Supplementary Materials

Structural phase transitions coupled with prominent dielectric anomalies and dielectric relaxation in $[(CH_3)_3NH]_2[KCo(CN)_6]$ and mixed $[(CH_3)_3NH]_2[KFe_XCo_{1-X}(CN)_6]$ double perovskite hybrids

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CAPTIONS OF FIGURES

CAPTIONS OF TABLES

Table S1. Masses and the number of moles of mixed crystals **TrMAFe$_x$Co$_{1-x}$**.

Theoretical X molar fraction of Fe^{3+}	$K_3Fe(CN)_6$		$K_3Co(CN)_6$		trimethylammonium hydrochloride		Obtained X molar fraction of Fe^{3+}
	$m_{Fe^{3+}}$ [g]	$n_{Fe^{3+}}$ [mol]	$m_{Co^{3+}}$ [g]	$n_{Co^{3+}}$ [mol]	$m_{TrMA.HCl}$ [g]	$n_{TrMA.HCl}$ [mol]	
TrMACo, 0	0.00	0.00	2.59	7.78E-03	2.23	2.33E-02	**TrMACo**, 0
0.1	0.20	6.07E-04	1.82	5.47E-03	1.74	1.82E-02	**0.12**
0.2	0.50	1.52E-03	2.02	6.07E-03	2.18	2.28E-02	**0.18**
0.4	2.00	6.07E-03	2.02	6.07E-03	3.48	3.64E-02	**0.49**
0.5	3.00	9.11E-03	2.02	6.07E-03	4.35	4.56E-02	**0.56**
0.6	3.00	9.11E-03	0.76	2.28E-03	3.27	3.42E-02	**0.73**
0.8	0.20	6.07E-04	1.82	5.47E-03	1.74	1.82E-02	**0.81**
TrMAFe, 1	2.79	8.48E-03	0.00	0.0E+00	2.43	2.54E-02	**TrMAFe**, 1

