Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Materials
Reorientational dynamics of organic cations in perovskite-like coordination polymers

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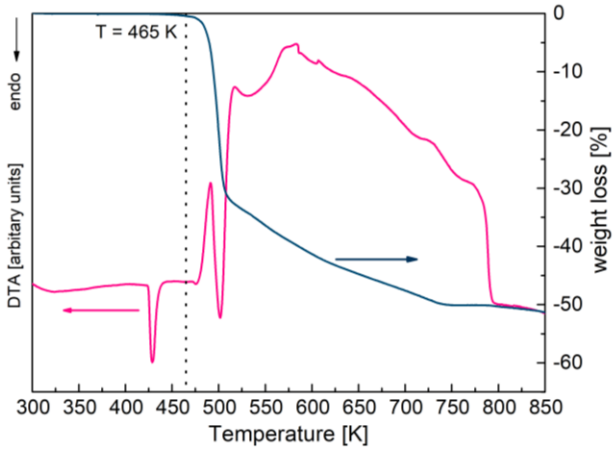
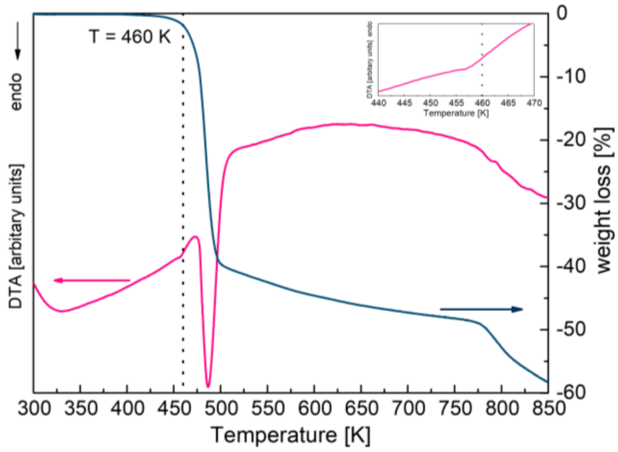
CAPTIONS OF FIGURES

CAPTIONS OF TABLES

a) MAFe



b) DMAFe



c) TrMAFE

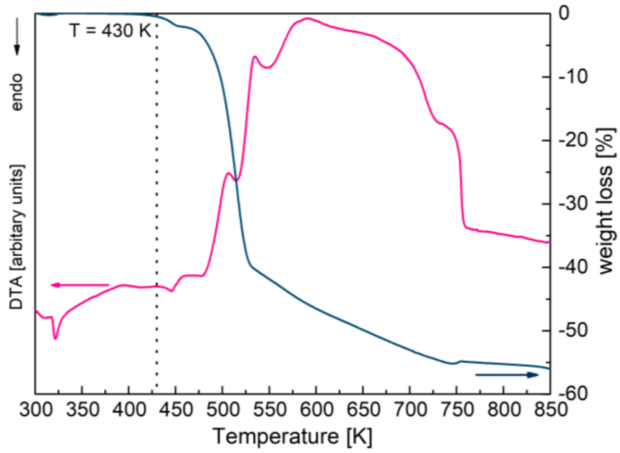
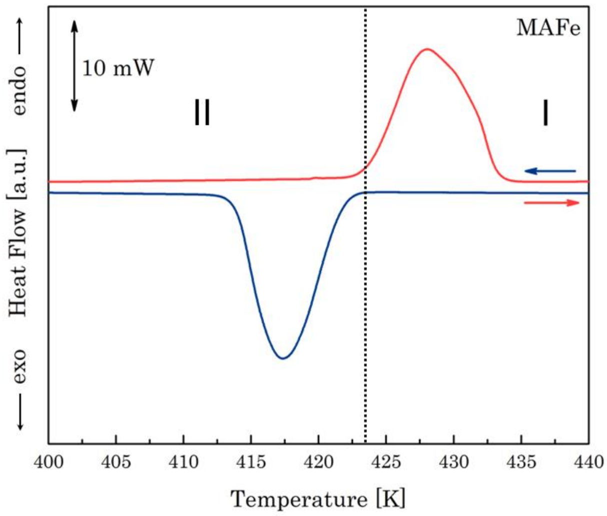
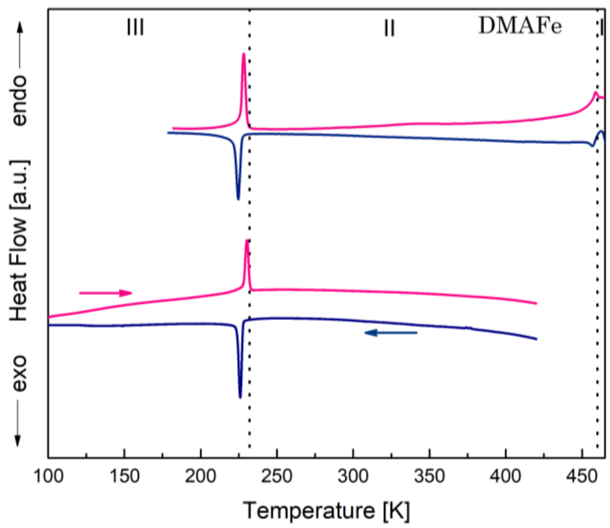


