Supporting Information

Flexible crystals of perovskite-like coordination polymers with tunable and switchable organic guest: $(CH_3NH_3)_2[KFe(CN)_6]$ and $(CH_3NH_3)_2[KCo(CN)_6]$

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Table 4S. Thermodynamic parameters of the phase transition for **1** and **2** in the condensed state.

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Fig. 1S. TGA and DTA thermograms between 300 and 900 K for (a) $(CH_3NH_3)_2[KCo(CN)_6]$ (**1**), (b) $(CH_3NH_3)_2[KFe(CN)_6]$(**2**).

Fig. 2S. The temperature dependence of (a) the real part, ε′, and (b) the imaginary part, ε ″, of the electric permittivity for the pure $K_3Co(CN)_6$ complex along the [10-1] direction.

Fig. 3S. The temperature dependence of (a) the real part, ε′, and (b) the imaginary part, ε ″, of the electric permittivity for the pure $K_3Fe(CN)_6$ complex along the [10-1] direction.

F**ig. 4S.** The comparison of a) real and b) imaginary part of permittivity between the pure host ($K_3Fe(CN)_6$) and the quest-host crystals (**2**).

Table 1S. Summary of crystal data and structural refinements for $(CH_3NH_3)_2[KCo(CN)_6]$ at 100 and 443K temperatures.

Complexes:	**$(CH_3NH_3)_2[KCo(CN)_6]$ LT**	**$(CH_3NH_3)_2[KCo(CN)_6]$ HT**
Formula	$C_8H_{12}N_8KCo$	$C_8H_{12}N_8KCo$
Formula weight	318.29	318.29
T (K)	100.00	443.15
Crystal system	monoclinic	cubic
Space group	C2/c	Fm-3m
a (Å)	13.626(5)	11.388(18)
b (Å)	7.821(3)	11.388(18)
c (Å)	13.610(5)	11.388(18)
α (°)	90	90
β (°)	108.55(3)	90
γ (°)	90	90
V (Å^3)	1375.0(9)	1477.00(7)
Z	4	4
Radiation type	Mo Kα	Mo Kα
Crystal size (mm)	0.39 x 0.22 x 0.14	0.33 x 0.32 x 0.2
Diffractometer	Xcalibur, Ruby	Xcalibur, Sapphire 1
θ Range (°)	6.09 to 57.87	6.196 to 52.374
ρ_{calc}(g cm^{-3})	1.537	1.431
Index ranges	$-14 \le h \le 17$, $-8 \le k \le 10$, $-16 \le l \le 18$	$-14 \le h \le 13$, $-8 \le k \le 14$, $-14 \le l \le 14$
μ(Mo K_α) (mm^{-1})	1.55	1.440
Absorption correction	Analytical	Analytical
T_{min}, T_{max}	0.760, 0.838	0.665, 0.766
No. of reflections collected	3013	3079
No. of independent reflections	1562 [R_{int} = 0.0227, R_{sigma} = 0.0378]	104 [R_{int} = 0.0241, R_{sigma} = 0.0066]
Goodness-of-fit on F^2	1.065	1.280
Final R_1, wR_2 indices [$F > 4\sigma F$)]	R_1 = 0.0263, wR_2 = 0.0609	R_1 = 0.0702, wR_2 = 0.1299
Final R_1, wR_2 indices (all data)	R_1 = 0.0303, wR_2 = 0.0647	R_1 = 0.0702, wR_2 = 0.1299
$\Delta\rho_{max, min}$ (*e* Å^{-3})	0.25, -0.43	0.75, -0.63

Table 2Sa. Experimental bond lengths and angles for $(CH_3NH_3)_2[KCo(CN)_6]$ in LT phase. (Å, °)

