

Novel Coordination Compounds Based on Copper Complexes with new Synthesized Schiff bases and Azo-dyes as Sensitizers for Dye-Sensitized Solar Cells: Spectral and Electrochemical Studies

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Four new compounds using 5-amino-3-methyl-1-phenylpyrazole were neatly prepared. A 2-((3-methyl-1-phenyl-1H-pyrazol-5-yl)diazenyl)benzene-1,3,5-triol (A1) and 2-((3-methyl-1-phenyl-1H-pyrazol-5-yl)diazenyl)benzene-1,3-diol (A2) were taken as examples of azo-dyes. Also, the two Schiff bases, 4-((3-Methyl-1-phenyl-1H-pyrazol-5-ylimino) methyl) benzene-1,3-diol (S1) and 4-Bromo-2-((3-methyl-1-phenyl-1H-pyrazol-5-ylimino) methyl) phenol (S2) were prepared and all these prepared compounds were isolated and purified. The synthesized reagents A1, A2, S1 and S2 were chelated with Cu(II) to form (1:1) (R:Cu(II)) solid complexes and well characterized using FT-IR, UV/visible and molar conductance. The conductivity studies revealed the electrolyte nature of all prepared copper complexes. From both electronic absorption spectra and cyclic voltammetry, the energy gaps for all free ligands and their copper complexes were determined. After a comparison of the representative IR bands of the free compound with the copper complexes formed, compounds were found to binding to the Cu(II) through phenolic OH and azomethine-nitrogen in S1 and S2 while in case in A1 and A2 chelation was taken place through OH and nitrogen of azo group. Furthermore, the date obtained from the electrochemical characterization indicated that these prepared Cu(II) complex can used as an inorganic dye sensitizers in dye-sensitized solar cells (DSSCs).

Keywords: Azo dyes; Schiff bases; Solar cells; Energy gap, Copper complexes.

1. INTRODUCTION

No one can deny the extent of the increasing consumption of energy at the global level due to the huge increase in population and their needs. As a solution to this problem, the solar cell was developed to reach the third generation, which including in its composition and design dyes and/or metal complexes. This type is called dye-sensitized solar cells (DSSCs) [1,2]. This generation of solar cell has many advantages, including low cost, environmental preservation, ease of manufacturing and high efficiency [3,4]. Ruthenium complexes were considered as the most important sensitizers [5-8] due to the easy of charge transfer. Indeed, there are many other metals used in fabrication of DSSCs as Ni, Fe, Ag Mn Co [9-12]. Also, organic dyes either synthetic or natural side-by-side with some the metal ions were used in DSSCs [13–16]. There is an inversely relation between temperature and the most solar cell efficiency specially which attached with heliacal concentrator [17,18]. The main disadvantages of the DSSC compared with the silicon-based solar cells is the more temperature affecting. To overcome this problem, both structure and composition of sensitizer were subjected to change during fabrication tell obtain the optimum conditions giving high performance at high temperatures [19,20]. As yet, three modules of sensitizers were established. These modules included inorganic, organic and natural dyes. The syntheses of palladacyclic complexes was considered as a new class of metal complexes with many attractive advantages in numerous scopes [21-24]. The selection of organic moiety in metal complexes provides the stability of electronic transitions between metal ion and ligand in the sensitizer. This phenomenon was clearly observed from UV/Vis absorption spectra [25,26]. Also, the ligand type which used in complex effluences the ability of DSSC to absorb sunlight and produce a photocurrent [1]. Azo dyes and Schiff bases are the most famous organic compounds used in metal complexes [27,28]. The azo dye compounds are characterized by containing azo group ($-N=N-$) which acts as a strong chromophore used in enormous applications [29]. Moreover, the azo compounds have extraordinary physico-chemical and optical features [30]. With respect to Schiff base compounds, which containing the azo methine chromophore ($R-HC=N-R$), are generally synthesized by coupling between amines with aldehyde/ketone [30]. Many fields have been used Schiff base reagents. Of these, organometallic chemistry in addition to bioinorganic chemistry and similarly in several biological areas. The influence of the ($-HC=N-$) bonding for Schiff bases was investigated [31-34]. In this study, the mono bivalent copper complexes with novel azo-dyes and Schiff bases were synthesized. Also, the obtained Cu(II) complexes were characterized and utilized as an example of sensitizer in DSSCs. The newly prepared azo dyes and Schiff bases in addition to their copper complexes were recognized via spectral and electrochemical tools.

2. EXPERIMENTAL

2.1. Reagents and chemicals:

All chemicals in this paper were used as obtained unless otherwise stated. Copper (II) chloride dihydrate, sodium nitrite, sodium hydroxide, hydrochloric acid, absolute ethanol, paraffin oil, dimethyl

formamide (DMF), benzene-1,3,5-triol, 1,3-dihydroxybenzene and 5-amino-3-methyl-1-phenylpyrazole were obtained from Sigma-Aldrich company. Graphite powder was purchased from Fluka.

