Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Multifunctional properties and multi-energy storage in the $[(CH_3)_3S][FeCl_4]$ plastic crystal

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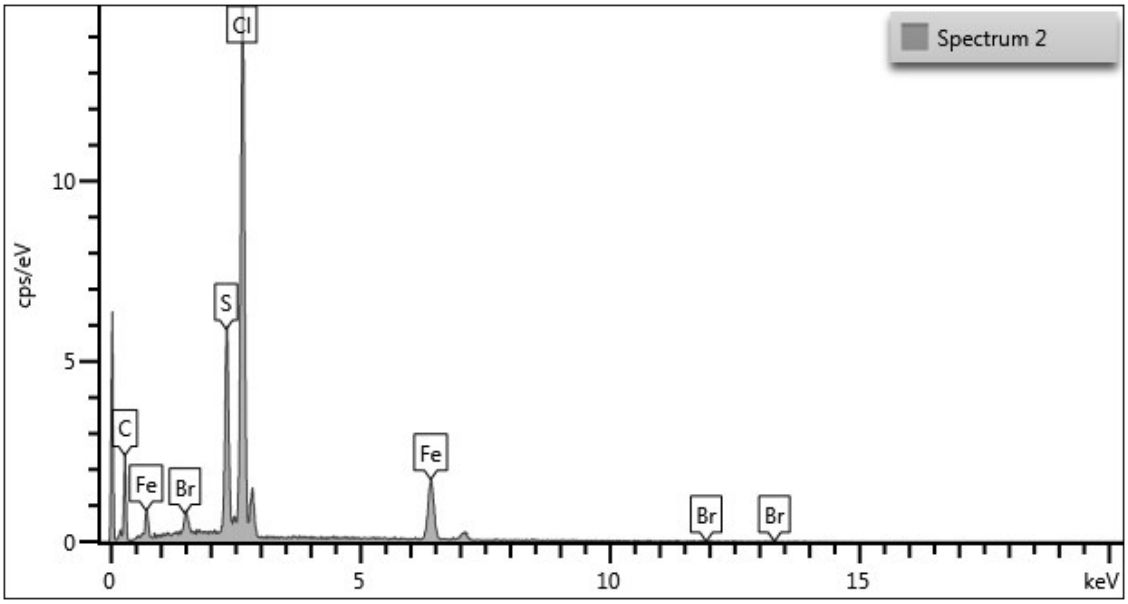

Figure S1. Energy dispersive X-ray spectrum of the $[(CH_3)_3S][FeCl_4]$ compound.

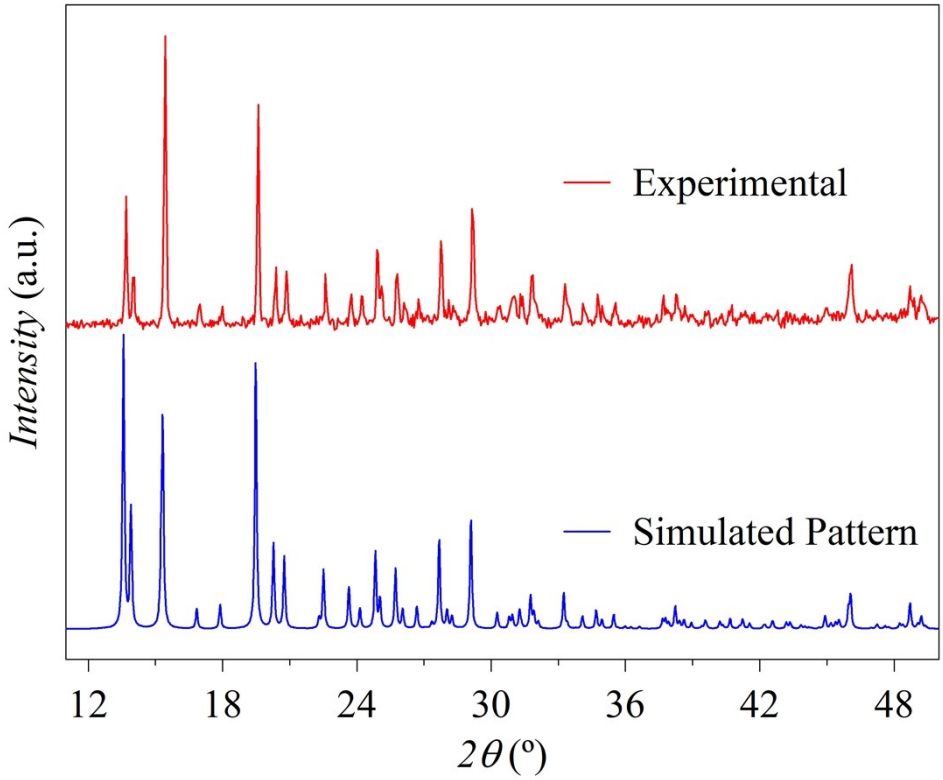

Figure S2. Room temperature experimental PXRD patterns for the obtained $[(CH_3)_3S][FeCl_4]$ compound together with the simulated patterns based on its single crystal structure at room temperature.

