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

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Abstract: The Schiff base ligand H_2SB derived from the condensation of 4-formyl-3-hydroxybenzoic acid with *N*-(2-aminobenzyl)-5-(dimethylamino)naphthalene-1-sulfonamide has been investigated as a chemosensor for the detection of CdSe-Cys QDs in water samples. We immobilized H_2SB 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_2SB-modified paper demonstrated its immobilization. A linear decrease in the absorbance of the band at 270 mm is observed, when the CdSe-Cys QDs concentration increased from 100 ppb to 2 ppm. The LOD and LOQ calculation results were 245 and 815 ppb, respectively. An interaction via metal-ligand coordination between CdSe-Cys QDs and H_2SB has been demonstrated with ^1H NMR, ATR-FTIR and UV-Vis spectrometries.

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), laser, thin-film transistors, or solar cells [1,2]. A clear negative consequence of this extensive use is the discharge 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 color analysis provides fast response, 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_2SB [3]. In addition, we present here our progress in the study of the interaction between H_2SB and CdSe-Cys QDs. The usefulness of the H_2SB-modified paper (Figure 1) for the detection of CdSe-Cys QDs was demonstrated registering the decrease in the absorbance of the band at 270 mm, with the increase in CdSe-Cys QDs concentration from 100 ppb to 2 ppm [4]. In order to help elucidate how H_2SB interacts with CdSe-Cys QDs, $Cd_2(SB)_2(H_2O)_4$, has been synthesized and studied by ^1H NMR, ATR-FTIR and UV-Vis spectrometries.

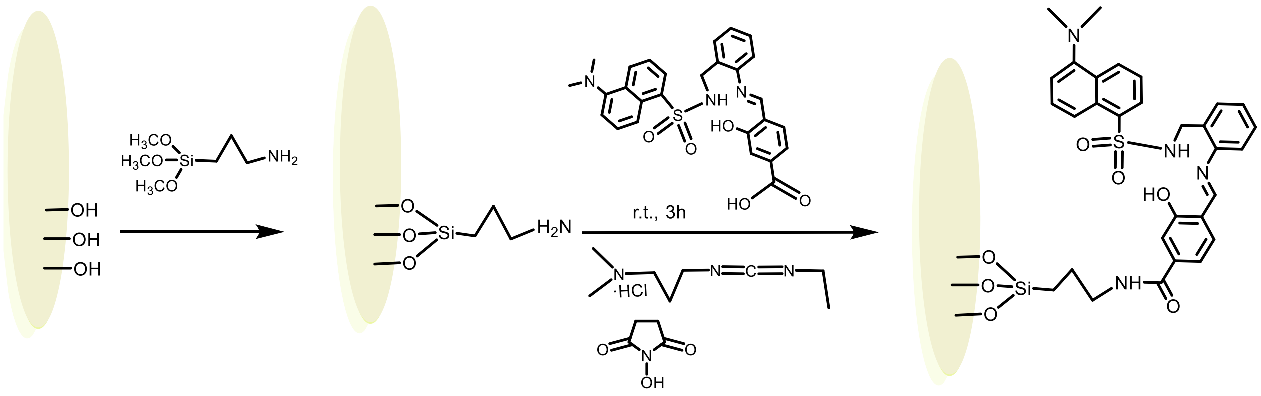

Figure 1. Schematic representation of the chemosensor-modified cellulose paper.

2. Results and Discussion

The cellulose paper was first primed with 3-aminopropyl)trimethoxysilane (APTMS) by soaking it in a DMF solution for 2 h (Scheme 1). In a second reaction step, *N*-hydroxysuccinimide (NHS) and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl) were added together with the chemosensor H_2SB 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 band appears around 30 nm red-shifted, with respect to the spectrum of an ethanol solution of the chemosensor (390 nm).

