

Proceeding Paper

# Immobilization on Cellulose Paper of a Chemosensor for CdSe-Cys QDs<sup>†</sup>

Yeneva Alves-Iglesias<sup>1,2</sup>, Pilar Bermejo-Barrera<sup>2</sup>, Ana María García-Deibe<sup>1</sup>, Matilde Fondo<sup>1</sup> and Jesús Sanmartín-Matalobos<sup>1,\*</sup>

<sup>1</sup> Coordination and Supramolecular Chemistry Group (Suprametal), Institute of Materials (iMATUS), Department of Inorganic Chemistry, Faculty of Chemistry, Universidade de Santiago de Compostela, Avenida das Ciencias s/n, 15782 Santiago de Compostela, Spain

<sup>2</sup> Trace Element, Speciation and Spectroscopy Group (GETEE)—Institute of Materials (iMATUS), Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, Universidade de Santiago de Compostela, Avenida das Ciencias, s/n, 15782 Santiago de Compostela, Spain

\* Correspondence: [jesus.sanmartin@usc.es](mailto:jesus.sanmartin@usc.es)

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**Abstract:** The Schiff base ligand H<sub>2</sub>SB derived from the condensation of *N*-(2-aminobenzyl)-5-(dimethylamino)naphthalene-1-sulfonamide with 4-formyl-3-hydroxybenzoic acid has been investigated as a chemosensor for the detection of CdSe-Cys QDs in water samples. We immobilized H<sub>2</sub>SB onto cellulose paper by forming an amide bond, which results from the condensation of a carboxylic acid and an amine. Three dominant signals located around 270, 330, and 420 nm in the diffuse reflectance spectrum of the H<sub>2</sub>SB-modified paper demonstrated its immobilization. A linear decrease can be observed in the absorbance of the 270 nm band with the increase of the CdSe-Cys QDs concentration from 100 ppb to 2 ppm. The LOD and LOQ show values of 245 and 815 ppb, respectively. An interaction via metal–ligand coordination between CdSe-Cys QDs and H<sub>2</sub>SB has been demonstrated with <sup>1</sup>H NMR, ATR-FTIR, and UV-Vis spectroscopy.

**Keywords:** chemosensor; Schiff base; CdSe-Cys QDs; UV-Vis spectroscopy



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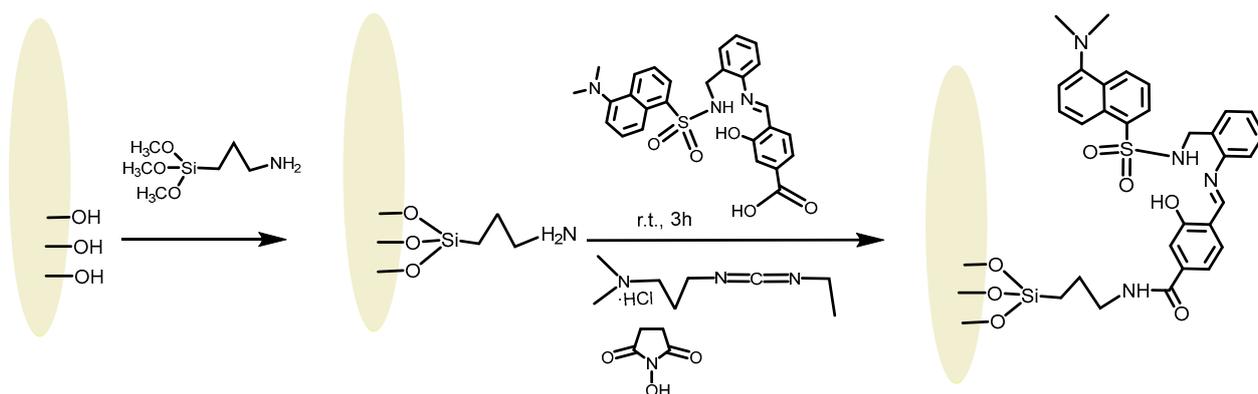
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## 1. Introduction

Cadmium-based QDs are one of the most widely used semiconducting QDs, as they have useful properties for biochemical sensors, biomedical imaging, photovoltaic applications, light-emitting diodes (LEDs), thin-film transistors, lasers, and solar cells [1,2]. A negative consequence of this widespread use is the release into the environment of such noxious material. To prevent their uncontrolled discharge, it is essential to develop simple methods to detect them in waste or even in the environment. The implementation of paper sensors for colour analysis provides fast responses, simple operation, and low cost in the detection of CdSe QDs. Here, we report new spectroscopic data about the immobilization on cellulose paper of a Schiff base containing a carboxylic acid substituent, H<sub>2</sub>SB [3]. In addition, we present here our progress in the study of the interaction between H<sub>2</sub>SB and CdSe-Cys QDs. The usefulness of the H<sub>2</sub>SB-modified paper (Figure 1) for the detection of CdSe-Cys QDs was demonstrated by registering an absorbance decrease in the band at 270 nm, with a simultaneous increase in the CdSe-Cys QDs concentration from 100 ppb to 2 ppm [4]. In order to help elucidate how H<sub>2</sub>SB interacts with CdSe-Cys QDs, Cd<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> has been synthesized and studied by <sup>1</sup>H NMR, ATR-FTIR, and UV-Vis spectroscopy.

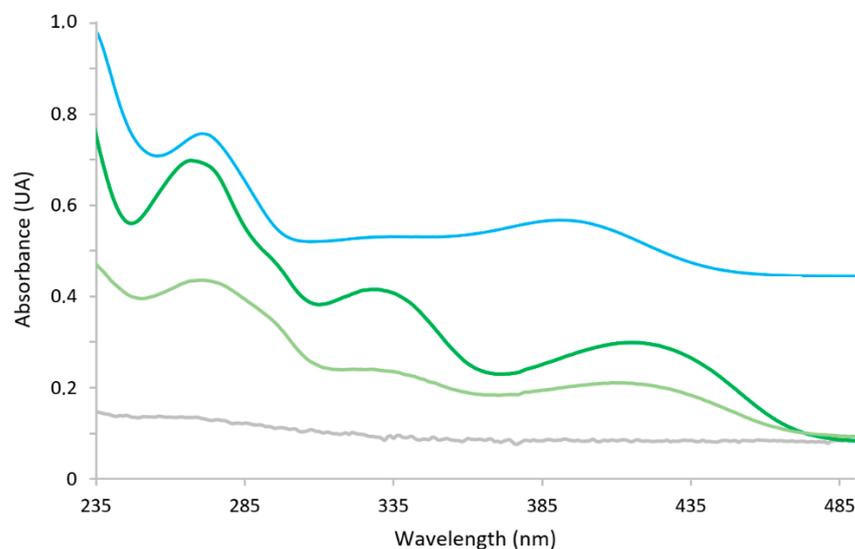


**Figure 1.** Schematic representation of the chemosensor-modified cellulose paper.

## 2. Results and Discussion

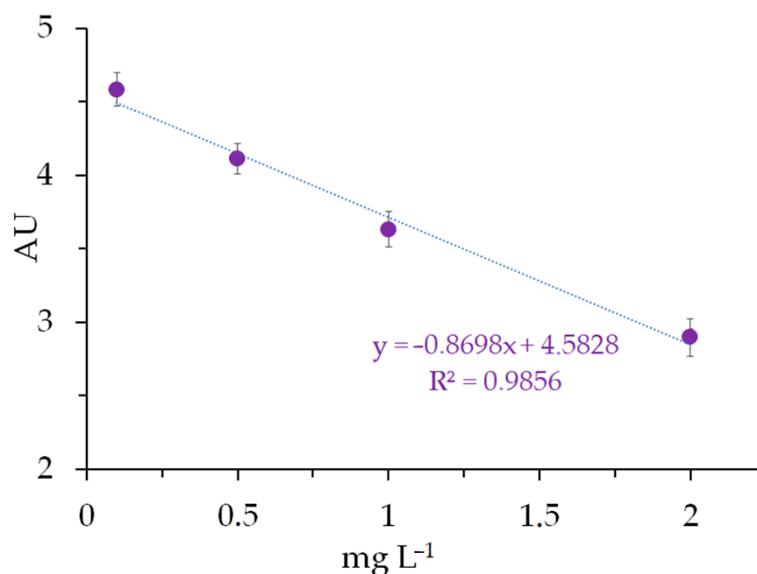
The cellulose paper was first primed with (3-aminopropyl)trimethoxysilane (APTMS) after soaking it in a DMF solution for 2 h (Figure 1). In the second reaction step, *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl), *N*-hydroxysuccinimide (NHS), as well as the chemosensor H<sub>2</sub>SB, were added together to achieve its immobilization on the amine-modified paper (by forming an amide bond) [4].

The observation of three dominant signals located around 270, 330, and 420 nm in the diffuse reflectance spectrum of the chemosensor-modified paper demonstrated its immobilization (Figure 2). One of the dominant absorption bands appeared to red-shifted around 30 nm, with respect to the spectrum of an ethanol solution of the chemosensor (390 nm).



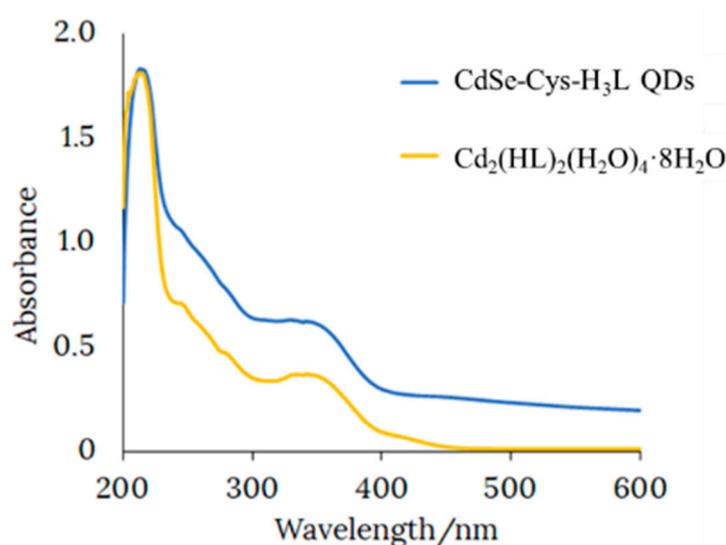
**Figure 2.** View of the diffuse reflectance spectrum of H<sub>2</sub>SB-modified cellulose paper previously (green) and after (pale green) the interaction with CdSe-Cys QDs. The diffuse reflectance spectrum of cellulose paper (grey) and the UV-Vis spectrum of H<sub>2</sub>SB in water solution (blue) have been included for comparison.

The chemosensor-modified cellulose paper after being soaked in CdSe-Cys QDs water solutions for two hours exhibited a decreased absorbance of each band of its diffuse reflectance spectrum. As the most pronounced decrease was observed for the band at 270 nm, this wavelength was chosen to carry out the measurements (Figure 3). The limits of detection (LODs) and of quantification (LOQs) of H<sub>2</sub>SB were expressed as  $LOD = 3SD/M$  and  $LOQ = 10SD/M$ , where SD is the standard response deviation and M is the slope of the calibration curve. The LOD and LOQ calculation results were 245 and 815 ppb, respectively.



**Figure 3.** Decrease in the absorbance at 270 nm with increasing CdSe-Cys QDs concentration from 100 ppb to 2 ppm.

To study the type of interaction between the CdSe-Cys QDs and H<sub>2</sub>SB, we obtained Cd<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·8H<sub>2</sub>O from the reaction of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O and H<sub>2</sub>SB in an ethanol solution at room temperature. The similarities between the UV-Vis spectra of Cd<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·8H<sub>2</sub>O and CdSe-Cys-H<sub>2</sub>SB QDs (Figure 4), with three bands at about 220, 250, and 340 nm, evidenced an interaction via metal–ligand coordination between CdSe-Cys QDs and H<sub>2</sub>SB.



**Figure 4.** View of the UV-Vis spectra of CdSe-Cys-H<sub>2</sub>SB QDs and Cd<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·8H<sub>2</sub>O in ethanol solution.

The binding constant value of H<sub>2</sub>SB with Cd<sup>2+</sup>, at room temperature, has been determined from UV-Vis absorption data following the Benesi–Hildebrand equation [5] ( $K_b = 3.686 \times 10^3 \text{ M}^{-1}$ ) for 1:1 (metal:ligand) complexes (Figure 5). The binding stoichiometry used in the determination of  $K_b$  was obtained by elemental analysis.



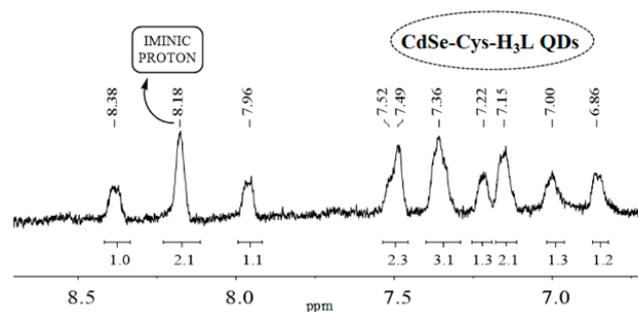


Figure 7. Aromatic region of the  $^1\text{H}$  NMR spectrum of CdSe-Cys- $\text{H}_2\text{SB}$  QDs (in methanol- $\text{d}_4/\text{D}_2\text{O}$ ).

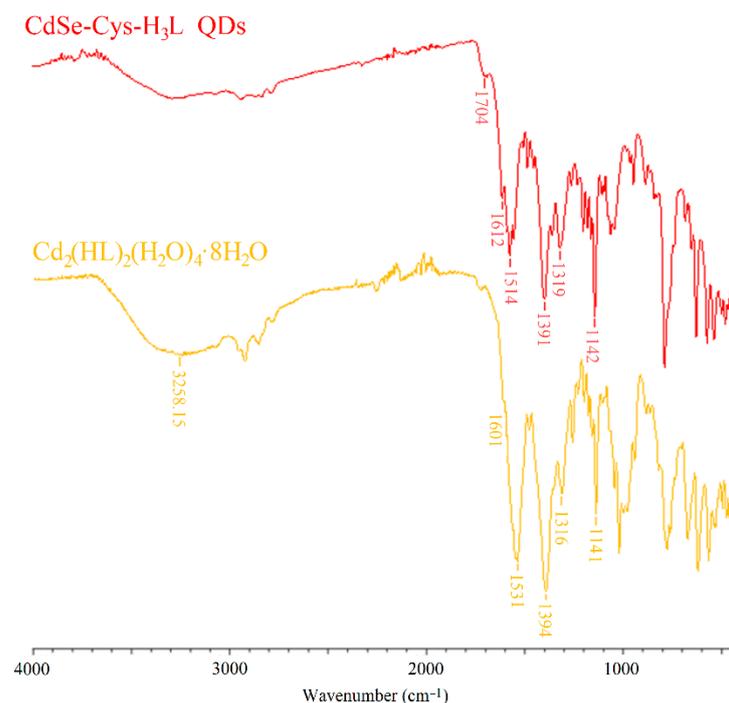


Figure 8. ATR-IR spectra of CdSe-Cys- $\text{H}_2\text{SB}$  QDs (top) and  $\text{Cd}_2(\text{SB})_2(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  (bottom).

The IR spectrum of  $\text{Cd}_2(\text{SB})_2(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  showed a broad band centred at about  $3360\text{ cm}^{-1}$ , attributable to  $\nu(\text{OH})$ , which evidences the hydration of the obtained complex (Figure 8). The observation of two bands attributable to  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  at ca.  $1574$  and  $1393\text{ cm}^{-1}$ , respectively, seems to indicate the deprotonation of the carboxylic groups of the Schiff base in its complex. The neutrality of this complex is related to the zwitterionic nature adopted by the ligand units, where the carboxylic groups are deprotonated, while their amine N atoms are protonated.

The IR spectrum of CdSe-Cys- $\text{H}_2\text{SB}$  QDs evidences the bideprotonation of the Schiff base ligand, as it showed the absence of bands attributable to  $\nu\text{ OH}/\nu\text{ NH}$  modes. Likewise, the presence of two bands attributable to  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$ , at about  $1574$  and  $1391\text{ cm}^{-1}$ , respectively, evidences the deprotonation of the carboxyl group in the ligand, as it is indicative of the formation of the carboxylate sodium salt. In addition, the clear presence of a strong sharp band (ca.  $1615\text{ cm}^{-1}$ ) is attributed to the C=N group of the ligand. The similarity between the spectra of the ATR-IR spectra of CdSe-Cys- $\text{H}_2\text{SB}$  QDs with  $\text{Cd}_2(\text{SB})_2(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  (Figure 8) supports that the interaction between  $\text{H}_2\text{SB}$  and CdSe-Cys QD surfaces occurred via metal–ligand coordination through the  $\text{N}_{\text{sulfonamide}}$ ,  $\text{N}_{\text{imine}}$ , and  $\text{O}_{\text{phenol}}$  atoms.

### 3. Conclusions

In conclusion, we can say that we have immobilized H<sub>2</sub>SB onto cellulose paper by forming an amide bond, which results from the condensation of a carboxylic acid and an amine. Three dominant signals located around 270, 330, and 420 nm in the diffuse reflectance spectrum of the H<sub>2</sub>SB-modified paper demonstrated its immobilization. Diffuse reflectance spectrophotometry allows the detection of CdSe-Cys QDs using H<sub>2</sub>SB-modified cellulose paper (LOD = 245 ppb and LOQ = 815 ppb). UV-Vis, <sup>1</sup>H NMR, and ATR-FTIR spectroscopy evidenced that the interaction between H<sub>2</sub>SB and CdSe-Cys QDs takes place through the O<sub>phenol</sub>, N<sub>imine</sub>, and N<sub>sulphonamide</sub> atoms of the dianionic ligand (as phenolate and sulphonamide anion).

### 4. Experimental Section

#### 4.1. Materials and Methods

The synthesis and characterisation of H<sub>2</sub>SB and CdSe-Cys QDs have been previously reported [3,4]. The sample used for investigating the interaction of CdSe-Cys QDs with H<sub>2</sub>SB was obtained by stirring, at room temperature, an ethanol solution of H<sub>3</sub>L (pH = 9) with a suspension of CdSe-Cys QDs in 2:1 molar ratio, for about 15 min. The sample was subsequently air-dried.

<sup>1</sup>H NMR spectra (400 MHz) were measured in dmsO-d<sub>6</sub> using a Varian Inova 400 Spectrometer. *J* values are provided in Hertz. Diffuse reflectance spectra were measured on a PerkinElmer LAMBDA 1050+ UV/Vis/NIR spectrophotometer, equipped with an integrating sphere. The infrared spectra were measured in the 4000–400 cm<sup>-1</sup> wavenumber range, using an FTIR spectrometer PerkinElmer Spectrum Two coupled with a Platinum Diamond ATR, consisting of a diamond disc as an internal reflection element.

#### 4.2. Synthesis of Cd<sub>2</sub>(SB)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>·8H<sub>2</sub>O

An ethanol solution of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (40 mL, 0.0212 g, 0.0794 mmol) was added to of an ethanol solution (60 mL) of H<sub>2</sub>SB (0.0400 g, 0.0794 mmol). The resulting solution was refluxed for 4 h. During the reaction time, the coloured solution changed from greenish yellow to deep yellow. This solution was evaporated under vacuum to dryness. Then, the powdery solid was washed with diethyl ether, filtered, and air-dried.

Yield: 42 mg (40.6 %). <sup>1</sup>H NMR (400 MHz, dmsO-d<sub>6</sub>, δ in ppm): 8.60 (d, 1H), 8.30 (s, 1H), 8.28 (d, 1H), 8.17 (d, 1H), 7.49 (t, 1H), 7.43 (t, 1H), 7.27 (d, H), 7.27 (d, 1H), 7.22 (s, 1H), 7.15 (d, 1H), 7.07 (t, 1H), 7.07 (t, 1H), 6.97 (d, 1H), 6.97 (d, 1H), 3.97 (s, 2H), 2.81 (s, 6H). ATR-IR (ν in cm<sup>-1</sup>): 3347 br (ν OH, ν NH), 1614 m (ν CN), 1574 s (vas OCO), 1394 s (vs OCO), 1316 s (vas OSO), 1143 s (vs OSO). UV-Vis (ethanol, λ in nm) 217, 261, 349, 410 sh. Elemental analysis (found): C 45.1; H 5.0; N 5.5; S 4.4%; calc. for C<sub>54</sub>H<sub>54</sub>Cd<sub>2</sub>N<sub>6</sub>O<sub>14</sub>S<sub>2</sub>·8H<sub>2</sub>O: C 44.9; H 4.9; N 5.8; S, 4.4 (Mw: 1444.1 g·mol<sup>-1</sup>).

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