



# Spectroscopic investigation of Tb(III) porphyrin in solid and solutions

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## Abstract

Characteristic Q and S (Soret) bands of metal porphyrins in the visible and near ultraviolet region are assigned as excited  $S_1$  singlet and the second excited  $S_2$  states. Upper excited-state emission has been observed for variety of diamagnetic metal porphyrins. In the paramagnetic systems emission depends on the position of CT, d- and f- excited states that could take part in the porphyrin emission quenching. In some kinds of porphyrins with f-electron metals, TPPEr(III)dpm types, porphyrin emission depends on the energy of the triplet and singlet states of  $\beta$ -diketone. The TPPTb(III)acac porphyrin was obtained in the solid state. Its structure was earlier described by different methods. Absorption, emission, IR and Raman spectroscopy were used to characterize Tb(III) porphyrin in solid and solution. Absorption spectra were measured at room temperature, emission and excitation ones at 293 and 77 K. Correlation of the spectroscopic results in solids makes possible considerations about the role of solvent molecules in modifications of the structure of porphyrin complex in solutions. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Tb(III) porphyrin; TPPEr(III)dpm; TPPTb(III)acac

## 1. Introduction

Lanthanide porphyrins exhibit two features: (1) ability to be accumulated in many kinds of cancer cells and (2) 'specific' paramagnetic and optical properties of lanthanide(III) ions. These characteristics make them useful in the photodynamic method of therapy and cancer diagnoses [1–3]. Lanthanide porphyrins can be also used as a paramagnetic contrast in MRI spectroscopy as was described by Marzalo and Cannistrato [4] for gadolinium porphyrin. The earlier published papers dealt mainly with synthesis of lanthanide porphyrin monocomplexes but full their characterization was not carried out. The X-ray structure was described for ScTPP(CL) (TPP, 5,10,15,20-tetraphenylporphyrin) [5] but not for any f-electron elements. The structures proposed for such systems (e.g. GdTPP(acac) [6]) and schemes of describing lanthanide porphyrin complexes are based on the scandium porphyrin data [5]. The main goal of this paper is to investigate the spectroscopic properties of TbTPP(acac) (I),  $H_2$ TPP (II) in solids and to compare them with similar data in solutions at room and 77 K temperatures. For comparison some results for Tb(acac) (III) compounds will be presented, too. In particular, we tried to elucidate the effect of structure changes on optical properties of complex under study and the role of solvent molecules. Compounds I, II and III in which the axial substituents are coordinated in I and

arranged in the similar order as in II are good candidates for that kind of investigation.

## 2. Experimental

Compounds I, II and III were obtained according to the procedures described in [6]. Absorption spectra of solids I and II were measured in nujol and methanol solutions using a Cary-Varian 5 spectrophotometer and emission spectra on SLM Aminco SPF-500 spectrofluorometer using neodymium excimer laser and xenon lamp as the excitation sources. IR spectra were recorded using Bruker FS 88 FTIR spectrometer.

## 3. Results and discussion

Fig. 1 shows the absorption spectra of TbTPP(acac) (I),  $H_2$ TPP (II) in methanol, where  $H_2$ TPP has  $D_{2h}$  (*mmm*) symmetry, but that of metal complex is  $D_{4h}$  (*4 mmmm*). The simple axial ligand can disturb the symmetry but does not change it drastically [6]. In the UV–vis absorption spectra of porphyrin in the Q bands one can distinguish four components [ $Q_x(0,0)$ ,  $Q_x(1,0)$ ,  $Q_y(0,0)$ ,  $Q_y(1,0)$ ] but in the case of the metal porphyrin of  $D_{4h}$  (*4 mmmm*) symmetry only two components [ $Q(0,0)$ ,  $Q(1,0)$ ];  $x$  and  $y$

