Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Near-Room-Temperature Tunable Dielectric Response Induced by Dual Phase Transitions in a Lead-Free Hybrid: $(C_3H_8N)_2SbBr_5$

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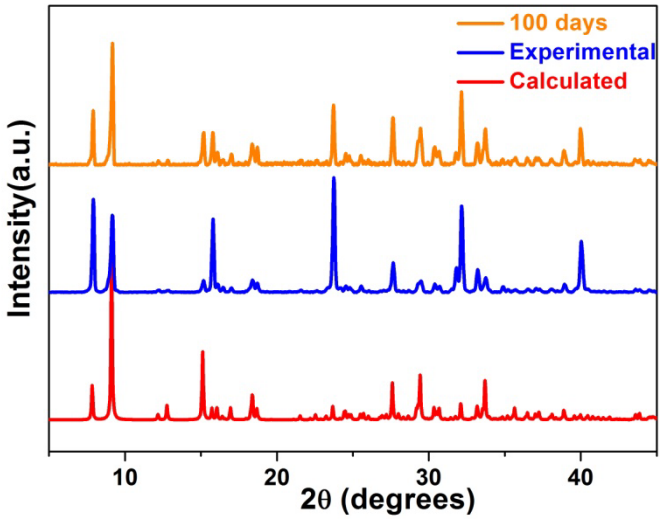
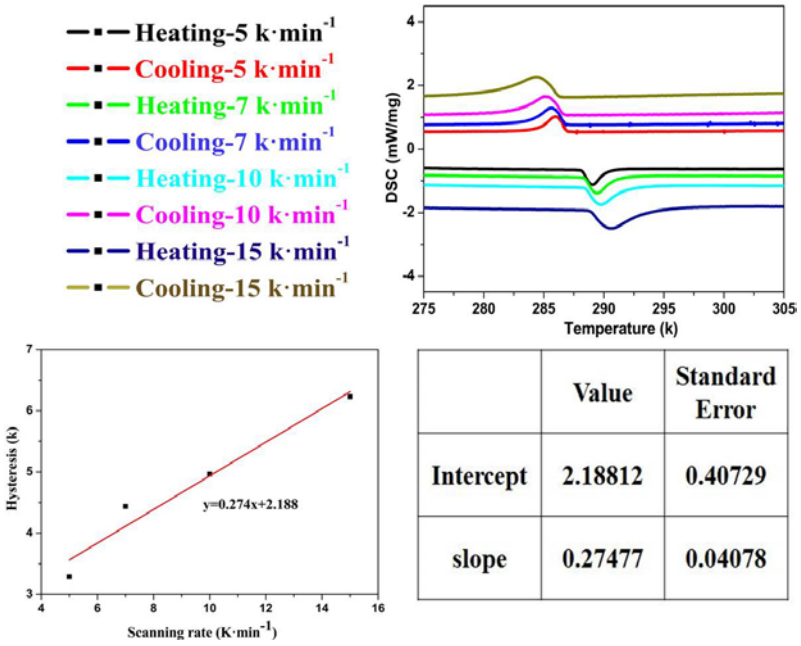
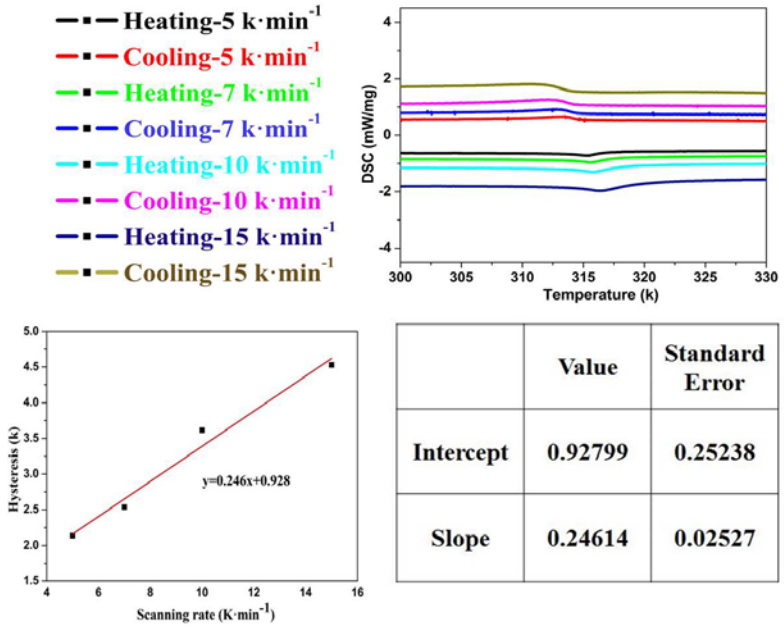


Figure S1. Powder X-ray diffraction patterns of **1** recorded on the sample after 100 days.



	Value	Standard Error
Intercept	2.18812	0.40729
slope	0.27477	0.04078

Figure S2. DSC measurements of **1** around T_1 with the scanning rates of 5, 7, 10 and 15 K·min^{-1}.



	Value	Standard Error
Intercept	0.92799	0.25238
Slope	0.24614	0.02527

Figure S3. DSC measurements of **1** around T_2 with the scanning rates of 5, 7, 10 and 15 K·min^{-1}.

