Quantum Dot-Driven Stabilization of Liquid-Crystalline Blue Phases

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Liquid crystals hosting nanoparticles comprise a fascinating research field, ranging from fundamental aspects of phase transitions to applications in optics and photonics. Liquid-crystalline phases exhibit topological defects that can be used for assembly of nanoparticles in periodical arrays, and at the same time, the nanoparticles can increase the stability range of liquid-crystalline phases. This has been experimentally demonstrated over the past few years in the case of blue phases that are present in some strongly chiral liquid crystals. Experimental results in quantum dot-driven blue phase stabilization are presented here by means of high-resolution calorimetry and polarizing optical microscopy. It is demonstrated that quantum dots essentially stabilize the macroscopically amorphous blue phase III. There are discussed similarities and differences between the effects of spherical and anisotropic nanoparticles on blue phase stabilization; moreover, future prospects and trends in the field are addressed.

Keywords: liquid crystals, blue phases, topological defects, disclination lines, nanoparticles, quantum dots

INTRODUCTION

Liquid crystals (LCs) form a fascinating class of soft materials exhibiting a plethora of mesophases between the isotropic liquid and the crystal phases. Being discovered in the end of the 19th century [1], LCs made inroads into optical display technologies in the second half of the 20th century [2]. Upon reducing temperature, LCs undergo several phase transitions along which they progressively obtain a long-range orientational and partial positional order. The competition between the incompatible structures of adjacent mesophases often results in the appearance of topological defects such as disclinations and screw and edge dislocations. In addition, LCs exhibit anisotropy in their elastic, dielectric, and optical properties. Hence, they form a multidisciplinary scaffold, where fundamental science, and envisioned applications meet [3–7]. The former consists of studies of quenched-random disorder and inclusions on symmetry-breaking phase transitions [8–11], critical phenomena, and universality classes [12–16]. The latter is related to attempts for assembly and orientation of nanoparticles (NPs) [17], as well as to search of tunable photonic crystals and lasers [18, 19], soft magnetoelectrics [20–22], and metamaterials [23]. Moreover, liquid-crystalline cholesteric and blue phases comprise a testing ground for the study of active materials [24, 25], with rapidly increasing interest in physics and biology [26].

Among the most interesting liquid-crystalline phases for applications in optics and photonics are the so-called blue phases (BPs). These phases are inherently present in some strongly chiral...
LCs and only within a narrow temperature range (in most cases from 1 to 3 K) between the isotropic (I) and chiral nematic (N*) phases. Three such phases have been identified, denoted as blue phase III (BPIII), blue phase II (BPII), and blue phase I (BPI), upon reducing temperature. The extension of the BP range as a function of increased chirality was demonstrated in phase diagrams of racemic-chiral mixtures [27]. Their thermodynamic stability was confirmed by identifying the distinct thermal signatures of I-BPIII, BPIII-BPII, BPII-BPI, and BPI-N* transitions for cholesteryl non-anoate [28]. In the late 90s, the BP phase diagrams were revisited and the critical behavior as a function of chirality was well-understood [29, 30].

Regarding structure, BPI and BPII consist of double-twisted cylinders, with the director being parallel to the cylinder axis in the center and gradually changing from $-45^\circ$ to $+45^\circ$, as it can be schematically depicted in Figure 1. This structure emanates from a continuous competition between two factors: the chirality and the packing topology. The double-twisted cylinders are packed in such a way that BPII and BPI exhibit three-dimensional simple cubic and body-centered cubic defect lattices, respectively [31–33]. Between these cylinders, there is no LC molecular alignment, i.e., the cylinders coexist with lines of $-1/2$ disclinations as seen in Figure 1. The structure of BPIII, in particular, remained elusive for many years [34]. Though it was initially considered to be locally similar to BPII [35], recent systematic theoretical work by Henrich et al. [36, 37] yields a macroscopically amorphous network of disclination lines. These lines are interconnected in BPIII and BPII, whereas they do not intersect in the case of BPI.

The cubic lattice of BPs with periodicity in visible wavelengths could be exploited toward the fabrication of tunable photonic crystals, as proposed by Etchegoin [38]. Following work of Cao et al. [18] reported lasing in a three-dimensional photonic-bandgap BPII sample. Nevertheless, the narrow temperature stability range of BPs remained a long-standing, unsurpassed obstacle. The envisioning of applications revolved around the interest of the scientific community in exploring strategies to extend the BP temperature stability range. Kikuchi et al. [39] exploited bi-continuous phase separation phenomena in LC and polymer composites that, in case of a BPI defect lattice, could drive the polymer chains in the space between the double-twist cylinders, i.e., assemble them along the disclination lines. Indeed, this work resulted in the first experimental demonstration of BP stabilization. Posterior stabilization strategies were based on mixing of chiral and non-chiral molecules [40] and fast quenching in super-cooled states [41, 42]. The use of surface-functionalized NPs is a more recent, yet very effective strategy toward expanding the temperature range of BPs. The first reports came out almost simultaneously for spherical Au nanoparticles dispersed in a LC/chiral dopant mixture [43] and CdSe quantum dots (QDs) [44, 45] dispersed in single LC compounds. Subsequent studies used additional types of spherical NPs and QDs, by varying the core composition and diameter, as well as the surface functionalization [46–52]. Apart from the stabilization effect, it has been also reported that NPs could improve the electro-optical performance of blue phase-based optical displays [53].

