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Supplementary Materials

Synthesis, Crystal Structure and Phase Transitions of a Series of Imidazolium Iodide

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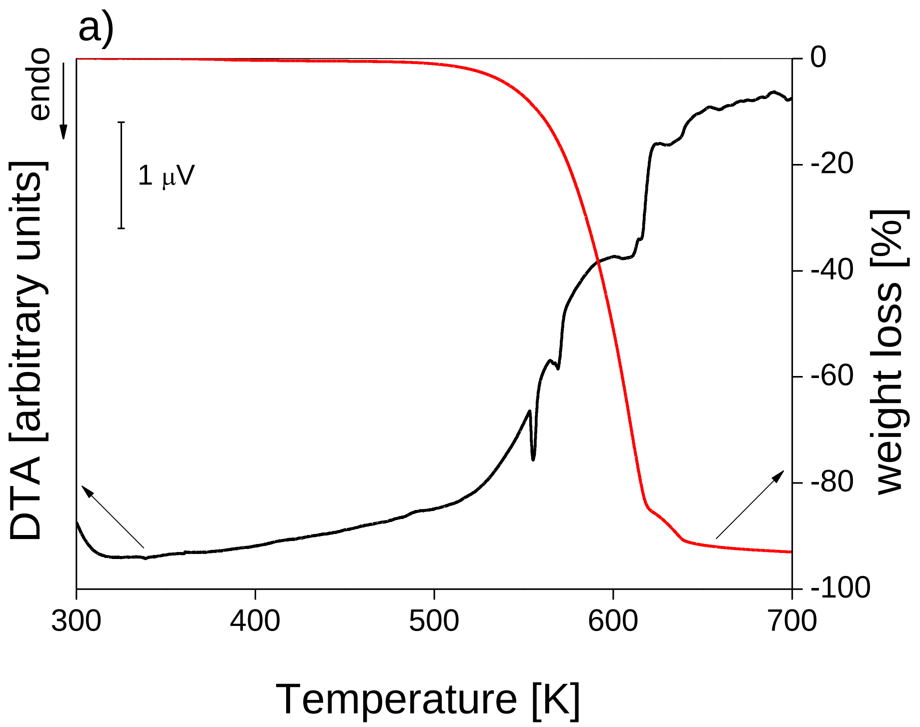

