

Accepted Manuscript

Photoluminescence spectra of CdSe/ZnS quantum dots in solution

K.H. Ibnaouf, Saradh Prasad, A. Hamdan, M. AlSalhi, A.S. Aldwayyan, M.B. Zaman, V. Masilamani

PII: S1386-1425(13)01246-8
DOI: <http://dx.doi.org/10.1016/j.saa.2013.10.089>
Reference: SAA 11218

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 25 December 2012
Accepted Date: 3 August 2013

Please cite this article as: K.H. Ibnaouf, S. Prasad, A. Hamdan, M. AlSalhi, A.S. Aldwayyan, M.B. Zaman, V. Masilamani, Photoluminescence spectra of CdSe/ZnS quantum dots in solution, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2013), doi: <http://dx.doi.org/10.1016/j.saa.2013.10.089>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Photoluminescence spectra of CdSe/ZnS quantum dots in solution

K. H. Ibnaouf^{1*}, Saradh Prasad², A. Hamdan^{2,3}, M. AlSalhi^{2,3}, A.S. Aldwayyan³, and M. B. Zaman^{4,5}, V. Masilamani^{2,3}

1 - Al Imam Mohammad Ibn Saud Islamic University, Physics Department, college of science
P.O.Box 9095,Riyadh 11623, Saudi Arabia.

2 - Research Chair for Laser Diagnosis of Cancer, King Saud University.

3- Department of Physics& Astronomy, College of science, King Saud University.

4 - CEREM, College of Engineering – King Saud University Saud University.

5 -Advanced Medical Research Institute of Canada, Sudbury, Canada

* For correspondence: kheo90@gmail.com

Abstract:

The spectral properties of CdSe/ZnS core-shell quantum dots (QDs) of 3 nm size have been studied under different organic solvents, concentrations and temperatures. Our results showed that the absorption spectra of CdSe/ZnS in benzene have two humps; one around 420 nm and another at 525 nm, with a steady increase in absorption along UV region, and the absorption spectral profile under a wide range of concentrations did not change. On the other hand, the photoluminescence (PL) spectra of CdSe/ZnS in benzene showed two bands one around 375nm and the other around 550nm. It could be seen that the band at 375 nm is due to the interaction between the shell (ZnS) with the solvent species in high excited state, and the band at 550 nm is due to core alone (CdSe).

Keywords: *Photoluminescence Spectra; quantum dots; solvent influence;*

Introduction:

The semiconductors quantum dots (QDs) are nanoparticles or clusters-like particles with a typical size of 2-20 nanometers (nm) consisting of few hundreds to few thousand atoms in each particle. Quantum dots are new nanomaterials which have properties that are intermediate between those of bulk materials and those of isolated or discrete molecules [1].

Quantum dots can be made from a wide variety of material; the most common QDs are the binary semiconductor materials containing the II-VI elements, e.g, cadmium sulfide (CdS), cadmium selenide (CdSe), cadmium telluride (CdTe), zinc selenide (ZnSe), lead sulfide (PbS), and mercury sulfide (HgS) etc. These semiconductor QDs, in the bulk, usually have band gap energy less than 3eV. In all these nanocrystals QDs (or the clusters) the atoms are aligned periodically with certain crystal lattice structure, such as the cubic zinc blende or hexagonal wurtzite structure of the CdS and ZnS QDs [2]. Because of these reasons, these clusters-like particles display unique electronic and optical properties including size-tunable light emission, simultaneous excitation of multiple fluorescence, high quantum yield and long-term photostability. They have attracted a lot of both theoretical and experimental research interest for more than two decades [3-7]. These properties can be drastically changed, while maintaining the material morphology, by simply varying the number of atoms in each quantum dot. In such nanoparticles, the size of the quantum dot can be used to tune the emission spectral range over a major part of visible spectrum due to quantization effect: e.g., in the case of CdSe, the spectral range can be tuned from deep red ~ 1.7 eV to green ~ 2.4 eV by reducing the dot diameter from 20 to 2nm [8-10]. It has been also shown that the core-shell quantum dots over coated with higher band gap inorganic materials exhibits high PL quantum yield compared to the uncoated QDs, perhaps due to the elimination of surface defects promoting non-radiative recombination [11].

The photoluminescence spectra of CdSe/ZnS were found to be red shifted from the absorption maximum. This was observed more strongly in very small size quantum dots; such a shift towards red in emission of CdSe/ZnS quantum dots has been attributed to the recombination of weakly overlapping surface-localized carriers. This effect has also been explained as a recombination of the optically forbidden ground state exciton split from the first optically active state by quantum dots shape, electron-hole exchange interaction and intrinsic asymmetry of lattice[12].

Shu-Man Liu et al studied CdSe semiconductor nanoclusters over-coated with CdS shell in aqueous solution. Based on their experimental results and theoretical calculation, a model of excimer formation within nanoclusters was proposed to explain the large Stokes' shift [13].

In our work presented here, the spectral properties of CdSe/ZnS in different concentrations and temperatures were described in a particular solvent environment. The results showed that semiconductor CdSe/ZnS quantum dots could exhibit two bands of emission; one due to the core and another due to the interaction between solvent and shell. Similar experiments done in three more different types of the solvent environments showed that such interaction was strongly pronounced in polar solvents.

Experimental

CdSe/ZnS quantum dots were prepared following the previously reported procedures: TBP (tributylphosphine), TOPO (trioctylphosphine oxide), HDA (hexadecylamine) or ODPA (octadecyl phosphonic acid) capped CdSe nanocrystals were synthesized using standard published methods [14]. We deposited about five monolayers of ZnS around the CdSe cores by using the recently developed successive ion layer adhesion and reaction (SILAR) technique [15]. To optimize the ZnS shell growth around the CdSe core by SILAR using ZnO and S as precursors, a stock solution of 0.1 M concentration was prepared for ZnO, oleic acid and ODE (1-octadecene) that were used for Zn coating and elemental sulphur and ODE for S coating. The purified CdSe QDs were added to a reaction flask consisting of HDA and ODE where Zn and S stock solutions were added under argon flow to grow the ZnS shell. To optimize the shell growth, the reaction temperature was controlled between 200 °C to 240 °C.

The absorption and photoluminescence (PL) spectra of CdSe/ZnS core-shell quantum dots in various organic solutions were studied under wide range of concentrations and temperatures. The spectra for the fresh solutions were measured in a small quartz cuvette with the dimensions 1×1×4 cm with an optical path length of 1 cm.

UV-Vis absorption spectra were taken using a Perkin Elmer spectrophotometer (Lambda 950) and the photoluminescence (PL) was measured on a Perkin Elmer LS55 spectrofluorometer.

Results and discussions:

The purified quantum dots nanocrystals were dispersed in different solvents in different concentrations and U-V absorption and photoluminescence emission spectra were taken and presented below to give insight into the excited state behavior of these nanocrystals.

Fig.1 shows the absorption spectra of CdSe/ZnS quantum dots of different concentrations ranging from 9.0mg to 300mg of CdSe/ZnS in 5ml of benzene. It shows that there were two humps; one at 420 nm and another at 525 nm with high absorbance in the UV region. When the concentration was increased, the optical density increased. Note that the absorbance was not to the scale.

CdSe/ZnS in benzene at low concentration (9 mg/ 5ml) was prepared. The photoluminescence emission spectra (PLES) depicted in fig.2, it could be seen that the PLES, as excited at 300 nm have a primary band at 375nm and small shoulder at 550nm.

The PLES of CdSe/ZnS in benzene at low concentration (18 mg in 5ml) were obtained under two different wavelengths of excitation (280nm and 330nm).In both cases one could get the same spectral profile (with the primary band at 375nm and secondary at 550nm) but with different intensity as shown in fig.3. This is indicative for *spectral purity* of the sample.

The fluorescence spectrum of CdSe (core alone) of size 3 nm in benzene at 300 mg/ 5 ml was recorded. It could be seen that there was only one band at 550 nm. There was no traces of signal have been detected at 375 nm as shown in fig.3.

Similarly, the fluorescence spectrum of ZnS (shell alone) in benzene at 300 mg/ 5 ml was recorded. The result showed that there was only one band at 375 nm. There was no other band at 550 nm as shown in fig.4. By comparing, fig.3&4 with fig.2, the bands at 375 nm and 550 nm are due to the shell (ZnS) and core (CdSe) respectively.

The PLES were recorded for three types of solvents under the same concentration. Figs.5a display the PLES spectra of CdSe/ZnS core shell quantum dots dissolved in hexane and benzene at same concentration (150 mg in 5ml). It could be seen that the bands at 550 nm and was strongly pronounced in non-polar solvents.