2.2. Instrumentations:

Shimadzu-1800 UV/Vis spectrophotometer, matched with 10 mm quartz cell, was used for all absorption measurements. The IR measurements were performed using IRAffinity-1S from Shimadzu company using KBr tablets within a range of 400-4000 cm^{-1} . Voltammetric measurements were carried out using PGSTAT30 Potentiostat /Galvanostat. An Ag/AgCl (KCl sat.) electrode was used as the reference electrode. A conventional three-electrode cell was used. JENWAY conductivity meter (model 4510) was used for conductivity measurements.

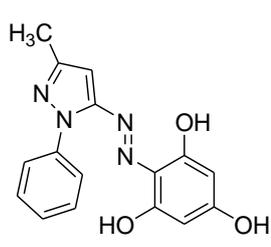
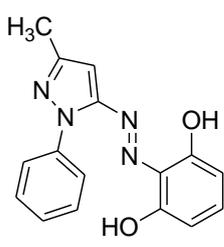
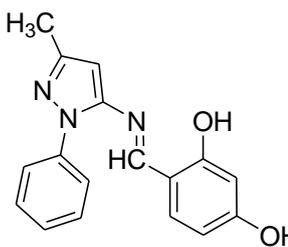
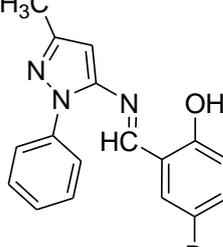
2.3. Synthesis of azo-dye compounds:

2-((3-methyl-1-phenyl-1H-pyrazol-5-yl)diazenyl)benzene-1,3,5-triol (A1) and 2-((3-methyl-1-phenyl-1H-pyrazol-5-yl)diazenyl)benzene-1,3-diol (A2) were prepared according to our work described previously [27]. A solution of 5-amino-3-methyl-1-phenylpyrazole (1.73 g) (10 mmol) was dissolved in 30 mL HCl (1:1) in presence of a small amount of acetic acid as catalyst. Then the dissolved amine was cooled in an ice bath till its temperature reach about $-5.0\text{ }^{\circ}\text{C}$. A 0.69 g of sodium nitrite, dissolved in bi-distilled H_2O , was also cooled and added slowly to the cooled amine solution to form the diazonium salt of the used amine. Benzene-1,3,5-triol (1.26 g) (10 mmol), 1,3-dihydroxybenzene (1.10 g) (10 mmol), were dissolved in 10% NaOH and cooled to about $-5.0\text{ }^{\circ}\text{C}$. Cautiously, a coupling reaction between the diazonium salt and the last solutions was performed separately to obtain the proposed two azo-dyes A1 and A1.

2.4. Synthesis of Schiff base compounds:

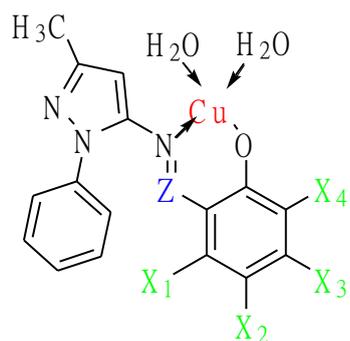
To a hot ethanolic solution of 5-amino-3-methyl-1-phenylpyrazole (1.73 g) (10 mmol), 5-bromo-2-hydroxy-benzaldehyde (Aldrich) (2.01 g) (10 mmol) and 2,4-dihydroxy benzaldehyde (Merck) (1.38 g) (10 mmol), dissolved in absolute ethanol, were poured directly [28]. Then these mixtures were subjected to reflux on a water-bath for 8 h. After that, the obtained solution was concentrated by vaporization. After cooling, the obtained precipitate was separated by filtration. washed with ether. The two Schiff bases were 4-((3-Methyl-1-phenyl-1H-pyrazol-5-ylimino) methyl) benzene-1,3-diol (S1) and 4-bromo-2-((3-methyl-1-phenyl-1H-pyrazol-5-ylimino) methyl) phenol (S2). The purity and chemical structures were noticed by sharp melting point and IR spectra. The propose structure of the prepared azo dyes (A1, A2) and Schiff bases (S1, S2) were presented in Table 1.

Table 1. The proposed structure of the prepared azo-dyes and Schiff base compounds

Azo-dye compounds		Schiff base compounds	
			
A1 (M.Wt = 310.3)	A2 (M.Wt = 294.3)	S1 (M.Wt = 293.3)	S2 (M.Wt = 356)

2.5. Synthesis of Cu(II) complexes:

To a hot solution of 5 mmol A1 (1.55 g), A2 (1.45 g), S1 (1.45 g) and S2 (1.9 g), dissolved in 30 mL absolute ethanol, a solution of 5 mmol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, (0.85 g), dissolved in 10 mL ethanol, was added drop-wise. Then obtained mixture was refluxed on water bath for at least 6 h. During this period of reflux, the color of the solution was changed indicating the formation of (1:1) copper complexes. After that the solution was condensed to a volume of about 10 mL using rotary evaporator. The final solid product was filtered, washed and subject to dry at 80 °C. The proposed structures of the prepared complexes are shown in Fig. 1.