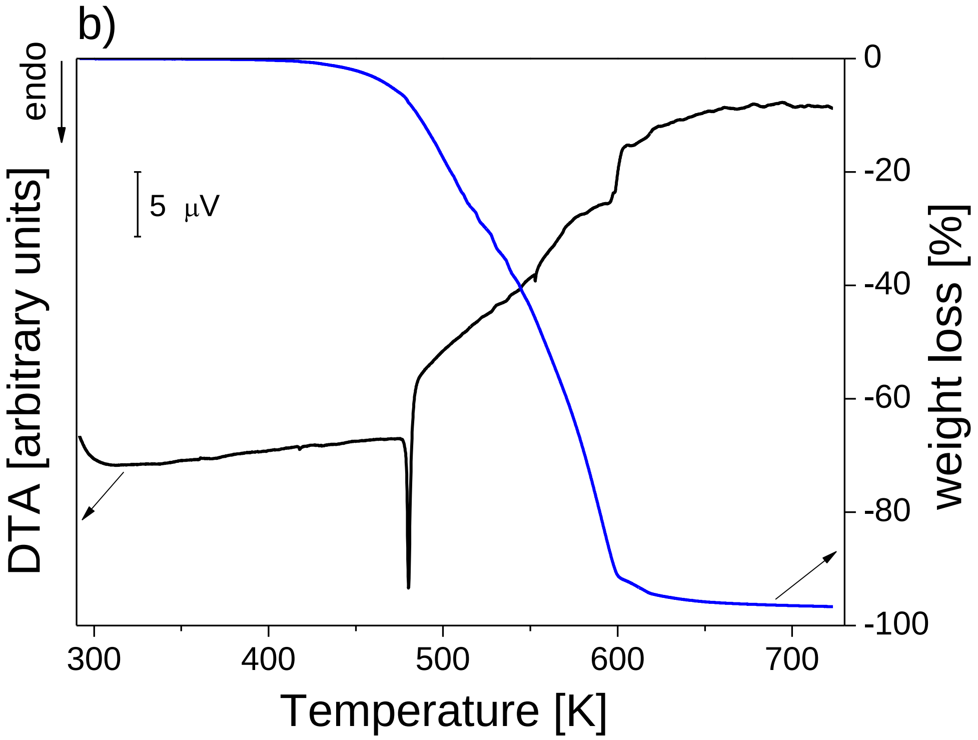

Figure S1 Simultaneous thermogravimetric analysis and thermal analysis scan (with temperature rate of 2 K min^{-1}) for a) **(1)** (sample mass 9.34 mg) and b) **(3)** (sample mass 10.9 mg).

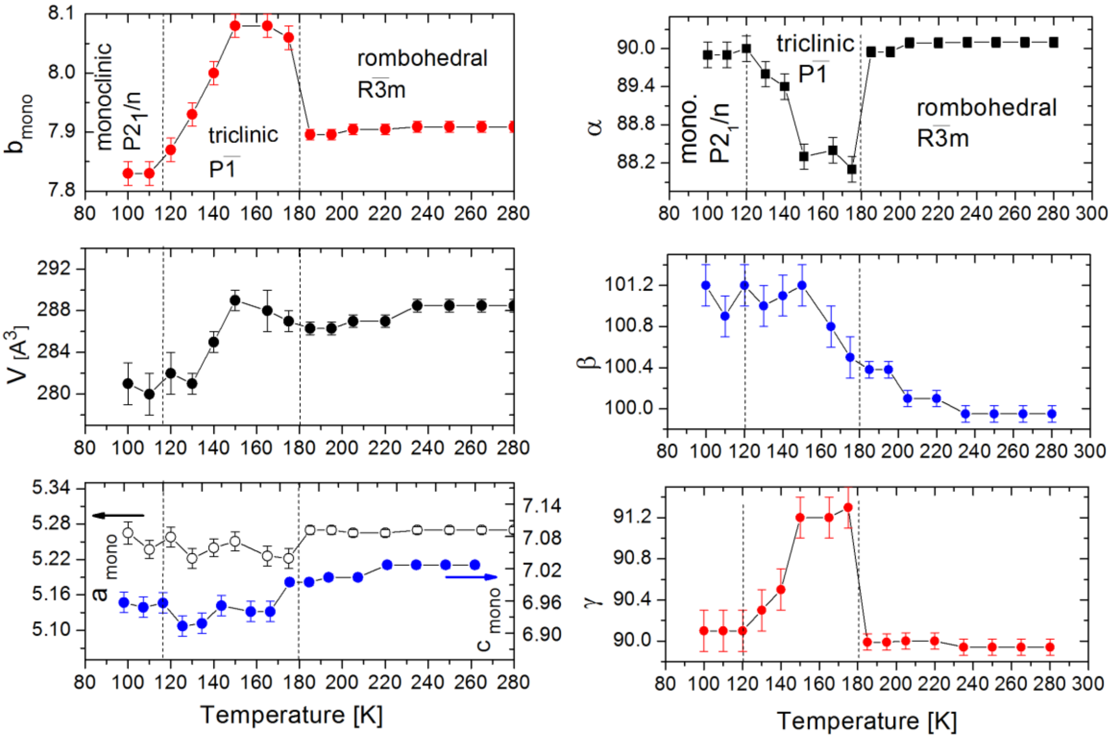

Figure S2 Temperature dependencies of the lattice parameters, angles and volume for **(1)**

