



## CdSe quantum dots capped PAMAM dendrimer nanocomposites for sensing nitroaromatic compounds

M. Algarra<sup>a</sup>, B.B. Campos<sup>b</sup>, M.S. Miranda<sup>a</sup>, Joaquim C.G. Esteves da Silva<sup>b,\*</sup>

<sup>a</sup> Centro de Geologia da Universidade do Porto, Departamento de Geociências, Ambiente e Ordenamento do Território do Porto, Faculdade de Ciências da Universidade do Porto, Porto, Portugal

<sup>b</sup> Centro de Investigação em Química, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Porto, Portugal

### ARTICLE INFO

#### Article history:

Received 20 September 2010

Received in revised form 20 October 2010

Accepted 29 October 2010

Available online 13 November 2010

#### Keywords:

CdSe quantum dots

PAMAM-G<sub>4</sub> dendrimer

Nanocomposites

Explosives

Nitroaromatic compounds

### ABSTRACT

The detection of nitroaromatic compounds, best known as raw materials in explosives preparations, is important in many fields including environmental science, public security and forensics. CdSe quantum dots capped with PAMAM-G<sub>4</sub> dendrimer were synthesized in water and used for the detection of trace amounts of three nitroaromatic compounds: 4-methoxy-2-nitrophenol (MNP), 2-amine-5-chloro-1,3-dinitrobenzene (ACNB) and 3-methoxy-4-nitrobenzoic acid (MNB). To increase the apparent water solubility of these compounds  $\alpha$ -cyclodextrin ( $\alpha$ -CD) was used to promote the formation of inclusion complexes. The studied nitroaromatic compounds (plus  $\alpha$ -CD) significantly quenched the fluorescence intensity of the nanocomposite with linear Stern–Volmer plots. The Stern–Volmer constants (standard deviation in parenthesis) were: MNB,  $K_{SV} = 65(5) \times 10^4 \text{ M}^{-1}$ ; ACNB,  $K_{SV} = 19(2) \times 10^4 \text{ M}^{-1}$ ; and, MNP,  $K_{SV} = 33(1) \times 10^2 \text{ M}^{-1}$ . These constants suggest the formation of a ground state complex between the nitroaromatic compounds and the sensor which confers a relatively high analytical sensitivity. The detection sensitivities are about  $0.01 \text{ mg L}^{-1}$  for MNB and ACNB and about  $0.1 \text{ mg L}^{-1}$  for MNP. No interferences or small interferences are observed for trinitrotoluene [ $K_{SV} = 10(2) \times 10^2 \times \text{M}^{-1}$ ], 2,4-dinitrotoluene [ $K_{SV} = 20(3) \times 10 \text{ M}^{-1}$ ], 2,6-dinitrotoluene [ $K_{SV} = 11(4) \times 10 \text{ M}^{-1}$ ] and nitrobenzene [ $K_{SV} = 2(1) \times 10^3 \times \text{M}^{-1}$ ].

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Nitroaromatic compounds are produced in large scale in the chemical industry. They are used in the manufacture of pesticides, dyes, pharmaceuticals and are raw materials in explosives preparations [1].

The detection of trace amounts of nitroaromatic compounds is an important task in many fields including environmental science, public security and forensic science. In environmental science, nitroaromatic compounds have received a great deal of attention over the years because these compounds present a high toxicity and have been proved to be potential carcinogens or mutagens which are dispersed to soils, water and air as consequence of their utilization [2]. Moreover, they are known to undergo microbiological and photochemical degradation processes in the environment leading to the formation of other nitroaromatic compounds. In public security, there is concern about unexploded land mines and to the increasing incidents and threats of terrorist attacks with explosive devices. In forensics, the detection of

trace amounts of nitroaromatic explosives in the body or clothes may lead to the identification of persons in recent contact with explosives.