Fig S1. Curves of thermogravimetric analysis and differential thermal analysis (2 K min^{-1}) (a) **MAFe**; (b) **DMAFe**; (c) **TrMAFe**.

a) MAFe



b) DMAFe



c) TrMAFe

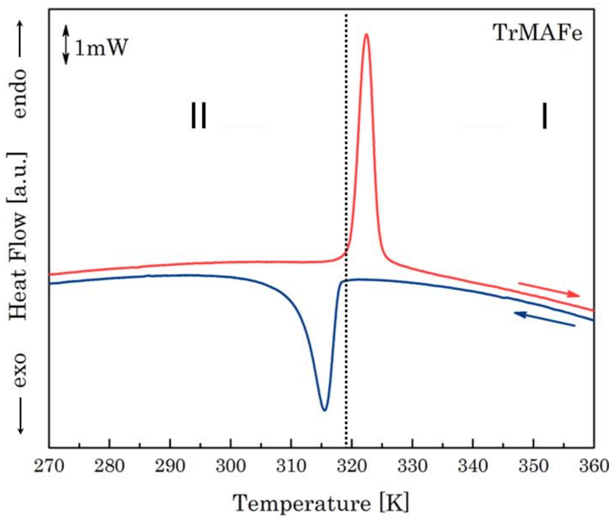


Fig. S2. DSC curves upon cooling and heating runs: a) **MAFe**, b) **DMAFe**, c) **TrMAFe**