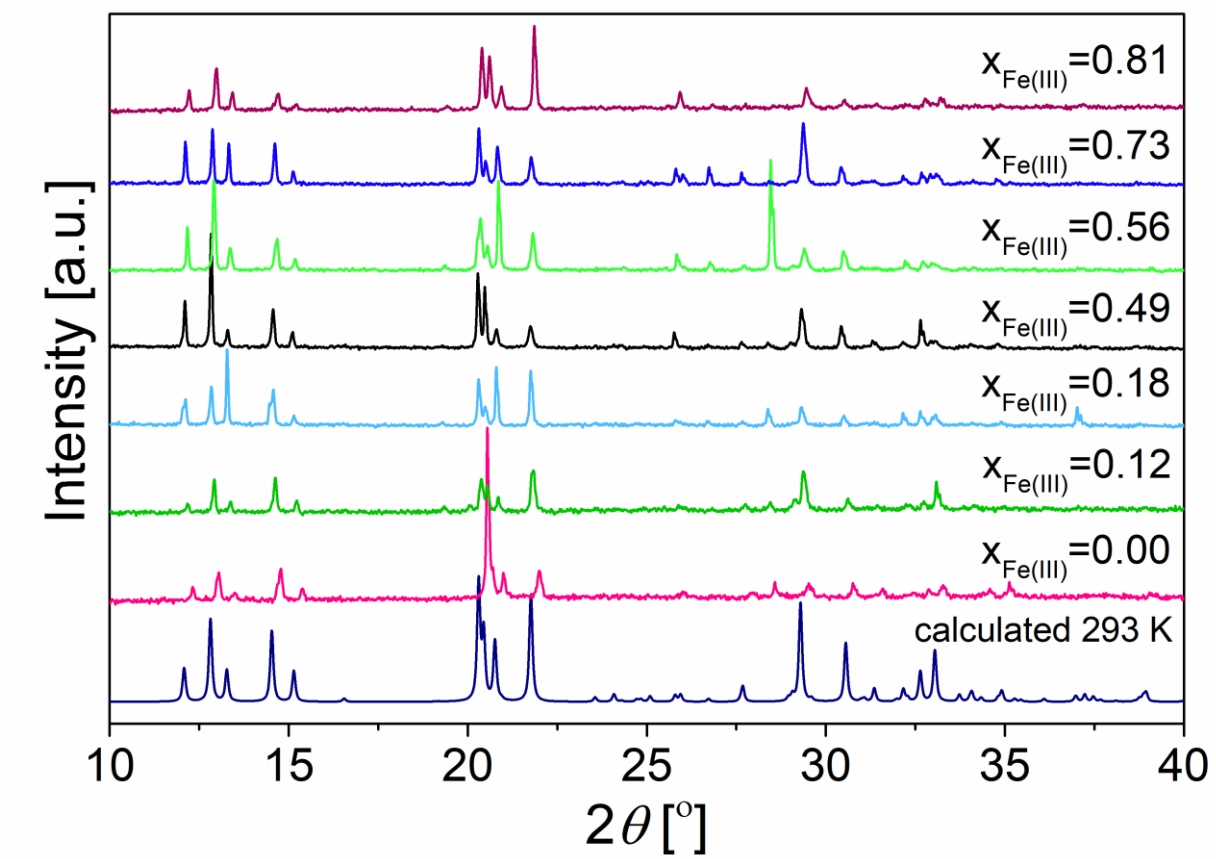


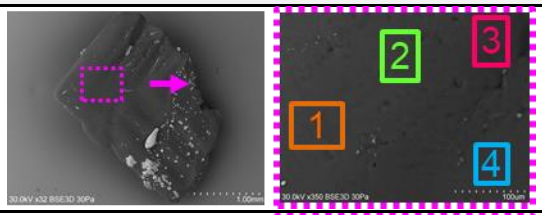
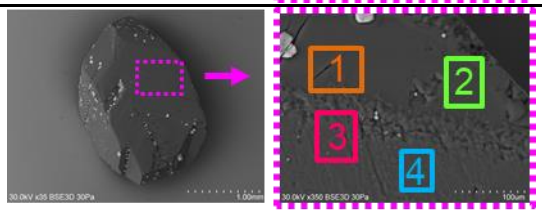
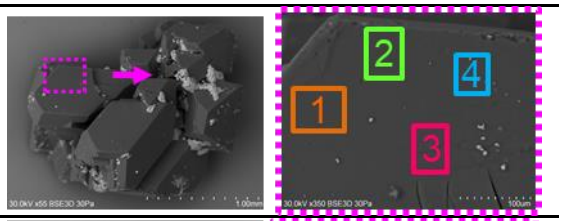
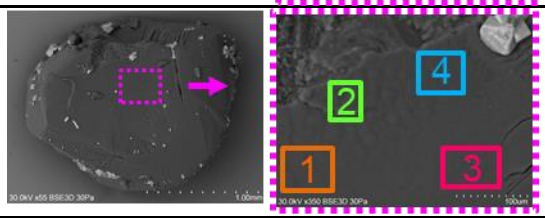
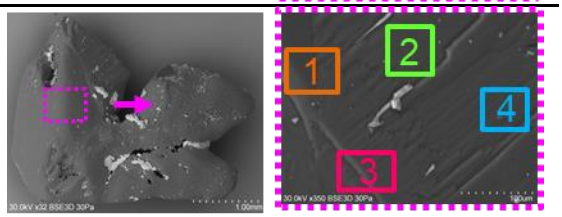
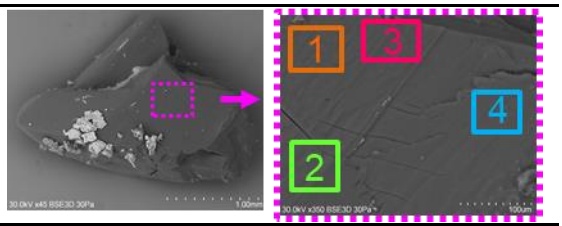
Fig. S1. X-ray diffraction pattern of **TrMAFe$_x$Co$_{1-x}$** (x: 0.00-0.8) at 293 K and calculated from crystal structure **TrMACo**.

Table S2. Crystal data, experimental details, and structure refinement results for **TrMACo** at 360 (HT) and 100 K (LT).

