

# Circular Dichroism Spectra and Optical Rotation of II-VI Molecules

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## Research Article

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### ABSTRACT

Spectra of ZnSe molecule with different type of impurity, model of dopant, geometric structure, ligand and solvent have been investigated combining the results of theory and experiment. Contrast of absorption spectra, Circular Dichroism (CD) spectra and optical rotation shows that absorption spectra and CD spectra can be used to judge the type of molecule, the type of impurity, the geometric structure, the type of ligand and solvent. The spectra can also be used to estimate the model of impurity (dopant or forming alloy) in ZnSe molecule. Besides, optical rotation is influenced by the type of impurity, the model of dopant and the type of ligand. For  $Zn_3Se_3$ ,  $Cd_3Se_3$  and  $Zn_3S_3$  and  $Zn_4Se_4$  molecules, they do not have optical rotation. The type of ligand has no influence on the optical rotation.

## INTRODUCTION

Quantum dots (QDs) have attracted major attention for their uniform quantum size effect. Specifically, the spectra of QDs shift to longer wavelength with increasing of size <sup>[1-3]</sup>. Conversely, the shapes and the peak positions of spectra can be used to specify QDs in terms of the type and the size <sup>[4-6]</sup>. Several, II-VI clusters, such as CdTe, ZnSe, CdSe etc. have been investigated <sup>[7-9]</sup>. The geometric structure and suitable calculated method have been confirmed. Computational research on the influence of solvent and the ligand on the spectra have been conducted <sup>[10]</sup>. The calculated data are good agreement with the experimental results.

In the course of the rapid development of QDs, their chirality has been studied in ever increasing detail. Although the concept of chirality drives from the field organic materials, it is useful to characterize QDs <sup>[11,12]</sup>. Therefore, it is important to determine the chirality of QDs. Circular Dichroism (CD), which can offer information about primary structure, secondary, and tertiary structures of organic materials is one of the best methods for analyzing chiral states of these materials <sup>[13]</sup>. CD is used to investigate QDs with respect to chirality <sup>[14-16]</sup>. Chiral D-Pen and L-Pen capped Cds QDs, which have potential for biomedical user, have been prepared <sup>[17]</sup>. ZnSe QDs capped with a chiral biomolecule (ligand), 1-glutathione, were studied for their optical activity <sup>[18]</sup>. A recent study has found that CD spectra are independent of the diameter of QDs <sup>[19]</sup>.

Traditional CD, named electronic CD (ECD), is range from 200 nm to 400 nm (the range of UV), which restricted the application of CD. Vibrational CD (VCD) is CD in the region of infrared spectrum <sup>[20-22]</sup>. Under the ideal condition, the wavelength of UV is equal to the wavelength of ECD and optical rotatory dispersion.

The kind of QDs, the type of impurity, the dopant method, the geometric structure, ligand and solvent have different influence on absorption spectra, ECD, VCD and optical rotation. All these factors have been detailed investigated in the following.

