

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Synthesis and Analytical Applications of Quantum Dots Coated with Different Generations of DAB Dendrimers

Joaquim G.G. Esteves da Silva<sup>1</sup>, Manuel Algarra<sup>2</sup> and Bruno B. Campos<sup>1</sup>

<sup>1</sup>*Centro de Investigação em Química*

<sup>2</sup>*Centro de Geologia. University of Porto.*

*Porto,  
Portugal*

## 1. Introduction

Quantum dots (QDs), also known as luminescent nanocrystals, are a special class of semiconductors that possesses remarkable fluorescence emission properties (Coe et al., 2002; Tessler et al., 2002). Due to their unique optical characteristics, which include sharp emission spectra, QDs have been utilized for fluorescent tagging applications, demonstrating the advantages of high photobleaching threshold, good chemical stability, and readily tuneable spectral properties (Lebedkin et al., 2003; Hartschuh et al., 2003; Li et al., 2007; Leitão et al., 2008; Gonçalves et al., 2009). QDs have semiconductor properties different from bulk material due to the quantum confinement effects on their molecular band structure (Chen et al., 2003).

The synthesis, modification, and applicability of cadmium chalcogenide nanocrystals, in particular cadmium sulfide (CdS), have been optimized (Alivisatos, 1996; Weller, 1993). The interaction of the CdS nanocrystals with its environment or capping agent plays crucial role in determining its photoluminescent properties and reactivity (Aldana et al., 2001; Talapin et al., 2001; Wuister & Meijerink, 2003a,b; Uchihara et al., 2005; Chen & Rosenzweig, 2002). Polymer coating of QDs, rendering them biocompatibility and biostability, confers an important biomedical role in diagnostics and biochemical sensing (Pileni et al., 1992; Gattas-Asfura & Leblanc, 2003; Gao et al., 2008). Dendrimers are a particularly interesting class of emerging nanopharmaceuticals that can be used as capping agents of QDs.

Diaminobutane-based poly(propyleneimine) dendrimers (DAB) (Fig. 1) have been synthesised (Etienne et al., 2005) and applied for *in vitro* diagnostics (Schatzlein et al., 2005; Bawarski et al., 2008; Hezinger et al., 2008; Dutta et al., 2008) tested in preclinical studies as contrast agent for nuclear magnetic resonance (Kobayashi et al., 2003; Talanov et al., 2006). There are attempts to use dendrimers in the targeted of delivery of drugs and other therapeutic agents (Crampton & Simanek, 2007). Drug molecules can be loaded both in the interior of the dendrimers as well as attached to the surface groups (Liu et al., 2000; Fernández et al., 2006) and used as therapeutic agents, for example in cancer treatment (Hollins et al., 2004; Svenson & Tomalia, 2005). Besides biomedical applications, dendrimers can be used to improve many industrial processes. The combination of high surface area and high solubility makes dendrimers useful as nanoscale catalyst (Yu et al., 2008). The high potential of these compounds opens new perspectives to

bioimaging diagnosis (Scott et al., 2005), photosensors (Hezinger et al., 2008) of heavy metals (Bawarski et al., 2008) and organic pollutants (Lubick, 2009) and in detection of fingerprints in forensic chemistry (Juan et al., 2008).

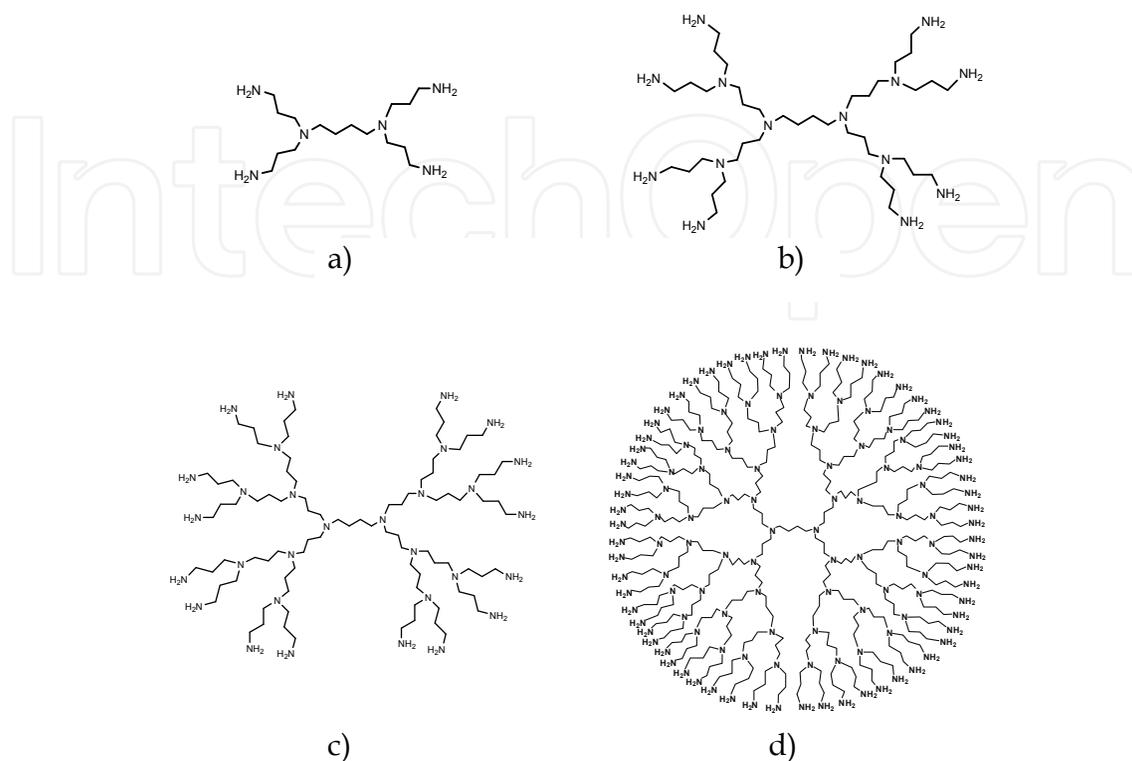


Fig. 1. Molecular structure of different generations DAB dendrimers [DAB-dend-(NH<sub>2</sub>)<sub>n</sub>]; a) n=8 (generation 2-G<sub>2</sub>); b) n=16 (generation 3-G<sub>3</sub>); c) n=32 (generation 4-G<sub>4</sub>); d) n=64 (generation 5-G<sub>5</sub>).

The most used dendrimer for QDs capping is poly(amidoamine) (PAMAM) polymer. CdS-QDs and/or ZnS-QDs have been synthesized using dendrimer structure, where polyamide dendrimer (PAMAM) is employed as host confinement (Juan et al., 2008; Sooklal et al., 1998; Wisher et al., 2006; Ling & Cong, 2008). Hybrid CdS DAB dendrimer nanocomposites have been synthesised and characterized in methanol (Lemon & Crooks, 2000; Gayen et al., 2007). These nanocomposites are formed by the arrested precipitation of nanometer-scale CdS clusters in the presence of polyamide dendrimers. Although we do not yet know the exact locus of cluster nucleation, the dendrimer clearly interacts with the clusters at a relatively early stage in the arrested precipitation, retarding further growth and producing small QDs clusters with unique photoluminescent properties. The dendrimer stabilized clusters then undergo further aggregation in solution to produce micrometer scale composite flocks. Despite this aggregation, the long term stability of the materials and its photoluminescent properties suggests that the QDs clusters do not coalesce but remain as distinct entities (Hedden et al., 2002; Huang & Tomalia, 2005).

A severe limitation of the biomedical or biochemical *in vivo* imaging applications of cadmium chalcogenide QDs is their potential cytotoxicity due to the release of cadmium ions. Moreover, hybrid dendrimer QDs nanocomposites are usually synthesised and kept in organic solvents, like methanol, which are toxic or bioincompatible. In order to reduce or eliminate health risk, cadmium ions should be replaced with other less or no toxic metal

ions like zinc and these nanoparticles should be synthesised and kept in aqueous media, *i.e.* using a green chemistry approach.

In this chapter, the simple aqueous synthesis and characterization of hybrid nanocomposites constituted by CdS, ZnS and CdS/ZnS-QDs and different generations (from 2 up to 5) of DAB dendrimer is presented. Moreover, the application of these nanocomposites as nanosensors of Hg(II) ion, pH, ionic strength and nitromethane is described.