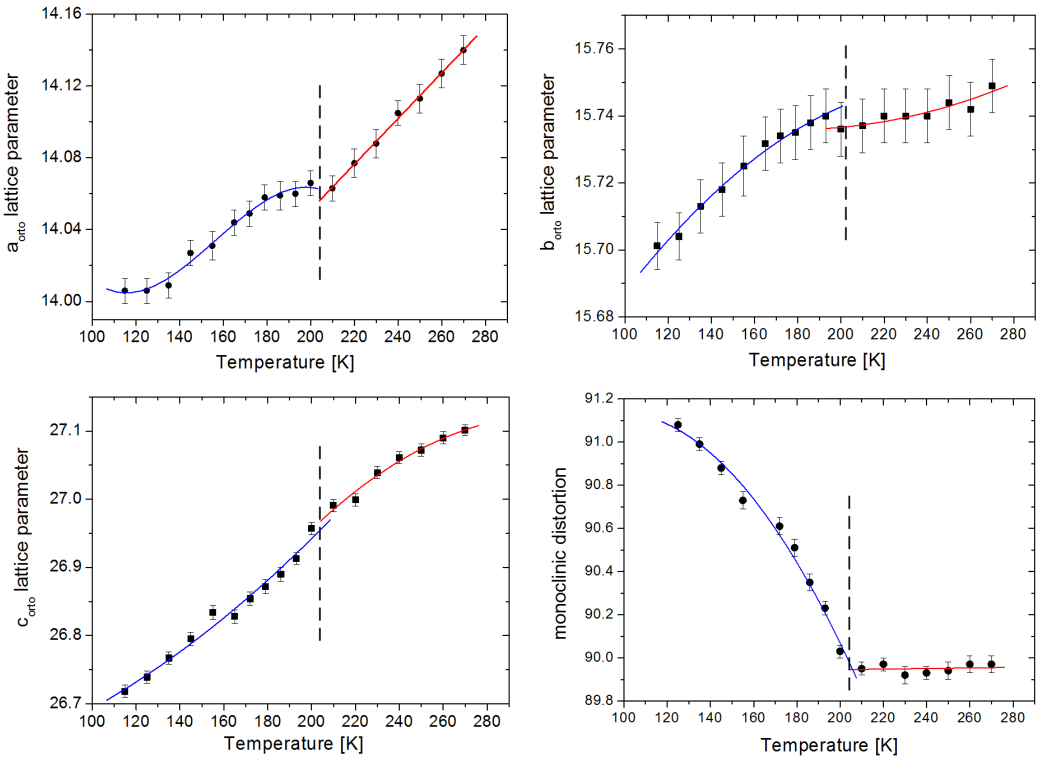

Figure S3 Temperature dependencies of the lattice parameters and monoclinic (β) angle for **(3)**

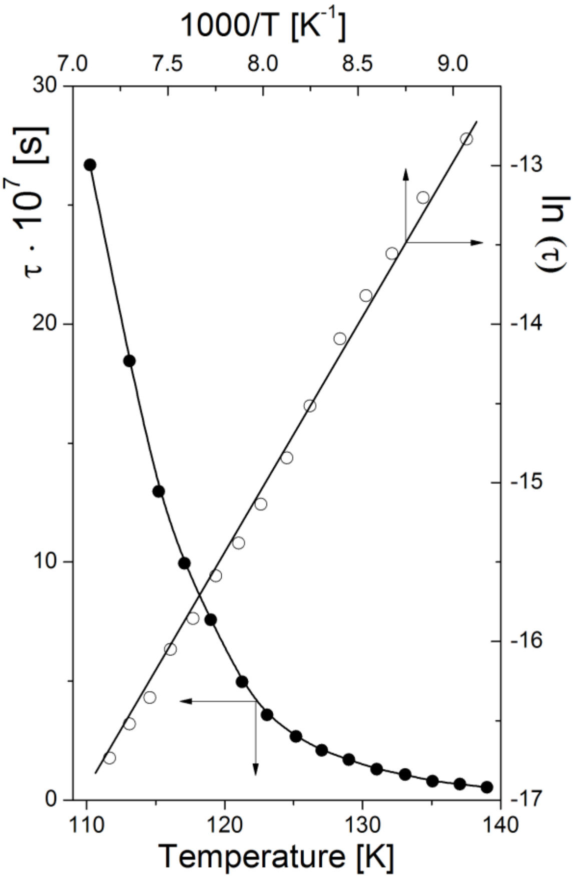

Figure S4 Temperature dependence of τ *versus* temperature and ln(τ) *versus* reciprocal temperature for **(3)**.

