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Synthesis, thermal behavior and optical characterizations of thin films of a novel thiazole azo dye and its copper complexes

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ABSTRACT

In the present paper, a novel dye of 4-methyl-5-(4-acetylphenyldiazenyl)thiazol-2-amine (**L**) and its corresponding copper complexes are synthesized and characterized using different techniques including elemental analysis, thermal analysis, ^{1}H NMR, Mass, and FT-IR spectra. The thermal behavior of **L** and its complexes is carried out and discussed using thermogravimetric analysis, and it observed that the type of copper substituent affects the thermal decomposition of complexes. Homogenous thin films of **L** and its complexes are successfully grown onto quartz substrates using spin coating technique. Optical features and spectral phenomena of the thin films are studied using spectrophotometric measurements of absorbance, transmittance and reflectance. The optical constants such as refractive index, extinction coefficient, optical conductivity and energy loss functions of the thin films of **L** and its complexes are calculated. The refractive index curves for all films show a normal dispersion behavior in the non-absorbing region of spectra, from which the dispersion parameters can be calculated using Wemple-DiDomenico model. The type of optical transition bands shows indirect allowed. The values of the optical energy gap are calculated in the range from 2.13 to 2.33 eV, depending on the nature of Cu(II) substituent. Indeed, the present results show that the complexes as organic semiconductors acquired good characterizations better than metal free ligand (**L**) such as more thermal stability, reducing in the optical band gap and increasing in the absorption coefficient that refers to light harvesting capacity.

1. Introduction

Azo compounds are widely using in several applications in different fields including industry, technology and biological activities [1–5]. Among large number and variety of azo dye compounds, thiazole dyes and their complexes are receiving much attention due to their interesting optical, electrical and geometrical structural features in connection with their practical use in many advanced technological applications for solar cells [6,7], light emitting diodes (OLEDs) [8,9], sensors [10,11], fluorescent probes [12], switching devices [13] nonlinear optical elements [14].

Azo complexes have more well features rather than metal free dyes such as they have more thermal stability than metal free dyes. They can also provide control of the shape of absorption spectrum and its transition bands that may be tuned by varying the substituted groups [15,16]. Additionally, they have better solubility than many metal free dyes in many organic solvents [17,18]. Several characterizations of numerous multifunctional azo dyes and their complexes have been studied [19–23]. Characterization of the structural and electrical properties of 5-(4′-derivatives phenylazo)-2-thioxothiazolidin-4-one [20] showed that the thermal stability of that compound was affected by the type of substituent. The dielectric constants (real and imaginary parts) increased with increasing the temperature for that ligand. Investigation of the structural and electrical properties of a series of azo rhodanine copper (II) complexes have been studied [21], it was concluded that the electrical conductivity of complexes showed semiconducting behavior and its value depends on the type of the substituents.

A series of nickel(II), copper(II) and cobalt(II) complexes of 5-(2,3-dimethyl-1-phenylpyrazol-5-oneazo)-2-thioxo-4-thiazolidinone dye have been synthesized, and the structural and electrical characterizations have been investigated [22,23]. The results showed that the thermal activation energy of the nickel(II) complex is greater than copper (II) and cobalt(II) complexes because of its lower ionic radius. Additionally, it is found that the electrical conductivity and the dielectric constants of these complexes showed semiconducting features with different rates depending on the type of the substituent ions. The applications of copper (II) complexes are largely varied and of great importance. The copper (II) complexes are widely used as polymer additives, fungicidal and crop protectors [24–26].

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Complexes have more light stability than their metal free ligands, where their absorption bands may be tuned by varying the substituents of derivatives. These substituents can give desirable changes in the intensity and wide of absorption spectrum of the synthesized molecule according to our demand. Also, the most important phenomenon of azo complex dyes is the good thermal stability because they have high thermal decomposition. Furthermore, the appropriate absorption spectra of complexes are essential features in their applications in the photovoltaic devices and optical recording materials [27–29].

Thiazole is a well-known molecule in the azole family and has electron-deficient properties due to the presence of the electron-withdrawing nitrogen replacing the carbon atom at the 3rd position of thiophene. This makes it act as an excellent potential for constructing functional electron donors. However, to our knowledge, the research on the thin solid films of thiazole compounds and their derivatives for studying of optical, electrical and photovoltaic features is still limited. The preparing of the thiazole compounds in the form of the thin solid films may be greatly affects their optical and structural properties and even changes the charges transport mechanism of thiazole compounds [30].

Herein, the aim of the present work is focusing on synthesis and physicochemical characterization as well as thermal behaviors of the 4-methyl-5-(4-acetylphenyldiazenyl)thiazol-2-amine and its Cu(II) complexes. The thermal analysis for the ligand and its complexes are also investigated. Additionally, the spectroscopic characterization and dispersion properties of these compounds in the thin solid films form are studied. The spectral distribution of optical conductivity and energy loss functions of the films are also calculated.

2. Experimental Details

2.1. Materials and Methods

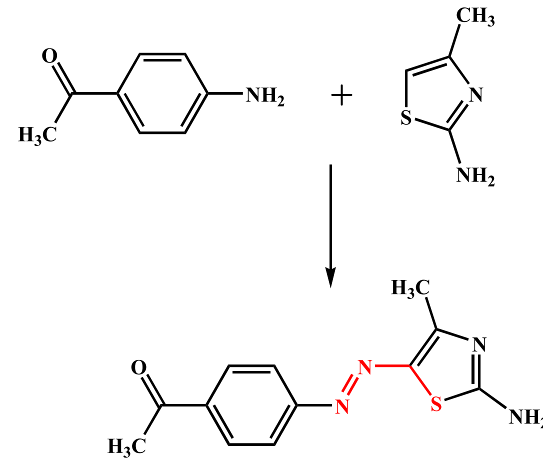
The used chemicals were purchased from BDH and Sigma-Aldrich companies. All chemicals were used without further purification.