A1-Cu(II) complex: Z= N, X₁ and X₃ = OH, X₂ and X₄ = H

A2-Cu(II) complex: Z= N, X₁ = OH, X₂, X₃ and X₄ = H

S1-Cu(II) complex: Z= CH, X₃ = OH, X₁, X₂ and X₄ = H

S2-Cu(II) complex: Z= CH, X₂ = Br, X₁, X₃ and X₄ = H

Figure 1. The proposed structure of the formed (1:1) complexes between the prepared reagents and Cu(II).

2.6. Preparation of the carbon paste electrode supported with the prepared compounds:

To measure the electrochemical behavior for both the prepared compounds and their copper complexes, a carbon paste electrode (CPE) was prepared using a recommended method [35]. CPE was prepared by mixing 20% paraffin oil, 75% graphite powder and 5% of either prepared compounds or their Cu(II) complexes. All components were subjected to perfect mixing in an agate mortar till very homogeneity. Then the obtained paste was pressed in polyethylene holder of a diameter 3.0 mm. Using a weighting paper, the surface of the CPE was smoothened. The electrochemical behavior, cyclic

Voltammetry (CV), of both prepared compounds and their Cu(II) complexes were scanned in a range +0.8 V to -0.9 V using scan rate of 100 mVs⁻¹.

3. RESULTS AND DISCUSSION

3.1. Characterization of ligand and its transition metal complexes:

3.1.1. Molar conductance measurements

To determine the nature of the prepared complexes, the molar conductivity measurements for the prepared Cu(II) complexes dissolved in the DMF solution were performed. The obtained values were found in the range of 14.55–16.74 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ showed that the prepared copper complexes are electrolytes as projected [36].

3.1.2. FT-IR studies on the prepared compounds and their copper complexes

The FT-IR spectra of A1, A2, S1, S2 and their Cu(II) complexes are shown in Figs 2 and 3. The most important IR bands for the prepared compounds, azo dyes and Schiff bases in addition to their copper complexes, are cited in Table 2 which extracted from Figs 2 and 3. The broad bands at 3396 and 3400 cm^{-1} for A1 and A2 respectively, which corresponding to the stretching vibration of hydroxide group (ν_{OH}), were changed to 3400 and 3387 cm^{-1} in case of A1-Cu(II) and A2-Cu(II), respectively. This shift in the position of ν_{OH} indicating the participating of -OH group in chelation with Cu(II) [27]. A same behavior was observed in case of Schiff base compounds S1 and S2, where ν_{OH} were cited at 3338 and 3363 cm^{-1} . Whereas in case of S1-Cu(II) and S2-Cu(II) complexes, the corresponding position changed to 3421 and 3444 cm^{-1} , respectively. Another evidence for the participating of -N=N- group in the chelation for azo-copper complexes was that $\nu_{\text{N=N}}$ was found at 1320 and 1311 cm^{-1} for A1 and A2, respectively. An observable shift in band positions for this azo group was found upon complexation with Cu(II) which found at 1301 and 1325 cm^{-1} for A1-Cu(II) and A2-Cu(II), respectively. The stretching vibration for the azomethine group -C=N- in the Schiff bases, S1 and S2 were found at 1620 and 1680 cm^{-1} . In case of Cu(II) complexes of S1 and S2, the position changed to 1608 and 1627 cm^{-1} due to a pull of electron density toward Cu(II) upon chelation [37]. A new bands which observed at wavenumber of 422, 547, 422 and 435 cm^{-1} referred to the binding between Cu(II) and nitrogen atom for A1-Cu(II), A2-Cu(II), S1-Cu(II) and S2-Cu(II), respectively. Also the band at about $\approx 520 \text{ cm}^{-1}$ was referred to the bonding between oxygen atom and the Cu(II) [37]. These observations gave an strong evidence for the proposed structure of Cu(II) chelates with the prepared azo dyes and Schiff bases as illustrated in Fig. 1.

Table 2. Results from IR analysis of azo dye, Schiff base and their prepared Cu(II) complexes.

Compound	νOH	νC=N	νC-H	νN=N	νC-N	νM-O	νM-N
A1	3396(b)	-	2935(w)	1320(m)	1490(w)	-	-
A1-Cu(II)	3400(b)	-	2935(w)	1301(s)	1512(w)	517(w)	422(w)
A2	3400(w)	-	2775(w)	1311(s)	1552(s)	-	-
A2-Cu(II)	3387(s)	-	2920(w)	1325(s)	1577(s)	522(w)	547(w)
S1	3338(m)	1620(s)	3930(w)	-	1570(m)	-	-
S1-Cu(II)	3421(b)	1608(b)	-	-	1537(w)	580(w)	422(w)
S2	3363(w)	1680(s)	2960(w)	-	1490(s)	-	-
S2-Cu(II)	3444(b)	1627(s)	2955(w)	-	1516(s)	534(w)	435(w)

s: strong, m: medium, w: weak, b: broad.

