Supplementary Materials for

Inverse "guest - host" effect: ferroelectric nanoparticles mediated switching of nematic liquid crystals

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This PDF file includes:

Materials and Methods Figs. S1 to S4 Table S1 Captions for Movies S1 to S5 References

Other Supplementary Materials for this manuscript include the following:

Movies S1 to S5

Materials and Methods

1. Preparation of liquid crystals doped with ferroelectric nanomaterials

1.1. Liquid crystal materials.

We tested a large variety of different nematic liquid crystals with both positive ($\Delta \epsilon > 0$) and negative ($\Delta \epsilon < 0$) dielectric permittivity: TL-205, ZLI-1132, LC-13739, 5CB, ZLI-4801, ZLI-2806, MLC-6610.

1.2. Ferroelectric nanoparticles.

Different ferroelectric materials were considered for making nanoparticles: BaTiO₃ (ref. 1), $Sn_2P_2S_6$ (ref. 2), SbSI (ref. 3), CuInP_2S_6 (ref. 4). These materials are well known due to their excellent ferroelectric, piezoelectric and dielectric properties.¹⁻⁴ Some of their physical parameters such as spontaneous polarization P_s , the Curie temperature T_{Curie} , and dielectric permittivity ε are listed in the Table S1. The ferroelectric nanoparticles were prepared by the wet grinding of ferroelectric powder in a zirconia ball mill (planetary ball mill PM200 manufactured by Retsch GmbH, Germany) by following well-documented procedure.^{5,6} The carrier fluid was heptane, to which oleic acid was added as a surfactant for the nanoparticles. The addition of a surfactant was necessary to prevent agglomeration of the ferroelectric nanoparticles and to enable their small sizes. Typically, the solutions were prepared using a 1:1:20 ratio of ferroelectric nanoparticles : oleic acid : heptane by weight, respectively. The size of the nanoparticles was controlled by the time of milling.⁵ The dependence of the size of ferroelectric nanoparticles on the time of milling was reported in several papers.^{5,6,7,8} The average size of nanoparticles gets smaller and approaches the saturation level as the milling time increases.^{5,6,7,8} For the studied ferroelectric materials this saturation level is typically achieved after 20 hour long milling. Independent electron microscopy, atomic force microscopy, and dynamic light scattering measurements revealed that the size of the prepared ferroelectric nanoparticles was in the range of 10-20 nm (BaTiO₃), 20-60 nm ($Sn_2P_2S_6$), 20-50 nm (CuInP₂S₆) and 40-90 nm (SbSI).

The ferroelectricity of the prepared nanoparticles was verified in the following way. Their suspensions in heptane (isotropic liquid dielectric) can be considered as a system of free-to-rotate electric dipoles.^{9,10} Under the action of the uniform external electric field these dipoles are reoriented, and this physical reorientation accounts for the polarization switching current. Thus, the observation of the polarization switching current is a direct evidence of the ferroelectricity of the produced nanoparticles.

The current *I* through the cell is a sum of three components: a conduction current I_c (due to the electrical conductivity of the media), capacitive current I_{cap} , and polarization switching current I_p .

$$I = I_{c} + I_{cap} + I_{p} = \frac{V}{R} + C\frac{dV}{dt} + A\frac{dP_{s}}{dt}$$
(1.1.)

where V is the voltage across the cell, R is the electrical resistance of the sample, C is the capacitance of the cell, A is the sample area, P_S is the spontaneous polarization, and t is time. In the case of the triangular voltage waveform and relatively small concentration (< 1 % w/w) of C^{dV}

ferroelectric nanoparticles in the heptane, the capacitive term c_{dt} is a constant. As a result, the time dependence of the total current I(t) is governed by the conduction $I_c(t)$ and polarization $I_p(t)$ components. An electrical conductivity of a heptane is negligibly small ($I_c << I_p$) resulting in easy separation of the polarization switching current, $I(t) \approx I_p(t)$. In this case the maximum of the switching current (I_{max}) and the maximum of the driving electric field (E_{max}) do not coincide (Fig.

S1,A). A well pronounced maximum shown in Fig. S1, B is caused by the reorientation of ferroelectric nanoparticles under the action of the electric field thus indicating their ferroelectricity. The polarization switching current similar to that shown in Fig. S1 was measured for all studied nanoparticles.