## 2. Aqueous synthesis of the nanocomposites

### 2.1 Materials

Polypropylenimine tetrahexacontaamine dendrimer, generations 2 to 5 (DAB- $G_n$ ,  $n=2-5$ ) (Fig. 1), cadmium chloride ( $\text{CdCl}_2$ , 99.9%), zinc chloride (99.9 %) sodium sulphide ( $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich Química S.A. (Spain) and 3-mercaptopropionic acid (MPA, 99%) from Fluka. Standard aqueous solutions of  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$ ,  $\text{CoCl}_2$  and  $\text{Zn}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  and nitromethane were obtained from Merck. All solutions were made with deionised water with resistivity higher than 4 M $\Omega$ /cm.

### 2.2 Synthetic procedures

#### 2.2.1 Synthesis of DAB-CdS QDs

DAB dendrimer of different generations (DAB- $G_n=2-5$ ) (10.0 mg) from Aldrich, were dissolved in 20.0 mL in deionised water and stirred for 24 hours. After that,  $\text{CdCl}_2$  (Aldrich) was added to the solution for a DAB- $G_n=2-5$ :Cd molar ratio of 1:10 and left to stabilize for 24 hours. 100  $\mu\text{L}$  of MPA was added and left to stabilize for 24 hours (Belcastro et al, 2004).  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was then added with a Cd:S molar ratio of 1:1, and stirred for 72 hours to obtain an aqueous solution that was centrifuged at 13000 rpm for 10 min. Then, the solid obtained was washed with water and acetone, frozen and lyophilized. When no precipitate was detected the aqueous solution was dialyzed for 12 hours against deionized water using a MW CO 12.000-14.000Da dialysis tube (Medicell International).

#### 2.2.2 Synthesis of DAB-CdS:ZnS QDs

This synthesis followed the same procedure previously described, except for DAB- $G_n(=2-5)$ :Cd:Zn molar ratio that was 1:5:5.

#### 2.2.3 Synthesis of DAB-ZnS QDs

The synthesis followed the same sequence of dendrimer-CdS QDs synthesis, except the pH of the solution, adjusted to 12 with tetrabutylammonium hydroxide (TBAH) (Li et al, 2007) in 2-propanol/methanol after addition of MPA. Firstly, the additions of TBAH provoke the precipitation of zinc hydroxide, followed by redissolution as soluble zinc hydroxyl complexes.

### 2.3 Characterization procedures

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) were done on a FEI Quanta 400FEG/EDAX Genesis X4M high resolution Scanning Electronic Microscope at 15 kV. For SEM analysis of aqueous dendrimer-QDs, a microliter sample was evaporated under vacuum at room temperature, and solid dendrimer-QDs were immobilized on a carbon fiber, both were held on an aluminium support.

Absorbance measurements were made in a Hewlett-Packard HP8452A diode-array spectrophotometer using 1 cm pathlength quartz cuvettes.

Fluorescence confocal microscopy was used to record the luminescence spectra of solid samples, acquired with a Leica SP2 AOBS SE (Leica Microsystems, Germany). The excitation of solid dendrimer-QDs was made with the Ar laser lines of 458 and 476 nm. A filter-free prism spectrophotometer head with a set of 3 photomultiplier tubes (PMT) allowed the addressing of distinct detection channels in three user-defined spectral ranges. All the image processing operations were done with ORIGIN50 and LCS Lite ([http://taltos.stanford.edu/pages/cocoa\\_leica.htm](http://taltos.stanford.edu/pages/cocoa_leica.htm)).

Steady state fluorescence measurements of aqueous solutions of dendrimer-QDs photoluminescence were done with a Spex 3D Spectrofluorimeter with a 75W xenon lamp and a CCD detector. Raw EEM were acquired, in an excitation wavelength range from 296.4 to 675.1 nm, and in an emission wavelength range from 350.7 to 721.8 nm, with a resolution of 2 nm, slit of 0.25 mm and 1 s integration time. A 1 mL quartz microcell was used. Lifetime measurements were recorded with a Horiba Jovin Yvon Fluoromax 4 TCSPC using the following instrumental settings: 368 nm NanoLED; time range, 1.6  $\mu$ s; peak preset; 10,000 counts; repetition rate, 500 kHz; synchronous delay, 25 ns; emission detection: 535 nm.

### 3. Characterization of the nanocomposites

#### 3.1 Morphological properties

In order to confirm the elemental composition of the synthesised dendrimer-QDs nanocomposites EDS analysis were done and, as example, Fig. 2 shows the EDS spectra of DAB-G<sub>2</sub> with CdS (Fig. 2.a), ZnS (Fig. 2.b) and CdS:ZnS (Fig. 2.c). These spectra confirm that the synthesized nanocomposites are indeed DAB capped with CdS, CdS:ZnS and ZnS QDs. Indeed, the presence of the signals due to elements Cd, Zn and S confirm the composition of the QDs, C and N confirms that the synthesized material contains QDs capped with DAB. Also, the presence of signals due to the elements C, O and S suggests that MPA is capping QDs. These results suggest that the QDs are stabilized in water due to the capping of both the dendrimer and MPA.

Fig. 3 shows, as example, SEM images of DAB-G<sub>2</sub> with CdS (Fig. 3.a), CdS:ZnS (Fig. 3.b) and ZnS (Fig. 3.c). Although SEM images could not give particularly useful information about the morphology of the synthesised nanocomposites, the analysis of these images usually shows macroscopic spherical structures on the surface topography of the nanocomposites. A general examination of all SEM analysis suggests an amorphous nanocomposites structure. Nevertheless, the analysis of some SEM images, where macroscopic spherical structures could be observed, reveals dimensions comprised between 320 to 735 nm.

#### 3.2 UV-Vis absorption properties

UV-Vis absorption spectra of all the DAB-QDs nanoparticles in water are shown in Fig. 4. The analysis of these spectra shows the following:

- i. DAB-CdS QDs (Fig. 4a) are characterized by a well defined shoulder in the range between 370 to 390 nm (DAB-G<sub>5</sub> - 370 nm; DAB-G<sub>4</sub> - 380 nm; and, DAB-G<sub>3</sub> - 390 nm). DAB-G<sub>5</sub>-CdS QDs show another well defined shoulder at about 325 nm. Also, there is a blueshift of the absorption band as the generation of the dendrimer is increased. This result is similar to that described in the literature when methanol was used as solvent (Gayen et al., 2007). The absorption shift that is observed for the different generations of DAB confirms that the amine groups are participating with MPA in the capping of the QDs.

