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# The study on determination interactions between liquid crystals and nanoparticle: Fluorescence spectra of nanoparticle-doped liquid crystals

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**Abstract -** Liquid crystals are compounds interesting molecular structures between the solid state and the liquid state. Nanoparticles are materials whose physical and more different properties change depending on the nano-particle size. In this study, interactions between ZnS, CdSe and CdS nanoparticles with 4-Penthylphenyl 4-Methoxybenzoate (4PP4MetoxB), 4-Pentilphenyl 4-Pentilbenzote (4PP4PentB) and 4-Penthylphenyl 4-(Octyloxy)Benzoate (4PP4OctoxB) were have been investigated determined by using fluorescence spectra in different solvent medium. The motivation of the study can determine the possible interactions of liquid crystals and nanoparticles. We have been observed to difference fluorescence spectra in different medium of new compose nanomaterials. So, it can be said that there are interactions between nanoparticle with liquid crystals. It can be said that possible interactions between 4PP4OctoxB liquid crystal and nanoparticles have been done more interactions than other LCs molecules. Solvents used in this study are DMSO (Polar aprotic), Methanol (polar protic) and Toluene (non-polar). Except for toluene, it can be said that nanoparticle-doped liquid crystals interact in two solvent environments.

**Keywords:** Liquid crystals, nanoparticles, fluorescence spectra, solvent effect, nanomaterial

## 1. Introduction

Liquids with a specific positional and orientational order are defined as liquid crystals [1]. Molecular structures of liquid crystals (L.C.) have fluidity with a long-range order that can act together. In addition, these self-organizing molecules are interesting materials with unique optical, electrical, and magnetic properties [2]. The discovery of liquid crystals was made by studying cholesteryl benzoate, which has two melting points and birefringence. Liquid crystals are called liquid crystals because they are between a solid state and a liquid state and show both crystal and liquid properties [3]. The molecular structures of liquid crystals are anisotropic and can interact with external fields and surfaces [4]. Liquid crystals are basically divided into two main groups thermotropic and lyotropic. The main parameter of thermotropic liquid crystals is temperature and they are composed of individual molecules and do not need another molecule for the formation of the liquid crystal phase [5]. Lyotropic liquid crystals form their molecular structures in the liquid crystal phase under the influence of solvents and consist of multiple molecules [6]. Weak external effects can significantly change the molecular structure of liquid crystals. Due to this sensitivity to external effects, they are used in application areas such as biomedical detectors from display technology [7].

The size of nanomaterials ranges from 100 nm (nanometer) to 1 nm and varies according to their size and shape. It is possible to synthesize nanomaterials of various shapes and sizes from different materials. Many nanomaterials show luminescence depending on their size. The production of small-sized electronic materials has caused semiconductor nanoparticles in nanomaterials to attract more attention from researchers [8]. Nano-sized particles are interesting materials due to their unique properties and ability to be synthesized in different sizes. It has also been reported that the physical

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and chemical properties of materials change when the size of the materials is reduced to the nm scale [9], [10]. Nano-sized materials have significant differences compared to bulk materials. Control over these nanomaterials will also enable them to be used in important technological applications [11].

There are studies on doping nanomaterials with different properties and molecular structures into liquid crystals. In these studies, optical-electronic changes, photoluminescence depending on size, and improved diffraction efficiency results were obtained from doping nanoparticles into liquid crystals [12]. It can be said that advanced photoluminescence and electronic-optical properties develop with nanoparticles in applications where liquid crystal materials are used. The doping of liquid crystals with nanoparticles may have caused the development of dielectric permeability and spontaneous polarization of material [13], [14].

The molecular structure of nanoparticles added to liquid crystals tries to form an aligned and regular structure and allows electron transfer to occur more easily in photovoltaic cells, which is one of the application areas of liquid crystal nanoparticles [15]. There are studies for the use of liquid crystal nanoparticles in display technology, which is another application area. These studies varied according to the size of the nanoparticles and the method of doping. There are studies where it is reported that the threshold voltage decreases with liquid crystal nanoparticle materials [16]. Both liquid crystals and nanoparticles are materials that have been studied with interest by researchers. The important reason for the interest in these materials is due to their molecular structures. In this study, the fluorescence spectra of new materials formed by combining liquid crystals and nanoparticles dissolved in three different organic solvents were investigated. While making this study, a comparison was made with the fluorescence spectra of liquid crystalline solutions. Energy band gaps (Eg) of the synthesized nanoparticles were found by the Tauc method [17], [18]. Here, electronic emission transitions are investigated in detail in order to determine the possible interactions of liquid crystals and nanoparticles. Thus, it is aimed to have information about the electronic behavior of nanomaterials.

## 2. Materials and Methods

### 2.1. Materials

The 4-Penthylphenyl 4-Methoxybenzoate (4PP4MetoxB), 4-Penthylphenyl 4-Penthylbenzote (4PP4PentB) and 4-Penthylphenyl 4-(Octyloxy)Benzoate (4PP4OctoxB) liquid crystals purchased from Sigma-Aldrich were used in this study. It can bee seen from Figure 1 to molecular structures of 4PP4MetoxB, 4PP4PentB and 4PP4OctoxB liquid crystals. The liquid crystals in figure 1 were drawn using ChemOffice programs. The nanoparticles used in the study are CdS, CdSe and ZnS. The synthesis and characterization of these nanoparticles are as given in the references [19]–[21].

### 2.2. Experimental Methods

Liquid crystals were prepared in $10^{-5}$ M solution of methanol, toluene and DMSO in solvents with different properties such as polarity and polarizability. CdS, CdSe and ZnS nanoparticles have been prepared as about $2x10^{-4}$ M in DMSO, $1.3x10^{-4}$ M in Toluene, and $1.6x10^{-4}$ M in Methanol solvent. The electronic absorbance spectra of the prepared nanoparticle solutions were measured in Perkin Elmer Lambda-35 UV-vis spectrophotometer. In the last step, liquid crystal and nanoparticle solution was prepared by taking 1 ml of nanoparticle solution from 9 ml of liquid crystal solution. Then they were mixed in a magnetic stirrer, and after the samples were ready, fluorescence spectrums were taken at room temperature. The fluorescence spectra have measured using the Perkin Elmer LS-55 fluorescence spectrophotometer. Electronic band analysis of absorbance and fluorescence spectra was performed with Spectragraphy v1.2.16 and Origin lab 2019b versions [22], [23].