Experiments were carried out with Mo *K*a radiation using a Oxford Diffraction Xcalibur System diffractometer. Absorption was corrected for by multi-scan methods, *CrysAlis RED*, Oxford Diffraction Ltd., Version 1.171.33.57 (release 26-01-2010 CrysAlis171 .NET) (compiled Jan 26 2010,14:36:55) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Refinement was with 0 restraints. H-atom parameters were constrained.

	TrMACo100K	**TrMACo360K**
Chemical formula	$(C_3H_{10}N)_2[KCo(CN)_6]$	
M_r	374.39	374.39
Crystal system, space group	Monoclinic, *C*2/*c*	Cubic, $Fm\bar{3}m$
Temperature (K)	100	360
a, *b*, *c* (Å)	15.2965 (5), 8.4134 (2), 13.8289 (4)	12.0813 (2), 12.0813 (2), 12.0813 (2)
a, b, g (°)	90, 107.437 (4), 90	90, 90, 90
V (Å^3)	1697.93 (9)	1763.36 (9)
Z	4	2
m (mm^{-1})	1.26	1.22
Crystal size (mm)	0.6 x 0.55 x 0.4	
Data collection		
T_{min}, T_{max}	0.957, 1.000	0.797, 1.000
No. of measured, independent and observed [I > 2 s (I)] reflections	5573, 2138, 1985	3564, 160, 134
R_{int}	0.014	0.019
(sin θ/l)$_{max}$ (Å^{-1})	0.690	0.688
Refinement		
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.023, 0.065, 1.04	0.031, 0.101, 1.16
No. of reflections	2138	160
No. of parameters	108	16
r_{max}, r_{min} (e Å^{-3})	0.60, -0.57	0.29, -0.38

Table S3. Atomic concentration (%) of mixed crystal obtained on EDS results. SEM photographs of pure and mixed-crystals. Four squares represent the measured areas.

$[(CH_3)_3NH]_2[KFe_XCo_{1-X}(CN)_6]$				
X Fe^{3+}	No.	Fe [%]	Co [%]	SEM photographs
0.12	1	2.45	21.04	
	2	2.64	21.83	
	3	3.31	24.24	
	4	3.41	22.19	
	Average	**2.95**	**22.33**	
0.18	1	3.30	15.32	
	2	3.63	15.64	
	3	3.47	17.20	
	4	3.28	14.20	
	Average	**3.42**	**15.59**	
0.49	1	8.72	9.23	
	2	7.71	8.54	
	3	8.11	8.47	
	4	8.11	8.34	
	Average	**8.16**	**8.65**	
0.56	1	13.89	11.67	
	2	13.73	11.41	
	3	14.59	11.93	
	4	14.89	10.43	
	Average	**14.28**	**11.36**	
0.73	1	15.54	5.94	
	2	17.44	6.35	
	3	17.56	6.7	
	4	18.79	6.85	
	Average	**17.33**	**6.46**	
0.81	1	20.31	5.13	
	2	20.89	4.65	
	3	20.37	4.25	
	4	20.65	5.05	
	Average	**20.56**	**4.77**	

