Electronic Supplementary Material (ESI) for CrystEngComm.

A perovskite-type cage compound as a temperature-triggered dielectric switchable material

Kun Qian*,[a] Shao Feng,[b] Yan Zhihong,[b] Pang Jie,[c] Cheng Xiaodong,[a] and Yang changxin[a]

a. College of Pharmacy, Jiangxi University of Traditional Chinese Medicine, Nanchang, 330004 P. R. China

b. Key Laboratory of Modern Preparation of TCM, Ministry of Education, Jiangxi University of Traditional Chinese Medicine, Nanchang 330004, P. R. China

c. State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023 P. R. China

*E-mail: qk0876@hotmail.com

Materials and instrumentations. All starting reagents and solvents employed for synthesis were commercially available and used without further purification. Elemental analyses (C, H, and N) were performed on a Model 240 Perkin-Elmer elemental analyzer. X-ray data for the title complex was collected on a Bruker Smart APEX II diffractometer with MoK_α radiation (λ = 0.71073 Å). The IR spectrum was recorded in the range of 4000 ~ 400 cm^{-1} on a Tensor 27 OPUS (Bruker) FT-IR spectrometer from KBr pellets. Differential scanning calorimetry was carried out on a PerkinElmer instrument in the temperature range 160-230 K under nitrogen at atmospheric pressure in aluminum crucibles with a heating rate of 10 K/min. Dielectric permittivity ε ($\varepsilon = \varepsilon' - i\varepsilon''$) was measured on a Tonghui TH2828A instrument in the temperature range from 160 to 280 K and over the frequency range of 10 Hz to 1 MHz with an applied electric field of 1 V.

Synthesis. A 5mL methanol solution of $[C_3H_6NH_2]Cl$ (10 mmol, 0.9355 g) salts was slowly layered into a 5 mL aqueous solution of $K_3[Co(CN)_6]$ (5 mmol, 1.65 g) and Na_2CO_3 (2.5 mmol, 0.265 g). The slightly turbid solution was allowed to stand at room temperature. Two days later, colorless block-shaped crystals of compound **1** were formed in the solution in a ca. 50% yield based on Co. Anal. Calcd. (%) analysis for $C_{12}H_{16}CoKN_8$, C, 38.92 ; H, 4.35 ; N, 30.25, found: C, 38.84 ; H, 28 ; N, 30.05.

Single crystal X-ray crystallography. Variable-temperature X-ray single-crystal diffraction data were collected on a Bruker Smart APEX II diffractometer. Data processing including empirical absorption corrections was performed using the Crystal Clear software package (Rigaku, 2005). The structures were solved by direct methods and refined by full-matrix methods based on F^2 by means of the SHELXLTL software package. Non-H atoms were refined anisotropically using all reflections with $I > 2\sigma(I)$. All H atoms were generated geometrically and refined using a "riding" model with $U_{iso} = 1.2\ U_{eq}$ (C and N). The asymmetric units and the packing views were drawn with DIAMOND (Brandenburg and Putz, 2005). Angles and distances between some atoms were calculated using DIAMOND, and other calculations were carried out using SHELXTL. Crystallographic data and structure refinement Details at 113-293 K are given in Table S**1**.

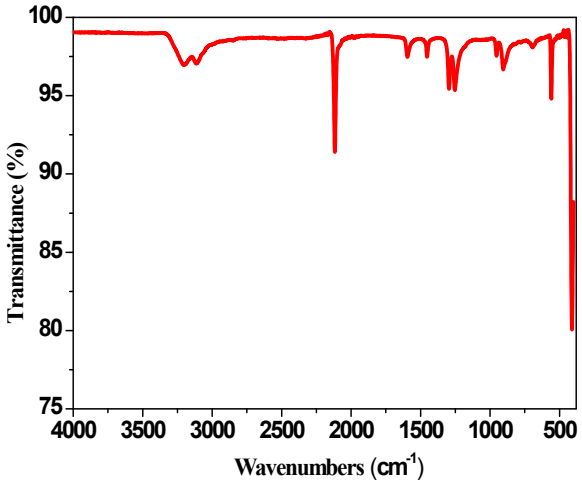

Figure S1. Infrared (IR) spectrum of solid compound **1** in KBr pellet was recorded at room temperature.

