Electronic Supplementary Material (ESI) for Dalton Transactions.

The lone-pair-electron-driven phase transition and order-disorder processes in thermochromic (2-MIm)SbI_4 organic-inorganic hybrid

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X-RAY POWDER DIFFRACTION

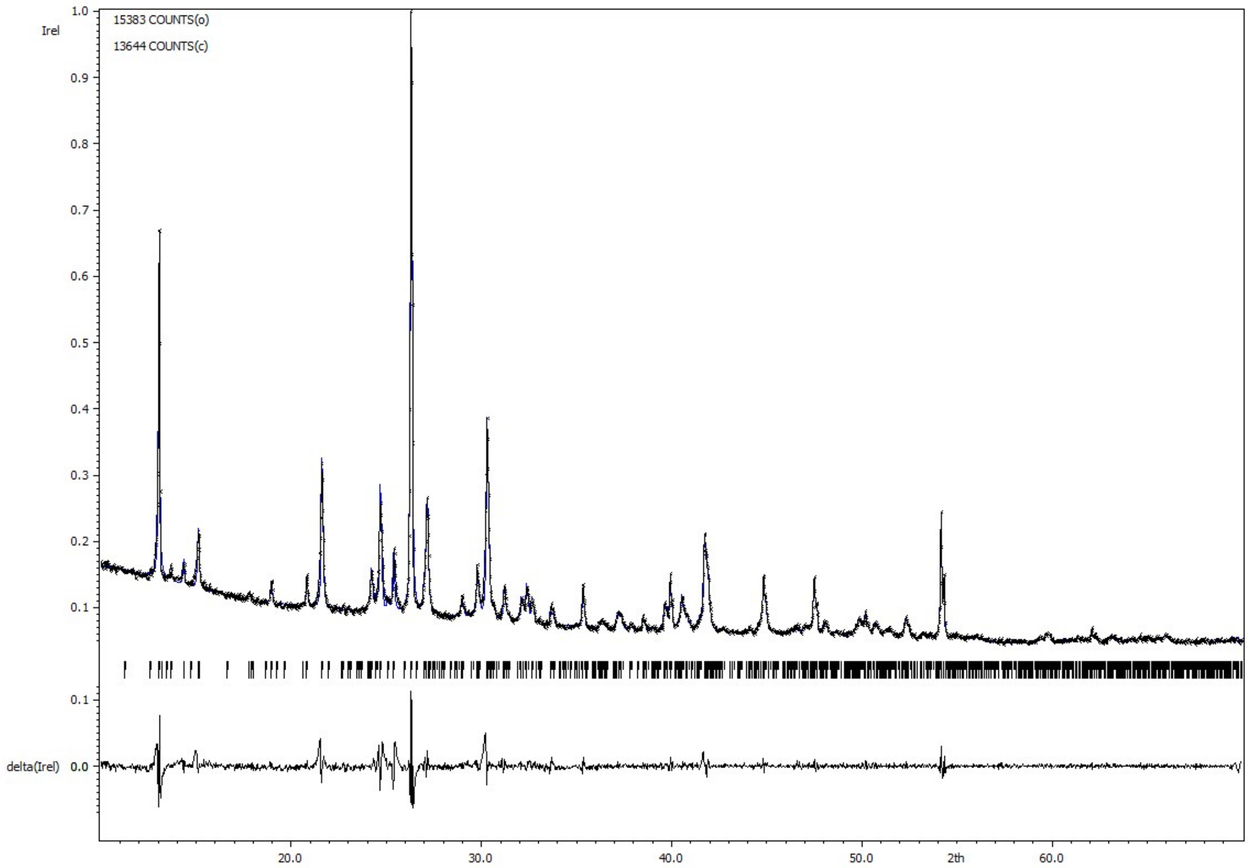

Fig. S1 The results of the Le Bail analysis made for (2-MIm)SbI$_4$ powders in Jana2006. The model of the high-temperature structure is used. The measurement was done at room temperature (around 290K). The difference diagram shows lack of the impurity phases. Differences in observed and calculated intensities come from the difficulties in correct profile refinement. The two most intense peaks are disturbed by the preferred orientation whereas the satellites may broaden the basis of the peaks.

