ELECTRONIC SUPLEMENTARY INFORMATION

Temperature Evolution of (quinuclidinium)[$FeCl_4$]; a Plastic/Polar Magnetic Hybrid Compound with Giant Dielectric Constant

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Table S1: Crystallographic data and single-crystal refinement details of (quinuclidinium)[$FeCl_4$] at 300 and 100 K from the refinement of the X-ray single-crystal data.

	Phase III @ 100 K	**Phase II @ 300 K**
Empirical formula	$C_7H_{13}Cl_4FeN_1$	$C_7H_{13}Cl_4FeN_1$
Formula weight	308.84	308.84
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	$Pbc2_1$
a (Å)	13.1204(3)	6.6991(2)
b (Å)	12.6450(4)	13.1984(5)
c (Å)	14.7155(5)	14.6266(5)
V (Å^3)	2441.41(13)	1293.25(8)
Z	8	4
ρ (g·cm^{-3})	1.686	1.591
wavelength (Å^{-1})	0.71073	0.71073
Reflections [I>2σ(I)]	2246	2069
Reflections [all data]	2606	2619
parameters	121	118
Goodness of fit (S)[a]	1.178	1.044
R_1[b]/wR^2[c] [I>2σ(I)]	0.0640 / 0.1203	0.0547 / 0.1740
R_1[b]/wR^2[c] [all data]	0.0731 / 0.1244	0.0680 / 0.5602

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R_1 = \sum||F_0|-|F_c|| / \sum|F_0|$; [c] $wR2 = [\sum w(F_0^2)^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2Fc^2)/3$, being a = 0.0528 and b = 3.3176

Table S2: Crystallographic data and single-crystal refinement details of (quinuclidinium)[$FeCl_4$] at 10 , 250 and 295 K from the refinement of the neutron single-crystal data.

	Phase III @ 10 K	**Phase III @ 250 K**	**Phase II @ 295 K**
Empirical formula	$C_7H_{13}Cl_4FeN_1$	$C_7H_{13}Cl_4FeN_1$	$C_7H_{13}Cl_4FeN_1$
Formula weight	308.84	308.84	308.84
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*P b c a*	*P b c a*	*P b c* 2_1
a (Å)	13.0822(5)	13.2030(10)	6.6726(19)
b (Å)	12.5799(6)	12.8939(12)	13.1429(8)
c (Å)	14.6292(5)	14.7769(10)	14.6275(15)
V (Å^3)	2407.57(17)	2515.6(3)	1282.8(4)
Z	8	8	4
ρ (g·cm^{-3})	1.710	1.636	1.604
wavelength (Å $^{-1}$)	0. 94558	1. 45566	1. 45566
Reflections [I>2σ(I)]	3821	1278	643
Reflections [all data]	3921	1743	957
parameters	245	244	118
Goodness of fit (S)[a]	1.254	1.606	2.485
R_1[b]/wR^2[c] [I>2σ(I)]	0.0961 / 0.2256	0.0770 / 0.2114	0.2046 / 0.5063
R_1[b]/wR^2[c] [all data]	0.0975 / 0.2262	0.0996 / 0.2255	0.2464 / 0.5602

[a] $S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$. [b] $R_1 = \sum||F_0|-|F_c|| / \sum|F_0|$; [c] $wR2 = [\sum w(F_0^2)^2 - F_c^2)^2 / \sum w(F_0^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (\max(F_0^2,0) + 2Fc^2)/3$, being a = 0.0528 and b = 3.3176

Table S3: Relevant distances of (quinuclidinium)[$FeCl_4$] at 10 K.

Quinuclidinium	**Length (Å)**	**FeCl4**	**Length (Å)**	**Fe···Fe**	**Length (Å)**
C7-C4	1.533(4)	Fe1-Cl4	2.189(2)	Fe1···Fe1^{I}	6.350(3)
C7-C8	1.535(3)	Fe1-Cl2	2.198(2)	Fe1···Fe1^{II}	6.541(2)
C3-C4	1.536(4)	Fe1-Cl3	2.205(3)	Fe1···Fe1^{III}	7.444(2)
C3-C2	1.537(4)	Fe1-Cl1	2.209(2)		
C2-N1	1.505(3)				
C6-N1	1.505(3)				
C6-C5	1.540(4)				
C4-C5	1.531(3)				
C8-N1	1.506(3)				

I: 1/2-*x*, -1/2+*y*, *z*; II: 1/2+*x*, *y*, 1/2-*z*; III: 1/2-*x*, -*y*, 1/2+*z*.

Table S4: Relevant distances of (quinuclidinium)[$FeCl_4$] at 250 K.

