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Optical properties of some synthesized azo thin films

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HIGHLIGHTS

- ▶ Thermal evaporation process does not affect the chemical structure of ligands.
- ▶ Thermally deposited PATT-L_n thin film can be considered as completely amorphous.
- ▶ The optical absorption showed many absorption bands.
- ▶ The type of optical transition is found to be direct allowed transition.
- ▶ The E_g values are in the range 1.78–2.29 eV according to *p*-(NO_2 > Cl > H > OCH_3 > CH_3).

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ABSTRACT

5-(4′-Alkyl phenylazo)-2-thioxothiazolidin-4-one (PATT-L_n) have been synthesized and characterized with various physico-chemical techniques. Thin films of PATT-L_n have been prepared by the thermal deposition technique in a vacuum of 3×10^{-5} mbar onto optical flat glass substrates. The absorption properties of thermally deposited PATT-L_n thin films were investigated in the wavelength range 190–2500 nm. The type of optical transition near the edge of the band gap is found to be direct allowed transition. The values of the energy gap for derivatives under investigation are calculated and found to be in the range 1.77–2.29 eV dependent on the nature of the substituent. They tend to the increase according to the following order *p*-(OCH_3 < CH_3 < H < Cl < NO_2) as expected from Hammett's constant σ^R.

1. Introduction

Azo compound, based on thioxothiazolidin (rhodanine), plays a central role as chelating agents for a large number of metal ions [1] as they form a stable six-member ring after complexation with a metal ion and can also be used as analytical reagents [2]. Rhodanine plays an important role in biological reactions [3]. Chemical properties of rhodanine and its derivatives are of interest due to coordination capacity and their use as metal extracting agents [4]. Azo compounds based on rhodanine were synthesized as potential medicinal preparations [3].

Rhodanine derivative attracted some attention in solar cell application [5]. Many authors studied the light-to-electricity conversion efficiency [6] for rhodanine derivative. They found that the value of conversion efficiency (η) is in the range 2.86% and 6.27%. A few triple rhodanine indoline derivatives showed comparable conversion efficiency [5]. A double rhodanine indoline dye has been reported to show a highest solar-to-electricity conversion efficiency (η = 9.0%) on titanium oxide [7].

Despite the importance of studying the optical absorption properties of rhodanine derivatives in solar cell applications, to the best of our knowledge, little efforts were done to study the optical absorption phenomena for 5-(4′-alkyl phenylazo)-2-thioxothiazolidin-4-one (PATT-L_n) in solution form whereas no studies on the materials under investigation in the thin films form has been done.

The objectives of the present work are synthesis and characterizing the 5-(4′-alkyl phenylazo)-2-thioxothiazolidin-4-one (Fig. 1), preparing the thin films by thermal evaporation technique, and to study the optical absorption properties of PATT-L_n thin films.

2. Experimental technique

All the chemicals used were of British Drug House quality.

2.1. Synthesis of 5-(4′-alkyl phenylazo)-2-thioxothiazolidin-4-one (PATT-L_n)

In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid were added to aniline (0.01 mol) or *p*-derivatives. To the resulting mixture stirred and cooled to 0 °C,