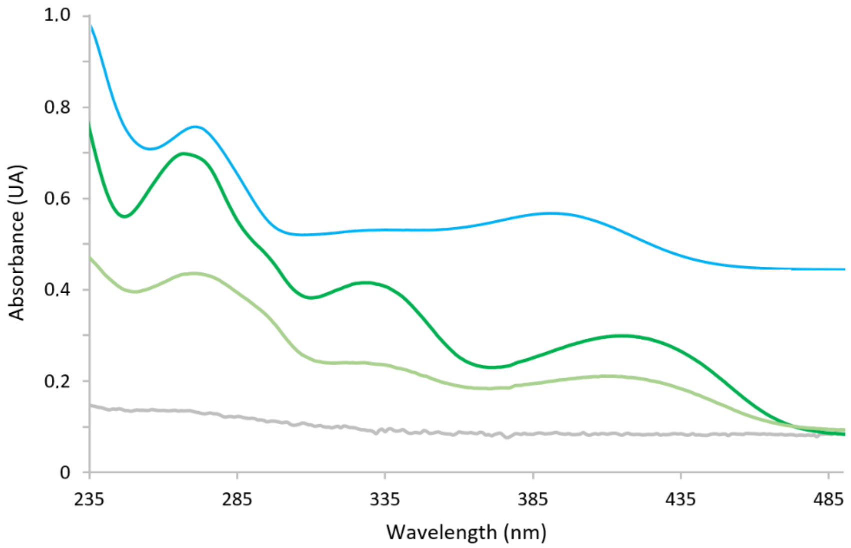

Figure 2. View of the diffuse reflectance spectrum of H_2SB-modified cellulose paper previously (green) and after (pale green) the interaction with CdSe-Cys QDs. The diffuse reflectance spectrum of cellulose paper (grey) and the UV-Vis spectrum of H_2SB in water solution (blue) have been included for comparison.

The chemosensor-modified cellulose paper upon soaking in CdSe-Cys QDs water solutions for 2 h exhibits a decrease in the absorbance of each band of the diffuse reflectance spectrum. As the decrease is more pronounced in the band observed at 270 nm, we have chosen this wavelength to carry out the measurements (Figure 3). The limit of detection (LOD) and limit of quantification (LOQ) of H_2SB have been expressed as LOD = 3SD/M and LOQ = 10SD/M, where SD is the standard deviation of the response and M is the slope of the calibration curveThe LOD and LOQ calculation result is 245 and 815 ppb, respectively.

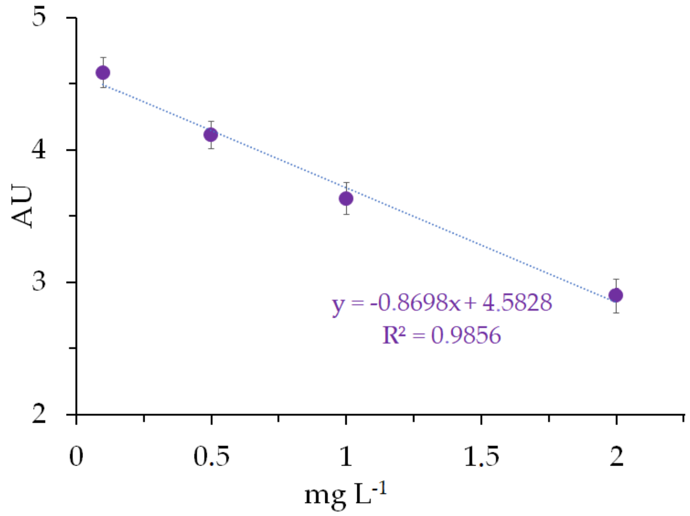

Figure 3. Decrease in the absorbance of the band at 270 mm, with the increase in CdSe-Cys QDs concentration from 100 ppb to 2 ppm.

To study the type of interaction between CdSe-Cys QDs and H_2SB, we obtained $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ from the reaction of $Cd(OAc)_2{\cdot}2H_2O$ and H_2SB in ethanol solution at room temperature. The similarities between the UV-Vis spectra of $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ and CdSe-Cys-H_2SB 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_2SB.

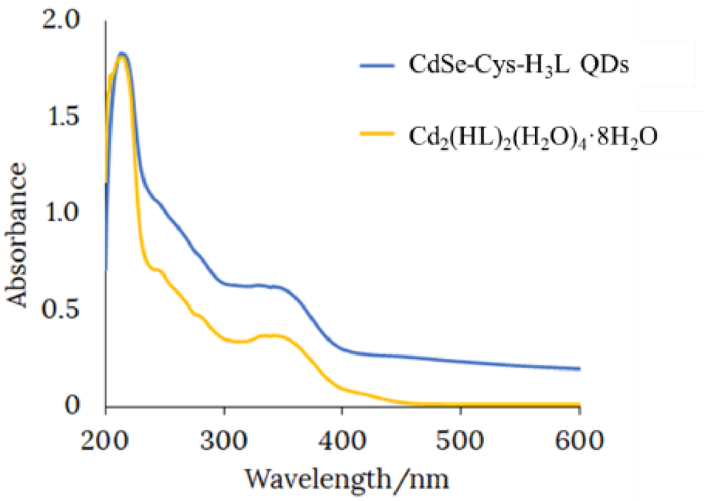

Figure 4. View of the UV-Vis spectra of CdSe-Cys-H_2SB QDs and $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ in ethanol solution.

The binding constant value of H_2SB with Cd^{2+}, at room temperature, has been determined from UV-Vis absorption data following the Benesi–Hildebrand equation [5] (K_b = 3.686 × 10^3 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.

