Electronic Supplementary Material (ESI) for Dalton Transactions.

Dielectric Relaxation and Anhydrous Proton Conduction in $[C_2H_5NH_3][Na_{0.5}Fe_{0.5}(HCOO)_3]$ Metal-Organic Framework

A. Sieradzki[1*], S. Pawlus[2,3], S. N. Tripathy[2,3], A. Gągor[3], M. Ptak[4], M. Paluch[2,3], M. Mączka[4]

[1]Departament of Experimental Physics, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

[2]Institute of Physics, University of Silesia, ul. Uniwersytecka 4, PL-40-007 Katowice, Poland

[3]Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1A, 41-500 Chorzow, Poland.

[4]Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Box 1410, 50-950 Wrocław 2, Poland

Authors of correspondence: sebastian.pawlus@us.edu.pl

FIG.S1: Powder XRD patterns for the as-prepared sample and sample after dielectric studies together with the calculated pattern based on the single crystal structure at room temperature (space group Pn) .

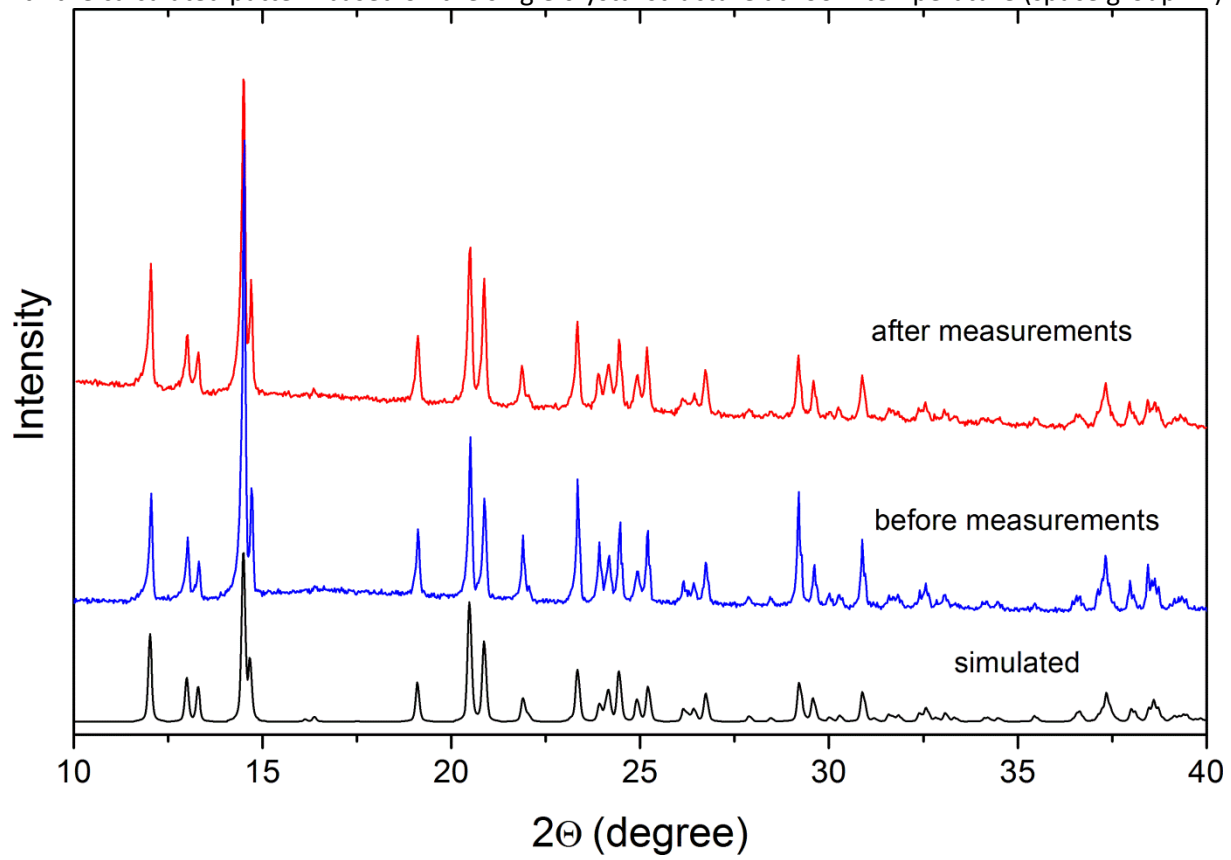

FIG. S2: Powder XRD patterns for pure cristalline sample together with the calculated pattern based on the single crystal structure for two phases.

