## Journal of Colloid and Interface Science 639 (2023) 401-407



Contents lists available at ScienceDirect

# Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

## Tuning of optical properties and phase behavior of Nanomaterialstabilized blue phase liquid crystals



Urice N. Tohgha<sup>a,b</sup>, Ecklin P. Crenshaw<sup>a,b</sup>, Michael E. McConney<sup>a</sup>, Kyung Min Lee<sup>a,b,\*</sup>, Nicholas P. Godman<sup>a,\*</sup>

<sup>a</sup> Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, United States <sup>b</sup> Azimuth Corporation, Fairborn, OH 45324, United States

## G R A P H I C A L A B S T R A C T



## ARTICLE INFO

Article history: Received 4 November 2022 Revised 10 February 2023 Accepted 14 February 2023 Available online 16 February 2023

Keywords: Nanoparticle Blue phase liquid crystal Phase behavior Stabilization and Optical property

## ABSTRACT

*Hypothesis*: Nanoparticles of various shapes and sizes can affect the optical properties and blue phase (BP) stabilization of BP liquid crystals (BPLCs). This is because nanoparticles, which are more compatible with the LC host, can be dispersed in both the double twist cylinder (DTC) and disclination defects in BPLCs.

Experiments.

This study presents the first systematic study of the use of CdSe nanoparticles having various sizes and shapes (spheres, tetrapods and nanoplatelets) to stabilize BPLCs. Unlike previous studies using commercial nanoparticles (NPs), we custom-synthesized NPs with the same core and nearly identical long chain hydrocarbon ligand materials. Two LC hosts were used to investigate the NP effect on BPLCs. Findings.

The size and shape of nanomaterials greatly influence the interaction with LCs, and the dispersion of NPs in the LC medium affects the position of the BP reflection band and the stabilization of BPs.

Abbreviations: BP, Blue phase; LCs, Liquid crystals; DTC, Double twist cylinder; NPs, Nanoparticles; NPLs, Nanoplatelets; QD-Ts, tetrapod quantum dots; QDs, Quantum dots.

<sup>\*</sup> Corresponding authors at: Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, OH 45433, United States (Kyung Min Lee).

E-mail addresses: kyungmin.lee.3.ctr@us.af.mil (K.M. Lee), nicholas.godman.2@us.af.mil (N.P. Godman).

Spherical NPs were found to be more compatible with the LC medium than tetrapod shape and platelet shape NPs, resulting in a wider temperature range of BP and a redshift of the reflection band of BP. In addition, the inclusion of spherical NPs tuned the optical properties of BPLCs to a significant extent, whereas BPLCs with nanoplatelets displayed a limited influence on the optical properties and temperature window of BPs due to poor compatibility with LC hosts. The tunable optical behavior of BPLC as a function of the type and concentration of NPs has not been reported.

© 2023 Elsevier Inc. All rights reserved.

## 1. Introduction

Blue phase liquid crystals are self-organized double twisted cholesteric liquid crystal (CLC) materials exhibiting a Bragg-type selective reflection. Various blue phases (BP) are observed in a small temperature range between the isotropic and the cholesteric phases of CLCs with relatively short pitch [1]. The director axes of LCs assemble into double twist cylinders (DTCs) with a diameter of 100 s nm. During cooling, three types of BPs are formed depending on the chirality of LC: blue phase III (BP-III), BP-II, and BP-I [2–17]. In BP-III, a DTC is in random orientation, while BP-II and BP-I are three-dimensionally ordered simple cubic (SC) and body-centered (BCC) states, respectively. In BP-II and BP-I, discontinuous points exist where the DTCs are in contact, and DTCs and disclination defects coexist [18].