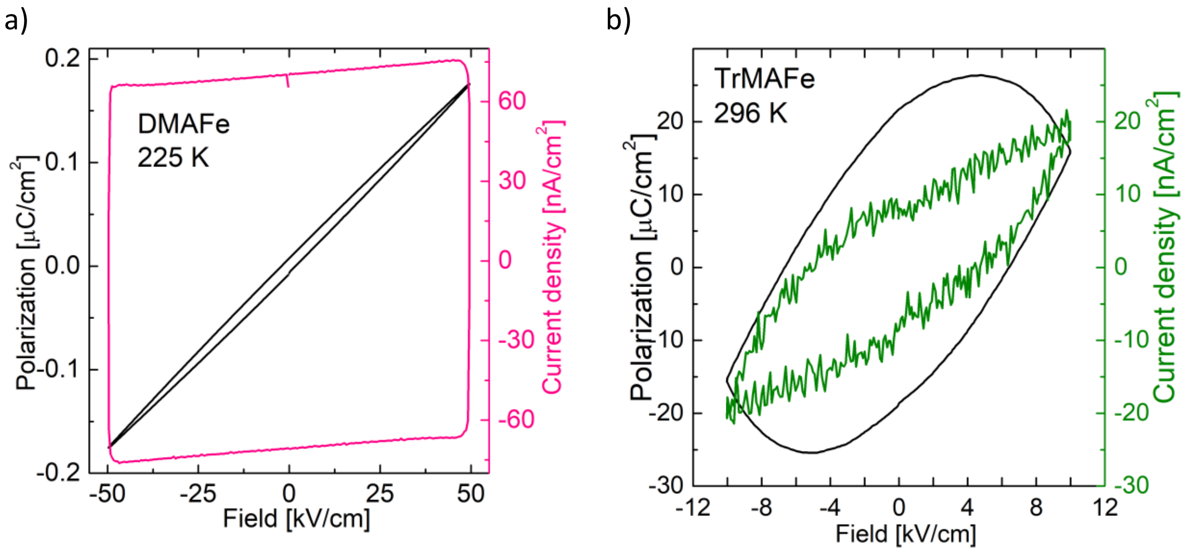


Fig. S3. Electric field dependence of the electric polarization of **DMAFe** (a) and **TRMAFe** (b) measured at 225 and 296 K, respectively.

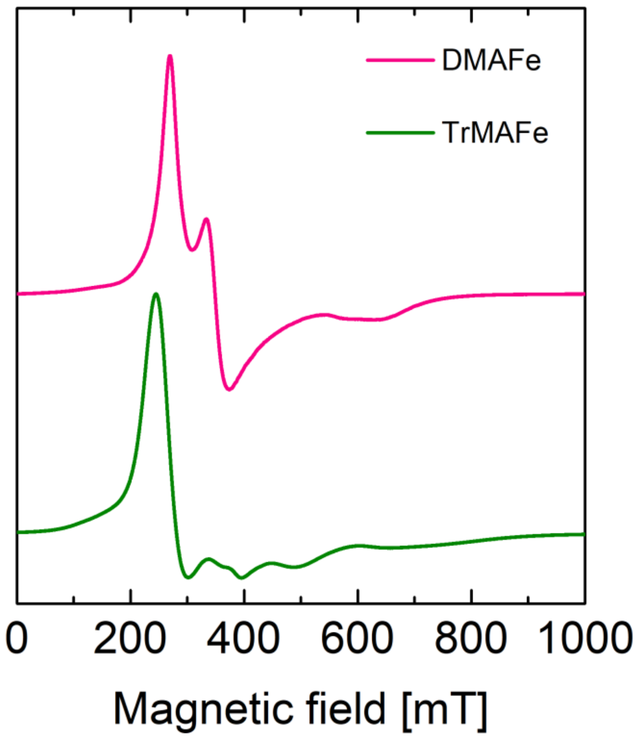
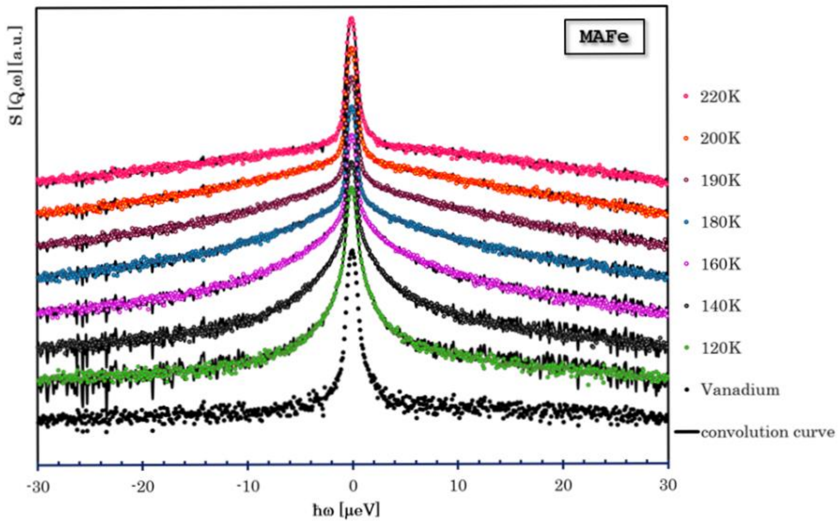
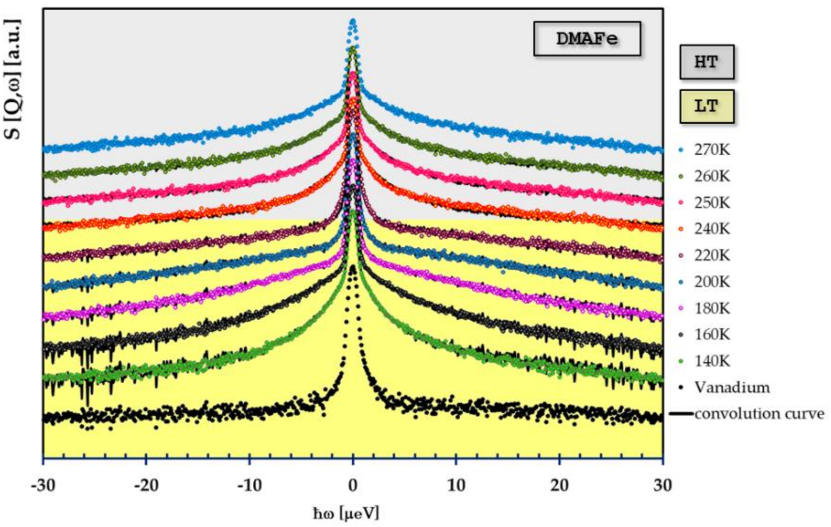


