Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPLEMENTARY MATERIALS

Unprecedented Transformation of $[I^- \cdot I_3^-]$ to $[I_4^{2-}]$ Polyiodides in the Solid State: Structure, Phase Transitions and Characterization of Dipyrazolium Iodide Triiodide

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Thermal properties:

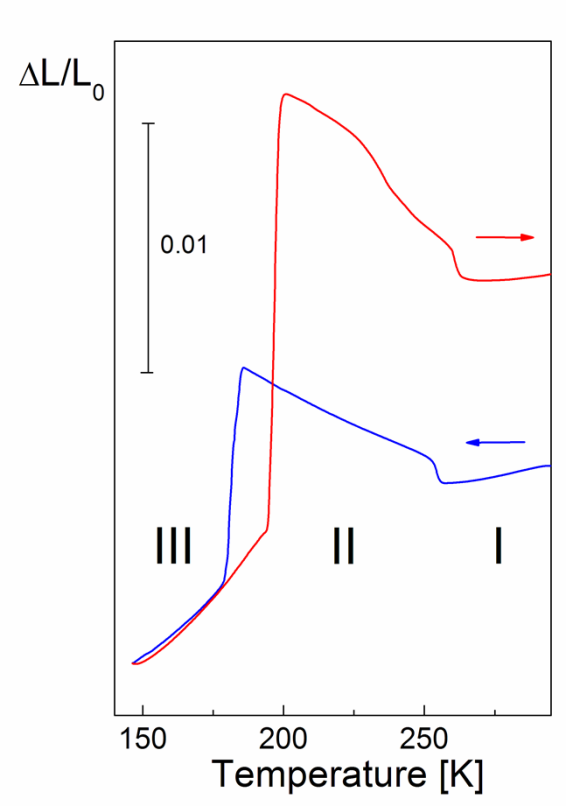


Figure S1. The linear thermal expansion along the *b*-axis of PI upon heating and cooling scans.

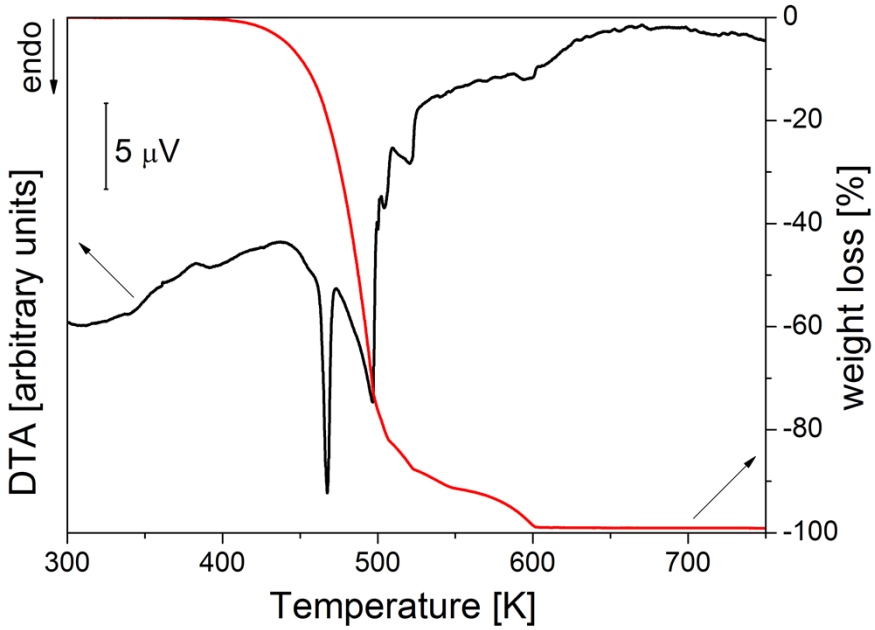
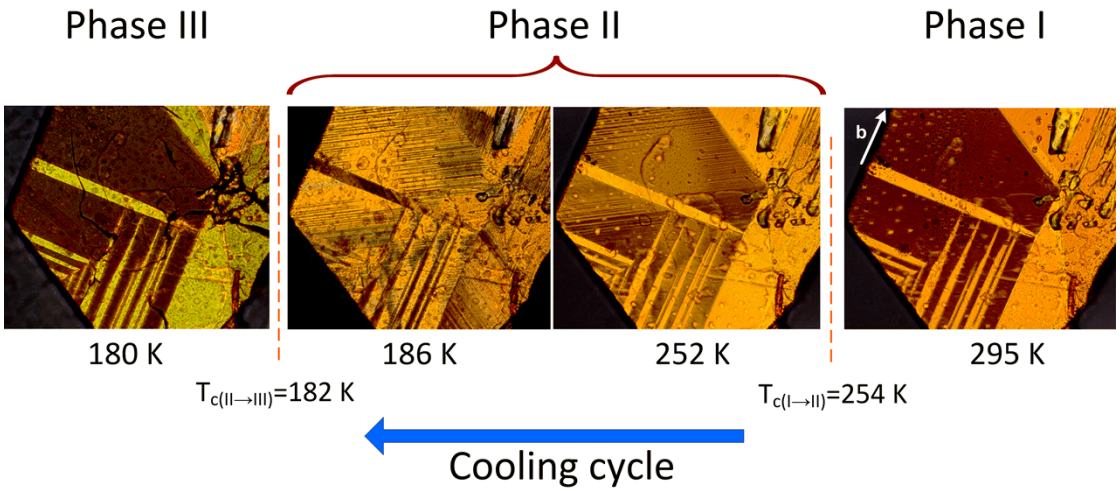