In contrast to many reports on the substantially reduced or even absence of ferroelectricity for nanoparticles below 100 nm, the nanoparticles prepared by means of the wet grinding do maintain spontaneous polarization. According to recent studies, an enhanced ferroelectric response of such tiny nanoparticles can be attributed to the existence of an induced surface strain as a result of the grinding process and mechano-chemical reactions.^{11,12}

1.3. Liquid crystals doped with ferroelectric nanoparticles.

Ferroelectric liquid crystalline nanocolloids were prepared using different concentrations of nanoparticles in liquid crystals (c = 0.25 - 5 wt. %). A necessary quantity of a dispersion of ferroelectric nanoparticles in heptane was added to a liquid crystal; the prepared mixture was placed in an ultrasound bath for ~ 30 seconds to ensure a complete dispersion of the nanoparticles, and then the heptane solvent was allowed to evaporate slowly at room temperature. Periodic weighing of the preparation vessel allowed us to determine when the heptane had been completely evaporated. A more detailed description of the ferroelectric nanoparticles and ferroelectric liquid crystalline colloids preparation is given in *ref. 5, 6.*^{5,6}

To prepare an empty cell, indium tin oxide (ITO) substrates were covered with a polyimide using a spin coating machine. Both planar alignment (on rubbed polyimide PI-5291), and homeotropic alignment (on unrubbed polyimide PI-7511) of liquid crystals were used. The thickness of the cells was controlled with spacers ($10 \mu m$).

In order to achieve more accuracy in experimental measurements a twin cell was developed (Fig. S2, Movie S1).^{6,8} The benefits of the twin cell are: 1) the same boundary conditions and alignment, 2) a more supported uniform thickness of the cell, 3) a correct comparison of the experimental results by simple visual observation. One region of a twin cell is filled with plain liquid crystals, and another region is filled with the same liquid crystals doped with ferroelectric nanoparticles. An immediate impact of the ferroelectricity of nanoparticles on optical properties of liquid crystals is clearly seen by utilizing a twin-cell (Fig. S2,A). The use of twin cell also allows for a simple yet fundamentally important proof-of-concept experiment unambiguously showing that intrinsic ferroelectricity of the nanoparticles is responsible for the alteration of physical properties of liquid crystals (Fig. S2,B,C and Movie S2). When the temperature of the cell is below the Curie point, there is a difference in colors, well perceived by the naked eye, between plain liquid crystals and liquid crystal nano-colloid (Fig. S2,A,B). Above the Curie point ferroelectricity disappears, and this phase transitions results immediately in the change of the observed colors – both plain liquid crystal and colloids exhibit the same colors unambiguously revealing effect of the intrinsic ferroelectricity of nanoparticles (Fig. S2,C).

To measure the electro-optical response, such a cell was inserted in between two crossed polarizers with the orientation of a liquid crystal director at 45 degrees relative to the polarizers' axes. Then, an electric field was applied to the cell and the transmittance versus voltage and time curves were measured using a computer-controlled system.¹³

2. Kinetics of orientational transitions

The kinetics of orientational transitions was observed in a twin cell with homeotropic boundary conditions. One part of the cell was filled with pure ZLI 2806 ($\Delta\epsilon$ <0) while the other part was filled with the colloid ZLI 2806 / Sn₂P₂S₆. The fast part of the curve (Figure S3, solid curve, from 2 to 2.5 s) corresponds to the liquid crystal switching from a homeotropic state to a planar; the slower part of the curve (dashed curve) shows partial returning of the liquid crystal alignment from a planar to some intermediate between the planar state and a homeotropic because of a screening effect. At the same time, colloid of ferroelectric nanoparticles in liquid crystals does not exhibit any reorientation (Fig.S3, dotted curve).

3. <u>Theoretical model predicting an inverse guest-host effect in liquid crystal doped with</u> <u>nanoparticles</u>

The goal of our theoretical part of investigation is to find the basic mechanisms of an inverse guesthost effect. Let us suppose that the direction of electric field E is perpendicular to the substrates (is along z-axis). First, let us consider the planar anchoring. Suppose that without electric field the director is oriented along x-axis. The applied electric field generally deforms the director field, so that the local director distribution can be written as follows: $n_x = \cos \theta(z) n_x - \sin \theta(z)$

$$= \cos \theta(z) n_z = \sin \theta(z)$$
⁽²⁾

The energy of the mixture of LC with ferroelectric nanoparticles can be written as a sum of elastic energy, the interaction of the electric field with LC matrix and interaction of electric field with ferroelectric nanoparticles:^{14,15}

