Title: Interaction and Characterization of The Triarylmethane Dye Bromophenol Blue with CdSeTe Quantum Dots

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Interaction and Characterization of The Triarylmethane Dye Bromophenol Blue with CdSeTe Quantum Dots

Erdem ELİBOL *, Tuna DEMİRCİ 2

Abstract

The use of hybrid associates in biological, optoelectronics and energy fields are increasing day by day. In this context, in this study, CdSeTe Quantum dots (QD): Bromophenol Blue (BPB) hybrid associates were studied for the first time in the literature and their spectroscopic characterizations were examined. In the study, CdSeTe QDs were synthesized with triocetylphosphine (TOP) ligands by hot injection method, and it was planned that the BPB would passivate the surface of the QD by interacting with the TOP ligand of the CdSeTe QDs. CdSeTe QD: BPB hybrid associates were prepared in different concentrations, and the effects of QD: BPB ratios on absorbance and emission characterizations were examined. Structures have been characterized using Uv-vis, PL, ICP-OES and FTIR. With the results found, the predictive mechanism has been put forward.

Keywords: CdSeTe QDs; bromophenol Blue; hybrid associate; emission; absorption

1. INTRODUCTION

Organic dyes have become an indispensable part of industrial applications, especially in many areas of daily life. They have a lot of advantages with their bright colours, easy applicability and colour sensitivity [1]. The main factor that determines the usage areas of organic dyes is their optical properties. In recent years, it has been shown that using hybrid associates can be beneficial both in order to increase the optical properties of organic dyes and to increase the areas of use [2,3]. For this reason, studies on hybrid associates of semiconductor nanocrystals (QDs) and organic dyes are increasing rapidly. These hybrid associates are highly related not only to the optical properties of their components, QD and dye, but also to the new characterization results resulting from the resulting composition [4]. So much so that hybrid associates can find application areas in many fields such as optoelectronic [5], biological imaging [6] and energy [7]. Stimulated electron transfer in hybrid associates plays an important role in the formation of these structures. In hybrid associates, QDs often act as donors, especially in associations in the aquatic environment. On the other hand,
organic dyes mostly take the role of acceptor [8]. At this process photon-induced charge transfer or irradiated energy transfers play a fundamental role.

Quantum dots have many advantages over bulk semiconductor materials with their unique optical and electronic properties. The energy levels of QDs, which are under the influence of quantum confinement in all three dimensions, turns from continuous to discrete [9]. This ensures that the QDs have adjustable energy band gap according to their size [10]. This feature paves the way for the quantum dots to be synthesized in the required absorbance and emission properties [11]. QDs have also started to be used in many fields with their multiple exciton production, easy and cheap production capacities, stability and high stability [12–14]. One of the main reasons for QDs to create hybrid associates with organic dyes is due to their long PL lifetime times and their ability to donor and adjust their absorbance and emission characteristics [15].

The optical properties of QD/organic dye hybrid associates have been investigated in many studies in the literature. Smirnow et al studied on CdS, passivated with TGA and Europium 1, 3-Diketonate, and methylene blue dye (MB) hybrid associate. In their study, it was observed that the maximum point of the absorbance peak did not shift with the addition of MB, but there was a 10-15% increase at the Full Width at Half Maximum (FWHM). In addition, nonradiative excitation energy transfer has been determined from Eu3+ and CdS QD to MB [16]. Rakovich et al. also worked on hybrid associates consisting of methylene blue and TGA capped CdTe QDs. As the amount of MB added to a fixed amount of CdTe solution increased, a decrease in absorbance was observed. They also showed that there was a certain electrostatic interaction between MB and QD while dimerization processes were observed due to the addition of MB. With their study, it has been shown that the efficiency of a light sensitive dye can be increased by using QDs. Orlova et al. worked on hybrid associates consisting of CdTe QD / Sulphophthalocyanine molecule and similar luminescence quenching was detected. In this study, it was stated that PL quenching resulted from FRET mechanism [17]. Ovchinnikov et al. found that in their study for CdS QD / methylene blue hybrid associates, CdSQDs behave as donors. However, it was found that dimerization increases as MB increases in the mixture formed with QD [18].