## CALCULATION METHOD

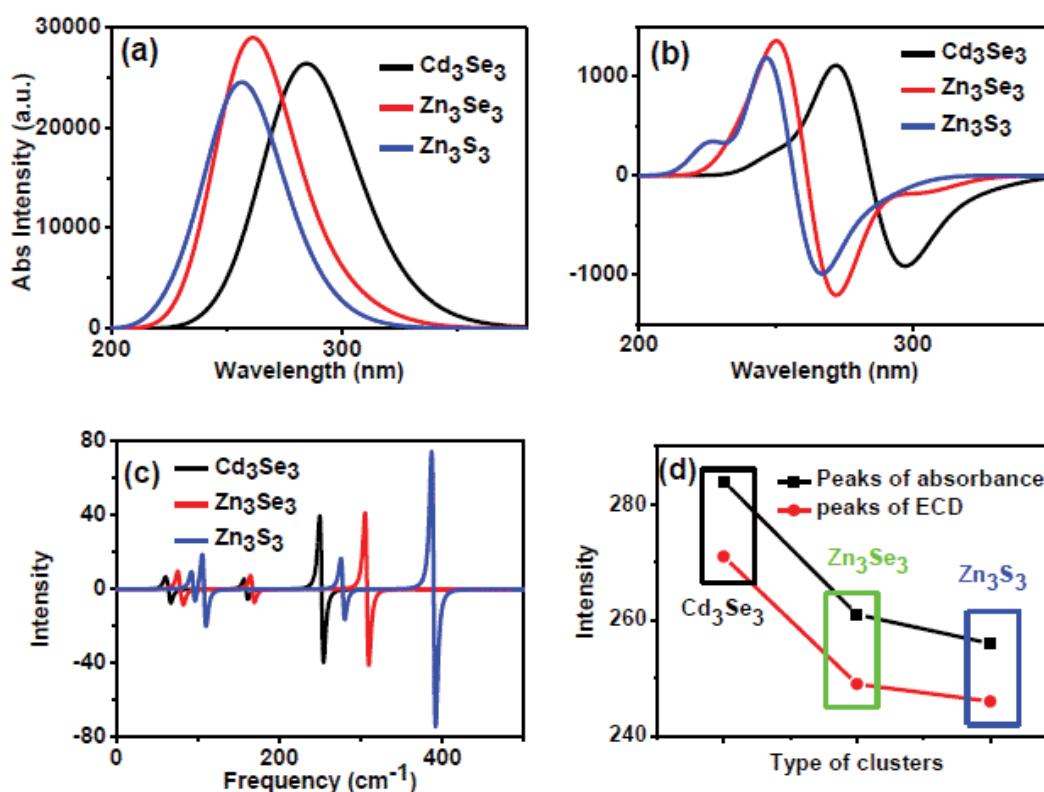
For DFT (density functional theory) calculation, we adopted Becke's three-parameter hybrid exchange functional with the correlation functional by Lee et al. (B3LYP) 6-31G basis set as it was implemented in Gaussian 03 program <sup>[23-25]</sup>. Figures of geometric structures were generated using GaussView program. Absorption spectra and ECD of these molecules were obtained with time-dependent DFT (TDDFT) <sup>[26-30]</sup>. Optical rotation and VCD are obtained at the same level with other data.

## RESULTS AND DISCUSSION

### $Cd_3Se_3$ , $Zn_3Se_3$ and $Zn_3S_3$ Molecules

Geometric structures of  $Cd_3Se_3$ ,  $Zn_3Se_3$  and  $Zn_3S_3$  molecules are hexagon with  $D_{3h}$  symmetry. Absorption spectra, ECD and VCD spectra of  $Cd_3Se_3$ ,  $Zn_3Se_3$  and  $Zn_3S_3$  molecules are depicted in **Figure 1**. The peaks wavelengths of absorption spectra of  $Cd_3Se_3$ ,  $Zn_3Se_3$  and  $Zn_3S_3$  molecules are located in 285 nm, 261 nm, and 257 nm. For the same size of  $Cd_3Se_3$ ,  $Zn_3Se_3$  and  $Zn_3S_3$  molecules, the wavelengths of peaks of absorption spectra shift to blue in the order of  $Cd_3Se_3 > Zn_3Se_3 > Zn_3S_3$  (**Figure 1a**). Namely, the order of peaks wavelengths is  $Cd_3Se_3 > Zn_3Se_3 > Zn_3S_3$ . ECD and VCD also has the order with absorption spectra (**Figure 1b and 1c**). The order of ECD is  $Cd_3Se_3 > Zn_3Se_3 > Zn_3S_3$ , which is the same order with absorption spectra. Frequency of VCD have opposite rule with absorption spectra and ECD. As we have known, absorption spectra of nanoparticle are influenced by the type and the size of materials for nanomaterials. From the data of ECD and VCD, we have confirmed that the type materials would influence ECD and VCD spectra. Therefore, ECD and VCD can be as data to judge the size and type of nanoparticle. Besides, the shift of ECD have the same quantity with absorption spectra, seen from **Figure 1d**.