$$U = \frac{1}{2}K\left(\frac{d\theta}{dz}\right)^2 - \frac{1}{2}(1-\alpha)\varepsilon_{LC}\Delta\chi_{LC}E^2\sin^2\theta - \frac{1}{2}\alpha\varepsilon_f\Delta\chi_fE^2\sin^2\theta - \alpha\varepsilon_fP_sE\sin\theta$$
(3)

where *K* is the elastic constant of the material in one-constant approximation, α is the molar fraction of ferroelectric nanoparticles, P_s is their spontaneous polarization, $\Delta \chi_e < 0$ is the anisotropy of the dielectric susceptibility of LC matrix, $\Delta \chi_f > 0$ is the anisotropy of the dielectric susceptibility of ferroelectric nanoparticles, $\varepsilon_{LC} > 0$ and $\varepsilon_f > 0$ are the dielectric permittivity of LC and ferroelectric nanoparticles, respectively. The minimization of energy finally yields:

$$\frac{d\theta}{dz} = \pm \frac{1}{\xi} \sqrt{\sin \theta_m + \eta E^* \sin^2 \theta_m - \sin \theta - \eta E^* \sin^2 \theta}$$
(4)

where the plus sign is for $\theta < \theta_m$, while the minus sign is for $\theta > \theta_m$, where θ_m is the maximum deviation angle from planar orientation.

$$\xi \equiv \frac{d}{2\sqrt{E^*}}, \quad E^* \equiv \frac{d^2 \alpha \varepsilon P_s E}{2K}, \quad \eta \equiv \frac{\left[(1-\alpha)\varepsilon_{LC}\Delta\chi_{LC} + \alpha\varepsilon_f \Delta\chi_f\right]K}{\left(\alpha\varepsilon_f P_s d\right)^2} \tag{5}$$

From Eq. (4) it follows

$$\sqrt{E^*} = \int_0^t \frac{dt}{\sqrt{(1 - k^2 t^2)(1 + k\eta E^* - t - k\eta E^* t^2)}}$$
(6)

where

$$k \equiv \sin \theta_m, \quad t \equiv \frac{\sin \theta}{\sin \theta_m} \tag{7}$$

For the numerical calculation of the integral in Eq. (6), to avoid zero in the denominator under the integral at t=1, let us change over from t variable to x variable in correspondence with the following equation:

$$x = \sqrt{1 - t + k\eta E^* (1 - t)}$$
(8)

4

from where it follows

$$\sqrt{E^*} = 2 \int_0^{\sqrt{1+k\eta E^*}} \frac{dx}{(1+2k\eta E^*t)\sqrt{(1-k^2t^2)}}$$
(9)

where

$$t = \frac{1}{2k\eta E^*} \left\{ -1 + \sqrt{1 - 4k\eta E^* \left[x^2 - (1 + k\eta E^*) \right]} \right\}$$
(10)

should be substituted at each step of integration. The numerical solution of Eq. (9) for $k(E^*)$ is presented in Fig. S4 at various η .

From Fig. S4 one concludes that below $E^*=4$ the orientation of the director in the whole sample remains planar. At $E^*=4$ the director starts reorienting along the electric field due to the presence of ferroelectric nanoparticles. At zero dielectric anisotropy of LC (curve 1) θ_m tends $\pi/2$ when the electric field further increases. At negative dielectric anisotropy of LC (curves 2 and 3) the maximal value of θ_m is smaller. The detailed distribution of the director between two glasses in the presence of electric field is shown in Fig. 4 of the main part of the text.

If the anchoring is homeotropic, the orientations of director and electric field coincide within the same range of electric field value.





Fig. S1.

Experimental evidence of the ferroelectricity of the produced nanoparticles¹⁰. (A) Current (red solid line) through the cell filled with $BaTiO_3$ nanoparticles dispersed in heptane. The electric field applied across the cell is represented by black dashed curve. (B) The measured current (red solid curve) is decomposed into the capacitive current (grey horizontal curve) and the polarization switching current (black dotted curve). For additional information refer to paper¹⁰.



Fig. S2.

Twin cell (each cell is separated with a polymer stripe into two identical regions of the same thickness, boundary conditions, anchoring strength of liquid crystals and aligning surfaces). The optical view of the cells placed in between two crossed polarizers and the difference in colors in two regions (Fig. S2,A,B) reveals immediately whether the liquid crystal (LC) is influenced by the embedded ferroelectric nanoparticles (FNP). At temperatures higher than the Curie temperature T_{Curie} ferroelectricity of nanoparticles vanishes. As a result, optical properties of liquid crystal colloids are the same as that of plain liquid crystals (Fig. S2,C). This experimental result unambiguously proves an impact of the ferroelectricity: non-ferroelectric phase of the same nanoparticle does not alter optical properties of liquid crystals (Fig. S2,C) while the ferroelectric phase does (Fig. S2,A,B). Actual temperature of the studied sample: (A) 293 K; (B) 323 K; (C) 343 K.



