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OPTIMIZATION OF CHEMICAL STRUCTURE OF COMPATIBILIZERS BASED ON LIQUID CRYSTALLINE DIBLOCK COPOLYMERS FOR RECONCILIATION BETWEEN INORGANIC QUANTUM DOTS AND ORGANIC CHOLESTERIC LIQUID CRYSTALS

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One of the key challenge of designing hybrid liquid crystalline (LC) materials is to combine organic and inorganic constituents in one stable system. To overcome this challenge, specially designed substances called compatibilizers may be used but the chemical structure of these substances and their content in the system should be adjusted properly. In this work, we optimized the chemical structure and the weight fraction of a compatibilizer between CdSe/ZnS quantum dots (QDs) and low molecular weight cholesteric liquid crystalline (CLC) matrix. As compatibilizers we used LC diblock copolymers containing a mesogenic block consisting of phenyl benzoate monomer units and poly(vinylpyridine) block of different polymerization degree, which is capable of binding to the surface of various nanoparticles. Using polarized optical microscopy and absorbance spectroscopy we found that the polymerization degree of poly(vinylpyridine) block can exert the influence on the CLC matrix properties such as a photonic band gap width and light scattering. The obtained results allowed us to prepare the hybrid CLC materials, which combine the high loading of QDs and unique optical properties of the cholesteric phase. Our approach to creation hybrid CLC materials might be employed as a “flexible template” for the design of many other hybrid LC systems.

Key words: cholesteric liquid crystals, quantum dots, liquid crystalline block copolymers, fluorescence, hybrid nanomaterials.

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ОПТИМИЗАЦИЯ ХИМИЧЕСКОГО СТРОЕНИЯ СОВМЕСТИТЕЛЕЙ НА ОСНОВЕ ЖИДКОКРИСТАЛЛИЧЕСКИХ ДИБЛОК-СОПОЛИМЕРОВ ДЛЯ ОБЪЕДИНЕНИЯ НЕОРГАНИЧЕСКИХ КВАНТОВЫХ ТОЧЕК И ОРГАНИЧЕСКИХ ХОЛЕСТЕРИЧЕСКИХ ЖИДКИХ КРИСТАЛЛОВ

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Одна из ключевых задач при дизайне гибридных жидкокристаллических (ЖК) материалов заключается в объединении органической и неорганической составных частей в одну стабильную систему. Чтобы решить данную задачу могут быть использованы специально разработанные соединения, называемые совместителями, однако химическое строение этих соединений и их содержание в системе должны быть подобраны подходящим образом. В данной работе, мы оптимизировали химическое строение и массовую долю совместителя между квантовыми точками (КТ) CdSe/ZnS и низкомолекулярной хо-

лестерической матрицей. В качестве совместителей мы использовали жидкокристаллические diblock-сополимеры содержащие мезогенный субблок состоящий из фенилбензоатных мономерных звеньев и субблоки поли(винилпиридина) разной степени полимеризации, которые способны связываться с поверхностью различных наночастиц. Используя поляризационную оптическую микроскопию и абсорбционную спектроскопию мы обнаружили, что степень полимеризации субблока поли(винилпиридина) может оказывать влияние на свойства холестерической матрицы, такие как ширина запрещенной фотонной зоны и рассеяние света. Полученные результаты позволили нам получить гибридные холестерические материалы которые объединяют в себе высокое содержание КТ и уникальные оптические свойства холестерической фазы. Продемонстрированный подход к созданию гибридных холестерических материалов может быть использован как гибкий «шаблон» для дизайна многих других гибридных ЖК-систем.

Ключевые слова: холестерические жидкие кристаллы, квантовые точки, жидкокристаллические блок-сополимеры, флуоресценция, гибридные наноматериалы.