In polar solvents like dimethyl fumarate (DMF) and acetonitrile (AN), as illustrated in fig.5c, the band at 550 nm for the CdSe/ZnS core shell is totally absent, and there was only one

band at 375 nm. This because the interaction between CdSe/ZnS with polar solvents in excited state is very strong. It is important to note that for CdSe/ZnS in polar solvents, the peak around 375 nm is due to the dipole-dipole interaction between the solvent and shell (ZnS) in excited state. Here the solvent surrounds the shell and traps it as in cage. In non-polar solvents the peak at 375 nm was very weak for CdSe/ZnS; this is because the interaction between the solvent species and the quantum dots is very weak

In some of intermediate polar solvents like ethyl acetate and n-butyl acetate, the intensity of the 375 nm and 550 nm bands of the core shell became almost comparable. (See fig.5b)

Fig.6 shows the PLES as excited at 300 nm for different concentration (9.0mg to 300mg of CdSe/ZnS in 5ml of benzene). It clearly shows that the weak secondary band at 550nm became stronger and stronger; and for the concentration around 300mg of CdSe/ZnS in 5ml of benzene the band around 550nm became the primary band and the one at 375nm became the secondary band.

The fig.6 also displays that the intensity of the band of 550nm increased by increasing the concentration. For the same set of concentrations; the profile of the absorption spectra remained unchanged as shown in fig.1. This could be due to increase in the ratio between CdSe/ZnS to the solvents species, in turn decreases the number of solvents species interacting with CdSe/ZnS. Therefore the intensity of the band at 375 nm was decreased and the band at 550 nm increased.

The spectral profiles of 300 mg of CdSe/ZnS in 5ml of benzene were taken under different temperatures, Fig.7 shows the PLES as excited at 300nm for three different temperatures. It's clear that as the temperature was increased above room temperature, (from 298K to 323K) the band at 550nm became weaker than at 375 nm. i.e,

$$\left[\frac{I_{550}}{I_{375}}(323K) < \frac{I_{550}}{I_{375}}(298K) \right]$$

The reverse took place with 550nm becoming stronger and stronger than 375nm band when temperature was lowered. .ie,

$$\left[\frac{I_{550}}{I_{375}}(283K) > \frac{I_{550}}{I_{375}}(298K) \right]$$

Fig.8 is a representation of I_{550}/I_{375} , the relative photoluminescence (PL) emission intensity at 550 nm and 375 nm bands, as a function of polarity (dielectric constant) of solvents.

The linear fit is a strong indication that polar solvent enhances the interaction between the shell and the solvent species.

The solvent environment not only changes the properties of solvent- shell interaction, but also the quantum efficiency of photoluminescence [16]. This is shown in table I where it can be clearly seen that quantum efficiencies increase in non- polar solvents like benzene.

Another important property of solvents influence upon the spectral properties is Stokes' shift, which is a measure of changes in the dipole moment of the species when it goes to the excited state from the ground state.

We observed a very small change in the fluorescence spectra for CdSe/ZnS in all of the above solutions at low concentrations, the only difference being a small shift in the band of the emission wavelength. In cases where the polarization interaction is the major contributing factor, Malaga et al. [15] have shown that the Stokes shift has a linear variation with the dipole factor.

The dipole factor is a measure of the interaction between the solute dipole and the solvent dipoles surrounding the solute as a cage. If the solute undergoes great delocalization of electron cloud (hence more polar) in excited state than the ground state, the dipole interaction becomes stronger in excited state than the ground state. This leads to more and more red shift of absorption and emission bands, and hence the Stokes' shift.

Fig.9 gives the variation of Stokes' shift as a function of dipole factor of the solvent as defined by Mataga et al [17]. It can be seen that this quantum dot undergoes significant changes in the electron delocalization and becomes more polar in the excited state than in the ground state.

Conclusion:

In this communication, we have been able to show that the quantum dot nanocrystals of CdSe/ZnS in organic solvents exhibits two bands one due to the interaction between solvent and shell at 375 nm, pronounced in highly polar solvents, and other one is due to core at 550 nm. This is analogous to the exciplex behaviour of the many organic dyes. All these because of the excitons of these nanoparticles undergo gross changes in the electronic configuration. These nanocrystals behave very much like organic dye molecule.

Acknowledgement:

This project was supported by King Saud University, Deanship of Scientific Research, College of Science Research Center.

ACCEPTED MANUSCRIPT

References:

- [1] Guozhong Cao, Jeffrey Brinker, Annual review of nano research - Volume 1. World Scientific 470 (2006)
- [2] Hines MA, Guyot-Sionnest P, "Synthesis and Characterization of Strongly Luminescing ZnS-Capped CdSe Nanocrystals." *J Phys Chem* 100(2):468–471, (1996)
- [3] Dabbousi BO, Rodriguez-Viejo J, Mikulec FV, Heine JR, Mattoussi H, Ober R, Jensen KF, Bawendi MG "(CdSe)ZnS Core–Shell Quantum Dots: Synthesis and Characterization of a Size Series of Highly Luminescent Nanocrystallites." *J Phys Chem B* 101 (46):9463–9475 (1997)
- [4] Alivisatos P, "The use of nanocrystals in biological detection." *Nature Biotechnology* 22:47–52 (2004)
- [5] Gao XH, Yang LL, Petros JA, Marshall FF, Simons JW, Nie SM, "In vivo molecular and cellular imaging with quantum dots." *Cur Opin in Biotechnol* 16(1):63–72, (2005)
- [6] Michalet X, Pinaud FF, Bentolila LA, Tsay JM, Doose S, Li JJ, Sundaresan G, Wu AM, Gambhir SS, Weiss S, "Quantum dots for live cells, in vivo imaging, and diagnostics" *Science* 307(5709): 538–544, (2005)
- [7] Smith AM, Duan HW, Mohs AM, Nie SM "Bioconjugated quantum dots for in vivo molecular and cellular imaging." *Adv Drug Deliv Rev* 60(11):1226–1240, (2008)
- [8] Alivisatos AP Semiconductor Clusters, "Nanocrystals and Quantum Dots." *Science* 271(5251): 933–937, (1996)
- [9] Murray CB, Norris DJ, Bawendi MG, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. *J Am Chem Soc* 115 (19):8706–8715, (1993)
- [10] Gorner S, Hodes G, "Quantum size effects in the study of chemical solution deposition mechanisms of semiconductor films." *J Phys Chem* 98(20):5338–5346, (1994)
- [11] Reiss P, Protiere M, Li L, "Core/Shell Semiconductor Nanocrystals." *Small* 5(2):154–168, (2009)
- [12] Bawendi MG, Wilson WL, Rothberg L, Carroll PJ, Jedju TM, Steigerwald ML, Brus LE, *Phys Rev Lett* 65(1623), (1990)
- [13] Liu Shu-Man, Guo Hai-Qing, Zhang Zhi-Hua, Li Rui, Chen Wei, Wang Zhan-Guo, "Characterization of CdSe and CdSe/CdS core/shell nanoclusters synthesized in aqueous solution." *Physica E* 8(2):174–178, (2000)
- [14] Zaman MB, Nath TB, Zhang J, Whithfield D, Yu K, "Single-Domain Antibody Functionalized CdSe/ZnS Quantum Dots for Cellular Imaging of Cancer Cells." *J Phys Chem C* 113:496–499, (2009)
- [15] Li JJ, Wang YA, Guo W, Keay JC, Mishima TD, Johnson MB, Peng X, "Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents via Successive Ion Layer Adsorption and Reaction." *J Am Chem Soc* 125(41):12567–12575, (2003)
- [16] Grabolle M, Spieles M, Lesnyak V, Gaponik N, Eychmuller A, Genger RU, "Determination of the fluorescence quantum yield of quantum dots: suitable procedures and achievable uncertainties." *Anal Chem* 81: 6285, (2009)
- [17] Metaga N, Tsuno S, "Hydrogen Bonding Effect on the Fluorescence of Some Nitrogen Heterocycles." *Bull Chem Soc Japan* 30(4):368–374, (1957)
- [18] Masilamani V, Aldwayyan AS, "Structural and solvent dependence of superexciplex" *Spectrochimica Acta Part A* 60:2099–2106 (2004)

