Electronic Supplementary Materials (ESI)

Para-Ferroelectric Phase Transition Induces Excellent Second Harmonic Generation Response and Prominent Switchable Dielectric Constant Change based on a Metal-Free Ionic Crystal

Ding-Chong Han, Yu-Kong Li, Yao Liu, Yu-Hui Tan*, Yun-Zhi Tang*, Wen-Juan Wei, Peng-Kang Du, Hao Zhang

*Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi Province, P. R. China

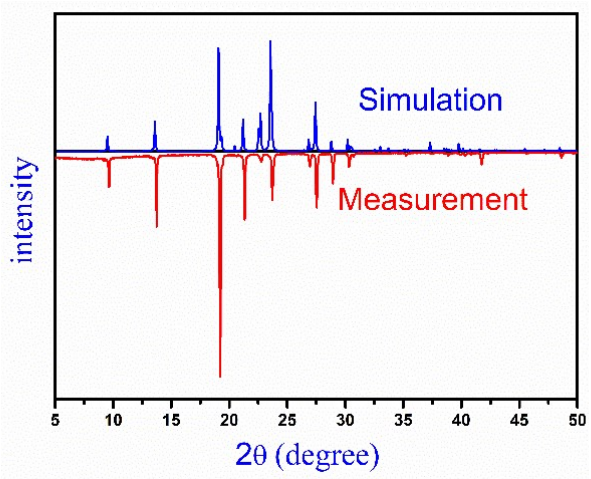

Fig. S1. PXRD (powder x-ray diffraction) measurement comparison with single crystal simulation of compound **1** at room temperature.

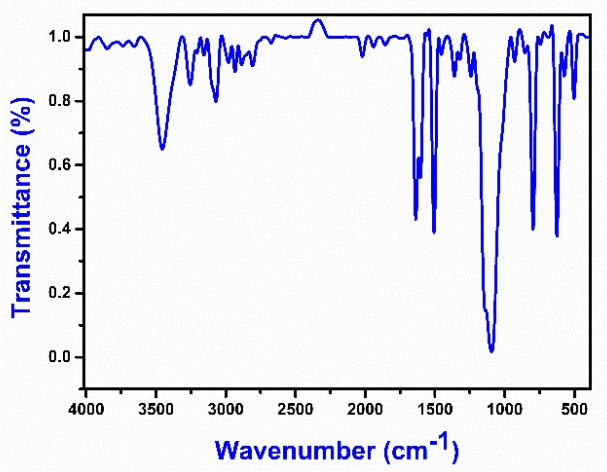

Fig. S2. The infrared (IR) spectra of solid compound **1** at room temperature.

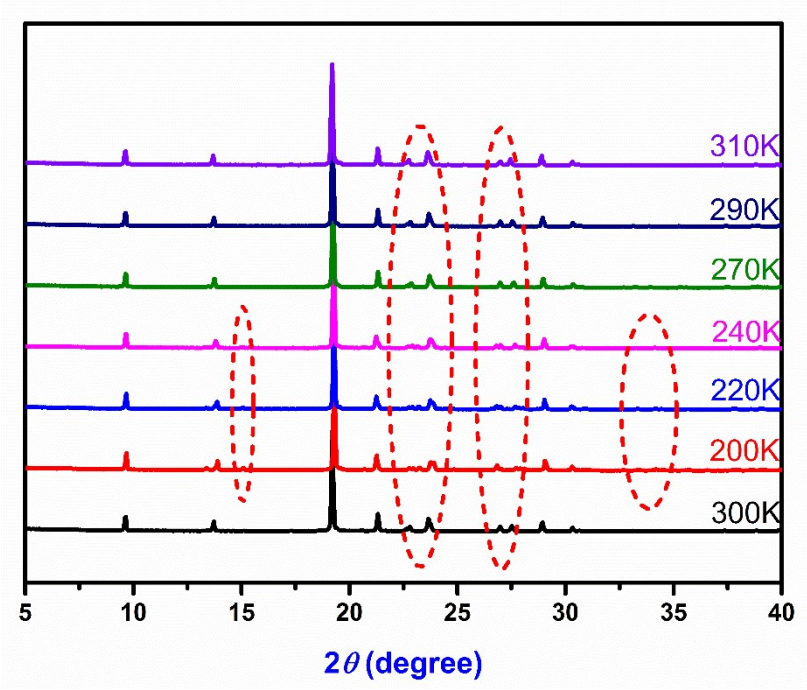

Fig. S3. The Variable-Temperature PXRD of compound **1** at different temperatures (200 K, 220 K, 240 K, 270 K, 290 K, 300 K, 310 K).

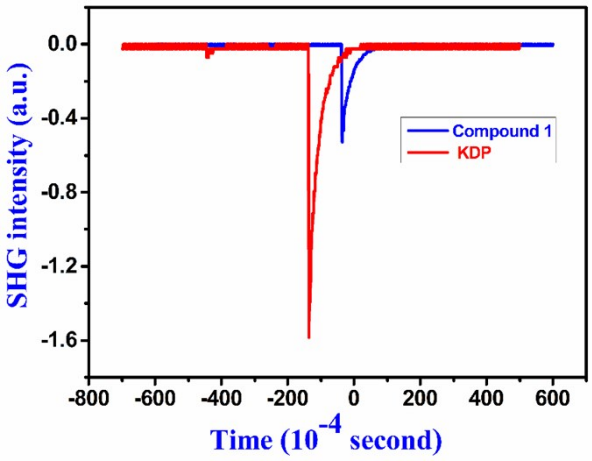

Fig. S4. The comparison of KDP, SHG response at **1-LTP** under the same condition.