Quinuclidinium	Length (Å)	FeCl4	Length (Å)	Fe···Fe	Length (Å)
C1-C2	1.530(7)	Fe1-Cl3	2.175(3)	Fe1···Fe1^{IV}	6.488(4)
C1-C3	1.530(8)	Fe1-Cl1	2.181(3)	Fe1···Fe1^{II}	6.602(3)
C1-C5	1.537(6)	Fe1-Cl4	2.187(5)	Fe1···Fe1^{VI}	7.420(2)
C2-C6	1.519(7)	Fe1-Cl2	2.192(3)		
C3-C4	1.497(7)				
C4-N1	1.489(6)				
C5-C7	1.499(7)				
C6-N1	1.476(5)				
C7-N1	1.485(5)				

II: 1/2+*x*, *y*, 1/2-*z*; IV: 1-*x*, 1/2+*y*, 1/2-*z*; VI: 1-*x*, 1-*y*, -*z*.

Table S5: Relevant distances of (quinuclidinium)[$FeCl_4$] at 295 K.

Quinuclidinium	Length (Å)	FeCl4	Length (Å)	Fe···Fe	Length (Å)
C2A-C6A	2.48(4)	Fe1-Cl4	2.138(19)	Fe1···Fe1^{VII}	6.621(13)
C2A-C8A	2.50(4)	Fe1-Cl2	2.172(12)	Fe1···Fe1^{VIII}	6.67(10)
C7A-N1A	2.35(4)	Fe1-Cl1	2.207(17)	Fe1···Fe1^{IX}	7.417(16)
C7A-C3A	2.48(4)	Fe1-Cl3	2.218(19)		
C7A-C5A	2.49(4)				
C8A-C6A	2.49(4)				
C4A-C6A	2.471(4)				
C4A-N1A	2.48(3)				
C5A-N1A	2.44(4)				
C5A-C3A	2.48(5)				
C3A-N1A	2.40(4)				
C2B-C6B	2.49(4)				
C2B-C8B	2.49(4)				
C7B-N1B	2.44(4)				
C7B-C3B	2.48(4)				
C7B-C5B	2.49(4)				
C8B-C4B	2.48(3)				
C8B-C6B	2.49(4)				
C4B-N1B	2.48(3)				
C4B-C6B	2.48(3)				
C5B-N1B	2.44(4)				
C5B-C3B	2.48(4)				
C3B-N1B	2.32(4)				

VII: -*x*, 1/2+*y*, *z*; VIII: 1+*x*, *y*, *z*; IX: -*x*, -*y*, 1/2+*z*.

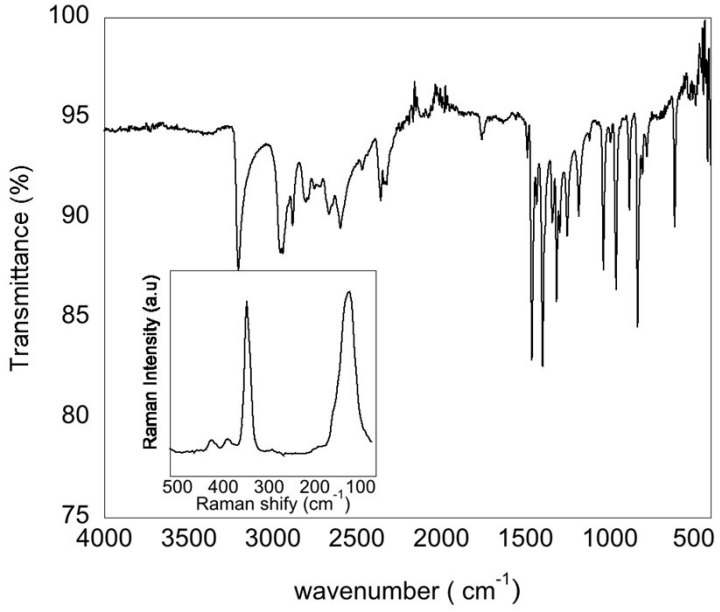

Fig. S1. FTIR and Raman (inset) spectra of (quinuclidinium)[$FeCl_4$].

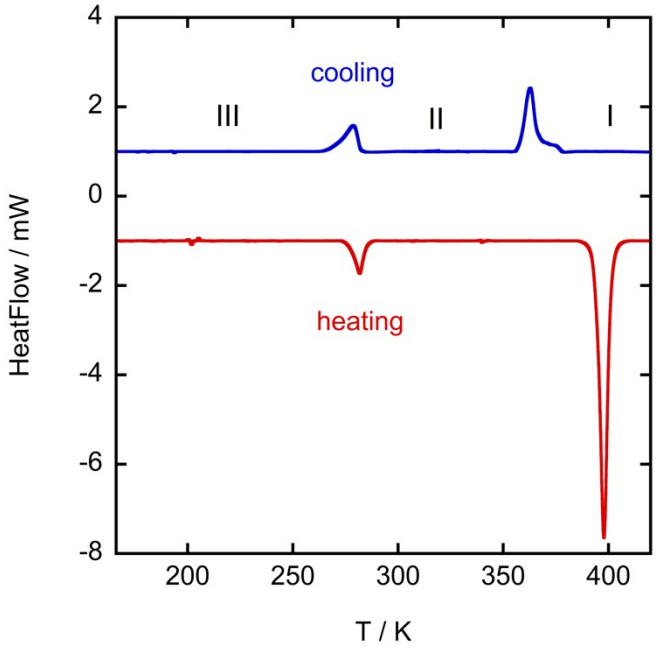

Fig. S2. DSC-thermogram of (quinuclidinium)[FeCl4]. Heating rate: 10 K/min.