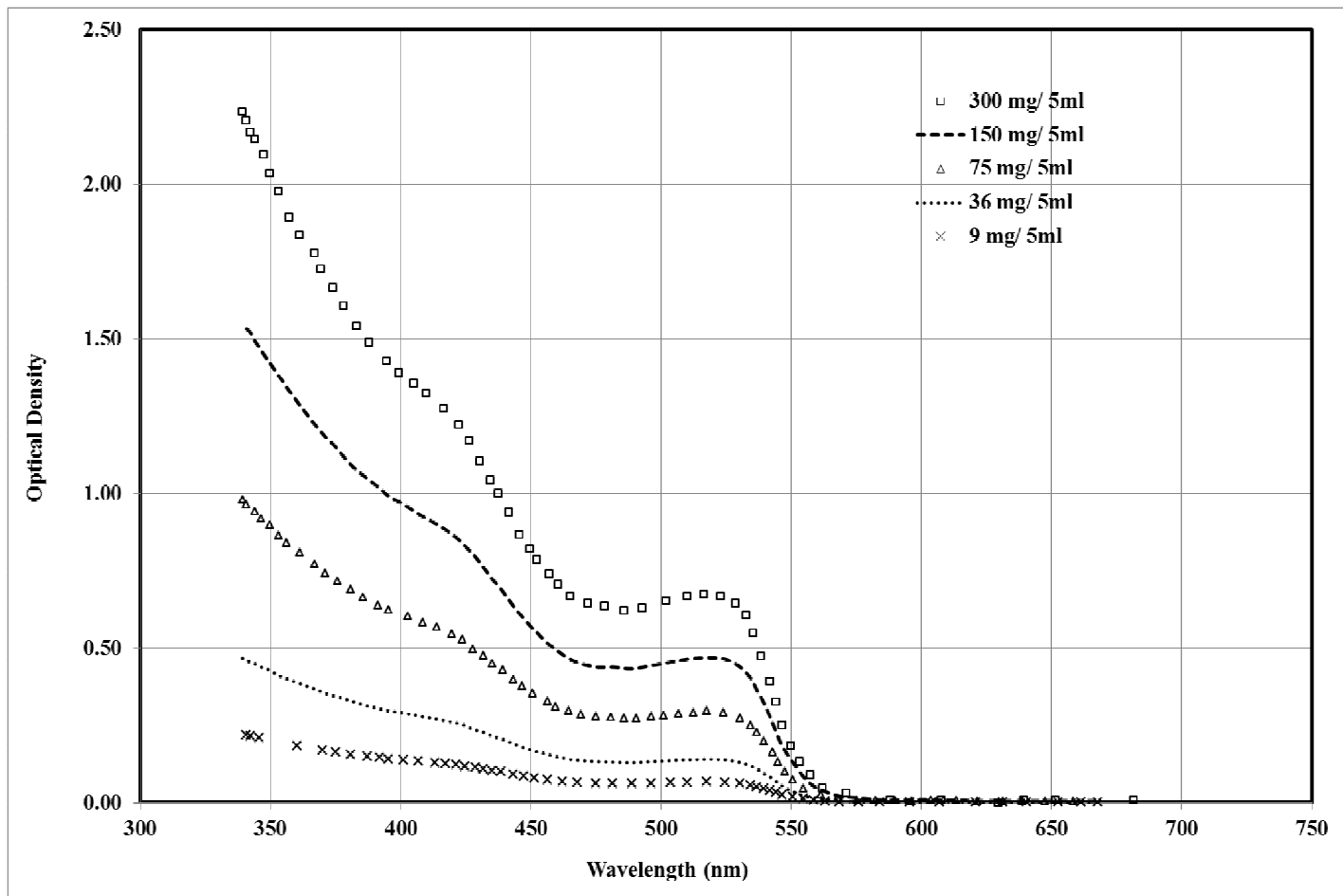


Fig.1

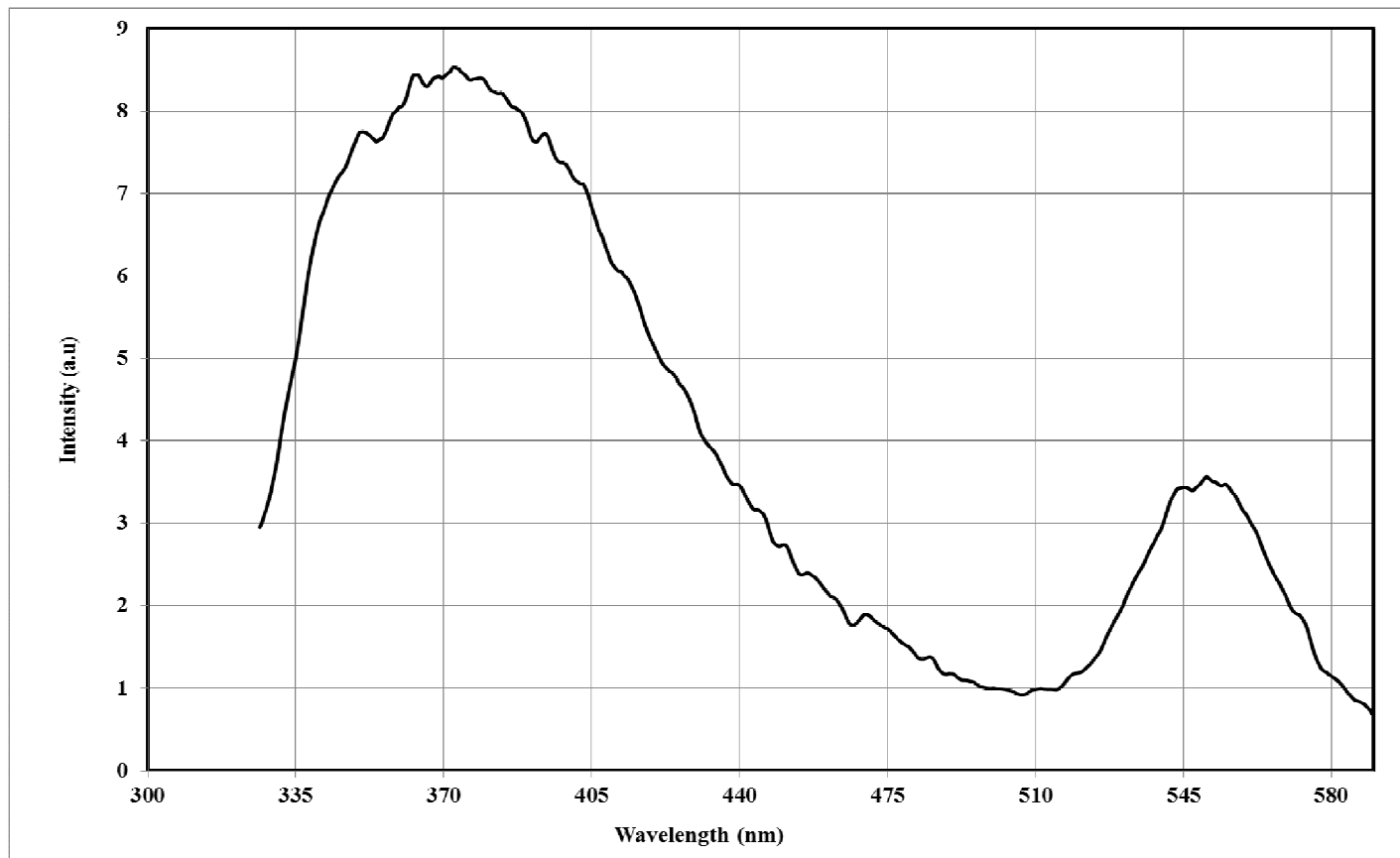