Figure S2. Simultaneous thermogravimetric analysis and thermal analysis scan (with temperature rate of 2 K min^{-1}, sample mass m=12.20 mg).



Optical properties:

Figure S3. Domain structure seen along the *a*-axis.

Figure 8 shows a rather typical domain pattern in a crystal over a wide temperature range. It should be emphasized that ferroelastic domains are really observed starting from the room temperature phase I. However, the virgin crystal samples are usually monodomain and the domain pattern seen on the right side (perpendicular daggers or lenses) was induced by a gentle squeezing between the finger tips. The parallel domain walls arise and move under an uniaxial stress applied approximately along the *b*-axis. Apart from that a system of parallel needle shaped domains is present in phase I independently of the external stress. The domains intersect at angles close to 120°, (see Fig. 8 in the main text), which may suggests a hexagonal or trigonal symmetry of the paraelastic phase. The I→II PT is accompanied by an appearance of stripe-like domain structure with domain walls perpendicular to the *a*-axis which form an angle close to 60° or 120°. The change in the domain pattern is presumably a result of a decrease in symmetry of the crystal from orthorhombic to monoclinic in the PT at 254 K. Further cooling through the lowest temperature PT at 182 K unexpectedly leads to a disappearance only these types of domain walls which were spontaneously induced through the I→II PT at 254 K. The domain pattern in the phase (III) resembles exactly that observed in the phase (I). This seems to be now consistent with the fact that both phases (I) and (III) adopts the same orthorhombic symmetry.

Dielectric properties:

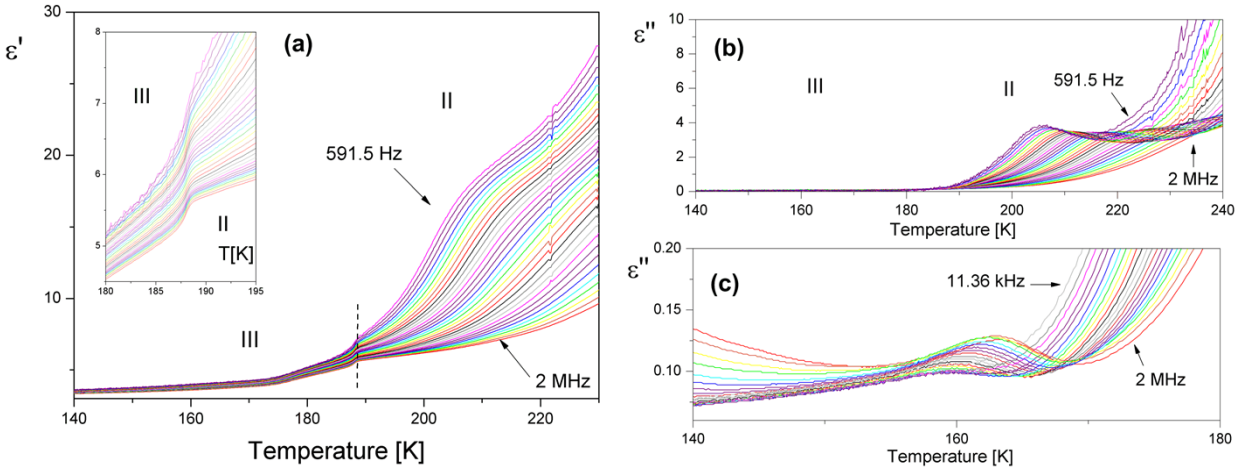


Figure S4. The temperature dependence of the (a) real and (b, c) imaginary part of complex electric permittivity for the polycrystalline sample of PI.