3.2. Spectrophotometric measurements

In order to understand better about the chelation manner between the prepared compounds and Cu(II), the UV-Vis absorption spectra for A1, A2, S1, S2 and their Cu(II) complexes are measured and shown in Figs. 4 and 5. The reagents and the complexes were dissolved in DMF to obtain 1.0×10^{-4} M solution which measured against DMF as a blank. The spectra of free compounds A1, A2, S1 and S2 showed an absorption peak at 438, 394, 364 and 378 nm, respectively, which assigned to the $\pi-\pi^*$ electronic transitions of the conjugated system inside the molecules [38]. For Schiff bases S1 and S2, the very broad peak observed in the range 520-670 nm can be assigned to an intramolecular interaction involving the whole molecule between hydroxyl group in ortho position of the azomethine [39-41]. Anyway, an observable change in both the position and the intensity of the absorption were noticed in case of all copper complexes with both azo dyes and Schiff bases. A blue shift for $\pi-\pi^*$ peak was observed with an appearance of a new charge transfer peak (CT) for all formed complexes. The higher energy reagent peaks are assigned to $\pi-\pi^*$ and ligand to copper charge transfer (LMCT) [42,43]. The λ_{\max} for these peaks are cited in Table 3.

The ionization potentials (I_P) for the charge-transfer peaks inside the prepared complexes, were calculated using equation (1) [44]:

$$I_P = 5.76 + 1.53 \times 10^{-4} \nu_{CT} \dots\dots\dots (1)$$

where ν_{CT} is the wavenumber in cm^{-1} that corresponds to the charge-transfer band formed from the interaction between Cu(II) and reagent. Results found that, the order of increasing ionization potentials was S2-Cu(II) > A2-Cu(II) > A1-Cu(II) > S1-Cu(II). This order indicates that the electron donating power of a donor molecule is highest in case of S2-Cu(II).

Also, the energy values (E_{CT}) between the copper ion and the prepared compounds were obtained using the subsequent equation [44]

$$E_{CT} = h\nu_{CT} = 1243.667/\lambda_{CT} \dots\dots\dots (2)$$

where λ_{CT} is the wavelength of charge transfer peak of the established chelate. The order of energy for CT was in the same above order for the prepared copper complexes. This result indicated that as the ionization potential increases, the energy of the CT peak also increases. Table 3.

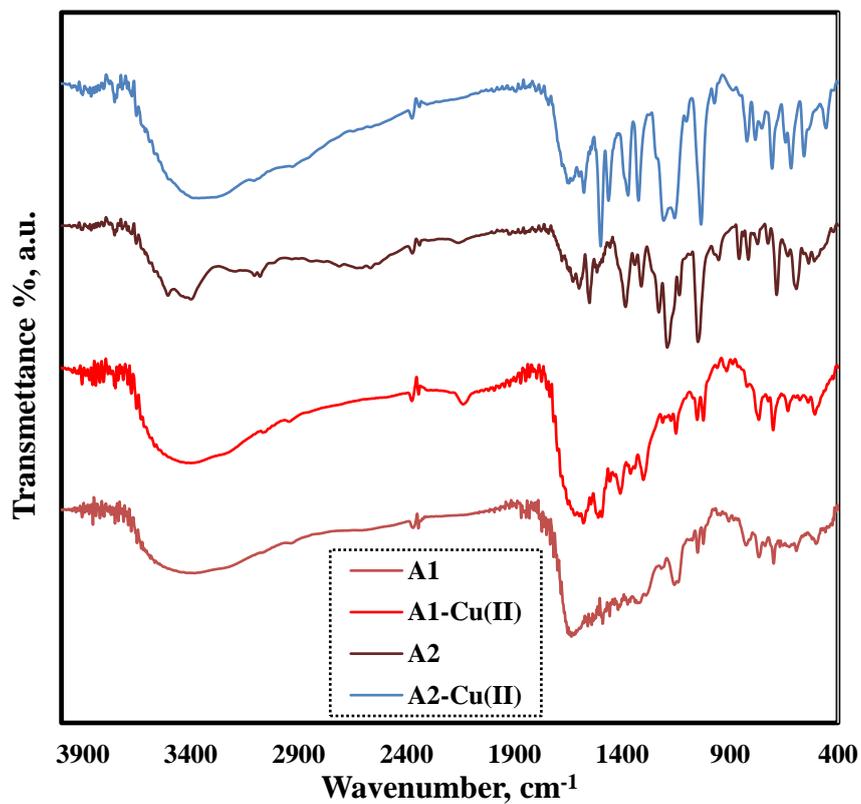


Figure 2. FT-IR spectra for the prepared Azo-dyes A1, A2 and their complexes with Cu(II).