Cordinate	Experimental
$(CH_3NH_3)^+$	
C(4) – N(4)	1.487(3)
$[KCo(CN)_6]^{2-}$	
Co(1) – C(2)	1.9008(18)
Co(1) – C(2)^1	1.9008(18)
Co(1) – C(1)	1.8986(18)
Co(1) – C(1)^1	1.8986(18)
Co(1) – C(3)^1	1.9073(18)
Co(1) – C(3)	1.9073(18)
N(2) – C(2)	1.153(2)
N(2) – K(1)	2.8536(17)
N(3) – C(3)	1.154(2)
N(3) – K(1)^2	2.8186(17)
N(1) – C(1)	1.153(2)
N(1) – K(1)^3	2.8186(17)
K(1) – N(2)^4	2.8535(17)
K(1)^5 – N(3)	2.8846(18)
K(1) – N(3)^6	2.8846(18)
K(1) – N(3)^7	2.8846(18)
K(1) – N(1)^8	2.8186(17)
C(2)^1 – Co(1) – C(2)	180.00(10)
C(2) – Co(1) – C(3)	89.39(7)
C(2)^1– Co(1) – C(3)	90.61(7)
C(2) – Co(1) – C(3)^1	90.61(7)
C(2)^1 – Co(1) – C(3)^1	89.39(7)
C(1) – Co(1) – C(2)^1	89.97(8)
C(1) – Co(1) – C(2)	90.03(8)
C(1)^1 – Co(1) – C(2)^1	90.03(8)
C(1)^1 – Co(1) – C(2)	89.97(8)
C(1)^1 – Co(1) – C(1)	180.0
C(1)^1 – Co(1) – C(3)^1	91.27(7)
C(1) – Co(1) – C(3)^1	88.73(7)

C(1) – Co(1) – C(3)[1]	88.73(7)
C(1) – Co(1) – C(3)	91.27(7)
C(3)[1] – Co(1) – C(3)	180.0
C(2) – N(2) – K(1)	138.97(12)
C(3) – N(3) – K(1)[5]	152.85(13)
N(2) – C(2) – Co(1)	179.61(16)
C(1) – N(1) – K(1)[2]	132.02(13)
N(1) – C(1) – Co(1)	178.49(16)
N(3) – C(3) – Co(1)	177.91(15)
N(2)[4] – K(1) – N(2)	169.69(6)
N(2) – K(1) – N(3)[7]	78.47(5)
N(2)[4] – K(1) – N(3)[7]	107.37(4)
N(2)[4] – K(1) – N(3)[6]	78.47(5)
N(2) – K(1) – N(3)[6]	107.38(5)
N(3)[7] – K(1) – N(3)[6]	113.23(7)
N(1)[8] – K(1) – N(2)[4]	96.67(5)
N(1)[8] – K(1) – N(2)	75.80(5)
N(1)[3] – K(1) – N(2)	96.67(5)
N(1)[3] – K(1) – N(2)[4]	75.80(5)
N(1)[3] – K(1) – N(3)[7]	84.60(5)
N(1)[8] – K(1) – N(3)[6]	84.60(5)
N(1)[8] – K(1) – N(3)[7]	152.23(4)
N(1)[3] – K(1) – N(3)[6]	152.23(4)
N(1)[3]– K(1) – N(1)[8]	88.14(7)

symmetry codes: (1) 1/2-x,1/2-y,-z; (2) 1/2+x,1/2+y,+z; (3) -1/2+x,-1/2+y,+z; (4) -x,+y,1/2-z; (5) 1/2+x, -1/2+y, +z; (6) 1/2-x,1/2+y,1/2-z; (7) -1/2+x,1/2+y,+z; (8) 1/2-x,-1/2+y,1/2-z;

Table 2Sb. Experimental bond lengths and angles for $(CH_3NH_3)_2[KCo(CN)_6]$in HT phase. (Å, °)