DIELECTRIC PROPERTIES

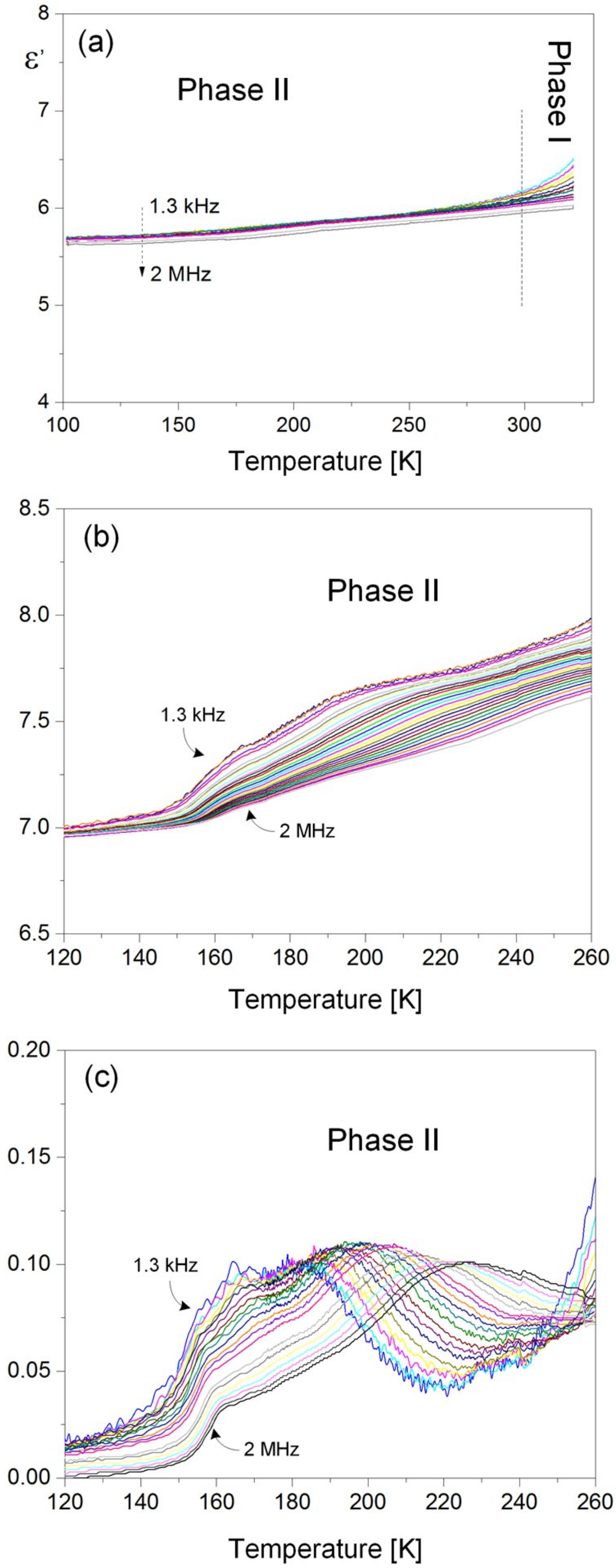

Fig. S2 Results of dielectric measurements obtained for (2-MIm)SbI_4 along the (a) [001] (b, c) [1-10] directions.

