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Influence of gamma ray irradiation and annealing temperature on the optical constants and spectral dispersion parameters of metal-free and zinc tetraphenylporphyrin thin films: A comparative study

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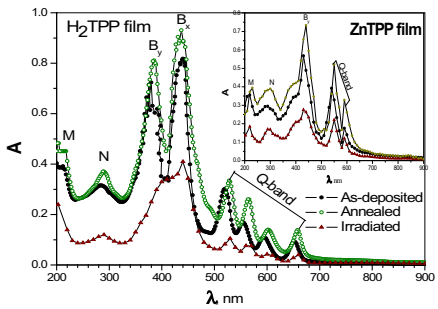
HIGHLIGHTS

- H_2TPP and ZnTPP thin films were prepared by thermal evaporation technique.
- A comparative study has been done between optical properties of H_2TPP and ZnTPP films.
- Influence of annealing temperature and γ-ray irradiation on the optical constants of H_2TPP and ZnTPP thin films have been reported.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report on the effect of γ-ray irradiation and annealing temperature on the optical properties of metal-free tetraphenylporphyrin, H_2TPP, and zinc tetraphenylporphyrin, ZnTPP, thin films. Thin films of H_2TPP and ZnTPP were successfully prepared by the thermal evaporation technique. The optical properties of H_2TPP and ZnTPP films were investigated using spectrophotometric measurements of the transmittance and reflectance at normal incidence of light in the wavelength range from 200 to 2500 nm. The absorption spectra of H_2TPP showed four absorption bands, namely the Q, B, N and M bands. The effect of inserting Zn atom into the cavity of porphyrin macrocycle in ZnTPP molecule distorted the Q and B bands, reduced the width of absorption region and influenced the optical constants and dispersion parameters. In all conditions, the type of electron transition is indirect allowed transition. Anomalous dispersion is observed in the absorption region but normal dispersion occurs in the transparent region of spectra. We adopted multi-oscillator model and the single oscillator model to interpret the anomalous and normal dispersion, respectively. We have found that the annealing temperature has mostly the opposite effect of γ-ray irradiation on absorption and dispersion characteristics of these films.

Introduction

Applications of porphyrins are not only limited to biological systems, but also to other fields of science and technology. The technological applications of porphyrins and their derivatives

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include: γ-ray and gas sensors [1,2], solar cells [3], photochromic recording media [4], photonic devices [5], catalysis [6] and photo-electrochemical cells [7]. Porphyrins also show relatively high efficiencies in the dye-sensitized solar cells (DSSCs) [8,9]. Porphyrins have been regarded as promising dye sensitizers in DSSCs due to their good absorption properties and synthetic versatility. Active efforts in the modifications of porphyrin molecules have recently led to a reasonable power conversion efficiency exceeding 13% in an optimized DSSC [10].

Porphyrins are a conjugated organic macrocycles consisting of four pyrrole-derived units (C_4H_4NH) fused together through the bridging carbon atoms. The porphyrin skeleton has an extended π-conjugation system with 18-π electrons leading to a wide range of wavelengths for light absorption; this can also be tuned by attaching different functional groups to the porphyrin ring [11,12]. Linker groups can be attached to different parts of the molecule for binding it to the surface [11,12]. This may be done as well by choosing proper central metal atoms [11–13]. These molecules play an important role for the life of plants; they are a central light-absorbing unit in the chlorophyll II molecule, as well as the life of animals and humans, as a main part of the hemoglobin molecule, the red blood cell pigment responsible for transport of oxygen and CO_2 in the blood [14,15]. Most of porphyrins often form so-called H-aggregates, where the neighboring molecules are stacked with their macrocycles "face-to-face" [16–18]. The physicochemical functions and spectroscopic properties of porphyrins and metalloporphyrins are related to the group and position of substituent at the porphyrin macrocycles. Therefore, the synthesis, structure and spectroscopic properties of porphyrins and metalloporphyrins continue to be an active and productive area [19,20].

Porphyrins have been used for the photosensitization of metal oxides, the most common of them are the metal-free tetraphenylporphyrin, H_2TPP, and zinc tetraphenylporphyrin, ZnTPP, they are also occupy the central interest to the study presented in this paper. These molecules consist of a central porphyrin ring and four phenyl (C_6H_5) rings attached to it through four C–C bonds, as shown in Fig. 1(a). As the Zn atom is introduced into the cavity of the H_2TPP molecule and bounded by four nitrogen atoms during the metalation process, the molecule becomes the zinc tetraphenylporphyrin, ZnTPP, as shown in Fig. 1(b). Due to the steric interaction between the hydrogen atoms on the porphyrin ring and phenyl rings, these rings are oriented nearly perpendicular to one another which decreases the overlap of the π-orbital located on these two parts of the molecule and consequently makes them almost completely electronically decoupled [21].