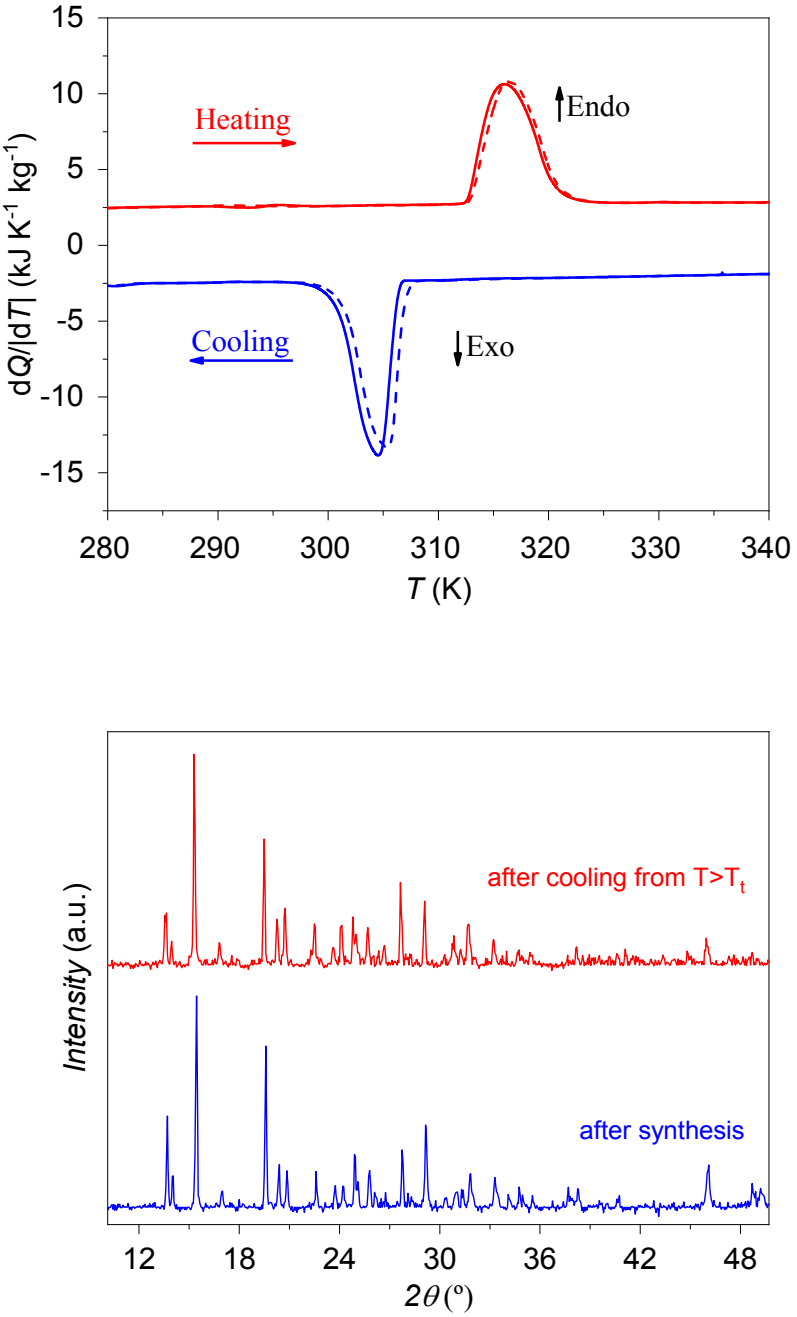

Figure S3. **Top**: Several DSC curves (solid line first cycle and dash line second cycle) for $[(CH_3)_3S][FeCl_4]$ compound. **Bottom:** Room temperature PXRD patterns for the obtained $[(CH_3)_3S][FeCl_4]$ compound after synthesis (blue line) and after cooling from $T > T_t$ (red line).