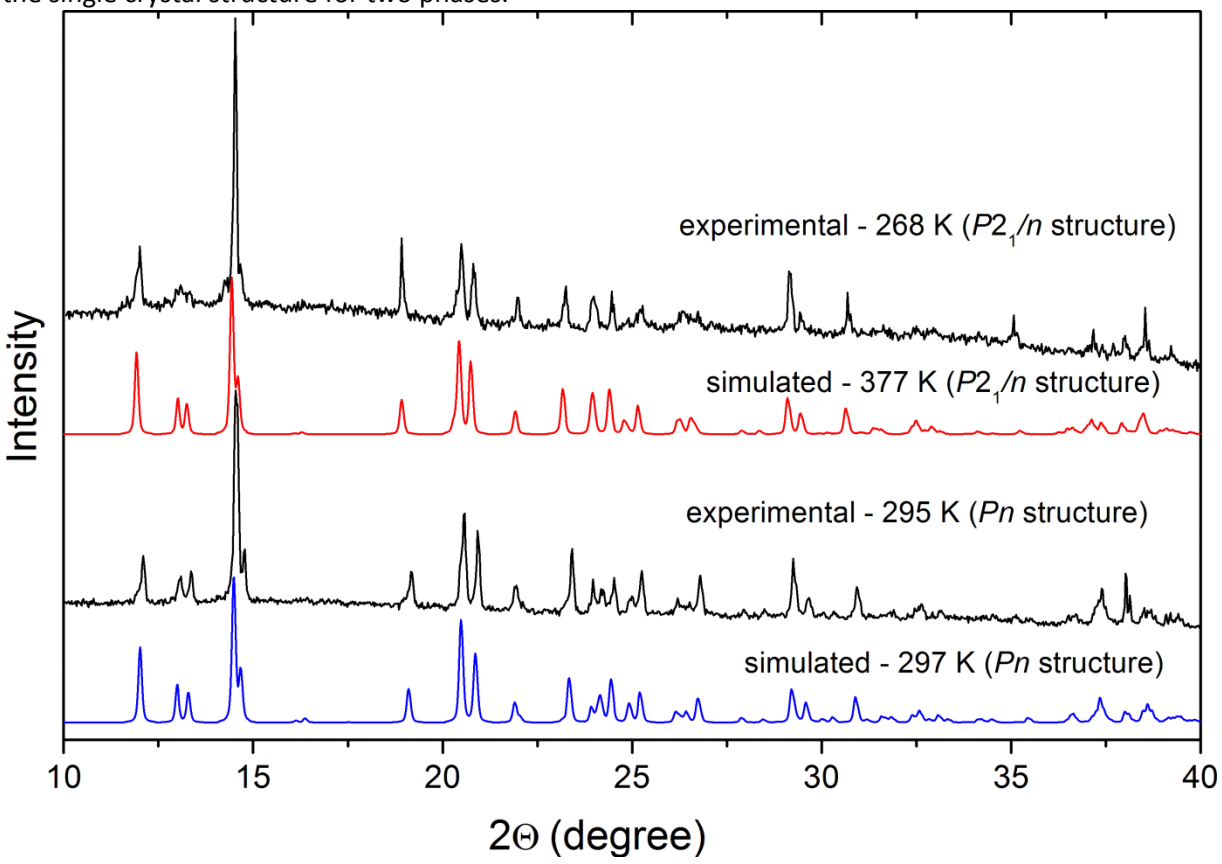

FIG.S3: The arrangement of the cations in the EtANaFe crystal; (a) high temperature phase I, T=360K, (b) polar phase II, T=297K demonstrating H-bonded network