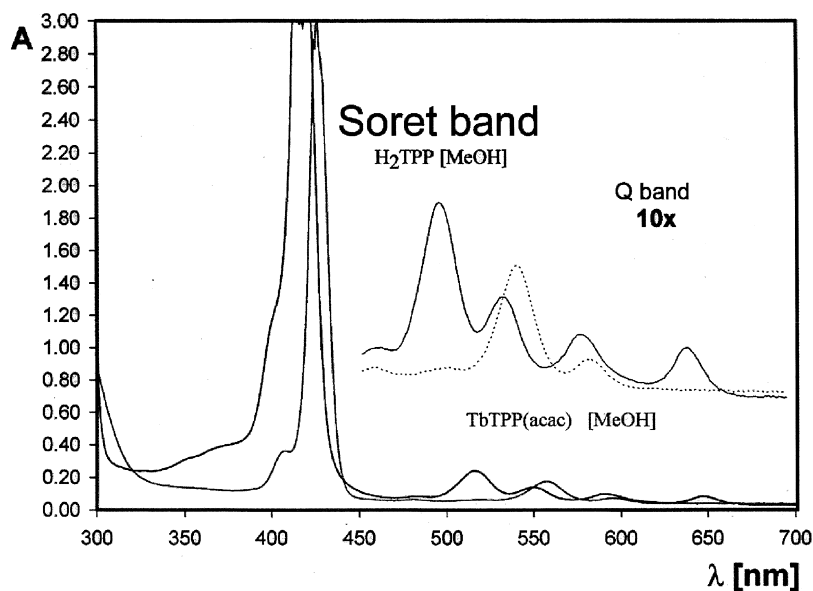


Fig. 1. Absorption spectra of TbTPP(acac) (I) and  $H_2TPP$  (II) in methanol.

are axes which are parallel and perpendicular to the line linking hydrogen atoms connected to nitrogen atoms in the pyrrol chain of porphyrin. Disappearance of Q components

with symmetry changing from  $D_{2h}$  to  $D_{4h}$  can be attributed to increasing possibilities of oscillation in free porphyrin. On contrary, B-Soret band did not change in por-