Stabilizing BPLCs has been achieved through various methods. Kikuchi et al. reported the stabilization of BP-I with a polymer network and widened the temperature range by more than 60 °C [3]. The polymer network mainly disperses within the disclination defects and stabilizes the BPLCs. The energy costly defect lines are replaced by polymer chains, which reduce the free energy of the BPLCs and lead to a more stable BP structure [19]. Recently, we reported the effect of amorphous crosslinker on the phase behavior of BPLCs [20]. The amorphous crosslinker greatly suppresses the formation of BP-II and induces a direct transition from isotropic to BP-I phase. Nakata et al. reported that achiral bent-core liquid crystal molecules induced BP-I and BP-II phases and studied the effect of chirality and bent shape of guest molecules [21]. A variety of nanomaterials including metal oxide nanoparticles (NPs), metallic NPs, carbon NPs [22] and guantum dots (QDs) [19,23] have been utilized with varying success to stabilize BPLCs by widening the temperature range [24]. While several nanomaterials have been investigated in the literature, the stabilization of BPLCs is dictated by the size, core materials and surface chemistry of the nanomaterials. QDs have emerged as more compatible materials with LCs due to their unique size, surface chemistry and shape-dependent properties. For QDs, surface ligands having the flexible oleyl moieties, such as oleylamine, have been shown to be compatible with the defect lattices of LCs [24]. However, few studies have systematically investigated the effect of QD properties on BPLC stabilization. Karatairi et al. [19] utilized CdSe QDs with an average diameter of 3.5 nm to stabilize two chiral BPLCs. The authors reported complete suppression of the BP-II phase at small QD concentrations (0.02 mass ratio of QD to LC). On the other hand, the widening of the temperature range (20 K) of BP-III was observed at high QD concentration (mass ratio of QD to LC = 0.02) for CE8 BPLC. A more recent study by Cordoyiannis et al. [25] used  $CdS_xSe_{1-x}$  (x = 0.5) QDs with an average diameter of 3.4 nm with 1-5 % QD content in CE8 BPLC. The increase in OD content widened the range of BP-III, while suppressing BP-II and BP-I phases. The authors explained that the mild stabilization effect was attributed to the lower NP core density of CdS<sub>x</sub>Se<sub>1-x</sub> compared to CdSe used in previous studies. Khan et al. [26] studied the effect of nanoparticle shape on the properties of BPLC by utilizing CdSe/CdS rods and CdSe spheres. The authors reported an

enhanced stabilization of BPLC using nanorods and a more limited stabilization using QD spheres. However, the QDs they used were commercially available QDs having different surface chemistries (ligands and shell material) and material compositions (CdSe and CdSe/CdS). Considering that the compatibility of NPs and LCs is mainly determined by their surface chemistry, it is important to use the same ligand material to eliminate/minimize the ligand effect to better understand the shape effect of NPs.

In this study, we report a systematic investigation of the size and shape of nanoparticles on the stabilization of BPs, which is affected by the compatibility and dispersion of nanoparticles in the LC medium. Three NPs with different shapes and sizes were customsynthesized to have identical core and nearly identical hydrocarbon ligand materials. CdSe nanoplatelets (NPLs) and CdSe spherical nanoparticles having different sizes were capped with oleylamine/ oleic acid. CdSe tetrapods (QD-Ts) were synthesized using oleic acid (OA) and cetyltrimethylammonium bromide (CTAB) as a co-ligand at a 114:1 M ratio (OA:CTAB). However, given the overwhelming molar excess of oleic acid employed during the reaction, [2] it is reasonable to assume that the majority of the ligands on the final QD-T surface are oleate. Since the majority of ligands present on the surfaces of all NPs used in this study were oleyl-based ligands, the ligand effect on the phase behavior and stabilization of the BPLC can be minimized. We observed a significant nanoparticle size and shape effects where small and isotropic spherical QDs are more compatible with LC hosts and dispersed in the BP double twist cylinders (DTCs) as well as disclination defects. The well-dispersed spherical nanoparticles in the DTC expand their cubic size, causing the reflection band to shift to longer wavelengths. Good compatibility between NP and LC medium stabilizes the BPs and widens the temperature window of BPs. QD-Ts showed moderate stabilization of the BPLC, whereas NPLs did not stabilize the BPLC. The poor dispersion of NPLs did not affect the temperature windows of BP.

#### 2. Experimental

## 2.1. Materials

A BPLC mixture (BPLC-0) was prepared using 8.8 wt% SL04151 (chiral liquid crystal, AlphaMicron, Inc.), chiral dopants (6.1 wt% R1011 and 17.3 wt% R811 from Merck), and 67.8 wt% BL038 (nematic mixture,  $T_{NI} = 100$  °C,  $\Delta n = 0.272$ ,  $\Delta \epsilon = 16.9$  from Merck). The chemical structures of the materials for BPLC-0 used in this study are summarized in **Figure S1** (Supplementary Materials). Cadmium oxide (CdO, 99.99 %, Aldrich), Selenium powder (Se, 99.9 %, Alfa Aesar), Oleic acid (OA, 90 %, Aldrich), Oleylamine (OLA, 70 %, Aldrich), 1 Octadecene (ODE, 90 %, Aldrich), Trioctylphosphine (TOP, 90 %, Strem chemicals), Trioctylphosphine oxide (TOPO, 90 % Aldrich), Cetyl trimethylammonium bromide (CTAB, 98 %, Alfa Aesar), were used as received.

