

The Solvent Effect on Nanomaterials Composed of Liquid Crystals and Nanoparticles: uv-vis Absorbance and Fluorescence Spectra

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Abstract: We have been investigated in different solvent medium to interactions between 4-Ethoxybenzoic acid (4EOBA), 4-Pentylbenzoic acid (4PentBA), and 4-Pentylphenyl 4-Methylbenzoate (4PP4MetB) liquid crystals with CdS, CdSe and ZnS nanoparticles. For this, the new materials composed from LC compound including the solvent and nanoparticle were investigated by use absorbance and fluorescence spectra. Electronic transitions and differences in absorbance and fluorescence spectra were interpreted. The fluorescence of liquid crystals has been defined in the shifts between wavelengths of the fluorescence of nanomaterials. It can be said that it has occurred blue shift at the maximum fluorescence wavelengths of the 4EOBA-CdS-DMSO and 4EOBA-CdSe-DMSO compared to 4EOBA-DMSO. On the other hand, we can say that in the 4EOBA-ZnS-DMSO solution occurs red shift in the fluorescence band, while the peaks seen in the fluorescence band occur in result of interaction of liquid crystals and nanoparticles.

Key words: Fluorescence spectrum, liquid crystals, nanoparticles, solvent effect, nanomaterials.

Sıvı kristaller ve Nanoyapılardan Oluşan Nanomalzemeler Üzerine Çözücü Etkisi: uv-vis Absorbans ve Floresans Spektrumları

Öz: 4-Etoksibenzoik asit (4EOBA), 4-Pentilbenzoik asit (4PentBA) ve 4-Pentilfenil 4-Metilbenzoat (4PP4MetB) sıvı kristaller ve CdS, CdSe ile ZnS nanopartikülleri arasındaki etkileşimleri farklı çözücüler içerisinde incelenmiştir. Bunun için çözücü ve nanopartikül içeren LC bileşiklerden oluşan yeni malzemelerin absorbans ve floresans spektrumları kullanılarak incelenmiştir. Absorbans ve floresans elektronik geçişleri yorumlanır. Sıvı kristallerin floresansı, nanomalzemelerin floresansının dalga boyları arasındaki kaymalarda incelenmiştir. 4EOBA-CdS-DMSO ve 4EOBA-CdSe-DMSO'nun maksimum floresans dalga boylarında 4EOBA-DMSO'ya göre maviye kayma meydana geldiği söylenebilir. Öte yandan, 4EOBA-ZnS-DMSO çözeltisinde, floresan bandında kırmızıya kayma meydana gelirken, floresan bandında görülen tepe noktaları, sıvı kristaller ve nanopartiküllerin etkileşim meydana geldiğini söyleyebiliriz.

Anahtar Kelimeler: Floresans spektrumu, sıvı kristaller, nanoparçacıklar, çözücü etkisi, nanomalzemeler.

1. Introduction

Liquid crystals in the phase diagram appear as an interphase between solid crystals and liquids. These materials are called liquid crystals because they show the properties of both solid crystals and liquids [1]. In that, liquid crystals are interesting due they are fluid and have a long-range order. At this long distance, the position and orientation of the building blocks of liquid crystals are interrelated [2]. Liquid crystalline compounds have a molecular structure with p-conjugates such as fused benzene and cyclopentadiene rings. These liquid crystals result in delocalized p orbitals of conjugates that facilitate charge transfer to gain or lose electrons. With the realization of intermolecular charge transfer, the materials become organic semiconductors and carry the charge [3]. Liquid crystals are divided into lyotropic and thermotropic. They are formed when more than one substance forms a solution in lyotropic liquid crystals. Thermotropic liquid crystals, on the other hand, are the type formed by temperature change [4]. The structures of liquid crystals can change with external stimuli. Temperature change or low voltage electric fields are the factors that cause this change. Liquid crystals that respond easily to external stimuli are used in many display technologies [5]. Depending on the structure and properties of liquid crystal molecules, they can also interact with nanoparticles and cause their fluorescence to change [6]. It has been previously reported in many studies that nanoparticles cause changes on different properties of liquid crystal compounds [7-9]

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The physical properties of materials in bulk can change when materials are reduced to nano-sizes. Studies are showing that when the size of semiconductor nanoparticles is below 5 nm, their electro-optical properties change [10, 11]. The optical and physical properties of materials with nanometer dimensions can vary depending on the size of these materials. The physical and chemical properties of materials occur when the particle size reaches the nanometer level. For a material to be defined as a nanomaterial, it must have a particle size between 1 nm and 100 nm [12, 13]. It has been reported that a wide photonic band gap of CdSe/ZnS nanoparticles doped into cholesteric liquid crystals is formed and these materials are used in optoelectronic applications [14].