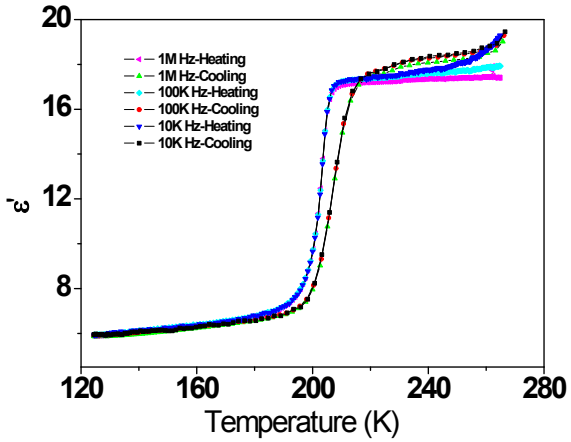

Figure S2. Temperature dependence of the real part of dielectric constant of **1** at different frequencies.

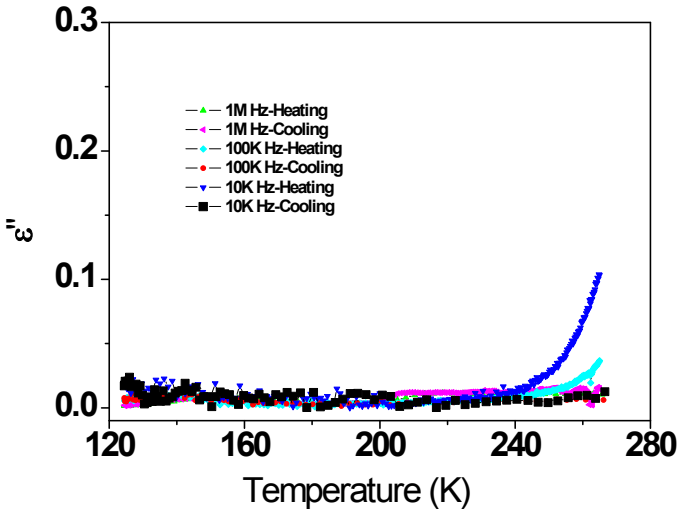

Figure S3. Temperature dependence of the imaginary part of dielectric constant of **1** at different frequencies.

Table S1. Summary of crystallographic data for compound **1**.

T, K	113(2) K	293(2) K
Empirical formula	$CoKC_{12}H_{16}N_8$	$CoKC12H_{16}N_8$
Formula weight	370.36	370.36
Crystal system	cubic	cubic
Space group	$Fm\bar{3}m$	$Pm\bar{3}m$
a , b, c, Å	11.759(7)	11.8233(15)
a, β, γ deg	90	90
V, $Å^{-3}$	1625.96(17)	1652.8(4)
Z	4	4
$D_{calc.}$, g m^{-3}	1.513	1.488
F (000), e	760	760
θ Range, deg	3.00 to 27.66	2.44 to 25
Data / Restraints / parameters	129/ 0/ 15	427/ 0/ 39
Reflections collected/ unique	2781/ 129	10420/427
R_{int}	0.0193	0.0135
Goodness-of-fit on F^2	1.018	1.053
$R1/wR_2$ [I >2σ(I)]	0.0274/0.0808	0.0405/0.1336
$R1/wR_2$ (all data)	0.0285/ 0.0812	0.0452/0.1353

Table S2. Bond lengths [Å] and angles [deg] for **1** at 293 K.

