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Pyronin Y as new organic semiconductors: Structure, optical spectroscopy and electrical/dielectric properties

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ABSTRACT

Pyronin Y (PY) is an organic dye which is used extensively before in staining RNA and other organo-cells. Nowadays, it can be used in electronic and optoelectronic devices as an organic semiconductor. X-ray diffraction (XRD) showed that PY is a polycrystalline material and both the lattice structure and the lattice constants were calculated for the first time by using crysfire and checkcell software. In addition, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been studied. Diffused reflectance (DR) of pyronin Y in the wavelength 200–2300 nm was measured and analyzed to calculate the optical parameters and the absorption region of pyronin Y. The optical band gap was calculated on the basis of Kubelka–Munk theory (KMT). It is clear that there are three optical band gaps in the studied range of photon energy and equal 2.13, 1.82 and 1.67 eV. The high band gap (2.13 eV) is corresponding to the fundamental band gap (between HOMO and LUMO) and other two gaps (1.82 and 1.67 eV) are corresponding to the trap energy inside the band gap (i.e. onset gaps). On the basis of the DR measurements and applicable of KMT, we are able to calculate the refractive index, absorption index and the dielectric constants for pyronin Y in powder form. Pyronin Y is an organic semiconductor due to the increasing of DC (direct current) electrical conductivity with increasing temperature and the electronic parameters of direct current was calculated. Ac electrical conductivity, dielectric constant and dielectric loss were calculated and interpreted on the basis of ac fields causes the different kind of polarization inside the materials. Hence, pyronin Y can be used as a new materials for advanced technology.

1. Introduction

Organic semiconductors are the key material for new technology and applications. Most electronic and opto-electronic technology are focusing on the organic materials and their fabrication technologies [1,2]. Organic devices have special features in comparable to the inorganic one such as, light weight, low cost manufacture, large area deposition on different substrates, flexibility, environmental friendly, room temperature deposition and bio-degradable. Organic semiconductors poses unique optical, electrical and opto-electronic features [3–6]. Dyes are an organic material and extensively applied in technological in the different applications because of their low cost manufacture and ease design of molecular level to get special optical characteristics [7].

Xanthene chemical dyes have high absorption coefficient and can be processed and then employed to uncover the optical and electrical properties [8]. Pyronin Y is a cationic dye from Xanthene derivatives and it is sensitive to the molecular environment [9,10]. It is a water-soluble with specific electrical, optical and surface properties. It has been extensively applied in the labeling of cell organelles and proteins, also by doping in organic thin films, and in constructing diodes by depositing it on the surface of a p-type silicon [10,11]. The photo-physical properties of pyronin Y has been studied widely because of their commercial significance in different fields, for example, in biological, in synthesis poly-electrolyte systems and in dyes laser [12]. Pyronin Y as an organic semiconductor can be used in electronic and optoelectronic devices such as schottky diode, thin films transistors, light emitting diode and solar cell, ...etc.

In the present study, XRD pattern of pyronin Y was analyzed for the first time. The pyronin Y lattice parameters and lattice

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structure will be calculated and interpreted. The optical band gaps and optical constants (i.e. absorption index, dielectric constant and the dielectric loss) were determined of Pyronin Y in powder form by using a diffused reflectance spectroscopy as a new technique to characterize the organic semiconductors. Ac and dc electrical conductivity, dielectric constants were measured, calculated and interpreted on the basis of the applied theories in this field.

2. Experimental details

Pyronin Y with high purity was bought from Sigma Aldrich, the pyronin Y molecular structure is shown in Fig. 1. No further purifications was made for pyronin Y. A 3626CARVER Mini-C Manual hydraulic pressure system was used to form a pellet with diameter 13 mm and thickness 1 mm. The method of uses is very simple, just weight 0.25 gm of PY using electronic balance, then arranged in the Evacuable Pellet, which an important piece used to form the pellet, and inserted between the fixed and movable rods of the above system and applying 10 ton to produce a compacted pellet disc in a circular shape.

Structure properties of powder pyronin Y was determined by Shimadzu Lab XRD-6000 with *CuK*α (λ = 1.5406 Å) radiation and secondary monochromator. The applied accelerated voltage was 30 kV and the current 30 mA with speed scan 0.02°. All the obtained XRD data was analyzed with the attached software to this device. Thermogravimetric and differential thermal analyses (TGA/DTA) of thesamplewere studied using TGA-50 and DTA-50 Shimadzu equipments, respectively, in the temperature range from RT (room temperature) to 600 °C.

The FTIR spectra of pyronin Y was performed by means of Thermo Nicolet NEXUS 470 FTIR Spectrophotometer. The samples were subjected to this analysis by preparing 100 mg highly grade of potassium bromide containing 2% of finely ground pyronin Y powder.

