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Metallomesogens as Biaxial Dopants in a Calamitic Nematic Liquid Crystal

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The electric field induced nematic order reconstruction is a way to achieve controlled transitions between uniaxial nematic textures with different topologies, hence allowing intrinsic textural bistability. The order reconstruction connects perpendicular nematic director orientations by exchanging two eigenvalues of the nematic order tensor \mathbf{Q} , implying intermediate transient biaxial order. This phenomenon avoids the full nematic melting; in fact the nematic scalar order parameter does not vanish. The Biaxial Order Reconstruction in a calamitic Nematic (BORN) is mainly governed by the biaxial coherence length ξ_b . Therefore, by varying ξ_b , one can favour or inhibit the transient biaxial order. Recently, it has been demonstrated that ξ_b can be controlled by suitable dopants and in this work we study the BORN transition threshold for liquid crystal mixtures made of the commercial nematic liquid crystal E7 and three different metallomesogens with board-like shape.

Recently, the high electric field induced Biaxial Order Reconstructions in Nematics (BORN) has been proposed as a new tool to achieve nematic textural changes with variable topology [1,2]. This fast transition has a threshold depending on the order and on the biaxial coherence length ξ_b of the nematic material, which can be controlled by suitable dopants [3]. In this work, we study the electric BORN transition threshold for liquid crystal mixtures [4] of the commercial nematic liquid crystal E7 doped with three different complexes whose molecules have board-like shape, synthesized in the Chemistry Department of the University of Calabria. The BORN behaviour has been investigated by means of dynamical electro-optical observations [1,2].

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A few years ago, surface switched bistable nematic displays were presented by using the breaking of surface anchoring, obtaining fast electro-optical transitions in the microseconds range. The first fast bistable nematic display using monostable surface switching was developed ten years ago [5]. In this case (π -cell) the electrically induced anchoring breaking allows for the switching between a uniform planar texture (with strictly zero pre-tilt) and a π -twisted state. These two textures have distinct topologies. The change of topology is due to the breaking of the nematic texture on the anchoring substrate [5]. Later, a mechanism for breaking tilted nematic anchoring, always by an electric field normal to the boundary plates in a sandwich cell, was proposed [6]. This last kind of surface anchoring breaking represents a discontinuous first-order transition, unlike the second order breaking discussed in the first case. Very recently, the research on nematic electro-optics has been strongly stimulated by the demonstration of fast coherent switching between two topologically distinct textures by means of the electrically controlled BORN. This transition, whose effects have been experimentally observed long time ago [7], has been correctly interpreted for the first time by Martinot-Lagarde et al. [8], who presented a static biaxial melting model. The first dynamical description of the biaxial order reconstruction has been proposed by Barberi et al., together with experimental results, qualitatively interpreted through a Landau-Khalatnikov dynamical model [1]. Later, it has been presented the time resolved experimental analysis of the nematic order reconstruction by using electric current measurements coupled with texture transformation observations [2].

The uniaxial nematic order can be represented in terms of a traceless symmetric tensor \mathbf{Q} , which, in the uniaxial state, presents two equal eigenvalues λ_y and λ_z and a third larger one λ_x . It is known that the spatial order variation crossing the core of a nematic defect implies the exchange between, for instance, the λ_x and λ_z eigenvalues [9]. The electrically induced BORN can be considered the dynamical equivalent of the spatial order evolution inside a defect. In both cases, two distinct uniaxial orientations, perpendicular each other, are connected by intermediate biaxial states. This fast biaxial transition is basically driven by the biaxial coherence length ζ_b , which gives a characteristic scale for the variation of the tensor order parameter of the nematic, in the range of tenth of nanometer.

This work will present experimental investigations which confirm the possibility to control ζ_b in common uniaxial nematics. This result is relevant both from a fundamental point of view, for a better understanding of the nematic order, and for applications, as it allows decreasing the electric BORN threshold.

Our experiments are carried out by using common sandwich type cells. The typical cell consists of two 15×20 mm parallel transparent Indium Tin Oxide (ITO) coated glass plates. On each plate there are two electrically conductive stripes of 1 mm width, made by photolithography on the ITO film. The two stripes are crossed to make one pixel of about 1 mm^2 area. The glass plates are coated with the polyimide acid LQ1800 (PI) by Hitachi chemical, dissolved in a mixture with 1-methyl-2-pyrrolidinone. The spin coating process is followed by two thermal baking steps: 1 h at 140°C , followed by 1 h at 250°C . The cured films are rubbed with a velvet cloth, which is wrapped around a rotating drum. With this procedure we obtain tilted nematic anchoring, necessary to build the required starting splayed symmetric texture [1,2,3]. Two plates are glued together to have a cell with a thickness of about $2 \mu\text{m}$, measured by means of an optical interference technique before filling the cell with the nematic liquid crystal E7 from Merck, in a vacuum chamber in the isotropic phase. The nematic E7 is a eutectic mixture of cyanobiphenyls with a dielectric anisotropy comparable with 5CB and also similar optical and visco-elastic properties in a larger temperature range from -20°C to 62°C which allows a direct comparison with previous experimental works. The cell spacers are mixed with the glue, which is deposited outside the pixel area, to avoid the biaxial wall breaking by defects around spacers. The thickness uniformity over the cells area is always better than 3%. We applied to the cell an electric pulse of width τ and we vary its amplitude until the threshold is reached.