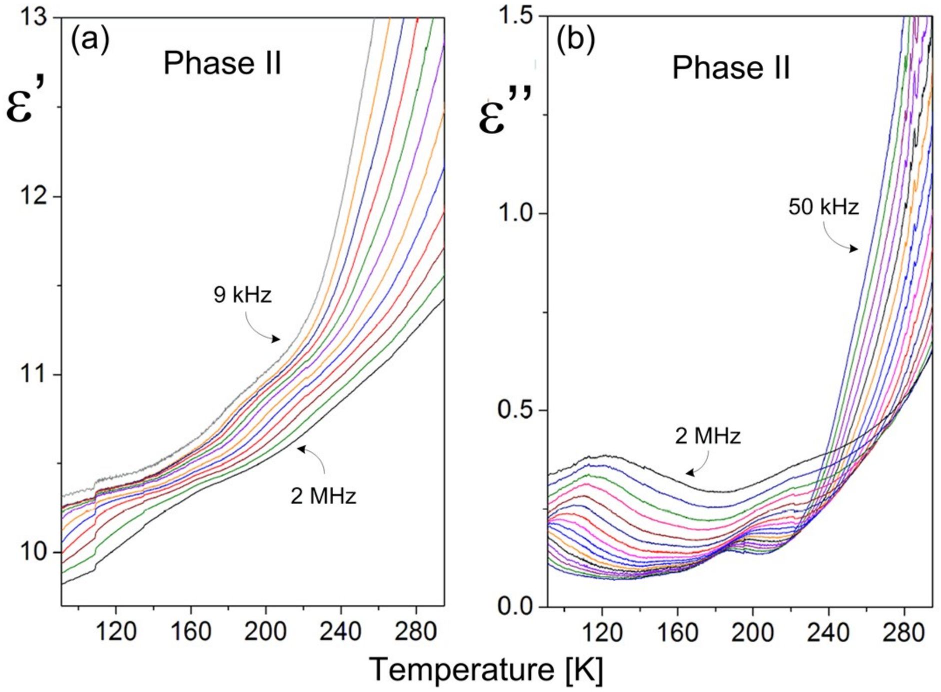

Fig. S3 Temperature dependence of the (a) real (ε') and (b) imaginary (ε'') parts of the complex dielectric constant (ε*) measured for the powder sample of (2-MIm)SbI_4 upon heating.

Temperature dependence of the real and imaginary parts of the dielectric constant measured on the powder sample is shown in Figure S3. Two low frequency dielectric relaxation processes are disclosed over the low temperature phase II. The lower frequency relaxation visible near 200 K is characterized by a weak dielectric increment ($\Delta\varepsilon_1'' \approx 0.15$-$0.2$), whereas the higher frequency one (**2**) ($\Delta\varepsilon_2'' \approx 03$) is observed in a wide temperature region 100~180 K.

Roughly estimated, energy activation E_a was found to be *ca*. 70 and 9 kJ/mol for the lower frequency and the higher frequency relaxation process, respectively. Dynamic dielectric properties of (2-MIm)SbI_4 appear to be quite similar to these encountered for (2-MIm)BiI_4. In both cases dielectric function is characterized by the presence of two relaxation processes which exhibit analogous dynamic properties. However, the activation energy of the low-frequency relaxation process is remarkably smaller in (2-MIm)SbI_4 analog (70 *vs.* 120 kJ/mol). Additionally, in (2-MIm)SbI_4 the change of the relaxation process taking place around 200 K points to the change in the motion of the 2-MIm^+.

Table S1. The geometry of hydrogen bonds at 330 K in (2-MIm)SbI_4.

	N-H	H···I (Å)	N…I (Å)	N-H-I angle (□)
N1-H1···I1$^{[-x,-y+1,-z]}$	0.860	3.157	3.710(11)	124.30
N1-H1···I1$^{[x,-y+1,z-1/2]}$	0.860	3.452	4.215(10)	149.47
N2-H2···I2$^{[-x,-y,-z]}$	0.860	3.101	3.609(12)	120.06

N2-H2···I2$^{[x,-y,z-1/2]}$	0.860	3.215	4.026(11)	158.08

The Jeffrey cryterium for hydrogen-bond formation requires the N…I distance less than 4.03 Å.