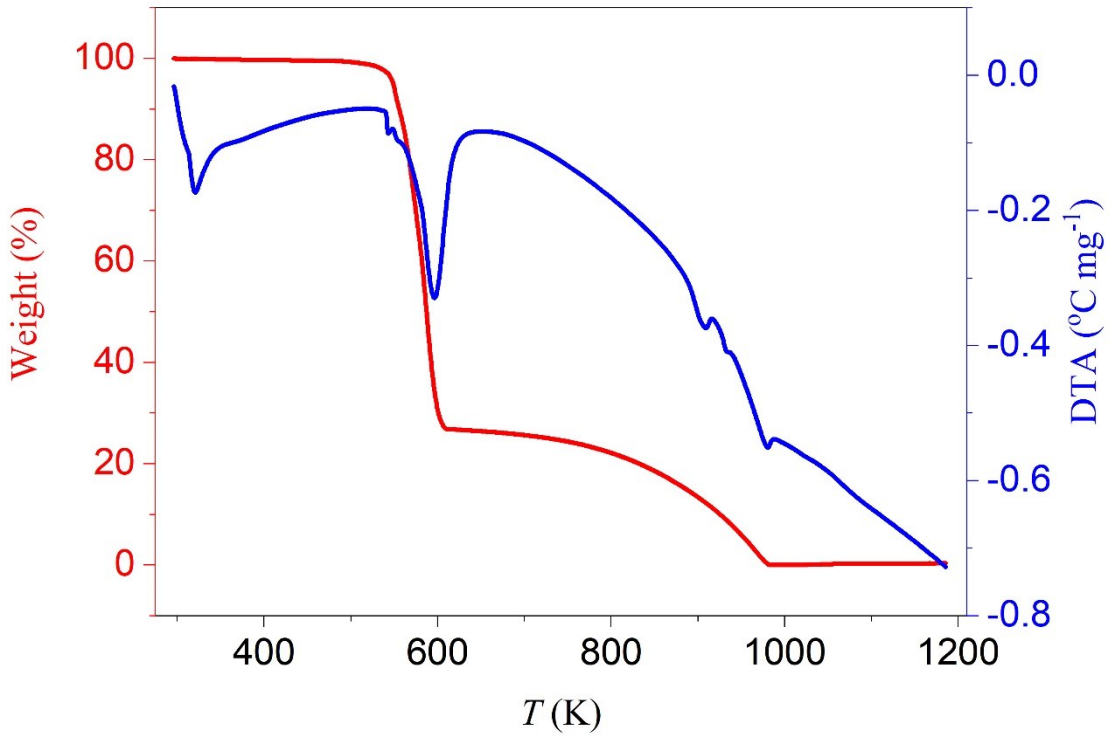

Figure S4. TGA and DTA decomposition curves for the $[(CH_3)_3S][FeCl_4]$ compound.

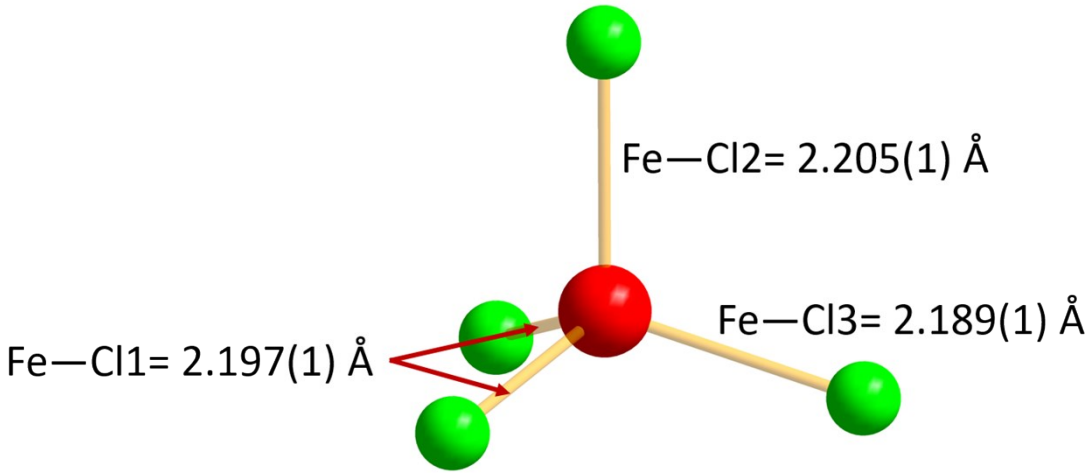

Figure S5. Detail of the crystal structure of the $[(CH_3)_3S][FeCl_4]$ compound showing the three different Fe-Cl distances present in the $[FeCl_4]^-$ anions at 100K.