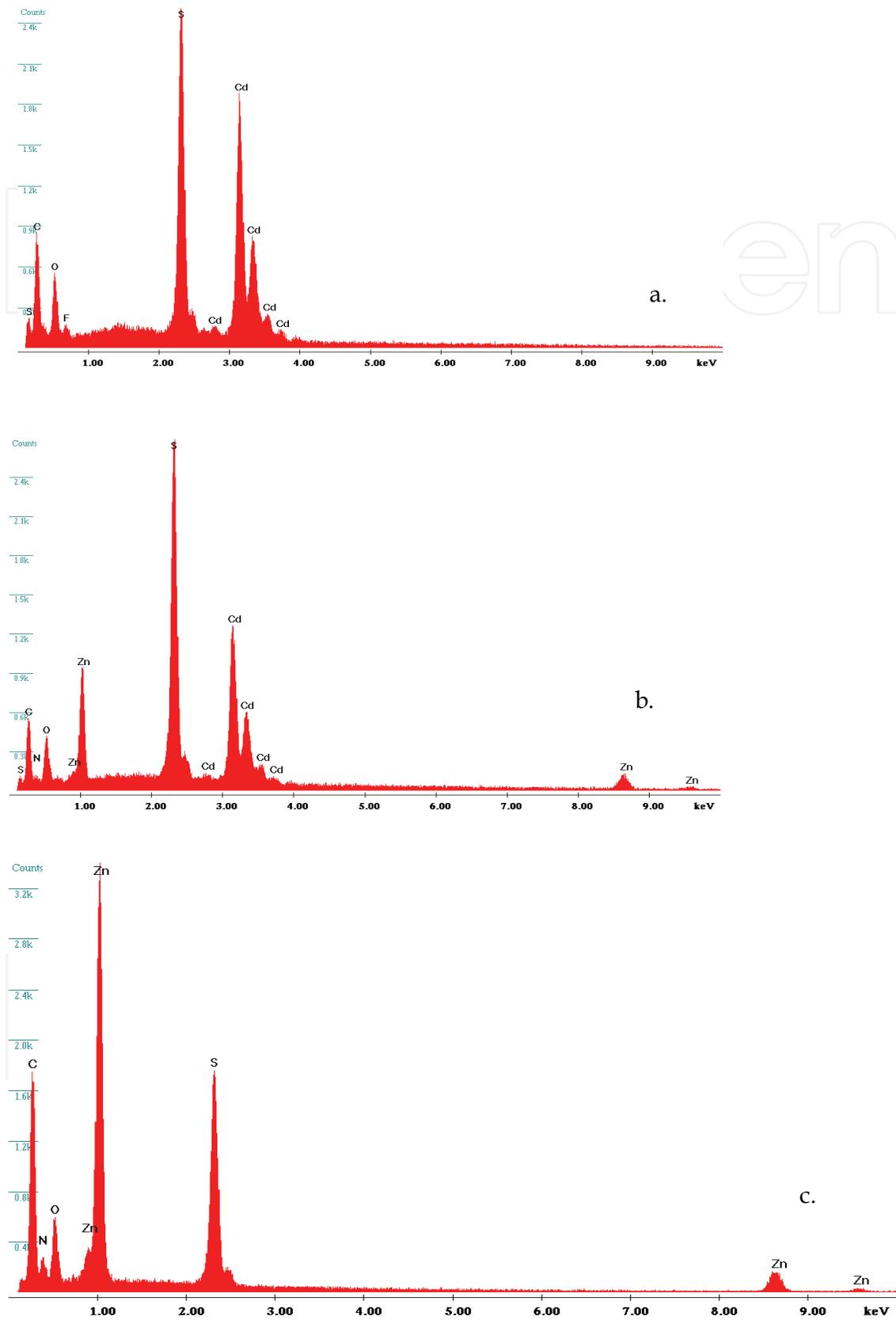


Fig. 2. EDS spectra of DAB-G<sub>2</sub>-CdS (a), DAB-G<sub>2</sub>-CdS:ZnS (b) and DAB-G<sub>2</sub>-ZnS (c) nanocomposites.

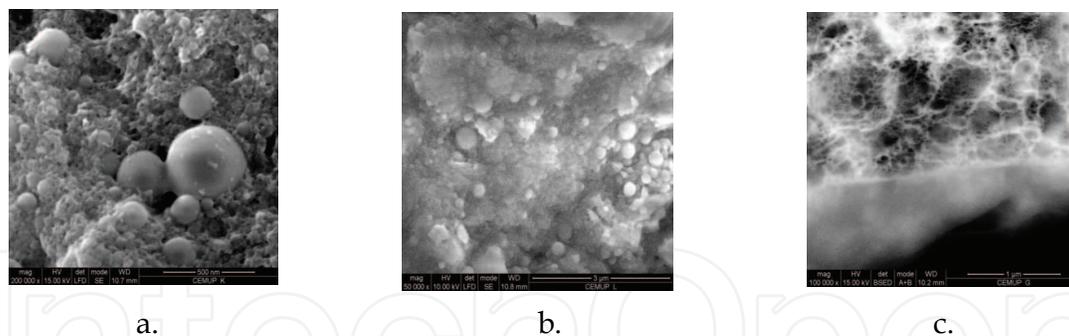


Fig. 3. SEM images of: a) DAB-  $G_2$ -CdS; b) DAB-  $G_2$ -ZnS; and, c) DAB- $G_2$ -CdS:ZnS.

- ii. DAB-ZnS QDs (Fig. 4.b) are all characterized by a poorly defined shoulder in the range between 250 to 260 nm. This shoulder is barely detected in the spectra of DAB- $G_2$ -ZnS QDs.
- iii. DAB-CdS:ZnS QDS (Fig. 4.c) are characterized by a well defined shoulder in the range 325 to 350 nm (DAB- $G_5$  - 325 nm; DAB- $G_4$  - 350 nm; and, DAB- $G_3$  - 330 nm). DAB- $G_5$ -CdS:ZnS QDs show another well defined shoulder at about 284 nm.

The absorptions of the DAB-CdS QDs and DAB-ZnS QDs are blueshifted from the expected values of bulk CdS and ZnS, respectively 510 and 335 nm (Unni et al., 2009). This result is a consequence of the quantum confinement effects in the nanoparticles confirming the existence of QDs. Also, the absorption wavelengths suggest that the sizes of the QDs are in the nanometers range (Gayen et al., 2007; Unni et al., 2009). The absorptions of the hybrid DAB-CdS:ZnS QDs occur at intermediate wavelengths of the absorptions of the single QDs. This hybrid system can be seen as  $Cd^{2+}$  doped DAB-ZnS QDs and the presence of  $Cd^{2+}$  provokes a redshift that has been previously described in the literature (Unni et al., 2009).

### 3.3 Steady state fluorescent properties

All the synthesized nanocomposites were fluorescent either in the solid or in aqueous solution. The fluorescence of the purified solid nanocomposites were analysed by confocal microscopy. Fig. 5.a shows, as an example, the confocal image of DAB- $G_3$ -CdS:ZnS where the green fluorescence (emission at 525 nm) can be observed. Table 1 summarizes the maximum wavelength of the emission of fluorescence of the solid nanocomposites. The general trends in the maximum wavelength of emission are: (a) within the same DAB generation a blue shift is observed in the maximum emission of fluorescence when CdS QDs is replaced by ZnS QDs; (b) a blue shift in the maximum fluorescence emission is also observed when the DAB generation is increased.

The solid nanocomposites emit in the range between 483 nm (DAB- $G_2$ -ZnS) up to 545 nm (DAB- $G_2$ -CdS) with a relatively high emission full width of half maximum (FWHM) (between 113 to 165 nm) when compared with typical narrow emission bands of QDs. This relatively high FWHM suggests that the CdS and ZnS QDs show a high degree of size heterogeneity probably because they are bounded to different chemical environments of the DAB dendrimer. The asymmetrical dispersion of QDs on the surface and the inner of dendrimers show the possibility of DAB to have focal regions where QDs can easily be linked and deposited controlling the growth of QDs. Being nanosized structures, dendrimers may respond to stimuli from the surroundings and can, like proteins, adapt a tight-packed conformation ("native") or an extended ("denaturated") conformation, depending on solvent, pH, ionic strength and temperature (Ballauf et al., 2001).