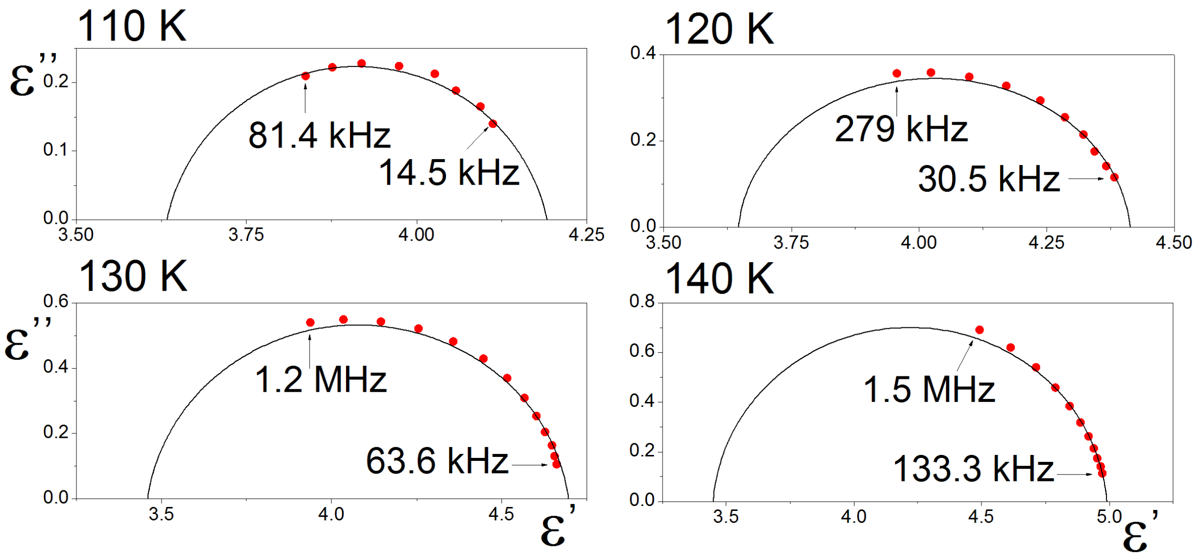

Figure S5 Cole–Cole plots at selected temperatures for **(3)**.

Molecular motions in (1) and (3) studied by ^{1}H NMR

Proton magnetic resonance (^{1}H NMR) T_1 relaxation times were measured with ELLAB TEL–Atomic PS 15 spectrometer working at the frequency of 25 MHz. The temperature of the sample was automatically stabilized by UNIPAN 650 temperature controller operating on Pt–100 sensor. The spin–lattice relaxation times (T_1) were determined using saturation recovery technique. The powdered sample for ^{1}H NMR study was degassed and sealed under vacuum in a glass ampoule.

The temperature dependence of the ^{1}H NMR spin–lattice relaxation time (T_1) for **(1)** and **(3)** is shown in Figure S6. In the low temperature region for both compounds two components of the T_1 relaxation times are found. For **(1)** the exponential character of FID (Free Induction Decay) starts above 193 K whereas for **(3)** it appears above 130 K.

In **(1)** two different regions in the ^{1}H NMR spin–lattice relaxation time (T_1) *versus* reciprocal temperature dependence are visible (see Figure S6(a)). The first region, below 130 K, forms a plateau, while the second one, at higher temperature, appears as doubled minimum with a small jump discontinuity around the phase transition (185 K). In the lower temperature region, very weak dependence of the relaxation time on temperature can be explained by the presence of interacting quadrupole nuclei. The temperature dependence of the relaxation time (T_1) above 240 K, shows the certain bending of the slope which can be also assigned to the beginning of the in-plane reorientation of imidazolium ring.