Experimental results are presented here on two mixtures of Cd$_x$S$_{1-x}$ quantum dots (QDs) dispersed in the chiral LC compound S-$(+)-4-(2$-methylbutyl) phenyl-$4\cdot n$-octylbiphenyl-4-carboxylate), henceforth referred to as CE8. The thermal and optical properties of the mixtures have been investigated by means of high-resolution ac calorimetry and polarizing optical microscopy. It is shown that the presence of CdSSe increases the total BP range and especially promotes the BPIII stabilization. In the succeeding sections, the materials and methods are presented, followed by the presentation of experimental results and discussion with respect to other recent advances and trends.

**MATERIALS AND METHODS**

CE8 of high purity has been purchased from Merck and exhibits all three BPs within a total range of 5 K [44]. QDs of the Cd$_x$Se$_{1-x}$ core (where $x = 0.5$) have been synthesized in the National Center for Scientific Research “Demokritos” (Greece). They have a core diameter of 3.4 nm, and they are surface-functionalized by flexible oleyl amine and tri-octyl phosphine molecules [54]. The oleyl amine-based functionalization has proven very effective in obtaining high-quality dispersions of spherical and anisotropic NPs in LCs [44, 45, 54–57]. Two mixtures of CE8 and CdSSe QDs have been prepared, with concentrations $\chi = 0.01$ and $\chi = 0.05$, where $\chi$ is defined as the ratio of the mass of QDs over the total sample mass (QDs and CE8). The mixing protocol has been described in previous studies [44, 45]. High-resolution ac calorimetry and polarizing optical microscopy have been used to study the mixtures’ properties.

The calorimetric apparatus at Jožef Stefan Institute (Slovenia) is home-made and fully automatized. It achieves an excellent thermal stability (better than 50 μK) and operates at slow scanning rates. This way, the samples are kept close to thermal equilibrium and the temperature profiles of heat capacity $C_p(T)$ are accurately derived. For calorimetric measurements, quantities of ~30 mg of the mixtures are placed immediately after preparation in home-made, high-purity silver cells. A glass bead thermistor and a heater are attached to the cell prior to measurements.

Polarizing optical microscopy yields the characteristic textures of liquid-crystalline phases. The apparatus in National and Kapodistrian University of Athens (Greece) consists of a Leica DM2500P microscope equipped with a Leica DFG420 digital image-acquisition camera. An Instec HCS402 heating stage with temperature stability better than 10 mK is attached to the microscope, allowing for temperature scans. The samples were placed between glass slides of 10-μm thickness.

The combination of ac calorimetry and polarizing optical microscopy provides a solid picture for the mixtures’ phase transition behavior. By checking the thermal and optical properties with two methods, upon heating and cooling, the possibility that BPs are super-cooled, i.e., thermodynamically unstable, is ruled out. Moreover, calorimetry provides robust evidence that these phases exist in bulk (thick) samples and are not induced or stabilized by the interfaces in thin samples. The
latter has been recently demonstrated by means of microscopy as a function of the cell thickness, the anchoring conditions, and the effective anchoring strength [58].

RESULTS

The $C_p(T)$ profiles of the two mixtures, $\chi = 0.01$ and $\chi = 0.05$, have been obtained at the same scanning rates of 0.25 Kh$^{-1}$ upon cooling from the I down to the N$^*$ phase. They are shown in Figure 2, at the middle and top layers, respectively. At the bottom layer, the $C_p(T)$ profile of pure CE8 [44] is shown at the same temperature range for comparison. The presence of CdSSe QDs has a strong impact on the phase transition behavior of the mixtures with respect to pure CE8. In particular, a widening of the total BP range is observed, from 5.0 K for CE8 to 7.2 K for $\chi = 0.05$. Although the increase of the total BP range is moderate, an impressive increase of the BPIII range by a factor of six times is found.