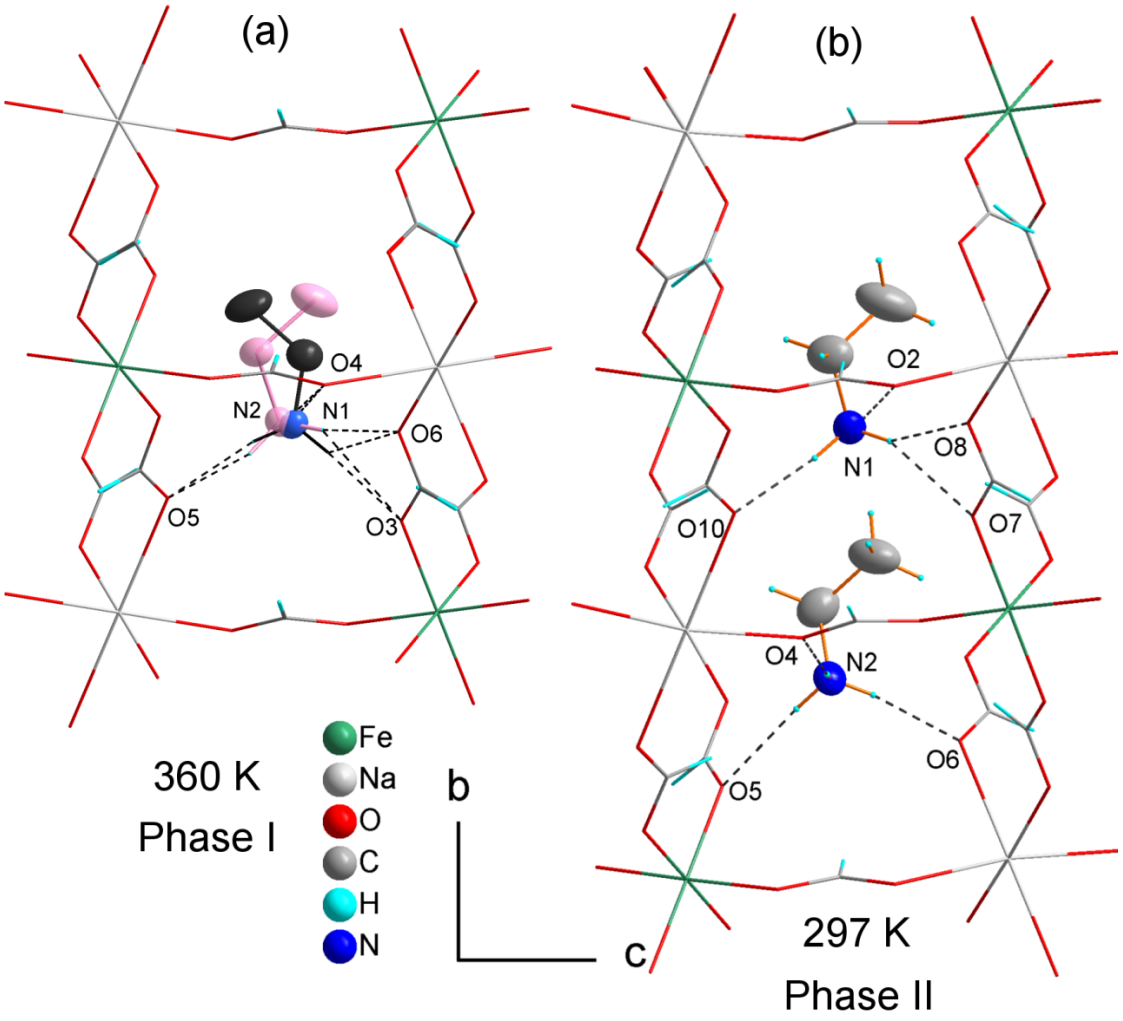

Fig.S4. EtA^+ cations in (a) Phase I, (b)-(c) polar Phase II. Hydrogen atoms have been omitted for the picture clarity. Two disordered positions are drawn for EtA^+ in Phase I. The site occupation factor is equal to 0.56 and 0.44 for A and B, respectively.