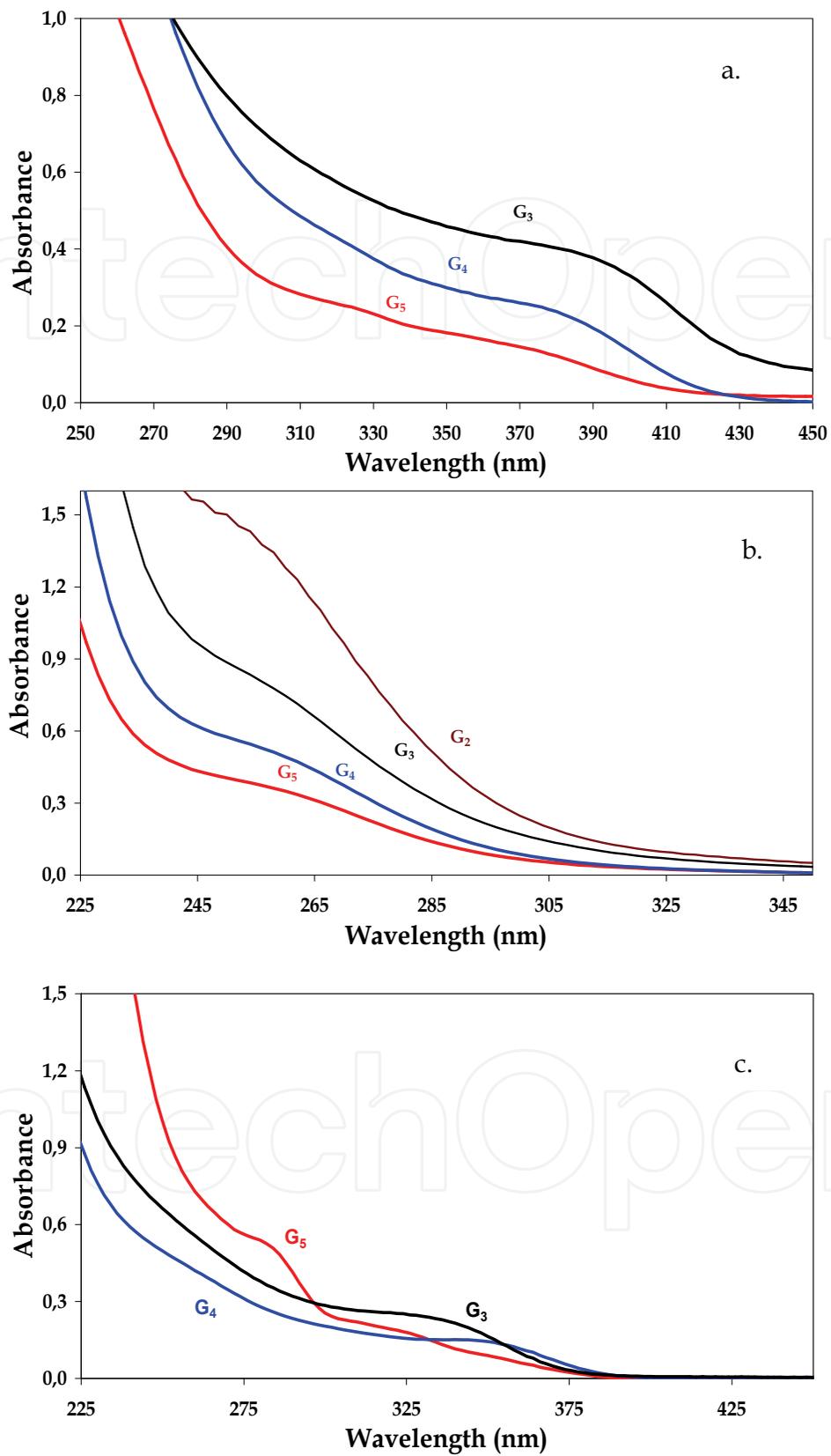


Fig. 4. Absorption spectra of DAB-CdS (a), DAB-CdS:ZnS (b) and DAB-ZnS (c) in water synthesized using DAB-G<sub>2</sub>, G<sub>3</sub>, G<sub>4</sub> and G<sub>5</sub> dendrimers.

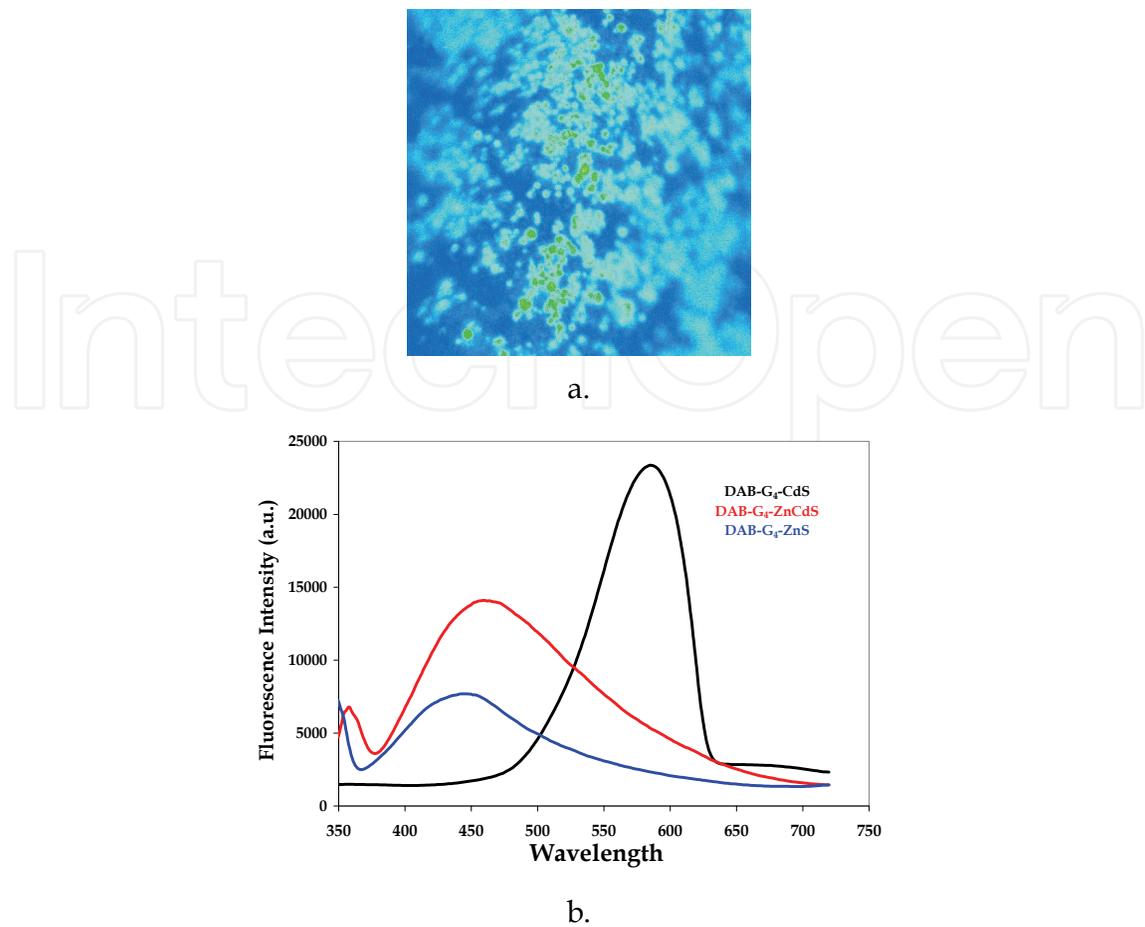


Fig. 5. Fluorescence emission image of DAB-G<sub>3</sub>-CdS:ZnS obtained by confocal microscopy (a) and spectra of the three nanocomposites synthesized using DAB-G<sub>4</sub> (b).

	G <sub>2</sub>				G <sub>3</sub>			
	pH	$\lambda_{ex}$	$\lambda_{em}$	FWHM	pH	$\lambda_{ex}$	$\lambda_{em}$	FWHM
CdS <sub>s</sub>	3.18		545	156				
CdS <sub>aq</sub>					3.27	344	607	227
CdS:ZnS <sub>s</sub>	3.19		545	165	3.40		525	163
CdS:ZnS <sub>s</sub>					3.40	382	555	170
ZnS <sub>s</sub>	12.00		483	129	12.06		476	113
ZnS <sub>aq</sub>	12.00	353	441	140	12.06	342	451	142
	G <sub>4</sub>				G <sub>5</sub>			
	pH	$\lambda_{ex}$	$\lambda_{em}$	FWHM	pH	$\lambda_{ex}$	$\lambda_{em}$	FWHM
CdS <sub>s</sub>								
CdS <sub>aq</sub>	3.10	369	584	82	3.22	342	535	201
CdS:ZnS <sub>s</sub>					3.22		485	146
CdS:ZnS <sub>s</sub>	3.40	344	460	157	3.22	344	453	158
ZnS <sub>s</sub>								
ZnS <sub>aq</sub>	12.02	342	443	140	12.04	333	431	132

Table 1. Fluorescence properties of the synthesized DAB-QDs nanocomposites.

The water soluble synthesized nanocomposites show similar fluorescence properties as the solid materials (Table 1). Fig. 5.b shows, as example, the fluorescence emission spectra of the three soluble DAB-G<sub>4</sub> nanocomposites. The same trends of the maximum emission wavelengths with the QDs type and DAB generation are observed. This last generation trend has already been described in the literature for different generations of DAB-CdS nanocomposites in methanol solution (Gayen et al., 2007). The aqueous solutions of nanocomposites emit in the range 431 nm (DAB-G<sub>5</sub>-ZnS) up to 607 nm (DAB-G<sub>3</sub>-CdS) with FWHM usually higher than the solid nanocomposites - a FWHM of 227 nm is observed for DAB-G<sub>3</sub>-CdS.

The synthesized nanocomposites show similar emission maximum to literature reports of mercaptoacetic acid-capped-CdS (541 nm) (Wisher et al., 2006) and thioglycerol-capped-ZnS (411 nm) (Unni et al., 2009; Jie et al., 2007). Also, the synthesized CdS nanocomposites have similar emission spectral characteristics to those reported in the literature, namely broad spectra with maximum intensity wavelength in methanol solution at about 470 nm (Gayen et al., 2007).