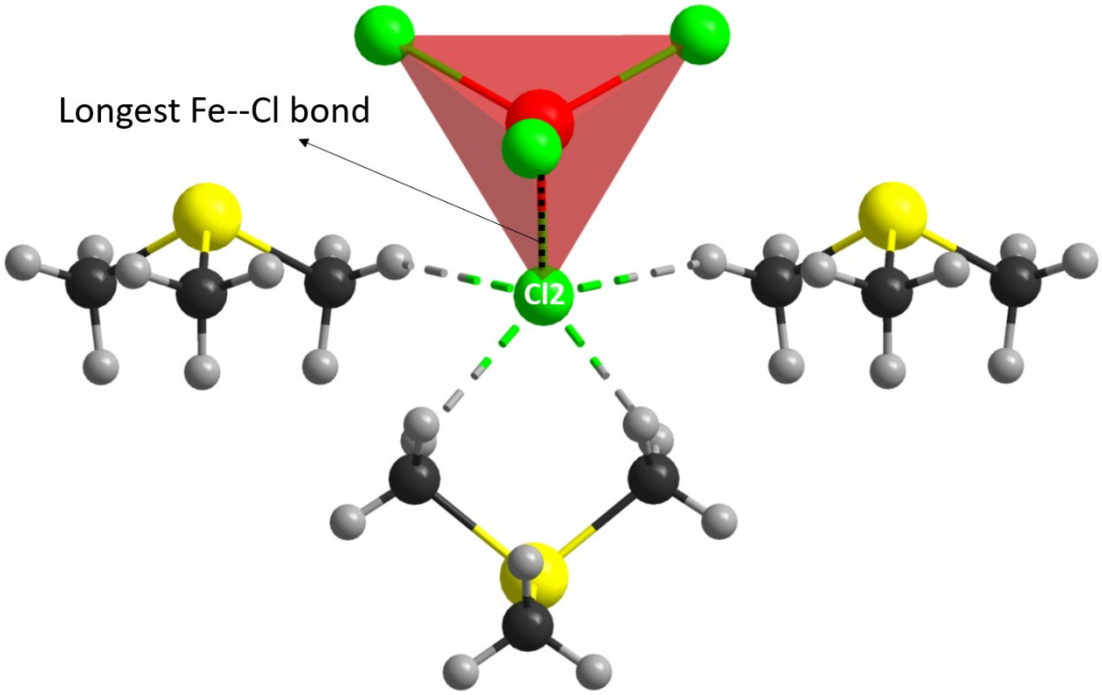

Figure S6. Detail of the crystal structure of the $[(CH_3)_3S][FeCl_4]$ compound at 100K showing the interactions between one Cl-atom of $[FeCl_4]^-$ with four H-atoms of methyl groups of three $[(CH_3)_3S]^+$ cations.

