Supporting information

A high-T_c organic-ionic phase transition crystal obtained from trivalent cation

Yu-Hua Liu,‡ Jun-Chao Liu,‡ Hang Peng,‡ Xue-Qin Huang, Wei-Qiang Liao* and Zhong-Xia Wang*

Experiment

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Synthesis. The chemical reagent was purchased and can be used directly without further purification. A large amount of colorless bulk crystals of **1** were collected by slow evaporation of an aqueous solution containing a stoichiometric ratio of the reactants.

Differential scanning calorimetry. Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 200F3 instrument. The powder samples were placed in aluminum crucibles and measured in the temperature range between 320 K and 400 K under a nitrogen atmosphere at heating and cooling rates of 20 K min^{-1}.

Single-crystal X-ray diffraction measurement. Single-crystal X-ray diffraction data of compound **1** was performed on a Rigaku Saturn 924 diffractometer with Mo-Kα radiation (λ = 0.71073A˚) at 293 K and 403 K. Structures of the complexes were determined by the direct methods routines in the SHELXS program and refined by full-matrix least-squares methods on F^2 in SHELXL.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) data for compound **1** from 293 K to 413 K were obtained using a Rigaku D/MAX 2000 PC X-ray diffractometer and the diffraction patterns were collected in the range of 2θ = 5° – 40° with a step size of 0.02°.

IR spectrum and TGA measurement. IR spectra were recorded at ambient temperature using a Shimadzu model IR-60 spectrometer with KBr pellets. TGA test for **1** at a rate of 10 K min^{-1} in the range of 300 K-1000 K.

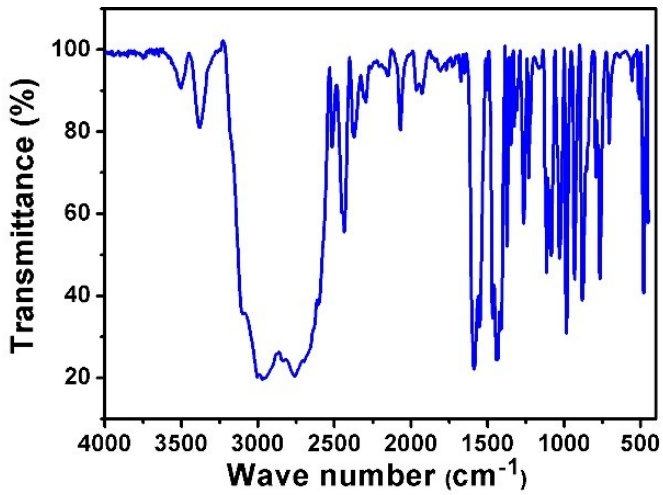

Figure S1. IR spectrum of **1**.

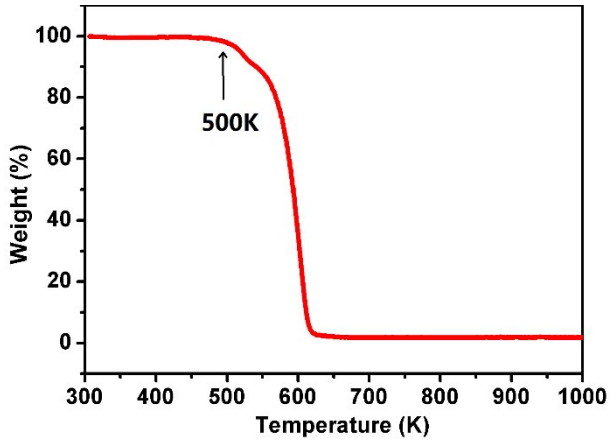

Figure S2. TGA curve of **1**. TGA test results showed that **1** is stable up to 500 K.

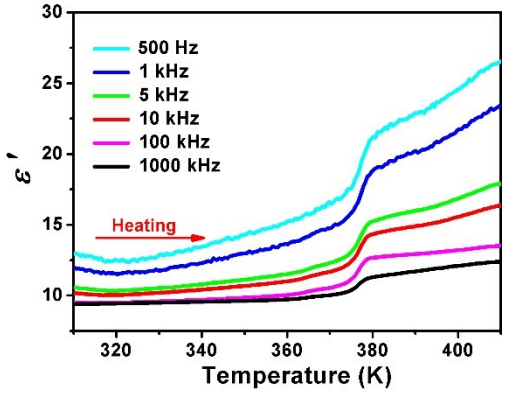

Figure S3. The real part (ε') of dielectric constant of **1** during heating at 500 Hz, 1 KHz, 5 KHz, 10 KHz, 100 KHz and 1000 KHz.

