Supplementary Material

Temperature symmetry breaking and properties of lead-free organic-inorganic hybrids: antimony(III) iodide and bismuth(III) iodide: $[S(CH_3)_3]_3Sb_2I_9$ and $[S(CH_3)_3]_3Bi_2I_9$

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Table S1. Experimental details of x-ray measurements.

	PHASE I	**PHASE II**	**PHASE III**
Crystal data			
Chemical formula		$[C_3H_9S]_3Bi_2I_9$	
M_r	1764.33	1791.54	1791.54
Crystal system, space group	Hexagonal, $P6_3/mmc$	Monoclinic, $C2/c$	Triclinic, P-1
Temperature (K)	325	200	100
a, b, c (Å)	9.759 (1), 9.759 (1), 23.153 (3)	19.005 (1), 33.199 (1), 22.897 (1)	18.854 (1), 18.993 (1), 22.686 (1)
α, β, γ (°)	90, 90, 120	90, 91.88 (1), 90	89.06 (1), 88.08 (1), 60.27 (1)
V (Å^3), Z	1909.8 (5), 2	14439.3 (6), 16	7050.5 (3), 8
μ (mm^{-1})	16.64	17.61	18.03
Data collection			
No. of measured, independent and observed [$I > 2\sigma(I)$] ref.	5576, 981, 294	56080, 17382, 12160	54603, 32278, 22968
R_{int}	0.079	0.056	0.063
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.088, 0.375, 0.98	0.048, 0.109, 1.22	0.102, 0.229, 1.17
No. of reflections	981	17382	32278
No. of parameters	14	427	599
No. of restraints	3	0	0
H-atom treatment	–	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, -1.09	1.9, -1.4	5.9, -4.1

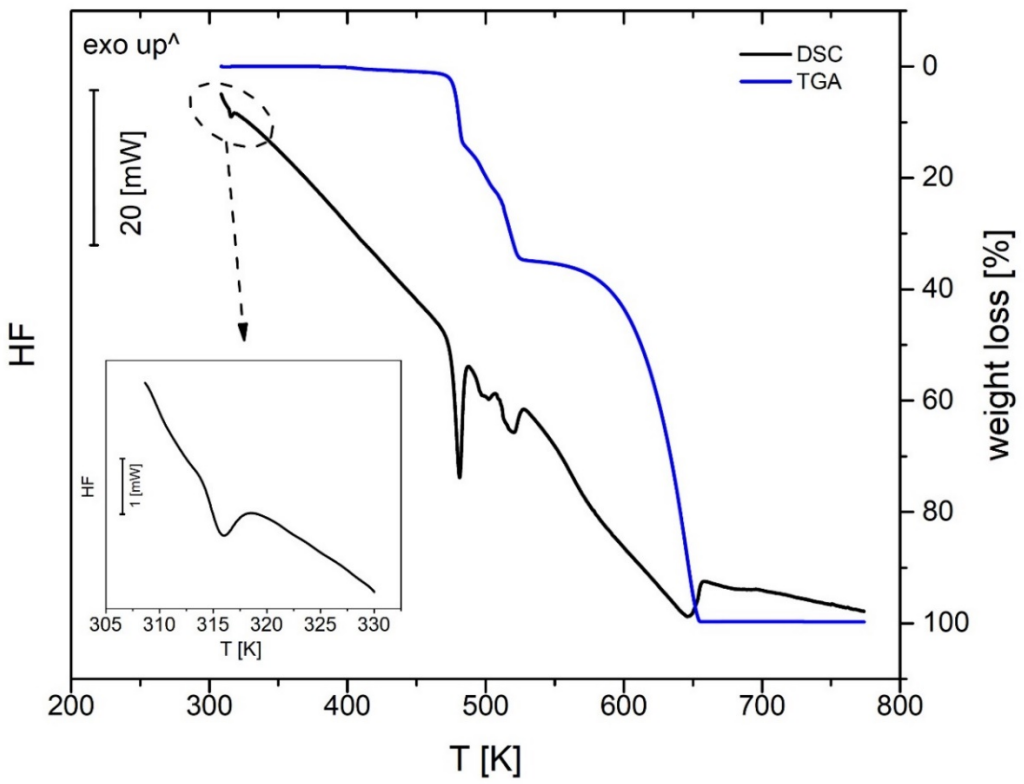

Fig. S1. The TGA and DSC signals for **TBI** (m_s=16.3794 mg).