UV–VIS–NIR spectrophotometer model (Shimadzu UV-3600) in the wavelength range from 200 to 2300 nm was employed to determine the diffused reflectance (DR) measurements. The system was designed by using the integrating sphere attachment with $BaSO_4$ as a reference material. Before any measurements, the base line was adjusted using $BaSO_4$ followed by the measured diffused reflectance for $BaSO_5$ in which 100% must be obtained. Now, the device setup was ready for DR measurements. Special designed holder attached to the integrating sphere system was used as a reference for $BaSO_4$ and the other holder to compact the PY inside the holder. The thickness of the holder represents the thickness of the pyronin Y.

At different elevated temperatures, the dc electrical conductivity was determined by using current-voltage characteristic circuit linked with PID controllable. This circuit Consists of a digital picoammeter (DPM-111/SVS labs Inc. USA), high-voltage power supply (EHT-11/SVS labs Inc. USA) and PID controlled oven (PID–200) attached with two probe holder fixed in special oven attached to the system. Pyronin Y was pressed on a compact disc under 10 ton of diameter 13 mm and thickness 1 mm.

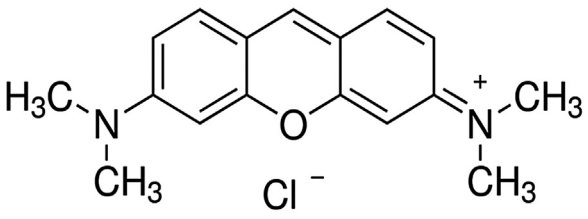

Fig. 1. The molecular structure of pyronin Y [13].

Ac conductivity and dielectric constants were performed by using Keithley 4200-SCS semiconductor characterization system. Two pre-Amplifier was connected throughout the device to control all the connection cables. The output of the pre-Amplifier is connected directly to a special design holder made from brass and Teflon. All measurements were don in the frequency range from 3 kHz–10 MHz and mounted at room temperature.

3. Results and discussion

3.1. Structure and thermal properties of pyronin Y in powder form

3.1.1. X-ray diffraction pattern (XRD) pyronin Y

Crystallographic structure of the powder pyronin Y was investigated by using X-ray diffraction (XRD) pattern in the range of 2θ from 10° to 90°. It is clear from Fig. 2 that PY is a polycrystalline material with monoclinic structure. The lattice parameters were calculated on the basis of crysfire (as indexing software) and checkcell (as refinement software) for the first time [14,15]. The intensity of the peaks more than 10% were considered in our XRD analysis. The values of the lattice parameters are a = 19.0067 Å, b = 13.7778 Å, and c = 9.0519 Å, α = 90°, β = 91.64° and γ = 90°. The volume of the Pyronin Y cell is 2369.475 nm^3. The XRD data analysis of pyroninY as the observed (2θ), the calculated (2θ) and the difference with (hkl) are tabulated in Table 1.

3.1.2. Thermal gravimetric analysis (TGA)

Thermal analysis is important method to determine the thermal stability of organic material. In addition to thermal stability, the curve of weight loss can be illustrated information such as kinetic parameters for chemical reactions in the sample, the changes in sample composition, and used to determine the point at which weight loss is most apparent. The thermal stability has been studied in the temperature range between 20 and 600 °C. Thermal gravimetric analysis (TGA) determines the changes in the mass of a sample as the temperature increases linearly. Pyronin Y dye shows the following stages of mass loss as shown in Fig. 3: between 25 and 100 °C the dehydration of dye gives 0.25 mg weight loss, between 100 °C and 200 °C the dye have thermal stability and up to 200 °C followed by as small decreasing in its mass up to 600 °C due to the decomposition of pyronin Y with further increasing of the surrounding temperature [16–19].

3.2. Optical properties of pyronin Y in powder form

3.2.1. Diffused and specular reflectance

There are two basic classes of reflectance measurements: Internal and external reflectance. The internal reflectance measurements are measured by employing attenuated total reflection (ATR) technique, so the incident beam is passed through an ATR crystal that is in good attached to the sample [20–26]. The measurements of external reflectance is based on the incident beam totally reflected from the sample [20–26]. These measurements can be divided into two types as follows: diffuse reflectance (DR), specular reflectance (SR). Diffused reflectance is a spectroscopic technique for powdered samples. It based on reflection of light in different spectral ranges. It created by irregular surfaces, such as powdered, that tend to reflected light in all directions. It is depend onto the concentration of incident spectrometer beam into the sample. For the incident beam, there are four possible results, it can be reflected, transmitted, absorbed or scattered [20–26]. The scattered beam inside the sample that returned to the surface is the only part of the beam is considered as the diffuse reflection. As a function of the wavelengths, the spectrum of DR is a ratio of the scattering light from a sample and the light scattered from the non-absorbing reference sample [20–26]. Specular reflectance is an