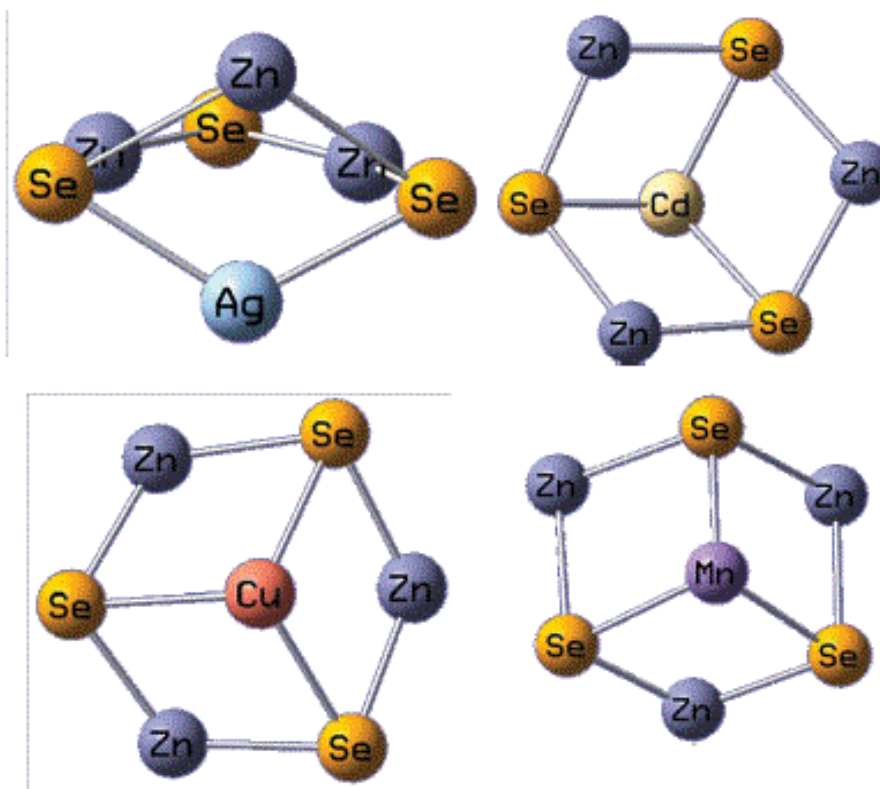
Moreover, we have calculated the optical rotation of  $Cd_3Se_3$ ,  $Zn_3Se_3$  and  $Zn_3S_3$  molecules. The results show that three molecules have no optical rotation. It is clear that optical rotation of nanoparticle does not relate to the type of materials. Therefore, for hexagon structure with  $D_{3h}$  symmetry, they have no optical rotation. From this view, substitution doping  $Zn_3Se_3$  molecules such as  $Zn_2AgSe_3$ ,  $ZnAg_2Se_3$ , they would do not have optical rotation.



**Figure 1:** Absorption spectra (a), ECD (b) and VCD (c) spectra of  $Zn_3Se_3$ ,  $Cd_3Se_3$  and  $Zn_3S_3$  molecules, the location of absorbance peak and the location of the first ECD peak (d).