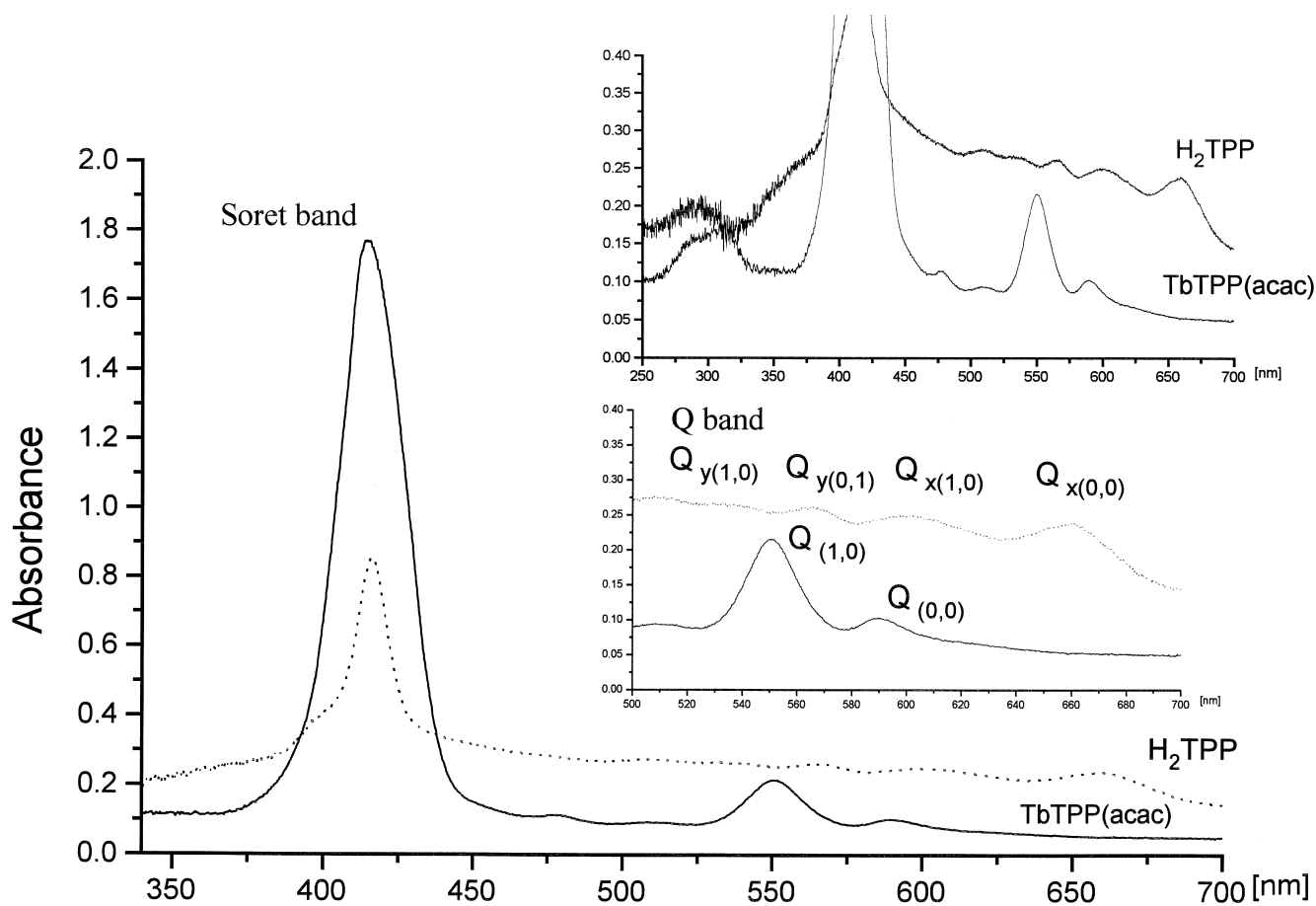


Fig. 2. Absorption spectra of TbTPP(acac) (I) and  $H_2TPP$  (II) in nujol.

phyrin. In metal porphyrin spectrum the tail at 400 nm became more distinct. This tail is visible at the edge of  $B_{(0,0)}$ -Soret band, both in the spectrum of porphyrin in nujol and that of  $H_2TPP$  in methanol (Fig. 2). However, the component of Q band ( $Q_{y(1,0)}$ ) which was the most intense in the spectrum of  $H_2TPP$  in methanol, in the solid state spectrum is present as two low intense components. Because the rest of the band did not exhibit any changes in solid state one can conclude that the structure of porphyrin in alcoholic solution is undisturbed and the observed changes are due to hydrogen bonding formation. In the spectrum of  $TbTPP(acac)$  in nujol (Fig. 2) the  $B_{(0,0)}$ -Soret band is compact and the tail, visible in the spectrum of  $TbTPP(acac)$  in methanol, disappeared. Moreover, the Q band in solid state, like in the case of  $TbTPP(acac)$  in methanol, consists of two components [ $Q_{(0,0)}$ ,  $Q_{(1,0)}$ ]. This band did not change in transition from solution to solid state. Comparison of solid state spectra of porphyrin and metal porphyrin indicates sensitivity of Q band (at 500 nm) on complexing process because its energy and intensity changed. The band at 650 nm in the spectrum of metal porphyrin almost disappeared (Fig. 2). Two explanations are possible: (1) the metal ion position is out of plane of the porphyrin ring, what was suggested by Kaizu et al. [7], and then attachment the solvent molecule in axial position

in relation to  $\beta$ -diketone disturbs the symmetry of the system insignificantly, (2) the process of exchanging solvent molecule and fluctuation in the metal position with respect to porphyrin ring is fast enough and the mean structure is close to that in solid state.

The IR spectra of three types of compounds given in Figs. 3 and 4 confirm metal–porphyrin interaction.

Our efforts to detect emission in complexes I and II in solid failed. Most probably self quenching is the reason for the lack of emission in II but in I more complex processes could be considered. Full emission properties of the three systems investigated will be the subject of our future studies.

#### 4. Conclusions

1. Absorption spectra of metalporphyrin in solution and solid state indicate similarities of the structure of both systems.
2. It was shown that the Q band (550 nm) is the most sensitive on complexing process.
3. Electronic and IR spectra provide information about complexing porphyrin to lanthanide ions.