#### 2.2. Cells and sample preparations

Alignment cells were prepared from ITO-coated glass slides (Colorado Concepts). The glass substrates were cleansed in acetone and methanol, and treated with air plasma for 30 s. The substrates were spin-coated with a polyimide solution (PI2551, HD Microsystems) and baked at 200 °C for 1 hr. The alignment layers were rubbed with a velvet, and the cell was constructed to ensure a planar alignment condition. The cell gap was controlled by mixing 12  $\mu$ m thick glass rod spacers into an optical adhesive. The cell was filled with the BPLC mixtures with/without NPs at 120 °C (isotropic phase) and cooled slowly at a cooling rate of 0.2 °C min<sup>-1</sup>. All materials were used as received without any purification.

BPLCs were stabilized with various concentrations (0.25 ~ 6 wt%) of NPs. Table 1 summarizes the sample code. The helical twisting power (HTP) of R1011, R811 and SL04151 with BL038 is approximately 25, 8, and 12  $\mu$ m<sup>-1</sup>, respectively. A single mixture was used to fill three separate alignment cells, and temperature-dependent optical measurements were performed 3–5 times to obtain phase transition temperatures. Errors in phase transition temperatures were evaluated using the method of standard deviation of the mean values in SigmaPlot 12.0 software.

## 2.3. Preparation of Nanoparticle-BPLC nanocomposites

Different concentrations of nanoparticles in LC were prepared by adding hexane solutions (with known nanoparticle weights) into pre-weighed LC samples in a vial. The solvent was removed by heating the mixture while vortexing. The remaining nanoparticle-LC mixture was kept for further characterization.

#### 2.4. Synthesis of NPs

See the Supplementary Material.

#### 2.5. Characterization

The phase behavior of the samples was monitored during cooling using an Ocean Optics spectrometer with an INSTEC temperature controller (mK1000) and a polarized optical microscope (POM) (Nikon, Eclipse 50iPol) with a hot stage (Mettler FP-90). The mixture was heated to an isotropic state and cooled slowly at a cooling rate of 0.2 °C min<sup>-1</sup>. Transmission Electron Microscope (TEM) images of NPL, QD-T, QD-2.9, and QD-18 (measured using Talos 200KV TEM) are shown in Fig. 1.

## 3. Results and discussion

The phase behavior of BPLC-0 containing 8.8 wt% SL04151, 6.1 wt% R1011, 17.3 wt% R811 and 67.8 wt% BL038 is shown in Fig. 2(a). Upon cooling, four distinct phases are observed: isotropic, BP-II, BP-I, and focal-conic (FC)/cholesteric phases. The tempera-