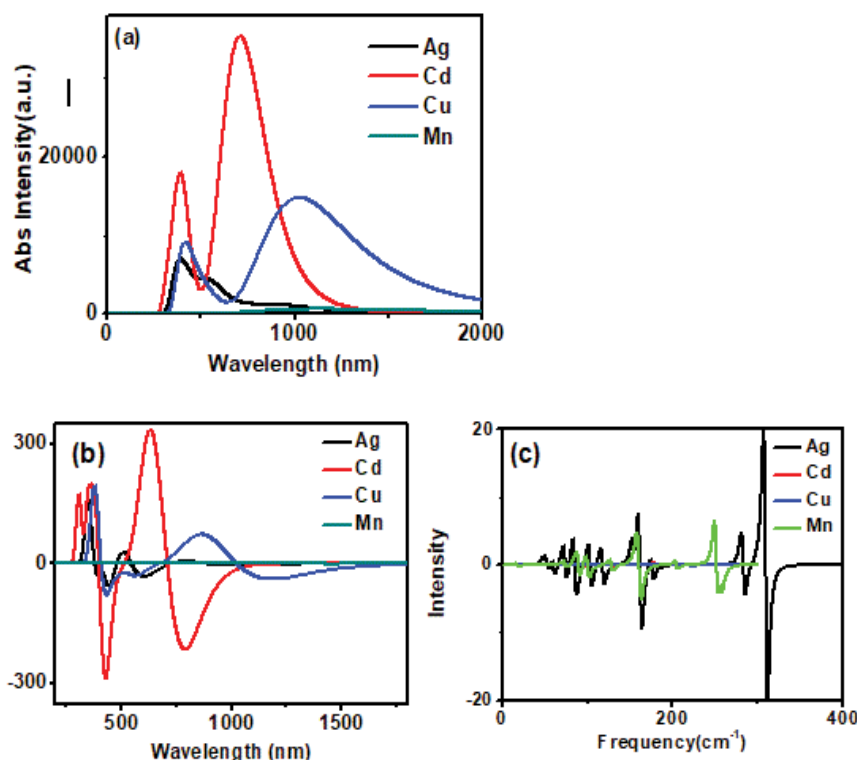
### $Zn_3Se_3$ Molecules with Different Type Impurities Dopant

Geometric structures of  $Ag-Zn_3Se_3$ ,  $Cd-Zn_3Se_3$ ,  $Cu-Zn_3Se_3$ ,  $Mn-Zn_3Se_3$  molecules are showed in **Figure 2**. The impurities are put in the center of hexagon before optimization. The whole molecule is planar (**Figure 2**),  $Ag-Zn_3Se_3$  have different geometric structure with  $Cd-Zn_3Se_3$ ,  $Cu-Zn_3Se_3$  and  $Mn-Zn_3Se_3$  molecules.  $Ag$  atom is not in the center of hexagon after optimizing.  $Cd$ ,  $Cu$  and  $Mn$  atoms are in the center of hexagon, but they are not in a plane with  $Zn_3Se_3$  molecule.



**Figure 2:** Geometric structures of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub> and Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules.

Absorption spectra, ECD and VCD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub>, Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules are depicted in **Figure 3a-3c**. Clearly, the spectra show Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub> and Cu-Zn<sub>3</sub>Se<sub>3</sub> molecules have two peaks. Mn-Zn<sub>3</sub>Se<sub>3</sub> molecule only has one peak. From experiment, we have known that Ag and Cu doped ZnSe quantum dots (QDs) had the photoluminescence (PL) of ZnSe QDs and impurities of Ag or Cu [31,32]. Mn doped ZnSe QDs has one peak which is PL of Mn impurity [33]. The reason is that conduction band or valence band of Ag and Cu is among the band gap of ZnSe and both conduction band and valence band of Mn is among the band gap of ZnSe. Therefore, Cd doped ZnSe QDs have the same band structure with Ag and Cu doped ZnSe QDs.

