Electronic Supplementary Material (ESI) for RSC Advances.

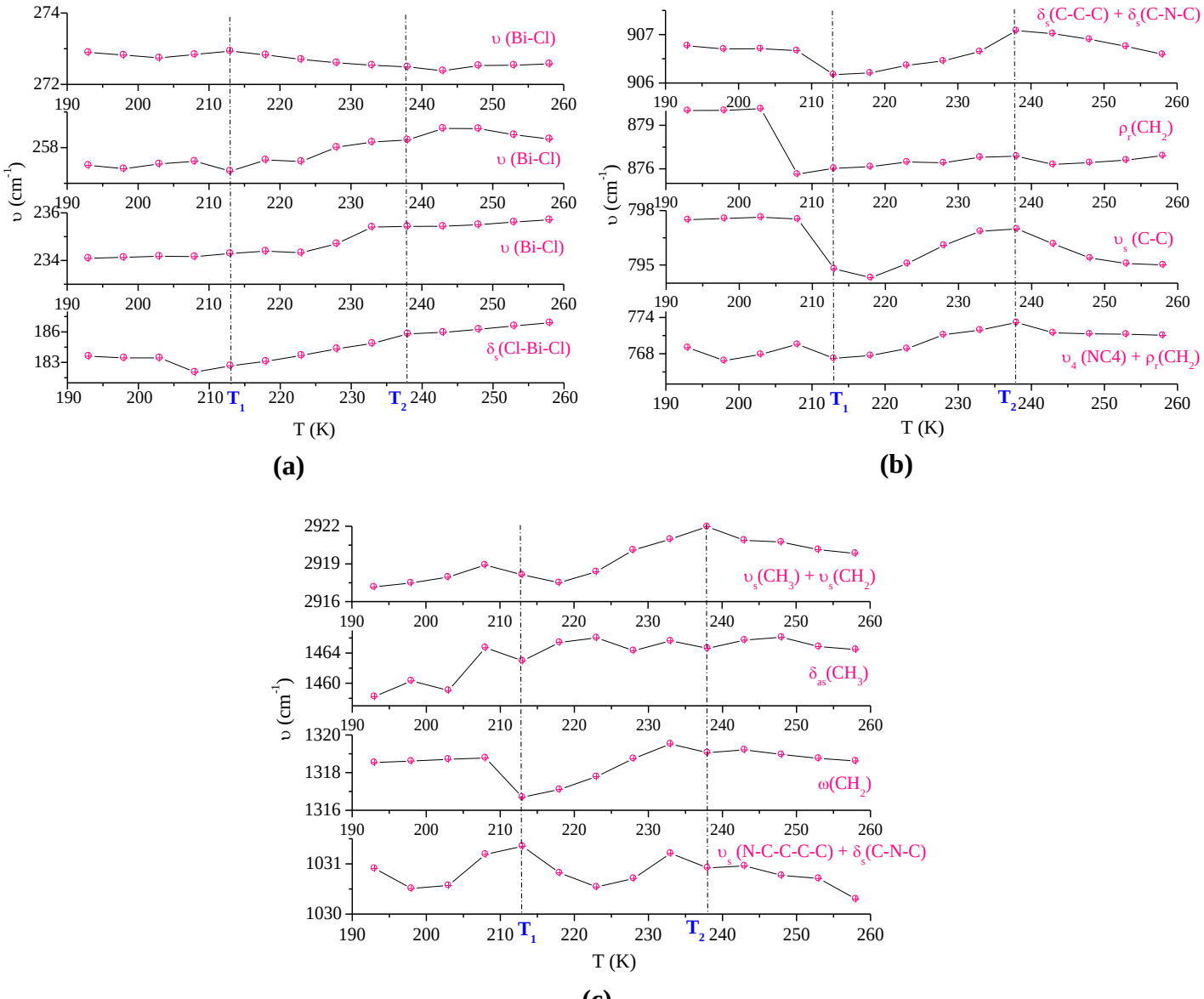
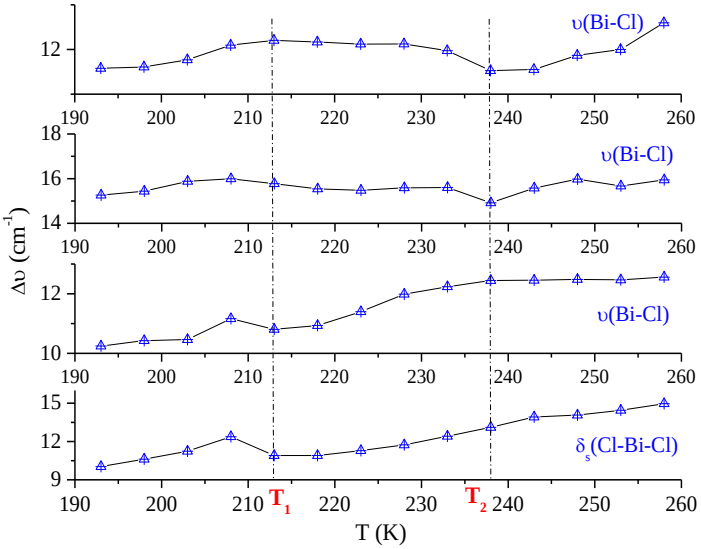
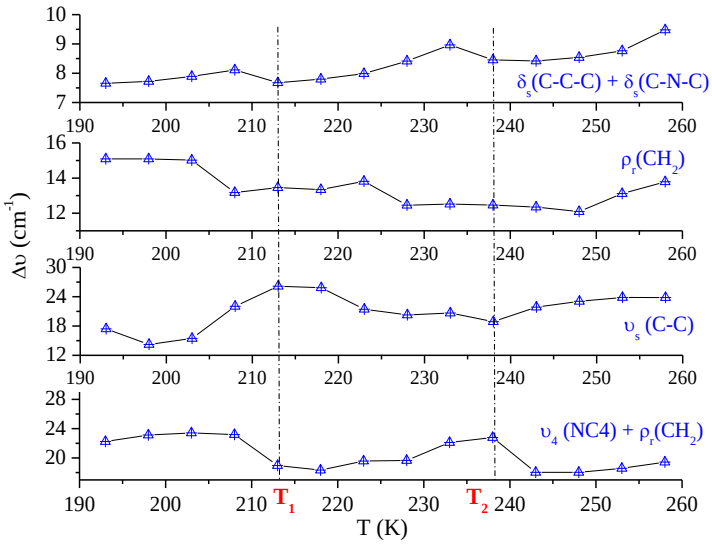