Fig.2

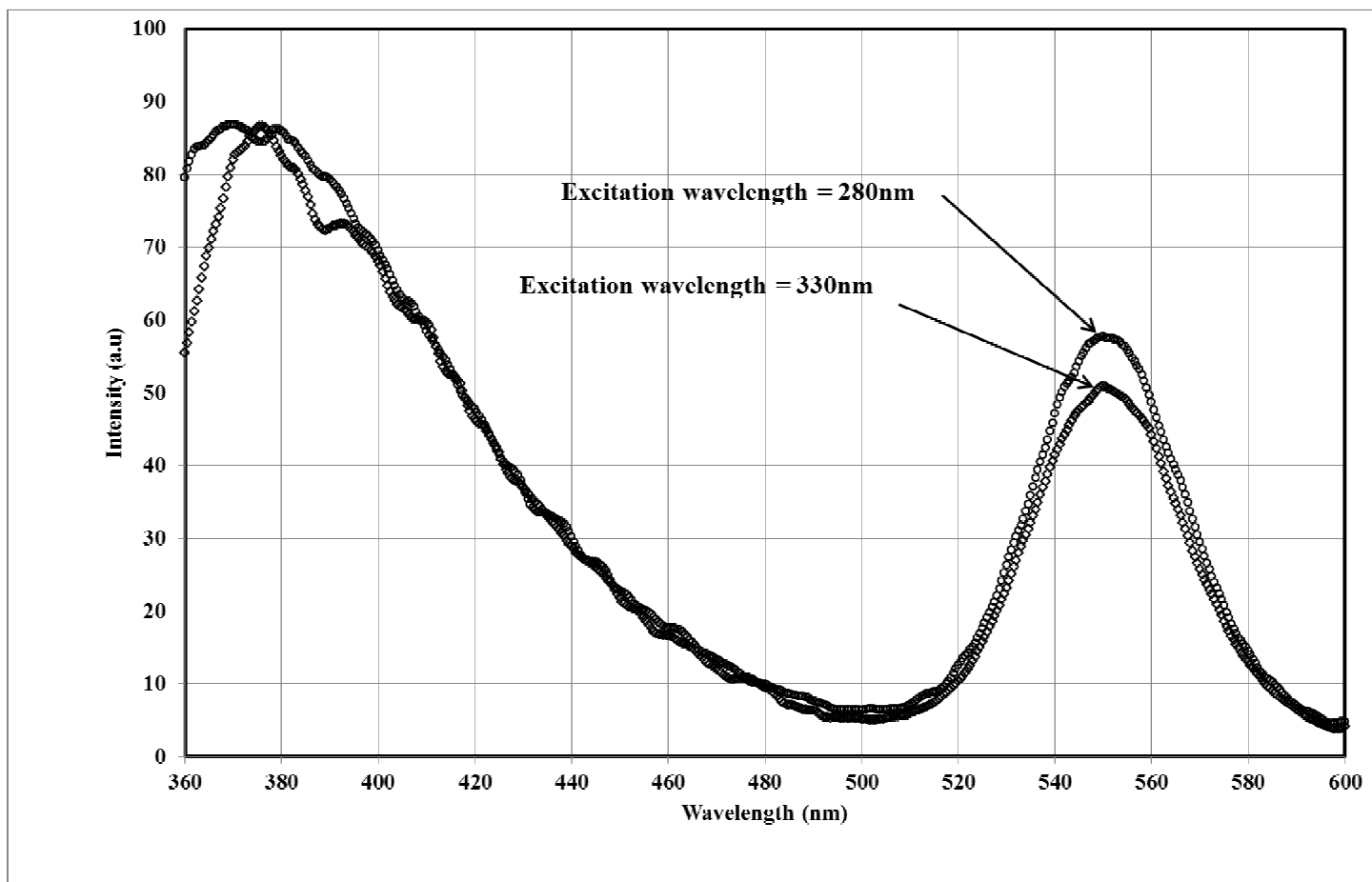
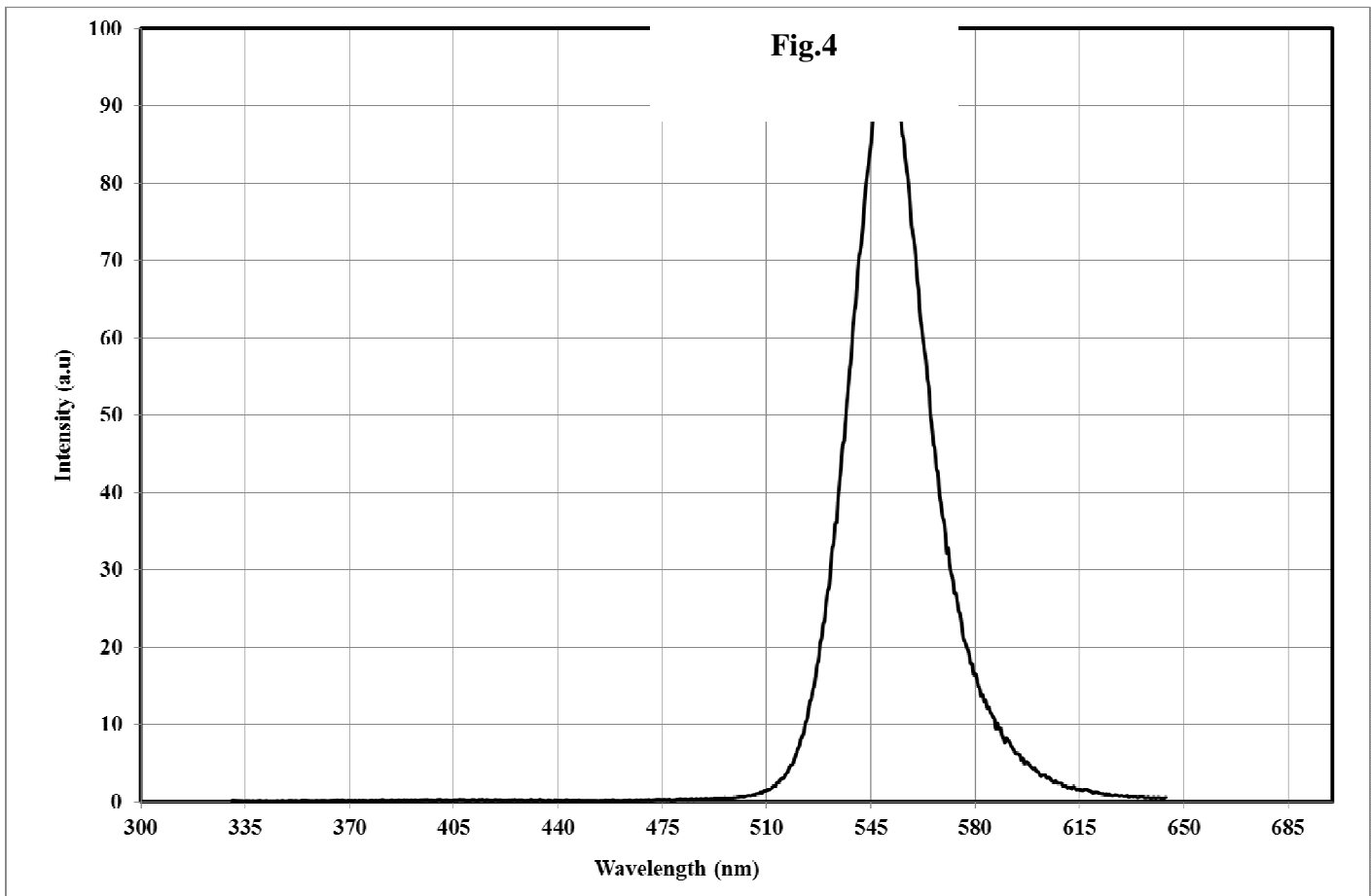