Bromophenol blue (BPB), which is one of these anionic dyes, is an acid organic dye, but it is used for especially in textile products [19], biological applications [20], and cosmetics [21], monitoring electrophoresis processes. However, it has recently been used as a photosensitizer material in dye-sensitive solar cells [22]. Bromophenol blue (BPB), is used in polyacrylamide gel electrophoresis and agarose gel electrophoresis processes due to its most commonly used electrophoretic colour marker feature. The main reason for this is that, since the structure contains a low density negative charge in the neutral close pH, it performs linear progress with DNA during the electrophoresis process. In addition to this feature, many drugs are used as colour markers in the UV analysis of the active substance [23]. If it is necessary to give examples, examples such as Atorvastatin Calcium [23], Ofloxacin [24], Levetiracetam [25] can be given. Still exploiting this property Beryllium [26], Calcium/Magnesium [27] being used in quantitative analysis of structures.

However, a study in which BPB is studied as QD/BPB hybrid associates is not available in the literature. For the QD/Dye hybrid associate, alloy CdSeTe QDs were preferred specifically for this study. Alloy CdSeTe QDs have the potential to be synthesized more precisely with their 3-component structures in a wider absorbance range to other QDs. However, according to many QDs, it is possible to synthesize them to cover the entire spectrum of the sunlight [28]. In this study, optical properties of CdSeTe QD / BPB hybrid associates were tested. Absorbance characterization and PL characterizations were studied depending on both QD and BPB. In the study, FT-IR analyses were done to make sense of the interactions of the mixes.
2. MATERIALS AND METHOD

2.1. Materials

Technical-grade trioctylphosphine (TOP, 90 %), trioctylphosphine oxide (TOPO, 99 %), cadmium oxide (CdO, 99 %), selenium powder (Se, 99 %), tellurium powder (Te, 99 %), 1-tetradecyl phosphonic acid (TDPA, 99 %), 1-Octadecene technical grade (ODE, 90 %), Bromophenol blue (BPB, 99 %).

2.2. Synthesis of CdSeTe QDs

In this study, alloy CdSeTe QDs were performed based on the method proposed by Debnath et al [29]. Minor changes were made in the applied method.

For synthesising the alloy CdSeTe firstly Cd, TOP-Se and TOP-Te precursors must be ready in at three different 3-neck flasks. For TOP-Se precursors Se (0.019 g, 0.25 mmol), TOP (0.57 ml) and ODE (1.25 ml) were mixed in 3-neck flasks while Te (0.011 g, 0.085 mmol), TOP (0.57 ml) and ODE (1.25 ml) were mixing for have TOP-Te precursors. After TOP-Se and TOP-Te were heated to 70°C and 200°C respectively. When precursors were ready TOP-Se was injected to TOP-Te precursors fastly for have TOP-Se-Te precursors. At the same time for prepare the Cd precursors, CdO (0.013g, 0.095 mmol), TDPA (0.075 g, 0.27 mmol), TOPO (1 g, 2.098 mmol) were mixed in ODE (2.5 ml). The solution was heated to 300°C and kept at this temperature until the clear solution had seen. When all precursors were ready, TOP-Se-Te precursors were injected in Cd precursors and the solution kept at the 260°C. At this temperature CdSeTe QDs were growing with time and solutions were taken at different grown times. Alloy CdSeTe QDs were washed with methanol and centrifuged and dissolved in chloroform for using. Synthesized steps of CdSeTe QDs are showed at Figure 1 and images of synthesized CdSeTe QDs in daylight and fluorescent light are shown in Figure 2.

2.3. Preparing Bromophenol Blue

Bromo phenol blue 0.669 g (0.01 mmol) is taken as main stock and completed with 50.0 ml of chloroform. The prepared main stock solution displays a colourless appearance.

2.4. Sample Preparation

Bromophenol blue colourless solution was mixed with 100 ul withdrawn CdSeTe QD solution in various concentrations. The final concentration was used as about 1.0x10^-4 M. CdSeTe QD solution molarity calculation by ICP-OES analysis. This result was shown CdSeTe QD concentration 2.0x10^-6 M.
Table 1. Concentrations and mixing ratios in CdSeTe QD: BPB hybrid associate.