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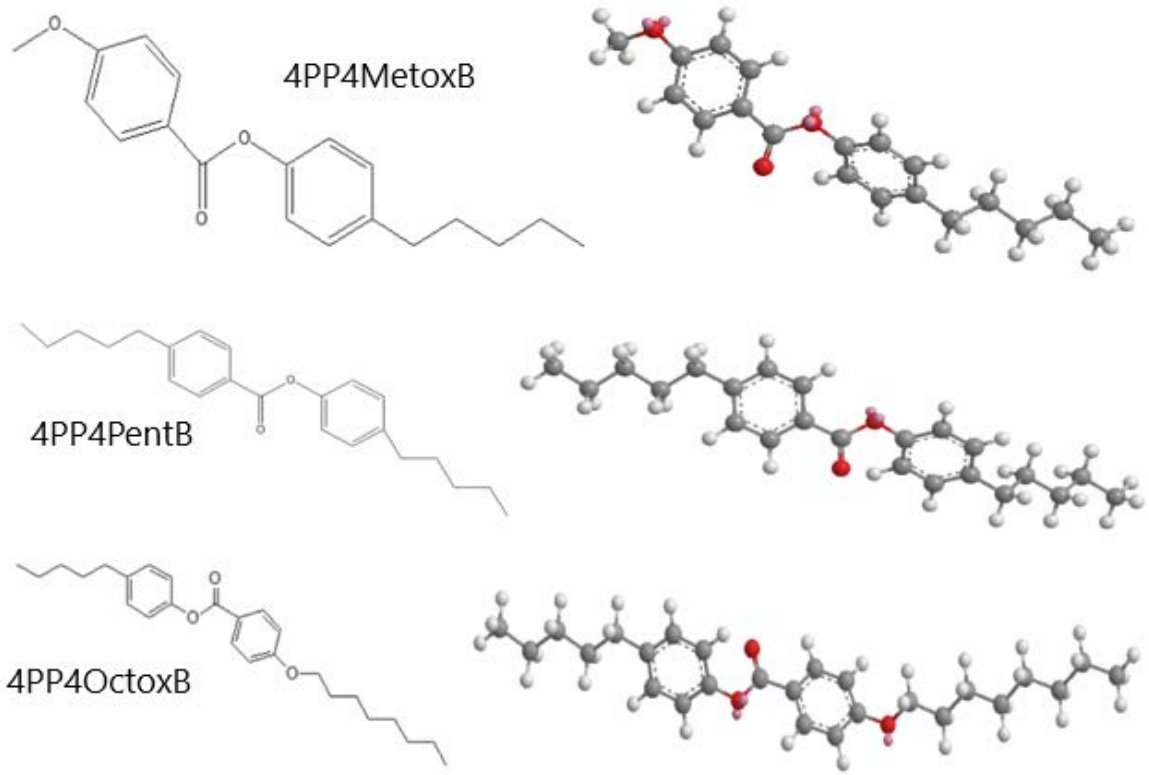


**Figure 1**. Molecular structures of 4PP4MetoxB, 4PP4PentB and 4PP4OctoxB liquid crystals.

## 3. Results and Discussions

The absorbance-wavelength and αhυ-energy graphs of CdS, CdSe, and ZnS nanoparticles are shown in Figure 2-4, 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.

$$\alpha h\upsilon = B^{*}(h\upsilon - Eg)^{p} \quad (1)$$

Here, hυ is the energy of the incident light, Eg is the band gap value, B is a unitless constant expressing the transition probability between energy levels, and p is a unitless constant whose value is 0.5 for direct transitions and 2 for indirect transitions [24], [25].

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 sizes of these materials are very small.

In some studies on nanoparticles, absorbance spectrum of CdSe nanoparticle with particle size smaller than 5.4 nm has been reported [8]. Based on this, it can be said that the particle size of the CdSe nanoparticle used in this study is around 5 nm.


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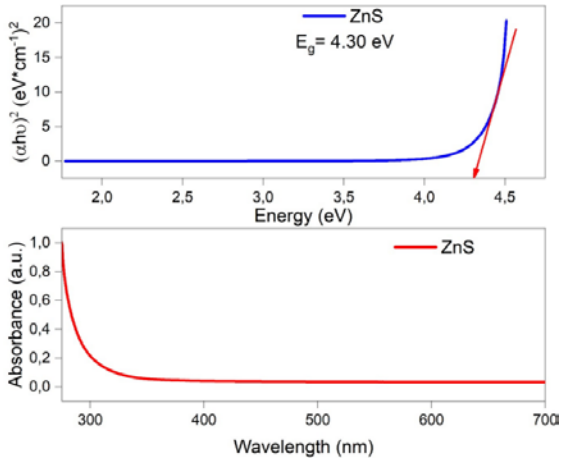


**Figure 2**. The absorbance spectra and graph of αhυ vs. energy for ZnS nanopartıcle.

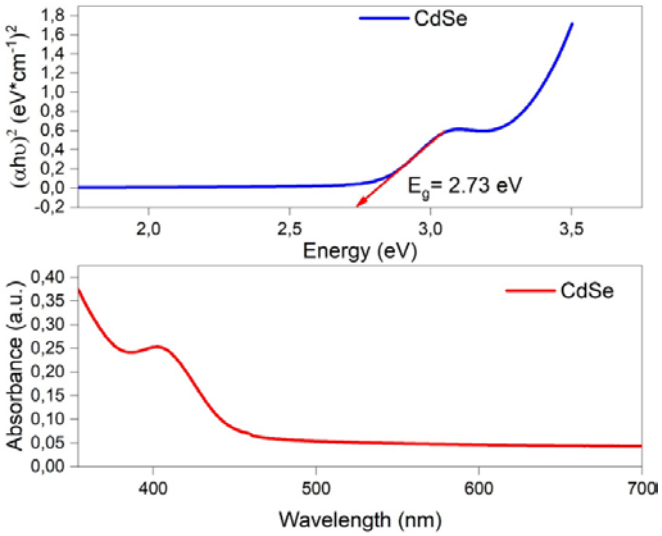


**Figure 3.** The absorbance spectra and graph of αhυ vs. energy for CdSe nanoparticle.

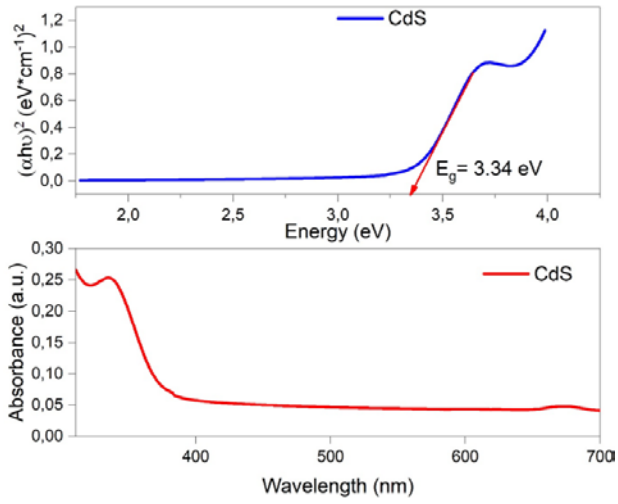


**Figure 4.** The absorbance spectra and graph of αhυ vs. energy for CdS nanoparticle.

Fluorescence spectra of nanomaterials are given in figure 5-13. Fluorescence spectra of nanomaterials with the liquid crystal solutions can be examined and compared. Changes in the maximum wavelengths of fluorescence spectra of nanoparticle doped liquid crystal solutions and liquid crystal solutions only were also evaluated. Some excitation peaks seen in fluorescence spectra


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are not given in the tables. The reason for this is not to confuse the wavelengths seen in the spectra with the excitation peaks and to perform better spectrum analysis.