Cordinate	Experimental
$(CH_3NH_3)^+$	
C(2) – N(2)	1.07(6)
C(2) – N(2)[1]	1.07(6)
C(2) – N(2)[2]	1.07(6)
C(2) – N(2)[3]	1.07(6)
C(2) – N(2)[4]	1.07(6)
C(2) – N(2)[5]	1.07(6)
$[KCo(CN)_6]^{2-}$	
Co(1) – C(1)	1.862(11)
Co(1) – C(1)[6]	1.862(11)
Co(1) – C(1)[7]	1.862(11)
Co(1) – C(1)[8]	1.862(11)
Co(1) – C(1)[9]	1.862(11)
Co(1) – C(1)[10]	1.862(11)
K(1) – N(1)	2.716(12)
K(1) – N(1)[11]	2.716(12)
K(1) – N(1)[12]	2.716(12)
K(1) – N(1)[13]	2.716(12)
K(1) – N(1)[14]	2.716(12)
K(1) – N(1)[15]	2.716(12)
C(2) – C(2)[16]	1.57(10)
C(2) – C(2)[17]	1.57(10)
C(2) – C(2)[18]	1.57(10)
N(1) – C(1)	1.116(16)
C(1) – Co(1) – C(1) [3]	90.0
C(1)[4] – Co(1) – C(1)[1]	90.000(1)
C(1)[4] – Co(1) – C(1)[5]	90.0
C(1) – Co(1) – C(1)[4]	180.0
C(1) – Co(1) – C(1)[5]	90.0
C(1)[3] – Co(1) – C(1)[4]	90.0
C(1)[3] – Co(1) – C(1)[1]	90.000(1)

C(1) – Co(1) – C(1)^{2}	90.000(1)
C(1)^{2} – Co(1) – C(1)^{1}	180.0
C(1)^{3} – Co(1) – C(1)^{2}	90.0
C(1)^{3} – Co(1) – C(1)^{5}	180.0
C(1)^{4} – Co(1) – C(1)^{2}	90.0
C(1)^{2} – Co(1) – C(1)^{5}	90.0
C(1) – Co(1) – C(1)^{1}	90.0
C(1)^{1} – Co(1) – C(1)^{5}	90.000(1)
N(1) – K(1) – N(1)^{10}	90.000(2)
N(1)^{9} – K(1) – N(1)^{7}	180.0
N(1)^{9} – K(1) – N(1)^{6}	90.000(2)
N(1) – K(1) – N(1)^{8}	180.0
N(1)^{10} – K(1) – N(1)^{6}	180.0
N(1)^{10} – K(1) – N(1)^{8}	90.000(1)
N(1)^{8} – K(1) – N(1)^{7}	90.0
N(1)^{10} – K(1) – N(1)^{9}	90.000(1)
N(1) – K(1) – N(1)^{6}	90.0
N(1)^{8} – K(1) – N(1)^{9}	90.000(1)
N(1)^{8} – K(1) – N(1)^{6}	90.000(2)
N(1) – K(1) – N(1)^{6}	90.000(1)
N(1)^{7} – K(1) – N(1)^{6}	90.000(1)
N(1)^{10} – K(1) – N(1)^{7}	90.000(2)
N(1) – K(1) – N(1)^{9}	90.0
C(2)^{11} – C(2) – C(2)^{12}	60.003(2)
C(2)^{13} – C(2) – C(2)^{11}	60.001(1)
C(2)^{13} – C(2) – C(2)^{12}	60.001(1)
N(2)^{15} – C(2) – C(2)^{11}	144.734(11)
N(2) – C(2) – C(2)^{12}	144.734(16)
N(2)^{15} – C(2) – C(2)^{13}	144.74(3)
N(2) – C(2) – C(2)^{11}	144.734(12)
N(2)^{14} – C(2) – C(2)^{12}	144.734(16)
N(2)^{17} – C(2) – C(2)^{11}	144.734(11)
N(2)^{15} – C(2) – C(2)^{12}	144.734(16)
N(2)^{18} – C(2) – C(2)^{12}	144.734(15)