<table>
<thead>
<tr>
<th>QD:BPB ratio</th>
<th>CdSeTe QD concentration (M)</th>
<th>BMB concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>-</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>0.5:1</td>
<td>2.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>1:1</td>
<td>4.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>2:1</td>
<td>8.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>3:1</td>
<td>16.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>4:1</td>
<td>64.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>1:0</td>
<td>4.0x10^{-6}</td>
<td>-</td>
</tr>
<tr>
<td>1:0.25</td>
<td>4.0x10^{-6}</td>
<td>2.5x10^{-5} M</td>
</tr>
<tr>
<td>1:0.5</td>
<td>4.0x10^{-6}</td>
<td>5.0x10^{-5} M</td>
</tr>
<tr>
<td>1:1</td>
<td>4.0x10^{-6}</td>
<td>1.0x10^{-4} M</td>
</tr>
<tr>
<td>1:2</td>
<td>4.0x10^{-6}</td>
<td>2.0x10^{-4} M</td>
</tr>
<tr>
<td>1:3</td>
<td>4.0x10^{-6}</td>
<td>3.0x10^{-4} M</td>
</tr>
</tbody>
</table>

Images of CdSeTe QD/BPB hybrid associates prepared at different concentration ratios are shown in Figure 3 under daylight (Figure 3-A) and fluorescent light (Figure 3-B).

Figure 3 Image of CdSeTe QD/ BPB hybrid associates samples A) under sunlight, B) under florescent light. a-h shows the different ratio of hybrid associates QD: BPB , a) 100:0, b) 1:0, c) 1:0.25, d)1: 0.5, e) 1 : 1, f)1:2, g) 1:3, h) 0:3.

2.5. Characterization

Absorption spectra of hybrid associates prepared in the study were tested using UV-1800 Shimadzu UV Spectrometer. It was chosen as the scanning range between 230-800 nm. It is known that bromophenol blue can give absorbance peaks in the range of 230-600 nm [30]. Absorption spectra scans for CdSeTe QD/BPB hybrid associates were performed based on their mixtures in different concentrations given in Table 1. Similarly, emission spectra scans of QD/BPB hybrid associates prepared with freshly synthesized CdSeTe QDs throughout the study were performed with Edinburgh Instruments FLS1000 Spectrometer. Emission scanning was performed in the range of 300-800 nm and excitation wavelength was preferred as 380 nm. The absorption and emission characteristic curves obtained were drawn with Origin Pro 8 and FWHM values were calculated again with this program.

Fourier transform infrared (FTIR) spectra of bromophenol blue and CdSeTe QD were recorded with ATR Attached Shimadzu IR Prestige 21 spectrometer. Spectrum was performed between 400-4000 nm and 32 scans. Metal contents of bromophenol blue and CdSeTe QD were measured on a Perkin Elmer 200 Avio ICP OES.
3. RESULTS and DISCUSSION

3.1. Absorption Spectra

Absorption analyses for the prepared QD / BPB hybrid associates were evaluated in two parts. In the first part, while the BPB concentrations in the hybrid associates were kept constant, the amount of QD added was gradually increased and changes in the absorption spectrum were followed. In the second part, the amount of BPB added was gradually increased by keeping the QD concentrations in the hybrid associates constant. With the study, the role of QD, which is usually a donor in the literature [31], and the absorption characterizations of the hybrid associate have been investigated. Remarkable results were obtained in both stages.

The absorption characteristic obtained in the first stage, where the BPB concentration in the hybrid associates is constant, is shown in Figure 4. The initial absorption peak of CdSeTe QDs, which were also added to hybrid associates, was calculated as 584 nm as shown in the bottom right figure in Figure 4. On the other hand, although the absorption of BPB used in hybrid associate comes at 410 nm levels (up right figure in Figure 4), it is not possible to obtain a clear absorption value of BPB which is very transparent in chloroform. With the addition of QDs into the hybrid associate, there was a marked increase in the BPB absorption peak. While the amount of BPB in the hybrid associates is constant, the addition of QDs showed a marked increase at the point where the absorbance peak of the BPB was present. Thus, while the maximum absorbance point of the reference BPB (0:1) was 0.1, the absorbance point increased 22.5 times and was observed as 2.25 with the addition of CdSeTe QD (half the concentration of BPB (0.5:1)) into the hybrid associate. Similarly, as the amount of QD added was increased, the increase in absorbance continued and the absorbance peak reached its maximum (2.6) with a mixture of 3:1. The QDs added (4:1) to the hybrid associate after this stage did not cause a change in the BPB peak at 408 nm, even though the absorbance peak of QD at 584 nm continued to increase minimally. Even if the ratio of QD: BPB in the hybrid associates varies, no obvious changes were observed in the wavelengths of the absorbance peak. This is an indication that there are no major chemical changes with the mixture. However, it is thought that there may be electrostatic attraction between QD and BPB [32], and the obvious increase in the absorbance peak is due to this interaction. It is also deducted that the QDs added to the hybrid associate cause dimerization in BPB and cause a marked increase in the maximum point at the peak [33].

