Journal of Luminescence 194 (2018) 507–518

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Linear and nonlinear optical properties of new azo aminosalicylic acid derivatives

N.A. El-Ghamaz[a], A.Z. El-Sonbati[b,*], L.S. Serag[b]

[a] Physics Department, Faculty of Science, Damietta University, 34517, Egypt
[b] Chemistry Department, Faculty of Science, Damietta University, 34517, Egypt

ARTICLE INFO

Keywords:
Linear and Nonlinear properties
Absorption and dispersion properties
Fluorescence phenomena
X-ray diffraction
Thermal evaporation

ABSTRACT

4-(3-Allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (4-ATS) and 5-(3-allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (5-ATS) were synthesized and characterized by different spectroscopic techniques. The XRD patterns of 4-ATS and 5-ATS in powder form were recorded and found to be polycrystalline with monoclinic crystal system. Thin films of 4-ATS and 5-ATS were successfully prepared by thermal evaporation technique onto optical flat quartz substrates. Linear and nonlinear optical properties of 4-ATS and 5-ATS were investigated by spectrophotometric measurements. The spectral distribution of refractive index of 5-ATS thin films showed normal dispersion in the non-absorbing region of spectra, while 4-ATS showed nonlinear response. The optical energy gap and the electronic transition type for 4-ATS and 5-ATS were calculated. The electronic absorption and emission spectra were recorded for pristine and UV-irradiated 4-ATS and 5-ATS thin films. The absorption coefficient spectra for 4-ATS and 5-ATS were found to decrease with increasing UV exposure time, while the intensity of emission spectra for both of the derivatives were enhanced with increasing UV exposure time. Recovery in dark reversed the effect of UV- radiation.

1. Introduction

Among organic compounds, aminosalicylic acids and their derivatives showed interesting linear and nonlinear optical properties which propose them in many advanced technological applications, for example, communications [1], information storage devices [2], laser sources [3] and for infrared blocking windows [4]. Also, aminosalicylic acids are of high importance in optoelectronic devices [5,6] such as photodiodes and light emitting diodes due to their distinguished emission properties [7–9].

Investigation of linear and nonlinear optical properties of a material may lead to better understanding of its suitable applications [10]. The importance of such materials is appeared through their ability to form second and third harmonic generation effects when interact with radiation. Second harmonic generation (SHG) or frequency doubling is formed by the interaction of a nonlinear material with the incident light to duplicate the photons energy (double frequency or half the wavelength of incident light). Reversible symmetrical molecular configuration of these materials on thin layer gives high nonlinear optical effect. Amino salicylic acids and their derivatives are well known as nonlinear optical materials [11,12]. They have promising optical properties and photochromic effect that involve strong fluorescence emissions.

The simplest system for studying excited-state intra-molecular proton transfer (ESIPT) is the salicylic acid and its derivatives [13–16]. Absorption and emission properties of 4-aminosalicylic acid (4-ASA) and 5-aminosalicylic acid (5-ASA) have been investigated in water and methanol by Joshi et al. [8]. They showed that the absorption peaks intensity and position were affected strongly by pH of the solution. On the other hand, 4-ASA showed two absorption peaks at λ_{abs} = 303 and 565 nm and one emission peak at λ_{em} = 386 nm, while 5-ASA showed two absorption peaks at λ_{abs} = 290 and 334 and dual emission at λ_{em} = 405 and 490 nm. Ghoneim et al. [9] reported that the 4-ASA thin film has two absorption peaks at λ_{abs} = 230 and 287 nm and three emission peaks at λ_{em} = 514, 538 and 581 nm. 4-ASA in protic polar polymer matrices such as poly (vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA) and cellulose acetate (CA) showed two main absorption peaks around $\lambda_{abs} \approx$ 270 and 300 nm depending on the polymer nature [17]. Gao et al. [18] reported that the emission intensity of bonded salicylic acid (SA) on polystyrene side chain has been enhanced by increasing of SA coordinating to Eu^{3+} ion. Quenching of emission spectra of 4-ASA has been observed by increasing the percentage of Konjac glucomannan (KGM) in 4-ASA-KGM blends [19]. Arora et al. [20] reported that the intensity of emission spectra of 5-ASA have been enhanced in presence of iodide in aprotic solvents. Diazotization reaction of *N*-acryloyl-4-aminosalicylic acid