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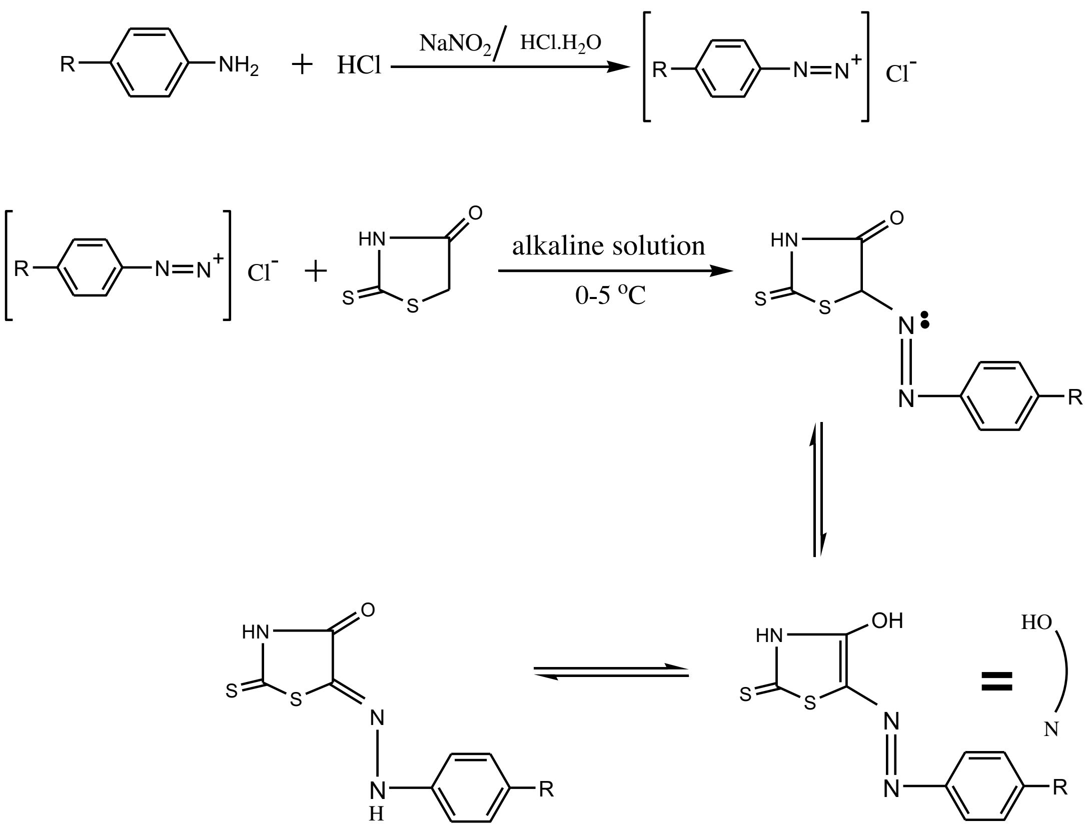
a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 2-thioxo-4-thiazolidinone, in 10 ml of pyridine. The colored precipitate, which formed immediately, was filtered through sintered glass crucible, washed several times with water and ether. The crude products was purified by recrystallization from hot ethanol, yield ~65% then dried in vacuum desiccator over P_2O_5.

The resulting formed ligands are: 5-(4′-methoxyphenylazo)-2-thioxothiazolidin-4-one (PATT-L_1), 5-(4′-methylphenylazo)-2-thi oxothiazolidin-4-one (PATT-L_2), 5-(4′-phenylazo)-2-thioxothiazoli din-4-one (PATT-L_3), 5-(4′-chlorophenylazo)-2-thioxothiazolidin-4-one (PATT-L_4) and 5-(4′-nitrophenylazo)-2-thioxothiazolidin-4-one (PATT-L_5).



n=1, R = OCH_3 (PATT-L_1); n=2, R = CH_3 (PATT-L_2); n=3, R = H (PATT-L_3); n=4, R = Cl (PATT-L_4); and n=5, R = NO_2 (PATT-L_5)

The formation mechanism of azodye ligands (PATT-L_n)

The ligands were also characterized by elemental analysis (Table 1), NMR and I.R. spectroscopy.

2.2. Preparation of 5-(4′-alkyl phenylazo)-2-thioxothiazolidin-4-one (PATT-L_n) thin films

Thin films of PATT-L_n were prepared by thermal evaporation technique onto optical flat and well-cleaned glass 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 to prepare thin films of PATT-L_n. The film thickness and the rate of deposition were monitored and controlled during deposition by a film thickness monitor (TM-350 MAXTEK). The film thickness of all samples was in the range 100–110 nm and the rate of deposition was ranged 0.5–1 nm/s.

2.3. Measurements

Elemental microanalyses of the separated solid chelates for C, H, and N were performed in the Microanalytical Center, Cairo University, Egypt. Infrared spectra were recorded using Perkin–Elmer 1340 spectrophotometer. ^{1}H NMR spectra were obtained on a JEOL FX 9000 Fourier transform spectrometer with deutrated dimethylsulfoxide (DMSO-d_6) as a solvent and TMS as an internal reference.

Structural analysis of the powder and thin film was performed at room temperature by a Philips X-ray diffractometer equipped with utilized monochromatic Cu Kα radiation (λ = 1.5418 Å). The X-ray tube voltage and current were 40 kV and 25 mA, respectively.

Measurements of transmittance $T(\lambda)$ of the thin film samples were carried out at room temperature and at normal incidence of light in the wavelength range 190–2500 nm in steps of 2 nm using a double-beam spectrophotometer (JASCO model V-570-UV/Vis/NIR).