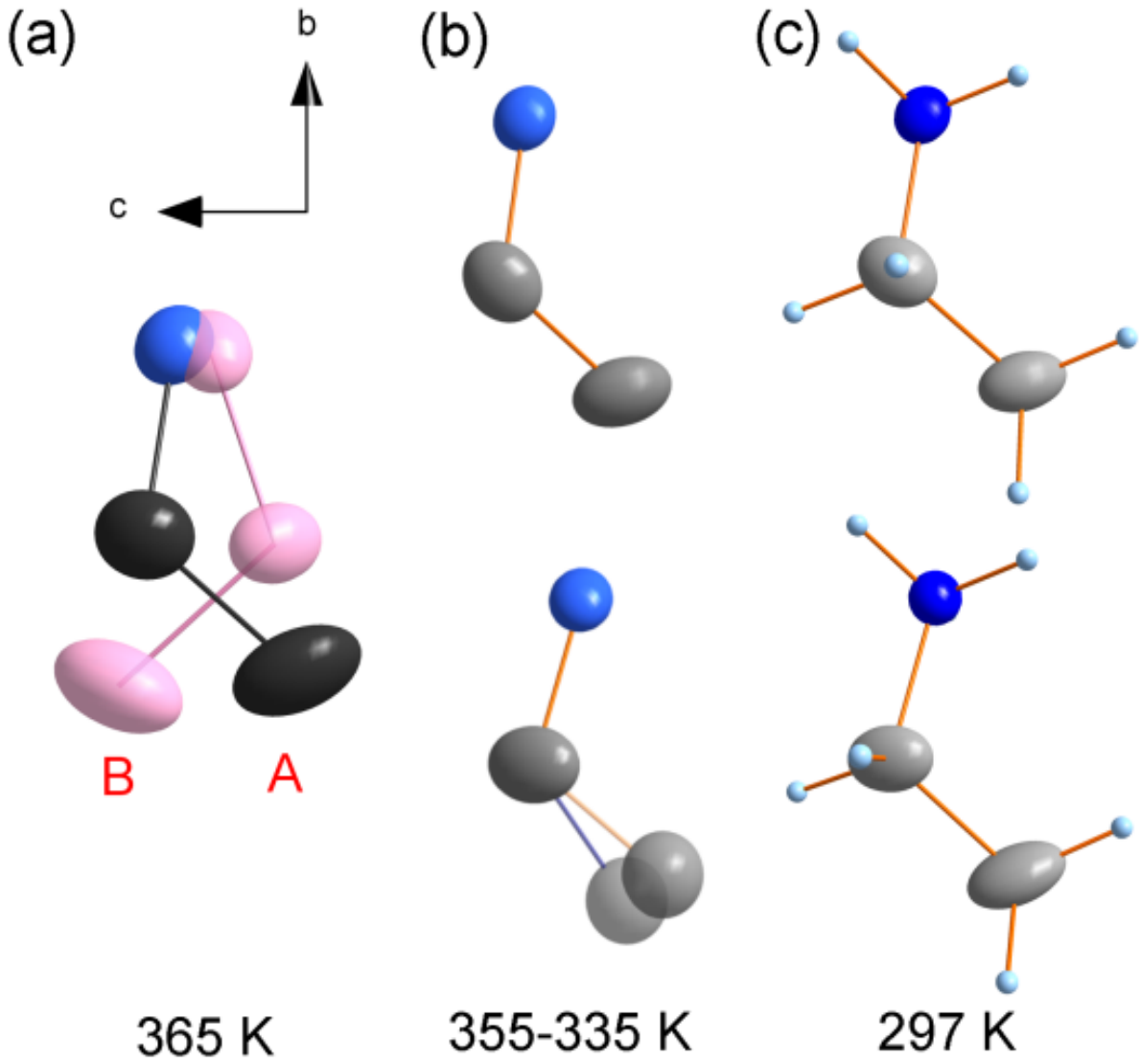

Fig.S5. The EtA^+ arrangement in the centrosymmetric Phase I and in the polar Phase II. Phase transition diminishes the rotational motion and lead to the polar organization of the template cations.

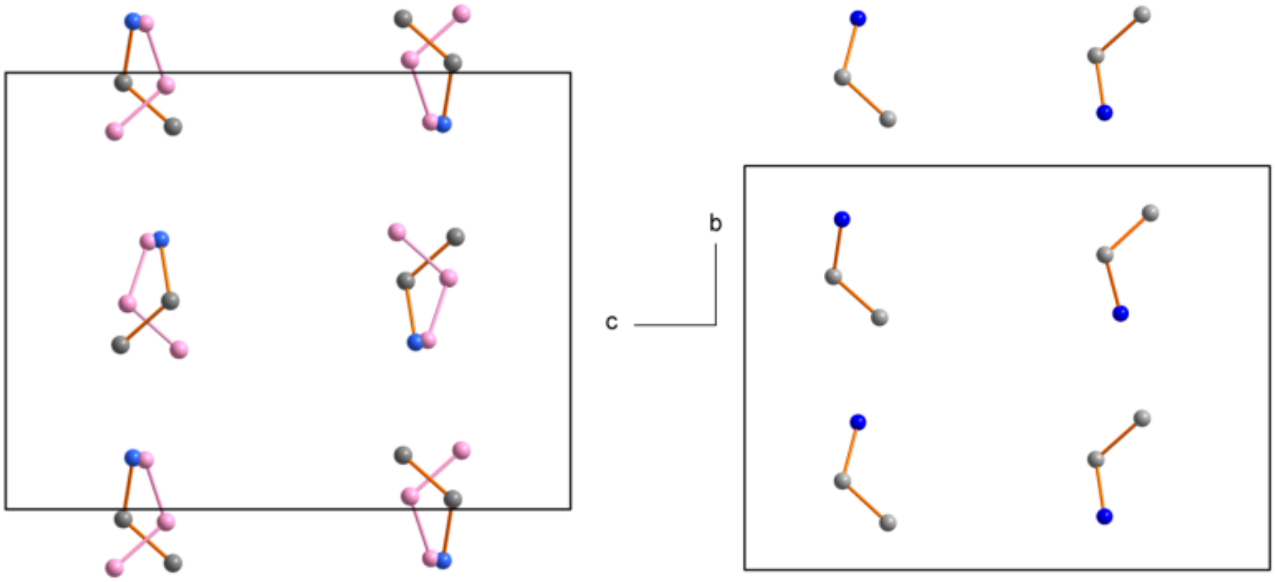

Fig.S6. The activation plot of the conductivity, σ. Vertical arrow indicate the transition temperature, T_c.

