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Structural and optical properties of $[M(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ $\{M = \text{Ni(II)}, \text{Co(II)}\}$ thin films deposited by chemical bath deposition method

Hadjer Mamine^a, Hacene Bendjeffal^{a,b}, Abdelkrim Djebli^c, Toufek Metidji^a, Mathieu Marchivie^d, Guillaume Chastanet^d, Nacer Rebbani^a, and Yacine Bouhedja^a

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ABSTRACT

The objective of this study was the deposition of thin films of 8-hydroxyquinolin (8-HQ) Cobalt(II) and Nickel(II) complexes onto glass substrates using the chemical bath deposition (CBD) method. The deposition experiments were carried out under the effect of some physicochemical factors such as solution temperature (25 °C–55 °C), medium pH (1–6), metal: ligand molar stoichiometric ratio (1:1–1:3), and immersion time (in the range 10–60 min). The obtained thin films were characterized using many analytical methods (UV-Vis spectrophotometry, infrared spectrophotometry, optical microscopy, scanning electron microscopy, and X-ray diffraction). The study of the optical properties of the obtained thin films showed that the complexes $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ have strong absorbance in UV area corresponding to a $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ electronic transition between the HOMO and the LUMO with a gap's energy in the range 4.1 and 4.4 eV. In the light of the optical measurements, $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ complexes can be considered as semiconductors.

Introduction

The idea of synthesis of nano-molecular materials based on organo-metallic complexes^[1–4] with optical, electrical, magnetic, and/or biological properties stimulates the scientific activity of laboratories across the world because of their novelties. These materials are very important. From technological point of view, they are found in different areas such as catalysis, electronics, optoelectronics, adsorption, and photovoltaic.^[1–6] One of the most promising strategies is based on the concept of hybrid molecular materials, resulting in the preparation of thin films of nickel(II)^[4–8] and cobalt(II)^[9–11] complexes which have the ability to solve several problems in various areas such as solar energy, information storage, catalysis, pollution sensor.^[7–10]

The elaboration of metallic-complexes thin layers has been studied using various deposition techniques, such as atomic layer deposition (ALD),^[12] molecular self-assembly (MSA),^[13] radio frequency co-sputtering (RFC),^[14] Langmuir–Blodgett technique (LB),^[15] spin-coating,^[16] chemical bath deposition (CBD),^[17–19] chemical vapor deposition (CVD),^[20] sol-gel process,^[21] and (successive ionic layer adsorption and reaction (SILAR)).^[9,10,22] However, the CBD technique is a simplified and not expensive method used for the synthesis of $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ with a very good homogeneity.

The objectives of this work were, firstly, the synthesis of complexes based on transition metals in order to elaborate thin films of light-sensitive property, and height quality and controlled thickness, as well as the deposition of these thin layers on micro-glass slides using the CBD method. Secondly, we attempted to optimize influencing parameters such as bath temperature, metal-ligand stoichiometric ratio, solution pH, and immersion time. In order to study the effects of these parameters on the structural, morphological, and optical properties of Ni(II) and Co(II) quinolates thin films, we used various analytical methods such as UV-Vis spectrophotometry, infrared spectrophotometry, optical microscopy, scanning electron microscopy, and X-ray diffraction. The UV-Vis spectrometry revealed large absorbance bands of the thin films in the UV range (190–300 nm), corresponding to the fundamental electronic transitions ($n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$), and an optical band gap energy (E_g) ranging between 4.1 eV and 4.4 eV. Consequently, the study proved that the $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ thin films have semiconductor properties.

Experimental

Chemical and materials

In this work, the used chemicals (nickel (II) sulfate-6-hydrated $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, cobalt (II) sulfate-6-hydrated

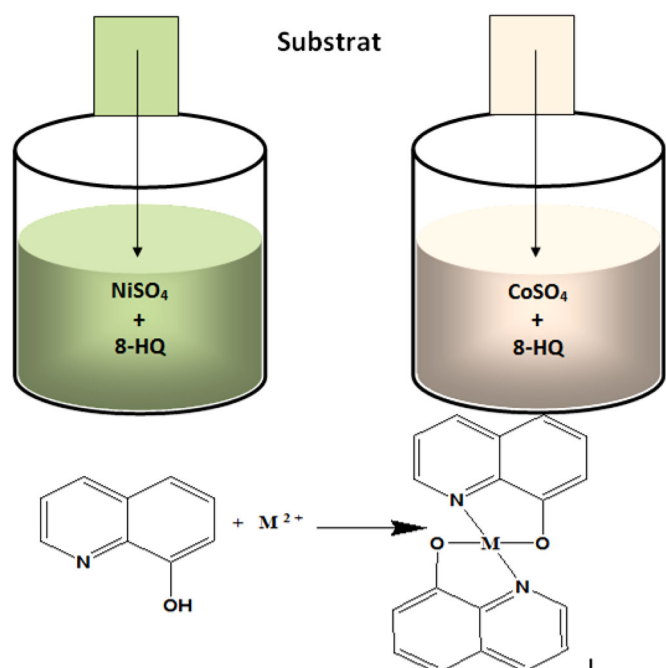
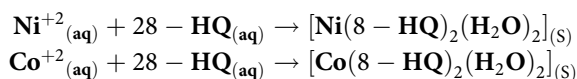


Figure 1. Schematic depiction of $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ using the chemical bath deposition method where $\text{M} = \text{Ni}$ or Co .

