Electronic Supplementary Information (ESI)

Halogen Regulating Induced Reversible High-*T*-Dielectric-Thermal Transitions in Novel Layered Organic-Inorganic Hybrid Semiconducting Crystals

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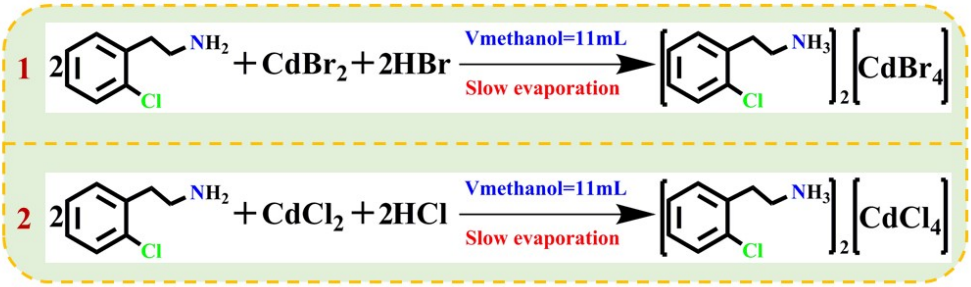

Fig. S1. The basic synthetic route of **1** and **2**.

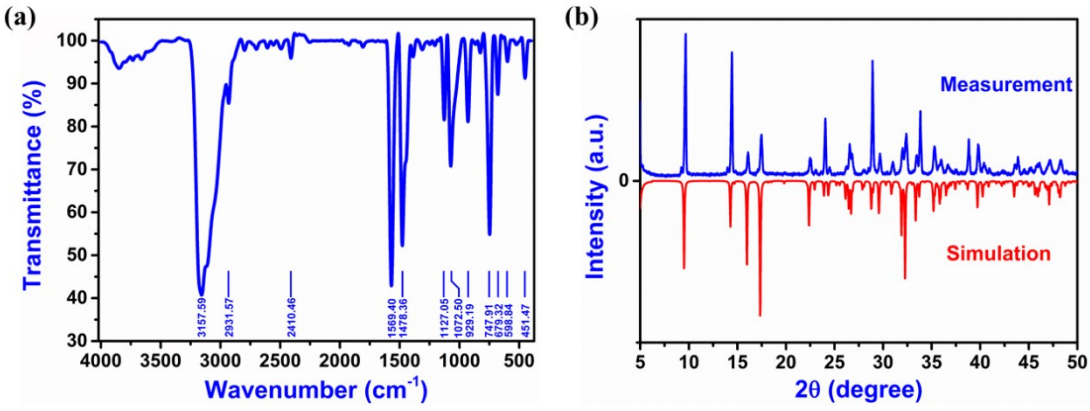

Fig. S2. PXRD (powder X-ray diffraction) measurement comparison with single crystal simulation (b) and the infrared (IR) spectra (a) of **1** at room temperature.