$N(2)^{17} – C(2) – C(2)^{12}$	144.734(15)
$N(2)^{17} – C(2) – C(2)^{13}$	144.74(3)
$N(2)^{16} – C(2) – C(2)^{12}$	144.734(16)
$N(2)^{14} – C(2) – C(2)^{13}$	144.74(3)
$N(2) – C(2) – C(2)^{13}$	144.734(3)
$N(2) – C(2) – C(2)^{14}$	144.734(11)
$N(2)^{18} – C(2) – C(2)^{13}$	144.74(3)
$N(2)^{16} – C(2) – C(2)^{11}$	144.734(12)
$N(2)^{18} – C(2) – C(2)^{11}$	144.734(11)
$N(2)^{3} – C(2) – C(2)^{3}$	144.735(16)
$N(2)^{3} – N(2) – C(2)$	92(10)
$N(2)^{1} – N(2) – C(2)$	92(10)
$N(2)^{1} – N(2) – C(2)$	92(10)
$N(2)^{3} – N(2) – C(2)$	92(10)
N(1) – C(1) – Co(1)	180.0
C(1) – N(1) – K(1)	180.0

symmetry codes: (1) 1/2-x, 1/2-y, -z; (2) 1/2+x, -1/2+y, +z; (3) -x, 1/2-y, 1/2-z; (4) -x, 1-y, -z; (5) +x, -1/2+y, 1/2+z; (6) 1/2-x, 1-y, 1/2-z; (7) 1/2+x, -1/2+y, +z; (8) -x, 1-y, 1-z; (9) 1/2-x, 1/2-y, 1-z; (10) 1/2+x, +y, -1/2+z; (11) 1/2-x, 1/2-y, +z; (12) 1/2-x, +y, 1/2-z; (13) +x, 1/2-y, 1/2-z; (14) 1/2-x, 1/2-y, +z; (15) 1/2-x, +y, 1/2-z; (16) +x, +y, +z; (17) 1/2-x, 1/2-y, +z; (18) 1/2-x, +y, 1/2-z;

Table 3S. Hydrogen bonds and short contacts for $(CH_3NH_3)_2[KCo(CN)_6]$ (**1**) and $(CH_3NH_3)_2[KCo(CN)_6]$ (**2**) in LT and HT phases

$(CH_3NH_3)_2[KCo(CN)_6]$ LT				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (°)**
N(4)–H(4A)···N(2)[1]	0.85(2)	2.14(2)	2.932(3)	155
N(4)–H(4B)···N(3)[2]	0.81(2)	2.42(2)	3.092(2)	141
N(4)–H(4C)···N(1)	0.88(2)	2.10(2)	2.911(2)	153
symmetry codes: (1) 1/2+x,1/2-y,1/2+z; (2) 1/2-x,1/2+y,1/2-z;				
$(CH_3NH_3)_2[KCo(CN)_6]$ HT				
D–H···A (Å)	**D–H (Å)**	**H···A (Å)**	**D···A (Å)**	**D–H···A (°)**
C(2)–H(2)···N(2)[1]	0.78(5)	1.77(5)	2.52(7)	161
symmetry codes: (1) 1/2-x,1+y,1/2-z;				

Table 4S. Thermodynamic parameters of the phase transition for **1** and **2** in the condensed state.