$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, 8-hydroxyquinoline, and ethanol) were Merck grade. The metal ion solutions were prepared in doubly distilled water and the 8-HQ solution was prepared in ethanol. The glass slides were cleaned in an ultrasonic bath with a commercial detergent for 10 min and then rinsed with distilled water pursued by a dipping in acetone for another 10 min. The substrates were then washed with dichloromethane. Finally, the whole was dried in vacuum at 105°C during 90 minutes.^[9,11]

Deposition procedure

The deposition of $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ thin films were performed on glass micro slide substrate by CBD method. The NiSO_4 , CoSO_4 , and 8-HQ solutions were prepared in suitable solvents. The substrate was then immersed in the appropriate metal complex. The formation mechanism of $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ thin films onto glass surface can be illustrated by Figure 1 and via the following reactions:



This same deposition protocol was repeated to study the effect of various parameters (metal: ligand molar stoichiometric ratio, pH, temperature, and immersion time) on the thickness growth of the studied complexes thin films. At the end of each deposition, the thicknesses of films were measured with a profilometer (Dektak 3030 Surface Profiler).

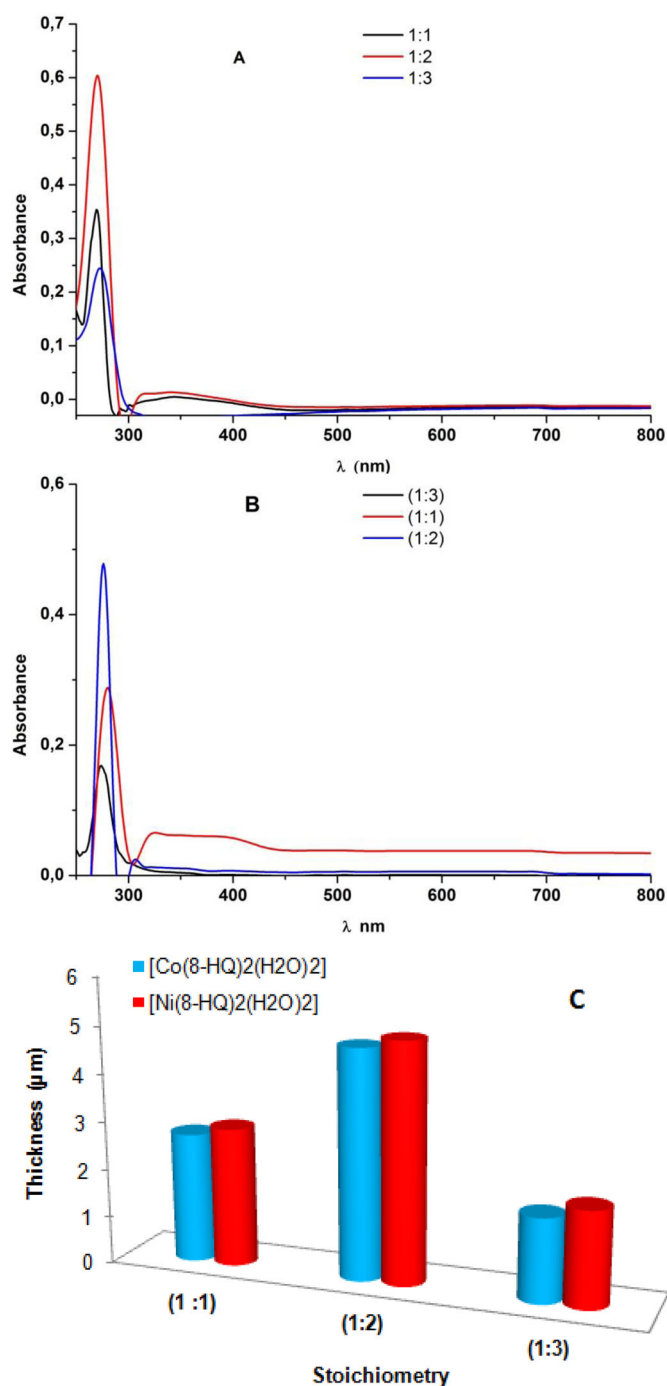


Figure 2. Absorption spectra of A: $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, B: $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, and the variation of thin films thickness of $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ at different molar stoichiometry (pH = 7, immersion time = 15 min, $T = 25^\circ\text{C}$).