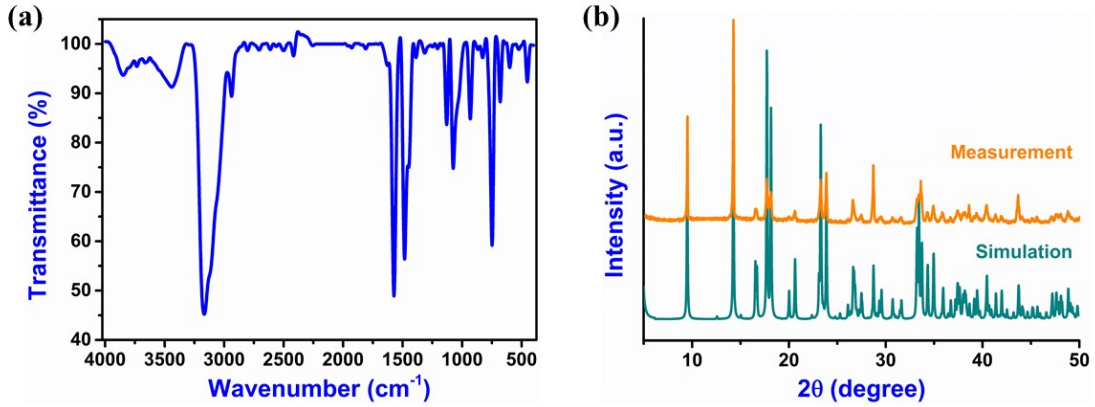

Fig. S3. PXRD (powder X-ray diffraction) measurement comparison with single crystal simulation (b) and the infrared (IR) spectra (a) of **2** at room temperature.

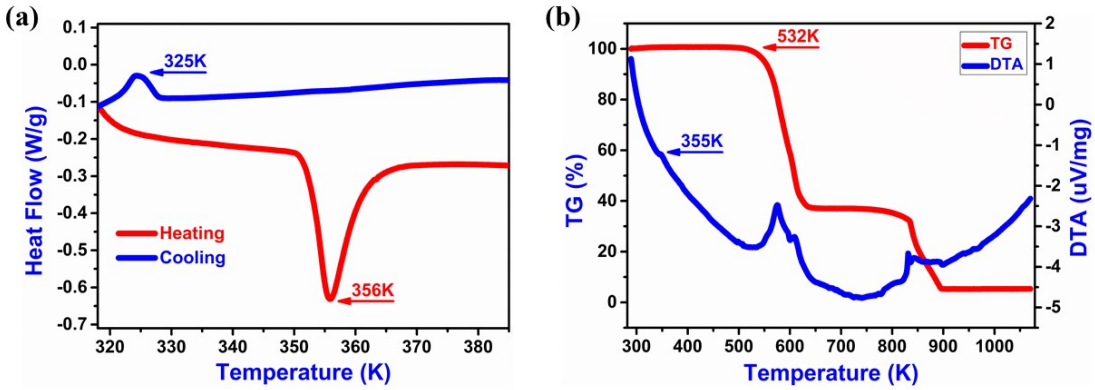

Fig. S4. The heat flow graph of **2** (a). TG-DTA curves ranging temperature from 290 K to 1075 K of **2** (b).

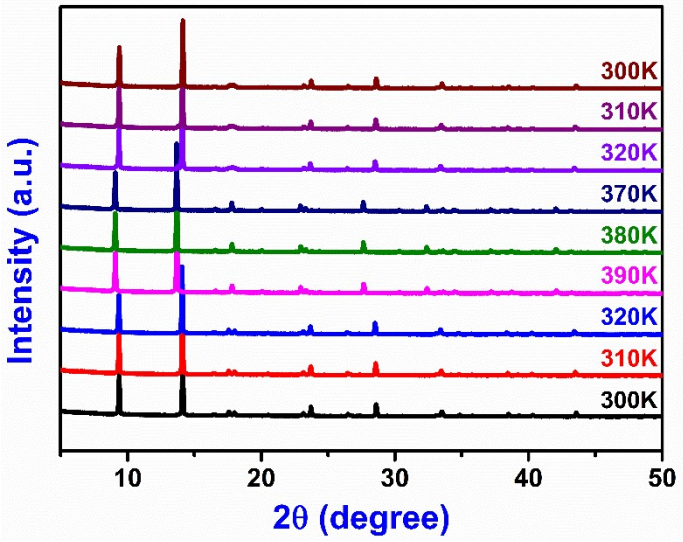

Fig. S5. The X-ray powder diffraction patterns of **2** at different temperatures.