The aim of this study is to examine possible interactions with nanostructures and liquid crystal compounds and to determine electronic structure by observing electronic changes and looking at changes in spectra. So, we have been investigated the interactions and electronic transitions between liquid crystals which is including benzoic acid and benzoate structures, and CdS, ZnS and CdSe semiconductor nanoparticles. In addition, we are by examining the absorbance and fluorescence spectra of nanomaterials formed from nanoparticles with liquid crystal; it is aimed to interpret the electronic structures of both nanoparticles and nanomaterials. In addition, solvent effects on nanoparticle have been determined with using electronic absorbance and fluorescence spectrum in different solvent medium.

2. Materials and methods

2.1. Used liquid crystals materials

Liquid crystals of 4-Ethoxybenzoic Acid (4EOBA), 4-Pentylbenzoic Acid (4PentBA), and 4-Pentylphenyl 4-Methylbenzoate (4PP4MetB) used in this study are of high purity. The molecular structures of these liquid crystals are shown in Figure 1. Methanol, Toluene and DMSO solvents are spectroscopic grade. Both the solvents used and the liquid crystal compounds used were taken from Sigma-Aldrich.

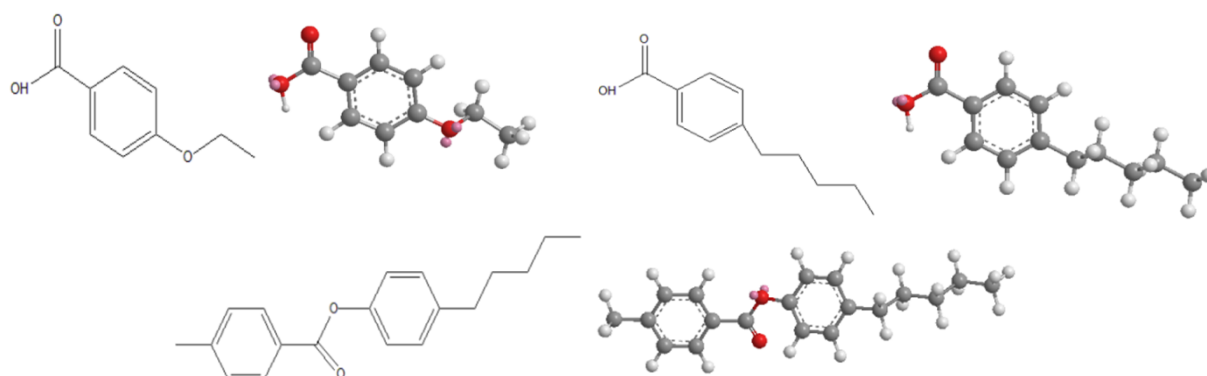


Figure 1. The molecular structure of investigated liquid crystals.

2.2. Syntheses and characterized of nanoparticles

2.2.1. ZnS synthesis and characterize

In a typical process, 100 ml of an aqueous solution containing 0.1 M of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and Na_2S were put into 250 ml of an ethanol solution containing citric acid (10 ml) and methacrylic acid (5 g). The resultant solution was then cooled to room temperature and refluxed under N_2 for several hours. The resulting powders were separated by centrifuging, and then dried at room temperature in a vacuum. XRD graph of ZnS nanoparticles has been shown in Figure 2.

2.2.2. CdS synthesis and characterize

In a typical process, 100 ml of an aqueous solution containing 0.1 M of $\text{Cd}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ and Na_2S were put into 250 ml of an ethanol solution containing citric acid (10 ml) and methacrylic acid (5 g). The resultant solution was then cooled to room temperature and refluxed under N_2 for several hours. The resulting powders were separated by centrifuging, and then dried at room temperature in a vacuum. The XRD graph of CdS nanoparticles have been shown in Figure 2.