Results and discussion

Optimization of deposition factors

Effect of molar concentration

The effect of molar concentration of $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ -8-hydroxyquinolin complexes thin films formation was studied by keeping the cobalt and nickel ion concentration constant at 10^{-2} M while the concentration of 8-HQ was varied to cover three different values of $1 \cdot 10^{-2}$, $2 \cdot 10^{-2}$ and $3 \cdot 10^{-2}$ M. The deposited thin films were obtained at 25°C . The study of the influence of the stoichiometry of complexes

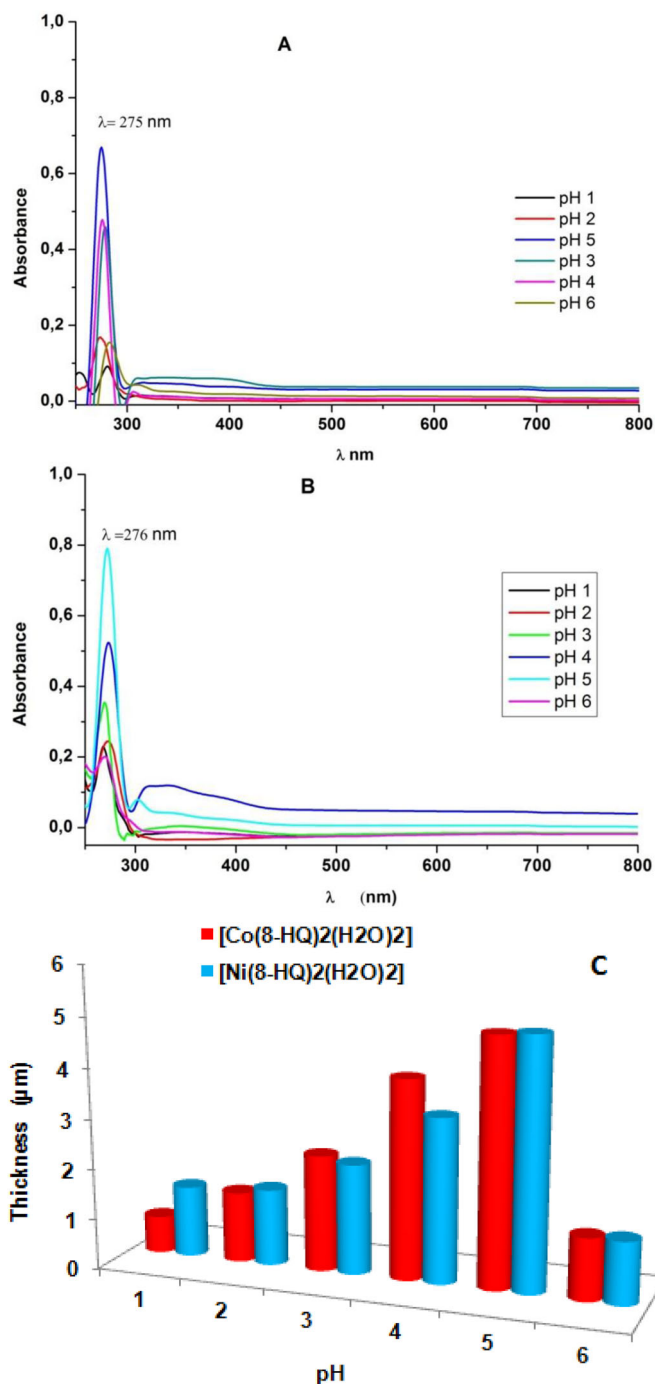


Figure 3. Absorption spectra of A: $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, B: $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, and the variation of thin films thickness of $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ at different pH's (stoichiometric ratio = 1:2, immersion time = 15 min, $T = 25^\circ\text{C}$).

deposition is illustrated by the dependency $A = f(\lambda)$ (Figure 2A and B) and by determining the thickness of the deposited layers $d = f(\text{M}:\text{R})$ (Figure 2C). The absorption spectra show that the maximum absorbance of the prepared complexes is observed for a convenient stoichiometry (1:2) which is in accord with the evolution of their thickness. However, at this conditions a small part of Ni(II) and Co(II) can change their oxidation degree and formed small quantity of another form of these complexes this phenomenon explains the observed halo on the UV-Vis absorbance spectrum in the region of 300–400 nm (Figure 2A and B).