Fig.3



ACCEPTED

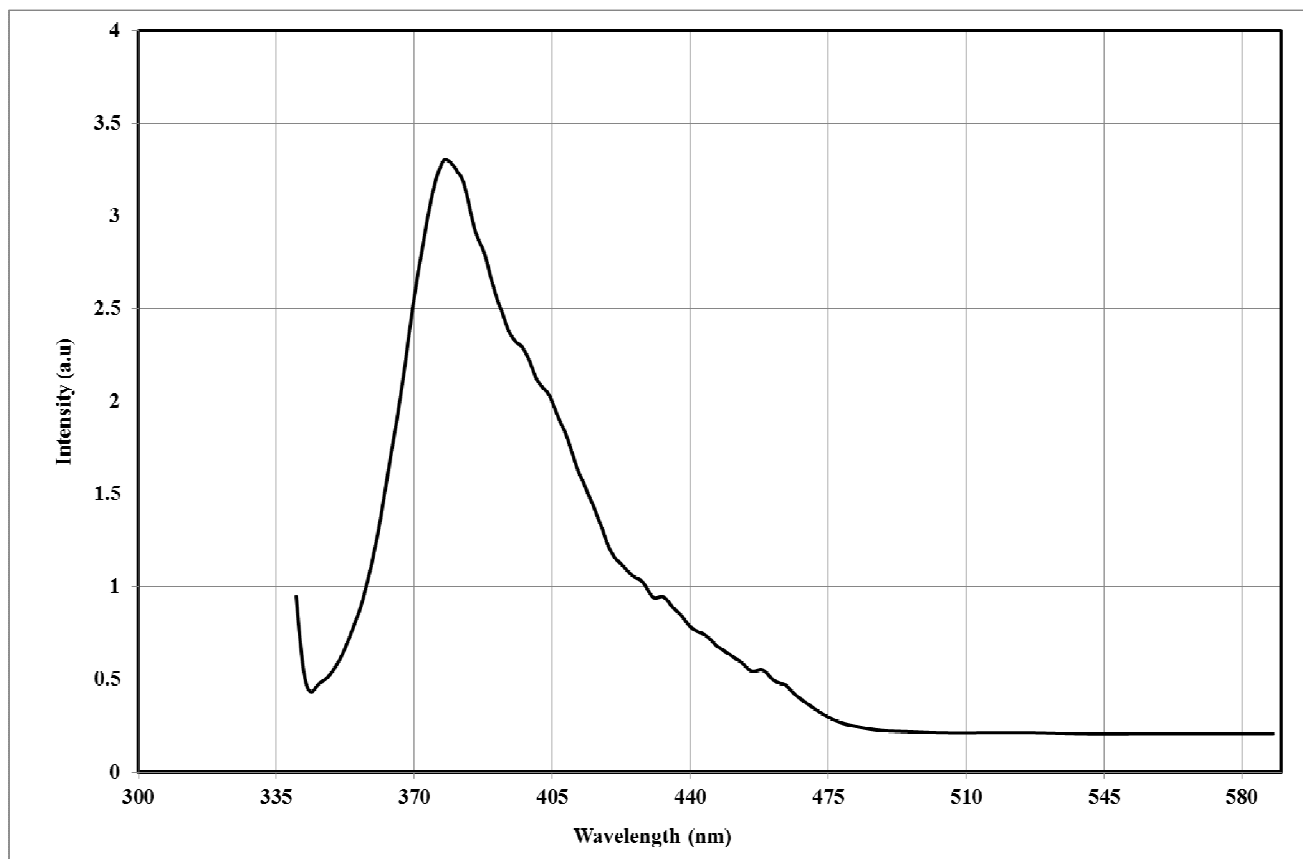


Fig.5

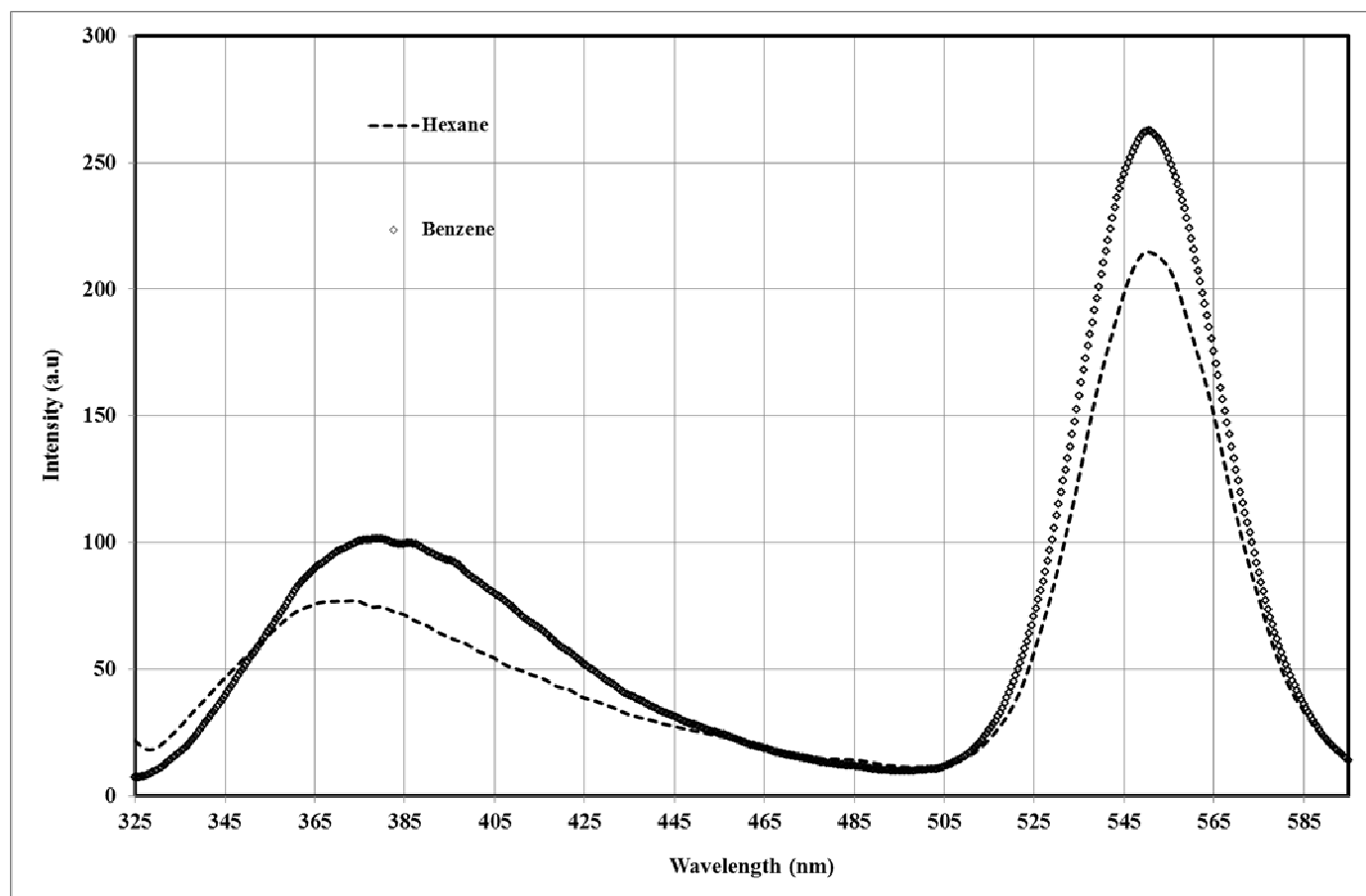


Fig.6 (a)

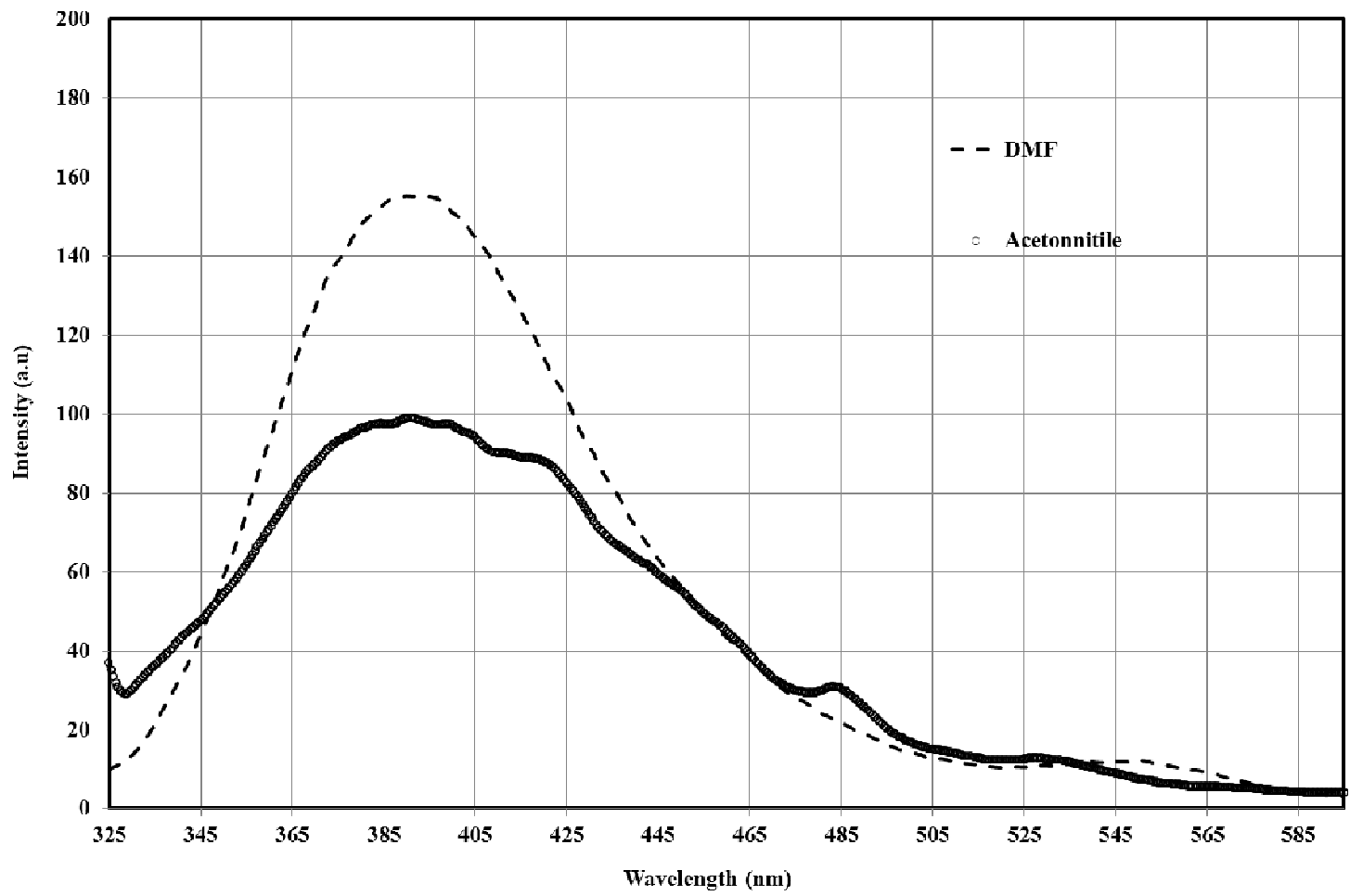


Fig.6 (b)