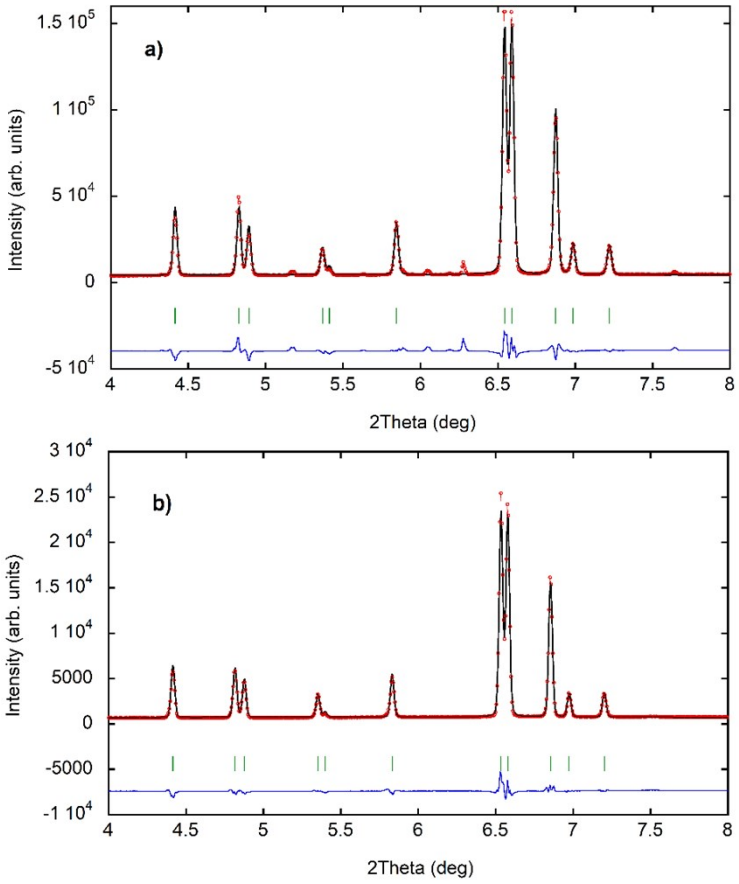

Fig. S3. Rietveld refinement at 300 K (a) and 300 K after increasing the temperature up to 470 K (b). The peaks corresponding to the second phase are not observed in the pattern after the annealing. Observed and calculated patterns are represented by red points and by a solid black line, respectively. Positions of the Bragg reflections are represented by vertical green bars. The observed-calculated difference pattern is depicted as a blue line at the bottom of the figure.

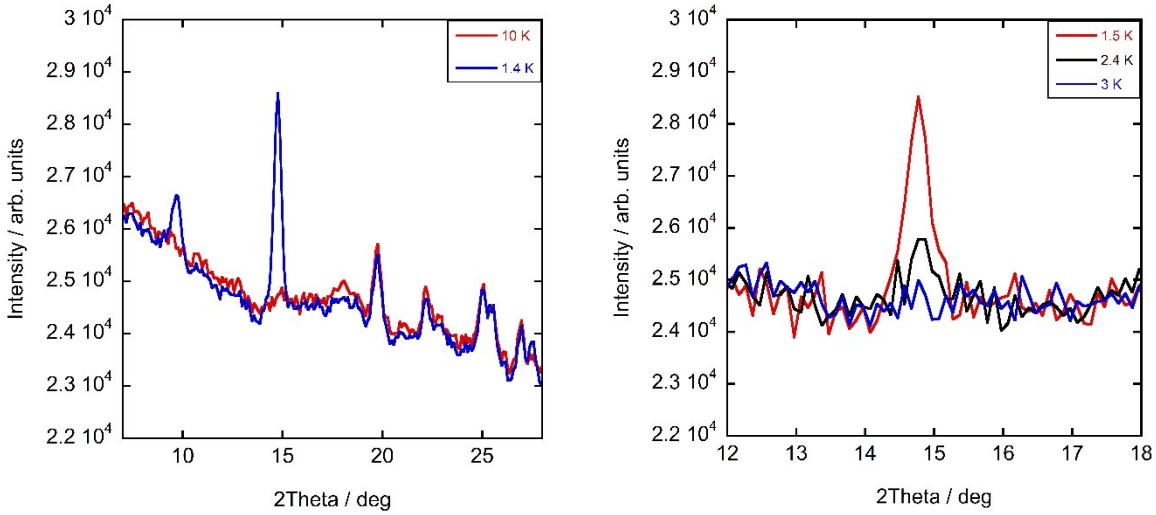

Fig. S4. (Left) D1B data at 10 (red) and 1.4 K (blue). (Right) Evolution of the main magnetic peak as function of temperature.