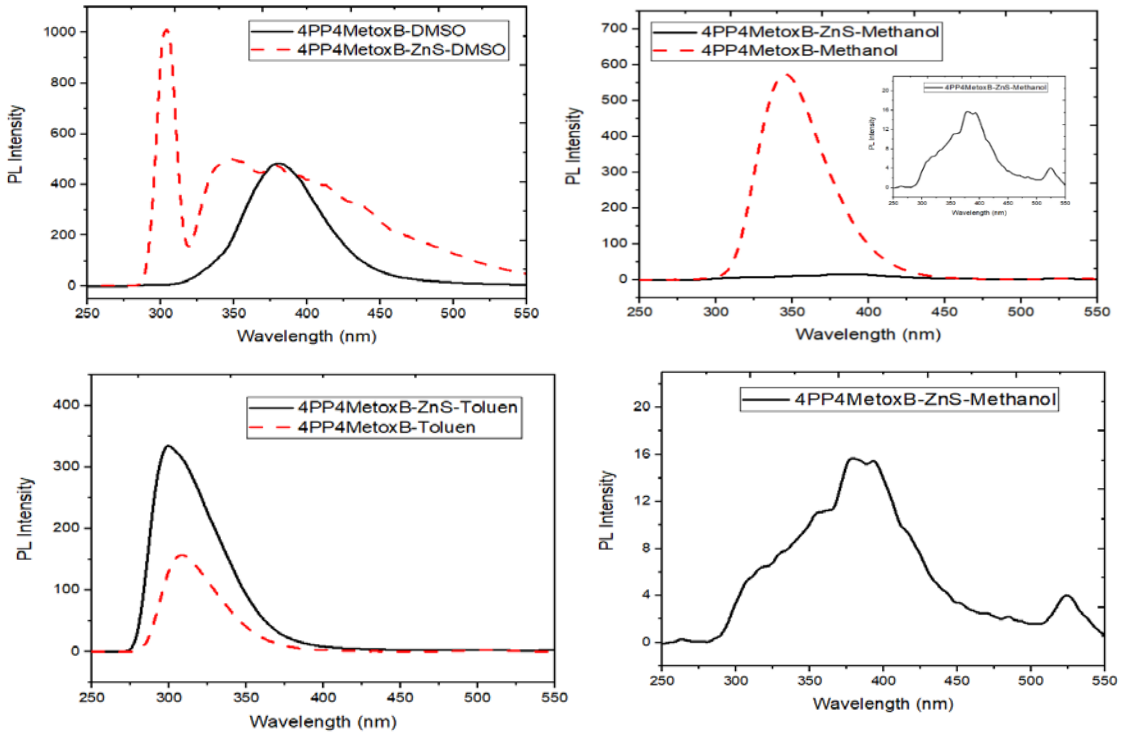


**Figure 5.** Fluorescence spectra of ZnS nanoparticle doped 4PP4MetoxB and 4PP4MetoxB liquid crystal.

**Table 1**. Data of fluorescence spectra of ZnS nanoparticle doped 4PP4METOXB and 4PP4METOXB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4MetoxB (nm) | 381 | 345 | 308 |
| 4PP4MetoxB-ZnS (nm) | 348-378-435 | 318-358-377-393 | 300 |

Fluorescence spectra of new nanomaterials formed with 4PP4MetoxB liquid crystal and ZnS nanoparticles in 3 different solvents are given in figure 5. The change in the maximum wavelengths of the fluorescence spectra of 4PP4MetoxB-DMSO liquid crystal solution and 4PP4MetoxB-ZnS-DMSO nanomaterial is seen as approximately 33 nms. In addition to this change, more peaks are observed in the 4PP4MetoxB-DMSO solution, while a single and wide peak is observed in the 4PP4MetoxB-ZnS-DMSO solution. The data of the fluorescence spectra of the 4PP4MetoxB-Methanol solution and the 4PP4MetoxB-ZnS-Methanol solution, which has a weak peak, are given in Table 1. By examining this table 1 and fluorescence spectra we obtained, it can be said that charge transfers occur between liquid crystals and nanoparticles in methanol solvent. It is seen that the fluorescence spectra of the 4PP4MetoxB-Toluene solution and the 4PP4MetoxB-ZnS-Toluene solution are similar to each other and the difference between the maximum wavelengths is 8 nms.


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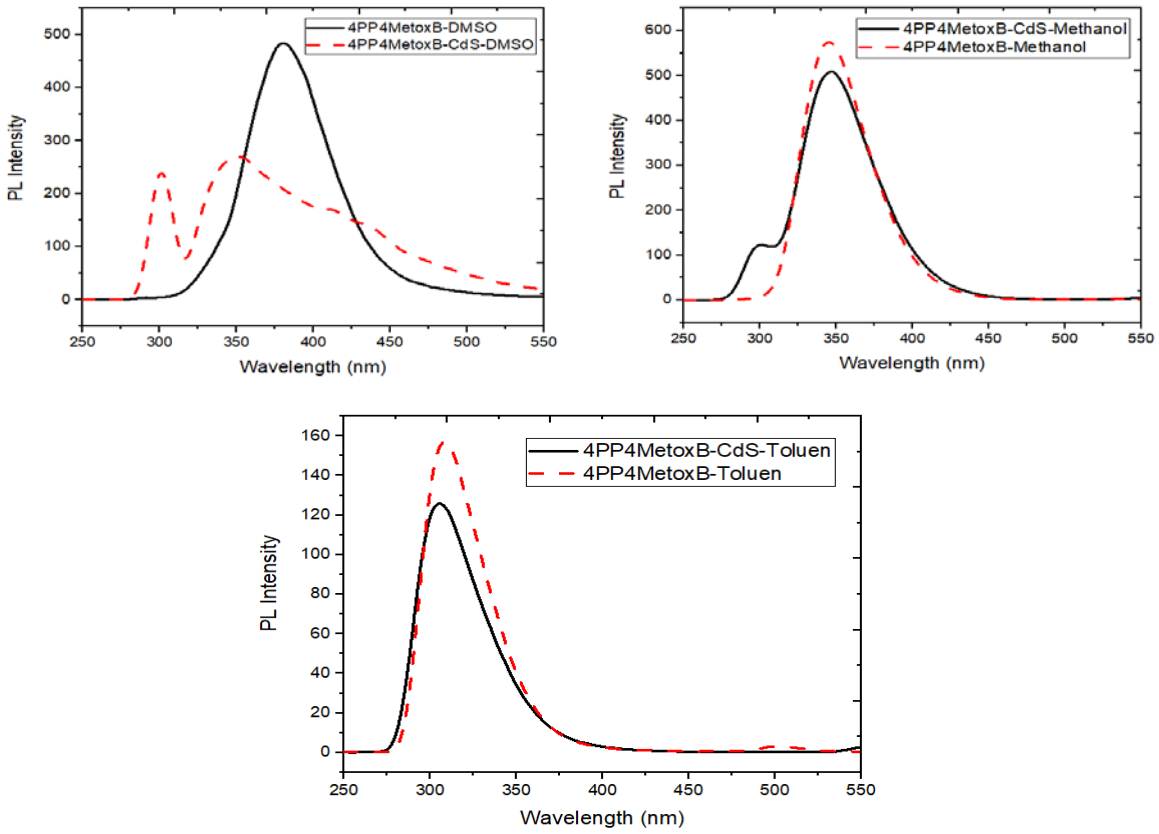


**Figure 6.** Fluorescence spectra of CdS nanoparticle doped 4PP4MetoxB and 4PP4MetoxB liquid crystal.

**Table 2**. Data of fluorescence spectra of CdS nanoparticle doped 4PP4MetoxB and 4PP4MetoxB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4MetoxB (nm) | 381 | 345 | 308 |
| 4PP4MetoxB-CdS (nm) | 350-407 | 300-346 | 305 |

Fluorescence spectra of new nanomaterials formed with 4PP4MetoxB liquid crystal and CdS nanoparticles in 3 different solvents are given in Figure 6. It is seen that there is a difference of approximately 31 nms in the maximum wavelengths on the fluorescence spectra between 4PP4MetoxB-DMSO and 4PP4MetoxB-CdS-DMSO solutions. There are an interaction between the 4PP4MetoxB liquid crystal and the CdS nanoparticle in the DMSO solvent and charge transfer occurred. The fluorescence spectra of the 4PP4MetoxB-Methanol solution and the 4PP4MetoxB-CdS-Methanol solution overlap each other. It can be said that charge transfer between the 4PP4MetoxB liquid crystal and the CdS nanoparticle in the methanol solvent does not occur and there is no interaction between them. Another nanomaterial in which liquid crystals and nanoparticles do not interact was the 4PP4MetoxB-CdS-Toluene solution. Here, it is seen that the fluorescence spectra of 4PP4MetoxB and 4PP4MetoxB-CdS solutions in toluene solvent are similar and there is only a difference of about 3 nm at their maximum wavelengths.