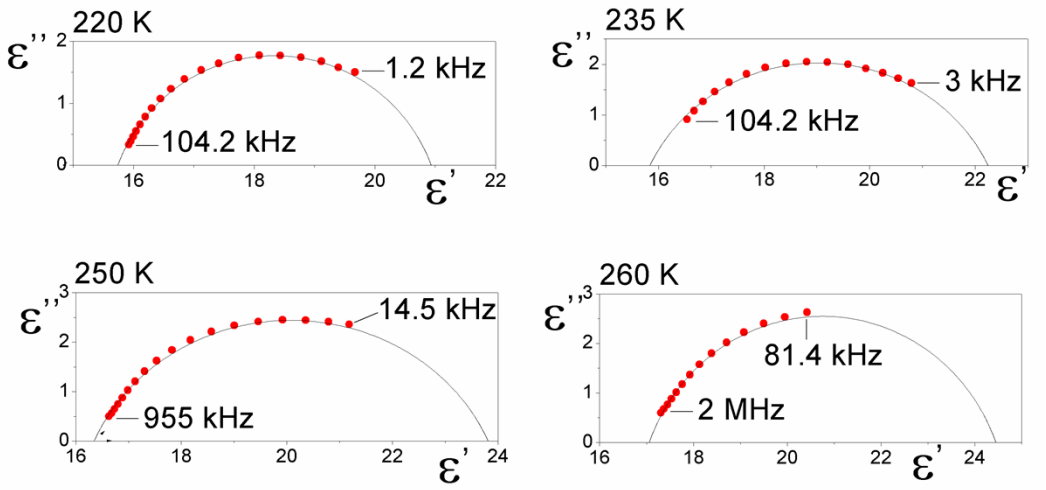


Figure S5. Cole-Cole plots of ε'' versus ε' a at selected temperatures showing the relaxation nature of the dielectric dispersion for PI.

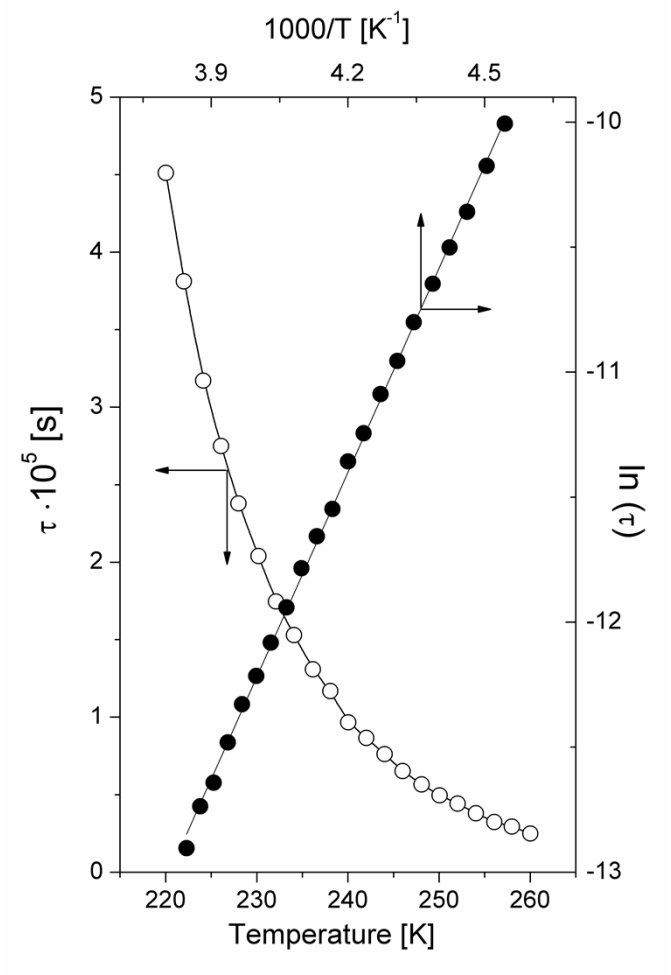


Figure S6. Temperature dependence of τ versus temperature and ln(τ) versus reciprocal temperature for PI.

Proton Magnetic Resonance studies (^{1}H NMR):

The theoretical second moment value for the rigid lattice was determined from the van Vleck formula:

$$M_2 = \frac{3}{5N}\gamma_H^4 \hbar^2 I(I+1)\sum_{j,k}^{N} r_{H\text{-}H}^{-6} + \frac{4}{15N}\gamma_H^2\gamma_S^2\hbar^2 S(S+1)\sum_{j,k}^{N} r_{H\text{-}S}^{-6}$$

where I denotes the hydrogen nuclei spin; S corresponds to the Nitrogen nuclei spins; γ_H – the gyromagnetic ratio of proton spin (γ_H= 26.75221 10^7 rad/Ts), γ_S - the gyromagnetic ratio of Nitrogen nuclei spins (γ_S= 1.93378 10^7 rad/Ts), $r_{j,k}$ - internuclear distance in whole sample; N - number of resonant spin in the molecule.