Introduction

Hybrid liquid crystalline (LC) nanomaterials has attracted great attention of many material scientists from different fields [1–6]. This attention is due to broad possibilities of the directed design of such materials to achieve a desirable range of their properties. Hybrid LC nanomaterials are comprised of organic and inorganic parts, thus combining features of these dissimilar matters. The organic part is generally a LC matrix, which provides self-assembly and anisotropy, and endows the nanomaterial with sensitivity to external fields. The role of the inorganic part can be played by various types of nanoparticles but fluorescent semiconductor quantum dots (QDs) is of considerable interest owing to their size-tunable properties, high optical stability, high fluorescence yield and emission brightness [7, 8]. Combining QDs and LC phase in one material results in mutual tuning characteristics of both constituents [9]. As example, being introduced in nematic LCs, QDs could lower switching voltage and time from planar to homeotropic transition in the cell [10]. On the other hand, the self-assembly of the LC matrix can organize QDs in a controlled way leading to the programmed pattern formation of nanoparticles [5].

A key feature of inorganic QDs is well known to be the superior emission capability. Consequently, introducing these nanoparticles in a LC media that is capable to interact with light is of specific interest for many applications. For this purpose, a cholesteric LC (CLC) phase can be involved due to its intrinsic helical structure. The presence of helical structure in CLC phase results in unique optical properties such as Bragg selective light reflection and huge optical rotation. CLC phase can be considered as one-dimensional photonic crystal with a photonic band gap for circular polarized light of the same handedness as the helical

structure. The spectral position of the photonic band gap is defined by the pitch of helical structure and average refractive index of the CLC phase. The pitch can be easily tuned under the action of various external fields making it possible to adjust the spectral position of photonic band gap [11–13]. Introducing QDs in CLC phase has allowed hybrid LC nanomaterials with controllable light emission to be designed [14]. The control of light emission could be realized by various external actions such as electrical field and light irradiation [15, 16]. Besides, thermo and electrically adjustable lasers [17, 18] as well as a single photon source [19, 20] have been developed by the use of QD dispersions in CLC phase. These features of CLC-QD hybrid nanomaterials make them promising for many practical applications such as nanophotonics, optical coding, display technology and telecommunication.

There have been reported a great number of hybrid LC-QD nanomaterials including ones based on CLCs but compatibility between inorganic nanoparticles and organic LC media remains one of the crucial problems related to the design of these materials [5, 21]. Low compatibility can result in the formation of QD aggregates, which may make worse properties of material or uncontrollable (or even unpredictable) change in them over time. Usually, QDs are covered with aliphatic ligands (oleylamine, oleic acid or others), which are compatible rather poorly with liquid crystals being mainly aromatic compounds. Such QDs form stable dispersion in LC media only at rather low concentration, about 0.01 wt. %, but even at this concentration small aggregates could be observed with light scattering measurements [5]. Sometimes, optical applications require such a low concentration and even lower, for instance, to create single-photon sources [19]. However, usually the concentration of QDs should be quite high, about a few percent, to ensure suitable intensity of light emission.

The aggregation of QDs dispersed in low molecular weight LCs can be suppressed with ligands containing mesogenic groups. CdSe/ZnS QDs decorated with mesogen-containing ligands could be successfully embedded in CLC phase and their weight fraction can be reached as high as 0.05–0.1 wt. % without aggregation [21, 22]. When excited with a continuous wave laser, these hybrid nanomaterials demonstrated characteristic emission for QDs coupling with a cholesteric cavity. Nevertheless, the reached QD content was not quite enough for optically pumped lasing. The higher QD content could be reached by the thoroughly design of complex dendritic mesogen-containing ligands together with addition of a certain amount of aliphatic co-surfactant [23]. The obtained hybrid LC nanomaterials with QD loading up to 0.25 wt. % were thermodynamically stable but this result was shown only for a nematic phase. Thus, the successful compatibilization of inorganic QDs and organic CLCs is still a challenge in the field of designing novel hybrid LC nanomaterials.