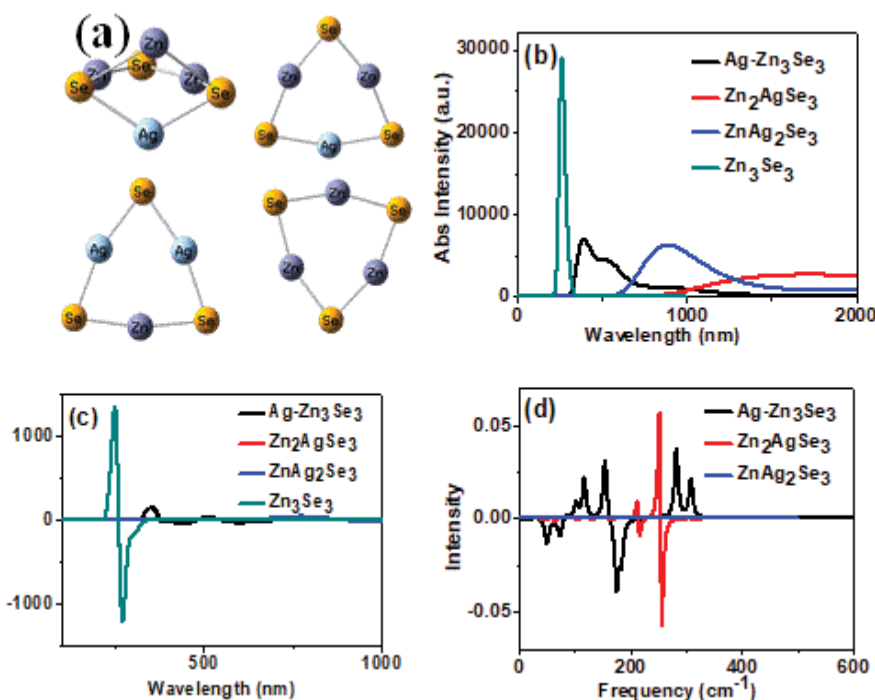


**Figure 3:** Absorption spectra (a), ECD (b) and VCD (c) spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub>, Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules.

ECD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub> and Cu-Zn<sub>3</sub>Se<sub>3</sub> are similar. Cd-Zn<sub>3</sub>Se<sub>3</sub> molecule has strong ECD spectra. ECD spectra of Mn-Zn<sub>3</sub>Se<sub>3</sub> is close to zero. Moreover, ECD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub>, Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules are different from Zn<sub>3</sub>Se<sub>3</sub> molecule. Thus, ECD spectra are related to type of impurities. VCD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub>, Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules are different. Ag and Mn doped ZnSe molecules have stronger VCD spectra than those of Cd and Cu doped ZnSe molecules. VCD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub> molecule is similar to that of Zn<sub>3</sub>Se<sub>3</sub> molecule. Obviously, the influence of structure and impurity type is little on VCD spectra. The calculated optical rotation data for Ag-Zn<sub>3</sub>Se<sub>3</sub>, Cd-Zn<sub>3</sub>Se<sub>3</sub>, Cu-Zn<sub>3</sub>Se<sub>3</sub>, and Mn-Zn<sub>3</sub>Se<sub>3</sub> molecules are -28, 12, 1 and 39, respectively. As we have known that Zn<sub>3</sub>Se<sub>3</sub> molecule have no optical rotation. The impurity in Zn<sub>3</sub>Se<sub>3</sub> molecule has obvious influence on the optical rotation.