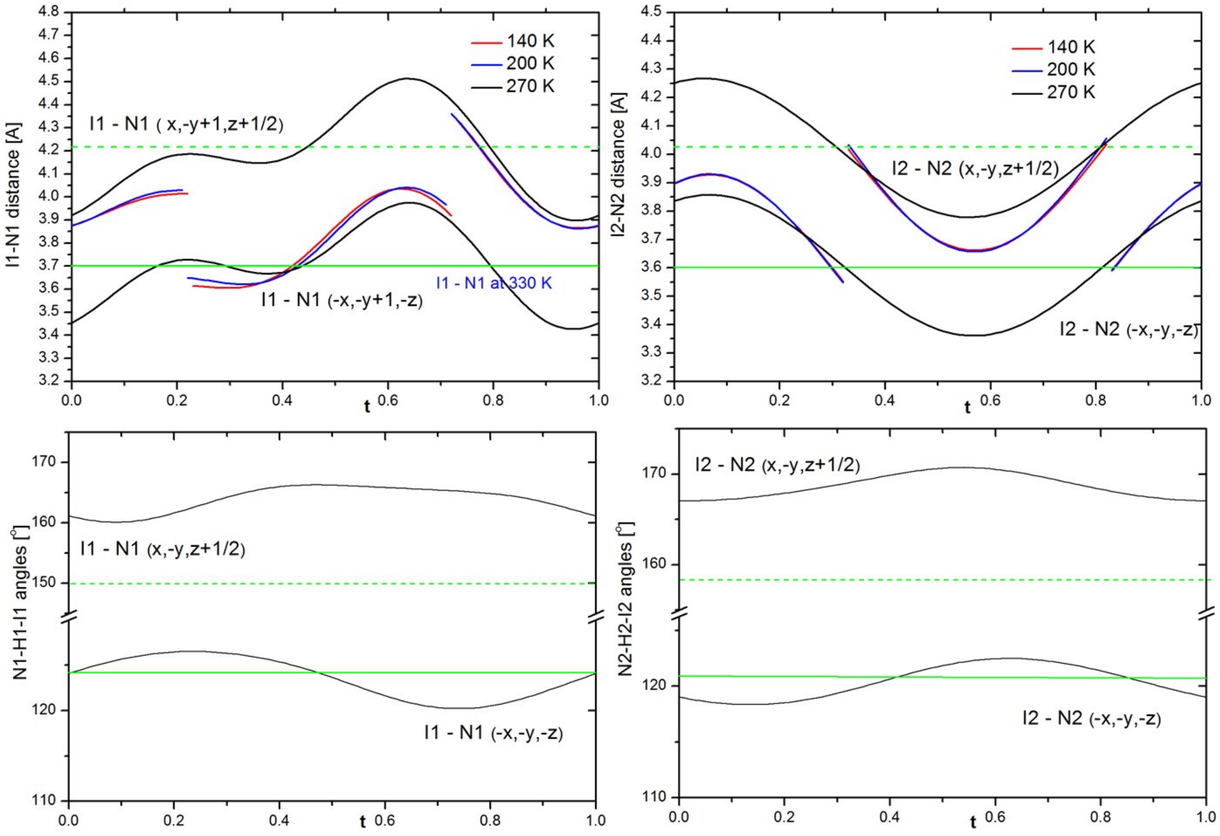

Fig. S4 The N···I distances and N-H-I angles as a function of internal coordinate t. The green lines denote non-modulated values form phase I (at 330K).

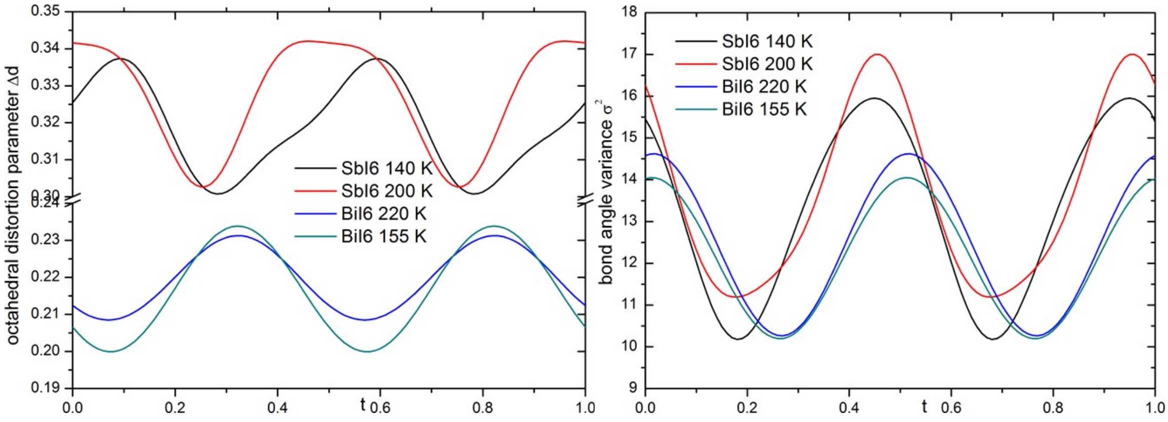

Fig. S5 Octahedral distortion parameter □d (left) and bond angle variance □^{2} (right) of SbI_6 and BiI_6 octahedra as a function of the phase of the modulation t; modulated at different temperatures