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Optical and dielectrical properties of azo quinoline thin films

N.A. El-Ghamaz [a], E.M. El-Menyawy [b], M.A. Diab [c], A.A. El-Bindary [c], A.Z. El-Sonbati [c,*], S.G. Nozha [c,1]

[a] *Physics Department, Faculty of Science, Damietta University, 34517, Egypt*
[b] *Solid State Electronics Laboratory, Solid State Physics Department, Physics Division, National Research Center, Dokki, Cairo 12615, Egypt*
[c] *Chemistry Department, Faculty of Science, Damietta University, 34517, Egypt*

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ABSTRACT

In this study, the optical and dielectrical properties of a novel series of quinoline azodyes (5-(4′-derivatives phenyl azo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_1–AQL_5) were investigated and the obtained results were analyzed. The X-ray diffraction (XRD) patterns of AQL_n show that the materials in the powder form are a mixture of amorphous and crystalline structure, while the thermally deposited thin films are completely amorphous. The optical constants such as the refractive index, n, the absorption index, k and the absorption coefficient, α, were determined using spectrophotometric measurements of transmittance (T) and reflectance (R) in the wavelength range 200–2500 nm. According to the single oscillator model (SOM), some related parameters such as oscillation energy (E_o), the dispersion energy (E_d), the optical dielectric constant (ε_∞), the lattice dielectric constant (ε_L) and the ratio of free carrier concentration to its effective mass (N/m^*) are estimated. The emission spectra of azo quinoline ligands (AQL_n) exhibit dual fluorescence peaks in the region 512–580 nm. This finding reveals the formation of two stoichiometric hydrogen-bonding in the ground and excited state. The dielectrical properties and alternating current conductivity (σ_{AC}) are investigated in temperature range 298–483 K and frequency range 0.1–100 KHz.

1. Introduction

Azodyes have received great attention due to their environmental stability, their ease of preparation, and their promising optical and electrical properties. Optical properties are directly related to their structural and electronic properties and subsequently optical [1]. Linear optical properties have been the subject of numerous investigations by both theoreticians and experimentalists in decades due to the potential applications in optical signal processing and computing [2]. Detailed investigations of the optical properties are vital to scrutinize the atomic structure, electronic band structure and electrical properties and helps in designing materials at the molecular level for specific applications such as optoelectronic devices. Substitution group variation influences the optical functions, dispersion parameters, and bond length of 5-sulfono-7-(4-derivatives phenyl azo)-8-hydroxy quinoline (SAHQ)–x ligands, x = NO_2 or CH_3 or Cl. It has no influence on mobility, relaxation time and plasma frequency of charge carriers. The obtained optical energy gaps for SAHQ–x ligands, x = NO_2, CH_3 and Cl were 1.89, 2 and 2 eV, respectively [3]. Also, the values of dispersion parameters E_o, E_d, ε_L, ε_∞ and N/m^* for copper(II) complexes of (4-alkylphenylazo)-5-sulfo-8-hydroxyquinoline, $[Cu(L_n)_2]$, were calculated according to the single oscillator model. The values of the fundamental and onset energy gaps, E_g and E_g^* were calculated and found to be in the range 2.48–3.51 eV and 1.8–3.01 eV, respectively; depending on the substituent [4].

Nonlinear optical responses of some ligands, azo ligands and its metal organic compounds have been studied recently [5–9]. A compact molecule possessing the tetrathiafulvalene (TTF) group with two backsides C=O groups with nonlinear optical response have been synthesized by Janczarek et al. [5]. They reported that the figure of merit factor decreases due to the increasing optical losses as a consequence of enhanced linear absorption at the same time. Experimental investigations of electroluminescent spectra for several pyrazoloquinoline and quinoksaline derivatives have been performed by Gondek et al. [6]. They suggested the possibility of using the materials like new electroluminophore. Organometallic materials based on ruthenium (II) have been investigated for nonlinear optical response [7,8]. Sahraoui et al. [7] have studied the

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[*] Corresponding author. Tel.: +20 1060081581; fax: +20 572403867.
E-mail address: elsonbatisch@yahoo.com (A.Z. El-Sonbati).

[1] Abstracted from her Ph.D.

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influence of the functionalization on the improvement of the second- and third-order nonlinear optical properties in particular the nature of the acceptor fragment and the π-conjugated transmitter. Gherab et al. [8] reported that the introduction of a metal acetylide fragment in the same conjugated chain as the azobenzene induces the *trans*–*cis*–*trans* isomerization of the azo unit, while the rate of the thermal *cis* → *trans* back isomerization increases with increasing overall electron richness of these compounds.

Substituted quinolines and isoquinolines are known to have interesting photochemical and photophysical properties. These compounds are commonly used as fluorescent probes, standards, and fluorogenic substrates for enzymatic assays and anion recognition [10]. Among these, 8-hydroxyquinoline is one of the most important chelators for metal ions, and has found significant applications in a variety of investigations involving metal complexes [11]. Phototautomerization from excited state intramolecular proton transfer (ESIPT) is of prime importance in biological and chemical systems [12] and as a result, there have been experimental and theoretical interests [13]. Photoexcitation leads to a shift in electron density that facilitates proton migration from a donor atom, usually oxygen, to a nearby acceptor atom, either oxygen or nitrogen, culminating in ESIPT. Occurrence of the red shifted emission makes such molecules interesting, and find a wide range of applications as photochromic dyes [14], laser dyes [15], fluorescent probes [16], sensors [17], organic electroluminescence optical materials [6,18], and photostabilizers [19] as well as in fluorescence recording techniques [20].