Table S1 Bond length (Å) and bond angle (°) of **1** at 293 K.

C1-N1	1.497(3)	N1-C1-C2	117.7(2)
C1-C2	1.511(3)	N2-C2-C1	114.7(2)
C2-N2	1.499(3)	N2-C3-C4	115.0(2)
C3-N2	1.494(3)	C3-C4-N3	113.5(2)
C3-C4	1.499(3)	N3-C5-C6	116.5(2)
C4-N3	1.509(3)	N1-C6-C5	117.4(2)
C5-N3	1.491(3)	N4-C7-C8	116.08(19)
C5-C6	1.511(3)	C7-C8-N5	114.3(2)
C6-N1	1.504(3)	N5-C9-C10	116.2(2)
C7-N4	1.491(3)	N6-C10-C9	116.3(2)
C7-C8	1.501(4)	N6-C11-C12	116.7(2)
C8-N5	1.506(3)	N4-C12-C11	116.2(2)
C9-N5	1.494(3)	C1-N1-C6	118.8(2)
C9-C10	1.512(3)	C3-N2-C2	116.7(2)
C10-N6	1.507(3)	C5-N3-C4	116.02(19)
C11-N6	1.502(3)	C7-N4-C12	116.2(2)
C11-C12	1.503(3)	C9-N5-C8	116.32(19)
C12-N4	1.501(3)	C11-N6-C10	117.2(2)

Table S2 Crystallographic data and structural refinement for **1**.

	1 (293 K)	**1** (403 K)
Formula	$C_6H_{18}Cl_3N_3$	$C_6H_{18}Cl_3N_3$
Formula weight	238.58	238.58
Crystal system	Monoclinic, $P2_1/n$	Trigonal, Rm
a / Å	10.9842(3)	8.0160(5)
b / Å	7.9342(2)	8.0160(5)
c / Å	25.1271(7)	15.1863(12)
α (deg)	90	90
β (deg)	91.717(2)	90
γ (deg)	90	120
V / Å ^{3}	2188.86(10)	845.08(12)
Z, D_{calcd} / g cm^{-3}	8, 1.448	3, 1.406
$F(000)$	1008	378
Goodness-of-fit on F^2	1.001	1.010
R_1[a] ($> 2\sigma$)	0.0508	0.0887
wR_2[b] ($> 2\sigma$)	0.1302	0.2290

[a] $R_1 = \mathbf{\Sigma}||F_o| - |F_c||/\mathbf{\Sigma}|F_o|$, [b] $wR^2 = [\mathbf{\Sigma}(|F_o|^2 - |F_c|^2) / \mathbf{\Sigma}|F_o|^2]^{1/2}$

Table S3 Hydrogen-bonding information of **1** at 293 K.

D-H…A	d(D-H)/Å	d(H-A)/Å	d(D-H)/Å	D-H…A/°
N1-H1C-Cl5[1]	0.89	2.21	3.062(2)	160.8
N1-H1D-Cl3[1]	0.89	2.24	3.075(2)	156.2
N2-H2C-Cl4[3]	0.89	2.31	3.088(2)	145.8
N2-H2D-Cl2[2]	0.89	2.28	3.121(2)	158.4
N3-H3C-Cl1[4]	0.89	2.86	3.324(2)	114.0
N3-H3C-Cl6[1]	0.89	2.52	3.209(2)	134.3
N3-H3D-Cl2[2]	0.89	2.27	3.153(2)	170.2
N4-H4C-Cl6[6]	0.89	2.29	3.120(2)	155.4
N4-H4D-Cl1[5]	0.89	2.31	3.099(2)	147.1
N5-H5C-Cl59[7]	0.89	2.71	3.285(2)	123.9
N5-H5C-Cl6	0.89	2.77	3.380(2)	127.0
N5-H5D-Cl1[5]	0.89	2.30	3.170(2)	166.6
N6-H6C-Cl3[7]	0.89	2.27	3.119(2)	159.7
N6-H6D-Cl2	0.89	2.28	3.132(2)	161.3

[1]1/2-X,-1/2+Y,1/2-Z; [2]-1+X,+Y,+Z; [3]1/2-X,1/2+Y,1/2-Z; [4]1-X,1-Y,1-Z; [5]3/2-X,-1/2+Y,1/2-Z; [6]+X,-1+Y,+Z; [7]1+X,+Y,+Z;