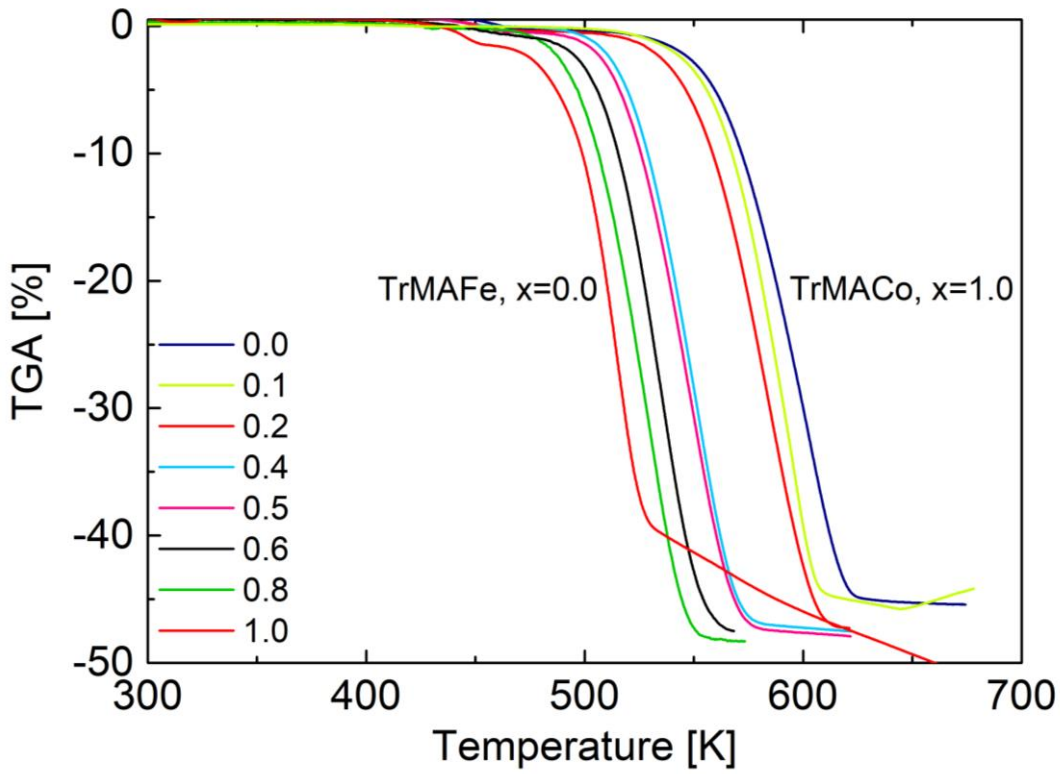


Fig. S2. TGA between 300 and 700 K measured for pure **TrMACo** and **TrMAFe**, as well as for mixed crystals **$TrMFe_xCo_{1-x}$**.

Table S4. Thermodynamic parameters of the phase transitions for **$TrMFe_xCo_{1-x}$**, x = 0, 0.12, 0.18, 0.49, 0.56, 0.73, 0.81, 1.0 in the condensed state indicated from DSC results and calculated according to equation: $\Delta S = R \ln N^2$, $N = N_2/(N_1=2)$.

PT	**LT → HT**							
$X_{Fe^{3+}}$	**0.0**	**0.12**	**0.18**	**0.49**	**0.56**	**0.73**	**0.81**	**1.0**
M [g/mol]	374.4	374.1	373.9	372.9	372.7	372.2	371.9	371.4
T [K]	347.2	343.2	337.6	333.0	327.1	324.9	321.2	317.9
ΔH [J·g^{-1}]	14.3	14.8	15.8	16.1	16.3	16.5	16.7	16.9
ΔH [J·mol^{-1}]	5335.1	5536.1	5907.2	5996.6	6071.4	6129.8	6211.3	6275.8
ΔS [J·mol^{-1}·K^{-1}]	15.4	16.1	17.5	18.0	18.6	18.9	19.3	19.7
N	2.5	2.6	2.9	3.0	3.1	3.1	3.2	3.3
N_2	5.0	5.3	5.7	5.9	6.1	6.2	6.4	6.6

Table S5. Selected geometric parameters (Å, º) measure for two phases LT (100 K) and HT (360 K). Redundant, symmetrically depended values are omitted.