Compounds	**$(CH_3NH_3)_2[KCo(CN)_6]$**	**$(CH_3NH_3)_2[KFe(CN)_6]$**
M [g·mol^{-1}]	318.3	315.2
Tc (heating) [K]	421.7	425.6
ΔH [J·g $^{-1}$]	59.2	60.9
ΔH [kJ·mol $^{-1}$]	18.8	19.2
ΔS [J·mol $^{-1}$·K^{-1}]	44.7	45.1
N	14.7	15.1

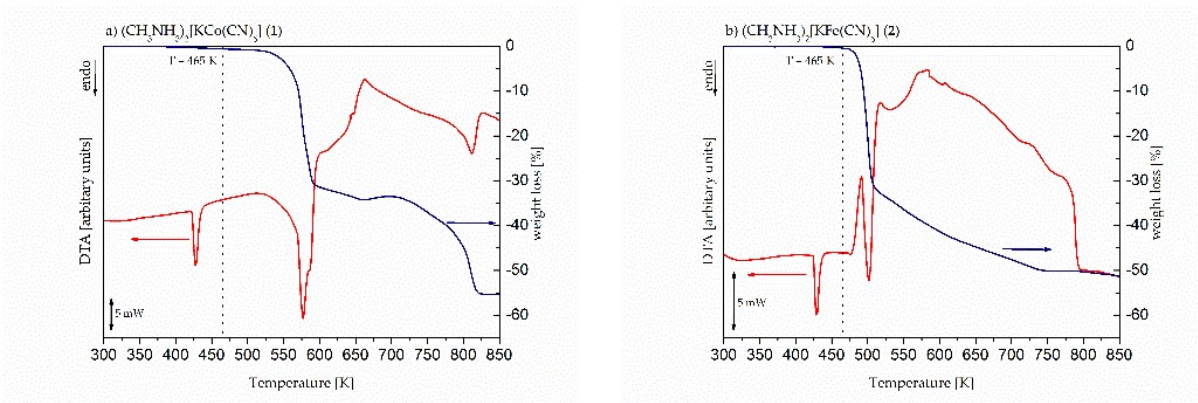

Fig. 1S. TGA and DTA thermograms between 300 and 900 K for (a) $(CH_3NH_3)_2[KCo(CN)_6]$ (**1**), (b) $(CH_3NH_3)_2[KFe(CN)_6]$ (**2**).

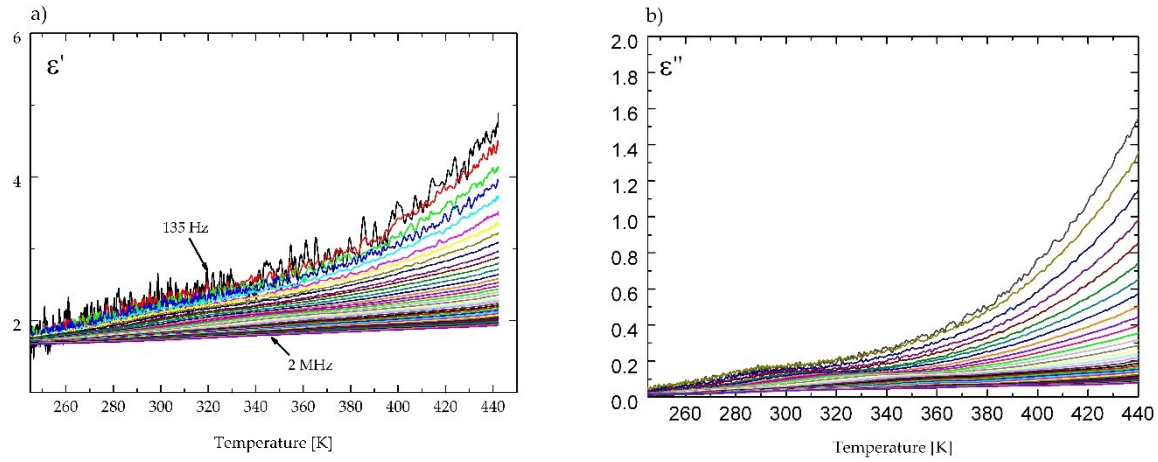

Fig. 2S. The temperature dependence of (a) the real part, ε′, and (b) the imaginary part, ε ″, of the electric permittivity for the pure $K_3Co(CN)_6$ complex along the [10-1] direction.