All observations are carried out with the sample in a temperature controlled oven under a polarizing microscope. In order to study the bistable behaviour of these cells, we used the same experimental setup and methods already described in Refs. 1, 2 and 3. In the first experiment we doped the commercial nematic E7 with a chlorine-bridged dinuclear platinum complex based on a cyclometallated azobenzene ligand with a high anisometric ratio (Chart 1) [10]. This complex, namely $[(\text{L}^1)\text{Pt}(\mu - \text{Cl})]_2$, shows a strong intrinsic biaxiality and does not exhibit a nematic phase but a Smectic C one. Figure 1 presents a comparison of experimental results between the pure E7 and the mixture of E7 with 3% *wt* of H-shape molecules, for fixed pulse width $\tau = 1 \text{ ms}$ and $\tau = 0.1 \text{ ms}$, as a function of the reduced temperature $T_C - T$. As expected, the threshold field decreases by increasing the temperature. The general behaviour of the two kinds of cells is similar, but it is interesting to note that the cell filled with the doped nematic shows a visible decrease of the BORN threshold E_{th} of about 13% for $\tau = 1 \text{ ms}$.

In the second experiment we used, as biaxial dopant in a *wt* concentration of about 6%, the mononuclear platinum derivative $[(\text{L}^1)\text{Pt}(\text{acac})]$ (Chart 2), whose asymmetric molecular structure led

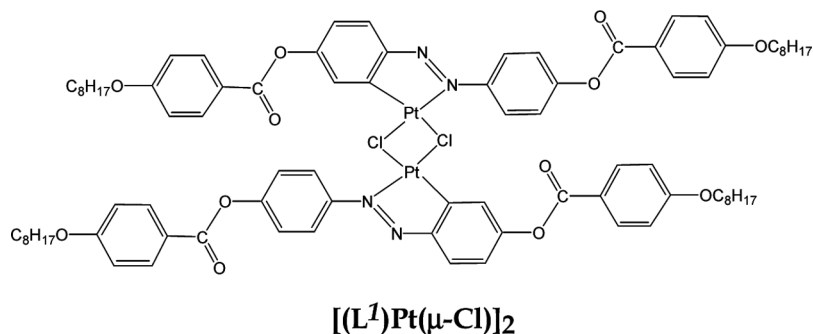


CHART 1 Graphical representation of the structure of the H shaped molecule.

the nematic phase to appear instead of the smectic one of the corresponding precursor, between 185°C and 250°C [10].

As in the previous case, we measure the BORN threshold E_{th} versus the reduced temperature $T_C - T$ for fixed τ at 1 ms and 0.1 ms. A slight decrease of the threshold is observed (Fig. 2).

Finally, we used as dopant, in a *wt* concentration of about 6%, a mononuclear palladium acetylacetonate derivative, AZPAC, based on a two phenyl ring azoxybenzene ligand, nematogenic between 94°C

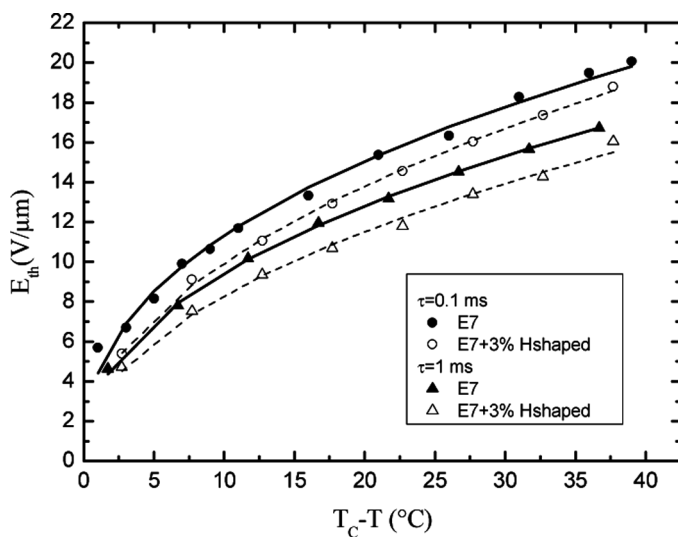


FIGURE 1 BORN threshold as a function of reduced temperature for E7 and E7 + 3% H shaped for $\tau = 0.1$ and $\tau = 1$ ms.