Many expensive and operator dependent analytical methodologies exist to detect nitroaromatic explosives: mass spectrometry [3–5]; surface enhanced Raman spectroscopy [6]; nuclear quadrupole resonance [7–9]; energy dispersive [10]; X-ray diffraction [11–13]; neutron activation analysis [14,15]; ion mobility spectrometry [16]; and, electrochemistry [17,20]. Fluorescence and luminescence based techniques for the detection of nitroaromatic compounds offer many benefits over other commonly used methodologies, although nitroaromatic compounds are not intrinsically fluorescent. Many nitroalkane explosives, such as nitroamines, nitrate esters, and peroxide explosives have non conjugated structures that allow efficient vibrational relaxation. Nitroaromatic explosives, despite having an aromatic structure, do not fluoresce as result of the strong electron-withdrawing nature of the nitro substituents. In spite of this lack of native fluorescence, many methods have been proposed in recent years for their detection using luminescence based techniques. In this respect fluorescence based sensors are very promising [21–25].

Nanotechnology designed new materials can be used for trace detection of nitroaromatic compounds [26]. Semiconduc-

\* Corresponding author. Tel.: +351 220 402 569; fax: +351 220 402 654.

E-mail address: [jcsilva@fc.up.pt](mailto:jcsilva@fc.up.pt) (J.C.G.E. da Silva).

tor nanocrystals, such as CdS, CdSe or CdTe, known as quantum dots (QDs) show high photoluminescence efficiency, robustness and flexibility of functionalization with conjugating ligands for the selective nanosensing of analytes [27–35]. The applications of QDs in the detection of nitroaromatic compounds, based on direct fluorescence quenching of QDs [36,37] or fluorescence resonance energy transfer [38], have been proposed. The detection of a nitroalkane explosive, nitromethane, based on the quenching of the fluorescence intensity of a hybrid cadmium sulfide QDs dendrimer DAB-G<sub>5</sub> nanocomposite has been studied [39]. Besides the capping agent of QDs using simple thiolate reagents that confers to them water solubility, stability and chemical reactivity, dendrimers are being used as coating polymers of QDs. The conjugation of dendrimers with QDs, originating hybrid nanomaterials, markedly increases their physico-chemical properties rendering them biocompatibility and biostability, increased reactivity, and confers an important biomedical role in diagnostics and biochemical sensing [40–42].

This paper reports the synthesis of a hybrid CdSe QDs dendrimer PAMAM generation 4 in water–CdSe–PAMAM-G<sub>4</sub> nanocomposites. The quenching of the fluorescence of CdSe–PAMAM nanocomposites by three nitroaromatic compounds 4-methoxy-2-nitrophenol (MNP), 3-methoxy-4-nitrobenzoic acid (MNB) and 2-amine-5-chloro-1,3-dinitrobenzene (ACNB) is presented and its potential application for sensing of these materials assessed. Nitrophenols nitrobenzoic acids and nitroanilines are known to be intermediates in the environmental degradation of nitroaromatic explosives [43]. Also, the effect of trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT) and nitrobenzene (NB) in the fluorescence of the nanocomposite was evaluated.

The nanocomposites synthetic procedure used in this work uses a green chemistry approach because it was based on water instead of using organic solvents [44,45]. The selection of the PAMAM-G<sub>4</sub> dendrimer was based on previous studies where it was demonstrated that the interaction with CdSe nanocrystals increased with the generation of the dendrimer [45].

## 2. Materials and methods

### 2.1. Reagents and apparatus

Polyamidoamine dendrimer-1,12-diaminododecane core-generation 4 (PAMAM-G<sub>4</sub>, solution in methanol 10%), cadmium chloride (99.9%, CdCl<sub>2</sub>), selenium powder (Se, 99.99%),  $\alpha$ -cyclodextrin, and nitroaromatic compounds: 4-methoxy-2-nitrophenol (MNP); 2-amine-5-chloro-1,3-dinitrobenzene (ACNB); 3-methoxy-4-nitrobenzoic acid (MNB); trinitrotoluene (TNT); 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); and, nitrobenzene (NB) were purchased from Sigma–Aldrich Spain; sodium borohydride (NaBH<sub>4</sub>,  $\geq 96\%$ ) and 3-mercaptopropionic acid (MPA, 99%) were purchased from Fluka and used without further purification. Stock solutions (50 mg L<sup>-1</sup>) of MNP, ACNB and MNB were prepared by rigorous weighting of the powders in aqueous solutions of  $\alpha$ -CD (10<sup>-2</sup> M). Concentrated stock solutions (1000 mg L<sup>-1</sup>) of TNT, 2,4-DNT, 2,6-DNT and NB were prepared in acetonitrile and diluted stock solutions (50 mg L<sup>-1</sup>) in aqueous solutions of  $\alpha$ -CD (10<sup>-2</sup> M) were obtained by rigorous dilution of the concentrated solution.