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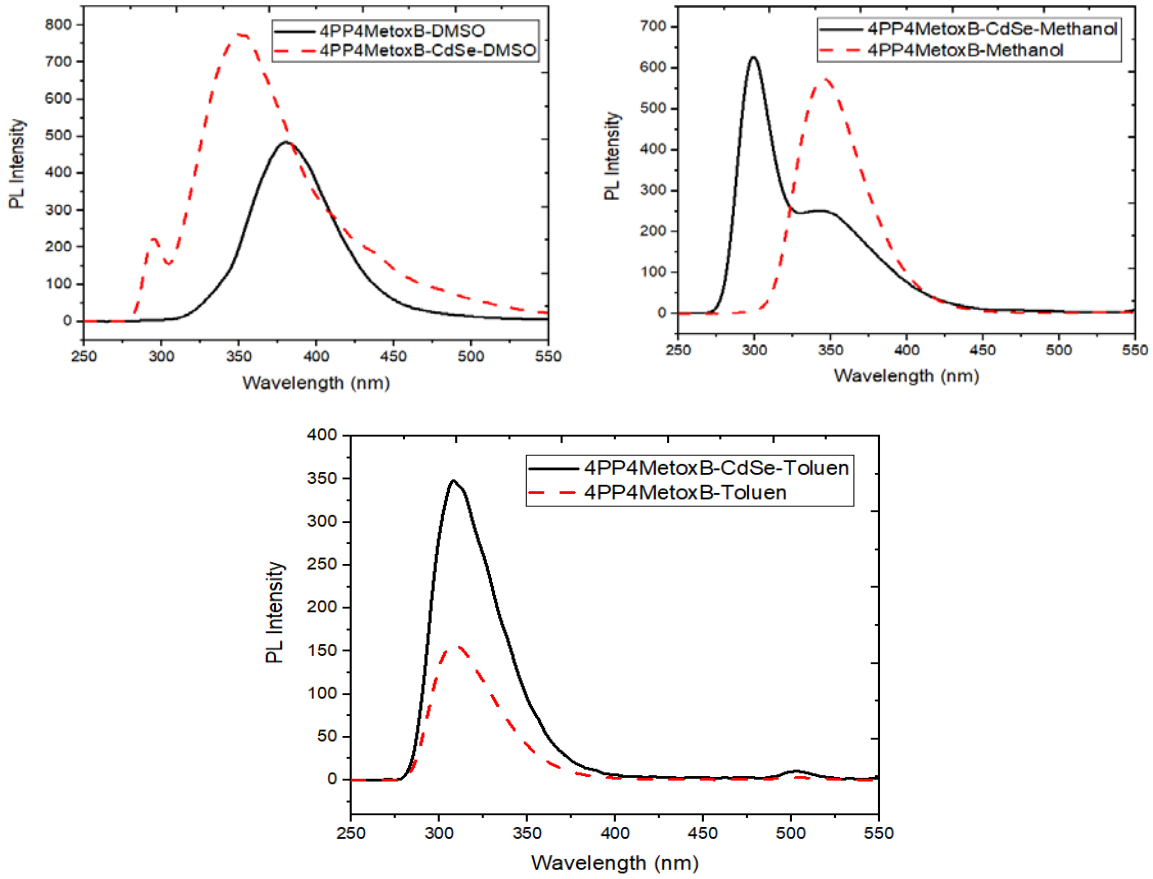


**Figure 7.** Fluorescence spectra of CdSe nanoparticle doped 4PP4MetoxB and 4PP4MetoxB liquid crystal.

**Table 3**. Data of fluorescence spectra of CdSe nanoparticle doped 4PP4MetoxB and 4PP4MetoxB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4MetoxB (nm) | 381 | 345 | 308 |
| 4PP4MetoxB-CdSe (nm) | 350 | 298-343 | 308 |

It is seen that there is a 31 nm difference in the maximum wavelengths of the fluorescence spectra of the 4PP4MetoxB-DMSO solution and the 4PP4MetoxB-CdSe-DMSO solution. It is seen that the fluorescence spectra of 4PP4MetoxB-DMSO solution and 4PP4MetoxB-CdSe-Methanol solution have a difference of 47 nms at their maximum wavelengths. It is seen that the fluorescence spectra of the 4PP4MetoxB-Toluene solution and the fluorescence spectra of the 4PP4MetoxB-CdSe-Toluene solution are quite similar to each other. When these fluorescence spectra are investigted, it can be said that 4PP4MetoxB liquid crystal and CdSe nanoparticle do not interact in Toluene solution.


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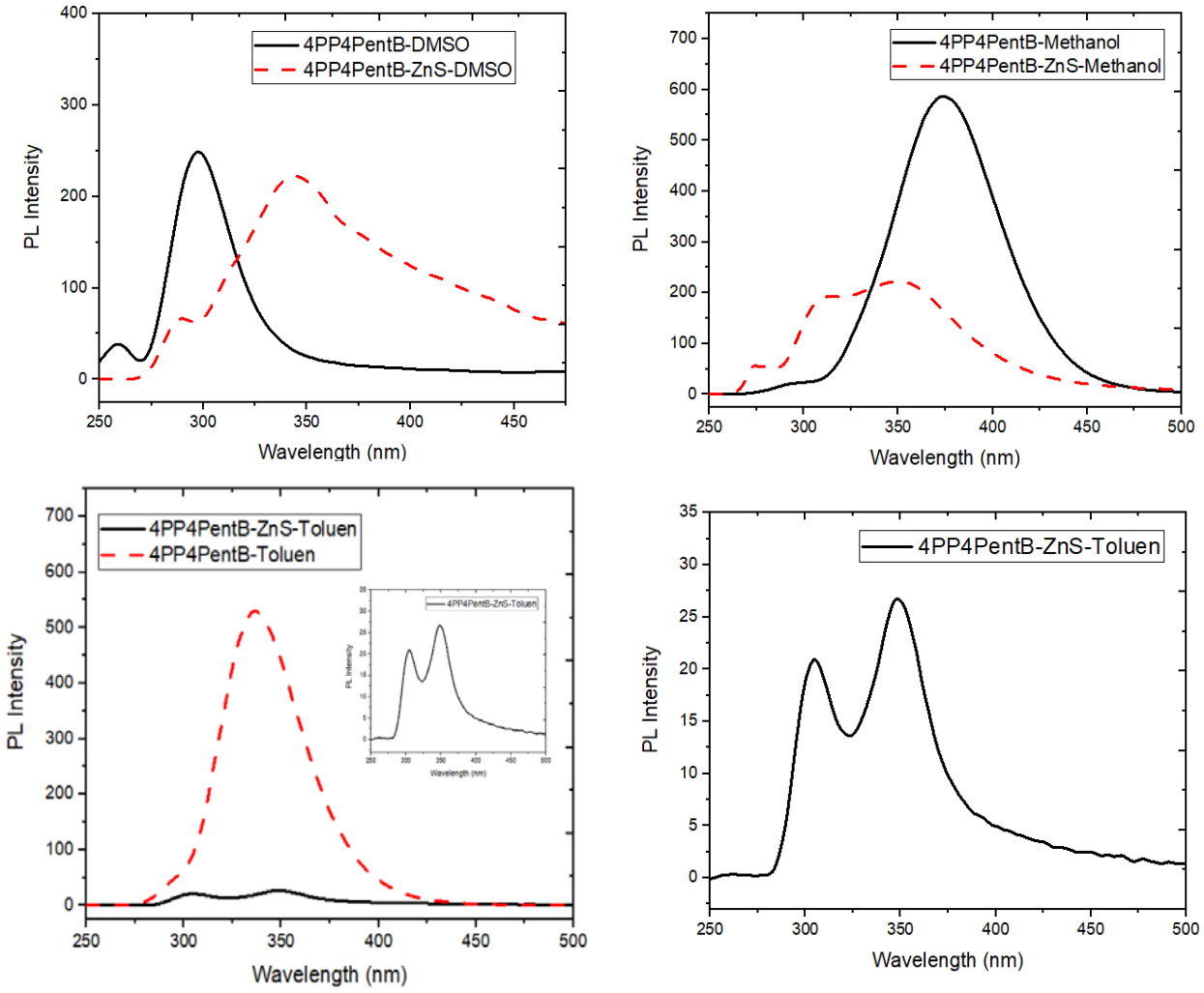