Recently, we have developed an approach to the design of hybrid CLC materials based on specially designed LC triblock copolymers [24]. CdSe/ZnS QDs coated with these LC triblock copolymers could form stable dispersions in low molecular weight CLCs and QD loading was as high as 1 wt. %. To assure compatibilizing effect, the constituent blocks of the LC triblock copolymers used as polymer QD ligands were endowed with clearly designated functionality. The end blocks of the LC triblock copolymers contained vinylpyridine (VP) units, which can form coordinate bonds with Zn^{2+} ions that are located on the QD surface. The central block was liquid crystalline due to the presence of nematogenic phenyl benzoate (PhM) groups, which provided compatibility with the CLC phase. However, some of the LC triblock copolymers we tested were able to provoke the aggregation of QDs supposedly due to the potential ability of macromolecules of triblock copolymers to connect two different nanoparticles forming a “bridge”. This behavior depended on the polymerization degree of the LC triblock copolymers and in the case of relatively high polymerization degree, the formation of QD aggregates was not observed. This fact restricts the potentialities of the application of LC triblock copolymers as compatibilizers between QDs and LC phase because LC block copolymers with high degree polymerization

may have poor compatibility with low-molecular weight LCs. At the same time, diblock copolymers cannot form any bridges between nanoparticles because they have only one binding block. Indeed, as it was proved in our further investigation, QDs embedded in LC diblock copolymers containing PhM and VP blocks did not form any aggregates regardless of the polymerization degree of the diblock copolymers [25]. LC diblock copolymers thus appear more promising and flexible agents for stabilization of QD dispersions in LC phase than LC triblock copolymers.

Here, we aim to enhance our approach to design of hybrid CLC materials by means of the tuning the chemical structure of the LC block copolymer and their weight fraction in the system. For this purpose, we considered a series of test mixtures consisted of the low molecular weight CLC matrix and the LC diblock copolymers containing VP blocks of different polymerization degree and PhM block of the invariable length. We focused on optimization of the polymerization degree of VP block because this part of the diblock copolymers is amorphous and it is likely to have poor compatibility with CLC phase. In addition, we varied the weight fraction of diblock copolymers in the test mixtures to optimize optical properties of the test mixtures.

Experimental

Chloroform, *pyridine*, *4'-pentyl-4-biphenyl-carbonitrile* (5CB), and *2,6-di-tert-butyl-4-methylphenol* (BHT) were purchased from Aldrich. *Chloroform* was passed through aluminum oxide and distilled. *Pyridine* was dried over KOH and distilled over CaH_2 . RM257 (Fig. 1a) were purchased from Synthon. The synthesis of LC diblock copolymers was performed by reversible addition-fragmentation transfer polymerization as described previously [26]. CdSe/ZnS QDs covered with oleylamine and surrounded by TOPO matrix were synthesized according to a previous literature [27]. To prepare QDs coated with LC block copolymers a ligand exchange procedure was used [24]. In the course of this procedure, oleylamine on the surface of CdSe/ZnS QDs was replaced by pyridine which was exchanged to a LC block copolymer containing poly(vinylpyridine) block. HexSorb and ButSorb (Fig. 1, a) were synthesized as described previously [28].

The low molecular weight cholesteric LC matrix doped with LC block copolymers was prepared according to the following procedure. As example, for the CLC-10%VPx samples, RM257 (14.0 mg), 5CB (27.9 mg), HexSorb (1.60 mg), ButSorb (1.40 mg), BHT (0.15 mg) and a LC block copolymer (5.0 mg) were dissolved in 1 ml of *chloroform*. The obtained mixture was thoroughly stirred and dried under reduced pressure. Then, the mixture was placed into the 20 μm -thickness plane-parallel glass cell, both inner surfaces of which were coated with rubbed polyimide layer (ZLI 2650). Sample was annealed at room temperature for 48 h. The hybrid CLC material was prepared using the same procedure but instead of the block copolymer, CdSe/ZnS QDs decorated with LC block copolymer were added.

Polarizing optical microscopic (POM) observations were conducted on LOMO P-112 polarizing microscope equipped with CCD camera and Mettler TA-400 heating stage.

Absorbance spectra of the composites were recorded by Unicam UV-500 UV-Vis spectrophotometer. Fluorescence spectra were recorded using M266 au-

tomated monochromator/spectrograph (SOLAR Laser Systems, Belarus) equipped with CCD U2C-16H7317 (Ormins, Belarus), homemade light-collecting inverted system using 100X/0.80 MPLAPON lens (Olympus, Japan) and homemade confocal unit with two 100 mm objective lenses. Exciting light was cut off by Semrock 488-nm RazorEdge® ultrasteep longpass edge filters (Semrock, USA). Fluorescence of QDs was excited by KLM-473/h-150 laser (Plazma, Russia) operating at 473 nm. An incident light intensity was equal to 50 mW/cm^2 as measured with LaserMate-Q (Coherent) intensity meter.