Fig. S4. X-band CW EPR spectra of **DMAFe** and **TrMAFe** recorded at 20 K.

a) MAFe



b) DMAFe



c) TrMAFe

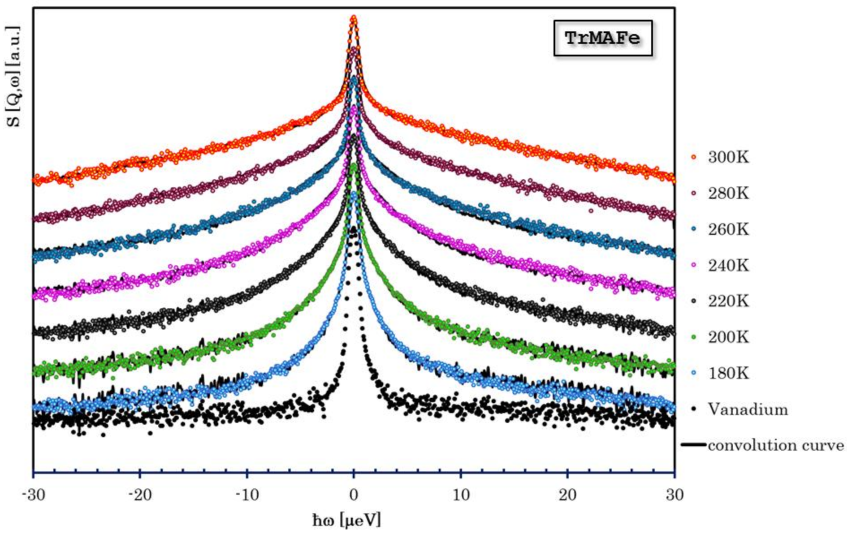


Fig.S5. QENS data collected for all samples: a) **MAFe**, b) **DMAFe**(two colours indicate the HT and IT phase), c) **TrMAFe**.