Azodye ligands of (5-(4′-derivatives phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) [HL_1–HL_5] are air-stable, high melting temperature, colored, insoluble in water, but partially soluble in hot ethanol, and soluble in coordinating solvent. Decomposition is near 275 °C. Around 350 °C the decomposition showed for a short period and became rapid again at about 430 °C. The ligands were completely decomposed at 590 °C [21].

Due to the clear importance of published work about the quinoline dyes and their derivatives in numerous applications. In this study, the optical, electrical and dielectrical properties of (5-(4′-derivatives phenyl azo)-8-hydroxy-7-quinolinecarboxaldehyde) azodye ligands (AQL_n) were investigated.

2. Experimental technique

2.1. Preparation of (5-(4′-derivatives phenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_n)

8-Hydroxy-7-quinolinecarboxaldehyde was prepared according to El-Sonbati and El-Bindary [22]. (5-(4′-derivatives phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_n) prepared according to El-sonbati et al. [21]. As follow azodye ligands (AQL_n) were prepared from aniline or its *p*-substituted derivatives (10 mmol) was dissolved in hydrochloric acid (20 mmol/25 ml distilled H_2O). The hydrochloric compound was diazotized below 0–5 °C with a solution of sodium nitrite (0.8 g, 10 mmol, 30 ml distilled H_2O). The diazonium chloride was coupled with an alkaline solution of oxine (1.7 g, 10 mmol) in 20 ml of pyridine. The crude dye was collected by filtration and was crystallized from DMF, then dried in a vacuum dessicator over P_2O_5. The preparation of (AQL_n) is summarized in Fig. 1.

The resulting formed ligands are:

(5-(4′-methoxyphenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_1)
(5-(4′-methylphenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_2)
(5-(4′-phenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_3)
(5-(4′-chlorophenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_4)
(5-(4′-nitrophenylazo)-8-hydroxy-7-quinolinecarboxaldehyde) (AQL_5)

2.2. Preparation of azo quinoline thin films

Thin films of azo quinoline ligands are prepared by thermal evaporation technique onto optical flat and well-cleaned quartz substrates. The vacuum chamber was pumped down to 3×10^{-5} mbar at room temperature before starting the evaporation process. A high vacuum coating unit (Edward's, E306A, UK) was used for preparing thin films of azo quinoline ligands ($AQL_{1,\ 3\ \text{and}\ 5}$). The film thickness and the rate of deposition were monitored and controlled during deposition by a film thickness monitor (TM-350 MAXTEK). The film thicknesses of the samples are 100, 85 and 125 nm for AQL_1, AQL_3 and AQL_5 respectively, with deposition rate of 0.5–1 nm/s.

2.3. Analysis and physical measurements

The FTIR spectra are recorded as KBr discs using Perkin–Elmer 1340 spectrophotometer. Elemental microanalyses of the separated ligands and solid chelates for C, H, and N were performed in the Microanalytical Center, Cairo University, Egypt. X-ray diffraction patterns of the powder and the thin film forms, are recorded on X-ray diffractometer (Philips x' pert) with CuKα-radiation ($\lambda = 1.541874$ Å) in the range of diffraction angle ($2\theta^\circ = 4$–70°) by (GNR APD-2000 PRO) (Central Laboratory, Tanta University, Egypt). The applied voltage and the tube current are 40 KV and 30 mA, respectively. Measurements of transmittance, $T(\lambda)$, and reflectance, $R(\lambda)$, of the thin film samples are carried out at room temperature and at normal incidence of light in the wavelength range 200–2500 nm using a double-beam spectrophotometer (JASCO model V-570-UV/Vis/NIR). The absolute values T and R which used to calculate optical constants are calculated according to the relation [4,23]

$$T(\lambda) = \left(\frac{I_{ft}}{I_q}\right)(1 - R_q) \tag{1}$$

and

$$R(\lambda) = \left(\frac{I_{fr}}{I_q}\right)R_{Al}\left[1 + \left(1 - R_q\right)^2\right] - T^2 R_q, \tag{2}$$

where I_{ft} and I_q are the intensities of light passing through film–quartz system and reference quartz substrate, respectively. I_{fr} and I_{Al} are the intensities of the light reflected from the sample and that from the reference mirror, respectively. R_{Al} is the reflectance of Al-mirror and R_q is the reflectance of the quartz. The emission spectra of ($AQL_{1,\ 3\ \text{and}\ 5}$) thin films are recorded using Fluorimeter Spectro Photometer (Model 6285; for excitation and emission spectra, 200–700 nm) equipped with monochromatic light with wavelength ($\lambda_{ex} = 365$ nm) for excitation process.

2.4. Electrical measurements

The powder of each azo quinoline AQL_n derivative is compressed by a hydraulic press under a pressure of 5 tons/cm^2 at room temperature. The thickness of each pellet is about 1 mm and surface area is about 25 mm^2. Silver paste is used as ohmic contact. The AC electrical measurements are performed with a LCR bridge model Stanford SR720 LCR meter. The measurements are carried out in the frequency range 0.1–100 KHz and in the temperature range 298–