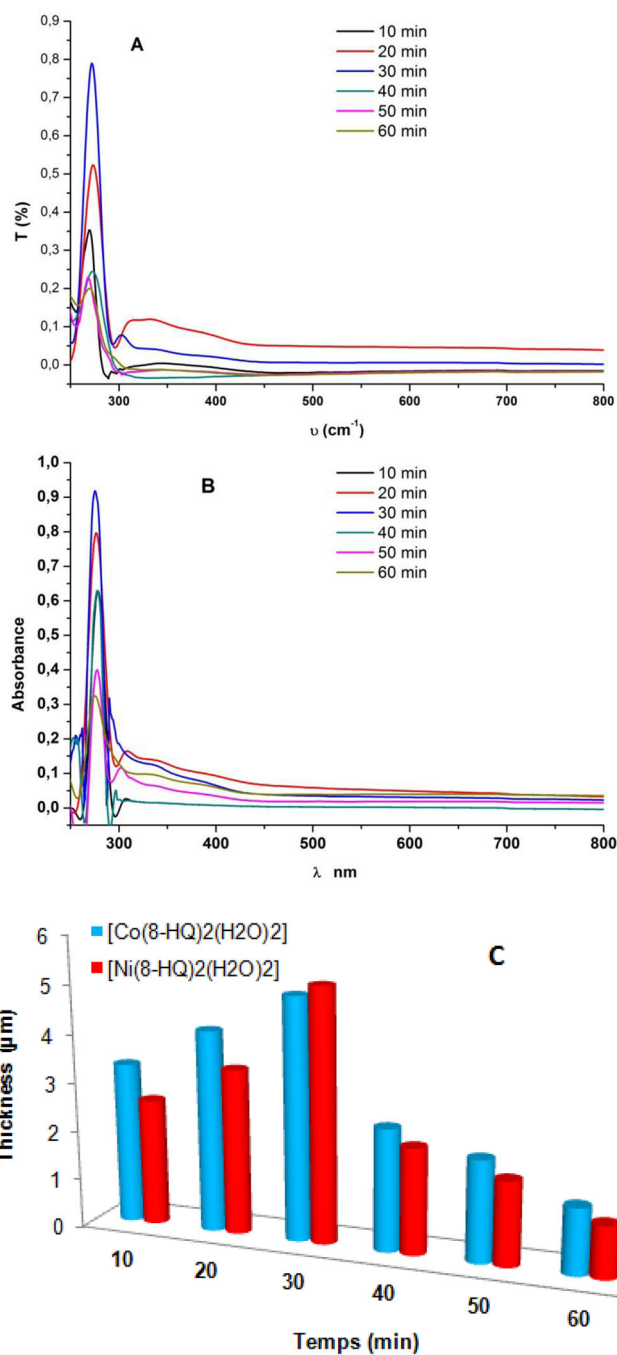


Figure 4. Absorption spectra of A: $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, B: $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ complexes thin film and the variation of thin films thickness of $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ at different dipping time (stoichiometric ratio = 1:2, immersion time = 15 min, $T = 25^\circ\text{C}$).

Effect of pH

The effect of pH on the formation of Co(II) and Ni(II)-8-hydroxyquinolin thin films was studied for pH's varying from 1 to 6 using the same procedure. The various precursors were prepared in the corresponding buffer solutions such as the acetic buffer solutions ($\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$) for a pH ranged between (3-6) and HCl/KCl for a pH of 1 and 2. This study was carried out at 25°C , The molar stoichiometric ratio of metal to ligand (1:2) and the immersion time (15 min) were kept constant. This study is illustrated by the dependencies $A = f(\lambda)$ (Figure 3A and B) and $d = f(\text{pH})$ (Figure 3C). For both studied complexes ($[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$), the thickness of the thin films generally increases with pH up to pH 5 and then decreases at pH 6.