Perkin Elmer-2400 elemental analyzer used for C, H, N analyses. Complexometric titration was used to determine the percent of Cu(II) ion of complexes [31]. IR spectra applied on a Nicolet FT-IR spectrophotometer. Bruker NMR spectrophotometer at 600 MHz is used to record the proton-NMR spectra in DMSO d_6. GCMS DFS-Thermo is used for mass analysis. The absorption electronic spectra were measured in nujol mulls using a Perkin Elmer Lambda 4B spectrophotometer. Molar conductivity is measured by CD6N Tacussel conductometer using DMSO solution (10^{-3} M). Shimadzu DAT/TG-50 thermal analyzer under control program "heating rate 10 °C/min, flowing rate 20 mL/min up to 1000 °C" is used for investigated the thermal decomposition behavior of compounds.

Magnetic susceptibilities were measured at room temperature by a modified Gouy method with using a Johnson Matthey magnetic susceptibility balance. Stuart melting point apparatus measures the inaccurate M.P. The absorbance, transmittance and reflectance spectra of the thin films are measured in the spectral range 200–2000 nm for ligand **L** and its complexes using a double-beam spectrophotometer (JASCO model V-570 UV-VIS-NIR. More details about the methodology of optical measurements and calculations are available in our previous works [32,33].

2.2. Synthesis of 4-Methyl-5-(4-acetylphenyldiazenyl)thiazol-2-amine (*L*)

The synthetic route for preparation of ligand **L** is shown in Scheme 1. A solution of aryl diazonium salt was prepared by adding $NaNO_2$ (0.01 mol, 10 mL H_2O) to cold solution of 4-aminoacetophenone (0.01 mol, 1.35 g) in 3 mL conc. HCl with stirring. The freshly prepared solution was added with continuous stirring to cold solution of 2-amino-4-methylthiazole (0.01 mol, 1.14 g) and 3 g of sodium acetate in 30 mL ethanol. The reaction mixture was stirred at 0–5 °C for 2 h, diluted with water. Upon recrystallization from EtOH, thiazole azo dye was obtained. Yield 75%; m.p. 192–194 °C. IR (KBr, cm^{-1}): 3350 (NH_2), 1680 (C═O), 1575 (C═N), 1505 (N═N), 815 (C—S). ^{1}H NMR (δ, ppm): 2.55 (s, 1H, CH_3-acetyl), 2.57 (s, 3H, CH_3-thiazole), 7.68 (d, 2H, J = 9.0 Hz, Ar-H), 8.00 (d, 2H, J = 8.4 Hz, Ar-H), 8.66 (s, 2H, NH_2, D_2O-exchangeable). MS: (m/z, %) = 260 (100%), 227 (22%), 120 (31%), 91 (16%), 72 (25%). Analysis calcd. for $C_{12}H_{12}N_4OS$ (260.31): C, 55.37; H, 4.65; N, 21.52%. Found: C, 55.30; H, 4.77; N, 21.30%.



Scheme 1. Synthetic route for novel aminothiazole dye (**L**).

2.3. Synthesis of Metal Complexes of Aminothiazole Dye

The metal complexes were prepared by adding 0.02 mol of appropriate Cu(II) salts (sulfate, acetate, chlorides and nitrate) to 0.01 mol of a suspended solution of ligand **L** in 50 mL ethanol in (2 M:1 L) molar ratio. The reaction mixture was refluxed at 90 °C for 6 h. The obtained complexes were filtered off, washed several times with ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$ for one day. A New series of the Cu(II) complexes derived from ligand **L** are shown in Scheme 2 and the analysis data of their characterization is listed in Table 1.

2.4. Preparation of Complexes Thin Films

The powder form of thiazole ligand **L** and its complexes (**L-CuSO$_4$**, **L-Cu(AcO)$_2$**, **L CuCl$_2$**, and **L-Cu(NO$_3$)$_2$**) with weights of 30, 35 and 40 mg for each complex were measured. Each complex with certain weight is individually dissolved in 15 mL DMF solvent. The solution of each compound is stirred for 2 h, at ambient temperature. Then, the solution has been heated at 70 °C for 5 h during stirring process by using the thermo-stirrer hot plate. Finally, the solution was filtered. Cleaned optical flat quartz is used as substrate for growing the thin films for spectroscopic measurements. The spin coating technique is used for preparing homogenous films of Cu(II) complexes onto the quartz substrates. The speed of rotation of spin coater machine is 2500 rpm during the preparation of thin films. The subsequent drying process of the grown films on the quartz substrates are occurred using thermal oven at 70 °C for 12 h. The film thickness of each dried film of Cu(II) complex is calculated optically using an interferometer technique [34]. The average values of film thickness of ligand and its complexes are found as 260 nm with tolerance limit ±5 nm.

2.5. Method for Determining the Optical Constants of the Complex Thin Films

The optical constants such as refractive index (n) and extinction coefficient (k) can be calculated from the values of experimental $T(\lambda)$ and $R(\lambda)$ spectra of the complexes thin films by using the method of calculation in literature [35,36]. This method is based on a modified version of Abélés and Theye technique [37,38]. The different values of $T(\lambda)$