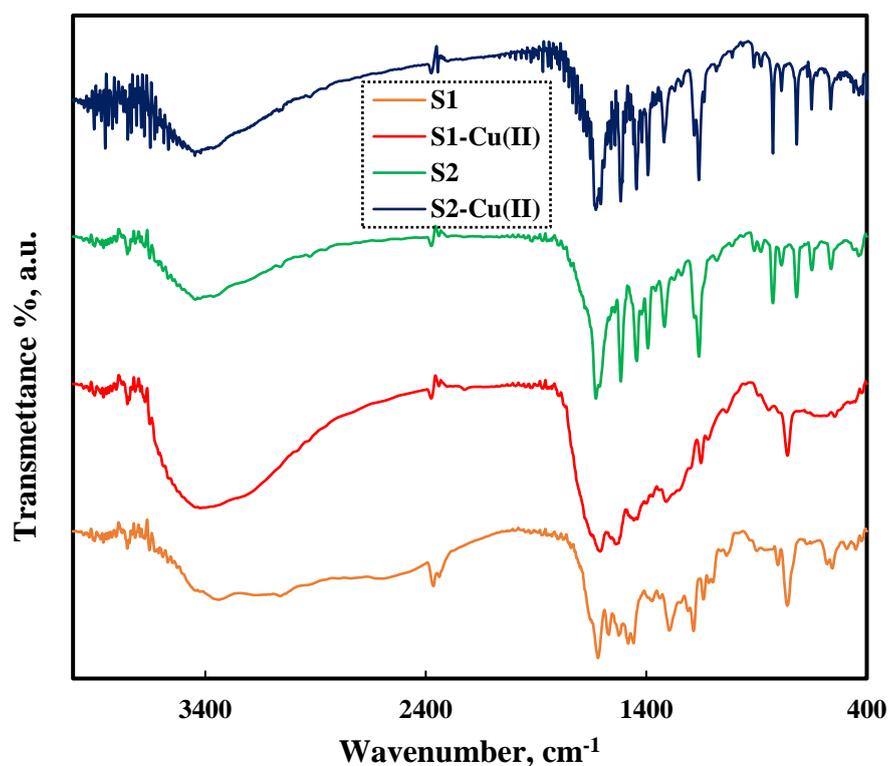


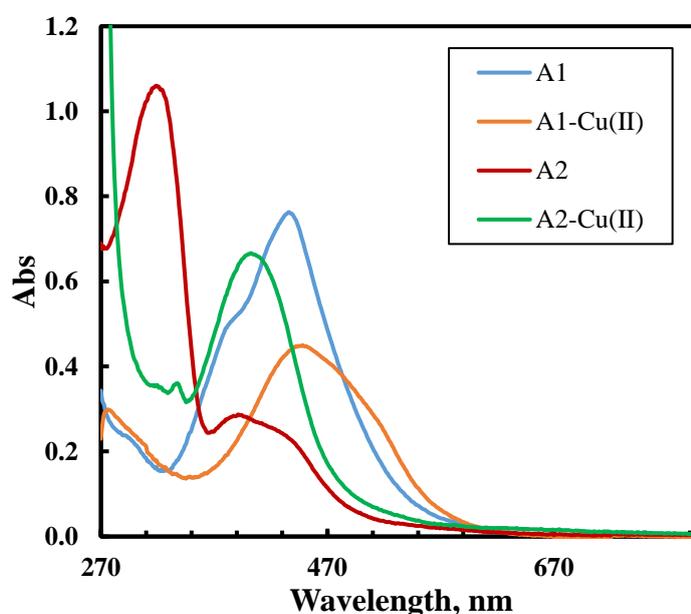
Figure 3. FT-IR spectra for the prepared Schiff bases S1, S2 and their complexes with Cu(II).

Table 3. The value of the energy gap extracted from Nujol mull spectra measurements and DMF for the prepared compounds and its complexes with copper ion

Compound	E _g , eV		λ _{CT}	ν _{CT} , cm ⁻¹	I _P	E _{CT}
	Nujol mull	DMF				
A1	1.97	2.17	---	---	---	---
A1-Cu(II)	1.76	2.28	705	14184	7.93	1.76
A2	2.37	2.61	---	---	---	---
A2-Cu(II)	2.17	2.71	680	14705	8.01	1.82
S1	2.23	2.47	---	---	---	---
S1-Cu(II)	1.91	2.48	732	13661	7.85	1.69
S2	2.12	2.33	---	---	---	---
S2-Cu(II)	1.89	2.41	588	17006	8.36	2.11

Table 4. Spectral and electrochemical parameters of Azo dyes, Schiff bases and their Cu(II) complexes.

Compound	Spectral parameters				Electrochemical parameters				
	λ _{max} (nm)	Abs	λ _{onset} (nm)	E _g (eV)	E _{ox} (V)	E _{red} (V)	E _{HOMO} (eV)	E _{LUMO} (eV)	E _g (eV)
A1	438	0.76	527	2.35	-0.05	-0.67	-4.35	-3.73	0.63
A1-Cu(II)	450	0.44	554	2.23	-0.04	-0.67	-4.36	-3.73	0.62
A2	394	0.28	490	2.52	-0.04	-0.71	-4.36	-3.69	0.67
A2-Cu(II)	402	0.66	476	2.61	-0.03	-0.57	-4.36	-3.83	0.53
S1	364	1.2	450	2.71	0.18	-0.73	-4.58	-3.67	0.91
S1-Cu(II)	446	0.24	495	2.51	-0.12	-0.47	-4.28	-3.93	0.35
S2	378	0.99	441	2.81	0.10	-0.67	-4.51	-3.73	0.77
S2-Cu(II)	478	0.21	508	2.42	-0.09	-0.65	-4.31	-3.75	0.56

**Figure 4.** Electronic absorption spectra of the prepared Azo compounds A1 and A2 and their copper complexes in DMF (1×10^{-4} M).