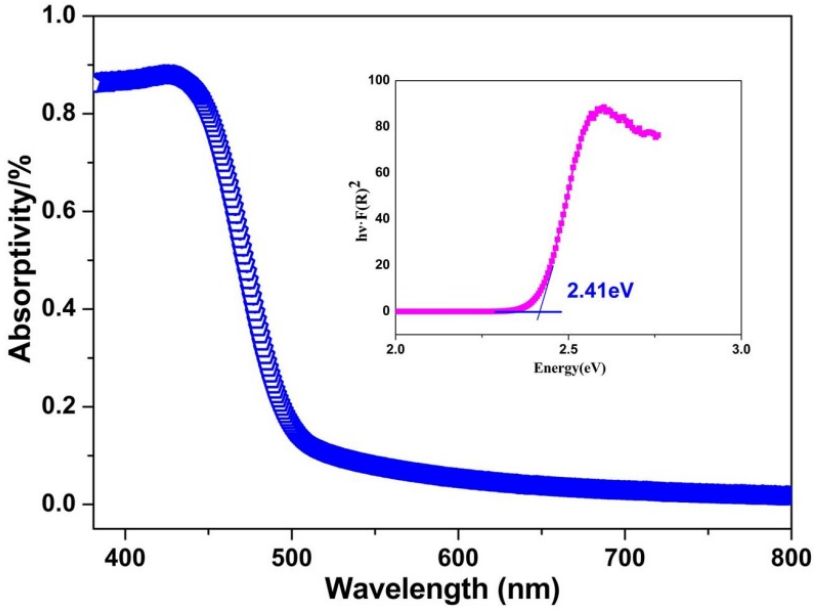


Figure S4. Absorption spectra with a sharp absorption edge of 525 nm. Inset: Calculation of the optical band gap using the Tauc method. The optical band gap is measured to be E_g = 2.41 eV.

Table S1 Crystal data and structure refinement for **1** at 270, 300 and 325 K.

Phase	LTP	ITP	HTP
phase	($C_6H_{16}N_2SbBr_5$)	($C_6H_{16}N_2SbBr_5$)	($C_6H_{16}N_2SbBr_5$)
T (K)	270 K	300 K	325 K
Formula weigh	637.51	637.51	637.51
Crystallgraphic system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pnca*[1]	*Bbcm*[2]
Z, Calculated density	4, 2.525 g/cm^3	8, 2.511 g/cm^3	8, 2.503 g/cm^3
a (Å)	11.8937(4)	22.5314(7)	22.4485(6)
b (Å)	19.0986(6)	18.9885(8)	18.9653(5)
c (Å)	7.8047(2)	7.8845(3)	7.9488(2)
β/°	108.9080(10)	90	90
F(000)	1168.0	2336.0	2256.0
Theta range fordata collection	4.266-55.228°	5.594-54.976°	4.296-55.014°
Limiting indices	-15≤h≤15 -24≤k≤24 -10≤l≤10	-29≤h≤28 -21≤k≤24 -9≤l≤10	-27≤h≤29 -24≤k≤24 -10≤l≤10
Reflections collected/unique	31235/3863 R_{int}=*0.0627*	19130/3868 R_{int}=0.0882	13466/2091 R_{int}=*0.0511*
Completeness	100%	100%	100%
Data/restraints/paraments	3862/36/131	3868/44/129	2093/74/89
Goodness-of-fit	1.091	1.005	1.023
Final R indices I>2sigma(I)	R_1=0.0313	R_1=0.0527	R_1=0.0454

1 Space group *Pnca* is a non-standard setting of space group Pbcn #60 in International Tables.
2 Space group *Bbcm* is a non-standard setting of space group Cmca #64 in International Tables.

Table S2 N-H···Br Hydrogen bonds of **1** at LTP**.**

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N2-H2A	0.890	2.703	143.39	3.479	Br4 [x, y, z-1]
N2-H2B	0.890	2.902	145.01	3.667	Br1 [-x+1, -y+1, -z+1]
N2-H2B	0.890	3.036	129.28	3.665	Br5 [-x+1, -y+1, -z+1]
N2-H2C	0.890	2.691	168.21	3.567	Br2
N1-H1A	0.890	2.510	152.79	3.326	Br3
N1-H1B	0.890	2.597	156.52	3.432	Br4 [x, -y+1/2, z-1/2]
N1-H1C	0.890	2.673	172.58	3.558	Br3 [x, -y+1/2, z+1/2]

Table S3 N-H···Br Hydrogen bonds of **1** at ITP

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N2-H2A	0.890	2.470	161.53	3.326	Br2 [x, -y+1/2, z +1/2]
N2-H2B	0.890	2.622	157.40	3.460	Br5
N2-H2C	0.890	2.882	163.66	3.745	Br2 [x, y, z +1]
N1-H1A	0.890	3.062	139.73	3.785	Br1 [-x+1, -y, -z+1]
N1-H1A	0.890	2.897	140.77	3.630	Br4 [-x+1, -y, -z+1]
N1-H1B	0.890	2.657	157.24	3.495	Br5
N1-H1C	0.890	2.865	153.31	3.682	Br3 [x, y, z+1]

Table S4 N-H···Br Hydrogen bonds of **1** at RTP**.**

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.890	2.904	133.66	3.577	Br1 [x+1/2, y, -z+1/2]
N2-H1B	0.890	2.884	138.93	3.603	Br2 [-x+1, -y+1, -z+1]
N1-H1C	0.89	3.010	123.35	3.577	Br1 [x+1/2, y, z+1/2]
N2-H2C	0.890	3.001	126.78	3.605	Br1 [x, -y+3/2, -z+1/2]
N2-H2C	0.890	3.113	128.54	3.733	Br3 [x, y, -z+1]
N2-H2D	0.890	2.740	164.55	3.605	Br1 [x, -y+3/2, z+1/2]
N1-H2E	0.890	2.490	157.91	3.331	Br4