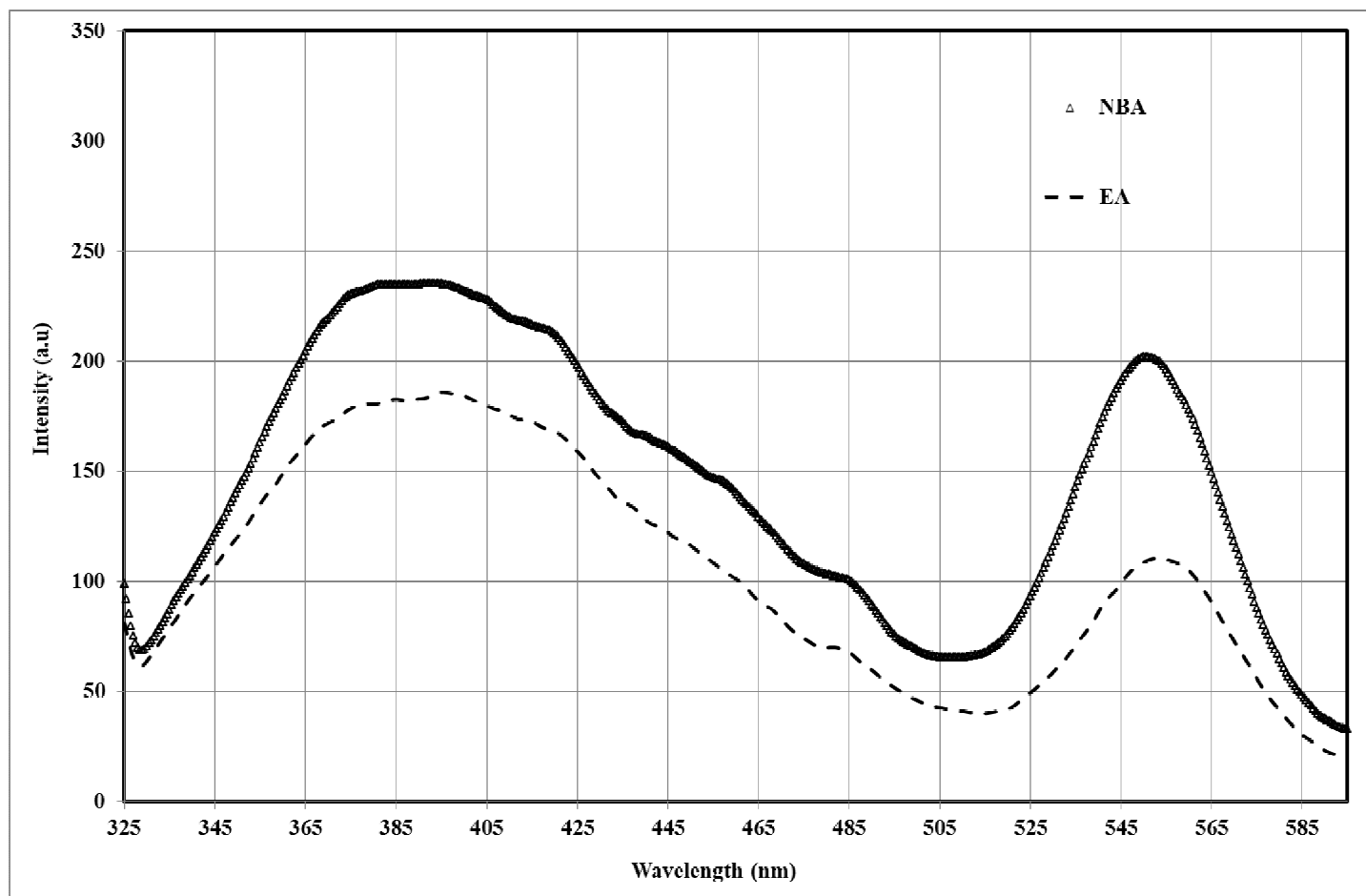


Fig.6 (c)