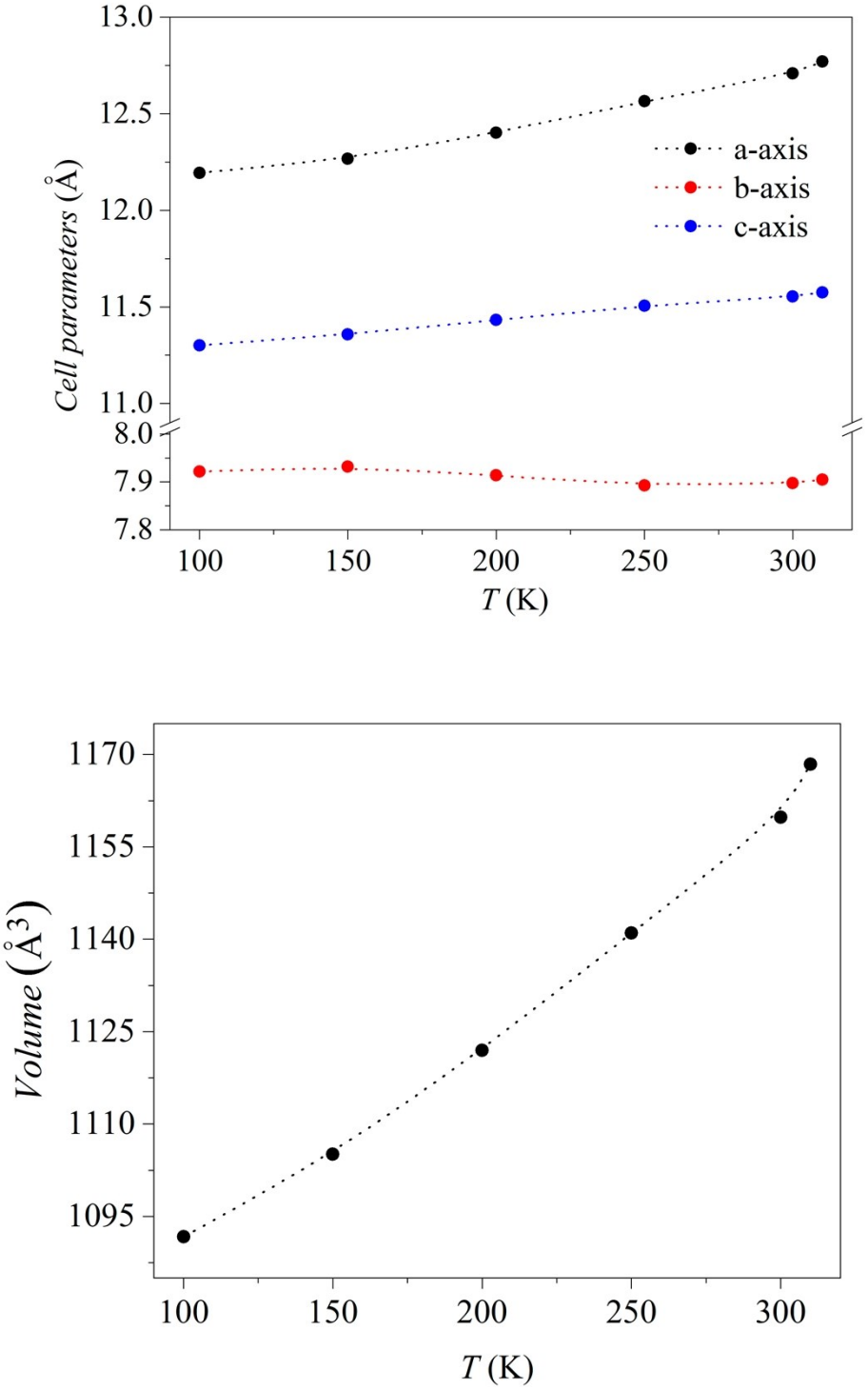

Figure S7. **Top:** Thermal evolution of the cell parameters of the LT-polymorph of $[(CH_3)_3S][FeCl_4]$. **Bottom:** Thermal evolution of the volume of the LT-polymorph of $[(CH_3)_3S][FeCl_4]$.

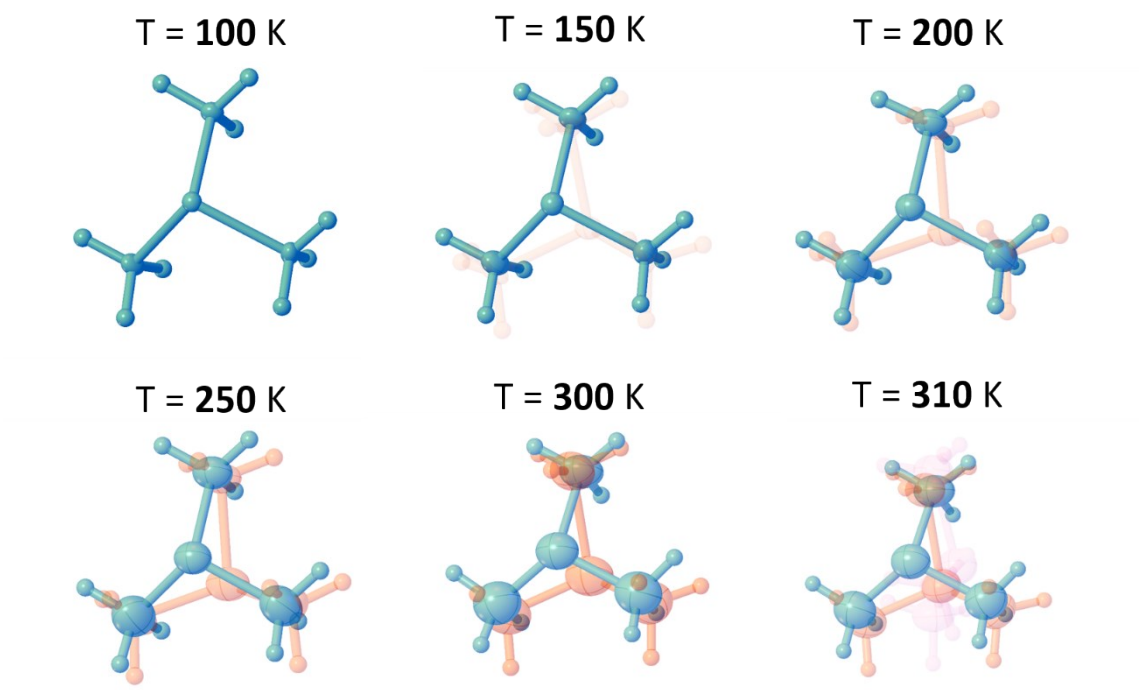

Figure S8. Detail of the crystal structure of $[(CH_3)_3S][FeCl_4]$ showing the disorder of the $[(CH_3)_3S]^+$ cations at different temperatures between 100, 150, 200, 250, 300 and 310K (from left top to right bottom). The ellipsoid shows a probability of 30%. Hydrogen atoms shown as spheres of fixed radius. Refined atomic population parameters are used for transparency level (%), see Table S3 for numerical values.