All phase transitions appear suppressed in the presence of QDs. An interesting feature is the apparent stronger suppression of I-BPIII anomaly for $\chi = 0.01$ with respect to $\chi = 0.05$. This does not imply any abnormality regarding the enthalpic content of phase transition behavior, taking into account that ac calorimetry in the conventional (so-call ac) mode of operation senses only the continuous part of enthalpy change. In case of first-order transitions (such as the I-BPIII) latent heat is present, being the major contribution to the total enthalpy. The latter can be in this case measured by operating the calorimeter in a different, so-called relaxation or non-adiabatic scanning mode [59]. Note that ac runs are more precise for the determination of the transition temperatures, and they have been chosen for the construction of the temperature-concentration phase diagram. Nevertheless, only the size of the anomalies obtained by relaxation runs can be used for a comparison of the total enthalpic content of first-order I-BPIII transition between pure CE8 and the mixtures. Such types of runs have not been performed, since the determination of enthalpy values is not the focus of the present work.

Another interesting feature of the phase transition behavior is that BPII is already absent at $\chi = 0.01$. The phase sequence I-BPIII-BPI-BPI-N$^*$ of pure CE8 has given its place to I-BPIII-BPI-N$^*$ in the case of $\chi = 0.01$. By additionally increasing the QD concentration to $\chi = 0.05$, BPI also disappears and BPIII occupies the full temperature range of 7.2 K between the I and N$^*$ phases. Hence, the presence of CdSSe QDs strongly promotes the stabilization of BPIII and yields an I-BPIII-N$^*$ sequence, with an extended BPIII range.

In order to additionally confirm the phase sequence derived by ac calorimetry, the optical textures have been examined upon sequential heating and cooling cycles. The temperature is slowly changed, using average scanning rates from 0.1 to 0.2 Kmin$^{-1}$. The images are captured at several temperatures in the transmission mode and under crossed polarizers, for the $\chi = 0.01$ mixture. Well-reproducible foggy blue textures of BPIII and vivid turquoise-green, large-size platelets attributed to BPI appearing on both heating and cooling. Oily streaks, characteristic of the N$^*$ phase in planar anchoring conditions, are also found. All the aforementioned textures remain stable when leaving the sample for longer time scales at a fixed temperature.

In Figure 3, the temperature-concentration ($T$-$\chi$) phase diagram of the CE8 and CdSSe nanocomposites is presented, based on the combined results from calorimetry and microscopy which agree well with each other. The three insets show the characteristic textures of the BPIII, BPI, and N$^*$ phases for $\chi = 0.01$. The phase diagram clearly demonstrates that by increasing the QD concentration, the range of the amorphous BPIII structure prevails over BPII and BPI.
FIGURE 2 | Heat capacity temperature profiles $C_p(T)$ obtained by ac calorimetry for two mixtures of chiral liquid crystal CE8 and CdSSe QDs. Top layer (A): $\chi = 0.05$, Middle layer (B): $\chi = 0.01$. Bottom layer (C): pure CE8 (from Ref. [44]). The inset in layer (B) shows a blow-up of the temperature regime around BPIII-I anomaly, which is greatly suppressed and barely visible in the full-scale plot.
**DISCUSSION**

This work shows that BPII and BPI gradually disappear and BPIII prevails, exhibiting a six-fold extended range in the presence of CdSSe QDs. BPIII has also been strongly stabilized in the case of CdSe QDs of almost identical size (3.5 nm) and similar surface treatment dispersed in CE8 \([44]\), as well as in another chiral LC compound CE6 \([45]\). In both these cases, BPIII already disappeared for small concentrations of QDs (below \(\chi = 0.02\) for CE8 and below \(\chi = 0.01\) for CE6). However, BPI was mildly affected and remained present for higher QD concentrations than in the current work. In particular, in the case of CE8 the CdSe-driven stabilization reaches saturation in concentrations well above \(\chi = 0.05\) \([44]\). On the contrary, the CdSSe-driven stabilization effect of this work essentially saturates around \(\chi = 0.01\). With the LC compound being the same and the QD core size almost identical, the different impact must be related to density changes and surface functionalization. Indeed, as mentioned above, the composition of the QDs used here is \(\text{CdS}_x\text{Se}_{1-x}\) (where \(x = 0.5\)). In addition, oleyl amine binds on both Cd and S, whereas tri-octyl phosphine only on Se. Hence, the partial replacement of Se by S yields a larger coverage of the CdSSe surface with oleyl amine combined with reduced core density. The latter is reflected in slower kinetics of CdSSe QDs in the LC volume, since they sense a more viscous medium with respect to their heavier CdSe counterparts. Hence, their trapping to the defect cores is slightly less effective and the overall stabilization milder. This reveals the great importance of NP chemistry, related to the modification of core composition and surface functionalization, in their trapping efficiency.