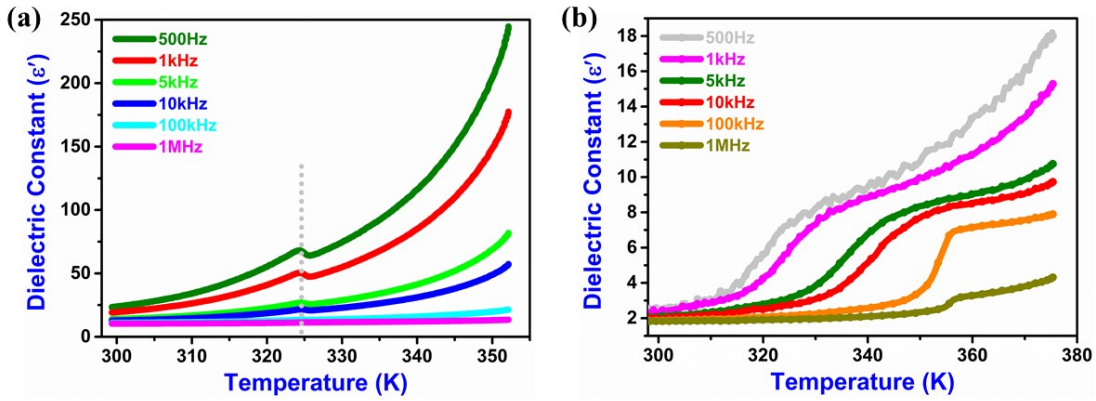

Fig. S6. The frequency-dependent ε′ curve of **1** (a) and **2** (b) with temperature changing.

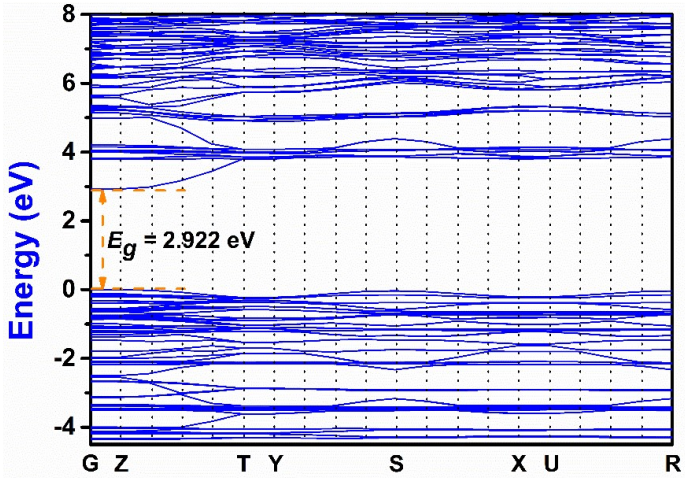

Fig. S7. The calculated energy band structures of **1**.

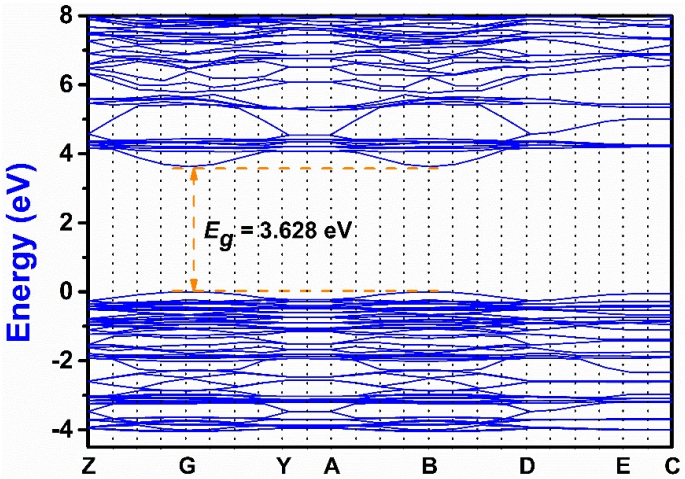

Fig. S8. The calculated energy band structures of **2**.