Results and Discussion

To prepare a cholesteric matrix we used the mixture of two nematogenic compounds, 5CB and RM257, doped with two chiral additives, HexSorb and ButSorb (Fig. 1, a). The role of RM257 was to increase the isotropization temperature of the cholesteric matrix. The ratio between 5CB and RM257 was equal to 2:1 resulting in appropriate clear temperature [29].

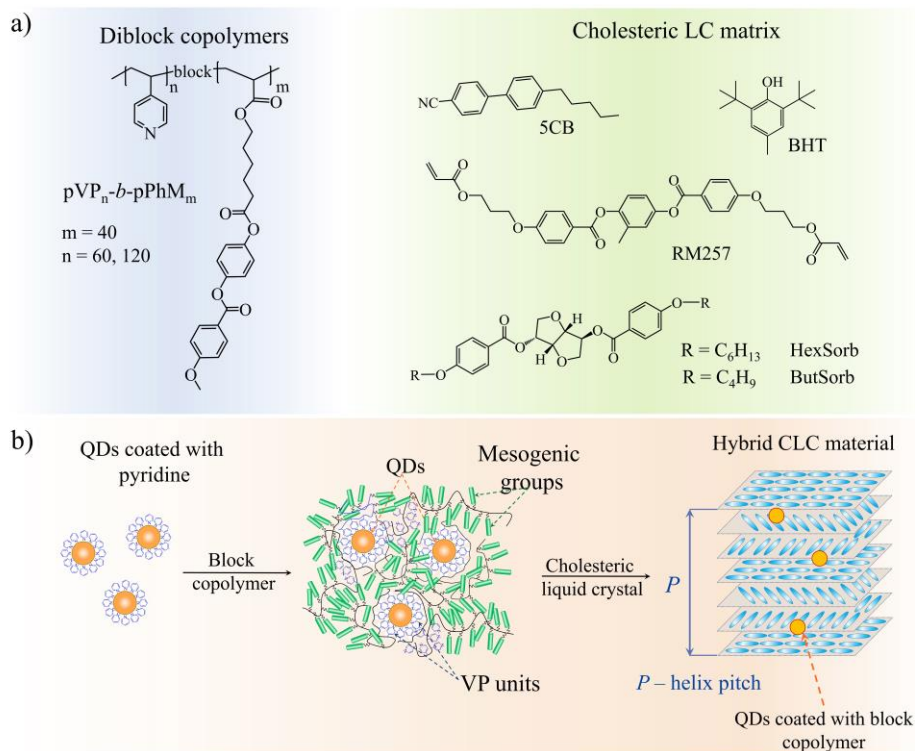


Fig. 1. The chemical structure of diblock copolymers and constituents of the CLC matrix (a), the schematic route of the preparation of hybrid CLC materials (b)

Two chiral additives were added to decrease the concentration of each of them due to their limited solubility in the cholesteric matrix. The total weight fraction of the chiral additives was 6 wt. % in all the prepared samples, which had the selective light reflection in the visible region of the spectrum. As RM257 is a cross-linkable compound inclined to a spontaneous polymerization, an inhibitor of radical polymerization, butylated hydroxytoluene (BHT), was included in the cholesteric matrix. The compositions of all the test mixtures are shown in Table 1. The test mixtures are marked as CLC- $w\%$ VP x , where w and x stand for the weight

fraction of a block copolymer and the polymerization degree of the VP block, respectively.

As seen from Fig. 1, *b*, the hybrid CLC materials were prepared by introducing CdSe/ZnS QDs decorated with the LC diblock copolymers in the CLC matrix. The same route was used for the test mixtures but instead of QDs coated with block copolymers, only the LC block copolymers were added. To study optical properties, the mixtures were placed in 20- μm -thickness cells because this type of samples is of interest for our future studies.