The fluorescence properties of the synthesised nanocomposites can be slightly modified if the reaction conditions are changed. For instance, the fluorescence intensity of the material increases with the stirring time which is related to the agglomeration of conjugated DAB-QDs. The amino groups of the DAB surface have a tendency to link with another dendrimer molecules by hydrogen bonding (Nourse et al., 2000). The solvent, pH, ionic strength and temperature are the experimental factors that can change the conformation and assembly of dendrimers (Ballauf et al., 2001). Maintaining the same chemical and physical conditions, the fluorescence intensity increases up to nearly 72 h and then decreased due to a high molecular density that cause the increasing of stereochemical repulsions leading to the split of agglomerated dendrimers.

### 3.4 Fluorescence lifetime analysis

A typical fluorescence time decay profile of the nanocomposite DAB-G<sub>5</sub>-CdS is shown in Fig. 6. The time decay is complex showing the presence of lifetime ranges from the picoseconds and up to almost the microseconds. However, a four component decay time model originated a good fit ( $\chi = 1.20$ ) with the following lifetimes:  $\tau_1 = 657$  ps;  $\tau_2 = 10.0$  ns;  $\tau_3 = 59.42$  ns; and  $\tau_4 = 265$  ns. The existence of relatively long lived components in dendrimer stabilized QDs (in the range of  $\tau_3$  and  $\tau_4$ ) has already been observed in studies using methanol as solvent (Lakowicz et al., 1999; Gayen et al., 2007).

## 4. Applications of the DAB nanocomposites as nanosensors

The nanocomposites constituted by a dendrimer (DAB), a capping agent (MPA) and QDs show several reactive sites that make them potential chemical sensors. Indeed, both the dendrimer and the capping agent have ionisable and metal complexing groups and the dendrimer can undergo structural modifications as consequence of the presence of organic molecules soluble in water or ionic species. These modifications on the physico-chemical environment surrounding the QDs will affect their fluorescence emission properties because it will provoke modifications on the quantum confinement regime. In this section the nanocomposite DAB-G<sub>5</sub>-CdS will be used to demonstrate that these nanomaterials can be used as nanosensors for pH, mercury(II) ion [Hg(II)], ionic strength and nitromethane.

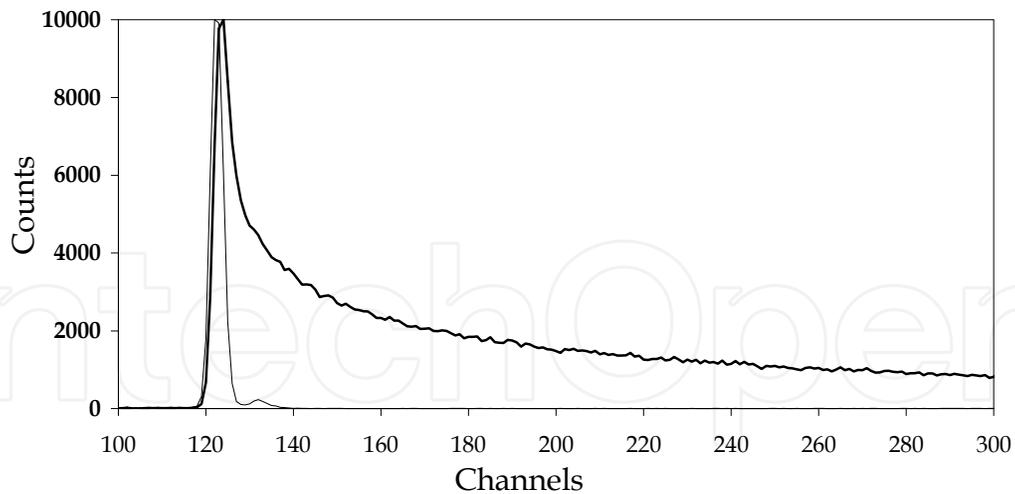


Fig. 6. Fluorescence time decay of fluorescence of aqueous solution of DAB-G<sub>5</sub>-CdS.

#### 4.1 Sensing the pH

The effect of the pH (range of pH between ca. 3 and 9) on the fluorescence intensity of aqueous solutions of the DAB-G<sub>5</sub>-CdS nanocomposites is shown in Fig. 7. A detailed analysis of this effect of the pH shows the existence of a marked fluorescent intensity decrease in the pH range from 5 to 7 and a relatively small increase for pH values higher than 7 (Campos et al, 2009). Also, a blue shift is observed from 518 to 500 nm as the pH increases. These variations are a consequence of the change of the quantum confinement of the QDs as consequence of the ionization of the carboxylic groups of MPA and amine groups of DAB capping the CdS QDs (Gonçalves et al., 2009; Leitão et al., 2008).

The variation of the fluorescence properties (intensity and wavelength at the maximum of the emission spectra) of DAB-G<sub>5</sub>-CdS with the pH was expected because QDs capped with ionisable ligands are quite promising pH sensors (Maule et al, 2010). However, when the

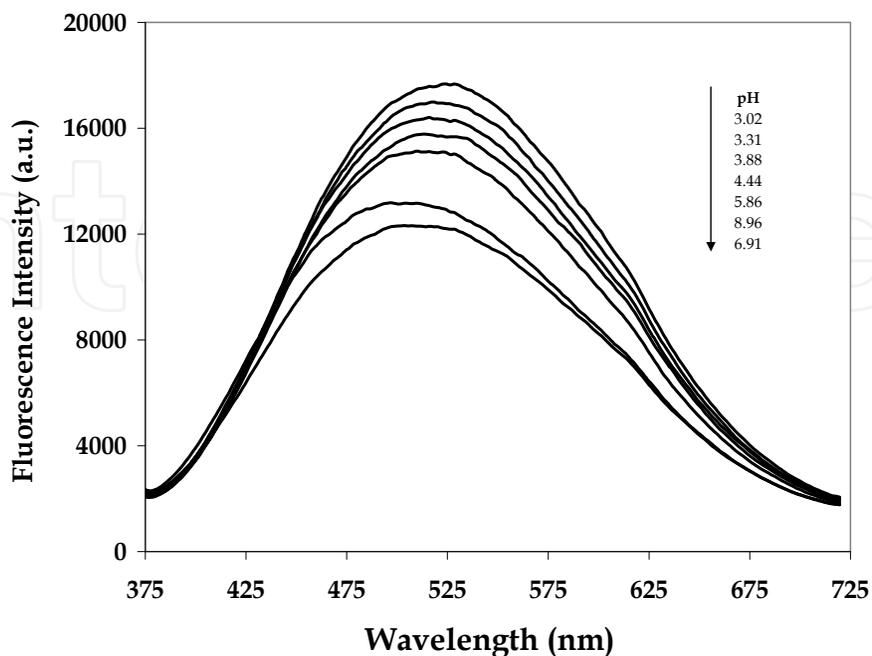


Fig. 7. Emission spectra of DAB-G<sub>5</sub>-CdS at different pH values.

QDs is attached to DAB other applications can be designed taking into consideration the unique properties of dendrimers.

#### 4.2 Sensing Hg(II) ion

The effect of the Hg(II) ion on the fluorescence intensity of aqueous solutions of the DAB-G<sub>5</sub>-CdS nanocomposites is shown in Fig. 8. This figure shows a marked quenching of the fluorescent intensity with the increase of the Hg(II) concentration without wavelength shift of the emission band (Campos et al, 2009). The analyze of the quenching mechanism provoked by Hg(II) ion was done using Stern-Volmer plots which show a static quenching with a Stern-Volmer constant for Hg(II) was  $1.5 \times 10^5 \text{ M}^{-1}$ . This result suggests the formation of a quite stable complex between the DAB-G<sub>5</sub>-CdS nanocomposites and Hg(II) ions.