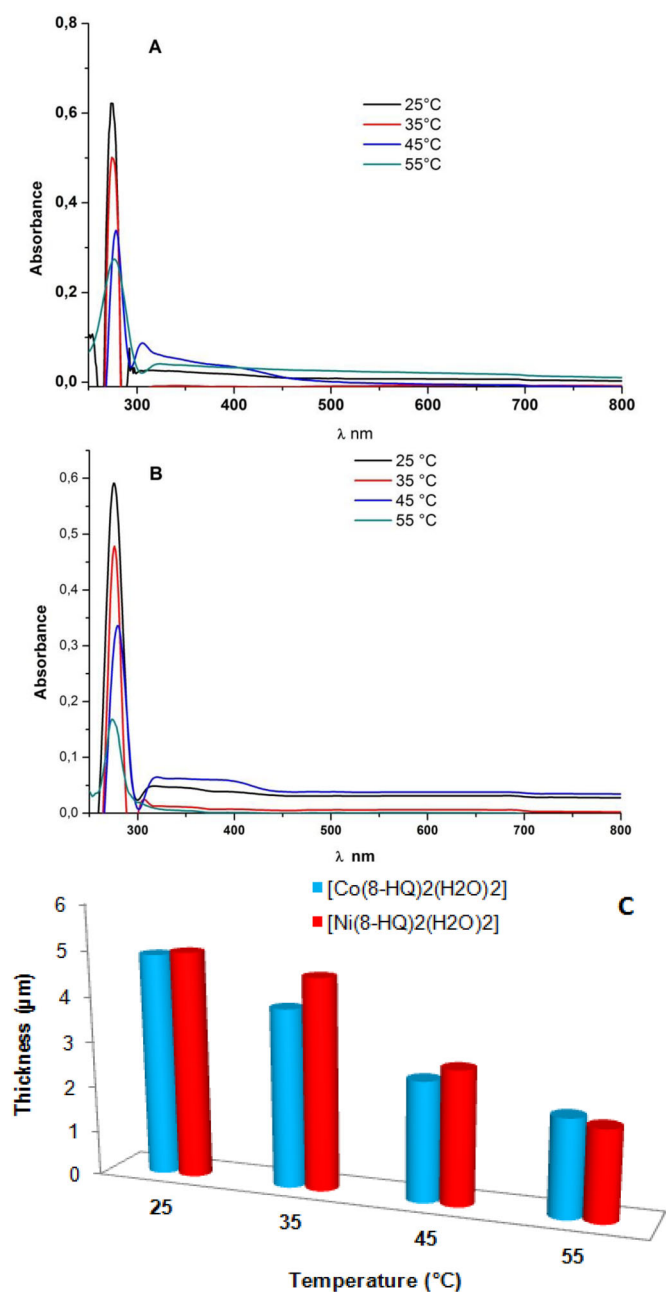


Figure 5. Absorption spectra of A: [Ni(8-HQ)₂(H₂O)₂], B: [Co(8-HQ)₂(H₂O)₂] thin film and the variation of thin films thickness of [M(8-HQ)₂(H₂O)₂] at different temperature (stoichiometric ratio = 1:2, immersion time = 30 min, pH 5).

HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] the optimum pH value was found to be 5 with a good thickness ranged between 0.9 μm and 5 μm as can be seen from Figure 3.

Effect of dipping time

The effect of immersion time in [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] solutions on thin films formation was also studied. The time of immersion was varied from 10 to 60 min. The selected molar stoichiometric ratio of metal to ligand was (1:2) prepared in a solution of pH = 5 at 25 °C. Results of this study are illustrated by the dependencies $A = f(\lambda)$ (Figure 4A and B) and $d = f(\text{time})$ (Figure 4C). For both studied complexes the best results were obtained after 30 min of immersion. Beyond this time there is a

decrease in the absorbance due to partial dissolution of the deposited complex.

Effect of temperature

The same procedure was used to study the influence of temperature on the deposition of [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂]. This study was conducted at different temperatures (25-55 °C). The stoichiometric metal to ligand ratio (1:2) and the time of immersion (30 min) were kept constant. The absorption spectra are given in Figure 5 (A and B) show that the maximum absorbances of the prepared complexes are observed at 25 °C. This result is in a good agreement with the thickness growth reported in Figure 5(C).

Thin film characterization

Infrared analysis

The as-deposited [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] thin films were characterized using a Shimadzu FTIR-8700 spectrometer in the range 400-4000 cm⁻¹. Several characteristic infrared peaks that are related to the bonding in the [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] complexes, as shown in Figure 6 are characterized at 1570 and 1500 cm⁻¹ consequent into stretching vibration for $\nu_{(C=C)}$ of aromatic ring. The appearance of a characteristic absorption peaks at 3051, 1650, 1230 cm⁻¹ due to the presence of $\nu_{(C-H)}$, $\nu_{(C-O)}$, and ν_{CN} , respectively. The presence of metal nitrogen bonding in the complexes is evident from the appearance of $\nu_{(M-O)}$ bands at 645-850 cm⁻¹ in the spectra of the complexes and $\nu_{(M-N)}$ appearance at 500 to 525 cm⁻¹. However, the thin films FTIR spectrum shows another peak at 3490.46 cm⁻¹ probably due to the existence of some adsorbed water molecules.^[5,23,24]

Surface morphological studies

The surface morphology of the deposited thin film of [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] was studied by Scanning electron microscopy (SEM) and optical microscopy (OM). From Figure 7A-D, it can be seen that the surface of the studied thin films on a glass substrate has a homogenous distribution of the deposited complex particles with the presence of crystallites. The calculated dimensions of particles ranged from 0.9 to 10 μm. Thus, CBD chemical deposition technique was found to be a highly rapid and efficient procedure for direct metal complex thin film formation.

Structural study

The X-ray diffractograms of [Ni(8-HQ)₂(H₂O)₂] and [Co(8-HQ)₂(H₂O)₂] were recorded on a Panalytical X-pert pro diffractometer using the Cu K α line. The diffractometer was equipped with a Ni filter and a back monochromator (graphite 200) which filters the K β line but passes the K α_1 and K α_2 lines of the copper. The corresponding wavelengths are 1.5406 Å and 1.5444 Å. The obtained results (Figure 8) show that the positions and intensities of the diffraction peaks are very similar, thus, the compounds studied are most probably made up of a single polymorph and are iso-

