

Optical absorption of tetraphenylporphyrin thin films in UV–vis–NIR region

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Abstract

The optical absorption of thermally evaporated tetraphenylporphyrin (TPP) in the UV–vis–NIR region have been studied. The absorption spectra recorded in the UV–vis region for the as deposited and annealed films showed different absorption bands, namely the Soret(B) at region 360–490 nm, Q-band region consist of four bands in the region 500–720 nm and two other bands labeled N and M in UV region. The Soret band always shows its characteristic effect splitting in all the TPP thin films and the effect of annealing on the intensities of these components have been observed. The spectra of the infrared absorption allow characterization of vibrational modes for the powder, as deposited and annealed thin films. Some of the optical absorption parameters, namely molar extinction coefficient, ϵ , half band width, $\Delta\lambda$, electronic dipole strength, q^2 and oscillator strength, f , of the principle optical transitions have also been evaluated.
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1. Introduction

Porphyrins compounds have attracted much attention as promising materials because of their interesting properties as a optoelectronic [1], electron transfer [2], catalysis [3], non-linear optics [4], photodynamic therapy [5] and molecular semiconductors [6]. These compounds absorb visible light and convert photo-energy to electric energy [7]. Porphyrins and their derivatives are a ubiquitous class of naturally occurring compounds having important biological representative including hemes, chlorophyll and Vitamins B₁₂ among several others [8,9].

The basic structure of porphyrin consists of four pyrrolic subunits linked by four methane bridges, the Porphyrin skeleton has an extended π -conjugation system with 24- π electrons leading to a wide range of wave lengths for light absorption, the absorption spectra of the porphyrins are well known and their bands in different spectral regions are

denoted as Q, B, N, L and M [10]. The most representative of these are the Q, weak absorption, in the visible region and the Soret bands, B, which occurs in the near UV region showing the more intense absorption, the N, L and M bands are weak absorptions in the UV region, variations of substituents on the porphyrin ring often cause minor change to the intensity and wave length of these absorptions. These optical properties gives much attention so they have more potential technological applications in optical devices [11].

In general, the physicochemical functions and spectroscopic properties of porphyrins and metallo-porphyrins are related to the group and position of substituents at the porphyrin macrocycle. Therefore, the synthesis, structure and spectroscopic properties of porphyrins and metallo-porphyrins continue to be an active and productive area [12,13]. Due to the relatively high symmetry of tetraphenylporphyrin (TPP) as shown in Fig. 1, many investigations of the structure and properties of metallo-porphyrins derive from metallo-TPP studies. Numerous experiments have been carried out by Raman and IR spectroscopy on TPP and metallo-TPP, and reasonably assignments and calculations

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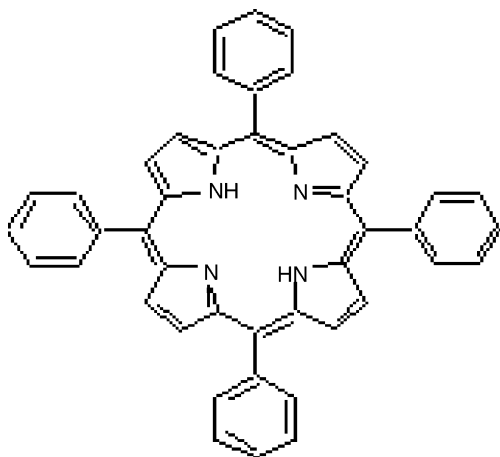


Fig. 1. Molecular structure for tetraphenylporphyrin (TPP).

have been reported [14–16]. Although the synthesis, electrochemistry and spectroscopic properties of porphyrins and their derivatives have been extensively studied [17–21], only a few studies concern the detailed assignment of the absorption bands in the infrared spectral region of tetraphenylporphyrin [17,19,21–23]. In particular, no precise work is reported in the case of infrared studies on TPP thin film and the influence of the heat treatment on this films.

The objective of this work is to study the optical absorption spectra of tetraphenylporphyrin thin films and determine important optical parameters: molar extinction coefficient, ϵ , half band width, $\Delta\lambda$, electronic dipole strength, q^2 and oscillator strength, f , of the principle optical transitions in the UV–vis–NIR region. The influence of the heat treatment on these parameters were also investigated.