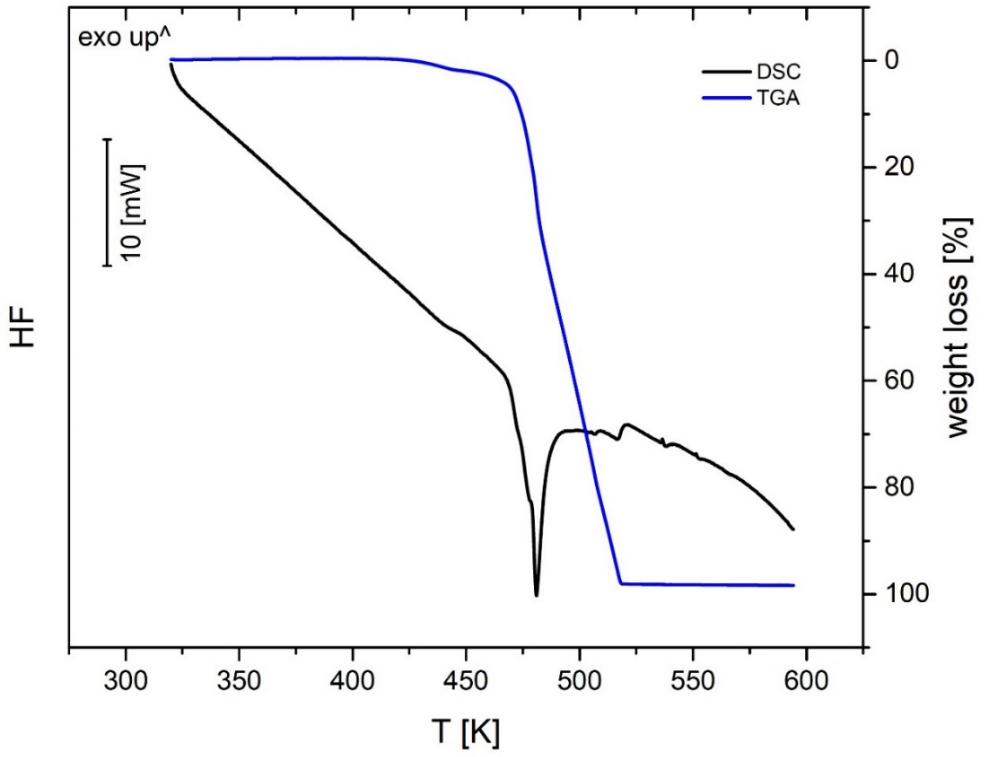

Fig. S2. The TGA and DSC signals for **TSI** (m_s=10.1380 mg).

Table. S2. Thermodynamic parameters of the phase transitions for **TBI** and **TSI** in the solid state.

Parameters	**TBI**	**TSI**
M [g·mol^{-1}]	1791.61	1617.17
T_{onset} [K] (coling/heating)		
I→II	314.2/314.8	303.9/304.1
II→III	-/181.5	212.9/221.4
$\triangle H_{PT}$ [J mol^{-1}] (coling/heating)		
I→II	7542.7/7811.4	6533.4/6484.8
II→III	-/2884.5	4641.3/4770.6
ΔS [J·mol $^{-1}$·K^{-1}] (coling/heating)		
I→II	24.0/24.9	21.5/21.3
II→III	-/15.9	21.8/21.6

Table. S3 . Activation energies, correlation times and motional constants evaluated for **TBI** and for **TSI**.

	Temperature range	E_a [kJ/mol]	τ_0 [S]	C [s^{-2}]
TBI	< 183K	6.8	$1.92\ 10^{-12}$	$3.83\ 10^{9}$
	183K-313K	26.8	$4.03\ 10^{-15}$	$1.8\ 10^{9}$
	313K <	8.4		
TSI	<223K	6.53	$2.33\ 10^{-12}$	$4.38\ 10^{9}$
	223K-293K	27.1	$3.94\ 10^{-15}$	$1.698\ 10^{9}$
	293K <	11.5		