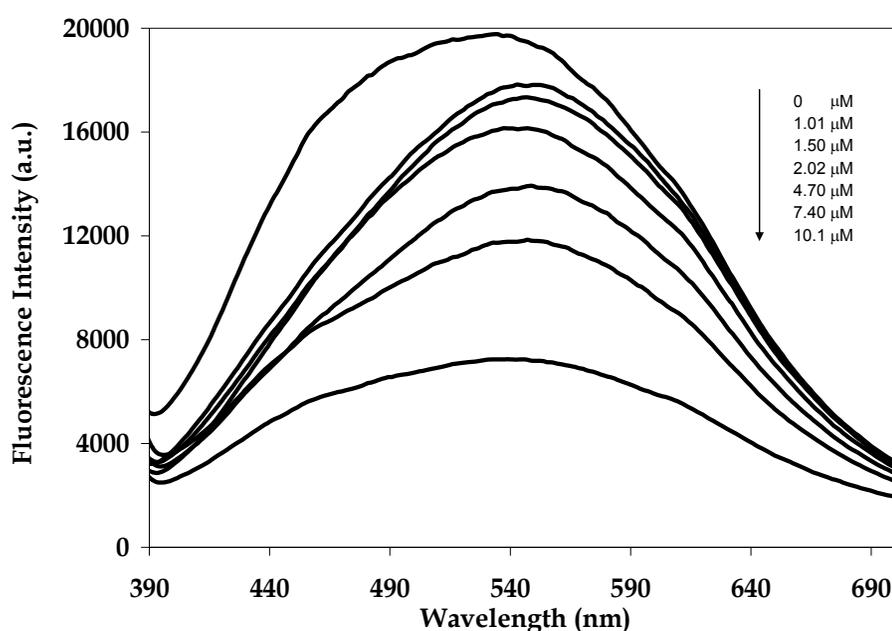


Fig. 8. Emission spectra of DAB-G<sub>5</sub>-CdS without and in the presence of increasing Hg(II) ion concentration.

The effect of micromolar concentration of the metal ions Pb(II), Cd(II), Zn(II), Cu(II), Co(II) and Ni(II) on the DAB-G<sub>5</sub>-CdS nanocomposite fluorescence has also been analysed and only Pb(II) and Cu(II) provokes measurable quenching (Campos et al, 2009). The Stern-Volmer constant for Cu(II) was  $1.9 \times 10^5 \text{ M}^{-1}$  and for Pb(II)  $2.2 \times 10^4 \text{ M}^{-1}$ .

#### 4.3 Sensing the ionic strength

The effect of alkaline metal ions in the molar concentration range (ionic strength effect) on the wavelength of the maximum of the emission spectra of aqueous solutions of the DAB-G<sub>5</sub>-CdS nanocomposites is shown in Fig. 9. This figure shows a marked redshift with the increase of the ionic strength (Campos et al, 2009).

Varying the ionic strength has a strong effect on charged DAB dendrimers and favours a contracted conformation with a high degree of back-folding somewhat similar to what is observed upon increasing pH or poor solvation (Welch and Muthukumar, 1998; Ramzi et al., 2002; Campos et al, 2009). This conformation changing provokes a modification of the chemical environment surrounding the QDs affecting the corresponding emission of fluorescence properties.

#### 4.4 Sensing nitromethane

The effect of the nitromethane on the fluorescence intensity of aqueous solutions of the DAB-G<sub>5</sub>-CdS nanocomposites is shown in Fig. 10. This figure shows a marked quenching of the fluorescent intensity with the increase of the nitromethane concentration without wavelength shift of the emission band (Campos et al, 2010). The analyze of the quenching mechanism provoked by nitromethane was done using Stern-Volmer plots which show a dynamic quenching with a Stern-Volmer constant of 25(6) M<sup>-1</sup> and a percentage of fluorophores accessible to the quencher of about 81%. This result shows that about 19% of the QDs (fluorophores) attach to the dendrimer are located in the inner layers of the dendrimer while about 81% are located in the external layer (Campos et al, 2010).

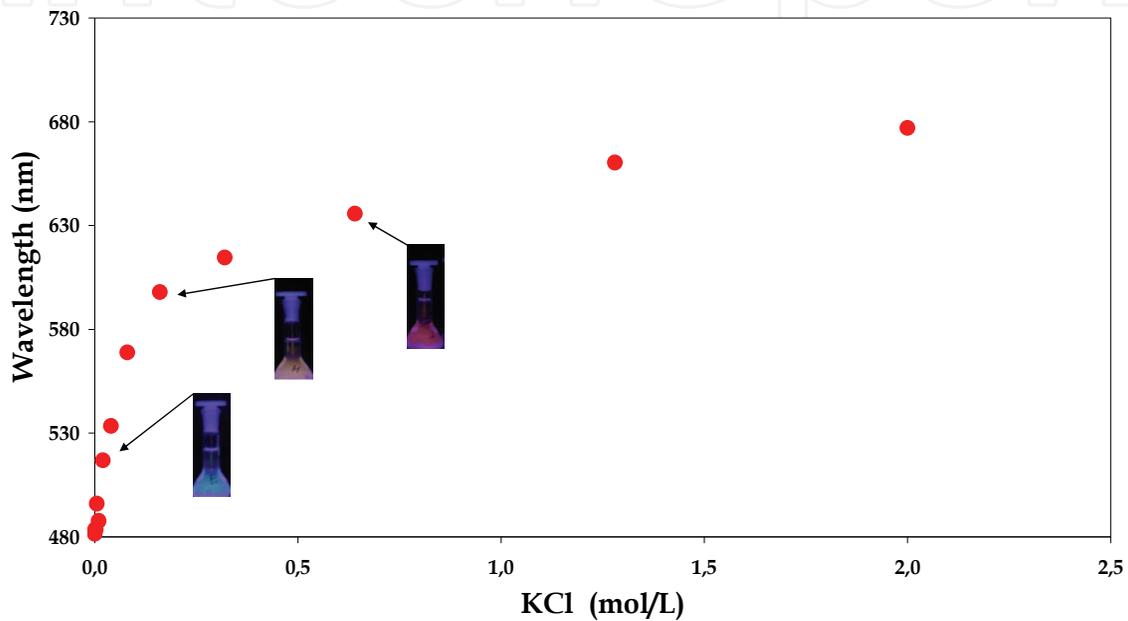


Fig. 9. Maximum wavelength of the emission spectra of DAB-G<sub>5</sub>-CdS in the presence of increasing potassium chloride concentration.

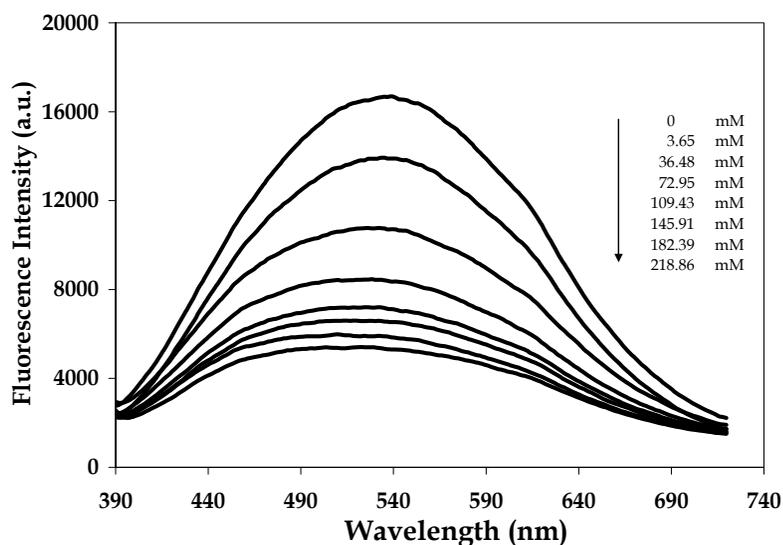


Fig. 10. Emission spectra of DAB-G<sub>5</sub>-CdS without and in the presence of increasing nitromethane concentration.

## 5. Conclusions and perspectives

This chapter described the successfully aqueous synthesis of hybrid nanocomposites of CdS, ZnS and CdS:ZnS QDs with different DAB dendrimer generations. Aqueous solutions of DAB-ZnS QDs based nanocomposites show absorption in the 250 to 260 wavelength range and a fluorescence emission in the 430 to 450 nm wavelength range (a Stokes Shift about 200 nm). Consequently stable water solutions of DAB-ZnS QDs nanocomposites could be obtained which are less toxic than the other cadmium based QDs methanol solutions. The synthesis of this stable, low toxic, high luminescent dendrimer based nanocomposites, opens new potential applications to this family of substances.

As shown in this chapter quite interesting applications of the DAB-QDs nanocomposites as nanosensors can be designed using different strategies. Indeed, the following approaches were observed:

- i. pH sensors can be developed taking advantage of the ionisable functional groups;
- ii. the metal ion coordinating ligands of the dendrimer and/or QDs capping agents can be used for metal ions sensing;
- iii. the collision of a quencher with the external layer of the dendrimer can deactivate the fluorescence of the fluorophore (QDs) and constitutes the bases for the development of the sensor for the quencher;
- iv. reorganization and/or modification of the dendrimer structure around the fluorophore (QDs) can be used as a sensor for example for the ionic strength.