* Corresponding author.
E-mail address: elsonbatisch@yahoo.com (A.Z. El-Sonbati).

http://dx.doi.org/10.1016/j.jlumin.2017.10.062
Received 21 August 2017; Received in revised form 24 September 2017; Accepted 23 October 2017
Available online 24 October 2017
0022-2313/ <outputStr5>

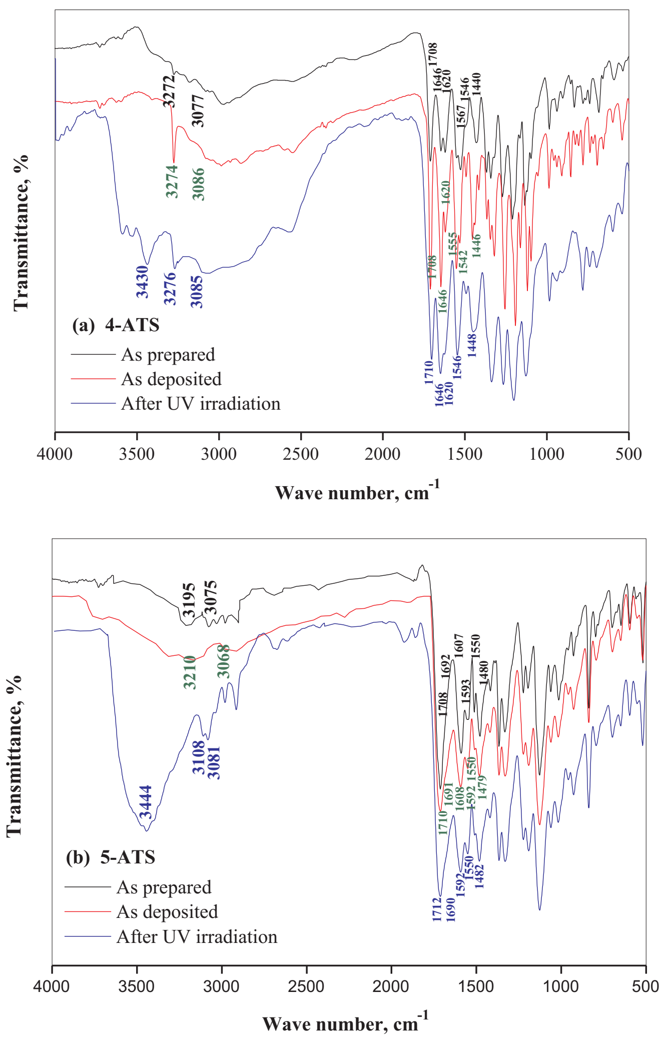


Fig. 1. The IR spectra of important peaks for (a) 4-ATS and (b) 5-ATS.