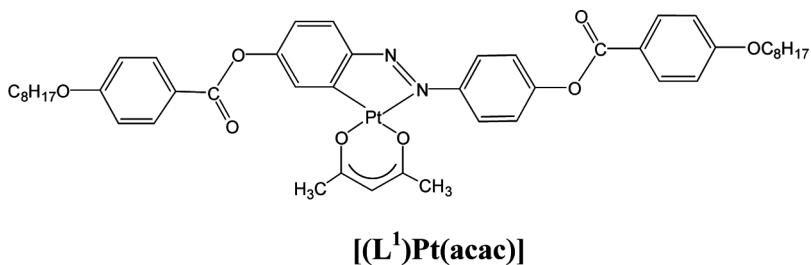


CHART 2 Graphical representation of the structure of the Pt(acac) molecule.

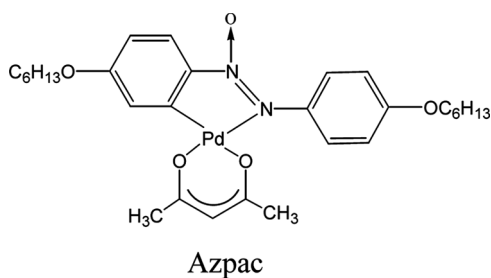


CHART 3 Graphical representation of the structure of the AZPAC molecule.

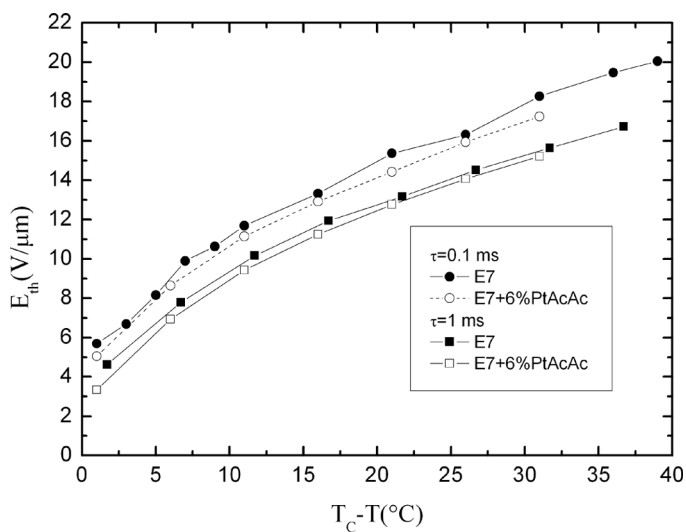


FIGURE 2 BORN threshold as a function of reduced temperature for E7 and E7 + 6% PtAcAc for $\tau = 0.1$ and $\tau = 1$ ms.

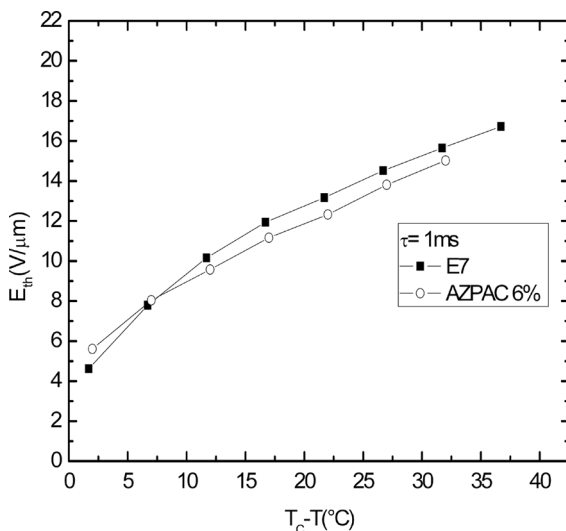


FIGURE 3 BORN threshold as a function of reduced temperature for E7 and E7 + 6% AZPAC for $\tau = 0.1$ and $\tau = 1$ ms.

and 105°C [11] with a negative dielectric anisotropy [12] which should increase the BORN threshold.

Also in this case an actual decrease of E_{th} has been observed (Fig. 3).

Note that the higher biaxiality at molecular level of the H-shaped molecules gives the stronger decrease of the BORN threshold at short electric pulses ($\tau = 0.1$ ms and $\tau = 1$ ms) with respect to the AZPAC and PtAcAc mixtures. Therefore, suitable metallomesogens are able to affect the biaxial coherence length i.e. the tendency of the nematic towards biaxial order. These metallomesogens are not well miscible with the nematic E7, but, even at low concentration, their effect on the BORN threshold is evident. It is interesting to note that in principle the miscibility problem could be solved with better optimized materials. Recently, in fact, it has been demonstrated that it is possible to have nematic thermotropic mixtures containing rod and disc shaped molecules, completely miscible one into an other [4]. We expect that also metallomesogens could confirm this behaviour.

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