C(1)-Co(1)	1.884(7)	Co(1)-C(1)$^{\#6}$	1.884(7)	C(2)-Co(1)	1.930(4)
Co(1)-C(2)$^{\#6}$	1.930(4)	Co(1)-C(2)$^{\#8}$	1.930(4)	Co(1)-C(2)$^{\#7}$	1.930(4)
Co(2) - C(3)	1.926(7)	Co(2)-C(3)$^{\#10}$	1.926(7)	Co(2)-C(3)$^{\#9}$	1.926(7)
Co(2)-C(3)$^{\#11}$	1.926(7)	Co(2)-C(3)$^{\#13}$	1.926(7)	Co(2)-C(3)$^{\#12}$	1.926(7)
C(2)-N(2)	1.155(5)	C(1)-N(1)	1.129(7)	C(4)-N(4)	1.543(16)
C(3)-N(3)	1.153(7)	C(6)-N(4)	1.474(14)	K(1)-N(1)	2.898(5)
K(1)-N(1)$^{\#14}$	2.898(5)	K(1)-N(1)$^{\#15}$	2.898(5)	K(1)-N(1)$^{\#16}$	2.898(5)
K(1)-N(1)$^{\#17}$	2.898(5)	K(1)-N(1)$^{\#18}$	2.898(5)	K(2)-N(2)	2.827(4)
K(2)-N(2)$^{\#19}$	2.827(4)	K(2)-N(2)$^{\#20}$	2.827(4)	K(2)-N(2)$^{\#21}$	2.827(4)
K(2)-N(3)	2.833(6)	K(2)-N(3)$^{\#21}$	2.833(6)	C(1)-Co(1)-C(2)	90.0
C(1)-Co(1)-C(2)$^{\#7}$	90.000(1)	C(1)$^{\#6}$-Co(1)-C(2)$^{\#8}$	90.000(1)	C(1)$^{\#6}$-Co(1)-C(2)$^{\#6}$	90.0
C(1)$^{\#6}$-Co(1)-C(2)$^{\#7}$	90.000(1)	C(1)-Co(1)-C(2)$^{\#8}$	90.000(1)	C(1)-Co(1)-C(2)$^{\#6}$	90.0
C(2)$^{\#8}$-Co(1)-C(2)$^{\#6}$	90.000(1)	C(1)$^{\#6}$-Co(1)-C(2)	90.0	N(3)-C(3)-Co(2)	180.0
N(4)-C(4)-C(5)	87.1(6)	C(6)$^{\#3}$-C(4)-N(4)	65.8(13)	C(6)$^{\#1}$-C(4)-N(4)	73(3)
N(4)-C(4)-C(6)$^{\#5}$	55.4(8)	C(6)$^{\#4}$-C(4)-N(4)	64.8(11)	N(4)-C(6)-C(5)	94.1(9)
C(4)$^{\#1}$-C(6)-N(4)	89(3)	N(4)-C(6)-C(4)$^{\#5}$	59.5(8)	C(4)$^{\#4}$-C(6)-N(4)	72.7(12)

C(4)$^{\#3}$-C(6)-N(4)	71.3(12)	C(1)-N(1)-K(1)	180.000(2)	C(2)-N(2)-K(2)	180.000(1)
C(3)-N(3)-K(2)	180.0	N(2)-K(2)-N(3)	90.0	N(2)-K(2)-N(3)$^{\#21}$	90.0
N(2)$^{\#20}$-K(2)-N(3)$^{\#21}$	90.0	N(2)$^{\#21}$-K(2)-N(3)$^{\#21}$	90.0	N(2)$^{\#20}$-K(2)-N(3)	90.0
N(2)$^{\#21}$-K(2)-N(3)	90.0	N(2)$^{\#19}$-K(2)-N(3)	90.000(1)	N(2)$^{\#19}$-K(2)-N(3)$^{\#21}$	90.0
C(6)-N(4)-C(4)	93.0(7)	C(6)$^{\#1}$-N(4)-C(4)	18.3(5)	C(6)$^{\#2}$-N(4)-C(4)	87.4(6)
C(6)$^{\#3}$-N(4)-C(4)	41.5(5)	C(6)$^{\#4}$-N(4)-C(4)	43.9(5)	C(6)$^{\#5}$-N(4)-C(4)	65.0(6)
C(6)$^{\#5}$-N(4)-C(4)$^{\#2}$	43.9(5)	C(6)-N(4)-C(4)$^{\#2}$	87.4(6)	C(6)$^{\#1}$-N(4)-C(4)$^{\#2}$	41.5(5)
C(6)$^{\#3}$-N(4)-C(4)$^{\#2}$	18.3(5)	C(6)$^{\#2}$-N(4)-C(4)$^{\#2}$	93.0(7)	C(6)$^{\#4}$-N(4)-C(4)$^{\#2}$	65.0(6)
C(6)$^{\#5}$-N(4)-C(4)$^{\#3}$	87.4(6)	C(6)-N(4)-C(4)$^{\#3}$	43.9(5)	C(6)$^{\#1}$-N(4)-C(4)$^{\#3}$	65.0(6)
C(6)$^{\#3}$-N(4)-C(4)$^{\#3}$	93.0(7)	C(6)$^{\#2}$-N(4)-C(4)$^{\#3}$	18.3(5)	C(6)$^{\#4}$-N(4)-C(4)$^{\#3}$	41.5(5)
C(6)-N(4)-C(4)$^{\#5}$	65.0(6)	C(6)$^{\#2}$-N(4)-C(4)$^{\#1}$	43.9(5)	C(6)$^{\#1}$-N(4)-C(4)$^{\#1}$	93.0(7)
C(6)$^{\#3}$-N(4)-C(4)$^{\#4}$	43.9(5)	C(6)-N(4)-C(4)$^{\#1}$	18.3(5)	C(6)$^{\#4}$-N(4)-C(4)$^{\#4}$	93.0(7)
C(6)$^{\#3}$-N(4)-C(4)$^{\#1}$	65.0(6)	C(6)-N(4)-C(4)$^{\#4}$	41.5(5)	C(6)$^{\#5}$-N(4)-C(4)$^{\#1}$	41.5(5)
C(6)$^{\#4}$-N(4)-C(4)$^{\#1}$	87.4(6)	C(6)$^{\#5}$-N(4)-C(4)$^{\#4}$	18.3(5)	C(6)$^{\#2}$-N(4)-C(4)$^{\#4}$	65.0(6)
C(6)$^{\#2}$-N(4)-C(4)$^{\#5}$	41.5(5)	C(6)$^{\#1}$-N(4)-C(4)$^{\#5}$	43.9(5)	C(6)$^{\#1}$-N(4)-C(4)$^{\#4}$	87.4(6)