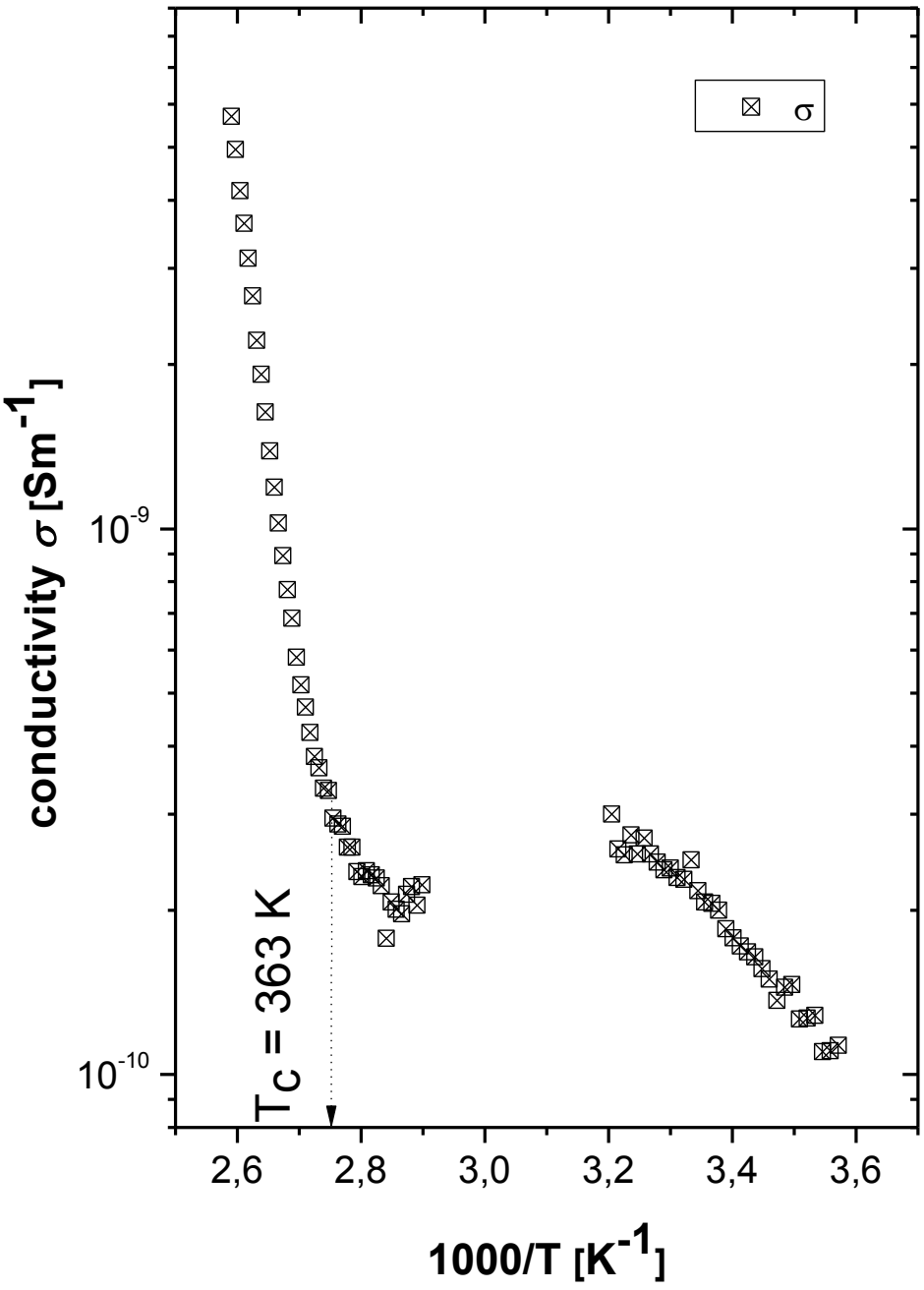

Fig.S7 Comparison of the conductivity range at the loss spectra collected at various temperatures