## 6. Acknowledgments

The authors would like to thank the Fundação para a Ciência e Tecnologia (Lisboa, Portugal) under the frame of the Ciência 2007 program. Financial support from Fundação para a Ciência e Tecnologia (Lisboa, Portugal) (FSE-FEDER) (Project PTDC/QUI/71001/2006) and (Project PTDC/QUI/71336/2006) is acknowledged.

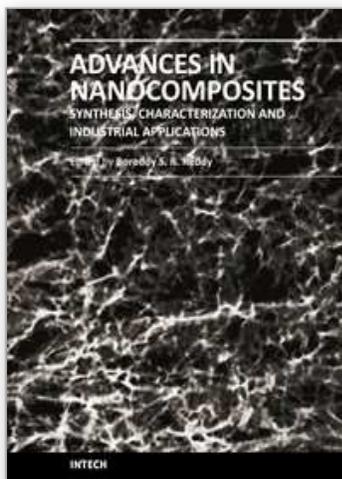
## 7. References

- Aldana, J.; Wang, Y. A. & Peng, J. (2001). Photochemical Instability of CdSe Nanocrystals Coated by Hydrophilic Thiols. *Journal of the American Chemical Society*, 123, 8844-8850, ISSN 1520-5126
- Alivisatos, A. P. (1996). Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science*, 271, 933-937, ISSN 0036-8075
- Ballauf, M.; Crooks, R.M.; Lemon B.I. III & Miller, M. (2001) Dendrimers III Design, Dimension, Function. *Topics in Current Chemistry*, 212, 177-194, ISSN: 0340-1022
- Bawarski, W. E.; Chidlow, E.; Bharali, D.J. & Mousa, S. A. (2008) Emerging nanopharmaceuticals. *Nanomedicine: Nanotechnology, Biology, and Medicine*, 4, 273-282, ISSN: 1549-9634
- Belcastro, M.; Marino, T.; Russo, N. & Sicilia, E. (2004). Structure and Coordination Modes in the Interaction between Cd<sup>2+</sup> and 3-Mercaptopropionic Acid. *The Journal of Physical Chemistry A*, 108, 8407-8410, ISSN: 1089-5639
- Campos, B. B.; Algarra, M.; Alonso, B.; Casado, C. M. & Esteves da Silva, J. C. G. (2009). Mercury(II) Sensing Based on the Quenching of Fluorescence of CdS-Dendrimer Nanocomposites. *Analyst*, 134, 2447-2452, ISSN: 0003-2654

- Campos, B. B.; Algarra, M. & Esteves da Silva, J. C. G. (2010). Fluorescent properties of a hybrid cadmium sulfide-dendrimer nanocomposite and its quenching with nitromethane. *Journal of Fluorescence*, 20, 143-151, ISSN: 1053-0509
- Chen, Y. F. & Rosenzweig, Z. (2002). Luminescent CdS quantum dots as selective ion probes *Analytical Chemistry*, 74, 5132-5138, ISSN: 0003-2700
- Chen, X. B.; Lou, Y. B.; Samia, A. C. & Burda, C. (2003). Coherency strain effects on the optical response of core/shell heteronanostructures *Nano Letters*, 3, 799-803, ISSN 1530-698
- Coe, S.; Woo, W.K.; Bawendi, M. & Bulovic, V. (2002). Electroluminescence from single monolayers of nanocrystals in molecular organic devices. *Nature*, 420, 800-803, ISSN: 0028-0836
- Crampton, H. L. & Simanek, E. E. (2007). Dendrimers as drug delivery vehicles: non-covalent interactions of bioactive compounds with dendrimers. *Polymer International*, 56, 489-496, ISSN: 0959-8103
- Dutta, T.; Garg, M. & Jain, N. K. (2008) Targeting of efavirenz loaded tuftsin conjugated poly(propyleneimine) dendrimers to HIV infected macrophages in vitro. *European Journal Pharmaceutical Science*, 34, 181-189, ISSN: 0928-0987
- Etienne M, Biney A, Walser, A, Dorsinville, Bauer DLV & Nair VB (2005) Third-order nonlinear optical properties of a cadmium sulfide-dendrimer nanocomposite. *Applied Physical Letters*, 87, 181913-181915, ISSN: 0034-6748
- Fernández, L.; González, M.; Cerecetto, H.; Santo, M. & Silber, J. (2006). Solubilization and release properties of dendrimers. Evaluation as prospective drug delivery systems. *Supramolecular Chemistry*, 18, 633-643, ISSN: 1061-0278
- Gao, Y.; Reischmann, S.; Huber, J.; Hanke, T.; Bratschitsch, R.; Leitenstorfer, A. & Mecking, S. (2008). Encapsulating of single quantum dots into polymer particles. *Colloid and Polymer Science*, 286, 1329-1334, ISSN: 0340-255X
- Gattas-Asfura, K. M. & Leblanc, R. M. (2003). Peptide-coated CdS quantum dots for the optical detection of copper(II) and silver(I). *Chemical Communications*, 21, 2684-2685, ISSN: 1364-548X
- Gayen, S. K.; Brito, M.; Das, B. B.; Comanescu, G.; Liang, X. C.; Alrubaiee, M.; Alfano, R. R.; González, C.; Byro, A. H.; Bauer, D. L. V. & Balogh-Nair, V. (2007). Synthesis and optical spectroscopy of a hybrid cadmium sulphide dendrimer nanocomposite. *Journal Optical Society of America B*, 24, 3064-3071, ISSN: 0740-3224
- Gonçalves, H. M. R.; Mendonça, C. & Esteves da Silva, J. C. G. (2009). PARAFAC Analysis of the Quenching of EEM of Fluorescence of Glutathione Capped CdTe Quantum Dots by Pb(II). *Journal of Fluorescence*, 19, 141-149, ISSN: 1053-0509
- Hartschuh, A.; Pedrosa, H. N.; Novotny, L. & Krauss, T. D. (2003). Simultaneous fluorescence and Raman scattering from single carbon nanotubes. *Science*, 301, 1354-1356, ISSN: 0036-8075
- Hedden, R. C.; Bauer, B. J.; Smith, A. P.; Gröhn, F. & Amis, E. (2002) Templating of inorganic nanoparticles by PAMAM/PEG dendrimer-star polymers. *Polymer*, 43, 5473-5481, ISSN: 0032-3861
- Hezinger, A. F. E.; Tessmar, J. & Gopferich, A. (2008). Polymer coating of quantum dots—A powerful tool toward diagnostics and sensorics *European Journal Pharmaceutics and Biopharmaceutics*, 68, 138-152, ISSN: 0939-6411
- Hollins, A. J.; Benboubetra, M.; Omid, Y.; Zinselmeyer, B. H.; Schatzlein, A. G.; Uchegbu, I. F. & Akhtar, S. (2004). Evaluation of generation 2 and 3 poly(propyleneimine) dendrimers for potential cellular delivery of antisense oligonucleotides targeting