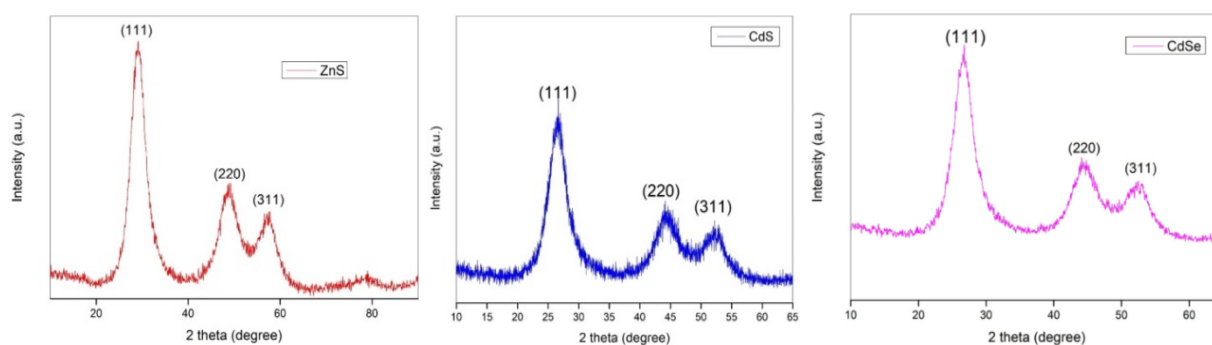


Figure 2. XRD graphs of ZnS, CdS and CdSe nanoparticles

2.2.3. CdSe synthesis and characterize

The cadmium supply was cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$), and the selenium source was sodium selenosulfate (Na_2SeSO_3). The pH of the aqueous mixture of mercapto acetic acid (HSCH_2COOH) and cadmium acetate (2 mmol) was adjusted to 10 by adding a 1 M solution of sodium hydroxide. N_2 bubbles were used to dehydrate the solution for 30 minutes. The sodium selenosulfate solution (Na_2SeSO_3) was made by combining the cadmium acetate solution with freshly made Se powder (0.02 mol) and Na_2SO_3 solution (0.2 mol). After that, 2-propanol was added drop by drop while the mixture was being stirred till it turned turbid. To obtain the dry powder, the precipitate was separated using centrifugation. The XRD graph of CdSe nanoparticles has been shown in Figure 2.

2.3. Experimental methods

We have been used in 4-Ethoxybenzoic Acid (4EOBA), 4-Pentylbenzoic Acid (4PentBA), and 4-Pentylphenyl 4-Methoxybenzoate (4PP4MetoxB) liquid crystals. We made the liquid crystals into solutions with 10^{-5} M in methanol, toluene and DMSO solvents. The CdS, CdSe, and ZnS nanoparticles have been used in our study. These nanoparticles have been prepared as about 2×10^{-4} M in DMSO, 1.3×10^{-4} M in Toluene and 1.6×10^{-4} M in methanol solvent. As a result, we have readied liquid crystals and nanoparticles solution, by taking 1 ml of nanoparticle solutions from 9 ml of liquid crystal solutions. The absorbance and fluorescence spectra have measured using the Perkin Elmer Lambda-35 UV-vis spectrophotometer and Perkin Elmer LS-55 fluorescence spectrophotometer.

3. Results and Discussion

3.1. The absorbance spectra of nanoparticles

The absorbance-wavelength and $\alpha h\nu$ -energy graphs of CdS, CdSe, and ZnS nanoparticles are shown in Figure 3-5, respectively. The band gaps of synthesized semiconductor nanoparticles using the Tauc equation given in Equation 1 were calculated as 3.34 eV for CdS, 2.73 eV for CdSe, and 4.30 eV for ZnS, respectively.

$$\alpha h\nu = B \cdot (h\nu - E_g)^p \quad (1)$$

Here, $h\nu$ is the energy of the incident light, E_g is the band gap value, B is a unit less constant expressing the transition probability between energy levels, and p is a unit less constant whose value is 0.5 for direct transitions and 2 for indirect transitions [15-16].