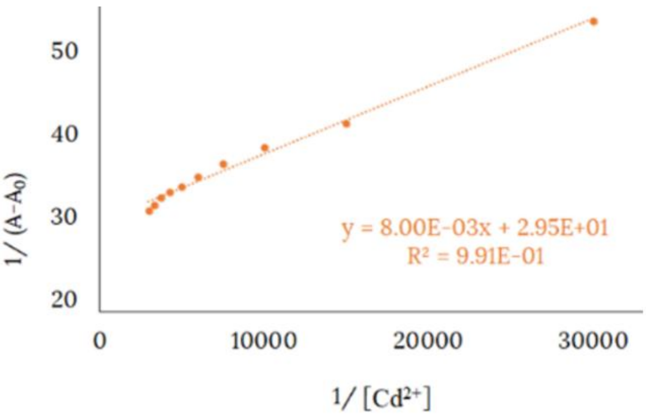

Figure 5. Benesi–Hildebrand plot from UV-Vis (left) and fluorescence (right) titration data of H_2SB (10^{-4} M, 1 mL) with Cd^{2+} (10^{-3} M, 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 mL) in an 80:20 ethanol:water solution.

The ^{1}H 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 observed at 8.63 ppm in H_3L. This is consistent with the formation of a sulfonamido-bridged cadmium complex, as those reported by us for complexes of similar Schiff base ligands [6,7]. The ^{1}H NMR spectrum of CdSe-Cys-H_3L QDs (Figure 7) shows the absence of the signals corresponding to OH_{phenol} and $NH_{sulphonamide}$, which indicates that the interaction between the QDs and the ligand occurs through its bideprotonated form. The obvious similarities between the ^{1}H NMR spectra of CdSe-Cys-H_2SB QDs and $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ (Figure 8) support that the interaction between CdSe-Cys QDs surface and H_2SB occurred via metal-ligand coordination. It must be noted that the differences in chemical shifts of CdSe-Cys-H_2SB QDs and $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ are due to the solvents used in each case, methanol-d_4/D_2O and dmso-d_6, respectively. The reason for this is the very different solubility of CdSe-Cys-H_2SB QDs and $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$.

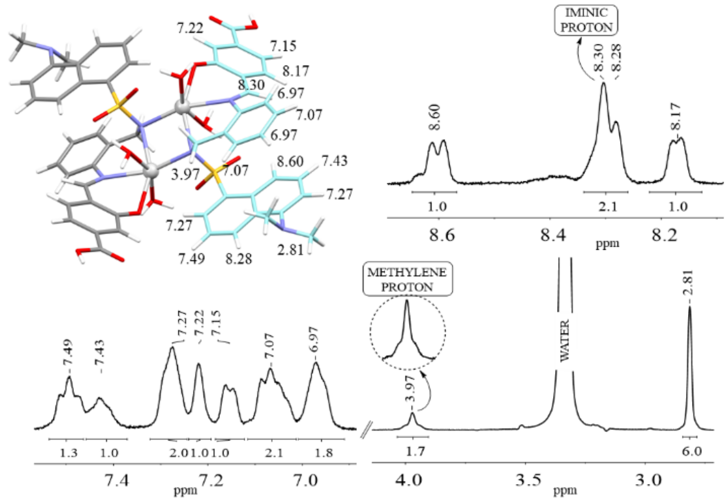

Figure 6. View of the ^{1}H NMR spectrum of the dinuclear cadmium(II) complex (in dmso-d_6), with signal assignment on a 3D model of the molecule.

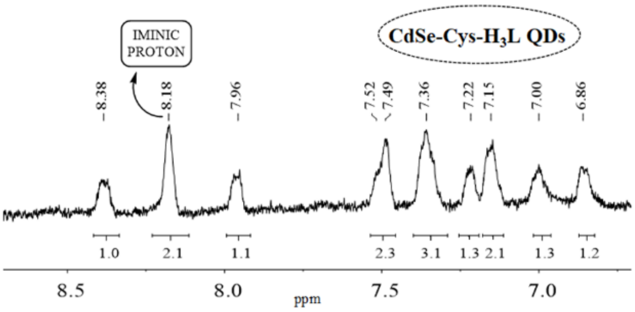

Figure 7. Aromatic region of the ^{1}H NMR spectrum of CdSe-Cys-H_2SB QDs (in methanol-d_4/D_2O).

The IR spectrum of $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ showed a broad band centred at about 3360 cm^{-1} attributable to ν(OH) which evidenced the obtaining of the hydrated complex (Figure 8). The observation of two bands attributable to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at about 1574 and 1393 cm-^{1}, respectively seems to indicate the deprotonation of the carboxylic groups of the Schiff base in its complex. The net charge zero of the complex can be achieved because the ligand units can adopt the zwitterionic form, in which carboxylic groups are deprotonated, while amine N atoms are protonated.