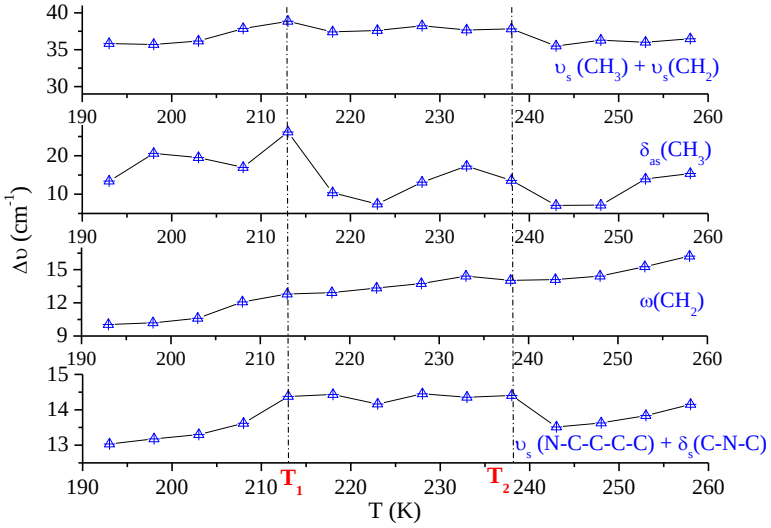
Fig. S1


υ(Bi-Cl)
υ(Bi-Cl)
υ(Bi-Cl)
δs(Cl-Bi-Cl)
Δυ (cm-1)
T (K)
T1
T2

(a)


δs(C-C-C) + δs(C-N-C)
ρr(CH2)
υs (C-C)
υ4 (NC4) + ρr(CH2)
Δυ (cm-1)
T (K)
T1
T2

(b)


υs (CH3) + υs(CH2)
δas(CH3)
ω(CH2)
υs (N-C-C-C-C) + δs(C-N-C)
Δυ (cm-1)
T (K)
T1
T2

(c)

Fig. S2

Table S

Raman shift (cm^{-1})	Assignments
170.1	υ_s(Bi-Cl)
184.4	δ_s(Cl-Bi-Cl)
193.1	υ_s(Bi-Cl)
229.2	υ_{as}(Bi-Cl)
239.3	υ_s(Bi-Cl)
270.5	υ_s(Bi-Cl)
769.8	υ_4 (NC_4) + ρ_r (CH_2)
786.0	υ_3 (NC_4)
797.4	υ_s (C-C-C-C)
811.1	
849.3	υ_s(N-C)+ δ_s(C-C-C)+ υ_s(C-N-C)
866.5	ρ_r (CH_2)
875.1	δ_s(C-C-C-) + δ_s(C-N-C)
883.2	
906.9	δ_s(C-C-C-) + δ_s(C-N-C)
926.2	ρ_r (CH_2)
973.6	υ_1 (NC_4)
991.2	υ_s(C-C)
1008.1	υ_{as}(C-C)
1031.0	υ_s (N-C-C) + δ_s(C-N-C)
1054.4	δ_s(C-C-C) + υ_s(N-C)
1080.7	
1094.2	Bending vibration of the cation skeleton
1108.1	δ_s(C-C-C)
1129.1	υ_s (N-C-C)
1151.4	τ (CH_2)
1183.6	
1206.2	
1271.0	τ (CH_2)
1284.3	ρ_r (CH_3) + υ_s(N-C)
1319.8	ω (CH_2)
1350.2	δ_s (CH_3)
1385.9	
1402.1	δ_{as} (CH_3)
1424.3	
1445.0	δ_s (CH_3)
1467.2	
1502.3	
1510.1	
1519.5	δ_s(CH_2)
2740.4	
2843.2	
2877.1	υ_s(CH_3) + υ_s(CH_2)
2926.0	υ_s(CH_2)
2936.3	
2963.6	υ_{as}(CH_3) + υ_{as}(CH_2)
2984.1	

υ_s: Symmetric stretching; υ_{as}: asymmetric stretching; δ_s: symmetric bending; δ_{as}: asymmetric bending; ω: wagging; τ: tortion; ρ_r: rocking.

Supplementary information captions

Fig. S1: Temperature dependence of the wavenumbers of different modes of the $[(C_4H_9)_4N]^+$ cation and the $[Bi_2Cl_9]^{3-}$ anion.

Fig. S2: Temperature dependence of the half-widths of different modes of the $[(C_4H_9)_4N]^+$ cation and the $[Bi_2Cl_9]^{3-}$ anion.

Table S: Assignments of Raman shift of $[(C_4H_9)_4N]_3Bi_2Cl_9$ compound.