The fitting procedure was done to a well-known Bloembergen–Purcell–Pound (BPP) equation (Eq. (1))[1]

$$\frac{1}{T_1} = C_{HH}\left[\frac{\tau_c}{1+\omega_H^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_H^2\tau_c^2}\right] \qquad \text{(Eq. 1)}$$

where: τ_c is the correlation time of the motion involved in the relaxation process according to the Arrhenius law ($\tau_c = \tau_0 \exp(E_a/RT)$), where τ_0 is the correlation time at the limit infinite temperature, E_a – the height of the barrier, R – gas constant), ω_H - the Larmor angular frequency of proton, and C_{HH} is the dipolar relaxation constant.

It should be emphasised, that the fitting procedure applied here is in accordance with the treatment used also to the compound possessing the quadrupole iode nuclei[2]. In Eq. (1) the entire relaxation is attributed to the ^{1}H–^{1}H dipole–dipole interactions. However, beside this essential relaxation mechanism, the other relaxation pathways are possible *e.g.* interactions between hydrogen and quadrupole nuclei, like: ^{1}H–^{14}N and ^{1}H–^{127}I.

In the case of **(3)** at lower temperature (below *ca.* 140 K), two sets of points were found to exhibit a linear temperature behaviour of T_1 *vs.* T^{-1} (see Figure S6(b)). The estimated activation energies from the slope of these curves are 5 kJ/mol and 3.3 kJ/mol for the long and short time components, respectively. The symmetrical minimum at about 175 K (58 ms) is broken at 245 K. It may be a result of overlapping of the higher temperature minimum of T_1 with somewhat higher estimated activation energy equal to about 19.9 kJ/mol.

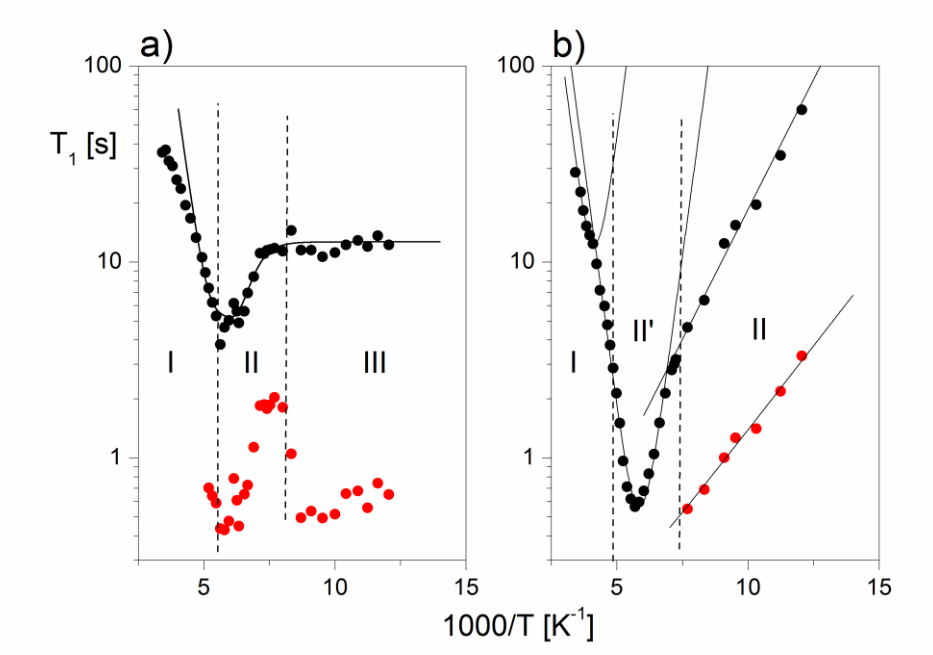

Figure S6 Comparison of ^1H NMR spin-lattice relaxation time (T_1) for a) (1) and b) (3). The solid line in (a) represents fitting to a double minimum for two inequivalent cations with added very strong quadrupolar mechanism (Eq. 2). Solid black lines (b) show both the slopes of both components (red and black points) of spin-lattice relaxation time and the fit of experimental points according to Eq. (1).

