Supporting Information for Publication

Room-temperature Ferroelectricity in Diisopropylammonium Bromide

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Differential scanning calorimetry (DSC) runs were recorded using a Perkin-Elmer DSC-7 in the temperature range 100–450 K with a ramp rate 5 K·min^{-1}.

Thermogravimetric analysis (TGA) and Differential Thermal Analysis (DTA) measurements were performed on a Setaram SETSYS 16/18 instrument in the temperature range of 300 – 700 K.

XRD data were collected using KM4-CCD diffractometer operating in κ-geometry and equipped with a two-dimensional CCD detector. *Mo Kα* radiation (0.71073Å) was used. Data were collected in ω-scan mode with $\omega\Delta$=1.0^{o} using CrysAlis CCD program. The CrysAlis. RED software version 1.170.32 (Oxford Diffraction)[1] was used for data processing. The structures were solved by direct methods and refined using full-matrix least-squares methods with SHELXL-97[2]. Multiscan absorption collection was applied on all data. Some geometrical (DFIX) parameter restraints were used to fix disordered molecules to be chemically reasonable in $P2_1/m$ phase. C-H hydrogen positions were placed in calculated positions and refined as riding atoms. Hydrogen atoms from NH_2 groups were found in the electron density maps and refined with restraints on bond lengths to nitrogen atoms. Thermal parameters of hydrogen atoms were 1.5 (CH_3) and 1.2 (CH_2, NH_2) times the thermal parameters of the corresponding parent atoms. The crystal were mounted in a glass capillaries and the diffraction was measured at room temperature (DPB-O) at 435 K (DPB-M(I)) and again at room temperature (DPB-M(II)). High temperature was maintained in a simple high-temperature attachment with hot-air flow (Kuma Diffraction, covering the temperature range 300-770 K). All atomic displacements were calculated in AMPLIMODES[3].

The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured using the Agilent E4980A Precision LCR Meter in the frequency range between 20 Hz and 2 MHz and in the temperature range from 100 to 460 K. The amplitude of the ac measuring electric field was 1 V/mm. The samples were prepared as flat plates cut parallel to the (010) crystallographic plane and covered by silver paste. The dimensions of the sample were of the order of 5×3×1 mm^3. The overall error in estimation of the complex dielectric permittivity value was less than 5% and 10% for the real and imaginary part, respectively.

The hysteresis loops were collected with a standard Sawyer-Tower circuit at 20 Hz.

(1) CrysAlisCCD CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.33.42, release 29-05-2009 CrysAlis171.
(2) Sheldrick, G., M.; *Acta Cryst*. **2008**, A64, 112.
(3) Orobengoa, D.; Capillas, C.; Aroyo, M. I.; Perez-Mato, J. M.; *J. Appl. Cryst.* **2009**, A42, 820.

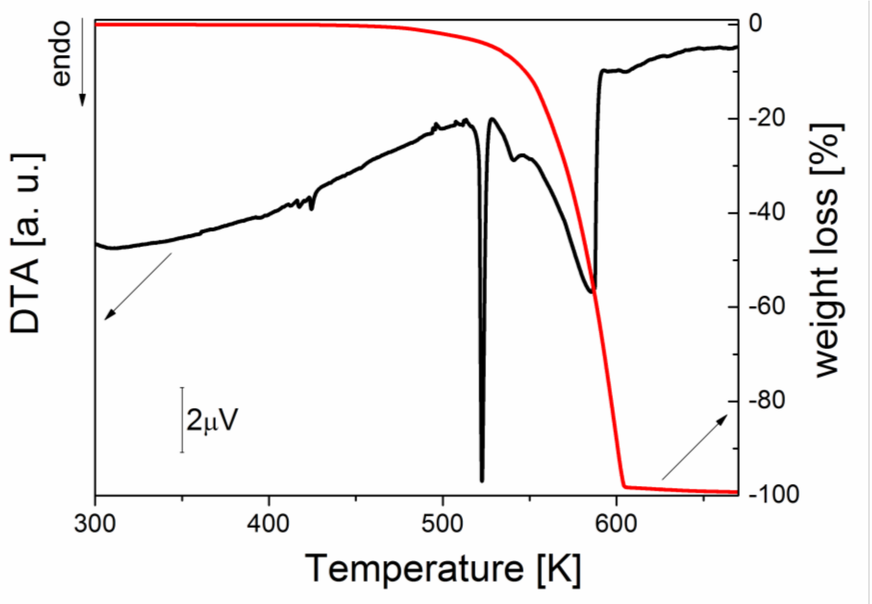

Figure S1 Simultaneous thermogravimetric analysis and thermal analysis scan (with temperature rate of 2 K min^{-1}, sample mass 15.1 mg) for **DPB**

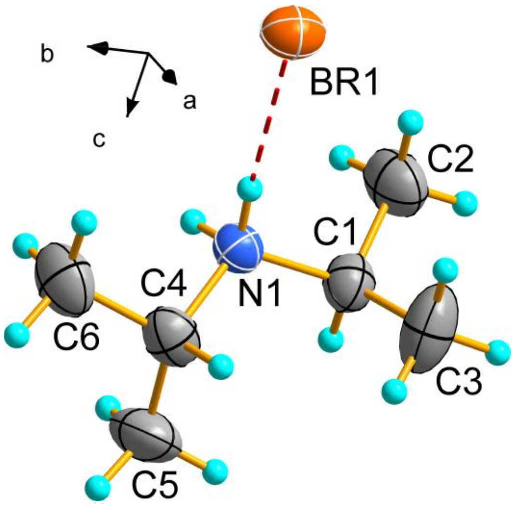

Figure S2. Content of the asymmetric unit in **DPB-O**, T=298K.