The most important observation obtained as a result of absorbance measurements is that the forbidden energy gaps calculated for the synthesized CdS, CdSe, and ZnS nanoparticles are larger than the bulk forbidden energy gaps of these materials. The bulk forbidden energy range for CdS is 2.42 eV, the bulk forbidden energy range for CdSe is 1.74 eV, and the bulk forbidden energy range for ZnS is 3.56 to 3.76 eV. As the band gap of the synthesized semiconductor quantum dots increases due to the quantum confinement effect, it can be said that the crystallite size of these materials are very small.

3.2. The solvent effect on nanoparticle

The graphs and data of nanoparticles obtained by fluorescence and absorbance spectrum are given in figures 3-5 and tables 1-3, respectively. These solvents which non-polar toluene, polar protic methanol and polar aprotic DMSO solutions are were used in this study to examine the changes between the electronic transitions in nanoparticles.

While taking fluorescence measurements of these nanoparticles, the excitation wavelength values were taken as 370 nm or 380 nm. It has been reported in previous studies that the absorption spectra of synthesized CdS nanoparticles were obtained in DMSO solution with a sharp peak at 327 nm and a shoulder peak at 346 nm [17]. We have been found as 335 nm wavelength in DMSO at room temperature. The have observed two different bands in the fluorescence spectrum of CdS nanoparticle in DMSO solvent are at 388 and 412 nm, while it has been observed fluorescence bands as 420, 440, and 470 nm.

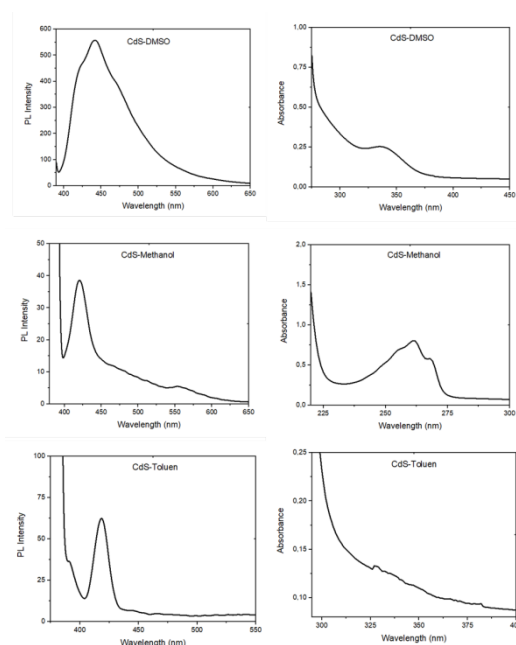


Figure 3. Absorbance and fluorescence spectra of Cadmium Sulfide (CdS) nanoparticle.

Table 1. The absorbance and fluorescence spectra CdS particle.

Solvent	(Excitation Wavelength, 370 nm)	Fluorescence Wavelength	Absorbance Wavelength
DMSO		420-440-470	335
Methanol		420-554	255-261-268
Toluene		391-420	327

As seen in Figure 3, absorbance spectra of CdS nanoparticles dissolved in methanol were observed at 255, 261, and 268 nm, while PL spectra were observed at 420 and 554 nm. In the previous study of CdS nanoparticles [18], the absorbance and fluorescence spectra of CdS in Toluene were found to be approximately 403.7 and 411 nm, and we have observed to 576 nm of CdS nanoparticles in toluene solvent. The UV-vis spectrum generally

decreases with the size of the nanocrystals and the absorption maximum wavelength decreases with the particle size [19]. CdS nanoparticles have unique properties due to their size and shape. It is widely used in fields such as biosensors, bioimaging, nanomedicine, molecular pathology, antimicrobial activities, photovoltaic cells, semiconductors, and drug delivery. It has been reported in the literature that CdS nanoparticles have a strong absorbance band at 420-440 nm in their UV-vis spectra. It is reported that 512 nm (2.42 eV) is the absorption limit for bulk hexagonal CdS [20].