Ta	ble	1
	~~~	-

Sample code of BPLCs with various NPs.

Sample code	Nanoparticl	Nanoparticle		
	Туре	Shape	Content (wt%)	
BPLC-0	-	-	0	
BPLC-NPL-0.25	NPL	Platelet	0.25	
BPLC-NPL-0.5	NPL	Platelet	0.5	
BPLC-NPL-1	NPL	Platelet	1	
BPLC-NPL-2	NPL	Platelet	2	
BPLC-QD-T-2	QD-T	Tetrapod	2	
BPLC-QD-T-4	QD-T	Tetrapod	4	
BPLC-QD-2.9-2	QD-2.9	Spherical	2	
BPLC-QD-2.9-4	QD-2.9	Spherical	4	
BPLC-QD-2.9-6	QD-2.9	Spherical	6	
BPLC-QD-3.5-2	QD-3.5	Spherical	2	
BPLC-QD-18-0.5	QD-18	Spherical	0.5	
BPLC-QD-18-2	QD-18	Spherical	2	

ture windows ( $\Delta T$ ) of BP-II and BP-I of BPLC-0 are  $\sim$  3 °C and  $\sim$  2.3 °C, respectively. Three NPs with different shapes and sizes were mixed with BPLC-0 to study the phase behavior and optical properties of BPLC doped with NPs. First, a spherical QD with a diameter of 2.9 nm was mixed with BPLC-0 (BPLC-QD-2.9), and the phase behavior of BPLC-QD-2.9 was studied at 2-6 wt% QD-2.9 concentration, as shown in Fig. 2(b, c) and Figure S2(a). In QD-2.9, 2.9 nm is the size of the inorganic CdSe core part obtained by TEM. Interestingly, the BP peak of BPLC-QD-2.9 shifts to a longer wavelength (redshift) with increasing QD-2.9 concentration. The small QD-2.9 disperse well in the LC medium in the range of up to 6 wt% without phase separation. This redshift of the reflection band indicates an increase in the size of the cubic structure. In addition to the redshift of the reflection band, a wider temperature window of BP is observed with increasing QD-2.9 concentration, as summarized in Fig. 2(d). As explained in Figure S3, the onset temperature and onset peak position during cooling are determined from the temperature and position at which the peak appears. Both the onset temperature and onset reflective peak position were determined by the average of 3-5 measurements. The BPLC-QD-2.9-4 sample (4 wt% QD-2.9) shows a wider temperature range of BPs compared to the other samples.

Transmission spectra of BPLCs with larger diameters of 3.5 nm and 18 nm QDs are shown in Figure S2(b, c). Figure S4 exhibits POM images of BPLC-QDs with 2-6 wt% QD-2.9 and 2 wt% QD-18. TEM images and absorption spectra of QD-2.9 and QD-18 are shown in Fig. 1(c, d) and Figure S5(a, b), respectively. BPLC with 2 wt% 3.5 nm and 18 nm diameter QDs show the same phase behavior as BPLC-QD-2.9. The larger diameter QDs are also well dispersed in the BPLC, showing a redshift of the reflection peak and a wider  $\Delta T$  of the BP. The  $\Delta T$  of the BP of all samples is summarized in Table S1 (Supplementary Materials). Cordoyiannis et al. [25] and Karatairi et al. [19] reported that the introduction of QDs with a diameter of 3.5 nm into a chiral LC suppressed BP-II and BP-I and significantly stabilized the BP-III. Cordoviannis et al. observed only BP-III with a total range of 7 °C when using 5 % QD-3.5. Karatairi et al. observed a large  $\Delta T$  of  $\sim$  18 °C ( $\Delta T$  of BP-III  $\sim$  16 °C and  $\Delta T$  of BP-I  $\sim 2 \,^{\circ}$ C) when using 2 % OD-3.5. Compared to these studies, no BP-III stabilization was not observed in our study and a total BP range of 9.3 °C (ΔT of BP-II and BP-I) was observed when using 2 % QD-3.5 content.

The effect of tetrapods (QD-Ts) on phase behavior of BPLC-QD-Ts was studied. The TEM image and absorption of QD-T are shown in Fig. 1(b) and Figure S5(a), respectively. Fig. 3 shows the transmission spectra, POM images and a summary of phase transition of BPLC-QD-T-2 and 4. Compared to the BPLC-NPL samples, a broadened temperature window of BP-II and BP-I is observed with increasing QD-T content, indicating that QD-T is more compatible with the LC host than NPL. This is because QD-Ts are more difficult to aggregate within the BP structure compared to NPLs.

Platelet shape NPs (0.25  $\sim$  2 wt% content) were mixed into this LC mixture and the phase behavior of the composites was studied. Fig. 4(a) shows the transmission spectra and POM images of BPLC with 0.25 wt% NPL (BPLC-NPL-0.25) upon cooling. BPLC-0 and BPLC-NPL-0.25 samples prepared in aligned cells show a relatively uniform crystal orientation [14,17,27,28]. The initial nucleation state determines the crystal orientation of the BPs. Transmission spectra of BPLCs with NPL concentrations of 0.5 wt%  $\sim$  2 wt%, as well as the onset transition temperature and onset reflective peak position of BPs are summarized in Figure S6. Fig. 4(b) summarizes the onset temperature of BPLC-NPLs, which decreases with increasing concentration of NPL in the LC mixture. For BPLC-NPL-0.25 and 0.5 samples with low NPL concentrations (0.25-0.5 wt% NPL), the temperature window of BP increases slightly, whereas for BPLC-NPL-1 and 2 samples with high NPL concentration, the temperature window of BP decreases. A small amount of NPL can