**Figure 8.** Fluorescence spectra of ZnS nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

**Table 4**. Data of fluorescence spectra of ZnS nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4PentB (nm) | 297 | 294-373 | 336 |
| 4PP4PentB-ZnS (nm) | 345 | 312-350 | 304-347 |

The fluorescence spectra of the solutions obtained by combining 4PP4PentB liquid crystal and ZnS, CdS and CdSe nanoparticles in a solvent medium and the fluorescence spectra of the liquid crystalline solutions are given in Figure 8-10. Between the 4PP4PentB-DMSO solution and the 4PP4PentB-ZnS-DMSO solution, a 48 nm red shift occurred at the fluorescence maximum wavelength. The ZnS nanoparticle added to the 4PP4PentB-DMSO solution was the element of change in the new 4PP4PentB-ZnS-DMSO solution. This change shows that 4PP4PentB liquid crystal and ZnS nanoparticle interact in DMSO solvent. In the fluorescence spectra of 4PP4PentB-Toluene solution and 4PP4PentB-ZnS-Toluene solution, a difference of 11 nm occurred at the maximum wavelength. In addition to this difference, it can be said that the fluorescence intensity of the 4PP4PentB-ZnS-Toluene solution is very low and the fluorescence spectra change compared to the 4PP4PentB-Toluene solution.


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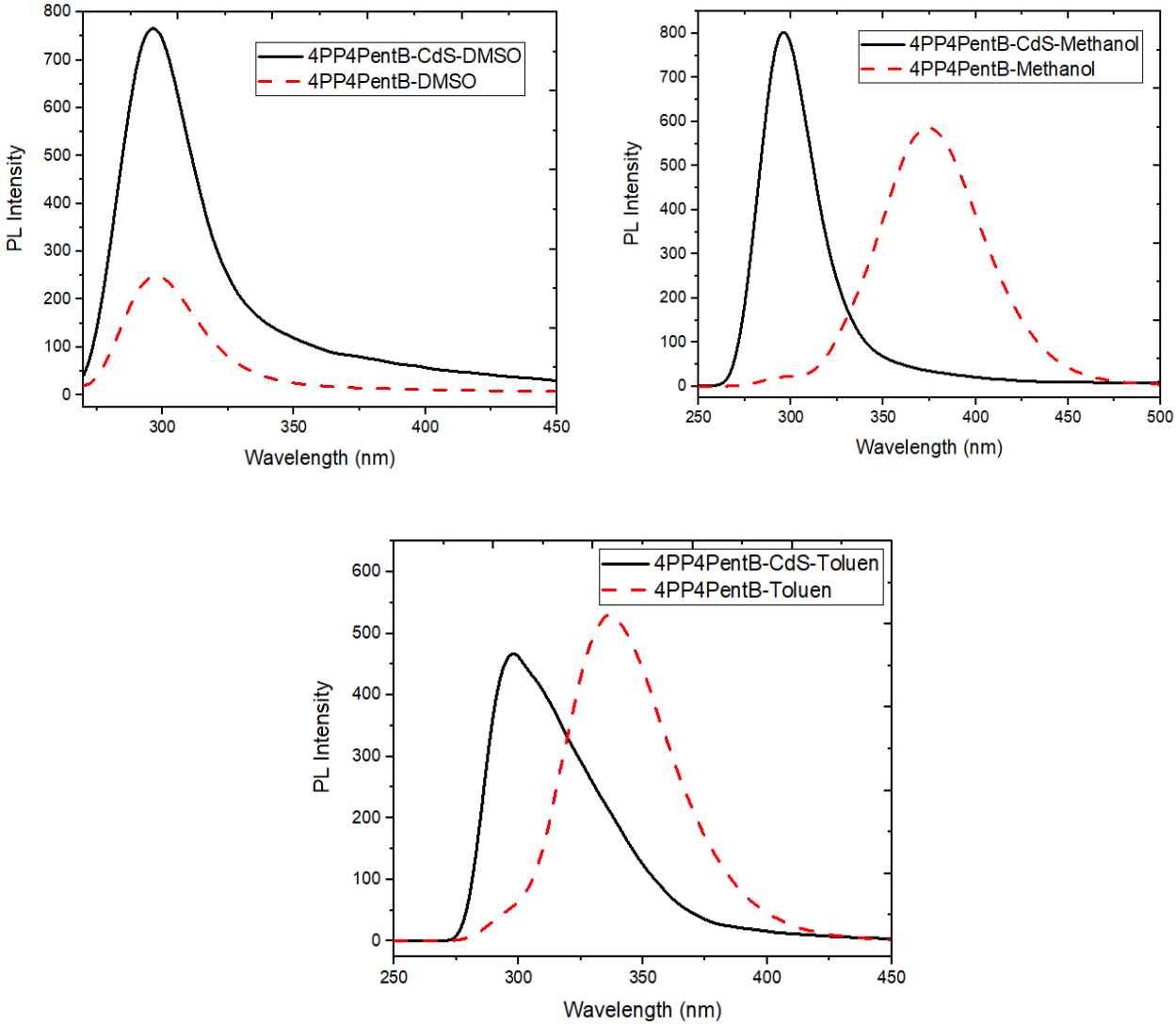


**Figure 9.** Fluorescence spectra of CdS nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

**Table 5**. Data of fluorescence spectra of CdS nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4PentB (nm) | 297 | 294-373 | 336 |
| 4PP4PentB-CdS (nm) | 295 | 296 | 297 |

It is seen that the fluorescence spectra of the 4PP4PentB-DMSO solution and the 4PP4PentB-CdS-DMSO solutions are similar except for the fluorescence intensities. No charge transfers or interaction was probably took place in the 4PP4PentB liquid crystal and the CdS nanoparticle DMSO solution. The fluorescence spectra of the 4PP4PentB-Methanol solution and the 4PP4PentB-CdS-Methanol solution are different, with a difference of 77 nm at the maximum wavelengths. It is observed that the maximum wavelength of the 4PP4PentB-CdS-Methanol solution is shifted towards the blue region compared to the maximum wavelength of the 4PP4PentB-Methanol solution. It was measured that there is a difference of 39 nm between the maximum wavelength of the fluorescence spectra of the 4PP4PentB-Toluene solution and the maximum wavelength of the fluorescence spectra of the 4PP4PentB-CdS-Toluene solution. It is seen that charge transfers take place by interacting with 4PP4PentB liquid crystal and CdS nanoparticle in Toluene solvent.