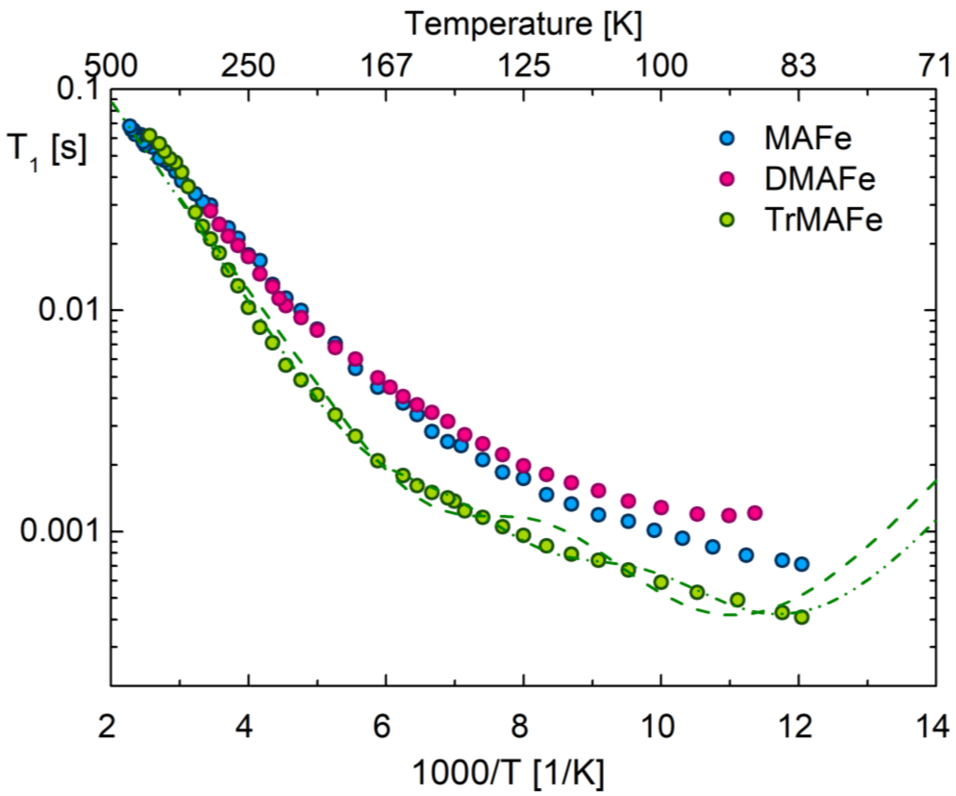


Fig. S6. The temperature dependence of the spin–lattice relaxation time (T_1) for all CPs crystals.

Table S1. Thermodynamic parameters of the phase transition for guest-host crystals in the condensed state.

Compounds	MAFe	DMAFe	TrMAFe
M [g·mol^{-1}]	315.2	343.2	371.3
T_c (heating) [K]	425.6	228	319
ΔH [J·g^{-1}]	60.9	8.4	13.84
ΔH [kJ·mol^{-1}]	19.2	2.9	5.1
ΔS [J·mol^{-1}·K^{-1}]	45.1	12.6	16.1
N	15	2	3

Table S2. The motion parameters obtained for protons in the CPS crystals obtained from the ^{1}H NMR and INS methods.

T_1				
parameter	**MAFe**	**DMAFe**		**TrMAFe**
E_{a1} [eV]	0.014	0.013	0.02	
τ_{01} [s]	$2.57\ 10^{-12}$	$7.12\ 10^{-12}$	$1.95\ 10^{-12}$	
K_1 [Hz^2]	$4.25\ 10^{11}$	$2.69\ 10^{11}$	$2.76\ 10^{11}$	
E_{a2} [kJ/mol]	0.016	0.016	0.016	0.024
τ_{02} [s]	$1.44\ 10^{-11}$	$2.67\ 10^{-11}$	$7.19\ 10^{-13}$	$5.02\ 10^{-12}$
K_2 [Hz^2]	$1.15\ 10^{11}$	$5.74\ 10^{10}$	$7.22\ 10^{11}$	$9.64\ 10^{10}$

M_2				
reduction	parameter	**MAFe**	**DMAFE**	**TrMAFe**
1	E_a[kcal/mol]	-	0.24	0.15
	τ_0 [s]	-	$3.7\ 10^{-13}$	$8.67\ 10^{-11}$
2	E_a[kcal/mol]	-	0.26	0.13
	τ_0 [s]	-	$5.0\ 10^{-11}$	$8.2\ 10^{-12}$