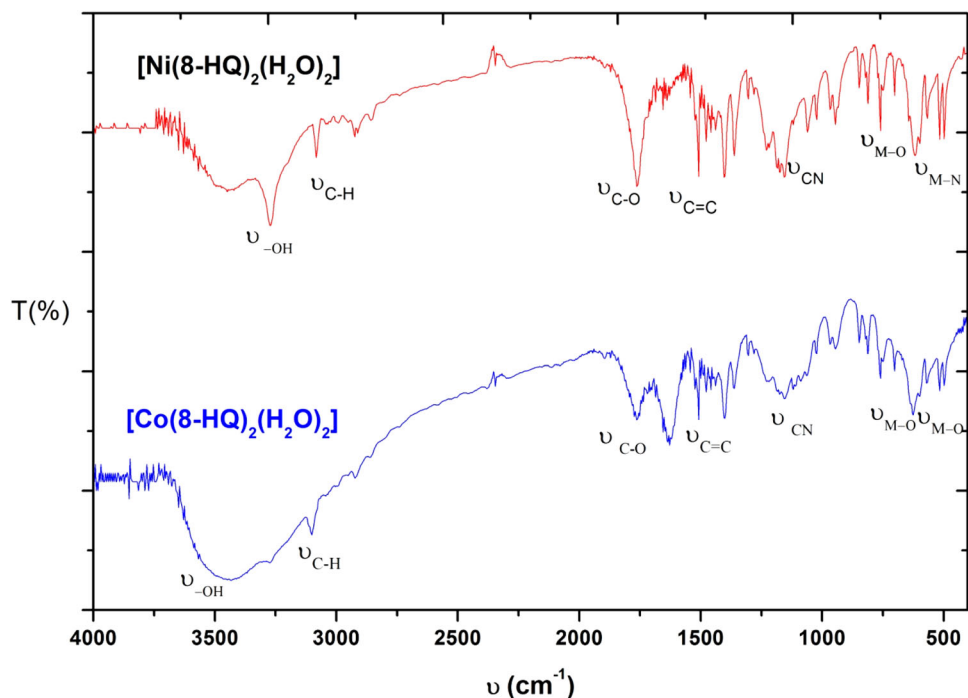


Figure 6. Infrared spectra of $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ thin film obtained at optimal conditions (stoichiometric ratio = 1:2, pH 5, immersion time = 30 min at 25 °C).

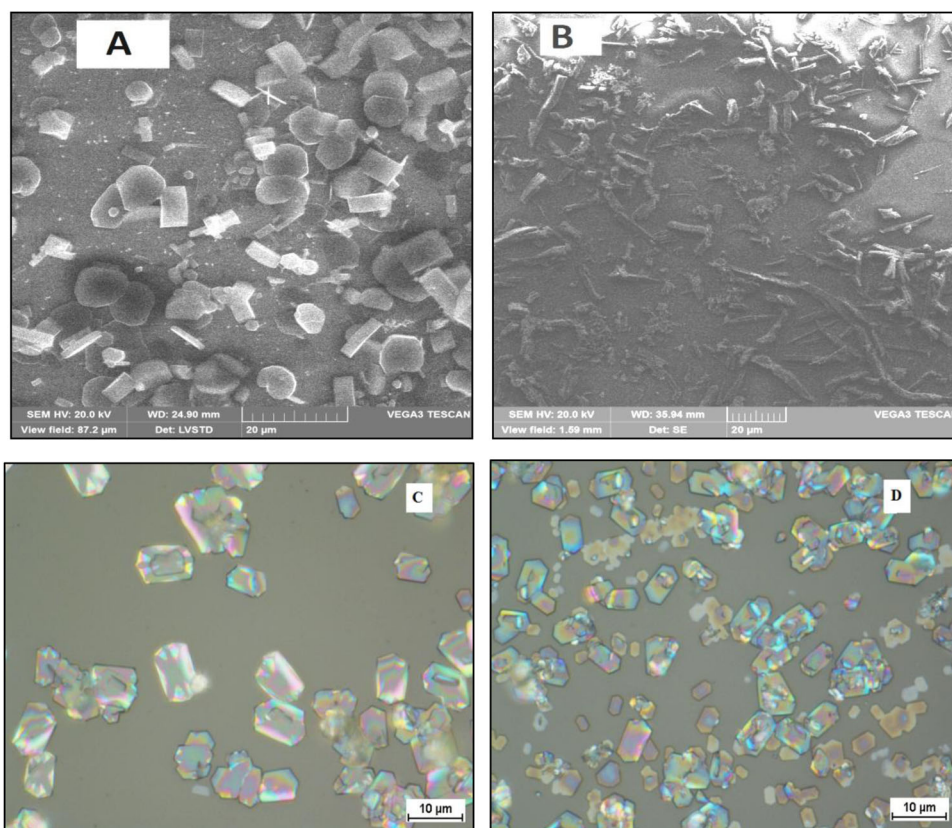


Figure 7. Scanning electron microscope (SEM) of A: $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, B: $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and optical microscope (OM) image of C: $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$, D: $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ complexes thin film obtained at optimal conditions (stoichiometric ratio = 1:2, pH 5, immersion time = 30 min at 25 °C).

structural. The complex $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ was used for a crystal lattice search by a dichotomy method using the DICVOL06 program.^[25,26] The primitive mesh found by this method is monoclinic with, after refinement, the following parameters:

$$a = 13,155\text{\AA} \quad b = 5,418\text{\AA} \quad c = 11,044\text{\AA} \quad \beta = 105,9^\circ$$

