Supplementary Material

Ferroelectricity in the nematic liquid crystal under the direct current electric field

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The phase transition sequence of the RM734 was investigated using the differential scanning calorimetry (DSC) method. DSC experiments were done by a Netzsch DSC 204 F1 Phoenix instrument in an atmosphere of flowing nitrogen. Figure S1 presents two phase transitions (exchange of heat) upon heating and cooling cycles at a rate of 1K/min. In the cooling cycle, the isotropic-nematic phase transition occurs at 184.1°C, while the nematic-ferronematic transition is at 127.2°C. The enthalpy of the first and the second phase transitions is 0.9915 J/g and 0.4955 J/g, respectively.
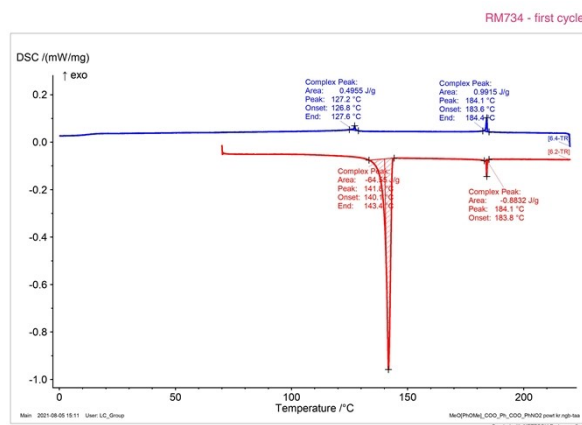

Figure S1 DSC thermogram of the heating (red line) and cooling (blue line) cycles obtained for the RM734.

The results presented in the main manuscript show that the DC field can strongly modify the electrical response of the nematic and ferroelectric nematic phases composed of highly polar molecules. No DC field (BIAS = 0 V) results in a clear border between N and N_F phases, around 127°C (Figure S2a). Electric permittivity in the nematic phase is about 50% of the low-frequency ($f = 100\,Hz$) electric permittivity measured in N_F. It is the result of the ionic contribution. If it was the result of strong dipoles built into the molecular structure it would give a strong contribution also for higher frequencies. Relatively low electric permittivity in N phase, at MHz range, is the result of the creation of dimers which is the common effect when highly polar molecules are considered. When a small DC field (2V) is applied, the situation changes (Figure S2b). Now the values of ε' in N_F are 3-4 times reduced ($\varepsilon' \sim 1800$) compared to the situation without the DC field. It can be concluded that the DC field latches the spontaneous polarization vector, and as the result, the low AC electric field (100mV) cannot repolarize the N_F phase. When the applied DC field is 4 V, then ε' is about 900 in the temperature range where N_F exists (Figure S2c). The further increase of the DC field reduces ε' in the ferronematic down to ~100 at 10 V DC field (Figure S2d-f). This effect is similar to the DC field influence on the

Goldstone mode in SmC* phase. When a strong enough DC field is applied (the helicoidal structure in SmC* is unwound) then electric permittivity in SmC* decreases. The spontaneous polarization vector is directed in one direction (defined by the DC field) and it cannot be changed by a low AC field. Hence, the real part of electric permittivity in N_F decreases under the DC field. The same effect is observed in the SmC* phase. The DC field annihilation of the ferroelectric modes in N_F shifts the dispersion of electric permittivity into the low-frequency region. For example, the electric permittivity measured in N_F under 10 V of DC field at a temperature around 100°C and at the frequency of 10 kHz is less than 30.

In the nematic phase, when the low DC field (2 V) is applied, it can be seen that the real part of electric permittivity is reduced, but this reduction is not so large as for N_F (Figure S2b). What can be the reason? On the one hand, the ionic contribution is reduced in N phase, as it is in N_F phase. On the other hand, a new mode (Ferro-C) appears in the nematic which can be related to "induced" ferroelectricity. In our opinion, this effect is similar to the electroclinic effect in the SmA* phase. The small DC field can force polar molecules to point their dipoles in one direction, and a small spontaneous polarization can be created in such a tense structure. The DC field-created ferroelectricity contributes to the real part of electric permittivity only when the low DC field (2 V) is applied. As it is for N_F phase, the small value of the AC field cannot change the direction of polarization. In the N phase, one can see the opposite effect than in N_F phase. For the fields with high DC voltage, the permittivity dispersion shifts to the higher frequency region (higher than for the measurements without the DC field).