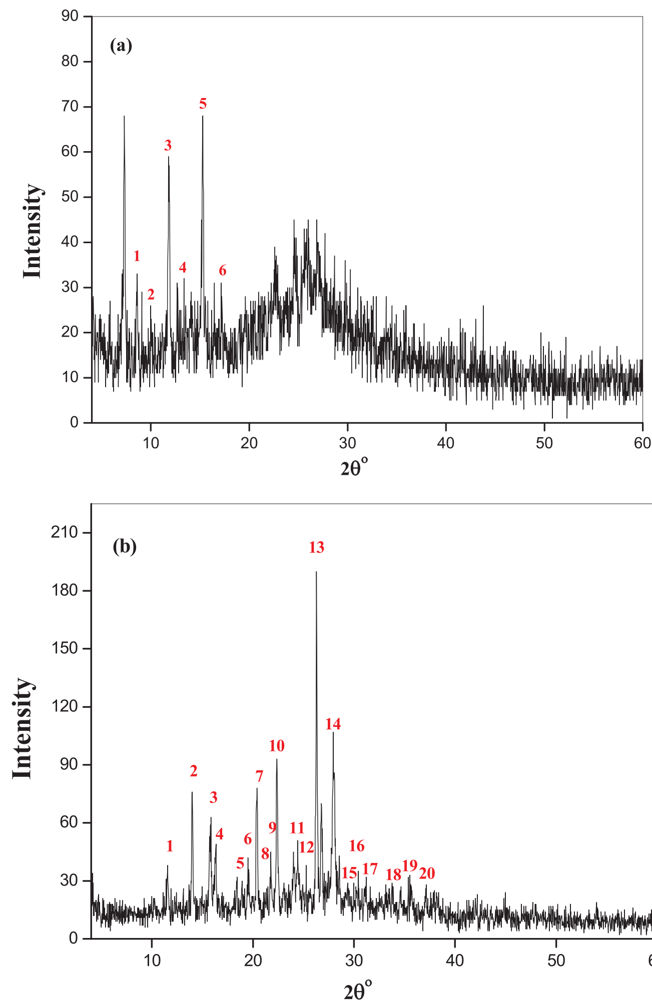
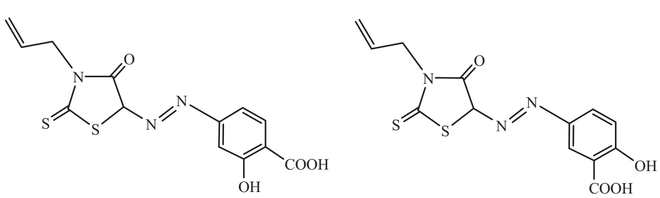


Fig. 2. The XRD patterns of the investigated compounds (a) 4-ATS and (b) 5-ATS.



(a) (b)

Scheme 1. The chemical structure of (a) 4-ATS (a) and (b) 5-ATS.

(4-AMSA) showed appearance of new absorption band in the range λ_{abs} = 430–470 nm and remarkably enhanced the emission intensity due to formation of azodye derivatives which are able to make an extra ESIPT [9].

In this work, we will focus our attention to study the difference of absorption, emission and dispersion properties of newly synthesized two azo aminosalicylic acids namely 4-(3-allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (4-ATS) and 5-(3-allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (5-ATS) to invest the enhancement effect of diazotization on emission spectra. Also, we will investigate the effect of UV- irradiation as an important environment operator on the chemical structure and spectral properties of 4-ATS and 5-ATS thin films. Also, we aimed to investigate the linear and non linear optical effects of the azo aminosalicylic acids thin films under investigation.

2. Experimental

2.1. Materials

3-Allylrhodanine, 4-aminosalicylic acid and 5-aminosalicylic acid are purchased from Aldrich Chemical Co., Inc. and used without purification. Organic solvents which are, pyridine (99.8%, Sigma), absolute ethyl alcohol and ethyl ether (BDH) are purified before use by standard methods. De-ionized water is usually used in all preparations.

2.2. Synthesis of aminosalicylic acid azo derivatives

4-(3-Allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (4-ATS) and 5-(3-allyl-4-oxo-2-thioxo-thiazolidin-5-ylazo) salicylic acid (5-ATS) are synthesized by the well established standard method [9,21,22]. The resulting solids (4-ATS and 5-ATS) are recrystallized with ethanol and then dried in a vacuum desiccator over anhydrous calcium chloride. The color of 4-ATS and 5-ATS azo ligands is dark orange and greenish brown, respectively. The melting point temperature is measured using Electrothermal IA9002 digital melting point and found to be 225 and 120 °C for 4-ATS and 5-ATS, respectively.

2.3. Thin films preparation

Thin films of 4-ATS and 5-ATS are prepared by thermal evaporation technique onto well cleaned optical flat quartz substrates. The vacuum coating unit is Edward's, E306A, UK. The vacuum chamber was pumped