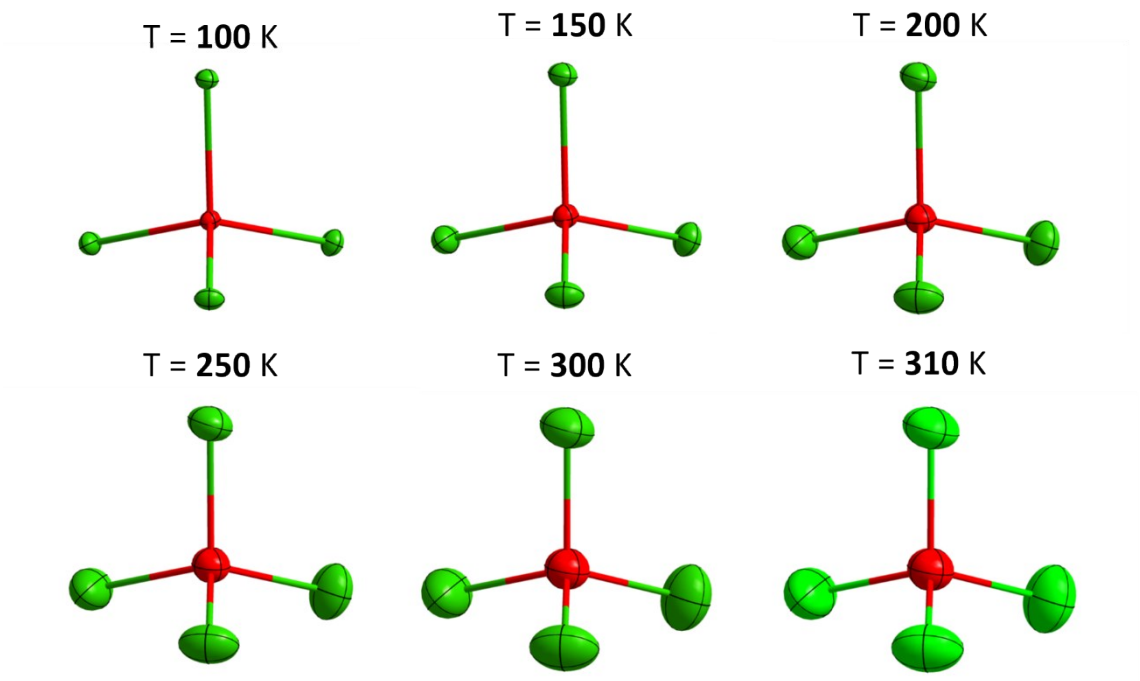

Figure S9. Detail of the crystal structure of $[FeCl_4]^-$ tetrahedral at different temperatures between 100, 150, 200, 250, 300 and 310 K (from left top to right bottom). The ellipsoid shows a probability of 30%.

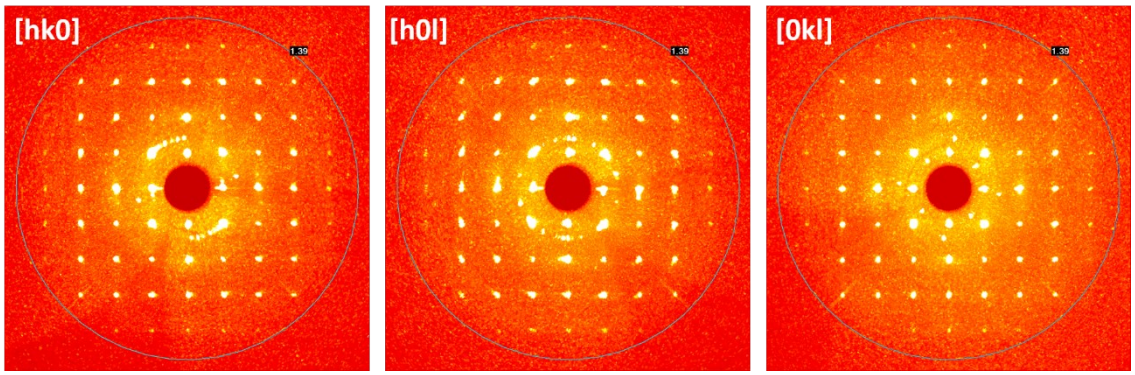

Figure S10. Precession images generated from single-crystal X-ray diffraction data of the HT-polymorph obtained along the main axis.