The IR spectrum of CdSe-Cys-H_2SB QDs shows the absence of the band at about 3283 cm^{-1} attributable to ν OH/ν NH modes, which evidences the bideprotonation of the Schif base ligand. The observation of two bands attributable to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at about 1574 and 1391 cm^{-1}, respectively is a clear sign of deprotonation of the carboxyl group in the ligand, which is coherent with the formation of the carboxylate sodium salt. Besides, it is clear the presence of a strong sharp band at about 1615 cm^{-1}, which is attributable to the imino group of the ligand. The similarity between the spectra of the ATR-IR spectra of CdSe-Cys-H_2SB QDs with $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ (Figure 8) supports that the interaction between H_2SB and CdSe-Cys QDs surface occurred via metal-ligand coordination through the $N_{sulfonamide}$,N_{imine} and O_{phenol} atoms.

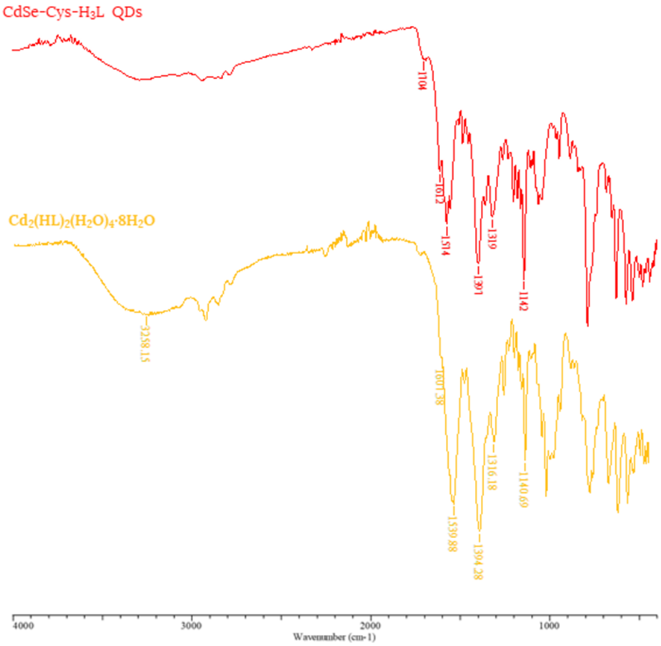

Figure 8. ATR-IR spectra of CdSe-Cys-H_2SB QDs (top) and $Cd_2(SB)_2(H_2O)_4{\cdot}8H_2O$ (bottom).

3. Conclusions

As conclusion, we can say that we have immobilized H_2SB 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_2SB-modified paper demonstrated its immobilization. Diffuse reflectance spectrophotometry allows to detect CdSe-Cys QDs using H_2SB-modified cellulose paper (LOD = 245 ppb and LOQ = 815 ppb). UV-Vis, ^1H NMR and ATR-FTIR spectrometries evidenced that the interaction between H_2SB 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 H_2SB and CdSe-Cys QDs has been previously reported [3,4]. The sample for investigations on the interaction of H_2SB with CdSe-Cys QDs were obtained by stirring an ethanol solution of H_3L at pH 9 and a suspension of NMs in 2:1 molar ratio, at room temperature, for about 15 min. Then, the sample was air-dried.

Diffuse reflectance spectra were measured on a PerkinElmer LAMBDA 1050+ UV/Vis/NIR spectrophotometer equipped with an integrating sphere. ^1H NMR spectra (400 MHz) were measured in deuterated solvents using a Varian Inova 400 Spectrometer. J values are given in Hertz. The infrared spectra were measured in the range 4000 to 400 cm^{-1} wavenumber using a FTIR spectrometer PerkinElmer Spectrum Two coupled with Platinum Diamond ATR, which consists of a diamond disc as an internal reflection element.

$Cd_2(SB)_2(H_2O)_4 \cdot 8H_2O$

An ethanol solution (60 mL) of H_2SB (0.0400 g, 0.0794 mmol) was added to 40 mL of an ethanol solution of $Cd(OAc)_2 \cdot 2H_2O$ (0.0212 g, 0.0794 mmol). The resulting solution was refluxed in a round bottom flask of 250 mL for 4 h. The colour of the solution changed from greenish yellow to deep yellow during the reaction time. Then, the solution was evaporated to dryness under vacuum. Then, the powdery solid was washed with diethyl ether, filtered, and air-dried.

Yield: 42 mg (40.6 %). 1H NMR (400 MHz, dmso-d_6, 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 (νas OCO), 1394 s (νs 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 $C_{54}H_{54}Cd_2N_6O_{14}S_2 \cdot 8H_2O$: C 44.9; H 4.9; N 5.8; S, 4.4 (Mw: 1444.1 g·mol 1).

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Conflicts of Interest: The authors declare no conflict of interest.

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