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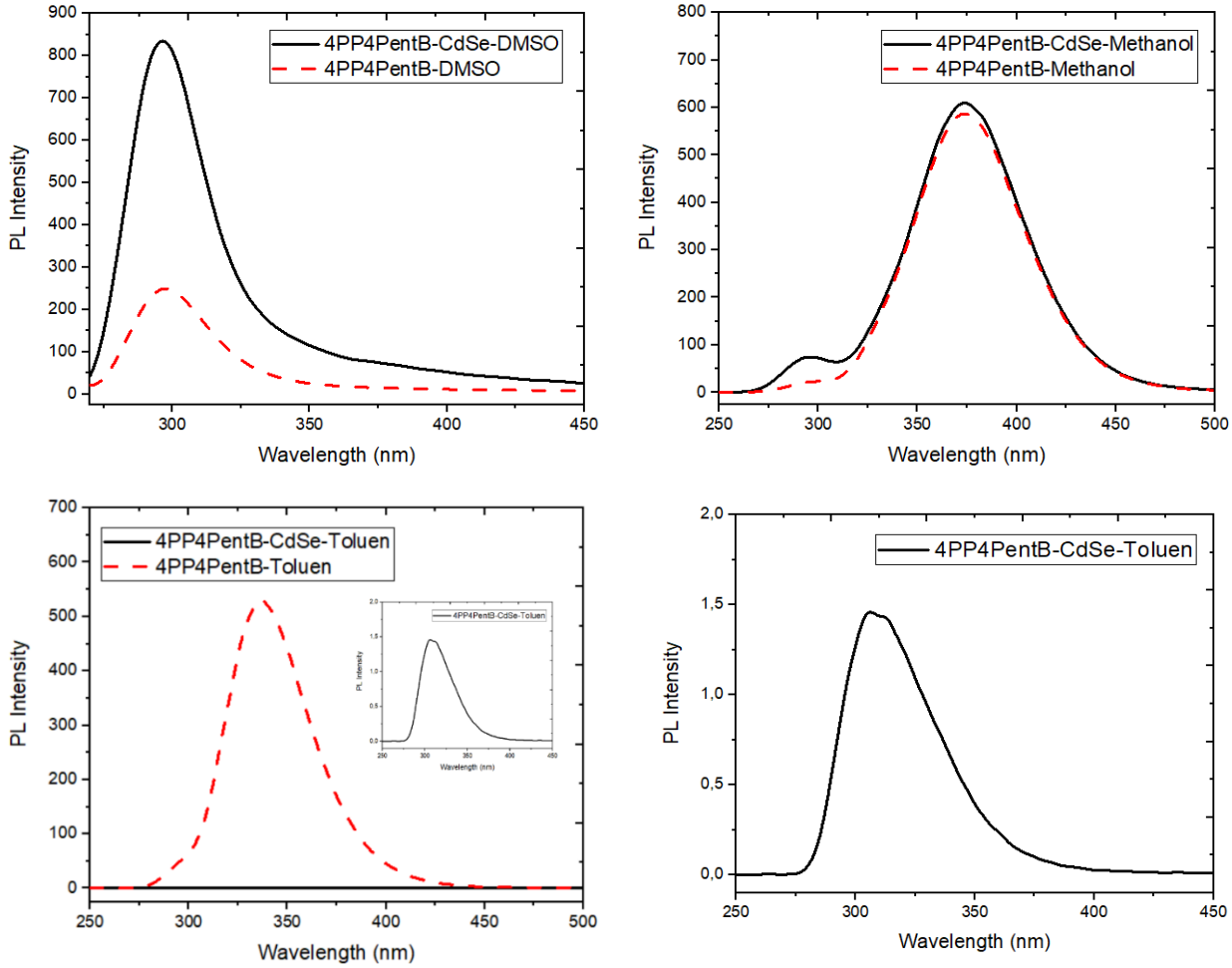


**Figure 10.** Fluorescence spectra of CdSe nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

**Table 6**. Data of fluorescence spectra of CdSe nanoparticle doped 4PP4PentB and 4PP4PentB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4PentB (nm) | 297 | 294-373 | 336 |
| 4PP4PentB-CdSe (nm) | 297 | 293-375 | 307 |

It is seen in Figure 10 that the fluorescence spectra of the 4PP4PentB-DMSO solution the and 4PP4PentB-CdSe-DMSO solution is similar. Likewise, the fluorescence spectra of the 4PP4PentB-Methanol solution and the 4PP4PentB-CdSe-Methanol solution is similar. It is understood that the CdSe nanoparticle of the 4PP4PentB liquid crystal does not interact in DMSO and Methanol solvents. It is observed that the fluorescence spectra of the 4PP4PentB-Toluene solution and the 4PP4PentB-CdSe-Toluene solution are different and there is a 29 nm difference in the maximum wavelengths. The intensity of the fluorescence spectra of the 4PP4PentB-CdSe-Toluene solution was also lower than the other solutions.