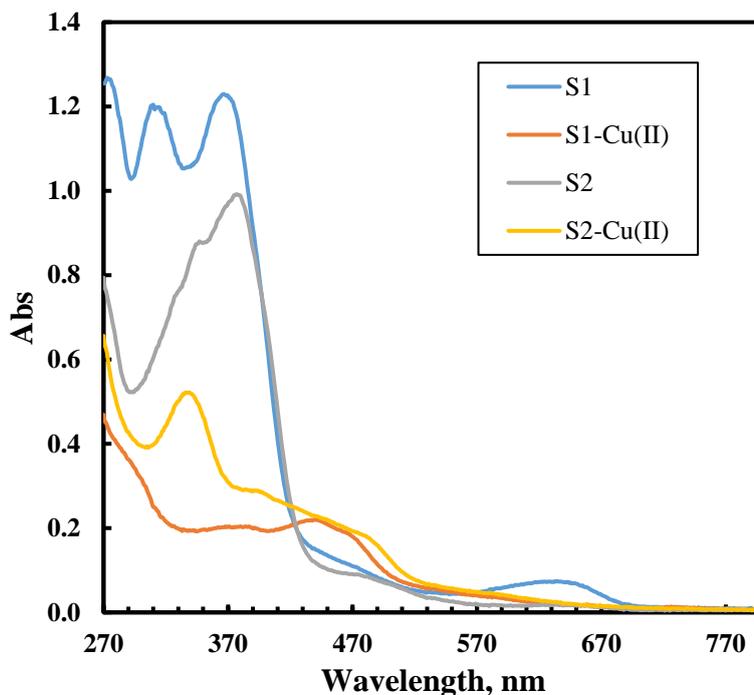


Figure 5. Electronic absorption spectra of the prepared Schiff base S1 and S2 and their copper complexes in DMF (1×10^{-4} M).

Figures 6-9 showed the absorption spectra for A1, A1-Cu(II), S1 and S1-Cu(II) using a Nujol mull technique. Inset the value of the energy gap was calculated using Tauc plot. The energy gaps for all complexes and free compounds were listed in Table 3. Results illustrated that, upon chelation with the bivalent copper ion, the energy gaps for the formed complexes were decreased which facilitate the moving of electrons between HOMO and LOMO orbitals.

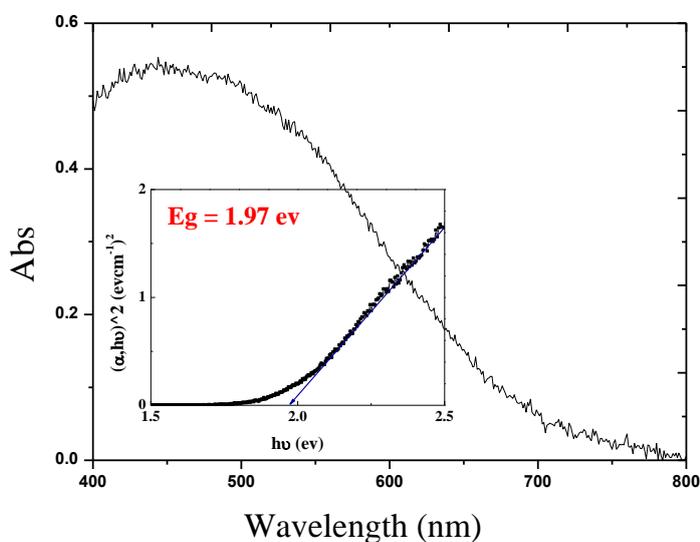


Figure 6. The electronic absorption spectrum of A1 using paraffin oil (Nujol mull) and its value of energy gap (Tauc plot) inset.

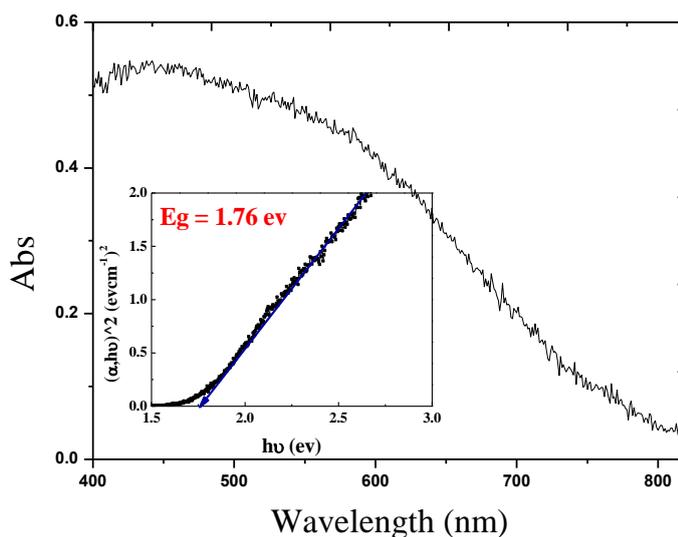


Figure 7. The electronic absorption spectrum of A1-Cu(II) complex using paraffin oil (Nujol mull) and its value of energy gap (Tauc plot) inset.