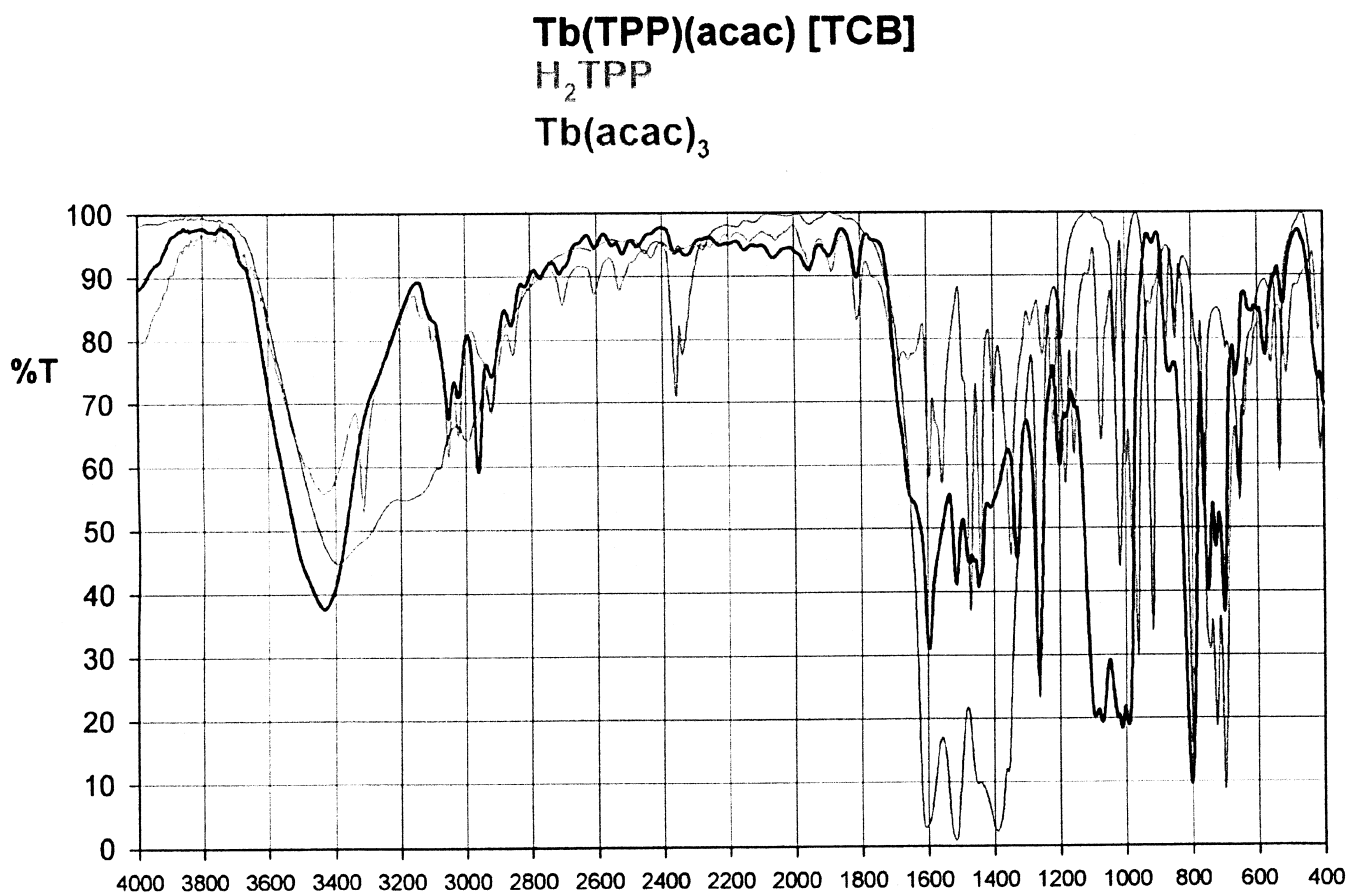


Fig. 3. IR spectra of I, II and III in the 400–4000  $cm^{-1}$  range.