No multiple meshes of higher symmetry correspond to these parameters. This mesh is compatible with the expected molecule by considering two molecules per cell, which

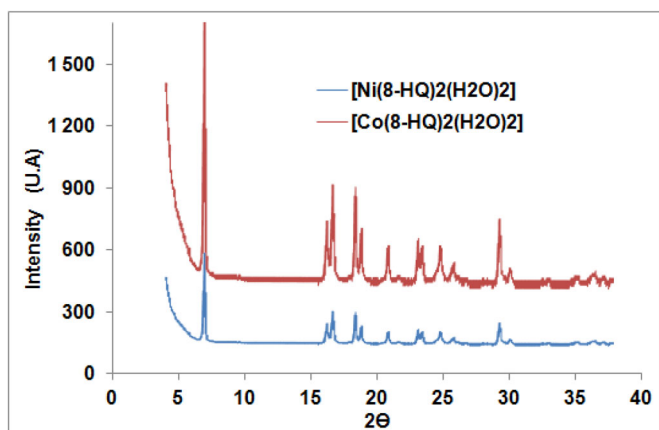


Figure 8. X-ray diffraction patterns of $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ deposited using CBD method at obtained at optimal conditions (stoichiometric ratio = 1:2, pH 5, immersion time = 30 min at 25 °C).

implies either (i) a non-centrosymmetric space group, or (ii) a centered group with an element of symmetry on the molecule which is more likely. A search of this mesh in the CSD (Cambridge Structural Database) permitted to find two iso-structural compounds. These are complexes of Zn and Cu published by several authors in the literature and with formula $[\text{Zn}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ ^[27] and $[\text{Cu}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ ^[28]

A Rietveld^[28] refinement could then be carried out on the 2 samples on the basis of the structure of the Zinc analog. Refinements led to good agreement on peak intensities and good quality factors ($R=0.062 - 0.076$, $wR = 8.2 - 10.8$, $wRp = 8.1 - 16.5$), thus validating that these compounds are isostructural to the Zn complex (Figure 9). The asymmetric unit of these compounds consists of 1/2 molecule of each complex. The application of the center of symmetry to the metal leads to the complex $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ where $\text{M}=\text{Ni}$ or Co . The two 8-HQ ligands and the two water molecules are in the Trans position around the metal (Figure 10).

Optical properties

UV-Vis spectrophotometry was used to study the optical properties, such as light absorption, electronic transition, and optical band gap of $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ thin films. The absorption spectra of the as-obtained complexes thin layers, prepared in optimal conditions show that all complexes thin films samples have large and intense absorption bands between 250 nm and 300 nm. The strong absorption bands observed in this area are essentially due to the principles electronic transition ($d \rightarrow \pi^*$, $\pi \rightarrow d$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) between the low unoccupied molecular orbital (LUMO) and the high occupied molecular orbital (HOMO) as previously reported by H. Bendjefal et al.^[8,11] and R.C. Evans.^[29]

The optical analysis is generally performed to identify the absorption coefficient (α) and the optical gap's energy (E_g) of film complex. The UV-Vis absorption spectra recorded for wavelengths ranging from 200 to 600 nm are shown in Figures 2–5. All studied Ni (II) and Co (II) complexes have a maximal absorbance ranging at (275 nm). The gap's

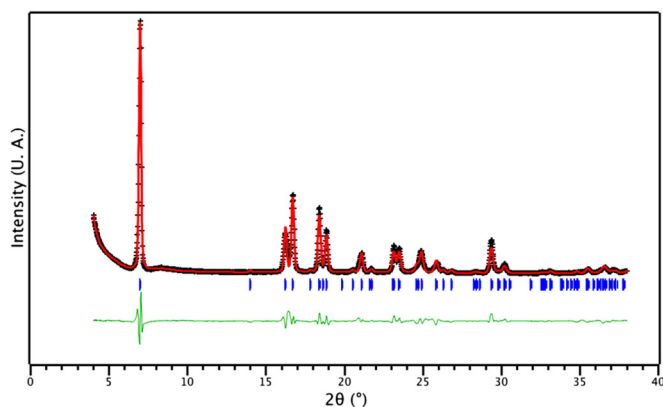


Figure 9. Result of the Rietveld refinement for the compound $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$. Experimental diagram (black crosses), calculated diagram (red continuous line), positions of Bragg peaks (blue vertical lines) and difference between calculated and experimental diagrams (green continuous line). Quality factor obtained: $R = 0.062$, $wR = 0.090$, $R_p = 8.2$ and $wRp = 0.116$.