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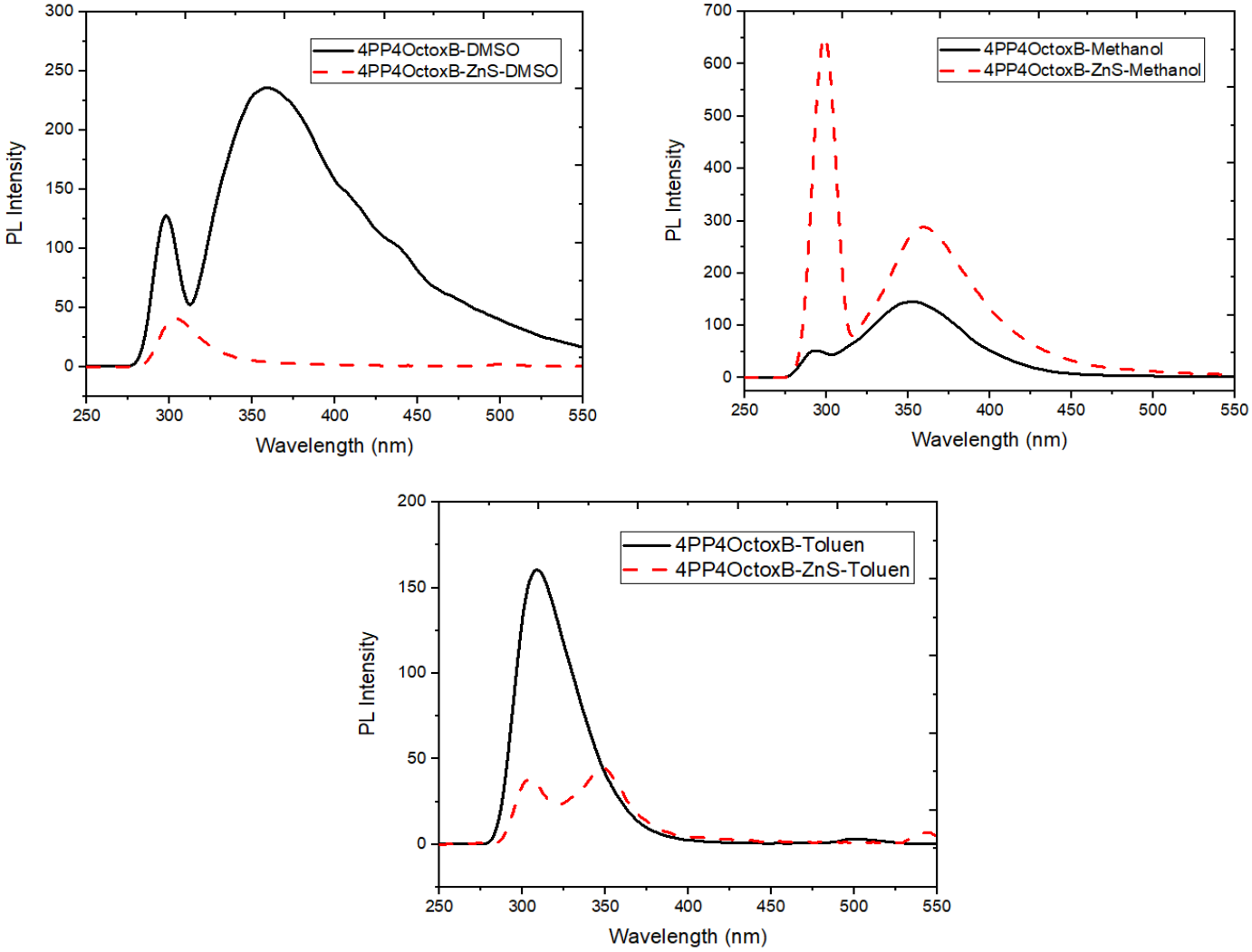


**Figure 11.** Fluorescence spectra of ZnS nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

**Table 7**. Data of fluorescence spectra of ZnS nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4OctoxB (nm) | 359-407-439 | 351 | 308 |
| 4PP4OctoxB-ZnS (nm) | 303 | 358 | 304-347 |

The fluorescence graphs of the 4PP4OctoxB liquid crystal solutions and the new solutions formed by the combination of 4PP4OctoxB liquid crystal and ZnS, CdSe, and CdS nanoparticles in the solvent are given in Figure 11-13. It was determined that the fluorescence spectra of the 4PP4OctoxB-DMSO solution and the 4PP4OctoxB-ZnS-DMSO solution were different and there was a 56 nm difference between the maximum wavelengths. A 56 nm blue shift occurred at the maximum wavelength of the 4PP4OctoxB-ZnS-DMSO solution compared to the 4PP4OctoxB-DMSO solution. It can be said that the fluorescence spectra of the 4PP4OctoxB-Methanol solution and the 4PP4OctoxB-ZnS-Methanol solution show close spectroscopy. It can be said that the fluorescence spectra of the 4PP4OctoxB-Toluene solution and the 4PP4OctoxB-ZnS-Toluene solution are different from each other. It can be understood that 4PP4OctoxB liquid crystal and ZnS nanoparticle interact in Toluene solvent.


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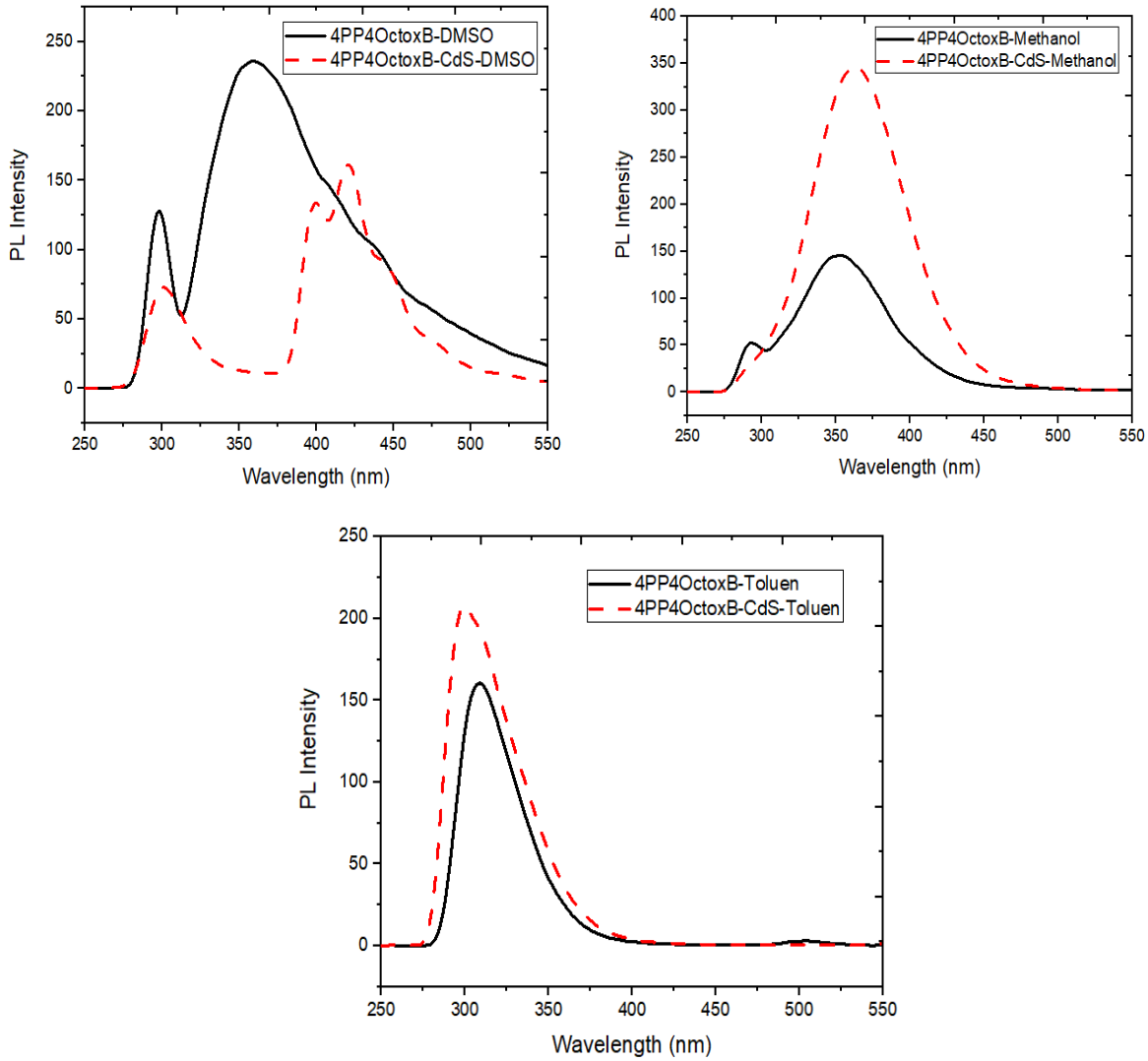


**Figure 12.** Fluorescence spectra of CdS nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

**Table 8**. Data of fluorescence spectra of CdS nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4OctoxB (nm) | 359-407-439 | 351 | 308 |
| 4PP4OctoxB-CdS (nm) | 300-399-420-445-479 | 363 | 300 |

There are remarkable differences in the fluorescence spectra of 4PP4OctoxB-DMSO solution and 4PP4OctoxB-CdS-DMSO solution. It can be said that fluorescence spectra of 4PP4OctoxB liquid crystal and CdS nanoparticle interact in DMSO solvent and differentiate as a result of charge transfers. It is seen that the fluorescence spectra of the 4PP4OctoxB-Methanol solution and the 4PP4OctoxB-CdS-Methanol solution are similar to each other. Likewise, it can be seen from figure 12 that the fluorescence spectra of the 4PP4OctoxB-Toluene solution and the 4PP4OctoxB-CdS-Toluene solution are similar to each other.