Fig. 1. TEM images of (a) nanoplatelet (NPL), (b) tetrapod (QD-T), (c) QD-2.9 and (d) QD-18.



**Fig. 2.** Transmission spectra of (a) BPLC-0 at isotropic (82 °C), BP-II (79 °C), BP-I (77 °C), (b) BPLC-QD-2.9–2 at isotropic (79 °C), BP-II (75 °C), BP-I (71.5 °C), and (c) BPLC-QD-2.9–4 at isotropic (80 °C), BP-II (73 °C), BP-II (69 °C). (d) Summary of the onset transition temperature of BPLC with QD-2.9 at concentrations of 2–6 wt%.

be dispersed in the LC medium and slightly widen the temperature window of BP. A very broad BP-II peak and a small BP-I peak of BPLC-NPL-2 (2 wt% NPL) are shown in Figure S6(c). In the POM images of BPLC-NPL-1 in Figure S6(d), many defects and low optical properties related to NPL aggregates are observed. Lower transmittance and smaller BP peaks observed in BPLCs containing more than 1 wt% NPL indicate poor dispersion of NPLs (NPL aggregation)

in the LC medium. NPLs appear to interact more strongly with each other than the liquid crystal medium, resulting in aggregation of NPLs. No significant stabilization was observed when NPLs were used. The absorption peak of NPL is shown in Figure S5(c).

Fig. 5 summarizes the onset transition temperature and onset peak position of the BPLC-0 and BPLCs with 2 wt% NPs. The addition of isotropic spherical QDs with sizes of 2.9 nm, 3.5 nm and



**Fig. 3.** Transmission spectra and POM images of (a) BPLC-QD-T-2 at isotropic (75 °C), BP-II (72 °C), BP-I (67.4 °C), and (b) BPLC-QD-T-4 at isotropic (73 °C), BP-II (68 °C), BP-I (62 °C). (c) Summary of onset transition temperature as a function of QD-T concentrations. Scale bar in the POM images are 200 μm.



Fig. 4. Transmission spectra of (a) BPLC with 0.25 wt% nanoplatelet (NPL) at isotropic (81 °C), BP-II (77 °C), BP-I (75.5 °C). Insets is POM images of BPLC-NPL-0.25. (b) Summary of onset temperature of BPLC-NPL with various NPL concentrations. Scale bar in the POM images are 200  $\mu$ m. Cells of 11  $\mu$ m thickness were used.

18 nm leads to a wider temperature range ( $\Delta T$ ) of BP-II and BP-I than for BPLC-O, BPLC-OD-T and BPLC-NPL samples, as shown in Fig. 5(a). The  $\Delta$ Ts for BPLC-OD-3.5–2 show the widest range (4.5 °C and 4.8 °C for BP-II and BP-I respectively), which are wider than those of BPLC-0 (3 °C and 2.3 °C). Samples containing QDs ranging in diameter from 2.9 nm to 18 nm show similar onset transition temperatures and onset peak positions, but higher than the 2 wt% OD-T and 2 wt% NPL samples. This widened  $\Delta$ T indicates that spherical ODs stabilize the BPs more effectively than NPL or OD-T. Platelet NPs have flat surfaces that can aggregate more than spherical ODs, and such aggregated NPLs are difficult to disperse in blue phase LCs (disclination line defects and DTCs). However, small and isotropic QDs can more easily disperse into line defects and DTCs. Less aggregated and well-dispersed spherical NP can stabilize BPs better than NPL and QD-T, so a wider temperature range of BPs is observed. This improved stability of BPs has also been previously reported by other researchers [19,25].

In addition to widened the temperature window of BPs, the inclusion of spherical QDs induces a redshift of the BP-I reflection

band in the BPLC-QDs, as shown in Fig. **5(b)**. The spherical QDs could be more compatible with the LC host than QD-T or NPL, and well dispersed QDs in the DTC increase the size of the BP cubic structure, causing a redshift of the reflection band. Small, less aggregated spherical QDs can be first dispersed into the disclination defects to lower their energy penalty and then dispersed without significant aggregation in the DTCs. As shown in Figures S8 and S9, no significant aggregation of spherical QDs was observed in both isotropic and cholesteric phases. Well-dispersed QDs in DTC can expand the cubic structure of BP, causing a redshift of the BP's reflection band (Fig. 5(b)). The large redshift of the BP's reflection band is greatly influenced by the shape of the NPs.

