# ELECTRONIC SUPPLEMENTARY INFORMATION

## 1. Detailed description of geometric changes parameters $\angle_{\varphi}$, $\angle_{\alpha}$ and $\angle_{\beta}$, and $\theta$ tilt and $\Psi$ tilt

To illustrate the mechanism and changes taking place of the alkylammonium cations at the phase transition, we have introduced three geometric parameters, which are the tilt angles $\angle_{\varphi}$, $\angle_{\alpha}$ and $\angle_{\beta}$, shown schematically in Fig. S1.[1] Similarly, to describe the movement of the octahedra in the 2-D inorganic layers, we describe two types of tilts: a tilt perpendicular to the inorganic sheets ($\theta$ tilt), so that adjacent corner-shared octahedra are rotated relative to each other. The angle of the $\theta$ tilt is mirrored in the bridging angle Pb-I-Pb, which deviates from the ideal 180°. The second kind of tilt is parallel to the layers ($\Psi$ tilt), so that the layers are corrugated in one particular direction. The corrugation angle is measured by the angle between the normal to the inorganic layers and the vector connecting the Pb atom and the terminal I. Finally, the relative displacement of the alkylammonium cations relative to the inorganic layers can be described by a parallelogram defined by the four bridging iodides . By projection onto this parallelogram the ammonium group is found in proximity to either an acute or an obtuse angle of the parallelogram. There is a correlation between the position of the ammonium group and the type of terminal halogen configuration: If the ammonium group is in the acute angled position, it has the right-angled configuration and if the ammonium group is in the obtuse angled position, it has the equilateral configuration.

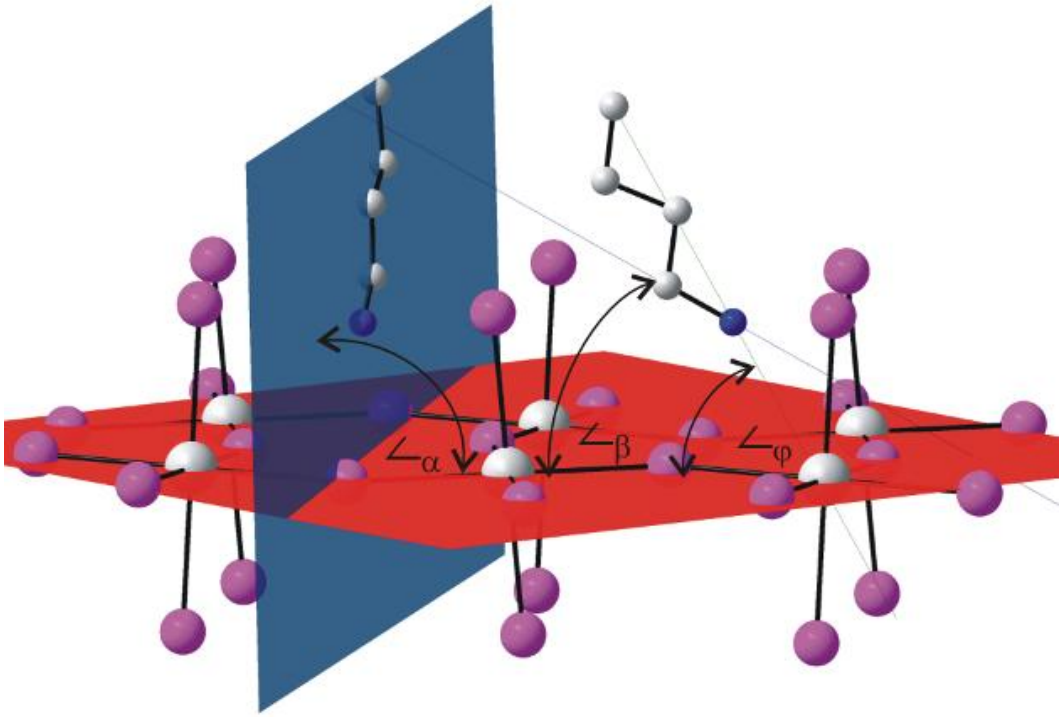


**Fig. S1** Tilt angles required to track the movement of the alkylammonium cations. Angle $\angle_{\varphi}$ between a plane through the inorganic layers and a vector connecting the first and last atom of each chain. Angle $\angle_{\alpha}$, which is defined as the dihedral angle between a plane containing all the atoms of the alkylammonium chains and the plane formed by the lead atoms of the inorganic layers. Angle $\angle_{\beta}$, which is defined as the angle between a vector connecting the atoms N1 and C1 and a plane through the lead atoms of the inorganic layers.