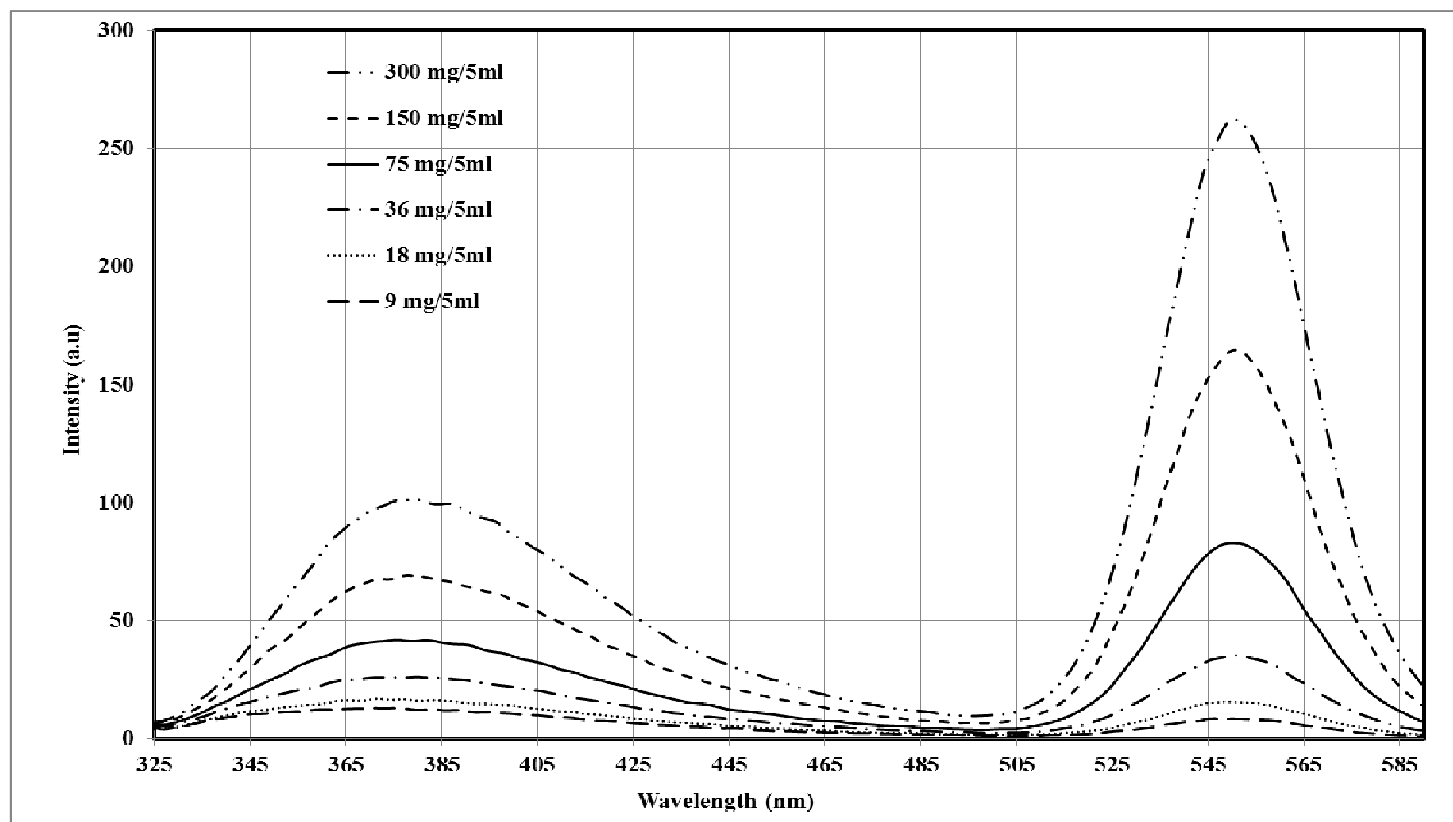


Fig.7

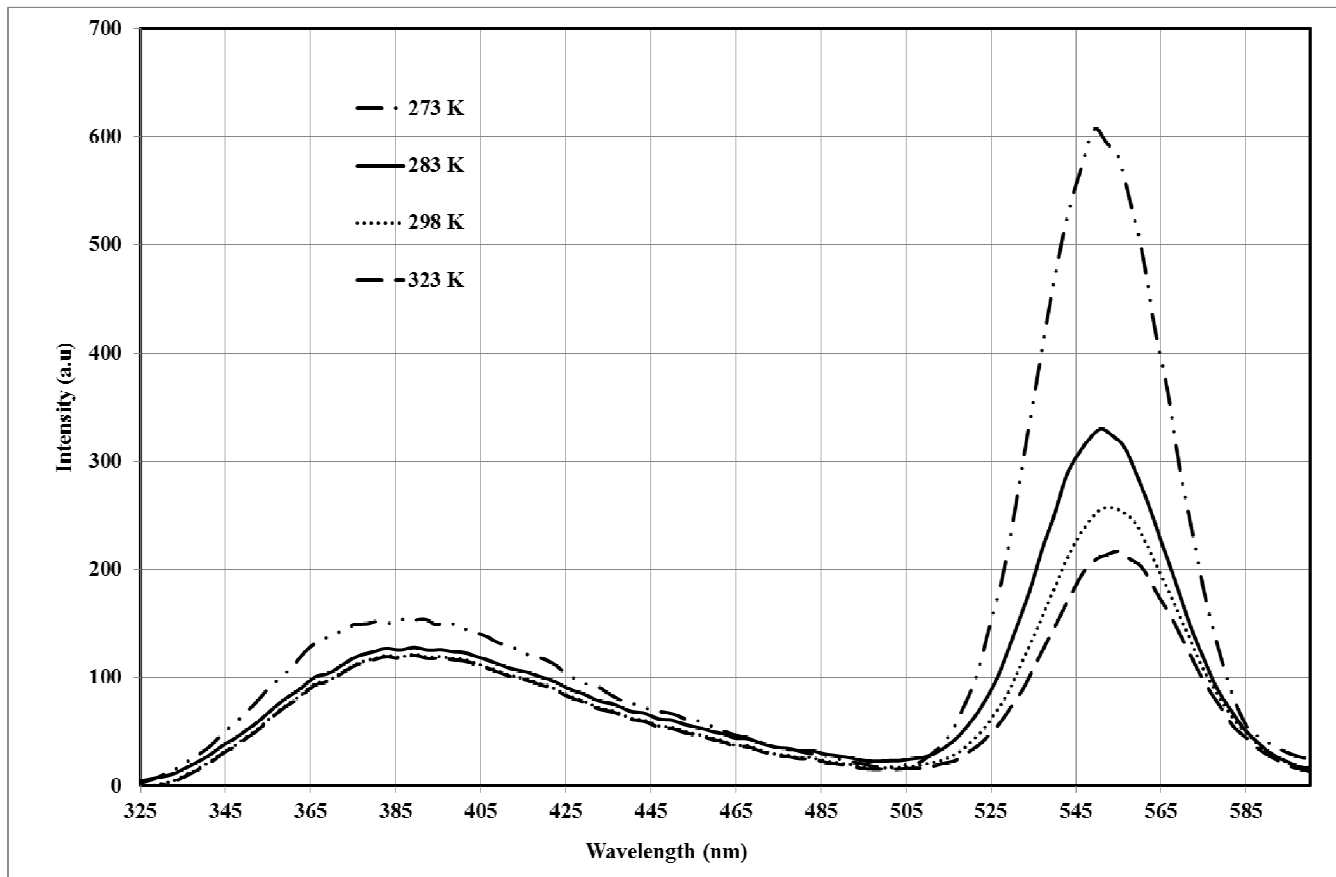
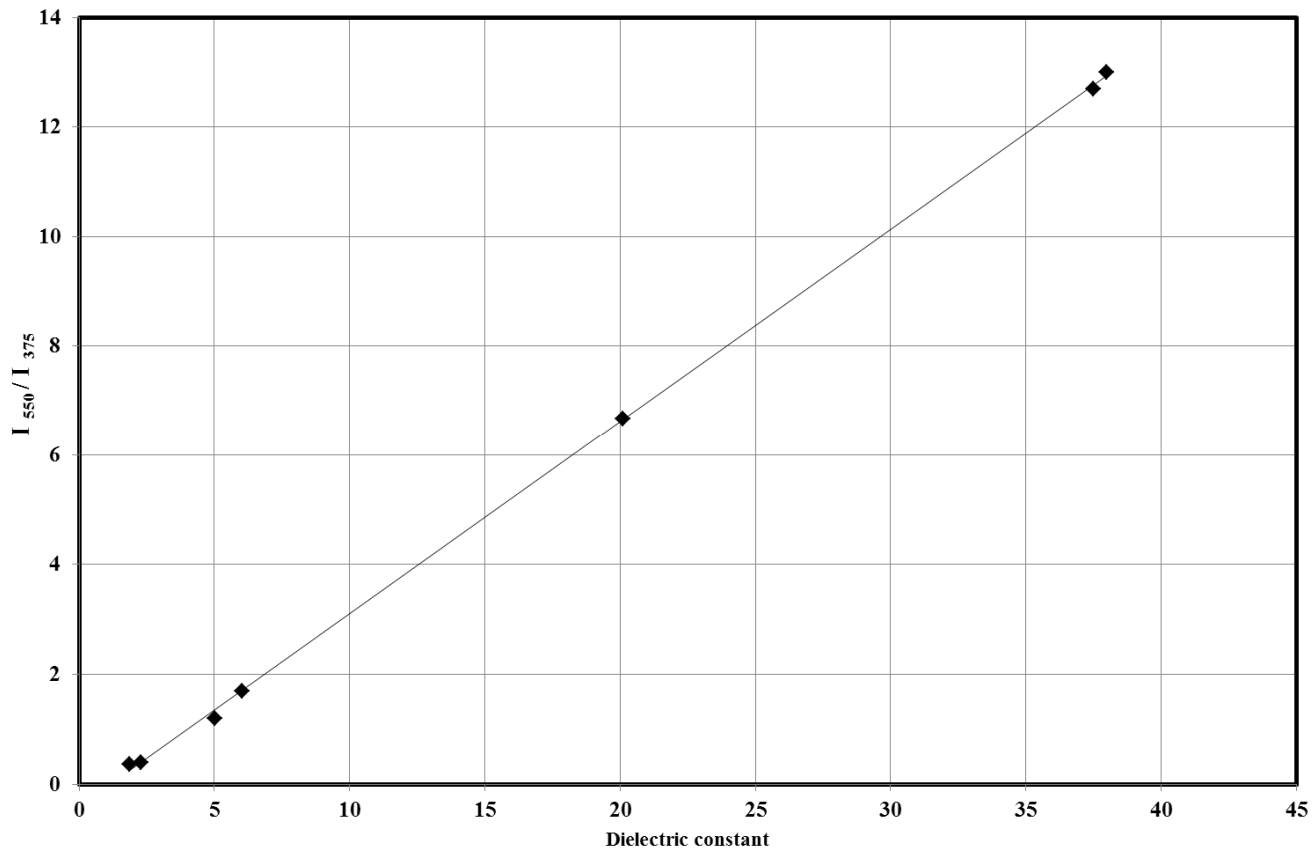