2. Experimental details

Thin films of TPP were prepared by conventional thermal evaporation technique using high vacuum coating system (Edward model 306A, England). The films were deposited on the optical flat of quartz substrates for optical measurements. The quartz substrates were carefully cleaned by putting them in chromic acid for 15 min and then rinsed by deionized water. The material was sublimated from a quartz crucible source heated by a tungsten coil in a vacuum of 10^{-4} Pa during the deposition. The rate of deposition was controlled at 2.5 nm s^{-1} using a quartz crystal thickness monitor (Edwards, Model FTM4, Edward Co., England). The thickness of films was also monitored by using the same thickness monitor. A shutter, fixed near to the substrate, was used at the initial and final stages of evaporation to be sure that the films are deposited at the same rate. The shutter could also be useful for obtaining films purer than the powder where it prevents the impurities, which have vapor pressures different from tetraphenylporphyrin, from reaching to the substrates.

The absorbance spectra of films were measured at normal incidence at room temperature in the spectral range

of 200–2200 nm by using a computer-aided double-beam spectrophotometer (JASCO model V-570 UV–vis–NIR). An uncertainty of 1% was given by the manufacturer for the measurements obtained by this spectrophotometer. A blank quartz identical substrate to the one used for the thin film deposition was used as a reference for the absorption scan. The other films were prepared on potassium bromide (KBr) single crystals for IR measurements to identify the chemical and thermal stabilities of the material under study.

3. Results and discussion

In free base porphyrin the characteristics infrared vibration frequencies range can be classified in two categories:

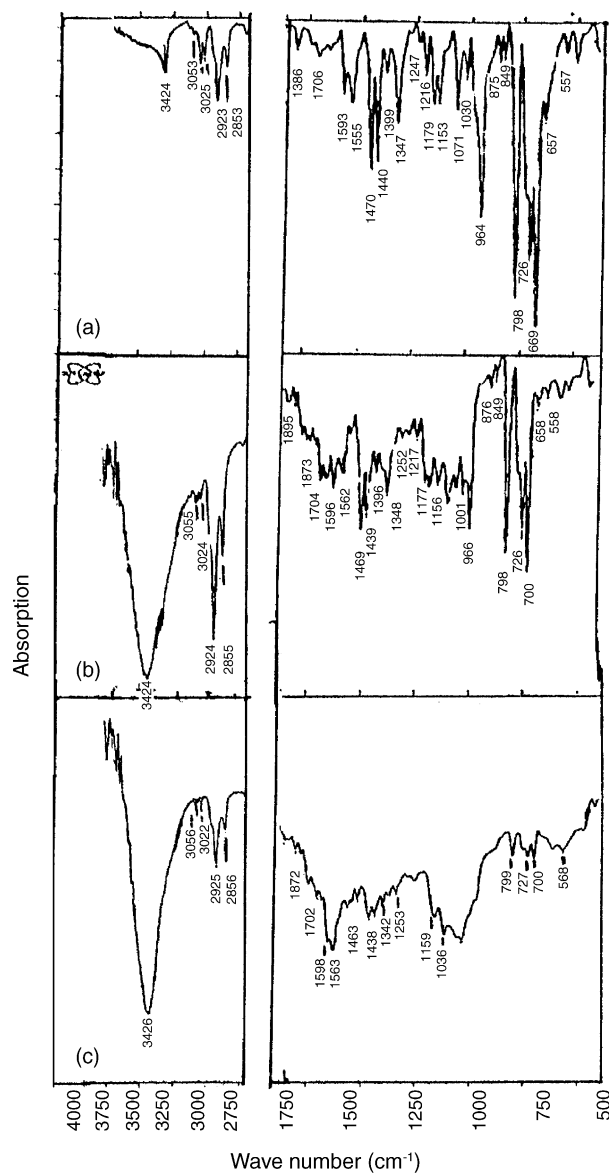


Fig. 2. Infrared spectra of TPP: (a) powder form; (b) thin film as deposited; (c) thin film, annealed at 373 K for 2 h.

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