Photoluminescence measurements were recorded with a Horiba Jovin Yvon Fluoromax 4 TCSPC spectrophotometer using an excitation of 380 nm and an emission range of 400–740 nm, with an integration time of 0.1 s and a slit of 5 nm. Samples were contained in 1-cm path length quartz cuvettes. The Quantum yield (QY) was determined using Rhodamine 6G as a standard. Rhodamine 6G has a QY of 90% at an excitation wavelength of 488 nm in methanol [18]. The calibration curve for Rhodamine was obtained

in methanol which has a refractive index ( $n_{st}$ ) of 1.329. The integrated area under the fluorescence curves (excitation at 488 nm) was plotted versus the absorbance at 488 nm (after subtraction of the solvent absorbance) for different concentrations. The same procedure was repeated for the QD samples dissolved in deionized water ( $n = 1.3749$ ). The excitation intensity and slit width were held constant for all measurements. The QY of the QDs was obtained from:

$$QY_{QD} = QY_{st} \left[ \frac{(dI/dA)_{QD}}{(dI/dA)_{st}} \right] \left[ \frac{n_{st}^2}{n_{QD}^2} \right]$$

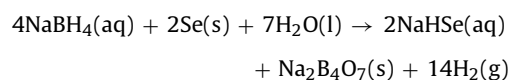
where  $I$  is the area under the PL curves and  $A$  is the corresponding absorbance [19]

Scanning electron microscopy (SEM) and Energy dispersive X-Ray analysis (EDS) were recorded by means of a FEI Quanta 400FEG/EDAX Genesis X4M high resolution scanning electronic microscope to examine the morphology of the nanocomposites obtained.

### 2.2. Preparation of CdSe–PAMAM nanocomposites

CdSe–PAMAM nanocomposites were prepared in three major steps:

- (i) Selenium was reduced according to the following chemical reaction:



60 mg of NaBH<sub>4</sub> and 50 mg of Se were dissolved in 3 mL of deionized water and left 12 h under nitrogen atmosphere. The obtained solution goes from colorless to brown-red.

- (ii) 90  $\mu$ L of PAMAM-G<sub>4</sub> ( $6.31 \times 10^{-4}$  mmol) were mixed with 25 mL of water and the mixture was stirred until the dissolution was completed. Then, 10 mg of CdCl<sub>2</sub> (0.05 mmol) was added and left to stabilize for 3 h followed by addition of 100  $\mu$ L (1.14 mmol) of MPA. According to previous experiments, this concentration for MPA is the best ratio to PAMAM (MPA:PAMAM 230:1) because as the concentration of MPA increases the pH of the aqueous solution decreases.
- (iii) After 24 h, 100  $\mu$ L of the reduced selenium solution (i), was added to solution (ii), with continuously stirring for more 24 h, yielding a orange-red solution that was dialyzed in cellophane membrane (using a MW CO 12,000–14,000 Dalton dialysis tube from Medicell International) for 12 h against deionized water at room temperature. The CdSe–PAMAM solution was centrifuged at 13,000 rpm for 10 min to remove unreacted reactants.

### 2.3. Quenching of CdSe–PAMAM nanocomposites by nitroaromatic compounds

For photoluminescent measurements CdSe–PAMAM (500  $\mu$ L) was transferred to a 5 mL calibrated flask together with aliquots containing from  $4.60 \times 10^{-5}$  to  $2.3 \times 10^{-1}$  M of nitroaromatic compounds and fulfilled with  $\alpha$ -CD (10<sup>-2</sup> M) – the problem of small solubility of these compounds in aqueous solution was solved by using the inclusion complex with  $\alpha$ -CD [20]. The samples were sonicated for 30 min, left until room temperature was reached, and then the fluorescence spectra were recorded.

### 2.4. Data analysis

A preliminary screening analysis was performed following a Plackett–Burman design, focusing on the effect's evaluation of the concentrations of the nitroaromatic compounds (MNP, ACNB, MNB)

Download English Version:

<https://daneshyari.com/en/article/10559529>

Download Persian Version:

<https://daneshyari.com/article/10559529>

[Daneshyari.com](https://daneshyari.com)