Table 1. The composition of the studied CLC samples

Sample	Weight fraction, %					
	5CB	RM257	Block copolymer	ButSorb	HexSorb	BHT
CLC	62.5	31.2	0	2.8	3.2	0.3
CLC-5 % VP x *	59.2	29.5	5.0	2.8	3.2	0.3
CLC-10 % VP x *	55.7	28.0	10.0	2.8	3.2	0.3

* $x = 60, 120$

According to POM, the initial CLC matrix has a planar texture with thin oily streaks, which are typical defects of the cholesteric phase (Fig. 2, *a*). Introducing either of the LC diblock copolymers provoked an increase in number of defects, as it can be seen for CLC-10%VP60 and CLC-10%VP120 (Fig. 2, *b* and *c*). The

texture of CLC-10%VP120 has an extremely dense network of oily streaks, which can cause substantial light scattering. CLC-10%VP60 shows a sparser network of oily streaks and dimensions of defect-free areas are not more than 100 μm .

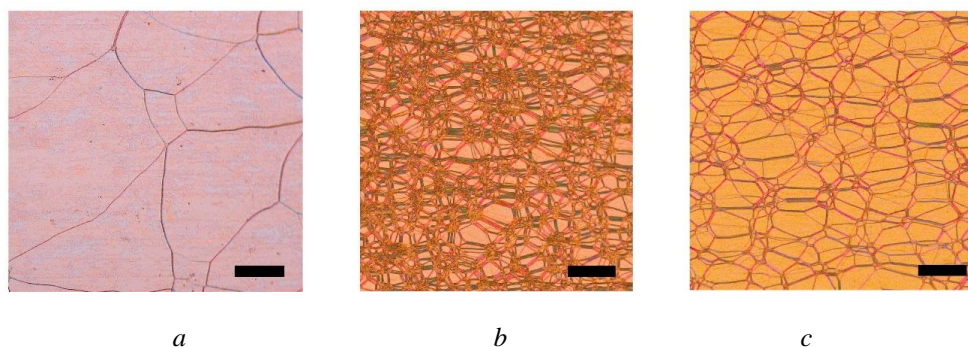


Fig. 2. POM images of (a) the CLC matrix and the samples (b) CLC-10%VP120, (c) CLC-10%VP60. Scale bar is 100 μm

As defects occupy appreciable volume of the samples, we tested CLC-5% VP60 and CLC-5% VP120 with the weight fraction of the diblock copolymers equal only to 5 wt. %. In the case of CLC-5% VP120, the texture is characterized by a dense network of oily streaks, which is the same as observed for CLC-10% VP120 (Fig. 3, *a*). Therefore, pVP₁₂₀-*b*-pPhM₄₀ appears to have poor compatibility with the CLC ma-

trix under examination. Strong incompatibility between pVP₁₂₀-*b*-pPhM₄₀ and the CLC matrix may be due to the high content of VP block in this diblock copolymer. Obviously, the amorphous VP block cannot be incorporated in the CLC phase without disturbance of the LC order. To put it in another way, the CLC phase should tend to eject the VP blocks, which is likely to be accumulated into defective areas.

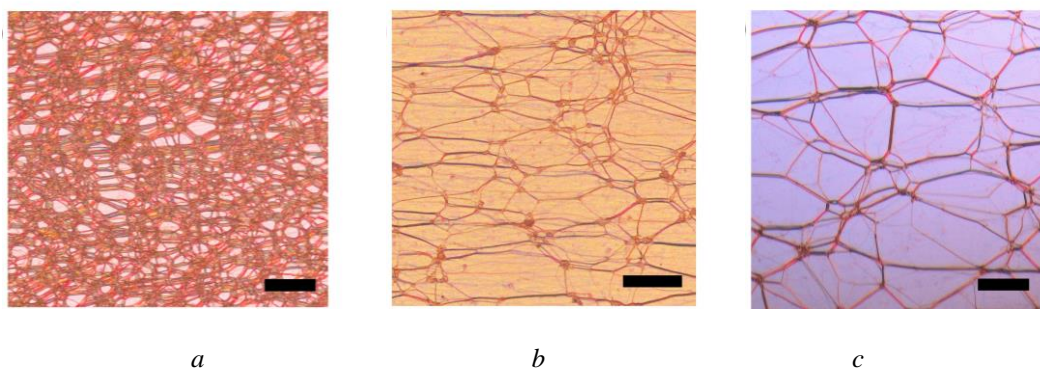


Fig. 3. POM images of the samples (*a*) CLC-5% VP120, (*b*) CLC-5% VP60, and (*c*) CLC-5% QDs@VP60. Scale bar is 100 μm