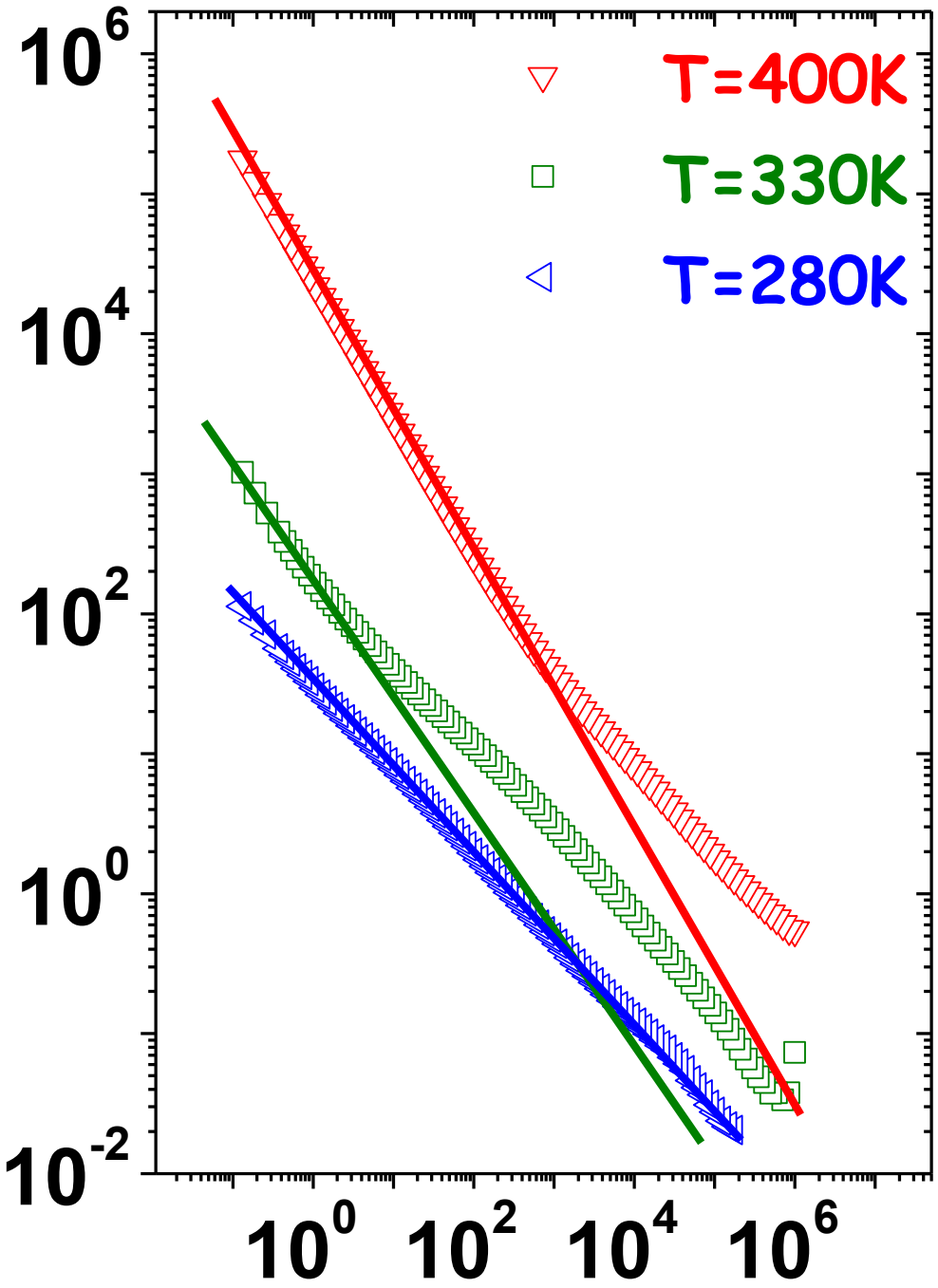

Table S1. Selected geometric parameters (Å)