The values of dynamical parameters obtained by fitting Eq. (1) to the experimental data are the following: E_a = 19 kJ/mol, τ_0 = 6.3 10^{-15} s, C = 1.95 10^8 s^{-2}. The obtained parameters, with quite small value of the correlation time, are comparable to those found previously in compounds containing aromatic organic cations in the crystal structure.[3,4] Given the fact that the in-plane reorientation of the imidazolium ring is released above 204 K one can conclude that a lower-temperature $T_1(1/T)$ minimum may be ascribed to a small-angle libration of the cations. The next expected minimum of T_1 at higher-temperature (only the left side is shaped) is believed to be assigned to a free reorientation of cation about the axis perpendicular to its plane.

It should be noted that probably ^1H–^1H dipole–dipole interactions take place in **(3)** at low temperatures where the characteristic plateau is not observed. The lack of the plateau may confirm the special reduction of the quadrupole effect efficiency by the mutual interacting (coupled) iodide nuclei in the $[I_4^{2-}]$ moiety. It seems to be clear that in the case of **(1)** the low temperature plateau comes from a very strong quadrupolar coupling of ^{127}I and this relaxation mechanism should be added to the equation Eq. 2:[5-8]

(Eq. 2)

$$\frac{1}{T_1} = C_{HH}\left[\frac{\tau_c}{1+\omega_H^2\tau_{ci}^2} + \frac{4\tau_c}{1+4\omega_H^2\tau_c^2}\right] + C_{HI}\left[\frac{\tau_{c,Q}}{1+(\omega_H-\omega_I)^2\tau_{c,Q}^2} + \frac{3\tau_{c,Q}}{1+4\omega_H^2\tau_{c,Q}^2} + \frac{6\tau_{c,Q}}{1+(\omega_H+\omega_I)^2\tau_{c,Q}^2}\right]$$

where: ω_I is the Larmor frequency of ^{127}I.

The correlation times $\tau_{c,Q}$ is defined as: $\tau_{c;Q}^{-1} = \tau_c^{-1} + R_Q$, where R_Q represents the quadrupolar spin–lattice rates of ^{127}I. From the perspective of ^{1}H the quadrupolar relaxation plays the role of a correlation time; it contributes to the effective fluctuations of the ^{1}H–^{127}I dipole–dipole coupling.[5,6] The numerical fitting to the experimental data (red line in Figure S6) leads to the following parameters: E_a = 18.9 kJ/mol, τ_c = 1.9 10^{-14} s for the first cation and E_a = 19.4 kJ/mol, τ_c = 2.1 10^{-15} s for the second one. The same value of C_{HH} = 9.2 10^8 s^{-2} means, that the relationship between both cations is 1:1. C_{HI} = 3.5 10^7 s^{-2} and R_Q^{-1}=2.3 10^{-10} s (as expected C_{HI} is significantly smaller than C_{HH} taking into account the gyromagnetic factor of ^{127}I and the structure of the compound, while the time scale of the quadrupolar relaxation is plausible because of the very strong quadrupolar coupling of ^{127}I). The quadrupolar relaxation has been assumed here as temperature independent. Contribution of the dipole-dipole coupling to the effective modulations of the ^{1}H–^{127}I causes that ^{1}H relaxation time appears to remain constant (the plateau in Figure S6) despite the fact that correlation time τ_c becomes very long at low temperatures. It should be emphasized that nonequivalence of the imidazolium cations seen as a doubled minimum of T_1 (the ratio of cations 1:1) seems to accord with the X-ray diffraction (two nonequivalent cations).

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