![Figure 4 Absorbance spectra for hybrid associates prepared at different QD: BPB ratios where the BPB concentration is constant.](image)

In the second stage, the absorbance characterization of hybrid associates prepared with different ratio of QD:BPB at constant CdSeTe QD concentration is shown in Figure 5. The absorbance spectra images for the reference samples with QD: BPB ratios 1:0 and 0:1 are given in the upright figure in Figure 4 and bottom right at Figure 5 respectively, since the absorbance maximum peak points were quite small. As can be understood from the figure at the upright in Figure 5, the absorbance peak of CdSeTe QDs with a QD: BPB ratio of 1:0 has reached 584 nm. With the increase in the BPB rate in the hybrid associate, it started to increase at the maximum peak point. When the QD: BPB ratio was 1:3, the maximum peak of the hybrid associate increased to 40 times the absorbance maximum peak of the BPB reference sample. An increase in the FWHM values of the absorbance peaks was observed, equivalent to an increase in the absorbance peak points. Although the amount...
of QDs in the hybrid associate is constant, minimal increases were observed in the absorbance peak of QD, as seen in the lower right corner of Figure 5. This is thought to be caused by the fact that QDs increase the absorbance feature by the interaction of TOPO ligands present on the surfaces of CdSeTe QDs and Br ions in BPB. There are case studies in the literature where ions such as Cl, Br and I have been used to treat surface ligands of QDs [34]. Here, although surface treatment is not applied with Br ions on its own, it can be considered that Br ions interact with the surface of the QD.

While the amount of QDs in the CdSeTe QD:BPB hybrid associate is constant, it is expected that the absorbance will increase depending on the amount of BPB [17]. However, when comparing both absorbance graphs (Figure 4 and Figure 5), the QD: BPB hybrid associate has an absorbance value much higher than the BPB and QD’s individual absorbance values.

![Figure 5 Absorbance spectra for hybrid associates prepared at different QD: BPB ratios where the CdSeTe QD concentration is constant.](image)

in the first stage, namely by keeping the BPB constant and increasing the amount of CdSeTe QDs, is shown in Figure 6. The emission characterization for the hybrid associates obtained in the first stage, namely by keeping the BPB constant and increasing the amount of CdSeTe QDs, is shown in Figure 6. As can be seen from the bottom left of Figure 6, the QD:BPB ratio is 0:1, that is, the emission value for BPB is shown. On the contrary, for the 1:0 ratio, the emission peak of CdSeTe QD is shown in Figure 6. The increase in the amount of CdSeTe QD in the hybrid associate naturally caused an increase in the luminescence peak [30]. When the hybrid associate is 1:0, the emission peak of QD is close to around 605 nm. As the ratio of QD in it decreased, the emission peak of QD shifted to 601 nm as seen at Figure 5. The 4 nm blue shift in the emission peak can be associated with the measurement sensitivity errors in the emission peak, and the continuity of this blue shift process has been determined by repeated analysis. This situation can be interpreted as that the long TOPO ligands of the QDs interact with the BPB, causing the QD to be partially passivated and the emission peak to blue. Another remarkable factor in Figure 6 is the decreasing amount of CdSeTe QDs, causing a noticeable change in the FWHM of the luminescence peak. Such that while the FWHM value of the emission peak of QD at 1:0 was 37.89 nm, the FWHM increased up to 38.28 nm with a ratio of 0.5:1. Partial increases in the emission peak of the BPB were observed with increasing QD in the hybrid associate ratio. This situation can be interpreted as the increase in the amount of QD present in the hybrid associate as a donor in the mixture causes an increase in the emission peak of the acceptor BPB [31][32].

### 3.2. Emission Spectra

The as in the absorbance study, emission characterization studies were also carried out in two stages. Similarly, emission studies were carried out due to keeping the QD and BPB amounts in the hybrid associate constant, respectively. The normalized emission characterization for the hybrid associates obtained...
In the second stage of the emission characterization study, while the amount of QD in the CdSeTe QD:BPB hybrid associate was kept constant, the amount of BPB was gradually increased and the emission graph obtained is given in Figure 7. In the study, quenching in luminescence started to appear with the increase amount of BPB in the hybrid associates. With the luminescent quenching process the peak length, 1 for QD:BPB ratio was 1:0, started to be minimalized. However, with the increase in the amount of BPB, the wavelength of the luminescence peak shifted towards blue up to 6 nm, while the luminescence peak FWHM values increased in proportion to the increase in BPB. In fact, while the FWHM value for 1:0 was 37.28 nm, this value increased to 45.72 nm for 1:3.

