Supporting Information for

Exploring a Lead-free Organic-Inorganic Semiconducting Hybrid with Above-Room-Temperature Dielectric Phase Transition

Yuyin Wang,[ab] Shiguo Han,[ab] Xitao Liu,[ac*] Zhenyue Wu,[ab] Zhihua Sun,[a*] Dhananjay Dey,[a] Yaobin Li,[a] and Junhua Luo[a*]

[a]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of*

Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R.China

[b]*University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100039,P.R.*

China

[c]*State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, China*

To whom correspondence should be addressed. E-mail:
jhluo@fjirsm.ac.cn；sunzhihua@fjirsm.ac.cn; xtliu@fjirsm.ac.cn
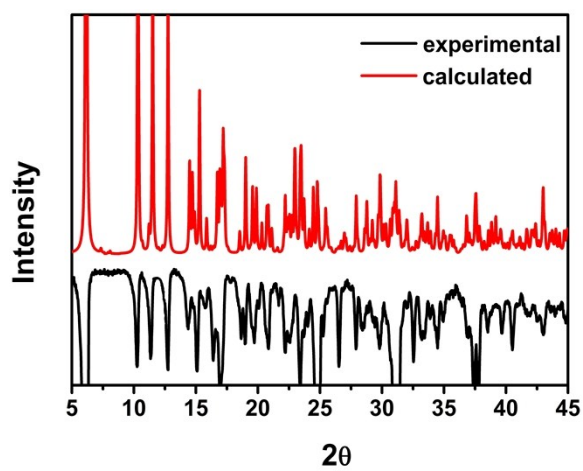
Figure. S1 Bulk crystal of CHA.

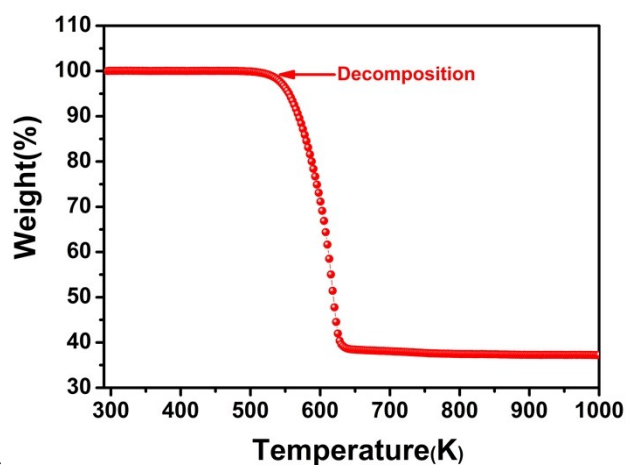Figure S2. Powder X-ray Diffraction (PXRD) patterns of experimental data and the calculated data
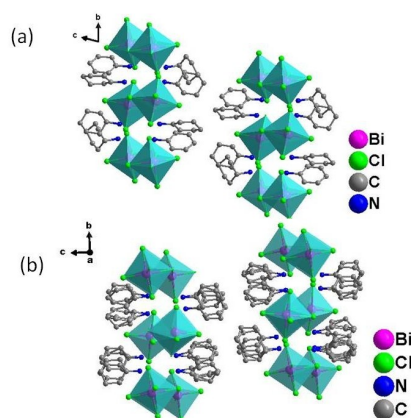

Figure S3. TG curves for CHA.

Figure S4. (a) Packing view of the unit cell at 200 K; (b) Packing view of the unit cell at 333K.
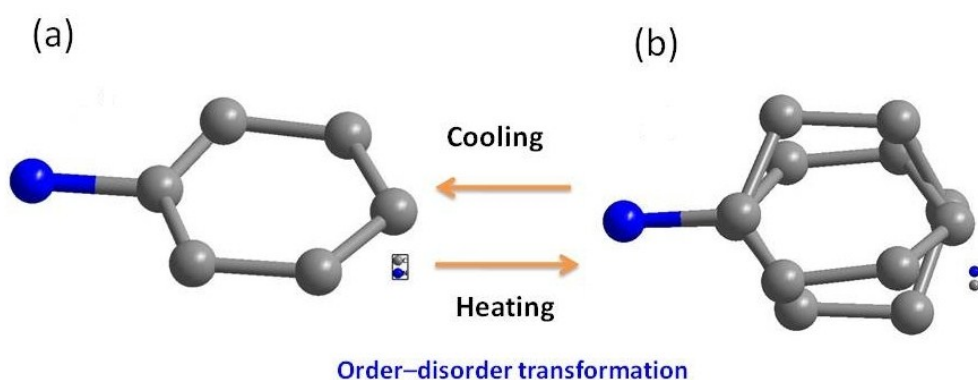

Figure S5. Order–disorder transformation of the cation in **CHA** during phase transition. cation attains (a) order state in RTP, and (b) disordered in HTP.
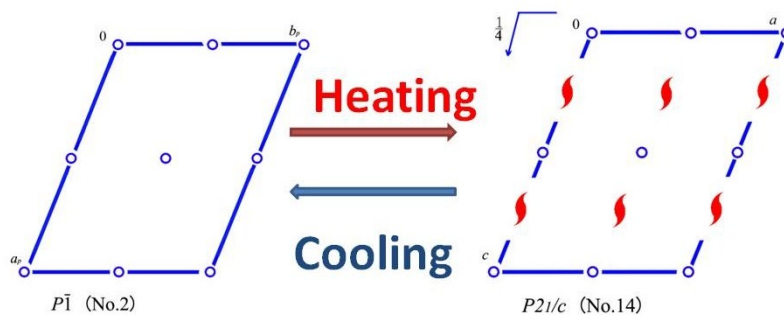

Figure S6. Symmetry transformation of CHA during the phase transition.

Table S1: Crystal structure and refinement detail of **CHA** at different temperatures.

Empirical formula	$C_{24}H_{56}N_4Cl_{10}Bi_2$	$C_{24}H_{56}Bi_2Cl_{10}N_4$
Formula weight	1173.19	1173.18
Temperature/K	200.15	333
Crystal system	triclinic	monoclinic

Space group	P-1	P2₁/c
a/Å	11.9718(4)	11.9592(3)
b/Å	12.4092(4)	12.7479(2)
c/Å	15.8390(6)	31.1058(6)
α /°	76.4740(10)	90
β /°	69.2450(10)	108.8270(10)
γ /°	89.3230(10)	90
Volume/Å³	2132.77(13)	4488.50(16)
Z	2	4
ρ_{calc}g/cm³	1.827	1.736
μ /mm⁻¹	8.887	8.446
F(000)	1128.0	2256.0
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.78 to 55.14	4.812 to 55.008
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -40 ≤ l ≤ 40
Reflections collected	43425	92899
Independent reflections	9781 [R_{int} = 0.0643, R_{sigma} = 0.0507]	10303 [R_{int} = 0.0816, R_{sigma} = 0.0427]
Data/restraints/parameters	9781/175/365	10303/347/541
Goodness-of-fit on F²	1.047	1.038
Final R indexes [I>=2σ(I)]	R_1 = 0.0520, wR_2 = 0.1444	R_1 = 0.0400, wR_2 = 0.0849
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.1556	R_1 = 0.0781, wR_2 = 0.1006
Largest diff. peak/hole /	5.63/-2.54	1.22/-1.21

e Å^{-3}

_____