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x,-z+1,-y+1 ; $^{\#2}$ -y+1,-x+1,z ; $^{\#3}$ z,-x+1,-y+1 ; $^{\#4}$ -y+1,-z+1,x ; $^{\#5}$ z,y,x; $^{\#6}$ -x+1,-y+2,-z+1 ; $^{\#7}$ -z+1,-y+2,x ; $^{\#8}$ z,y,-x+1 ; $^{\#9}$ -z,-y+2,x ; $^{\#10}$ z,y,-x; $^{\#11}$ -x,-y+2,-z ; $^{\#12}$ -y+1,x+1,z ; $^{\#13}$ y-1,-x+1,-z ; $^{\#14}$ -x+1,z,-y+1 ; $^{\#15}$ -x+1,-y+1,-z+1 ; $^{\#16}$ -y+1,x,z ; $^{\#17}$ y,-x+1,-z+1 ; $^{\#18}$ x,-z+1,y ; $^{\#19}$ -x+1,z+1,-y+1 ; $^{\#20}$ x,-z+1,y-1 ; $^{\#21}$ -x+1,-y+2,-z .

Table S3. Bond lengths [Å] and angles [deg] for **1** at 113 K.

Co(1)-C(1)	1.881(4)	Co(1)-C(1)$^{\#1}$	1.881(4)	Co(1)-C(1)$^{\#2}$	1.881(4)
Co(1)-C(1)$^{\#3}$	1.881(4)	Co(1)-C(1)$^{\#4}$	1.881(4)	Co(1)-C(1)$^{\#5}$	1.881(4)
K(1)-N(1)	2.863(3)	K(1)-N(1)$^{\#6}$	2.863(3)	K(1)-N(1)$^{\#7}$	2.863(3)
K(1)-N(1)$^{\#8}$	2.863(3)	K(1)-N(1)$^{\#9}$	2.863(3)	K(1)-N(1)$^{\#10}$	2.863(3)
N(1)-C(1)	1.135(4)	C(2)-C(3)	1.426(7)	C(2)-C(3)$^{\#11}$	1.426(7)
C(2)-C(3)$^{\#12}$	1.426(7)	C(3)-C(2)$^{\#11}$	1.426(7)	C(3)-C(2)$^{\#12}$	1.426(7)
C(3)-N(2)$^{\#11}$	1.426(7)	C(3)-N(2)$^{\#12}$	1.426(7)	N(1)-C(1)-Co(1)	180.0
N(2)$^{\#11}$-C(3)-C(2)	90.0(4)	N(2)$^{\#12}$-C(3)-C(2)	90.0(4)	N(2)$^{\#12}$-C(3)-C(2)$^{\#11}$	90.0(4)
N(2)$^{\#11}$-C(3)-C(2)$^{\#12}$	90.0(4)	N(2)$^{\#11}$-C(3)-N(2)$^{\#12}$	90.0(4)	C(1)-N(1)-K(1)	180.0

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x,z,-y ; $^{\#2}$ -x,-y,-z ; $^{\#3}$ -y,x,z ; $^{\#4}$ y,-x,-z ; $^{\#5}$ x,-z,y ; $^{\#6}$ -x,z+1/2,-y+1/2 ; $^{\#7}$ -x,-y+1,-z ; $^{\#8}$ -y+1/2,x+1/2,z ; $^{\#9}$ y-1/2,-x+1/2,-z ; $^{\#10}$ x,-z+1/2,y-1/2 ; $^{\#11}$ -y+3/2,x,-z+1/2 ; $^{\#12}$ y,-x+3/2,-z+1/2 ; $^{\#13}$ -x+3/2,-y+3/2,z.