Table S1. Crystal data and structure refinement for $[(CH_3)_3S]][FeCl_4]$.

Empirical formula	$C_3H_9S\ FeCl_4$						
Wavelength (Å)	0.71073						
Crystal size (mm^3)	0.170 x 0.100 x 0.056						
Formula weight	274.81						
F(000)	548						
							Proposed SG
Temperature (K)	100	150	200	250	300	310	320
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Cubic?
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pnma*	*Pm-3m*?
Unit cell dimensions (Å)	a = 12.1950(7)	a = 12.2667(8)	a = 12.4012(4)	a = 12.5644(5)	a = 12.707(4)	a = 12.7698(9)	a = 6.6626(13)
	b = 7.9217(4)	b = 7.9320(5)	b = 7.9136(2)	b = 7.8927(3)	b = 7.900(2)	b = 7.9044(5)	
	c = 11.3013(6)	c = 11.3580(7)	c = 11.4326(4)	c = 11.5059(4)	c = 11.551(4)	c = 11.5756(8)	
Volume ($Å^3$)	1091.71(10)	1105.13(12)	1121.97(6)	1141.01(7)	1159.6(6)	1168.41(14)	295.75(17)
Z	4	4	4	4	4	4	1
Density calculated (Mg/m^3)	1.672	1.652	1.627	1.600	1.574	1.562	-
Absorption coefficient (mm^{-1})	2.482	2.452	2.415	2.375	2.337	2.319	2.290
Tmin, Tmax	0.72, 0.87	0.65, 0.88	0.74, 0.88	0.74, 0.88	0.74, 0.88	0.72, 0.88	0.61, 0.82
Theta range for data collection (°)	2.46 - 36.37	2.44 - 33.16	2.42 - 33.13	2.40 - 29.57	2.38 - 27.13	2.38 - 26.72	3.06 – 15.15
Index ranges	-20<=h<=20 -13<=k<=13 -18<=l<=18	-17<=h<=18 -12<=k<=12 -17<=l<=17	-17<=h<=19 -12<=k<=12 -17<=l<=17	-16<=h<=17 -10<=k<=10 -15<=l<=15	-15<=h<=16 -10<=k<=10 -14<=l<=14	-15<=h<=16 -10<=k<=9 -14<=l<=14	-4<=h<=4 -4<=k<=4 -4<=l<=4
Measured reflections	65618	16182	17487	13914	11340	11256	2763
Independent reflections	2802 [R(int)=0.0488]	2241 [R(int)=0.0417]	2260 [R(int)=0.0369]	1702 [R(int)=0.0390]	1372 [R(int)=0.0365]	1324 [R(int)=0.0332]	24 [R(int)=0.0588]
Indep. Reflections [I>⍰(I)]	2420	1726	1715	1194	889	844	24
Completeness (%)	99.8	99.9	99.8	99.8	99.9	99.9	100
Refinement method	Full-matrix least-squares on F^2						-
Data / restraints / parameters	2802 / 0 / 63	2241 / 94 / 83	2260 / 94 / 83	1702 / 94 / 83	1372 / 94 / 83	1324 / 219 / 121	-
Goodness-of-fit on F^2	1.102	1.057	1.031	1.022	1.030	1.050	-
Final R indices [I>2sigma(I)]	R1 = 0.0288 wR2 = 0.0603	R1 = 0.0345 wR2 = 0.0601	R1 = 0.0343 wR2 = 0.0719	R1 = 0.0401 wR2 = 0.0938	R1 = 0.0484 wR2 = 0.1254	R1 = 0.0378 wR2 = 0.0933	-
R indices (all data)	R1 = 0.0377 wR2 = 0.0652	R1 = 0.0542 wR2 = 0.0680	R1 = 0.0514 wR2 = 0.0827	R1 = 0.0602 wR2 = 0.1090	R1 = 0.0764 wR2 = 0.1493	R1 = 0.0621 wR2 = 0.1113	-
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.628 and -0.657	0.652 and -0.469	0.439 and -0.410	0.560 and -0.374	0.522 and -0.262	0.230 and -0.215	-

Table S2. Interactions between Cl-atoms of $[FeCl_4]^-$ with t H-atoms of methyl group of $[(CH_3)_3S]^+$ cations at different temperatures (distances in Å, º). Atoms labelled as ^a, ^b or ^c according to different disordered positions for the cation.