As observed in Fig. 5(a), adding NPs lowers the transition temperature of LC. Osipov and Gorkunov reported that NPs effectively dilute the liquid crystal material and reduce the nematic-to-isotropic transition temperature [29]. Among the NPs used in this study, NPL tends to aggregate by itself, resulting in poor dispersion and the lowest transition temperatures. The poor dispersion is evidenced by haze values (Table S2) and POM images (Figure S6).



Fig. 5. Summary of (a) onset transition temperatures and (b) onset peak positions of BPLCs with 2 wt% NPs. The lines are the guide for the eyes.



Fig. 6. Transmission spectra of CLCs with (a) 0–6 wt% QD-2.9, (b) 0–4 wt% QD-18 and (c) 0–4 wt% QD-T at 25 °C. (d) Summary of the notch position of cholesteric phase with 0–6 wt% NPs: (i) QD-2.9, (ii) QD-18, (iii) QD-T, (iv) NPL.

However, spherical QDs are well dispersed in the LC medium and effectively stabilize the LC phase, leading to higher transition temperatures.

To investigate the miscibility between the NPs and the LC host, the position of the reflection band of the cholesteric phase is monitored, as shown in Fig. 6. Since these NPs have nearly identical hydrocarbon ligands, ligand effects are minimized and the effect of shape and size of NPs on compatibility with LC host is studied. Fig. 6(a, b) shows the transmission spectra of BPLC-QD-2.9 and BPLC-QD-18 samples with various NP concentrations. The reflection band of cholesteric phase shifts to longer wavelengths with increasing QD-2.9 concentration. The reflection band shifts from  $\sim$  390 nm initial position to  $\sim$  440 nm when 4 wt% QD-2.9 is added. BPLCs with larger spherical QD-18 (0.5 and 2 wt%) show a slight redshift of the reflection band, as shown in Fig. 6(d-ii). Small spherical particle QD-2.9 is more compatible than bigger size QD-18 with LC medium [30]. Tetrapod QD-T samples show a maximum  $\sim$  15 nm redshift when 2 wt% QD-T is mixed (Fig. 6(c) and (d-iii)). Platelet NPL samples show slight redshift at low NPL concentration (0.25 wt%) and then remain unchanged at high NPL concentrations (Fig. 6(d-iv) and Figure S7). The small spherical QDs are more compatible with LC hosts than tetrapod or platelet NPs, inducing a redshift of the peak positions of the CLC reflection bands. The dispersion of NPs in the LC host is further studied in the isotropic and cholesteric phases and are shown in Figure S8 and Figure S9. In the POM image of 2 wt% QD-2.9, only few aggregates are observed in both phases, indicating that the spherical NPs are well dispersed in the LC host. However, QD-T and NPL form several large aggregates due to poor compatibility with the LC host.

To further investigate the compatibility of NPs with the LC host, a haze meter was used to determine the degree of homogeneity of the NP-BPLC composite systems. The measured transmittance and haze of the QD-2.9, QD-T, and NPLs samples in the cholesteric phase are summarized in **Table S2**. BPLC-0 and BPLCs doped 2 wt % of either QD-2.9 or QD-T have similar overall transmittance (82–86 %) and haze (1.8–3 %), but BPLC with 2 wt% NPL has significantly lower overall transmittance (~65 %) and much higher haze

( $\sim$ 40 %). The incredibly high haze and the aggregation seen in the POM clearly indicate that the NPLs are acting as an impurity rather than forming a composite with the LC host.

To investigate the LC host effect on phase behaviour of BPLCs, 2 wt% nanoparticles were mixed with nematic liquid crystal E7. The onset transition temperature and BP peak position are summarized in **Figure S10**. BPLC containing 2 wt% QD-2.9 shows a wider BP window than other samples. This confirms that spherical NPs are more miscible with E7 LC medium than tetrapod or platelet NPs. Spherical NPs can fit within the line defects of BPs and are also well dispersed in DTC due to their good compatibility with LC hosts.