## 2. Detailed hydrogen bonding details for all 14 compounds.

**Table S1** Hydrogen bonding details and short contacts for compound **4** in its various phases.

| D-H···A | D-H/Å | H···A/Å | D···A/Å | <(D-H···A)/° | Symmetry transformations |
|---|---|---|---|---|---|
| **4a, IV** | | | | | |
| N(1)-H(1A)···I(1) | 0.90 | 2.64 | 3.43(3) | 147 | - |
| N(1)-H(1B)···I(2) | 0.90 | 2.83 | 3.68(4) | 157 | x+1/2,-y+3/2,z |
| N(1)-H(1C)···I(1 | 0.90 | 2.81 | 3.70(3) | 169 | x-1/2,-y+3/2,z |
| **4b, III** | | | | | |
| N(1)-H(1C)···I(1) | 0.89 | 2.89 | 3.59(3) | 137 | -x+5/2, y-1/2,z |
| N(1)-H(1B)···I(1) | 0.89 | 2.74 | 3.63(2) | 173 | x,y-1,z |
| N(1)-H(1A)···I(2) | 0.89 | 2.90 | 3.68(2) | 147 | -x+3/2,y-1/2,z |
| **4c, III** | | | | | |
| N(1)-H(1C)···I(1) | 0.89 | 2.89 | 3.59(3) | 136 | -x+5/2, y-1/2,z |
| N(1)-H(1B)···I(1) | 0.89 | 2.76 | 3.64(2) | 174 | x,y-1,z |
| N(1)-H(1A)···I(2) | 0.89 | 2.88 | 3.67(3) | 148 | -x+3/2,y-1/2,z |
| **4d, II** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.08 | 3.63(3) | 122 | -x+3/2,y-1/2,z |
| N(1)-H(1B)···I(1) | 0.89 | 2.74 | 3.61(3) | 168 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.75 | 3.62(3) | 167 | -x+5/2,y-1/2,z |
| **4e, II** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.09 | 3.65(6) | 123 | -x+3/2,y-1/2,z |
| N(1)-H(1B)···I(1) | 0.89 | 2.73 | 3.59(6) | 166 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.76 | 3.60(5) | 158 | -x+5/2,y-1/2,z |
| **4f, I** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.19 | 3.83(3) | 131 | -x+3/2,y-1/2,z |
| N(1)-H(1B)···I(2) | 0.89 | 3.29 | 3.83(3) | 122 | x+1/2,-y+3/2,-z+2 |

**Table S2** Hydrogen bonding details and short contacts for compounds **1-3** in their various phases.

| D-H···A | D-H/Å | H···A/Å | D···A/Å | <(D-H···A)/° | Symmetry transformations |
|---|---|---|---|---|---|
| **1a, IV** | | | | | |
| N(1)-H(1A)···I(1) | 0.89 | 2.65 | 3.44(3) | 148 | - |
| N(1)-H(1B)···I(2) | 0.89 | 3.01 | 3.77(4) | 145 | x + 1/2, -y + 3/2, z |
| N(1)-H(1C)···I(1) | 0.89 | 2.72 | 3.61(4) | 179 | x - 1/2, -y + 3/2, z |
| **1b, III** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.12 | 3.64(2) | 119 | -x + 3/2, y - 1/2, z |
| N(1)-H(1B)···I(1) | 0.89 | 2.77 | 3.64(2) | 165 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.72 | 3.60(2) | 168 | x - 5/2, y - 1/2, z |
| **1c, II** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 2.72 | 3.54(14) | 153 | -x + 3/2, y - 1/2, z |
| N(1)-H(1B)···I(1) | 0.89 | 2.82 | 3.67(15) | 160 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.96 | 3.79(16) | 156 | -x + 5/2, y - 1/2, z |
| **2a, III** | | | | | |
| N(1)-H(1A)···I(1) | 0.91 | 2.68 | 3.48(3) | 148 | - |
| N(1)-H(1B)···I(2) | 0.91 | 2.85 | 3.69(4) | 154 | x + 1/2, -y + 3/2, z |
| N(1)-H(1C)···I(1) | 0.91 | 2.72 | 3.62(4) | 172 | x - 1/2, -y + 3/2, z |
| **2b, II** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.11 | 3.642(16) | 121 | -x + 3/2, y - 1/2, z |
| N(1)-H(1B)···I(1) | 0.89 | 2.76 | 3.633(15) | 168 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.73 | 3.610(15) | 168 | -x + 5/2, y - 1/2, z |
| **2c, I** | | | | | |
| N(1)-H(1A)···I(1) | 0.89 | 3.02 | 3.73(2) | 138 | x + 1/2, -y + 3/2, -z + 2 |
| N(1)-H(1B)···I(1) | 0.89 | 2.86 | 3.72(3) | 164 | -x + 3/2, y - 1/2, z |
| N(1)-H(1C)···I(1) | 0.89 | 3.19 | 3.82(3) | 130 | - |
| **3a, III** | | | | | |
| N(1)-H(1A)···I(1) | 0.89 | 2.51 | 3.31(4) | 148 | - |
| N(1)-H(1B)···I(2) | 0.89 | 2.95 | 3.73(3) | 146 | x + 1/2, -y + 3/2, z |
| N(1)-H(1C)···I(1) | 0.89 | 2.91 | 3.81(4) | 176 | x - 1/2, -y + 3/2, z |
| **3b, II** | | | | | |
| N(1)-H(1A)···I(2) | 0.89 | 3.14 | 3.65(2) | 119 | -x + 3/2, y - 1/2, z |
| N(1)-H(1B)···I(1) | 0.89 | 2.79 | 3.67(2) | 168 | - |
| N(1)-H(1C)···I(1) | 0.89 | 2.72 | 3.59(2) | 163 | -x + 5/2, y - 1/2, z |