The lone-pair-electron-driven phase transition and order-disorder processes in thermochromic (2-MIm)SbI₄ 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.
Fig. S2 Results of dielectric measurements obtained for (2-MIm)SbI$_4$ along the (a) [001] (b, c) [1-10] directions.
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) ($\Delta\varepsilon''_2 \approx 0.3$) 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$_4$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>N-H</th>
<th>H-I (Å)</th>
<th>N-I (Å)</th>
<th>N-H-I angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1-...I$^{[x,y+1,z]}$</td>
<td>0.860</td>
<td>3.157</td>
<td>3.710(11)</td>
<td>124.30</td>
</tr>
<tr>
<td>N1-H1-...I$^{[x,y+1,z]}$</td>
<td>0.860</td>
<td>3.452</td>
<td>4.215(10)</td>
<td>149.47</td>
</tr>
<tr>
<td>N2-H2-...I$^{[x,y+1,z]}$</td>
<td>0.860</td>
<td>3.101</td>
<td>3.609(12)</td>
<td>120.06</td>
</tr>
</tbody>
</table>
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 SbI₆ and BiI₆ octahedra as a function of the phase of the modulation t; modulated at different temperatures.