#### 4. Conclusions

In summary, nanoparticles of various shapes and sizes affect the phase behavior of BPLCs to different extents. We prepared NPs with the same core and nearly identical hydrocarbon ligand materials but with different shapes and sizes. Since the same ligand material was used, the ligand effect on the phase behavior and stabilization of the BPLC can be minimized. The shape of the NPs affects their compatibility with the LC medium: spherical NPs > tetrapod NPs > platelet NPs. Highly compatible isotropic spherical NPs can be dispersed in line defects (discontinuous points) and DTCs in the cubic structure. The isotropic spherical NPs dispersed in the disclination defects reduce the free energy and stabilize the BPs, resulting in a wider BP temperature window. On the other hand, the spherical NPs dispersed in the DTC increase the size of the BP cubic structure. leading to a redshift of the reflection band of BPs. To the best of our knowledge, no nanoparticle-induced redshift of the BPLC reflection peak has been reported. The redshift of the reflection band of BPs is due to the high compatibility of the NPs with liquid crystal hosts. The compatibility of NPs does not depend on specific LCs (BL038 and E7).

Most of the existing studies have not reported systematic studies on the phase behavior and optical properties of BPLCs using nanomaterials [22,30–32]. In this study, we reported for the first time that the position of the blue phase reflection band varies depending on the type (shape and size) or concentration of the nanomaterial and is affected by the compatibility between nanomaterials and liquid crystal hosts. This tunable optical property and stabilized BPs could be a promising optical material for various optical applications. Further control of the optical properties of NPstabilized BPLCs by applying an electric field would be beneficial for the next generation displays, optical components, and photonics applications.

#### **CRediT authorship contribution statement**

**Urice N. Tohgha:** Data curation, Investigation, Formal analysis, Validation, Conceptualization, Writing – review & editing. **Ecklin P. Crenshaw:** Formal analysis, Writing – review & editing. **Michael E. McConney:** Formal analysis, Writing – review & editing. **Kyung Min Lee:** Conceptualization, Supervision, Data curation, Investigation, Formal analysis, Validation, Writing – original draft. **Nicholas P. Godman:** Conceptualization, Supervision, Methodology, Funding acquisition, Writing – review & editing.

## Data availability

No data was used for the research described in the article.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgements

The authors acknowledge funding from the Materials and Manufacturing Directorate of the Air Force Research Laboratory under contract #FA8650-16-D-5404.

#### **Appendix A. Supplementary material**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2023.02.076.

#### References

- J. Thoen, Adiabatic scanning calorimetric results for the blue phases of cholesteryl nonanoate, Phys. Rev. A 37 (5) (1988) 1754–1759.
- [2] F. Castles, F.V. Day, S.M. Morris, D.-H. Ko, D.J. Gardiner, M.M. Qasim, S. Nosheen, P.J.W. Hands, S.S. Choi, R.H. Friend, H.J. Coles, Blue-phase templated fabrication of three-dimensional nanostructures for photonic applications, Nat. Mater. 11 (7) (2012) 599–603.
- [3] H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, T. Kajiyama, Polymer-stabilized liquid crystal blue phases, Nat. Mater. 1 (1) (2002) 64–68.
- [4] H.J. Coles, M.N. Pivnenko, Liquid crystal 'blue phases' with a wide temperature range, Nature 436 (7053) (2005) 997–1000.
- [5] T.-H. Lin, T.-H. Lin, Y. Li, C.-T. Wang, H.-C. Jau, C.-W. Chen, C.-C. Li, H.K. Bisoyi, T. J. Bunning, Q. Li, Red, green and blue reflections enabled in an optically tunable self-organized 3D cubic nanostructured thin film, Adv. Mater. 25 (2013) 5050–5054.
- [6] S.-T. Hur, B.R. Lee, M.-J. Gim, K.-W. Park, M.H. Song, S.-W. Choi, Liquidcrystalline blue phase laser with widely tunable wavelength, Adv. Mater. 25 (21) (2013) 3002–3006.

- [7] F. Castles, S.M. Morris, J.M.C. Hung, M.M. Qasim, A.D. Wright, S. Nosheen, S.S. Choi, B.I. Outram, S.J. Elston, C. Burgess, L. Hill, T.D. Wilkinson, H.J. Coles, Stretchable liquid-crystal blue-phase gels, Nat. Mater. 13 (8) (2014) 817–821.
- [8] C.-W. Chen, C.-C. Li, H.-C. Jau, L.-C. Yu, C.-L. Hong, D.-Y. Guo, C.-T. Wang, T.-H. Lin, Electric field-driven shifting and expansion of photonic band gaps in 3D liquid photonic crystals, ACS Photonics 2 (11) (2015) 1524–1531.
- [9] I.C. Khoo, C.-W. Chen, T.-J. Ho, High efficiency holographic bragg grating with optically prolonged memory, Sci. Rep. 6 (2016) 36148.
- [10] W. Cao, A. Muñoz, P. Palffy-Muhoray, B. Taheri, Lasing in a three-dimensional photonic crystal of the liquid crystal blue phase II, Nat. Mater. 1 (2) (2002) 111–113.