TrMACo 100 K (LT)			
Bonds			
Co1—C1	1.9049 (14)	N3—C3	1.1521 (18)
Co1—C2	1.8999 (13)	N10A—C12	1.440 (3)
Co1—C3	1.9121 (13)	N10A—C11	1.467 (3)
K1—N1	2.8415 (12)	N10A—C10	1.526 (3)
K1—N2^{i}	2.8745 (13)	N10B—C10	1.4363
K1—N3^{ii}	3.2361 (12)	N10B—C12	1.5001 (19)
N1—C1	1.1515 (18)	N10B—C11	1.534 (2)
C2—N2	1.1513 (18)		
Angles			
C2—Co1—C2^{iii}	180.0	N1^{iv}—K1—N3^{ii}	89.59 (3)
C2—Co1—C1^{iii}	90.91 (5)	N1—K1—N3^{ii}	82.61 (3)
C2—Co1—C1	89.09 (6)	N2^{i}—K1—N3^{ii}	166.42 (4)
C1^{iii}—Co1—C1	180.0	N2^{v}—K1—N3^{ii}	89.45 (3)
C2—Co1—C3^{iii}	88.93 (5)	C1—N1—K1	170.32 (11)
C2^{i}—Co1—C3^{iii}	91.07 (5)	N1—C1—Co1	177.98 (12)
C1—Co1—C3^{iii}	87.68 (5)	N2—C2—Co1	178.95 (13)
C1—Co1—C3	92.32 (5)	C2—N2—K1^{i}	158.71 (12)
C3^{iii}—Co1—C3	180.00 (7)	C3—N3—K1^{vii}	165.13 (10)
N1^{iv}—K1—N1	167.47 (5)	N3—C3—Co1	176.29 (12)
N1^{iv}—K1—N2^{i}	86.97 (4)	C12—N10A—C11	113.76 (18)
N1—K1—N2^{i}	102.82 (4)	C12—N10A—C10	110.36 (18)
N2^{i}—K1—N2^{v}	78.53 (5)	C11—N10A—C10	108.17 (17)
N1^{ii}—K1—N3^{vi}	82.61 (3)	C10—N10B—C12	112.05 (8)
N1—K1—N3^{vi}	89.59 (3)	C10—N10B—C11	109.34 (8)
N2^{v}—K1—N3^{vi}	166.42 (4)	C12—N10B—C11	106.74 (13)
N3^{ii}—K1—N3^{vi}	103.14 (5)		
Torsion angles			
C12—N10B—C10—N10A	58.37 (17)	C10—N10B—C11—N10A	65.18 (16)
C11—N10B—C10—N10A	−59.76 (19)	C12—N10B—C11—N10A	−56.23 (17)
C12—N10A—C10—N10B	−61.25 (16)	C11—N10A—C12—N10B	−65.4 (2)
C11—N10A—C10—N10B	63.78 (17)	C10—N10A—C12—N10B	56.36 (15)
C12—N10A—C11—N10B	64.95 (19)	C10—N10B—C12—N10A	−63.44 (17)
C10—N10A—C11—N10B	−58.05 (15)	C11—N10B—C12—N10A	56.23 (19)

TrMACo 360 K (HT)			
Bonds			
Co1—C1^{viii}	1.897 (6)	N1—C1	1.139 (6)
K1—N1	3.004 (5)	N10—C10	1.360 (15)
Angles			
C1^{ix}—Co1—C1	90.0	N1—K1—N1^{xii}	180.0
C1^{x}—Co1—C1	180.0	C10^{xiii}—N10—C10^{xiv}	164.2 (8)
N1—K1—N1^{xi}	90.0		
Torsion Angles			
C10^{xxv}—N10—C10—C10^{xxvii}	−120.5 (2)		

Symmetry code(s): (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) −*x*+2, *y*, −*z*+1/2; (v) *x*, −*y*+1, *z*−1/2; (vi) *x*+1/2, *y*−1/2, *z*; (vii) *x*−1/2, *y*+1/2, *z*; (viii) −*y*+1, −*z*+1, −*x*+1; (ix) *y*, *z*, *x*; (x) −*x*+1, −*y*+1, −*z*+1; (xi) −*y*+1, −*z*+3/2, −*x*+3/2; (xii) −*x*+1, −*y*+1, −*z*+2; (xiii) *z*−1/2, −*x*+1, −*y*+3/2; (xiv) −*z*+1, *x*+1/2, −*y*+3/2.

Table S6. Hydrogen-bond geometry (Å, º) for **TrMACo** at 100 (LT) and 360K (HT).

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
TrMACo 100 K (LT)				
N10A—H10A···N3^{i}	0.89	2.33	3.190 (3)	162.0
C10—H10C···N1^{ii}	0.96	2.59	3.4102 (18)	144.1
C10—H10D···N3	0.93	2.68	3.2370 (17)	119.3
C11—H11E···N1^{iii}	0.95	2.64	3.550 (2)	160.0
C12—H12C···N3^{iv}	0.96	2.65	3.5132 (19)	149.7
TrMACo 360 K (HT)				
C10—H10D···N1^{v}	0.95	2.69	3.631 (8)	173.1

Symmetry code(s): (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1/2, *y*+1/2, *z*; (iii) −*x*+3/2, −*y*+1/2, −*z*+1; (iv) *x*−1/2, *y*−1/2, *z*; (v) −*z*+1, −*x*+1, −*y*+1.