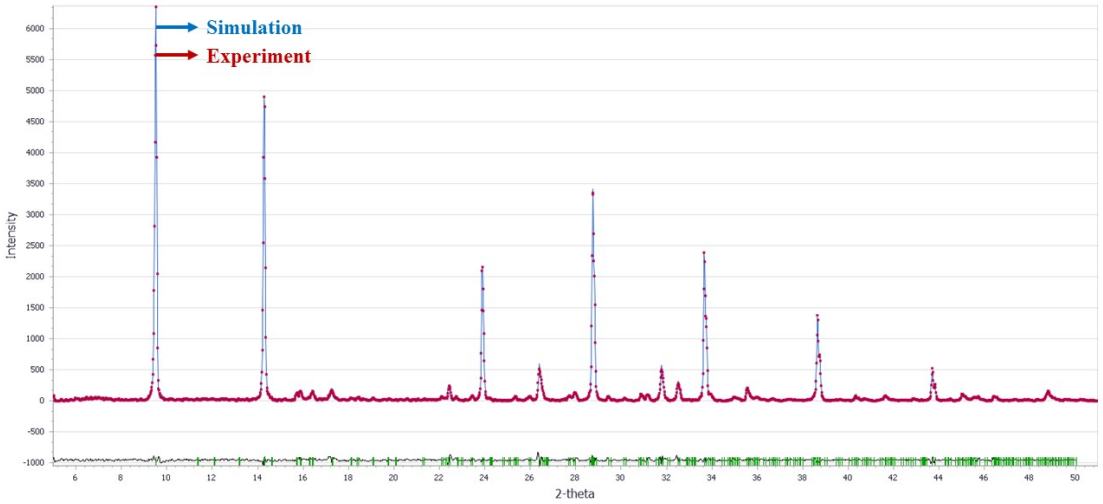

Fig. S9. The Pawley refinements results for **1** at 370 K. The refinements yielding tetragonal crystal system $P4_2/n$ space group with cell parameters are $a = b = 8.00325$ Å, $c = 37.33742$ Å, $\alpha = \beta = \gamma = 90°$ and $V = 2391.5368$ Å^3.

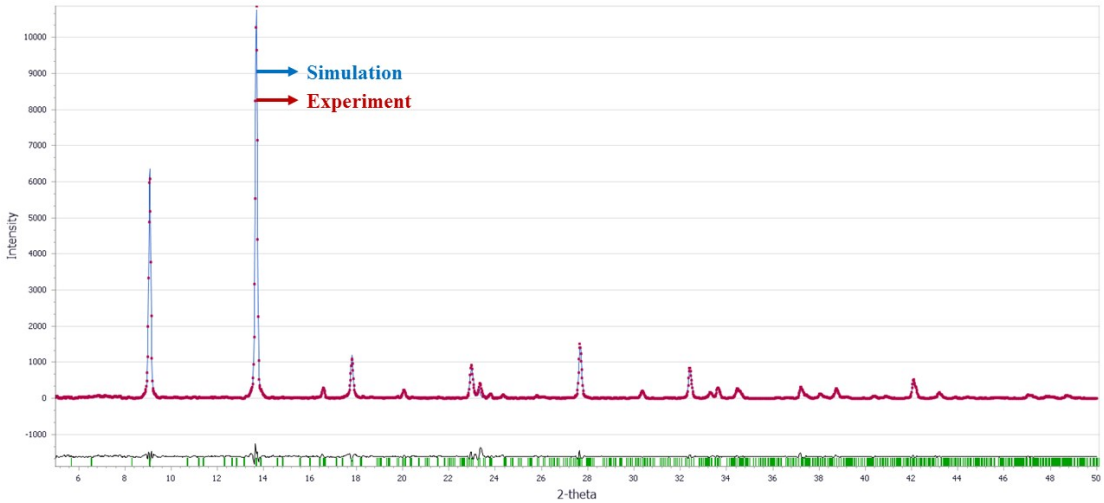

Fig. S10. The Pawley refinements results for **2** at 370 K. The refinements obtaining monoclinic crystal system $I2/m$ space group with cell parameters are $a = 19.68632$ Å, $b = 9.75979$ Å, $c = 13.50802$ Å, $\alpha = \gamma = 90°$, $\beta = 127.97999°$ and $V = 2045.7253$ Å^3.