(365K)			
Fe1—O1	2.0100 (18)	O1—C1	1.260 (3)
Fe1—O1^{i}	2.0100 (18)	O2—C3	1.249 (4)
Fe1—O3	2.0149 (19)	O3—C2	1.272 (3)
Fe1—O3^{i}	2.0149 (19)	O4—C1	1.218 (3)
Fe1—O2^{i}	2.0191 (18)	O5—C3	1.224 (4)
Fe1—O2	2.0191 (18)	O5—Na1^{iii}	2.534 (2)
Na1—O6^{ii}	2.414 (2)	O6—C2	1.212 (4)
Na1—O6^{iii}	2.414 (2)	O6—Na1^{v}	2.414 (2)
Na1—O4	2.443 (2)	C4—N2	1.4601 (10)
Na1—O4^{iv}	2.443 (2)	C4—C5	1.4995 (10)
Na1—O5^{v}	2.534 (2)	C6—N1	1.4601 (10)
Na1—O5^{vi}	2.534 (2)	C6—C7	1.4993 (10)
(355K)			
Fe1—O1	1.994 (5)	O7—C4	1.289 (7)
Fe1—O7	2.009 (4)	O5—C2	1.264 (7)
Fe1—O3	2.016 (4)	O6—C3	1.237 (7)
Fe1—O9	2.018 (4)	O9—C1	1.258 (7)
Fe1—O5	2.019 (3)	O10—C1	1.231 (7)
Fe1—O11	2.025 (5)	O11—C6	1.265 (11)
Na—O12^{vii}	2.387 (7)	O12—C2	1.220 (7)
Na—O8^{viii}	2.435 (7)		
Na—O4^{ix}	2.438 (8)	N2—C7	1.446 (9)
Na—O2^{x}	2.448 (8)	C7—C8	1.442 (12)
Na—O10	2.522 (5)	N1—C9	1.452(2)
Na—O6^{xi}	2.537 (5)	C9—C10B	1.470 (2)
O1—C5	1.260 (10)		
O2—C5	1.205 (10)		
O3—C3	1.248 (7)		
O4—C6	1.225 (10)		
(345K)			
Fe1—O11	2.009 (4)	O5—C2	1.272 (6)
Fe1—O1	2.009 (4)	O6—C3	1.236 (6)
Fe1—O7	2.010 (3)	O9—C1	1.261 (6)
Fe1—O3	2.016 (3)	O10—C1	1.233 (6)
Fe1—O9	2.019 (3)	O11—C6	1.266 (8)
Fe1—O5	2.021 (3)	O12—C2	1.219 (6)
Na—O12^{vii}	2.394 (5)		
Na—O8^{viii}	2.422 (5)	N2—C7	1.444 (8)
Na—O2^{x}	2.441 (6)	C7—C8	1.470 (10)
Na—O4^{ix}	2.447 (6)	N1—C9	1.505 (8)
Na—O6^{xi}	2.524 (4)	C9—C10B	1.470 (2)
Na—O10	2.526 (4)		
O1—C5	1.262 (8)		
O2—C5	1.209 (8)		
O7—C4	1.280 (6)		
O3—C3	1.247 (6)		
O4—C6	1.228 (8)		

(335K)			
Fe1—O7	2.006 (3)	O5—C2	1.275 (5)
Fe1—O11	2.010 (4)	O6—C3	1.240 (6)
Fe1—O1	2.009 (4)	O7—C4	1.278 (5)
Fe1—O3	2.018 (3)	O9—C1	1.258 (5)
Fe1—O9	2.022 (3)	O10—C1	1.235 (5)
Fe1—O5	2.022 (3)	O11—C6	1.257 (7)
Na—O12^{vii}	2.396 (4)	O12—C2	1.213 (6)
Na—O8^{viii}	2.416 (4)		
Na—O2^{x}	2.442 (5)	N2—C7	1.453 (7)
Na—O4^{ix}	2.445 (5)	C7—C8	1.475 (9)
Na—O6^{xi}	2.517 (4)	N1—C9	1.496 (7)
Na—O10	2.524 (3)	C9—C10B	1.470 (2)
O1—C5	1.268 (7)		
O2—C5	1.210 (7)		

Symmetry code(s): (i) -*x*, -*y*, -*z*+1; (ii) *x*-1/2, -*y*+1/2, *z*-1/2; (iii) -*x*+1/2, *y*-1/2, -*z*+1/2; (iv) -*x*, -*y*, -*z*; (v) -*x*+1/2, *y*+1/2, -*z*+1/2; (vi) *x*-1/2, -*y*-1/2, *z*-1/2; (vii) *x*, *y*-1, *z*; (viii) *x*-1, *y*, *z*; (ix) *x*-1/2, -*y*+1, *z*-1/2; (x) *x*-1/2, -*y*+1, *z*+1/2; (xi) *x*-1, *y*-1, *z*; (xii) *x*+1/2, -*y*+1, *z*-1/2; (xiii) *x*+1/2, -*y*+1, *z*+1/2; (xiv) *x*+1, *y*+1, *z*; (xv) *x*+1, *y*, *z*; (xvi) *x*, *y*+1, *z*.