**Vacancy Doping and Substitution Doping Zn<sub>3</sub>Se<sub>3</sub> Molecules**

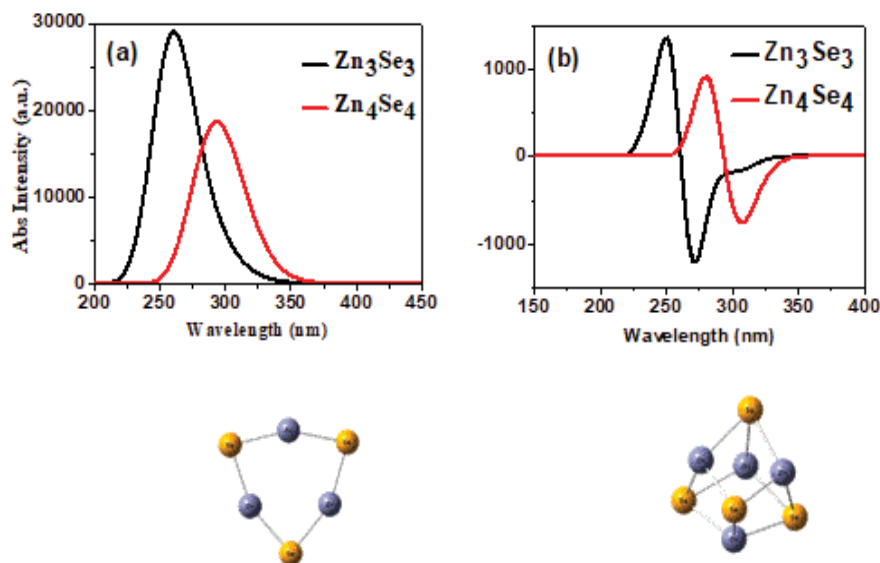
Geometric structures of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub> and Zn<sub>3</sub>Se<sub>3</sub> molecules are showed in **Figure 4a**. Absorption spectra, ECD and VCD spectra are depicted in **Figure 4b-4d**. Vacancy doping Ag-Zn<sub>3</sub>Se<sub>3</sub> has different structure from Zn<sub>3</sub>Se<sub>3</sub> molecule. Substitution doping Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub>, and Zn<sub>3</sub>Se<sub>3</sub> molecules have the similar geometric structures. Therefore, impurity in substitution doping has little influence on the geometric structure of Zn<sub>3</sub>Se<sub>3</sub> molecule. Absorbance spectra show that vacancy doping Ag-Zn<sub>3</sub>Se<sub>3</sub> has two peaks. Substitution doping Zn<sub>2</sub>AgSe<sub>3</sub> and ZnAg<sub>2</sub>Se<sub>3</sub> molecule have only one peak which is similar to that of Zn<sub>3</sub>Se<sub>3</sub> molecule. Therefore, substitution doping structure is inclined to forming alloy materials. Vacancy doping molecule may introduce an impurity band between band gaps of host material. ECD and VCD spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub> are close to zero, compared to Zn<sub>3</sub>Se<sub>3</sub> molecule. The dopant of impurity of Ag would change the characters of ECD and VCD. The optical rotation data of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub> and Zn<sub>3</sub>Se<sub>3</sub> molecules are -28, 1, -1 and 0. Ag-Zn<sub>3</sub>Se<sub>3</sub> molecule has strong optical rotation. Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub> and Zn<sub>3</sub>Se<sub>3</sub> molecules do not have optical rotation. Thus, optical rotation is influenced by geometric structure but not impurity.



**Figure 4:** Geometric structures (a), Absorption spectra (b), ECD (c) VCD and (d) spectra of Ag-Zn<sub>3</sub>Se<sub>3</sub>, Zn<sub>2</sub>AgSe<sub>3</sub>, ZnAg<sub>2</sub>Se<sub>3</sub> and Zn<sub>3</sub>Se<sub>3</sub>.