- the epidermal growth factor receptor. *Pharmaceutical Research*, 21, 458-466, ISSN: 0724-8741
- Huang, B. & Tomalia, D. A. (2005) Dendronization of gold and CdSe/cdS (core-shell) quantum dots with tomalia type, thiol core, functionalized poly(amidoamine) (PAMAM) dendrons. *Journal of Luminescence*, 111, 215-223, ISSN: 0022-2313
- Jie, G.; Liu, B., Pan, H.; Zhu, J.J. & Chen, H.Y. (2007) CdS Nanocrystal-Based Electrochemiluminescence Biosensor for the Detection of Low-Density Lipoprotein by Increasing Sensitivity with Gold Nanoparticle Amplification. *Analytical Chemistry*, 79, 5574-5581, ISSN: 0003-2700
- Juan, J. Y.; Jun, L. Y.; Ping, L. G.; Jie, L.; Feng, W. Y. & Qin, Y. R. (2008). Application of photoluminescent CdS/PAMAM nanocomposites in fingerprint detection. *Forensic Science International*, 179, 34-38, ISSN: 0379-0738
- Kobayashi, H.; Kawamoto, S.; Choyke, P. L.; Sato, N.; Knopp, M. V.; Star, R. A.; Waldmann, T. A.; Tagaya, Y. & Brechbel, M. W. (2003) Comparison of dendrimer-based macromolecular contrast agents for dynamic micro-magnetic resonance lymphangiography. *Magnetic Resonance Medical*, 50, 58-766, ISSN: 1880-2206
- Lakowicz, J. R.; Gryczynski, I.; Gryczynski, Z. & Murphy, C. J. (1999). Luminescence spectral properties of CdS nanoparticles. *The Journal of Physical Chemistry B*, 103, 7613-7620, ISSN: 1520-6106
- Lebedkin, S.; Hennrich, F.; Skipa, T. & Kappes, M. M. (2003). Near-infrared photoluminescence of single-walled carbon nanotubes prepared by the laser vaporization method. *The Journal of Physical Chemistry B*, 107, 1949-1956, ISSN: 1089-5647
- Lemon, B. I. & Crooks, R. M. (2000). Preparation and characterization of dendrimer-encapsulated CdS semiconductor quantum dots. *Journal of the American Chemical Society*, 122, 12886-12887, ISSN: 1520-5126
- Leitão, J. M. M.; Gonçalves, H. M. R.; Mendonça, C. & Esteves da Silva, J. C. G. (2008). Multiway chemometric decomposition of EEM of fluorescence of CdTe quantum dots obtained as function of pH. *Analytica Chimica Acta*, 628, 143-154, ISSN: 0003-2670
- Li, H.; Shih, W. Y. & Shih, W. H. (2007). Non-heavy-metal ZnS quantum dots with bright blue photoluminescence by a one-step aqueous synthesis. *Nanotechnology*, 18, 205604-205609, ISSN: 0957-4484
- Ling J. & Cong R. M. (2008). Fabrication of photoluminescent ultra-thin film by using CdS-ZnS core-shell structure quantum dot/PAMAM dendrimer nanocomposites. *Acta Chimica Sinica*, 18, 2070-2074, ISSN: 1872-1508
- Liu, M.; Kono, K. & Frechet, J. M. J. (2000). Water-soluble dendritic unimolecular micelles: their potential as drug delivery agents. *Journal Control Release*, 65, 121-131, ISSN: 0168-3659
- Lubick, N. (2009). Promising green nanomaterials. *Environmental Science Technology*, 43, 1247-1249, ISSN: 0944-1344
- Maule, C. D.; Gonçalves, H. M. R.; Mendonça, C.; Sampaio, P.; Jorge, P. A. S. & Esteves da Silva, J. C. G. (2010). Wavelength encoded analytical imaging and fiber optic sensing with pH sensitive CdTe quantum dots. *Talanta*, 80, 1932-1938, ISSN: 0039-9140
- Nourse, A.; Millar, D.B. & Minton A.P. (2000). Physicochemical characterization of generation 5 polyamidoamine dendrimers. *Biopolymers*, 53, 316-328, ISSN: 1097-0282

- Pileni, M. P.; Motte, L. & Petit, C. (1992). Synthesis of cadmium sulfide in situ in reverse micelles: Influence of the preparation modes on size polydispersity, and photochemical reactions. *Chemical Materials*, 4, 338-345, ISSN: 0897-4756
- Ramzi, A.; Scherrenberg, R.; Joosten, J.; Lemstra, P. & Mortensen, K. (2002). Structure-Property Relations in Dendritic Polyelectrolyte Solutions at Different Ionic Strength. *Macromolecules*, 35, 827-833, ISSN: 0024-9297
- Schatzlein, A. G.; Zinselmeyer, B. H.; Elouzi, A.; Dufes, C.; Chim, Y. T. A.; Roberts, C. J.; Davies, M. C.; Munro, A.; Gray, A. I. & Uchegbu, I. F. (2005). Preferential liver gene expression with polypropylenimine dendrimers. *Journal Control Release*, 101, 247-258, ISSN: 0168-3659
- Scott, R. W. J.; Wilson, O. M. & Crooks, R. M. (2005). Synthesis, characterization, and applications of dendrimer-encapsulated nanoparticles. *Journal Physical Chemistry B*, 109, 692-704, ISSN: 1089-5647
- Sooklal, B. K.; Hanus, L. H. & Murphy, C. J. (1998). A blue-emitting CdS/dendrimer nanocomposite. *Advanced Materials*, 10, 1083-1087, ISSN: 1468-6996
- Svenson, S. & Tomalia, D. A. (2005) Commentary: Dendrimers in biomedical applications. Reflections on the field. *Advanced Drug Delivery Reviews*, 57, 2106-2129, ISSN: 0169-409X
- Tessler, N.; Medvedev, V.; Kazes, M.; Kan, S. H. & Banin, U. (2002). Efficient near infrared polymer nanocrystal light-emitting diodes. *Science*, 295, 1506-1510, ISSN 0036-8075
- Talapin, D. V.; Rogach, A. L.; Kornowski, A.; Haase, M. & Weller, H. (2001). Highly luminescent monodisperse CdSe and CdSe/ZnS nanocrystals synthesized in a hexadecylamine-trioctylphosphine oxide-trioctylphosphine mixture. *Nano Letters*, 1, 207-211, ISSN: 1530-698
- Talanov, V. S.; Regino, C. A.; Kobayashi, H.; Bernardo, M.; Choyke, P. L. & Brechbiel, M. W. (2006). Dendrimer-based nanoprobe for dual modality magnetic resonance and fluorescence imaging. *Nano Letters*, 6, 459-463, ISSN: 1530-698
- Uchihara, T.; Fukuda, N. & Miyagi, E. (2005). Subpicosecond spectroscopic studies on the photochemical events of 2-dimethylaminoethanethiol-capped CdS nanoparticles in water. *Journal of Photochemistry and Photobiology A: Chemistry*, 169, 309-315, ISSN: 1010-6030
- Unni, C.; Philip, D. & Gopchandran, K. G. (2009). Studies on optical absorption and photoluminescence of thioglycerol-stabilized ZnS nanoparticles. *Optical Materials*, 32, 169-175, ISSN: 0925-3467
- Welch, P. & Muthukumar, M. (1998). Tuning the Density Profile of Dendritic Polyelectrolytes, *Macromolecules*, 31, 5892-5897, ISSN: 0024-9297
- Weller, H. (1993). Quantized semiconductor particles: A novel state of matter for materials science. *Advanced Materials*, 5, 88-95, ISSN: 1468-6996
- Wisher, A. C.; Bronstein, I. & Chechik, V. (2006). Thiolated PAMAM dendrimer-coated CdSe/ZnSe nanoparticles as protein transfection agents, *Chemical Communications*, 15, 1637-1639, ISSN: 1364-548X
- Wuister, S. F. & Meijerink, A. (2003a) A Synthesis and luminescence of CdS quantum dots capped with a silica precursor. *Journal of Luminescence*, 105, 35-43, ISSN: 0022-2313
- Wuister, S. F. & Meijerink, A. (2003b). Synthesis and luminescence of (3-mercaptopropyl)-trimethoxysilane capped CdS quantum dots. *Journal of Luminescence*, 102-103, 338-343, ISSN: 0022-2313
- Yu, J.; RajanBabu, T. V. & Parquette, J. R. (2008). Conformationally driven asymmetric induction in a catalytic dendrimer. *Journal of the American Chemical Society*, 130, 7845-7847, ISSN: 1520-5126



## **Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications**

Edited by Dr. Boreddy Reddy

ISBN 978-953-307-165-7

Hard cover, 966 pages

**Publisher** InTech

**Published online** 19, April, 2011

**Published in print edition** April, 2011

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

### **How to reference**

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Joaquim G.G. Esteves da Silva, Manuel Algarra and Bruno B. Campos (2011). Synthesis and Analytical Applications of Quantum Dots Coated with Different Generations of DAB Dendrimers, *Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications*, Dr. Boreddy Reddy (Ed.), ISBN: 978-953-307-165-7, InTech, Available from: <http://www.intechopen.com/books/advances-in-nanocomposites-synthesis-characterization-and-industrial-applications/synthesis-and-analytical-applications-of-quantum-dots-coated-with-different-generations-of-dab-dendr>

**INTECH**  
open science | open minds

### **InTech Europe**

University Campus STeP Ri  
Slavka Krautzeka 83/A  
51000 Rijeka, Croatia  
Phone: +385 (51) 770 447  
Fax: +385 (51) 686 166  
[www.intechopen.com](http://www.intechopen.com)

### **InTech China**

Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen