





Proceeding Paper

Immobilization on Cellulose Paper of a Chemosensor for CdSe-Cys QDs[†]

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Abstract: The Schiff base ligand H₂SB 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 H₂SB 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 H₂SB-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 H₂SB has been demonstrated with ¹H NMR, ATR-FTIR, and UV-Vis spectroscopy.

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



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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, H₂SB [3]. In addition, we present here our progress in the study of the interaction between H₂SB and CdSe-Cys QDs. The usefulness of the H₂SB-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 H₂SB interacts with CdSe-Cys QDs, Cd₂(SB)₂(H₂O)₄ has been synthesized and studied by ¹H NMR, ATR-FTIR, and UV-Vis spectroscopy.

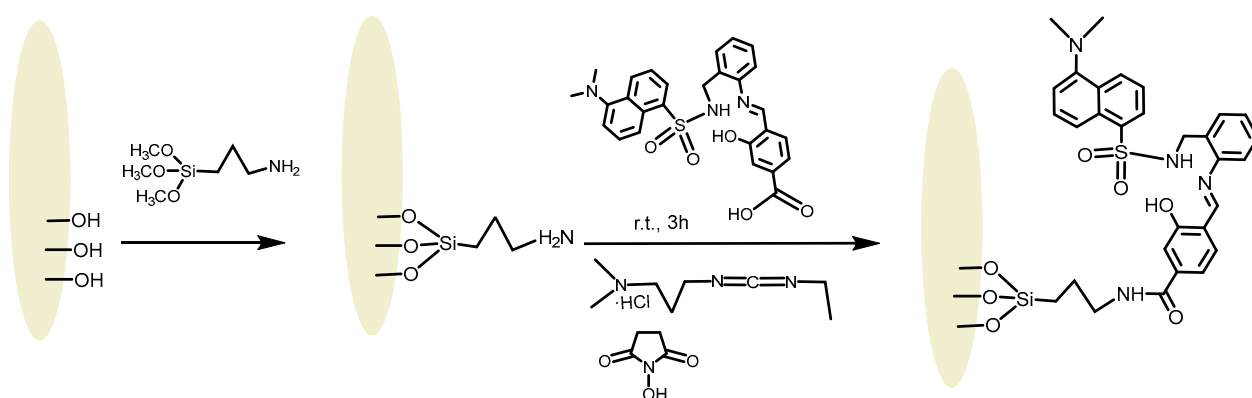


Figure 1. Schematic representation of the chemosensor-modified cellulose paper.

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 H₂SB, 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).

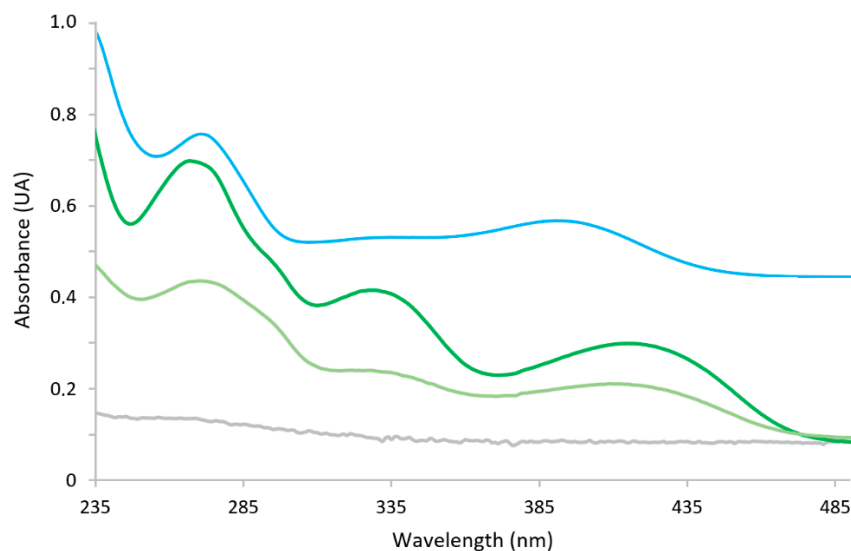


Figure 2. View of the diffuse reflectance spectrum of H₂SB-modified cellulose paper previously (green) and after (pale green) the interaction with CdSe-Cys QDs. The diffuse reflectance spectrum of cellulose paper (grey) and the UV-Vis spectrum of H₂SB in water solution (blue) have been included for comparison.

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 H₂SB 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.

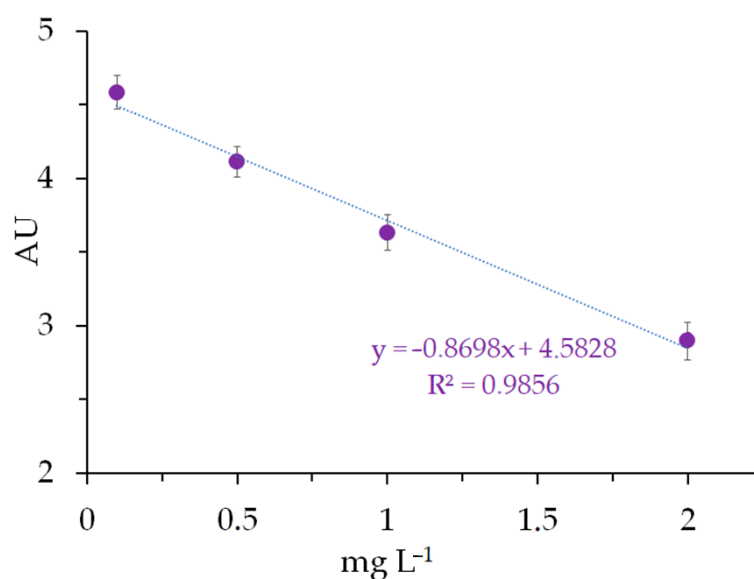


Figure 3. Decrease in the absorbance at 270 nm with increasing CdSe-Cys QDs concentration from 100 ppb to 2 ppm.

To study the type of interaction between the CdSe-Cys QDs and H₂SB, we obtained Cd₂(SB)₂(H₂O)₄·8H₂O from the reaction of Cd(OAc)₂·2H₂O and H₂SB in an ethanol solution at room temperature. The similarities between the UV-Vis spectra of Cd₂(SB)₂(H₂O)₄·8H₂O and CdSe-Cys-H₂SB 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 H₂SB.

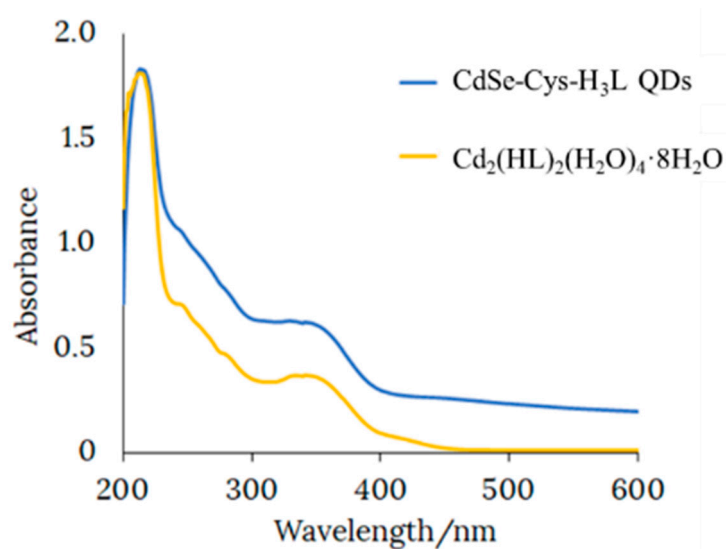


Figure 4. View of the UV-Vis spectra of CdSe-Cys-H₂SB QDs and Cd₂(SB)₂(H₂O)₄·8H₂O in ethanol solution.

The binding constant value of H₂SB with Cd²⁺, 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.

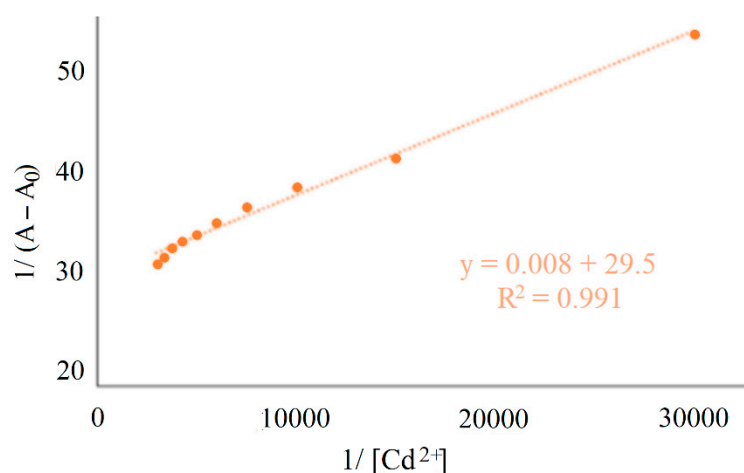


Figure 5. Benesi–Hildebrand plot from UV-Vis (left) and fluorescence (right) titration data of H₂SB (10^{-4} M, 1 mL) with Cd²⁺ (10^{-3} M, 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mL) in an 80:20 ethanol:water solution.

The ¹H NMR spectrum of the cadmium(II) complex revealed the chelating behaviour of the ligand through the O_{phenol}, N_{imine}, and N_{sulfonamide} atoms. Figure 6 shows the absence of the signal corresponding to OH_{phenol} (12.29 ppm) and NH_{sulfonamide} (8.37 ppm) as well as the upfield shift (about 0.3 ppm) of the -CH=N signal which was observed at 8.63 ppm in H₃L. This is consistent with the formation of a cadmium complex with a sulfonamide bridge, similar to those reported for complexes of similar Schiff base ligands [6,7]. The ¹H NMR spectrum of CdSe-Cys-H₃L QDs (Figure 7) showed the absence of the signals corresponding to OH_{phenol} and NH_{sulfonamide}, which indicates that the interaction between the QDs and the ligand occurs through its bideprotonated form. The obvious similarities between the ¹H NMR spectra of CdSe-Cys-H₂SB QDs and Cd₂(SB)₂(H₂O)₄·8H₂O (Figure 8) support that the interaction between CdSe-Cys QDs surface and H₂SB occurred via metal–ligand coordination. It must be noted that the differences in chemical shifts of CdSe-Cys-H₂SB QDs and Cd₂(SB)₂(H₂O)₄·8H₂O are due to the solvents used in each case, methanol-d₄/D₂O and dmso-d₆, respectively. The reason for this is the very different solubility of CdSe-Cys-H₂SB QDs and Cd₂(SB)₂(H₂O)₄·8H₂O.

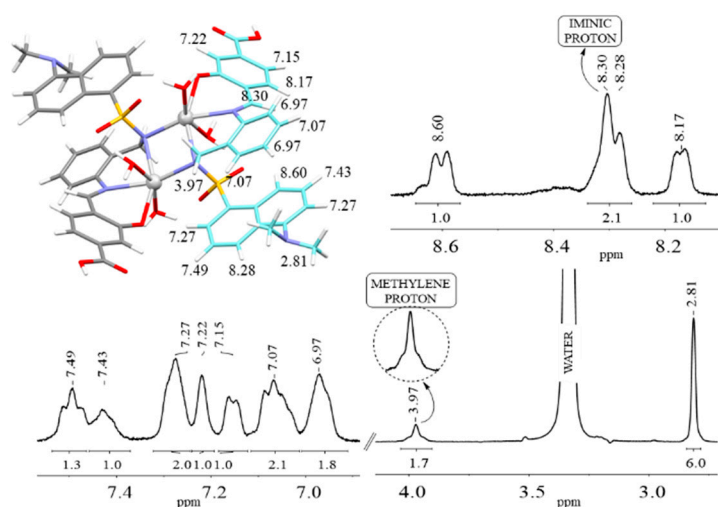


Figure 6. View of the ¹H NMR spectrum of the dinuclear cadmium(II) complex (in dmsO-d₆), with signal assignment on a 3D model of the molecule.

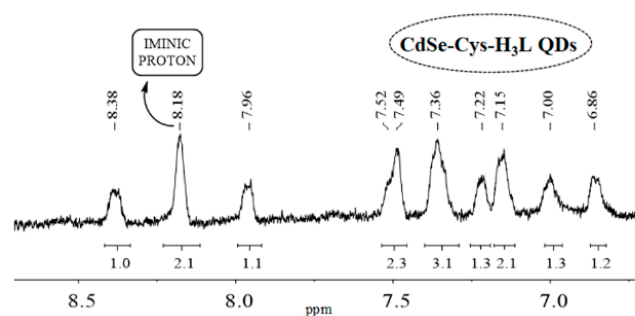


Figure 7. Aromatic region of the ^1H NMR spectrum of CdSe-Cys-H₂SB QDs (in methanol- $\text{d}_4/\text{D}_2\text{O}$).