Table S1. The crystallographic data and structure refinements at room temperature.

Compound	$[Cl\text{-}C_6H_4\text{-}(CH_2)_2NH_3]_2CdBr_4$	$[Cl\text{-}C_6H_4\text{-}(CH_2)_2NH_3]_2CdCl_4$
Formula weight	745.30	567.45
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn*	$P2_1/c$
a (Å)	7.917(3)	18.8581(14)
b (Å)	7.942(4)	7.6030(6)
c (Å)	37.185(13)	7.6418(6)
α (°)	90	90
β (°)	90	99.102(2)
γ (°)	90	90
V (Å^3)	2338.1(17)	1081.87(14)
Z	4	2
Density (g/cm^3)	2.117	1.742
m (mm^{-1})	8.002	1.753
F (000)	1416.0	564.0
Data/restraints/parameters	2691/0/115	2470/0/116
GOF	1.257	1.153
R_1, wR_2 [$I >= 2\sigma(I)$]	$R_1 = 0.0790$, $wR_2 = 0.1972$	$R_1 = 0.0403$, $wR_2 = 0.1078$
R_1, wR_2 (all data)	$R_1 = 0.0946$, $wR_2 = 0.2050$	$R_1 = 0.0447$, $wR_2 = 0.1125$
$\triangle\rho_{max}/\triangle\rho_{min}$ (eÅ^{-3})	1.09/-2.30	1.93/-0.59
CCDC	2263024	2263054

Table S2. Intermolecular hydrogen bond lengths (Å) and angles (º) for **1**.

D−H···A	D−H	H···A	D···A	∠D−H···A
N1−H1A···Br2	0.89	2.69	3.343(11)	131
N1−H1B···Br1	0.89	2.86	3.695(11)	156
N1−H1C···Br1	0.89	2.58	3.466(11)	171

Table S3. Intermolecular hydrogen bond lengths (Å) and angles (º) for **2**.

D–H···A	D–H	H···A	D···A	∠D–H···A
N1–H1A···Cl2	0.89	2.50	3.196(4)	135
N1–H1B···Cl3	0.89	2.69	3.479(4)	148
N1–H1C···Cl3	0.89	2.45	3.332(4)	169

Calculation of Δ*S* and *N*

$[Cl\text{-}C_6H_4\text{-}(CH_2)_2NH_3]_2CdBr_4$ ⟹

In the heating cycle mode

$\Delta S_1 = R\ln N_1$

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

$$= \frac{3.150 g^{-1} J \times 745.30 mol^{-1} g}{335 K}$$

$$= 7.01 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{7.01 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 2.32$$

In the cooling cycle mode

$\Delta S_2 = R\ln N_2$

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c}$$

$$= \frac{2.990 g^{-1} J \times 745.30 mol^{-1} g}{323 K}$$

$$= 6.90 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S_2}{R}\right) = \exp\left(\frac{6.90 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 2.29$$

$[Cl\text{-}C_6H_4\text{-}(CH_2)_2NH_3]_2CdCl_4$ ⟹

In the heating cycle mode

$\Delta S_1 = R\ln N_1$

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

$$= \frac{6.929 g^{-1} J \times 567.45 mol^{-1} g}{356 K}$$

$$= 11.04 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_1 = \exp\left(\frac{\Delta S_1}{R}\right) = \exp\left(\frac{11.04 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 3.77$$

In the cooling cycle mode

$\Delta S_2 = R\ln N_2$

$$\Delta S_2 = \int_{T_2}^{T_1} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c}$$

$$= \frac{5.790 g^{-1} J \times 567.45 mol^{-1} g}{325 K}$$

$$= 10.11 J \cdot mol^{-1} \cdot K^{-1}$$

$$N_2 = \exp\left(\frac{\Delta S_2}{R}\right) = \exp\left(\frac{10.11 J \cdot mol^{-1} \cdot K^{-1}}{8.314 J \cdot mol^{-1} \cdot K^{-1}}\right)$$

$$= 3.37$$