The adaptive character of NPs is related to their size and coating; both play an important role in the NP entrapment within the cores of defects. The trapping mechanism has been originally proposed by Kikuchi et al. \([39]\) for polymer-stabilized BPs, focusing on the energy gain when part of the defect volume is replaced by the guest (polymer) molecules. It was later on generalized for NPs \([44, 60]\), focusing on the adaptive character of the latter that should not significantly disrupt the surrounding LC ordering. This implies that the energy gain from the defect core replacement prevails over the energy cost for non-favorable boundary conditions in the interfaces between NPs and LC molecules \([61]\). Both CdSSe and CdSe QDs surface-functionalized with flexible molecules are highly adaptive to the defect lattices of LC structures. Apart from stabilizing BPs, it is also shown that they induce a stable twist-grain boundary phase, characterized by screw dislocations, in the cases of CE8 \([54]\) and CE6 LCs \([61]\). Au NPs with oleyl amine coating are also reported to stabilize BPIII and induce a twist-grain boundary phase in CE8 \([54, 62]\). Note that the aforementioned mechanism for NP assembly in the defect cores could be extended by including...
the contribution of saddle-splay elasticity; preliminary efforts to create a more general phenomenological model can be found in our recent study [62], and additional work is in progress. A new theoretical approach has been recently proposed by Machon and Alexander [63] and by Selinger [64] for analyzing the director deformations in liquid-crystalline phases, based on splay, twist, bend, and saddle-splay contributions in the free energy.

BP stabilization driven by spherical NPs is reported in several other studies in literature. The NP cores are composed of ZnS, Ni, MnO₂, Fe₂O₃, and SiO₂, and the sizes range from 2 nm to over 100 nm [46–52]. The effect is mostly on LC materials exhibiting BPI and, in few cases, BP II. According to theoretical predictions, BPI and BP II defect lattices could be used as matrices for large-scale, stable assembly of large (up to 100 nm) NPs that should remain unaffected by thermal fluctuations [65]. Nevertheless, most of the existing size-dependent studies [46, 48] suggest that the trapping becomes less effective and the stabilization effect milder as the NP size grows. When the size of particles becomes essentially larger, approaching the μm scale, the stabilizing effect may be associated with their assembly within the interfaces between platelets [66]. Moreover, it is worth investigating how the NPs affect the relaxation of a double-twist cylinder structure and if the larger sizes suppress the fluctuations, as theory suggests [65]. In the present ac calorimetric measurements, the frequency has been chosen to achieve a thermally thin sample, i.e., a sample without temperature gradients. In such slow timescales, the impact of QDs on the relaxation times of double-twist cylinder structures could not be assessed.

The small spherical QDs of the present and previous studies [44, 45] exhibit a minor shift of the BP III-I transition temperature to slightly higher or lower values (depending on the QDs size, surface functionalization, and the LC host). On the contrary, large anisotropic NPs, such as graphene, laponite, and MoS₂ nanosheets, systematically upshift the BP III-I transition temperature even at minute concentrations [55–57, 67]. This trend confirmed by other studies [68, 69] is attributed to the ordering of LC molecules induced within the I phase by the large surfaces of nanosheets. It also explains why large anisotropic NPs with similar surface functionalization promote the stabilization of the more ordered BP I structure over the less ordered, macroscopically amorphous BP III [55–57, 67].

SUMMARY

Soft nanocomposites of LCs and NPs constitute an exciting field of ongoing research. BPs hold a prominent position among liquid-crystalline phases due to their high potential for applications [70, 71]. The defect lattices could be used for assembly of NPs in regular templates or tuned by external fields [37, 50, 71]. Among various approaches, the nanoparticle-driven BP stabilization has attracted considerable interest over the last 10 years. Spherical quantum dots and nanoparticles, as well as anisotropic nanosheets, have been tested as stabilization agents. In this study, we have shown that small spherical QDs, surface-functionalized with flexible molecules, extend the total blue phase range of CE8 and strongly increase the stability of BP III. The outcomes of this work have been compared to other studies on QDs and other spherical and anisotropic NPs. The role of chemistry is very important since even moderate changes in the core composition and surface functionalization [56] have a noticeable impact on the stabilization effect. The results obtained so far have revealed certain trends, as well as the key mechanisms behind the BP stabilization. These mechanisms could be reformed to clearly include the saddle-splay contribution, using recently proposed mathematical formulations [63, 64]. It is anticipated that additional studies, both experimental and theoretical, will clarify the precise role of nanoparticle size, shape, core density, and coating.

DATA AVAILABILITY STATEMENT

The datasets generated for this study are available on request to the corresponding author.

AUTHOR CONTRIBUTIONS

ML, MT, and GC prepared the samples, performed the calorimetric measurements, and data analysis. GC and IL performed the optical measurements. VT synthesized and provided the quantum dots. GN and ZK conceived the idea and planned the work on blue phase stabilization. GC, MD, IL, GN, and ZK discussed and interpreted the results. GC, ML, and MT have prepared the figures. The manuscript was written by GC and reviewed by all authors.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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