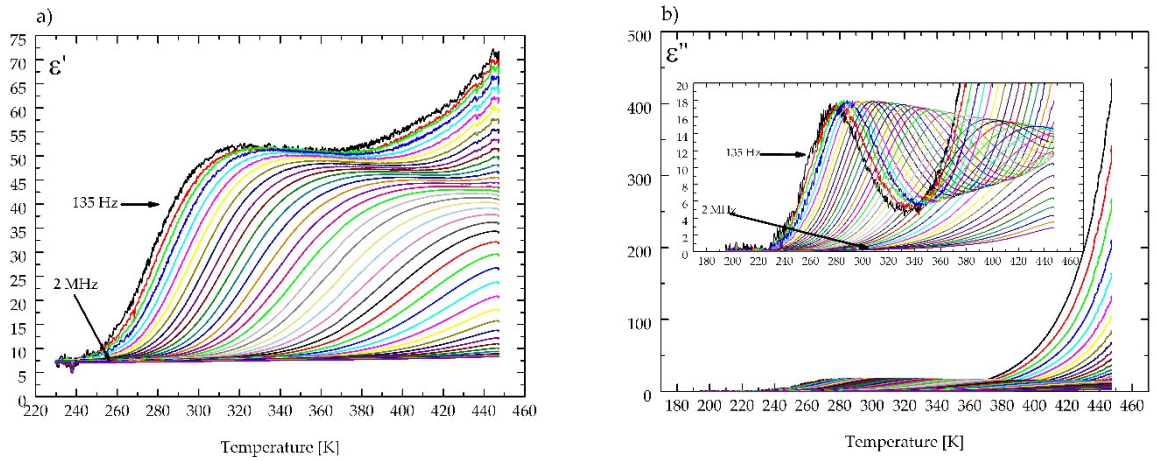

Fig. 3S. The temperature dependence of (a) the real part, ε′, and (b) the imaginary part, ε ″, of the electric permittivity for the pure $K_3Fe(CN)_6$ complex along the $[10\bar{1}]$ direction.

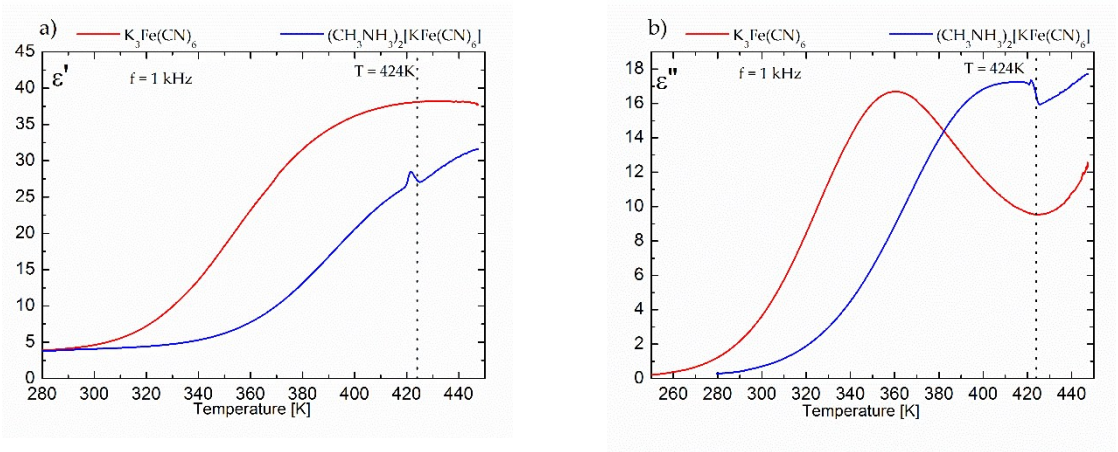

Fig. 4S. The comparison of a) real and b) imaginary part of permittivity between the pure host $K_3Fe(CN)_6$ and the quest-host crystals (**2**).