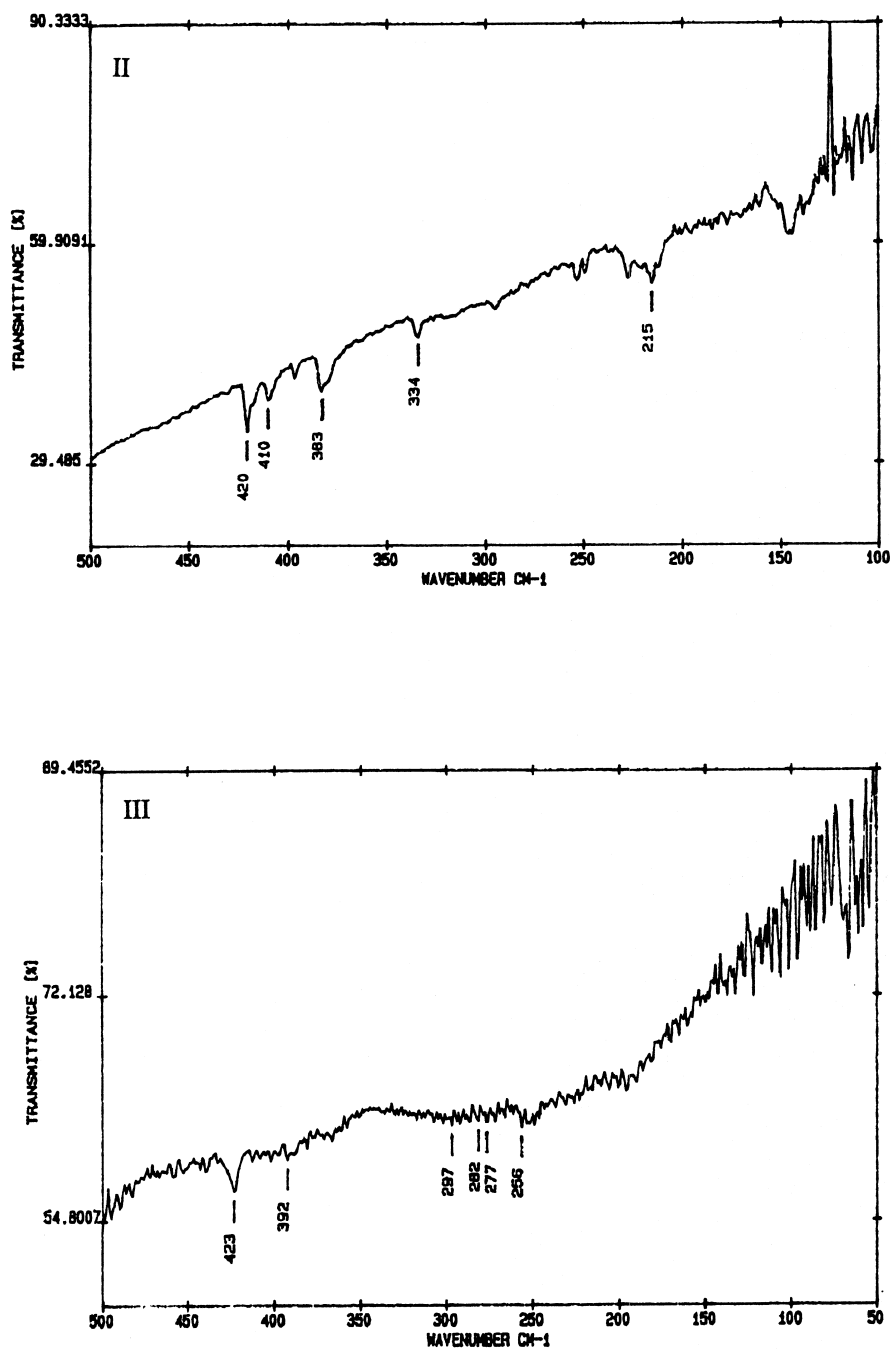


Fig. 4. IR spectra of II and III in the 100–500 cm<sup>-1</sup> range.

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