- [11] I.C. Khoo, K.L. Hong, S. Zhao, D. Ma, T.-H. Lin, Blue-phase liquid crystal cored optical fiber array with photonic bandgaps and nonlinear transmission properties, Opt. Express 21 (2013) 4319–4327.
- [12] Y. Chen, S.-T. Wu, Electric field-induced monodomain blue phase liquid crystals, Appl. Phys. Lett. 102 (2013) 171110.
- [13] S.-T. Wu, D.-K. Yang, Reflective Liquid Crystal Displays, Wiley: West, Sussex, UK, 2001.
- [14] S. Tanaka, H. Yoshida, Y. Kawata, R. Kuwahara, R. Nishi, M. Ozaki, Double-twist cylinders in liquid crystalline cholesteric blue phases observed by transmission electron microscopy, Sci. Rep. 5 (2015) 16180.
- [15] J. Kobashi, H. Yoshida, M. Ozaki, Planar optics with patterned chiral liquid crystals, Nat. Photonics 10 (6) (2016) 389-392.
- [16] S.-Y. Jo, S.-W. Jeon, B.-C. Kim, J.-H. Bae, F. Araoka, S.-W. Choi, Polymer stabilization of liquid-crystal blue phase II toward photonic crystals, ACS Appl. Mater. Interfaces 9 (10) (2017) 8941–8947.
- [17] K. Kim, S.-T. Hur, S. Kim, S.-Y. Jo, B.R. Lee, M.H. Song, S.-W. Choi, A well-aligned simple cubic blue phase for a liquid crystal laser, J. Mater. Chem. C 3 (21) (2015) 5383–5388.
- [18] Meiboom S., Sammon M., B.W. F., Lattice of disclinations: the structure of the blue phases of cholesteric liquid crystals, Phys. Rev. A 27 (1983) 438–454.
- [19] E. Karatairi, B. Rožič, Z. Kutnjak, V. Tzitzios, G. Nounesis, G. Cordoyiannis, J. Thoen, C. Glorieux, Nanoparticle-induced widening of the temperature range of liquid-crystalline blue phases, Phys. Rev. E 81 (2010) 041703.
- [20] K.M. Lee, U. Tohgha, T.J. Bunning, M.E. McConney, N.P. Godman, Effect of Amorphous Crosslinker on Phase Behavior and Electro-Optic Response of Polymer-Stabilized Blue Phase Liquid Crystals, Nanomaterials 12 (2022) 48.
- [21] M. Nakata, Y. Takanishi, J. Watanabe, H. Takezoe, Blue phase induced by doping chiral nematic liquid crystals with nonchiral molecules, Phys. Rev. E 68 (2003) 41710.
- [22] A.P. Draude, T.Y. Kalavalapalli, M. Iliut, B. McConnell, I. Dierking, Stabilization of liquid crystal blue phases by carbon nanoparticles of varying dimensionality, Nanoscale Adv. 2 (6) (2020) 2404–2409.
- [23] G. Cordoyiannis, P. Losada-Pérez, C.S.P. Tripathi, B. Rožic, U. Tkalec, V. Tzitzios, E. Karatairi, G. Nounesis, Z. Kutnjak, I. Musevic, C. Glorieux, S. Kralj, J. Thoen, Blue phase III widening in CE6-dispersed surface-functionalized CdSe nanoparticles, Liq. Cryst. 11 (2010) 1419–1426.
- [24] G. Cordoyiannis, M. Lavrič, V. Tzitzios, M. Trček, I. Lelidis, G. Nounesis, K. Samo, J. Thoen, Z. Kutnjak, Experimental Advances in Nanoparticle-Driven Stabilization of Liquid-Crystalline Blue Phases and Twist-Grain Boundary Phases, Nanomaterials 11 (2021) 2968.
- [25] G. Cordoyiannis, M. Lavrič, M. Trček, V. Tzitzios, I. Lelidis, G. Nounesis, M. Daniel, Z. Kutnjak, Quantum Dot-Driven Stabilization of Liquid-Crystalline Blue Phases, Front. Phys. 8 (2020) 315.
- [26] R.K. Khan, P. Ramarao, Selective stabilization of blue phase liquid crystals using spherical and rod-shaped colloidal nanocrystals, J. Appl. Phys. 129 (2021) 024702.
- [27] P.-J. Chen, M. Chen, S.-Y. Ni, H.-S. Chen, Y.-H. Lin, Influence of alignment layers on crystal growth of polymer-stabilized blue phase liquid crystals, Opt. Mater. Express 6 (2016) 1003.
- [28] M. Takahashi, T. Ohkawa, H. Yoshida, J.-I. Fukuda, H. Kikuchi, M. Ozaki, Orientation of liquid crystalline blue phases on unidirectionally orienting surfaces, J. Phys. D: Appl. Phys. 51 (2018) 104003.
- [29] M.A. Osipov, M.V. Gorkunov, Nematic liquid crystals doped with nanoparticles: phase behavior and dielectric properties, in: J.P.F. Lagerwall (Ed.), Liquid Crystals With Nano and Microparticles, World Scientific, Luxembourg, 2017, pp. 135–175.
- [30] A. Sharma, M. Worden, T. Hegmann, Nanoparticle-Promoted Thermal Stabilization of Room Temperature Cholesteric Blue Phase Mixtures, Ferroelectrics 431 (1) (2012) 154–163.
- [31] H. Yoshida, Y. Tanaka, K. Kawamoto, H. Kubo, T. Tsuda, A. Fujii, S. Kuwabata, H. Kikuchi, M. Ozaki, Nanoparticle-Stabilized Cholesteric Blue Phases, Appl. Phys. Express 2 (2009) 121501.
- [32] I. Dierking, W. Blenkhorn, E. Credland, W. Drake, R. Kociuruba, B. Kayser, T. Michael, Stabilising liquid crystalline Blue Phases, Soft Matter 8 (2012) 4355– 4362.