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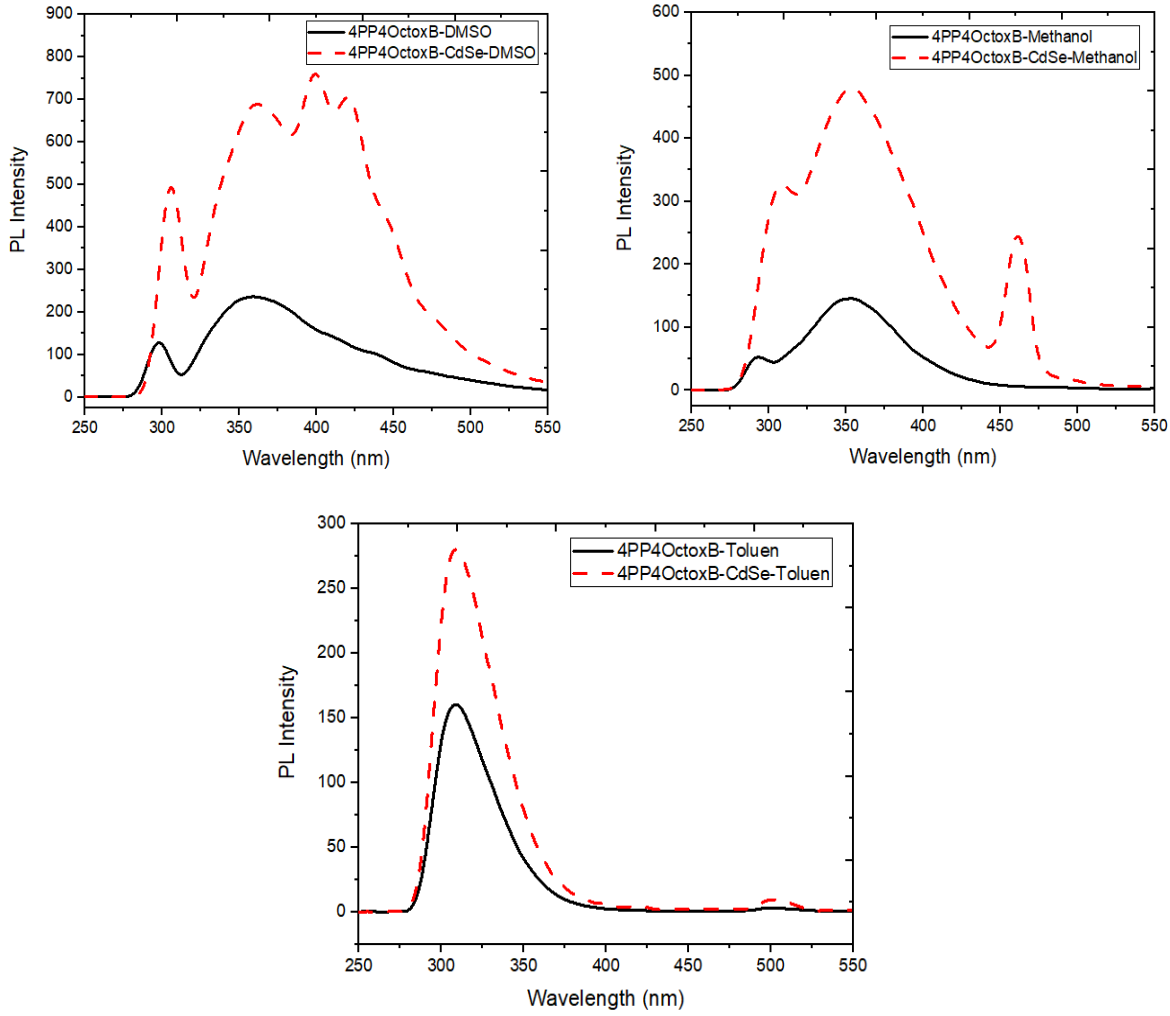


**Figure 13.** Fluorescence spectra of CdSe nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

**Table 9**. Data of fluorescence spectra of CdSe nanoparticle doped 4PP4OctoxB and 4PP4OctoxB liquid crystal.

| | **DMSO** | **Methanol** | **Toluene** |
|---|---|---|---|
| 4PP4OctoxB (nm) | 359-407-439 | 351 | 308 |
| 4PP4OctoxB-CdSe (nm) | 360-399-419 | 308-353 | 308 |

It is understood that there are significant differences between the fluorescence spectra of the 4PP4OctoxB-DMSO solution and the 4PP4OctoxB-CdSe-DMSO solution. It can be said that 4PP4OctoxB liquid crystal interacts with CdSe nanoparticle in DMSO solvent. It can be said that the fluorescence spectra of the 4PP4OctoxB-Methanol solution and the 4PP4OctoxB-CdSe-Methanol solution are similar. It is seen that the fluorescence spectra of the 4PP4OctoxB-Toluene solution and the 4PP4OctoxB-CdSe-Toluene solution are similar to each other. These similarities tell us that liquid crystals and nanoparticles do not interact and there is no charge transfer between them.

## 4. Conclusions

The changes in fluorescence spectra and maximum wavelengths of liquid crystals and nanoparticle doped liquid crystals were investigated. The CdS nanoparticle added to the 4PP4MetoxB liquid crystal interacted only in the DMSO environment and was blue-shifted at the maximum wavelength of the fluorescence spectrum. In the CdSe nanoparticle added to the 4PP4MetoxB liquid crystal, a blue shift occurred at the maximum wavelength of the fluorescence spectrum of this liquid crystal in the DMSO and Methanol solvent medium. The ZnS nanoparticle added to the 4PP4MetoxB liquid


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crystal showed a blue shift in DMSO and a red shift in Methanol. Since charge transfer did not occur between the 4PP4MetoxB liquid crystal in the toluene environment and the nanoparticles, the electronic structure of these molecules did not change. CdS nanoparticle doped into 4PP4PentB liquid crystal did not interact in DMSO while blue shifting occurred in Methanol and Toluene compared to the liquid crystal. While the CdSe nanoparticle added to the 4PP4PentB liquid crystal did not interact in DMSO and Methanol, electronic transitions occurred in Toluene and a blue shift occurred. In the ZnS nanoparticle added to the 4PP4PentB liquid crystal, charge transfers occurred in the entire solvent medium used and shifts occurred at the maximum wavelengths. CdS nanoparticle added to 4PP4OctoxB liquid crystal has been transferred in all solvents used, and the electronic structure of the liquid crystal has changed. Charge transfers took place in DMSO and Toluene solvents of ZnS and CdSe nanoparticles added to this liquid crystal in the same way. As a result, both blue-shift and red-shift occurred in the fluorescence spectrum compared to the liquid crystal.

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