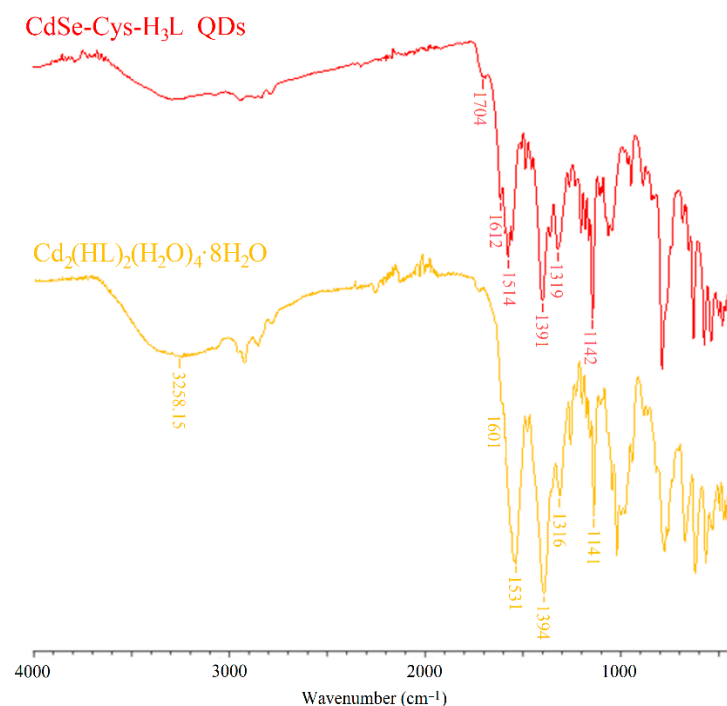


Figure 8. ATR-IR spectra of CdSe-Cys-H₂SB QDs (top) and Cd₂(SB)₂(H₂O)₄·8H₂O (bottom).

The IR spectrum of Cd₂(SB)₂(H₂O)₄·8H₂O showed a broad band centred at about 3360 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 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-H₂SB 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 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 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-H₂SB QDs with Cd₂(SB)₂(H₂O)₄·8H₂O (Figure 8) supports that the interaction between H₂SB and CdSe-Cys QD surfaces occurred via metal–ligand coordination through the N_{sulfonamide}, N_{imine}, and O_{phenol} atoms.

3. Conclusions

In conclusion, we can say that we have immobilized H₂SB 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 H₂SB-modified paper demonstrated its immobilization. Diffuse reflectance spectrophotometry allows the detection of CdSe-Cys QDs using H₂SB-modified cellulose paper (LOD = 245 ppb and LOQ = 815 ppb). UV-Vis, ¹H NMR, and ATR-FTIR spectroscopy evidenced that the interaction between H₂SB and CdSe-Cys QDs takes place through the O_{phenol}, N_{imine}, and N_{sulphonamide} atoms of the dianionic ligand (as phenolate and sulphonamide anion).

4. Experimental Section

4.1. Materials and Methods

The synthesis and characterisation of H₂SB and CdSe-Cys QDs have been previously reported [3,4]. The sample used for investigating the interaction of CdSe-Cys QDs with H₂SB was obtained by stirring, at room temperature, an ethanol solution of H₃L (pH = 9) with a suspension of CdSe-Cys QDs in 2:1 molar ratio, for about 15 min. The sample was subsequently air-dried.

¹H NMR spectra (400 MHz) were measured in dmso-d₆ 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^{−1} 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 Cd₂(SB)₂(H₂O)₄·8H₂O

An ethanol solution of Cd(OAc)₂·2H₂O (40 mL, 0.0212 g, 0.0794 mmol) was added to of an ethanol solution (60 mL) of H₂SB (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 %). ¹H NMR (400 MHz, dmso-d₆, 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^{−1}): 3347 br (ν OH, ν NH), 1614 m (ν CN), 1574 s (vas OCO), 1394 s (vs OCO), 1316 s (ν_{as} OSO), 1143 s (ν_s 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 C₅₄H₅₄Cd₂N₆O₁₄S₂·8H₂O: C 44.9; H 4.9; N 5.8; S, 4.4 (Mw: 1444.1 g·mol^{−1}).

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