	D-H	H...A	D...A	<(DHA)	
T=100K					
	0.97(2)	2.79(2)	3.6488(15)	147.0(17)	C1-H1B...Cl2_i
	0.92(2)	2.79(2)	3.6251(15)	150.9(17)	C1-H1C...Cl2_ii
T=150K					
	0.98	2.84	3.676(6)	144.0	C1^a-H1B^a...Cl2_i
	0.98	2.75	3.632(6)	150.0	C1^a-H1C^a...Cl2_iii
	0.98	3.00	3.73(6)	132.4	C1B^b-H1D^b...Cl2_iii
	0.98	2.72	3.46(5)	132.2	C1B^b-H1D^b...Cl3
	0.98	2.67	3.55(6)	149.1	C1B^b-H1E^b...Cl2_i
	0.98	2.92	3.63(5)	129.5	C1B^b-H1F^b...Cl1_iv
	0.965(19)	2.97(3)	3.64(6)	128(3)	C2B^b-H2E^b...Cl1_iii
T=200K					
	0.98	2.87	3.675(7)	140.5	C1^a-H1B^a...Cl2_i
	0.98	2.78	3.674(7)	152.5	C1^a-H1C^a...Cl2_iii
	0.98	2.83	3.59(2)	135.0	C1B^b-H1D^b...Cl2_iii
	0.98	2.88	3.547(16)	126.2	C1B^b-H1D^b...Cl3
	0.98	2.87	3.73(2)	147.9	C1B^b-H1E^b...Cl2_i
T=250K					
	0.97	2.88	3.630(15)	134.4	C1^a-H1B^a...Cl1_iv
	0.97	2.95	3.697(14)	134.8	C1^a-H1B^a...Cl2_i
	0.97	2.81	3.704(14)	154.0	C1^a-H1C^a...Cl2_iii
	0.97	2.84	3.63(3)	139.5	C1B^b-H1D^b...Cl2_iii
	0.97	2.93	3.50(3)	118.3	C1B^b-H1D^b...Cl3
	0.97	2.95	3.75(3)	141.1	C1B^b-H1E^b…Cl2_i
T=300K					
	0.96	2.75	3.576(15)	144.6	C1^a-H1B^a...Cl1_iv
	0.96	2.80	3.702(18)	157.4	C1^a-H1C^a...Cl2_iii
	0.96	2.77	3.44(2)	127.8	C1B^b-H1D^b...Cl3
	0.96	2.84	3.70(3)	149.5	C1B^b-H1E^b...Cl2_i
	0.94(2)	2.98(3)	3.65(3)	129.6(17)	C2B^b-H2E^b...Cl1_iii
T=310K					
	0.96	2.81	3.585(11)	138.0	C1^a-H1B^a...Cl1_iv
	0.96	2.84	3.707(14)	150.0	C1^a-H1C^a...Cl2_iii
	0.96	2.69	3.43(2)	134.9	C1B^b-H1D^b...Cl3
	0.96	2.79	3.69(3)	155.7	C1B^b-H1E^b...Cl2_i
	0.96	2.53	3.35(5)	143.4	C1C^c-H1I^c...Cl1_iii
	0.96	2.81	3.72(6)	158.3	C2C^c-H1J^c...Cl1_v
	0.96	2.71	3.48(7)	137.3	C2C^c-H1L^c...Cl1_iii
	0.96	2.92	3.70(6)	138.6	C3C^c-H1M^c...Cl1
	0.96	2.81	3.44(4)	124.6	C3C^c-H1O^c…Cl3_i

Symmetry operations:
(i) -x+1, -y+1, -z+1
(ii) x-1/2, -y+3/2, -z+1/2
(iii) x-1/2, y, -z+1/2
(iv) -x+1/2, -y+1, z+1/2
(v) x-1/2, -y+1/2, -z+1/2

Table S3. $[(CH_3)_3S]^+$ cation disorder vs temperature.

Temperature (K)	No disordered positions	Refined population parameters (%)
100	1*	100
150	2	92.3(2) / 7.7(2)
200	2	81.1(2) / 18.9(2)
250	2	71.4(3) / 28.6(3)
300	2	65.2(5) / 34.8(5)
310	4	60.0(3) / 25.7(3) / 7.11(14) / 7.11(14)**

(*) There are some low electron density residual peaks in the Fourier difference map that allow to construct and refine (with many constrains) a disordered model for $[(CH_3)_3S]^+$ in 2 orientations like that found at higher temperatures. The final refined population parameters are 99.07(13) / 0.93(13) %. It is a much more complicated model with no significant improvement in data fitting, therefore, the no disordered model is considered in the final refinement reported at 100K.
(**) Last two population values are identical because they correspond to disordered positions related by a mirror symmetry plane.