In the main manuscript the results of measured values of real ε' and imaginary ε'' part of electric permittivity in the ferronematic phase N_F were fitted to two dielectric modes, named Ferro-A and Ferro-B (Figure S3a). When the results were fitted considering the presence of only one ferroelectric mode, we observed the mismatch of experimental and model points for the lower frequencies (Figure S3b). Therefore, we assume the presence of two ferroelectric modes in the whole temperature range of N_F. In measurements with the applied DC field, there was no need to consider two modes in both the ferronematic and nematic phases. The temperature dependencies of the relaxation parameters are presented in the main manuscript.
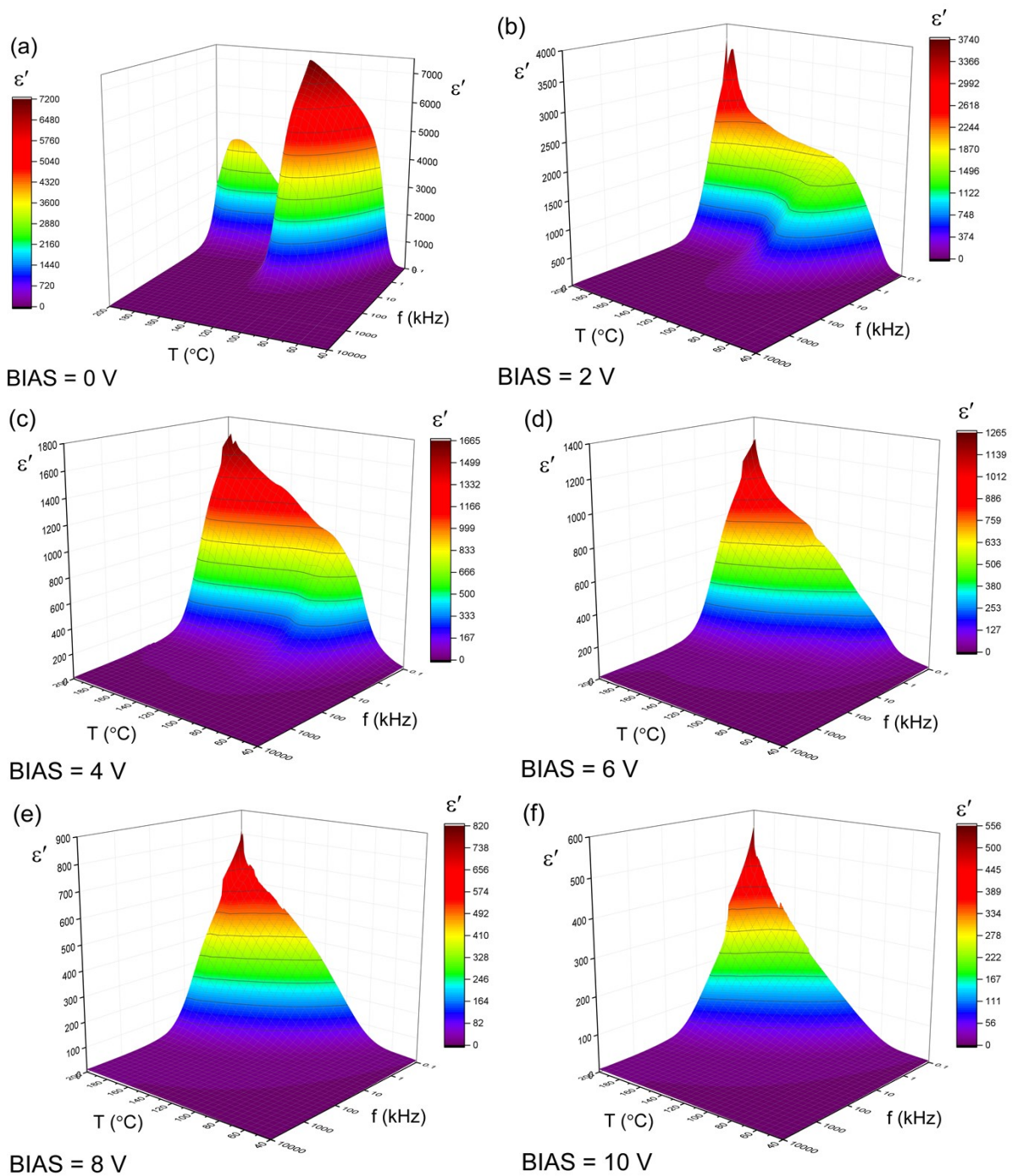
Figure S2 3D graph of real part ε' of electric permittivity versus frequency f and temperature T, measured in planarly aligned cell of RM734 with the bias electric field of (a) 0 V, (b) 2 V, (c) 4 V, (d) 6 V, (e) 8 V and (f) 10 V.
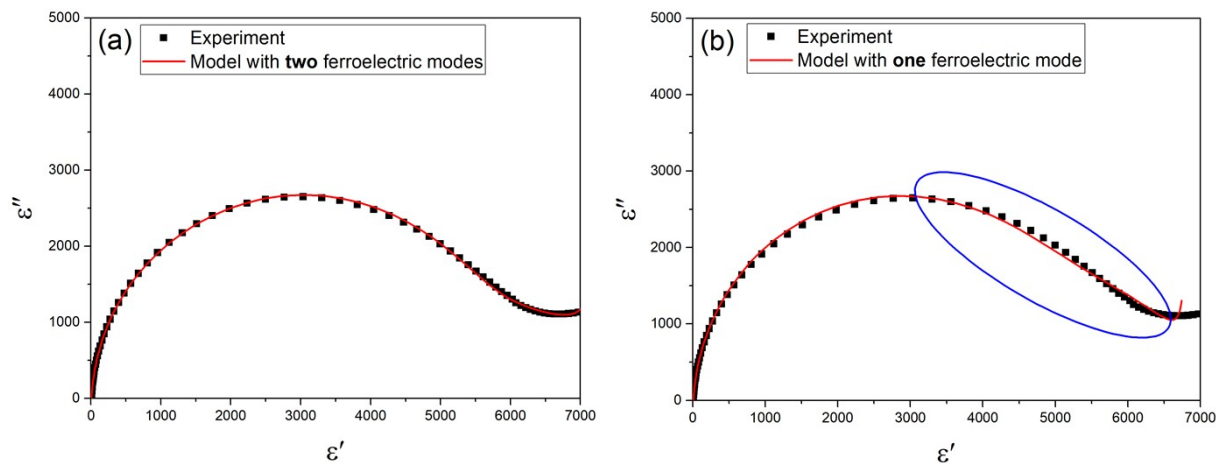
Figure S3 Fitting experimental results to the Cole-Cole model in the ferronematic phase at 120°C taking into account (a) two ferroelectric modes (Ferro-A and Ferro-B) or (b) one ferroelectric mode.