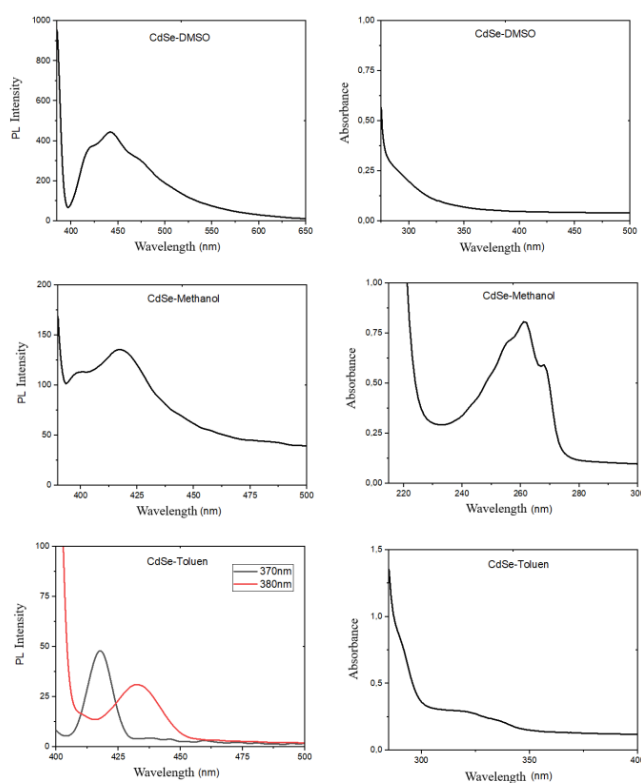


Figure 4. Absorbance and fluorescence spectra of Cadmium Selenide (CdSe) nanoparticle.

Table 2. The absorbance and fluorescence spectra CdSe particle.

Solvent	(Excitation Wavelength, 370 nm)	Fluorescence Wavelength (nm)	Absorbance Wavelength (nm)
DMSO		420-441-470	381
Methanol		400-417	256-261-268
Toluene		417	318-336
Toluene (380 nm)		432	

Electronic absorbance and fluorescence spectra of CdSe nanoparticles in DMSO, methanol, and toluene solvent are shown in Figure 4. Data about these measurements are given in Table 2. Semiconductor CdSe nanoparticles have been widely studied. The absorption spectrum of very small CdSe nanoparticles shifted from 402 nm to 417 nm depending on the size [11]. In our study, it has an absorbance band observed between 256-382 nm. The UV-Vis absorption spectra in previous studies for CdSe were observed in at 360 nm and 385 nm. In this study, an absorption band was observed at 382 nm in DMSO. It is known to have an absorbance band of 385 nm, so it can say as 5.4 nm for CdSe nanoparticle which is smaller than the Bohr radius [21]. Thus, we can say that the CdSe nanoparticle used in this study is around 5 nm. In the study by Ashtoputre [22] et al., a strong peak

at 435 nm and a weak peak at 414 nm were observed when the excitation peak was 362 nm, while a broad peak at 581 nm and a different peak at 437 nm was observed when the excitation peak was 371 nm. Here, a broad band was observed at 420, 441, and 470 nm in DMSO solvent at the excitation wavelength of 370 nm, while a peak was observed at 400 and 417 nm in methanol solvent. In toluene solvent, there are fluorescence bands at both 370 nm and 380 nm excitation values, which we observe in 417 and 418 nm wavelength.

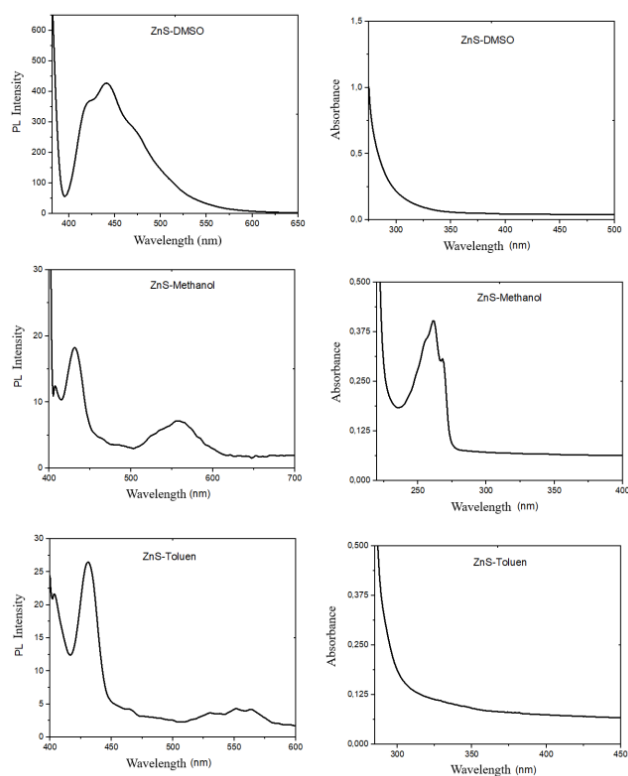


Figure 5. Absorbance and fluorescence spectra of Zinc Sulfide (ZnS) nanoparticle.