Fig.8



ACCEPTED

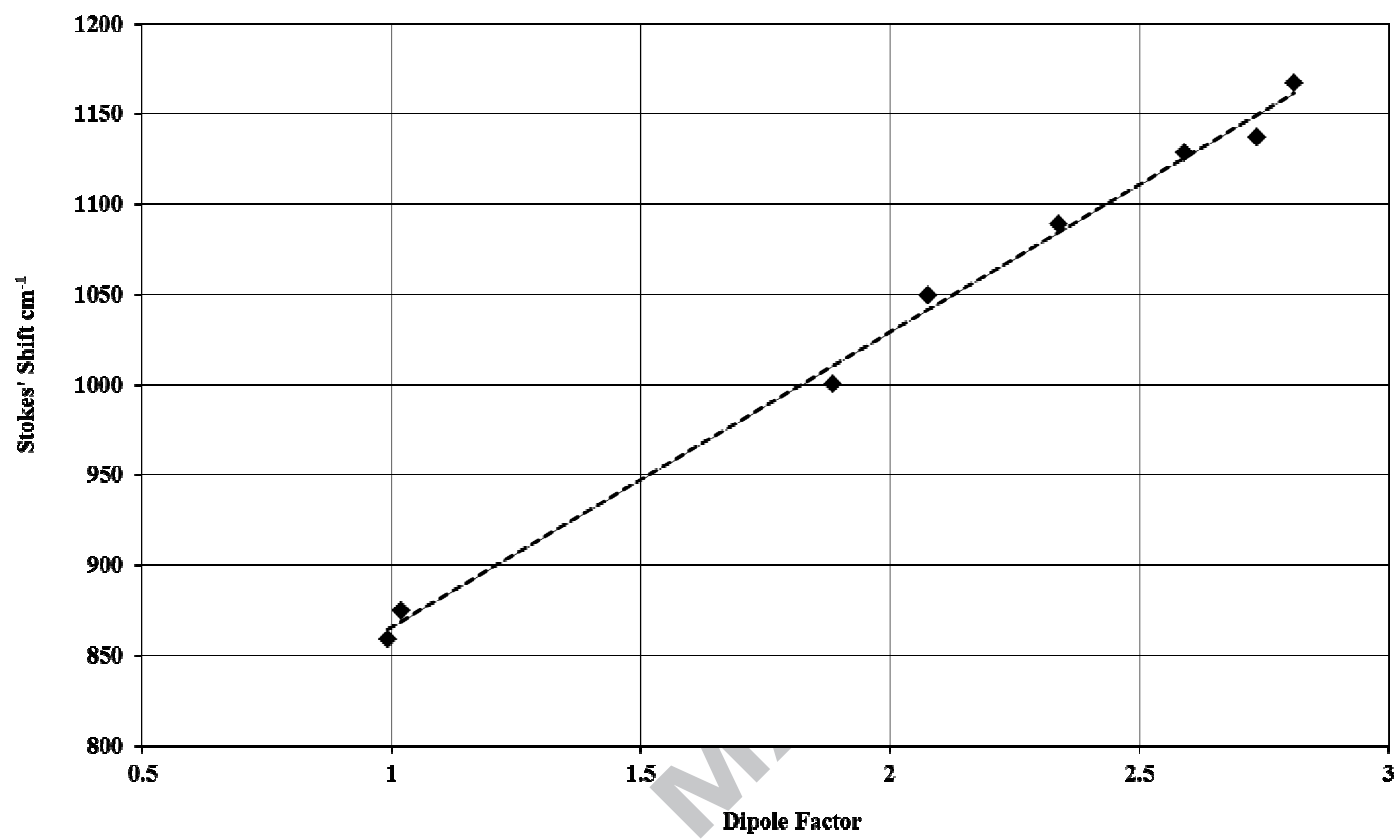


Fig.10

Figures Caption

Fig.1: Absorption spectra of CdSe/ZnS quantum dots for different concentrations from 9.0mg to 300mg in 5ml of benzene.

Fig.2: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentration of 9.0mg in 5ml.

Fig.3: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentration of 18 mg in 5ml for two different wavelengths of excitation (280nm and 330nm).

Fig 4: Photoluminescence emission spectra of CdSe quantum dots for concentration of 300mg in 5ml of benzene.

Fig 5: Photoluminescence emission spectra of ZnS quantum dots for concentration of 300mg in 5ml of benzene.

Fig.6: Photoluminescence emission spectra of CdSe/ZnS quantum dots for the concentration of 300mg in 5ml in different solvents (a) Non-polar solvents (b) High polar solvents (c) Intermediate polar solvents.

Fig.7: Photoluminescence emission spectra of CdSe/ZnS quantum dots for concentrations from 9.0mg to 300mg in 5ml of benzene.

Fig 8: Photoluminescence emission spectra of CdSe/ZnS quantum dots for concentrations of 300mg in 5ml of benzene under different temperatures.

Fig.9: The relative intensities of photoluminescence emission at 550nm and 375nm bands (I_{550}/I_{375}), as a function of polarity (dielectric constant) for different solvents.

Fig.10: The relationship between stokes shift and the dipole factor of quantum dots in different solvents at concentration concentrations 300mg in 5ml.

Table I

Solvent	Quantum Yield
Hexane	0.45
Benzene	0.58
n-Butyl acetate	0.42
Ethyl acetate	0.43
Acetonitrile	0.32
Dimethyl fumarate	0.35
Ethanol	0.31
Methanol	0.33

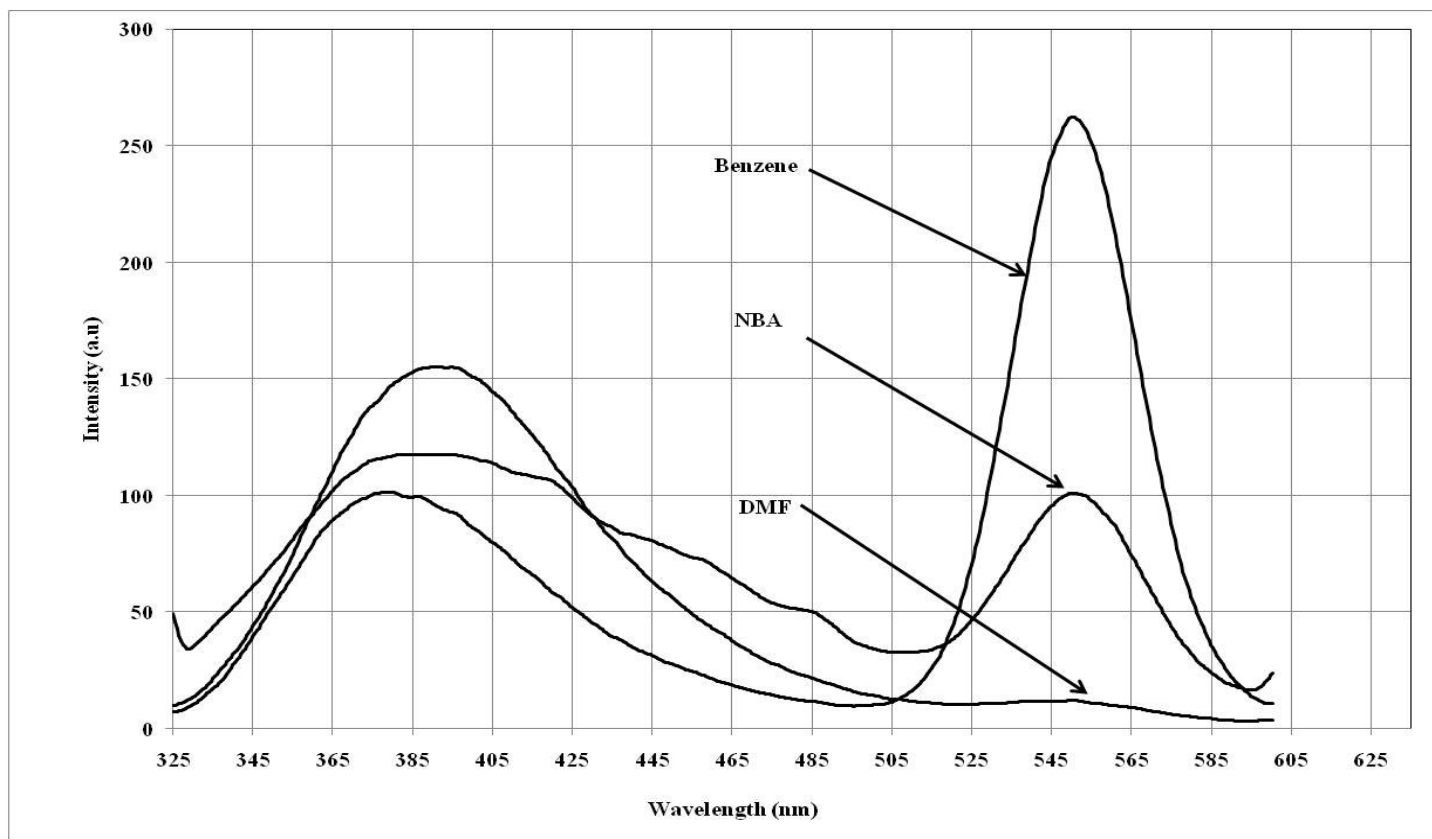
Table I

The quantum yields of (CdSe/ZnS) quantum dot in different solvents at concentration of 300 mg in 5ml.

Highlighting:

- Excimer like behavior of CdSe/ZnS core-shell quantum dots.
- Solvents influence on photoluminescence spectra of quantum dots.
- The band due to excimer becomes dominant in non polar solvents.
- Monomer and excimer bands become comparable for medium polar solvents.
- Monomer band becomes dominant in high polar solvents.

ACCEPTED MANUSCRIPT



ACCEPTED