240 s	240 s	238	ν_5 / F_{2g} : δ
172 vw, br [b)]		(168)[c)]	ν_6 / F_{2u} : δ
92 br	91 br		Lattice vibration

Estimated intensities: s: strong, m: medium, w: weak, v: very, br: broad. ν : stretching, δ : bending.

[a) b)] $[EMIm]^+$ bands, [c)] Estimated value.[30]

Footnote 1. *Raman* (cm^{-1} / intensity) of crystalline [EMIm] [PCl_6]: 3166 m, 3144 w, 3120 vw, 3106 vw, 2988 m, 2959 s, 2945 sh, 2922 w, 2885 vw, 2820 vw, 1566 w, 1450 w, 1420 m-s, 1386 vw, 1329 w, 1088 vw, 1036 sh, 1020 w-m, 962 w, 698 w, 597 w-m, 440 vw, br, 353 vvs, 270 vs, 240 s, 172 vw, br, 92 br.

Footnote 2. **Raman** (cm^{-1} / intensity) of crystalline [1,4-BMPy] [PCl_6]: 3094 s, 2997 sh, 2959 sh, 2923 vs, 2870 m, 1643 m, 1452 w, 1439 w-m, 1377w-m, 1211 m, 1175 m, 1048 w, 893 w, 837 m-s, 667 m, 351 vvs, 265 vs, 240 s, 91 br.

Table S3 Raman frequencies (cm^{-1}) of crystalline [EMIm] [$NbCl_6$] (**2**) and of crystalline, [1,4-BMPy] [$NbCl_6$] (**4**) and [1,3-BMPy][$NbCl_6$] (**5**) in the $[NbCl_6]^-$ relevant spectral region along with their estimated intensities and proposed assignment

[EMIm][$NbCl_6$] (**2**)	[1,4-BMPy][$NbCl_6$] (**4**)	[1,3-MPy][$NbCl_6$] (**5**)	$[NbCl_6]^{-20}$	Assignment / O_h mode description
	448 w			$[BMPy]^+$
370 vvs	375 vvs	368 vs	375 vs, br	ν_1 / A_{1g} : ν_s
	363 sh			(ν_3 / F_{1u} : ν_{as})
	336 w	332 w		$[BMPy]^+$
288 w-m	290 m	287 m-s	287 w	ν_2 / E_g : ν
240 vw				$[EMIm]^+$
179 vs	176 vs	177 vs	182m, sh	ν_5 / F_{2g} : δ
			177 s	
81 m	90 s	*92 br*		Lattice vibration

Estimated intensities: s: strong, m: medium, w: weak, v: very, br: broad. ν : stretching, δ : bending.

Footnote 3. *Raman* (cm^{-1} / intensity) of crystalline [EMIm][$NbCl_6$]: 3164 m, 3139 m, 3102 w, 2983 m-s, 2955 s, 2939 sh, 2916 w, 2876 w, 1563 w, 1421 w-m, 1332 w, 1250 vw, 1022 w, 964 w, 813 w (trace of $NbOCl_3$), 702 vw, 600 vw, 370 vvs, 340 vw (trace of $NbOCl_3$), 288 w-m, 240 vw, 179 vs, 81 m.

Footnote 4. *Raman* (cm^{-1} / intensity) of crystalline [1,4-BMPy][$NbCl_6$]: 3087 s, 2998 sh, 2955 sh, 2920 vs, 2871 m, 2728 w, 1641 m, 1454 w, 1438 m, 1375 m, 1210 m-s, 1172 m, 1049 w, 891 w, 836 m-s, 814 m, 666 m, 448 w, 375 vs, 363 sh, 336 w, 290 m, 176 vs, 90 s.

Footnote 5. *Raman* (cm^{-1} / intensity) of crystalline [1,3-BMPy][$NbCl_6$]: 3095 m, 3044 m, 2995 w, 2964 m, 2931 s, 2872 m, 1632 w-m, 1432 w-m, 1382 w, 1243 w, 1196 w-m, 1035 s, 826 w, 750 w, 721 w-m, 586 w, 537 w-m, 512 w, 368 vvs, 332 vw, 287 m-s, 227 w, 177 vs, 92 br.