Table S1. Selected geometric parameters (Å, º) in **DPB-O**, T=298K

N1—C1	1.508 (3)	C1—C2	1.503 (4)
N1—C4	1.516 (3)	C4—C5	1.512 (4)
C1—C3	1.507 (4)	C4—C6	1.514 (4)
C1—N1—C4	118.1 (2)	C5—C4—C6	112.0 (2)
C3—C1—C2	113.1 (2)	C5—C4—N1	109.4 (2)
C3—C1—N1	110.9 (2)	C6—C4—N1	107.1 (2)
C2—C1—N1	107.8 (2)		

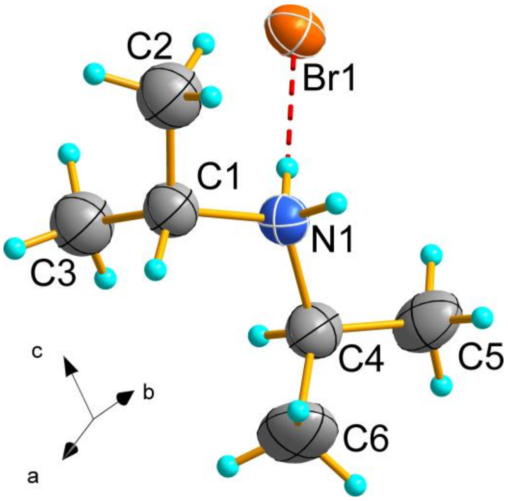

Figure S3. Content of the asymmetric unit in **DPB-M(I),** T=435K, Site occupancy factors for C4 and C6 are equal to 1 whereas s.o.fs of remaining atoms are equal to 0.5.

Table S2. Selected geometric parameters (Å, °) in **DPB-M(I)**, T=435K

C4—C6	1.501 (5)	C1—C2	1.495 (4)
C4—C5	1.494 (4)	C1—C3	1.492 (3)
C4—N1	1.514 (3)	C1—N1	1.526 (3)
C6—C4—C5	114.2 (3)	C2—C1—N1	105.4 (2)
C6—C4—N1	116.56 (19)	C3—C1—N1	108.3 (2)
C5—C4—N1	108.6 (2)	C4—N1—C1	117.9 (2)
C2—C1—C3	112.3 (2)		

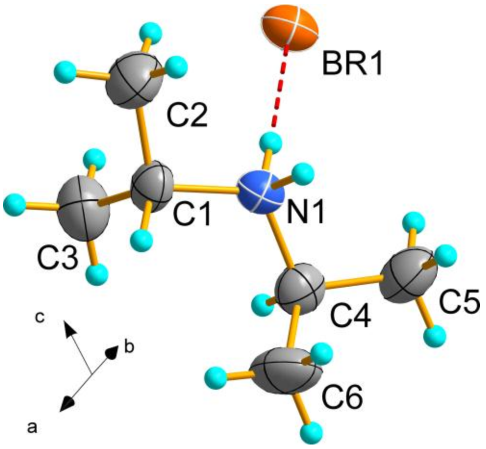

Figure S4. Content of the asymmetric unit in **DPB-M(II)**, T=298K.

Table S3. Selected geometric parameters (Å, º) in **DPB-M(II)**, T=298K

C4—C5	1.500 (5)	C3—C1	1.515 (7)
C4—C6	1.504 (4)	C1—N1	1.512 (6)
C4—N1	1.497 (7)	C1—C2	1.525 (6)
C5—C4—C6	112.2 (4)	C3—C1—C2	109.4 (6)
C5—C4—N1	108.0 (5)	N1—C1—C2	106.3 (4)
C6—C4—N1	110.5 (6)	C1—N1—C4	118.1 (3)
C3—C1—N1	110.4 (4)		

The relationship between the macroscopic and microscopic relaxation times is given by the Landau-Khalatnikov Equation 1 as follows:

$$\tau = \tau_0 \frac{T_c}{T - T_c} \qquad \text{(Equation 1)}$$

in which τ_0 is the microscopic relaxation time characteristic of the critical slowing down process. In ferroelectric crystals, the activation energy (ΔE) is usually estimated using the Eyring relation (Equation 2) as follows:

$$\tau_0 = \frac{h}{kT} \exp \frac{\Delta E^*}{RT} \qquad \text{(Equation 2)}$$

At temperatures approaching the Curie point, the activation energy was found to be ~100 kJ/mol. Therefore, the dielectric response is characteristic of the ferroelectric materials with an ‘order–disorder’ mechanism for the PT.

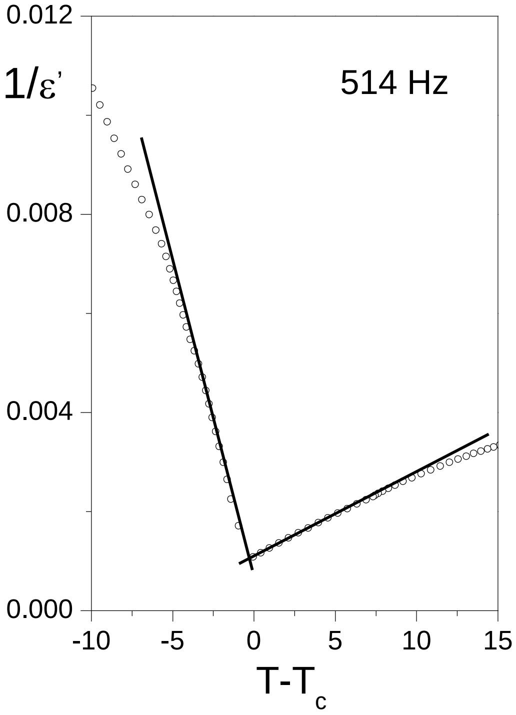

Figure S5 1/ε versus change in temperature (The Curie–Weiss law)