Fig. S3.

Electro-optical response of the homeotropic cell filled with pure liquid crystal (ZLI 2806, $\Delta \epsilon < 0$) and liquid crystal doped with ferroelectric nanoparticles under applying DC voltage of 10 V.



Fig. S4.

The electric field dependence of the maximal deviation of the nematic director from planar orientation at $\eta = 0$ (1); -0.01 (2); -0.03 (3).

Supplementary Tables

Table S1.

Table S1. Basic parameters of ferroelectric materials

Material	P_s , C/m ²	T _{Curie} , K	3	Ref.
BaTiO ₃	0.15 - 0.28	403	200 - 700	ref. 1
Sn ₂ P ₂ S ₆	0.14	339	200 - 9000	ref. 2
SbSI	0.023 - 0.30	292 - 338	4800	ref. 3
CuInP ₂ S ₆	0.0255	315	419	ref. 4

Supplementary Movie Captions

Movie S1.

Twin-cells placed in between two crossed polarizers at room temperature ($20 \circ C$). The cell to the left is filled with nematic liquid crystals TL205 doped with ferroelectric nanoparticles $Sn_2P_2S_6$ (green region) and pristine liquid crystals TL205 (light pink region). The cell to the right is filled with the same liquid crystals TL205 (top region) and liquid crystals TL205 doped with surfactant (oleic acid). Both regions exhibit similar light pink color indicting no or little impact of the surfactant on the birefringence of liquid crystals.

Movie S2.

Twin-cells taken off the hot plate and placed in between two crossed polarizers. The temperature of the hot plate was higher than the Curie point of ferroelectric nanoparticles $Sn_2P_2S_6$. The movie S2 shows a cooling process. Above the Curie point the ferroelectricity of nanodopants disappears, and this phase transitions results immediately in the change of the observed colors – both plain liquid crystal and colloids exhibit the same colors unambiguously revealing effect of the intrinsic ferroelectricity of nanoparticles (the cell to the left). On cooling once the temperature of the cell drops below the Curie point, there is a difference in colors, well perceived by the naked eye, between plain liquid crystals TL205 and liquid crystal nano-colloid: liquid crystal doped with ferroelectric nanoparticles $Sn_2P_2S_6$ turn green while pristine liquid crystals maintain light pink color (the cell to the left). The cell to the right is a reference cell filled with pristine liquid crystals and the same liquid crystals doped with surfactant (oleic acid). In this case both regions of the cell are of the same light pink color.

Movie S3.

Twin-cell with planar boundary conditions filled with pristine liquid crystals ZLI 2806 with negative dielectric anisotropy $\Delta \varepsilon < 0$ (top region), and the same liquid crystals doped with surfactant (bottom region). The cell is placed in between two crossed polarizers. As expected, the applied electric field orients the molecules of liquid crystals even more planar. As a result, the perceived bright yellow color of both regions of the cell becomes even more uniform.

Movie S4.

Twin-cell with planar boundary conditions filled with liquid crystals ZLI 2806 ($\Delta\epsilon$ <0) doped with ferroelectric nanoparticles Sn₂P₂S₆ .of different concentrations: ~ 1 wt% (top region), and 0.25 wt% (bottom region). The cell is placed in between two crossed polarizers. Ferroelectric nanoparticles, being homogeneously distributed in a nematic liquid crystal reorient in the external electric field and impose this alignment to an entire liquid crystal "host" (bright yellow region of the cell turns colorless), even though the "host" is required to be oriented in an orthogonal direction. The effect is stronger if higher concentrations of nanoparticles are utilized.

Movie S5.

Twin-cell with homeotropic boundary conditions filled with pristine liquid crystals ZLI 2806 ($\Delta \varepsilon < 0$) (top region) and the same liquid crystal doped with ferroelectric nanoparticles (bottom region). The cell is placed in between two crossed polarizers. In the region of the pure liquid crystal reorientation transition from homeotropic to planar was observed (initially dark region turns bright under the action of the applied electric field). At the same time, no reorientation was observed for the same liquid crystal doped with ferroelectric nanoparticles (the bottom region of the cell remains dark). The applied voltage was gradually changed from 10 V to 50 V. Ferroelectric nanoparticles, being aligned by an external electric field, hold liquid crystal molecules in homeotropic state.

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