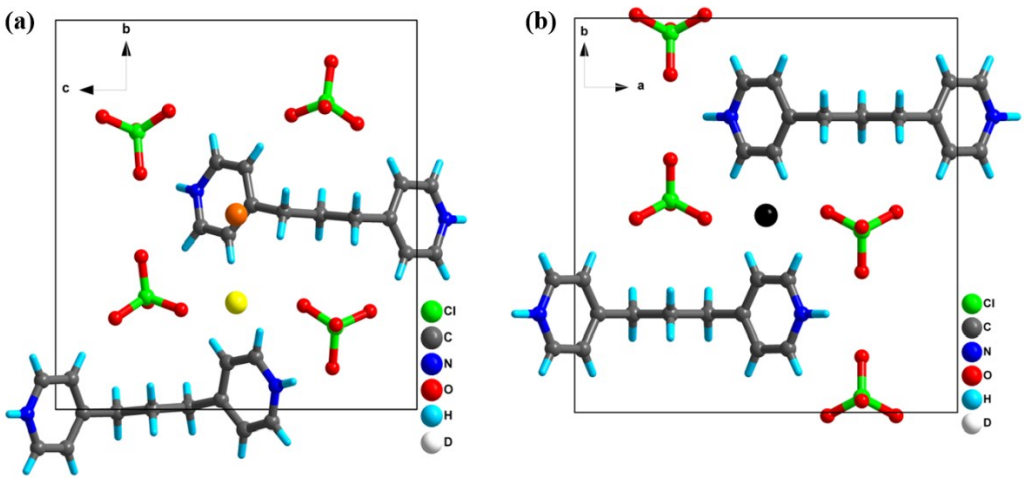

Fig. S5. The positive and negative charge centers of **1-LTP** (a) and **1-HTP** (b).

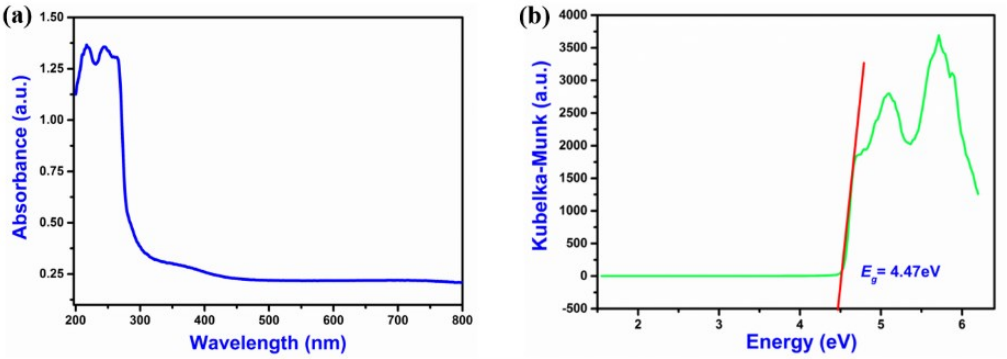

Fig. S6. UV-vis absorption spectrum at 293 K (a) and the optical bandgap calculation diagrams of compound **1** (b).

Table S1. The crystallographic data and structure refinements for compound **1** at 240K and 293K.

Temperature	240 K	293 K
Empirical formula	$C_{13}H_{16}Cl_2N_2O_8$	$C_{13}H_{16}Cl_2N_2O_8$
Formula weight	399.18	399.18
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12$
a (Å)	4.8478(2)	13.0155(7)
b (Å)	13.3356(5)	13.2744(7)
c (Å)	12.8520(5)	4.9013(2)
α (°)	90	90.00
β (°)	90.731(4)	90.00
γ (°)	90	90.00
V (Å^3)	830.79(6)	846.81(7)
Z	2	2
Density (g/cm^3)	1.596	1.566
m (mm^{-1})	0.437	0.429
F (000)	412.0	412.0
Data/restraints/parameters	4787/1/226	1483/35/115
GOF	1.047	1.182
R_1, $wR_2[I >= 2\sigma(I)]$	$R_1 = 0.0537$, $wR_2 = 0.1407$	$R_1 = 0.0657$, $wR_2 = 0.1970$
R_1, wR_2 (all data)	$R_1 = 0.0611$, $wR_2 = 0.1452$	$R_1 = 0.0766$, $wR_2 = 0.2120$
$\triangle\rho_{max}/\triangle\rho_{min}$ (eÅ^{-3})	0.52/-0.55	0.67/-0.62

Calculation of ΔS and N

In the heating cycle mode

$$\Delta S_1 = R\ln N_1$$

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{T_c}$$

$$= \frac{4.2430 J^{-1} mol \times 399.18 g^{-1} mol}{256.19 K}$$

$$= 6.61 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{6.61 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 2.22$$

In the cooling cycle mode

$$\Delta S_2 = R \ln N_2$$

$$\Delta S_1 = \int_{T_2}^{T_1} \frac{Q}{T} dT$$

$$\approx \frac{\Delta H}{Tc}$$

$$= \frac{4.7325 J^{-1} mol \times 399.18 g^{-1} mol}{252.09 K}$$

$$= 7.494 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{7.494 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 2.46$$