**Properties of Zn<sub>3</sub>Se<sub>3</sub> and Zn<sub>4</sub>Se<sub>4</sub> Molecules**

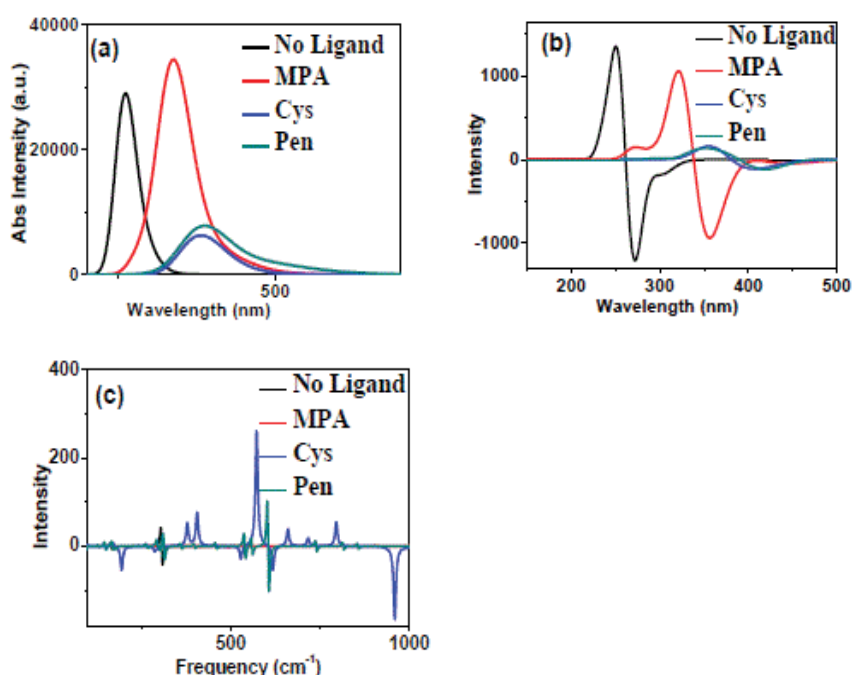
II-VI QDs have two kinds of structures zinc blende and Wurtzite. Zn<sub>3</sub>Se<sub>3</sub> is similar to Wurtzite. Zn<sub>4</sub>Se<sub>4</sub> molecule is close to zinc blende. Geometric structures of Zn<sub>3</sub>Se<sub>3</sub> and Zn<sub>4</sub>Se<sub>4</sub> molecules are inserted in absorption spectra of **Figure 5a** and ECD spectra of **Figure 5b**. Absorption spectra show that the peak of Zn<sub>4</sub>Se<sub>4</sub> molecule shift to longer wavelength than that of Zn<sub>3</sub>Se<sub>3</sub> molecule. This agree with quantum size effect. Namely, with increasing of size, the absorption spectra of QDs would shift to long wavelength. ECD spectra of Zn<sub>3</sub>Se<sub>3</sub> and Zn<sub>4</sub>Se<sub>4</sub> molecules have the same shape, which illustrate geometric structure of molecule would not change the shape of ECD spectra. VCD spectra of Zn<sub>4</sub>Se<sub>4</sub> molecule are zero. Namely, Zn<sub>4</sub>Se<sub>4</sub> molecule has weak VCD. To make clear, we have calculated the VCD spectra of Cd<sub>4</sub>Se<sub>4</sub> molecule. The result shows that Cd<sub>4</sub>Se<sub>4</sub> molecule has no VCD spectra. Therefore, the type of QDs has little influence on the VCD spectra. Optical rotation of Zn<sub>3</sub>Se<sub>3</sub> and Zn<sub>4</sub>Se<sub>4</sub> molecules are zero. Thus, two geometric structures of Zn<sub>3</sub>Se<sub>3</sub> and Zn<sub>4</sub>Se<sub>4</sub> molecules both have good symmetry that results in weak optical rotation.



**Figure 5:** Absorption spectra (a) and ECD spectra (b) of  $Zn_3Se_3$  and  $Zn_4Se_4$  molecules. Geometric structures of  $Zn_3Se_3$  and  $Zn_4Se_4$  molecules are inserted in (a) and (b).

**$Zn_3Se_3$  Molecules with Different Ligand**

Ligand has little influence on the geometric structure of  $Zn_3Se_3$  molecule. However, ligand would influence absorption spectra (**Figure 6a**), ECD (**Figure 6b**), VCD (**Figure 6c**) and optical rotation. Compared to that of structure without ligand, absorption spectra of  $Zn_3Se_3$  molecule with ligand shift to longer wavelength. Moreover, the data of shift are different for different type ligand. ECD have the same rule with absorption spectra. For absorption spectra and ECD,  $Zn_3Se_3$  molecule with ligand cysteine and penicillium amine have similar shape. Moreover, the intensity and the wavelength are similar. VCD spectra of  $Zn_3Se_3$  molecule with ligand cysteine and penicillium amine are different. Obviously, the influence of ligand on  $Zn_3Se_3$  molecule with different ligand is not the same. Data of optical rotation for  $Zn_3Se_3$  molecule without ligand, MPA, cysteine and penicillium amine are 0, -13, -356 and -353. Clearly, optical rotation of  $Zn_3Se_3$  molecule is related to the type of ligand. Therefore, optical rotation of QDs would be controlled through changing the type of ligand.