Table 3. The absorbance and fluorescence spectra ZnS particle.

Solvent	(Excitation Wavelength, 370 nm)	Fluorescence Wavelength (nm)	Absorbance Wavelength (nm)
DMSO		422-440-468	382
Methanol		431-557	256-261-267
Toluene		403-431-464-530 551-564	382

The absorbance and fluorescence spectra of ZnS nanoparticles in toluene, DMSO, and methanol are given in Figure 5, while the data of these spectra are given in Table 3. The ZnS nanoparticles give good absorption between 220-350 nm [23]. Generally, while ZnS absorbs around 300 nm, a blue shift occurs when bulk ZnS absorbs up to the 345 nm limit. As seen in Table 3, a wide band was observed in the absorbance spectrum for ZnS at 382 nm in DMSO, in addition, electronic absorbance bands in methanol solvent of ZnS nanoparticle have been found as 256, 261 and 267 nm. In toluene, the absorbance spectrum was observed at 382 nm.

Biswas et al. [24], Tamrakar et al. [25], and Chen et al. [26] have been found as about 400 nm in photoluminescence spectra of ZnS nanostructures. Chen et al. have compared the results with that of bulk. In this study, ZnS nanoparticles including methanol solvent have been found as about 422-440 nm as dependent

solvent, which is methanol, DMSO and toluene. Other fluorescence bands are observed to wavelength changed between 468-564 nm.

The reason for the change in absorbance and fluorescence bands of semiconductor nanoparticles due to solvent is that it can cause a change in the semiconductor band of NPs with solvent polarity. Radius lengths of very small nm show a three-dimensional quantum size effect in the electronic structure of semiconductor nanoparticles. The effect of quantum size on band gap absorption energy can be measured by UV-Vis absorbance spectroscopy.

3.3. The interaction between nanoparticle and LC compounds

Here, we have studied spectroscopic properties of doped nanoparticles in LC compounds for investigated possible interactions between nanoparticles with investigated LC compounds, in addition, so, we used liquid crystals and nanoparticles-doped liquid crystals in the same solvent environment. The graphs of fluorescence measurements of the analyzed 4EOBA, 4PentBA and 4PP4MetB LCs and the samples to which CdS, CdSe and ZnS nanoparticles were added are shown in Figures 6, 7 and 8, respectively. We set out to evaluate the fluorescence graphs of a new solution formed by nanoparticles added separately to liquid crystals and the changes in maximum wavelengths based on liquid crystals are listed in Tables 1, 2 and 3.

It is seen in Figure 6 that the maximum wavelengths of 4EOBA-CdS-methanol and 4EOBA-CdSe-methanol solutions consisting of nanoparticles added separately to liquid crystals in solvent media are almost the same.

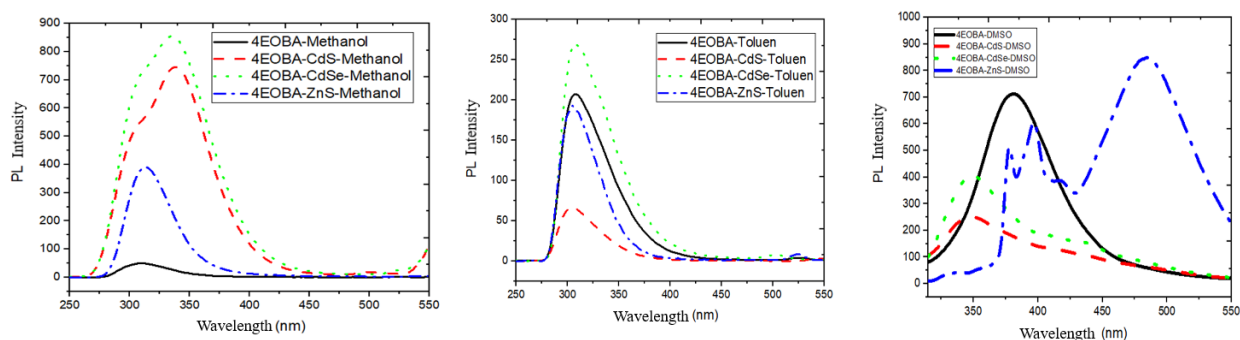


Figure 6. Fluorescence spectra of 4EOBA liquid crystal doped nanoparticles and 4EOBA liquid crystal in solvent environments.