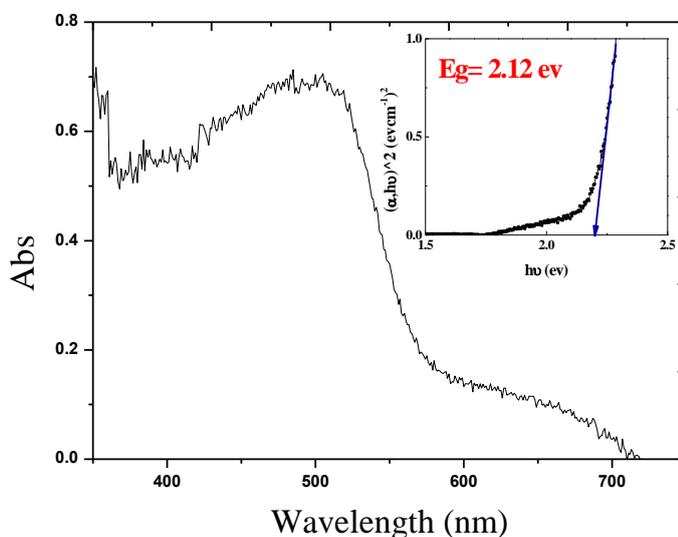


Figure 8. The electronic absorption spectrum of S2 using paraffin oil (Nujol mull) and its value of energy gap (Tauc plot) inset.

Figure 10 indicated the cyclic voltammograms for modified carbon paste electrodes of copper ion complexes and compared with their synthesized ligands A1, A2, S1 and S2. In the working potential +0.8 V to -0.9 V, a clear peak at about +0.35 V for both A1 and A1 was observed as an irreversible oxidation. These peaks are due to the reduction of azo groups in the ligands [45]. Upon chelation as shown in case of A1-Cu(II) and A2-Cu(II), the peak current was distinctly observed. This was due to the chelation effect [46,47]. Whereas in case of Schiff bases S1 and S2, the anodic peaks at about +0.05 and 0.0 V for S1 and S2, respectively, were vanished and a new peak at higher potential was appeared for Cu(II)-Schiff base complexes. These new anodic and cathodic peaks are due to redox couple Cu(II)/Cu(I) [47].

Equations 3, 4 and 5 were used to calculate the energy levels of both the highest occupied molecular orbital (HOMO) in addition to lowest unoccupied molecular orbital (LUMO) and the band gaps (E_g).

$$E_{HOMO} = -e(E_{Ox} + 4.40)eV \dots\dots\dots(3)$$

$$E_{LUMO} = -e(E_{Red} + 4.40)eV \dots\dots\dots(4)$$

$$E_g = E_{LUMO} - E_{HOMO} \dots\dots\dots(5)$$

where E_{HOMO} is the HOMO orbital energy, E_{LUMO} is the LUMO orbital energy, E_{Ox} is the first oxidation potential, E_{Red} is the first reduction potential and E_g is the energy gap. From figure 10, the first oxidation and reduction peak potentials were extracted.

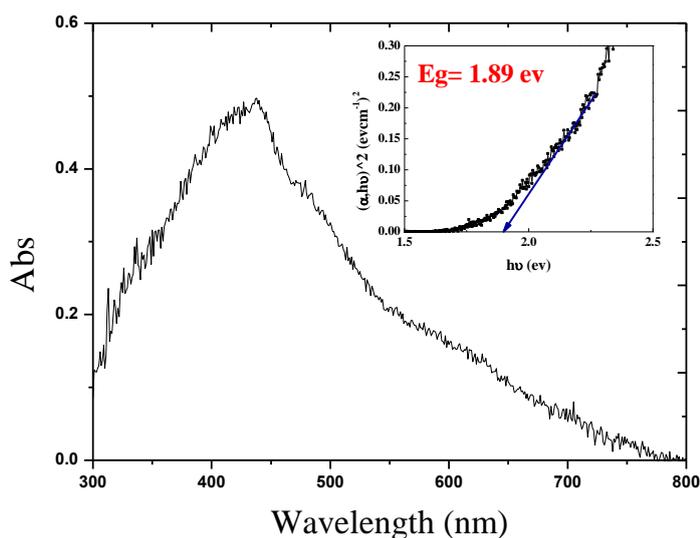


Figure 9. The electronic absorption spectrum of S2-Cu(II) complex using paraffin oil (Nujol mull) and its value of energy gap (Tauc plot) inset.

Table 4 showed the energy values of HOMO and LUMO levels. The attained results were compared with the reference ones, $I^- \leftrightarrow I^{3-}$ redox pair for HOMO and zinc oxide for LUMO [48]. The results indicated that, all the prepared copper complexes displayed inferior HOMO than iodide/triiodide pair electrolyte (-4.75 eV). That way, these prepared complexes permitting the sufficient driving force for dye regeneration. Furthermore, the LUMO energy levels of those complexes are more over that of the ZnO conduction band (-4.20 eV), which indicates that the electron injection is energetically favorable process. The comparison between electrochemical energy gap (E_g^{EC}) and optical energy gap (E_g^{opt}), we found that, both E_g^{EC} and E_g^{opt} are in a good agreement. However, these small differences between E_g^{EC} and E_g^{opt} are uncommon in literature [49]. These small differences can be attributed to the alteration of the media for both electrochemical and spectral determination. This lower E_g leads to more light absorption, and more easily electron excitation. Thus, E_g^{EC} and E_g^{opt} are in tuning with each other. Therefore, inconsistent E_g^{EC} and E_g^{opt} values were obtained.