On the contrary, CLC-5%VP60 demonstrates quite sparse network of oily streaks with thickness of oily streaks being comparable with the initial CLC matrix (Fig. 3, *b*). This fact indicates that pVP₆₀-*b*-pPhM₄₀ has proper compatibility with the CLC matrix and it is more suitable as a ligand of QDs to prepare hybrid CLC materials. Note that we did not continue decreasing the weight fraction of the diblock copolymers because the fraction of them should be as high as possible to stabilize the high content of QDs.

All the test mixtures formed the cholesteric phase at room temperature as well as the initial CLC matrix, but the isotropization temperature of the test mixture was slightly higher than that of the CLC matrix (Table 2). This fact is supposed to be associated with the doping of the CLC matrix with PhM blocks, which have relatively high isotropization temperature equal to about 120 $^{\circ}\text{C}$ [30].

Table 2. Phase behavior and parameters of the selective light reflection of the CLC matrix and the test mixtures

Sample	Phase behavior*	λ_{max} , nm	FWHM**, nm
CLC	Ch 56 Iso	587	75
CLC-10% VP60	Ch 59 Iso	574	95
CLC-10% VP120	Ch 59 Iso	562	110
CLC-5% VP60	Ch 59 Iso	580	89
CLC-5% VP120	Ch 59 Iso	561	110

*Ch is a cholesteric phase and Iso is a isotropic melt.

**Full width at half maximum

Absorbance spectra of the test mixtures and the CLC matrix have a typical peak in the visible region of the spectrum, which corroborates the presence of the cholesteric phase (Fig. 4). The peaks of the test mixtures are blue-shifted in comparison with that of the initial CLC matrix, the shift being higher for the test mixtures containing pVP₁₂₀-*b*-pPhM₄₀ (Fig. 4, Table 2). This fact indicates that the higher weight fraction of VP block in LC block copolymers, the more pronounced blue shift observed. As the amorphous VP block cannot participate in the formation of cholesteric phase, the number of mesogenic groups per one molecules of the chiral additives should be higher for the

test mixtures containing pVP₁₂₀-*b*-pPhM₄₀ in compared with those containing pVP₆₀-*b*-pPhM₄₀. Consequently, the pitch of the helix structure should be shorter for the test mixture containing pVP₁₂₀-*b*-pPhM₄₀. Note that when the weight fraction of pVP₆₀-*b*-pPhM₄₀ is decreased, the test mixtures CLC-*w*%VP60 show the decrease in blue shift and full width at half maximum (FWHM) of the peaks. In other words, the peak of the selective light reflection becomes more similar to that of the initial CLC matrix. At the same time, both mixtures containing pVP₁₂₀-*b*-pPhM₄₀ have almost the same peak position and FWHM of their peaks.