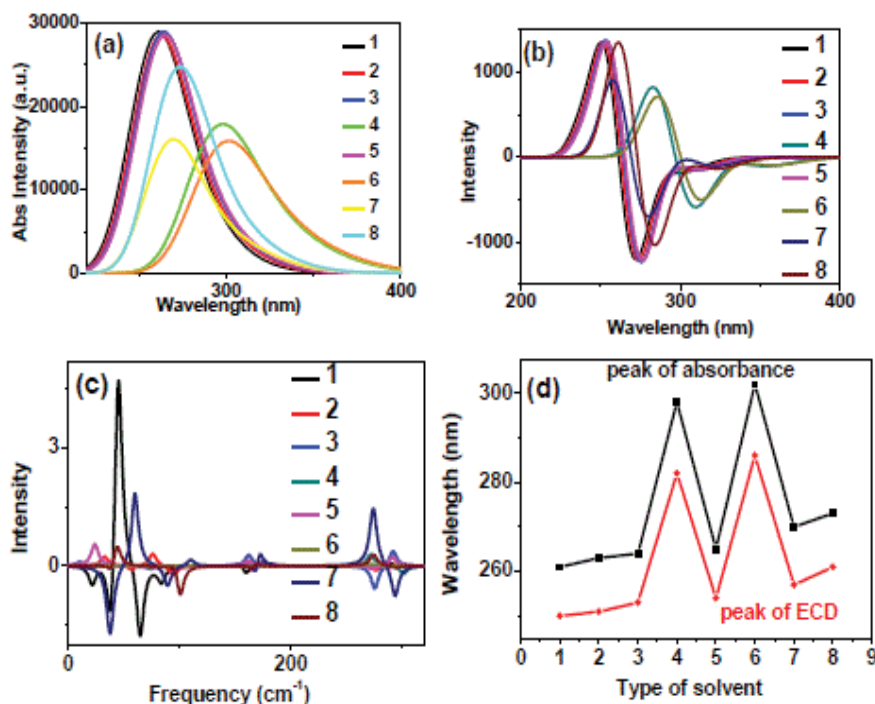


**Figure 6:** Absorption spectra (a), ECD (b) and VCD (c) spectra of  $Zn_3Se_3$  without ligand and with different ligands MPA ( $HS-CH_2-CH_2-COOH$ ), cysteine ( $HS-CH_2-CH(NH_2)-COOH$ ), and penicillium amine ( $CH_3-C(CH_3)(SH)-CH(NH_2)-COOH$ ).

**Influence of Solvent**

Absorption spectra, ECD and VCD are depicted in **Figure 7**. Obviously, solvent have influence on absorbance spectra, ECD

and VCD. Moreover, the shift rule of absorbance spectra is according to the change rule of ECD spectra (**Figure 7d**). Optical rotation of  $Zn_3Se_3$  molecule with different solvent are zero. Namely, optical rotation is not related to the type of solvent.



**Figure 7:** Absorption spectra (a), ECD (b) and VCD (c) spectra of  $Zn_3Se_3$  with different solvent. The location of absorbance peak and the location of the first ECD peak (d). 1-water; 2-methanol; 3-ethanol; 4-toluene; 5-acetone; 6-cyclohexane; 7-quinoline; 8-tetrahydrofuran (THF).

## CONCLUSIONS

The manuscript has investigated the influence of the type of impurity, model of dopant, geometric structure, ligand and solvent of  $ZnSe$  molecule on absorption spectra, CD spectra and optical rotation. The results show that CD spectra can be used to estimate the characters of molecules as absorption spectra. Therefore, CD spectra as a practical method are proposed for experimental investigation of  $ZnSe$  QDs. Optical rotation is an important nature of application of QDs. Calculated data illustrate that optical rotations of molecules are influenced by the type of impurity, the model of dopant and the type of ligand. For  $Zn_3Se_3$ ,  $Cd_3Se_3$  and  $Zn_3S_3$  and  $Zn_4Se_4$  molecules, they do not have optical rotation. The type of ligand has no influence on the optical rotation.

## ACKNOWLEDGEMENTS

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