Electronic Supplementary Material (ESI) for RSC Advances.

Multi-step phase transition crystal with dielectric constant bistability and temperature-dependent conductivity

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Experimental Section

1. Chemicals and reagents

All chemicals and solvents were reagent grade and used without further purification.

2. Physical measurements

TGA and DTA experiments were performed with a TA2000/2960 thermogravimetric analyzer from 25 to 800 °C for **1** at a warming rate of 10°C/min under a nitrogen atmosphere, and the polycrystalline samples were placed in an aluminum crucible. DSC experiments were carried out on on NETZSCH DSC 204F1 differential scanning calorimeter, and the heating and cooling rate is 10°C/min. Temperature-dependent power X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance powder diffractometer operating at 40 kV and 40 mA using Cu Kα radiation with λ = 1.5418 Å. Samples were scanned 2θ from 5 to 50° in the temperature range of 303-433 K. The measurements of temperature, frequency dependent dielectric permittivity were carried out using a concept 80 system (Novocontrol, Germany), the sample was prepared in the form of a disk with a 10 mm diameter and ca.1.5 mm thickness, and the disk was sandwiched between two parallel copper electrodes; the ac electrical field frequencies span from 1 to 10^7 Hz.

3. X-ray crystallography.

The diffraction data for **1** were collected at selected temperature with graphite monochromated Mo Kα (λ = 0.71073 Å) on an Oxford Diffraction Gemini-S Ultra CCD-detector diffractometer. Data reductions and absorption corrections was performed with the SAINT and SADABS software packages, respectively. Structures were solved by the direct method and refined by the full-matrix least-squares procedure on F^2 using SHELXL-97 program, all non-Hydrogen atoms were anisotropically refined. The H atoms were placed at calculated positions.

4. Preparation for 1

[C_4-bmim]Br and Na_2mnt were synthesized following the published procedures, respectively.[1,2] [C_4-bmim]$_2$[Ni(mnt)$_2$] was prepared employing a similar procedure

described in the literature.[1]

$[C_4\text{-bmim}][Ni(mnt)_2]$ **(1).** A MeOH solution (10 cm^3) of I_2 (205 mg, 0.80 mmol) was slowly added to a MeOH solution (25 cm^3) of $[C_4\text{-bmim}]_2[Ni(mnt)_2]$ (1.0 mmol), after stirred for 25 min, the mixture was allowed standing overnight. The microcrystalline precipitate formed were filtered off, washed with MeOH and dried in vacuum. Yield ~80%. Anal. Calc. for **1**: C, 40.14; H, 3.13; N, 17.56%. Found: C, 40.96; H, 3.41; N, 17.20%.

References

1. Ren, X. M.; Duan, C. Y.; Zhu, H. Z.; Meng, Q. J.; Hu, C. J.; Lu, C. S.; Liu, Y. J. *Trans. Met. Chem.* **2001**, 26, 295.
2. Davison, A.; Holm, H. R. *Inorg. Synth.* **1967**, 10, 8.

Table S1 Crystal and structural refinement data for compound **1**

Complex	1 at 298 K	1 at 353 K
Molecular formula	$C_{16}H_{15}N_6Ni\ S_4$	$C_{16}H_{15}N_6Ni\ S_4$
Molecular mass	478.26	478.26
Space group	P21/c	P21/c
Crystal system	monoclinic	monoclinic
Temp/K	296(2)	353
Wavelength (Å)	0.71073	0.71073
a/Å	10.5716(7)	10.7039(5)
b/Å	17.2583(4)	7.4586(4)
c/Å	26.5198(14)	26.8087(14)
α/°	90	90
β/°	93.924(6)	93.095(2)
γ/°	90	90
V/$Å^3$. Z	2030.1(2)	2137.18(19)
μ/mm^{-1}	1.381	1.312
ρ/g cm^{-3}	1.565	1.486
F000	980.0	1392.0
R_1	0.03809	0.0895
wR_2	0.0644	0.2386

Figure S1 TG curve of **1**

Figure S2 DSC curves for 1 in the heating/cooling cycle after melting

Figure S3 Temperature-dependent dielectric constant real part in the heating process

Figure S4 Nyquist plots at (a) 313-353 K