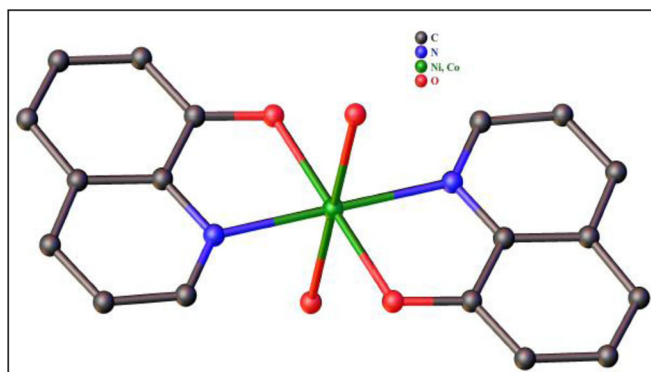


Figure 10. Molecular structure of $[\text{M}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ complexes where $\text{M}=\text{Ni}$ or Co .

energy, in this case, is defined as the difference between the high occupied molecular orbital and the low unoccupied molecular orbital. The absorption coefficient and gap's energy were determined using the UV-Vis absorbance spectra of deposited thin layers at optimal conditions. The relationship between the absorption coefficient (α) and photon energy ($h\nu$) for a direct transition is determined by the following equations:^[8,18]

$$\alpha = (1/d) \ln(100/T_{\%}) \quad (1)$$

$$\alpha(h\nu) = A(h\nu - E_g)^{1/2} \quad (2)$$

Where "T" is the transmittance (%), " α " the absorption coefficient (cm^{-1}), "d" the thickness of the thin film (cm), and E_g the gap's energy value (eV). E_g can be determined by extrapolating the straight-line portion at $\alpha=0$ as observed in Figure 11 (C and D). The band gaps found in this work were 4.4 eV and 4.1 eV for $[\text{Ni}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(\text{8-HQ})_2(\text{H}_2\text{O})_2]$ deposited films, respectively. These study findings indicate that these complexes have characteristics of semi-conductors.

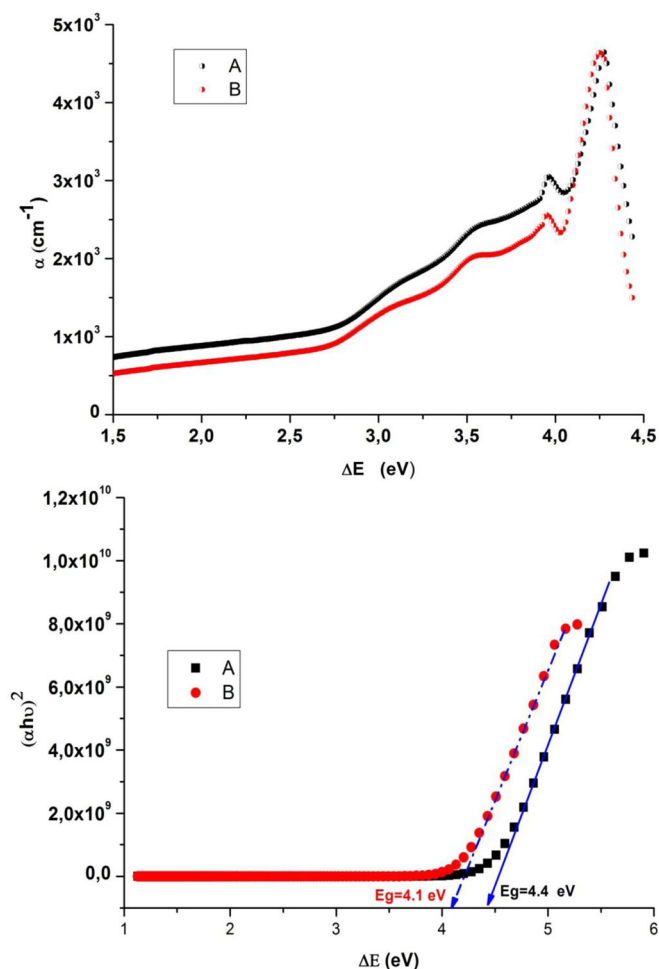


Figure 11. Plot of absorption coefficient (α) and $(\alpha h\nu)^2$ versus photon energy of A: $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$, B: $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ thin films deposited on glass substrate using CBD method.

Conclusion

This study showed that $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ thin films can be deposited by chemical bath deposition method. Several factors considered to be of great importance upon application of the CBD thin film formation of metal complexes have been explored in order to identify the optimum conditions. The best results were obtained at 30 min of dipping time with a molar stoichiometric metal to ligand ratio of 1:2. The optimal pH of the metal and ligand solutions, as well as the optimal temperature, were found equal to 5 and 25°C , respectively. The micrographs of the obtained films clearly show that surfaces of the thin films of the deposited complexes are characterized by a crystalline microstructure. Finally, the optical properties of Co(II) and Ni(II)-8-hydroxyquinolate complexes were studied and confirmed that the highest electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) energy levels. Upon these results, $[\text{Ni}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ and $[\text{Co}(8\text{-HQ})_2(\text{H}_2\text{O})_2]$ complexes can be considered as organic semiconductors.

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