The absorption spectra of H_2TPP and ZnTPP films showed different bands depending on the method of its preparation [22,23]. The absorption spectra of H_2TPP in nematic liquid crystals have been studied [23]; the spectrum showed characteristic Soret band in the visible region 400–500 nm and four small bands in the Q-band region 500–650 nm. Harime et al. [23] obtained similar absorption spectra for H_2TPP dissolved in chloroform solvents.

The influence of temperature changes on the thermal and structural behavior of crystalline solvates of H_2TPP with 1,4-dioxane and of CuTPP with benzene were investigated using X-ray diffraction, thermogravimetry and differential scanning calorimetry techniques [24]. X-ray diffraction measurements showed that desolation in benzene caused a minor decrease in the volume of the unit cell containing the same number of CuTPP molecules. The symmetry of the crystalline lattice changed from monoclinic to triclinic crystal system. There is a reversible thermal effect for crystals of H_2TPP obtained both by sublimation and by crystallization from 1,4-dioxane.

The exposure of solid materials to ionizing radiations such as γ or X-rays irradiation produce changes in the microstructural

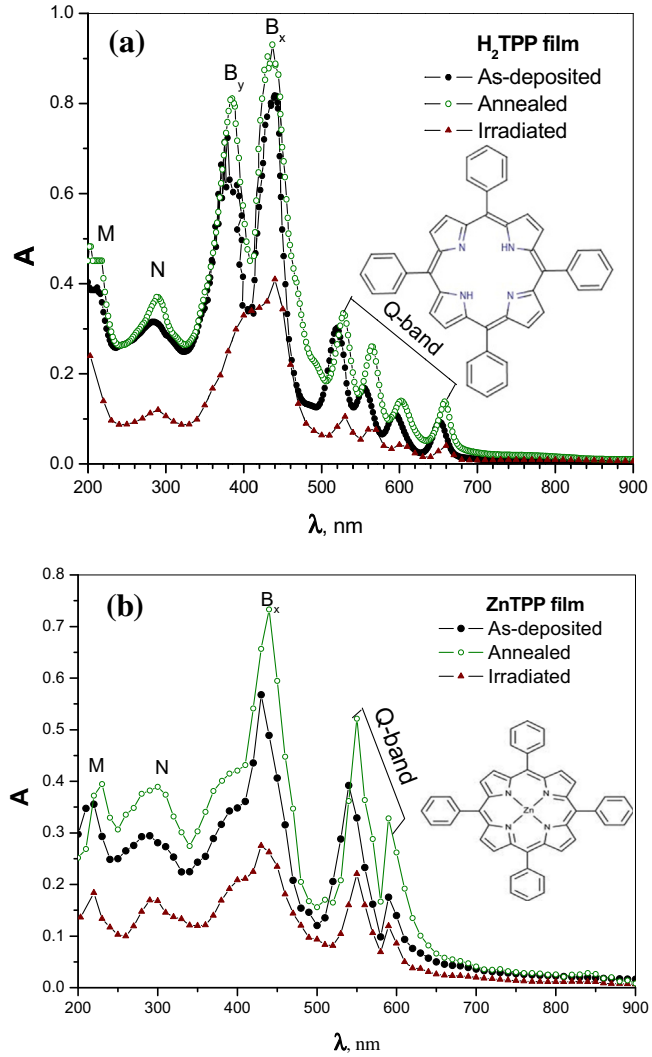

Fig. 1. Absorption spectra, *A*, as a function of wavelength, *λ*, for, (a) metal-free tetraphenylporphyrin, H_2TPP, and (b) zinc tetraphenylporphyrin, ZnTPP, thin films.

properties of the material as a result of inducing the structural defects, which in turn affect the optical properties. The change in structure depends on the type and dose of irradiation and sensitivity of the solid films to respective irradiation. The influence of γ or X-rays irradiation on the structural and optical properties of some porphyrins derivatives in the form of thin films has been investigated in Refs. [24–29]. The effect of γ-irradiation on the nickel tetraphenylporphyrin, NiTPP, thin film morphology has been investigated by XRD, AFM and TEM for as-deposited and γ-irradiated films [24]. The results show polycrystalline and amorphous nature for as-deposited and γ-irradiated NiTPP films, respectively. The optical properties of NiTPP thin films before and after gamma-irradiation have been investigated by means of spectrophotometric measurement. It is found that the energy band gap of 1.93 eV for as-deposited films, γ radiation decreased it to 1.65 eV. In addition, γ-irradiation affects the values of the calculated dispersion parameters such as oscillator energy, dispersion energy and dielectric constant. γ-Irradiation with doses up to 20 kGy decreases the refractive index, *n*, and extinction coefficient, *k*, of the iron(III) chloride tetraphenylphorphyrin, FeTPPCl [25]. The optical properties of 5,10,15,20-tetrakis (4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(II), CoMTPP thin films before and after irradiation have been studied in the spectral range 200–2500 nm and showed the energy