With assumed all hydrogen atoms in crystal structure we obtained the second moment value (M_{2rigid} as 4.5 × 10^{-8}T^2). In turn the H-N interaction contribution has been estimated to be 3.7 × 10^{-8}T^2 (for assumed N-H distance 1.03Å). The measured value of M_2 around 101K is definitely larger therefore we decided to estimated higher theoretical M_{2rigid} through manual changing of length of mentioned above H-H dipole. Both hydrogen atoms are attached to the same Iodine atom and it seems that the distance between them may shorten with lowering temperature. We have selected several possible shorter distances between both active protons and resulting dependence of calculated M_{2rigid} value (see Figure S6). The power like curve intersects with the measured value 14.6 × 10–^{8}T^2 at about 1.5-1.6 Å. Nevertheless, estimated M_2 value is rather shorter than usually used in the crystallographic standards.

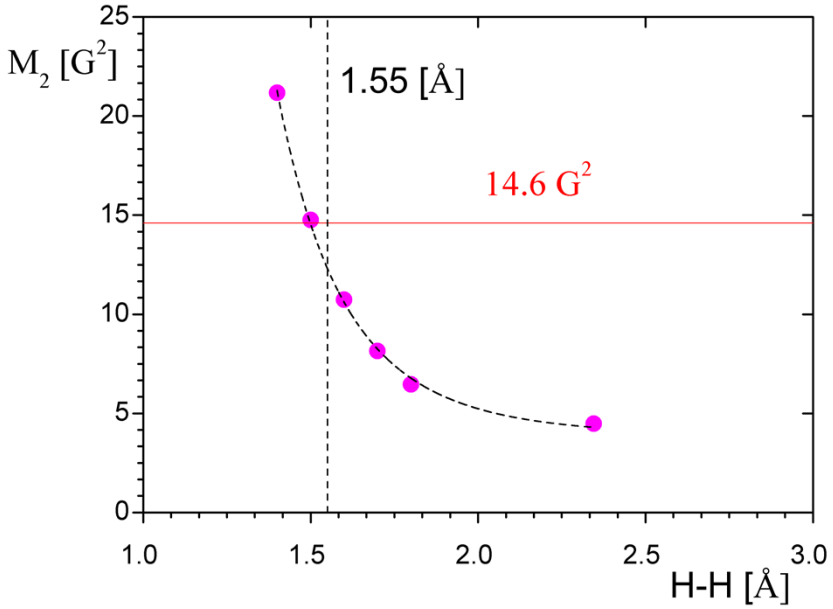


Figure S7. Relationship between H-H distance and calculated value of M_2.

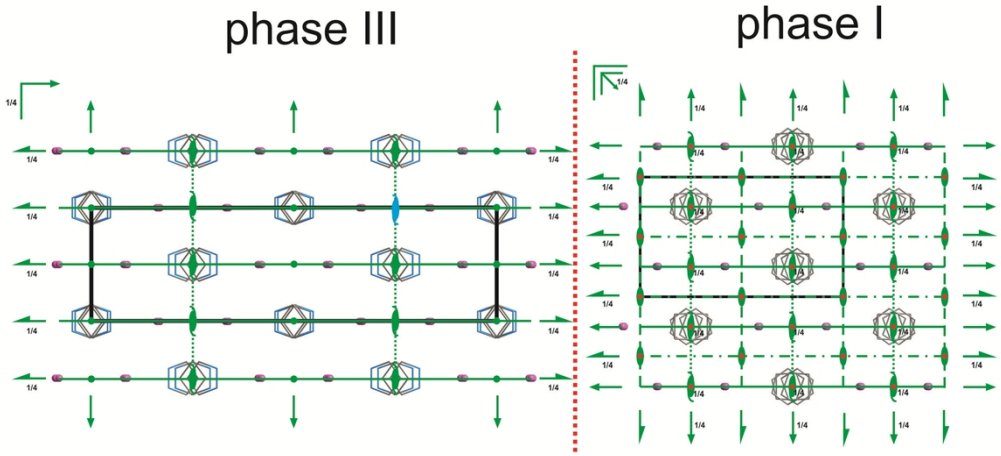


Figure S8. Crystal symmetry relationships during PTs.