The maximum wavelength of these nanoparticle-doped liquid crystals has a shift of approximately 25 nm compared to that of liquid crystals. In the resulting 4EOBA-ZnS-methanol solution, there is no shift compared to the liquid crystals.

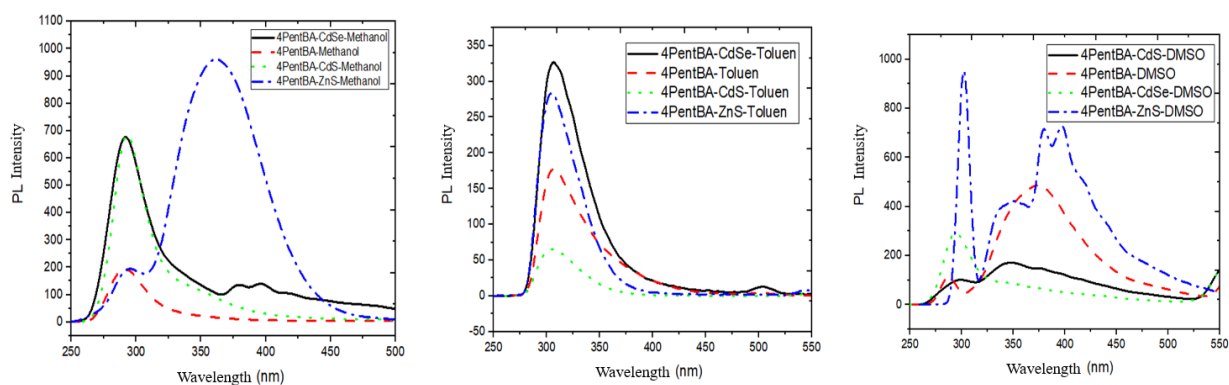


Figure 7. Fluorescence spectra of 4PentBA liquid crystal doped nanoparticles and 4PentBA liquid crystal in solvent environments.

It is seen that the fluorescence graphs of the liquid crystal and nanoparticle-doped liquid crystals are similar when the solvent is toluene in 4EOBA liquid crystal. As can be understood here, it has been observed that there is no interaction between liquid crystals and nanoparticles in toluene solutions.

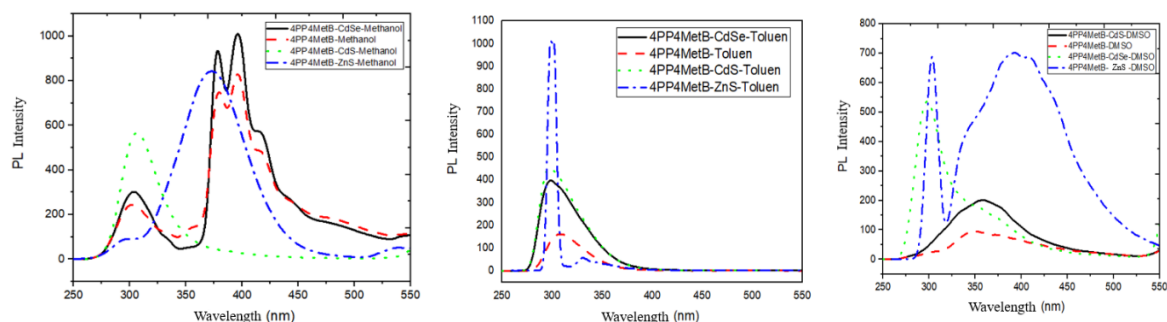


Figure 8. Fluorescence spectra of 4PP4MetB liquid crystal doped nanoparticles and 4PP4MetB liquid crystal in solvent environments.