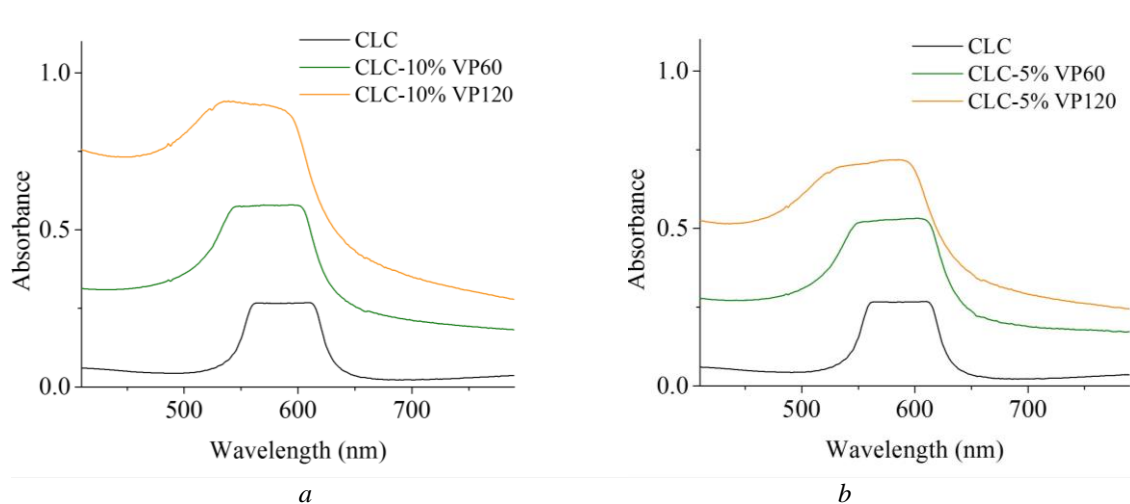


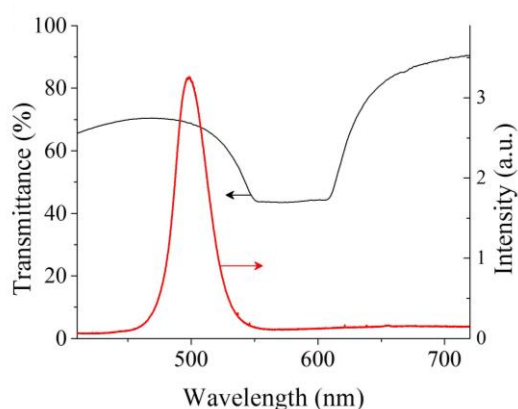
Fig. 4. Absorbance spectra of the initial CLC matrix and the test mixtures with the LC diblock copolymers

Besides blue shifting, the peak broadening in terms of FWHM is more pronounced for the mixtures doped with pVP₁₂₀-*b*-pPhM₄₀. This fact, along with the distortion of peak shape and strong light scattering, indicates that pVP₁₂₀-*b*-pPhM₄₀ has poor compatibility with the CLC matrix. These findings are in complete agreement with POM images, which indicate that introducing pVP₁₂₀-*b*-pPhM₄₀ gives rise to appearance of a strong network of oily streaks. On the contrary, the test mixtures with pVP₆₀-*b*-pPhM₄₀ demonstrate peaks with shape similar to the initial CLC mixture and relatively low light scattering. Therefore, this block copolymer was chosen for the preparation of hybrid CLC materials.

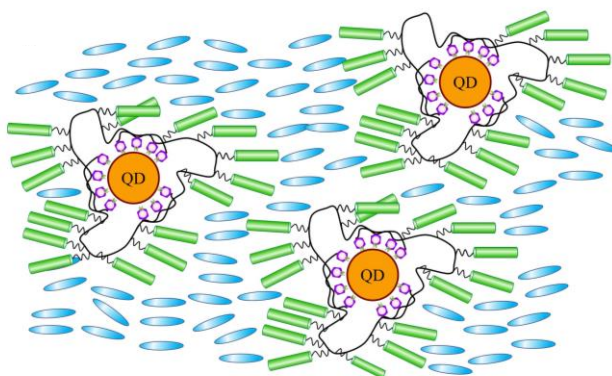
The hybrid CLC material CLC-5%QDs@VP60 was prepared similar to the test mixtures but instead of a LC block copolymer, an LC polymer-QD composite was added. The LC polymer-QD composite was made of the LC diblock copolymer pVP₆₀-*b*-pPhM₄₀ and CdSe/ZnS QDs as described previously [25]. Relying on the properties of the test mixtures discussed above, the weight fraction of the LC polymer-QD composite in CLC-5%QDs@VP60 was taken equal to 5 wt. %. Since the LC polymer-QD composite contained 20 wt. % of QDs, we reached 1 wt. % of QD loading in the hybrid CLC material.