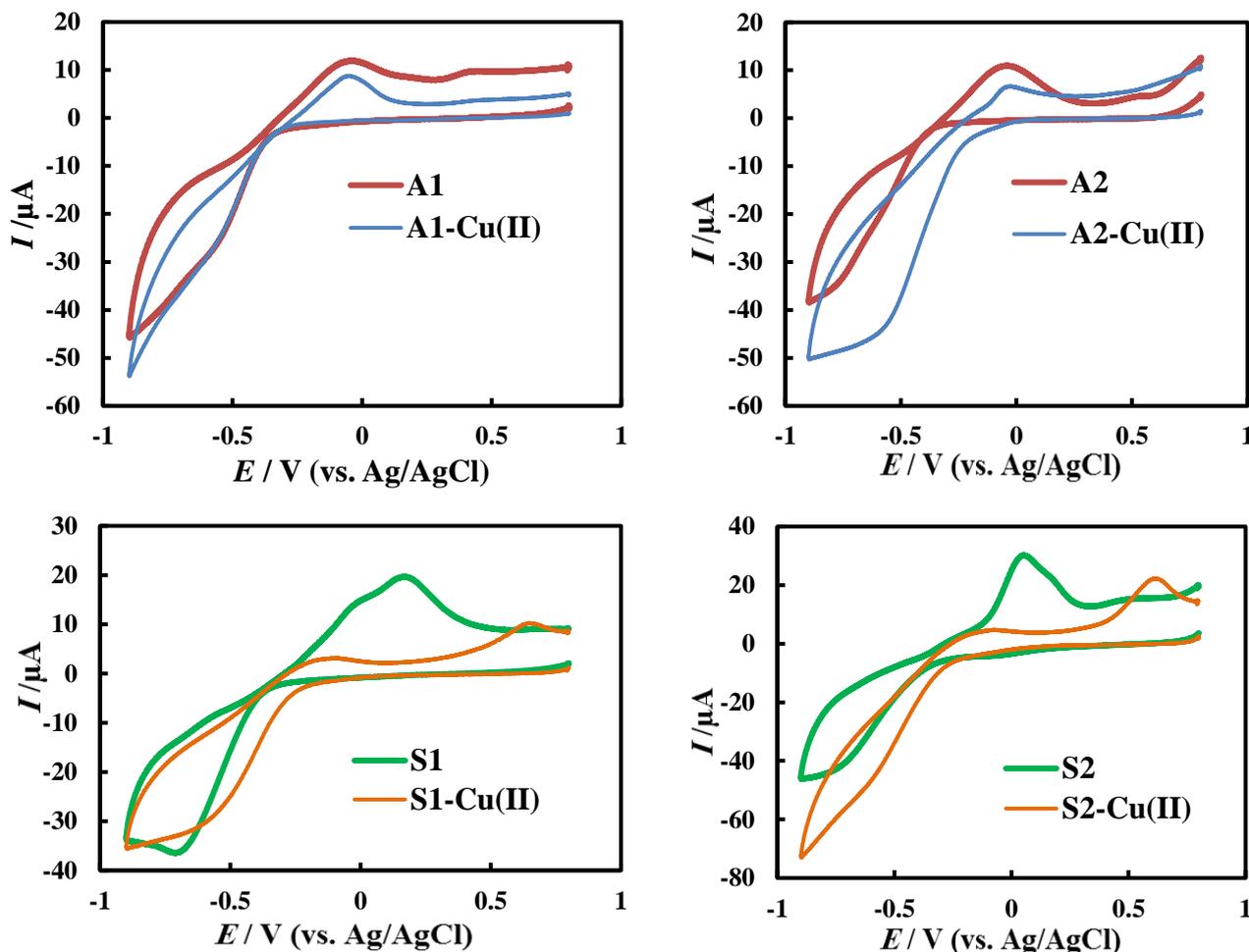


Figure 10. Cyclic voltammograms for the modified carbon paste electrodes using the prepared azo dyes, Schiff bases and their Cu(II) complexes, Scan rate is 100 mV/s.

4. CONCLUSIONS

In the present work, we have prepared a new four reagents, two azo dyes A1 and A2, and two Schiff bases S1 and S2. After that, we used a copper ion to form a complex with these reagents. Both compounds and complexes have been isolated, purified and well characterized and investigated by FT-IR spectroscopy, molar conductivity, UV-Visible absorption and through DMF and nujol mull. The electrochemical characterization was investigated through cyclic voltammetry (CV). The obtained results indicated that the new copper complexes showed good tuning of energy gaps and HOMO-LUMO energy levels in both electrochemical and optical measurements. The prepared Cu(II) complexes showed an easily electron transfer between energy levels in accordance with their intended application as sensitizers in solar cells.

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