The fluorescence graphs of the new 4EOBA-CdS-DMSO and 4EOBA-CdSe-DMSO solutions, which are formed by nanoparticles added separately to the 4EOBA-DMSO solution, are similar and their maximum wavelengths are the same. The maximum wavelength of the new 4EOBA-ZnS-DMSO solution formed by the ZnS nanoparticle added to the 4EOBA-DMSO solution has shifted compared to the liquid crystalline solution. Fluorescence graphs and maximum wavelengths of 4PentBA-CdS-methanol and 4PentBA-CdSe-methanol solutions formed by nanoparticles added separately to 4PentBA liquid crystal overlap. However, a shift of about 70 nm occurred in the maximum wavelength of the 4PentBA-ZnS-methanol solution. No significant difference was observed in the fluorescence graphs and maximum wavelengths of the nanoparticles added individually to the 4PentBA-toluene solution. Thus, we can say that 4PentBA liquid crystal and nanoparticles do not interact in the environment where toluene is used as a solvent. Different fluorescence graphs appeared in all new solutions formed with nanoparticles added separately to the 4PentBA-DMSO solution. 4PentBA liquid crystal and nanoparticles interacted in the DMSO solution. The maximum wavelengths are similar to the fluorescence graph of 4PP4MetB-methanol solution and 4PP4MetB-CdSe-methanol which is one of the new solutions formed by nanoparticles added separately to the 4PP4MetB-methanol solution. The maximum wavelength of the 4PP4MetB-ZnS-methanol solution creates a shift of about 43 nm concerning the liquid crystal solution. The new 4PP4MetB-CdS-methanol solution, on the other hand, showed a shift in the maximum wavelength compared to the liquid crystalline solution. It was observed that the fluorescence graphs of 4PP4MetB-CdS-toluene and 4PP4MetB-CdSe-toluene solutions obtained from the new solutions consisting of nanoparticles added separately to the 4PP4MetB-toluene solution were similar to each other. In the fluorescence graph obtained from the 4PP4MetB-ZnS-toluene solution, there was a 22 nm shift in the maximum wavelength compared to that of 4PP4MetB-toluene solution. We have seen that the 4PP4MetB-CdS-DMSO solution, which consists of nanoparticles added separately to the 4PP4MetB-DMSO solution, has a similar fluorescence graph to the liquid crystal solution. Maximum wavelength shift occurred in the 4PP4MetB-CdSe-DMSO solution compared to the 4PP4MetB-DMSO solution. In the 4PP4MetB-ZnS-DMSO solution, a wide peak was observed after the excitation peak. In the environment where methanol is used as a solvent, liquid crystals and solutions with CdS and CdSe nanoparticles interact and the electronic structure of the new solutions formed has changed. The change in the fluorescence graph of the new solutions formed and the difference in the maximum wavelengths are an indication that the charge transfers have taken place. In the environment where toluene was used as a solvent, there was generally no interaction between liquid crystals and nanoparticles. The fluorescence graph and maximum wavelengths of nanoparticle-doped liquid crystals are similar to liquid crystals. From investigated fluorescence spectra has different only in the 4PP4MetB-ZnS-Toluene solution. In the environment where DMSO is used as a solvent, interactions and charge transfers between liquid crystals and nanoparticles are seen from fluorescence graphs. The shifts observed in the maximum wavelengths of nanoparticle-doped liquid crystals compared to liquid crystals indicate that the energy band gaps also change. We can say that liquid crystals and nanoparticles can generally interact in a suitable solvent environment. Among the possible consequences of these interactions is the change of electronic structure with the realization of charge transfers.

Conclusions

In this study, fluorescence and absorbance spectra of nanomaterials consisting of liquid crystals and nanoparticles in solvents were investigated. In general, we observed that nanoparticles and liquid crystals do not interact in the toluene solvent. Solvent polarity may be the reason why the nanoparticle does not interact with liquid crystals in toluene. We can use the dielectric constant to compare the solvent polarity. Therefore, the values of the toluene solvent are 2.38, the values of the methanol solvent are 32.66 and the values of the DMSO solvent are 46.45 [27]. In addition, when looking at the types of solvents used, methanol is polar protic, DMSO is polar aprotic, and toluene is non-polar solvent. However, we observed interaction in the 4PP4MetB-ZnS-Toluene nanomaterial. The electronic structure of newly formed nanomaterials has changed. By changing the electronic structure, new nanomaterials with different optical and electronic properties can be obtained.

Observing the fact that different structure properties of nanoparticles have changed absorbance and fluorescence spectra, we can conclude that the solvent-solute interactions have been effected.

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