Although bromophenol blue has not been used in any hybrid associate studies before, it is known that when different types of hybrid associates are examined in the literature [3,18,31], such quenching occurring in luminescence is mainly caused by Förster resonance energy transfer (FRET) or charge transfer. In the emission spectrum, quenching at the luminescence peak of CdSeTe QD suggests that CdSeTe QDs function as donors in the hybrid associate. Similarly, a partial increase in the luminescence peak of BPB can be expected, as can be seen at Figure 6 and Figure 7. This indicates that the quenching mechanism in CdSeTe QD:BPB hybrid associate is due to FRET. The data obtained indicate that the CdSeTe QD:BPB hybrid associate can be used in solar energy systems, applications where electrochemical processes are required, in sensors and imaging areas. In fact, load transfer transitions between components are very important in terms of efficiency of these mechanisms.

3.3. FT-IR Spectra

FT-IR spectra of the CdSeTe QD structure synthesized into the TOPO substrate are shown in Figure 8. Firstly, when the structure was examined against the trioctylphosphine oxide (TOPO) spectrum, CH2 vibrations at 2945 cm−1 showed a progress towards a lower frequency thanks to the coated layer surface. Similarly, when the vibrations at 1450 cm−1 were examined, the asymmetric and symmetrical vibrations of the P=O were also observed. This observation shows that the TOP structure enters the structure by interacting with Cd+2 ions located on the outer surfaces of CdSeTe QD. The shear vibration of the methylene (CH2) shear vibration of the CdSeTe structure was observed at 750 cm−1 and 735 cm−1 between Cd+2 and the Se+2 and Te+2 ions, confirming the realization of CdSeTe QDs. Looking at the Bromo Phenol blue and CdSeTe spectrum, it corresponds to the C-H release and tensile vibration of the Bromo phenol blue groups at 1190 cm−1 and 1225 cm−1. S-O stretching
vibration and S=O symmetrical stretching vibrations within the bromophenol blue structure of the QD’s structure of the peaks coming around approximately 750 cm\(^{-1}\) and 1194 cm\(^{-1}\) increased. This has shown that the interaction is stronger with the QD and sulphate groups, but low level interaction with the hydrogen of the ring.

This has shown that the interaction is stronger with the QD and sulphate groups, but low level interaction with the hydrogen of the ring.

Figure 8 FT-IR spectra for hybrid associates prepared at different QD:BPB (1:1) ratios

The main reason for the transformation of yellow colour is the interaction between bromophenol blue and quantum dots. When viewed in FT-IR spectra, it is thought that the strength of S-O and S=O and 750 cm\(^{-1}\) and 1184 cm\(^{-1}\) vibrations, the intensity of the C-H peak coming around 1190 cm\(^{-1}\) and the visually the colour shift from yellow to low pH. Looking at the Uv-Vis spectra, Bromophenol blue appears to show a very low 425 nm in dichloromethane, while a QDs are added to a high absorbance of about 408 nm. In other words, it is thought that the way of interaction is estimated.

4. CONCLUSION

The spectroscopic characterization of CdSeTe:BPB hybrid associates has been studied in this study. The study has been examined in two basic stages. In the first stage, QD: BPB concentration was kept constant in the BPB hybrid associate and the amount of QD concentration in the solution was gradually increased and its spectroscopic characterizations were examined. The remarkable factor at this stage is the increase in BPB absorbance peak length with the addition of minimal QD. In the second stage, this time QD concentration was kept constant while the amount of BPB was changed. As a result of the study, it was determined that quenching occurred in the luminescence peak according to the amount of BPB added to the constant QD concentration. This led to the conclusion that while CdSeTe QDs act as donors in the associate, BPB acts as an acceptor and the FRET mechanism is active. As a result, CdSeTe QD:BPB shows that hybrid associate can be used especially in solar cells, biosensors and optoelectronic devices based on electron transfer. The enormous increase in absorbance peak, however, promises that CdSeTe QD: BPB can be used in the textile and cosmetic industries.

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