Table S2. Selected hydrogen-bond parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
(365K)				
N2—H2A···O4	0.89	2.18	2.98 (3)	148.5
N2—H2B···O3^{i}	0.89	2.38	3.132 (16)	143.0
N2—H2B···O6^{i}	0.89	2.47	3.26 (2)	147.8
N2—H2C···O5^{ii}	0.89	1.90	2.77 (2)	162.9
N1—H1A···O4	0.89	2.07	2.90 (2)	156.2
N1—H1B···O3^{i}	0.89	2.04	2.924 (12)	173.8
N1—H1B···O6^{i}	0.89	2.54	3.099 (18)	121.5
N1—H1C···O5^{ii}	0.89	2.08	2.960 (17)	170.2
(355K)				
N2—H2A···O4^{iii}	0.89	2.04	2.900 (7)	161.1
N2—H2B···O6^{iv}	0.89	2.00	2.872 (7)	164.3
N2—H2C···O5^{v}	0.89	2.12	3.009 (7)	175.9
N2—H2C···O12^{v}	0.89	2.53	3.162 (7)	128.2
N1—H1A···O2^{vi}	0.89	2.11	2.955 (7)	157.9
N1—H1B···O7	0.89	2.20	3.002 (6)	150.2
N1—H1B···O8	0.89	2.39	3.185 (8)	148.6
N1—H1C···O10^{vii}	0.89	2.02	2.885 (6)	165.0
(345K)				
N2—H2A···O4^{iii}	0.89	2.04	2.895 (6)	160.0
N2—H2B···O6^{iv}	0.89	1.99	2.870 (6)	169.5
N2—H2C···O5^{v}	0.89	2.11	2.999 (6)	176.1
N2—H2C···O12^{v}	0.89	2.54	3.155 (6)	126.9
N1—H1A···O2^{vi}	0.89	2.11	2.958 (6)	157.8
N1—H1B···O7	0.89	2.18	2.997 (5)	151.9
N1—H1B···O8	0.89	2.41	3.203 (6)	148.6

N1—H1C···O10^{vii}	0.89	2.01	2.874 (5)	164.7
(335K)				
N2—H2A···O4^{iii}	0.89	2.03	2.889 (5)	160.8
N2—H2B···O6^{iv}	0.89	1.99	2.868 (5)	169.8
N2—H2C···O5^{v}	0.89	2.10	2.991 (5)	175.4
N2—H2C···O12^{v}	0.89	2.53	3.152 (6)	127.6
N1—H1A···O2^{vi}	0.89	2.12	2.962 (6)	157.8
N1—H1B···O7	0.89	2.17	2.995 (5)	153.7
N1—H1B···O8	0.89	2.42	3.210 (6)	147.4
N1—H1C···O10^{vii}	0.89	2.00	2.872 (5)	165.6
(297K)				
N2—H2A···O4^{iii}	0.89	2.01	2.871 (5)	162.1
N2—H2B···O6^{iv}	0.89	1.98	2.861 (4)	170.1
N2—H2C···O5^{v}	0.89	2.11	2.994 (4)	175.3
N2—H2C···O12^{v}	0.89	2.53	3.153 (5)	127.4
N1—H1A···O2^{vi}	0.89	2.13	2.969 (5)	157.1
N1—H1B···O7	0.89	2.14	2.978 (4)	157.2
N1—H1B···O8	0.89	2.46	3.227 (5)	144.6
N1—H1C···O10^{vii}	0.89	1.99	2.862 (4)	166.9

Symmetry code(s): (i) *x*+1/2, -*y*+1/2, *z*-1/2; (ii) -*x*+1, -*y*, -*z*+1; (iii) *x*+1/2, -*y*+1, *z*-1/2; (iv) *x*-1/2, -*y*+1, *z*-1/2; (v) *x*, *y*-1, *z*; (vi) *x*-1/2, -*y*+1, *z*+1/2; (vii) *x*+1/2, -*y*+1, *z*+1/2.

The data have been assigned to the following deposition numbers.

CCDC 1526808-1526812

Summary of Data CCDC 1526808

Compound Name:
Formula: (C6 H6 Fe1 Na1 O12 2-)n,1.13(C2 H8 N1 1+),0.87(C2 H8 N1)
Unit Cell Parameters: a 8.1207(2) b 9.3921(4) c 12.1550(4) P21/n
---

Summary of Data CCDC 1526809

Compound Name:
Formula: (C6 H6 Fe1 Na1 O12 2-)n,2(C2 H8 N1 1+)
Unit Cell Parameters: a 8.12573(10) b 9.37296(10) c 12.1399(10) Pn
---

Summary of Data CCDC 1526810

Compound Name:
Formula: (C6 H6 Fe1 Na1 O12 2-)n,2(C2 H8 N1 1+)
Unit Cell Parameters: a 8.12950(10) b 9.35875(10) c 12.1287(10) Pn
---

Summary of Data CCDC 1526811

Compound Name:
Formula: (C6 H6 Fe1 Na1 O12 2-)n,2(C2 H8 N1 1+)

Unit Cell Parameters: a 8.13384(10) b 9.34542(10) c 12.11761(10) Pn
---

Summary of Data CCDC 1526812

Compound Name:
Formula: (C6 H6 Fe1 Na1 O12 2-)n,2(C2 H8 N1 1+)
Unit Cell Parameters: a 8.1394(1) b 9.3122(2) c 12.0951(2) Pn
---