As determined by POM, CLC-5%QDs@VP60 is characterized by a typical texture with oily streaks confirming the formation of the CLC phase (Fig. 3, *c*). The obtained POM image contains large defect-free areas, which have dimensions up to several hundreds of micrometers. Absorbance spectrum of CLC-5%QDs@VP60 demonstrates the fine peak in the visible region of the spectrum with $\lambda_{\text{max}} = 579$ nm and FWHM = 85 nm (Fig. 5, *a*). The obtained peak parameters are close to those of CLC-5%VP60 pointing out that QDs are successfully embedded in the cholesteric phase. At wavelengths outside the photonic band gap, transmittance is as high as 90 % indicating

quite low light scattering of this sample. Note that CLC-5%QD@VP60 shows lower intensity of light scattering as opposed to the test mixtures doped with pVP₆₀-*b*-pPhM₄₀. This fact may be associated with the structuring impact of QDs. Indeed, as VP blocks tend to be bound to the QD surface, the block copolymer pVP₆₀-*b*-pPhM₄₀ should form a shell around QDs (Fig. 5, *b*). Outside of this shell is decorated with mesogenic PhM groups, which conceal the VP block from the CLC matrix. Being shielded by PhM groups, the some parts of VP blocks cannot induce oily streaks and lower light scattering thus is observed.



a



b

Fig. 5. Absorbance and fluorescence spectra (*a*) and the proposed schematic representation of the inner structure of the hybrid CLC material CLC-5%QDs@VP60 (*b*) (for simplicity the cholesteric helix is omitted)

Under irradiation with a blue laser ($\lambda_{\text{ex}} = 473$ nm, $I = 200 \text{ mW cm}^{-2}$), the samples of CLC-5%VP60 demonstrate light emission due to the presence of QDs. Therefore, the obtained hybrid CLC material combines optical features of cholesteric phase and fluorescent properties of QDs. The emitted light is unpolarized because the peak of fluorescence and the spectral position of the photonic band gap do not match in the prepared hybrid CLC material. To overlap them, the concentration of the chiral additives should be adjusted properly in hybrid CLC materials. If overlapping between fluorescence spectrum and the photonic band gap happens, resonance between emitted light and cholesteric microcavity can be achieved and fine controlling of light emission can be realized [31]. Tuning the spectral position of the photonic band gap with

external fields, one can control the wavelength of the emission, its polarization state and intensity [14]. In addition, taking into account the high QD loading, our hybrid materials may be considered as a promising media for lasing. These phenomena will be the focus of our attention in the further studies.

Conclusions

In the present paper, we have attempted to enhance our approach to the preparation of hybrid materials that are based on inorganic CdSe/ZnS QDs and organic CLC matrix. This enhancement was to find the optimal weight fraction and chemical structure of LC diblock copolymers that provide compatibility between QDs and CLC matrix.

The LC diblock copolymers were consisted of polydentate ligand block of poly(vinylpyridine) and LC block containing phenyl benzoate groups. For optimization purposes, we have prepared and studied a series of test mixtures based on CLC matrix doped with LC diblock copolymers. Investigation of these test mixtures allowed optimal polymerization degree of poly(vinylpyridine) block and their weight fraction to be determined. The polymerization degree of poly(vinylpyridine) block was varied from 60 to 120 monomer units and the weight fraction of block copolymers was 5 or 10 wt. %. It was found that the block copolymer with long poly(vinylpyridine) block induced dense network of oily streaks in the CLC matrix resulting in strong light scattering. At the same time, the test mixtures containing the block copolymer with shorter poly(vinylpyridine) block had sparse network of oily streaks and low light scattering, especially at the weight fraction equal to 5 wt. %. Taking into account these results, we prepared the hybrid CLC material with the high QD loading equal to 1 wt. % that combine the fluorescence properties of QDs and the optical features of CLCs. Note that the obtained hybrid CLC materials were characterized by lower light scattering in comparison with the test mixtures that is likely to be due to the structuring impact of QDs on LC block copolymers. These findings is supposed to extend the potentials of the designing hybrid LC systems being promising materials for optical applications and fundamental research.

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