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Optical and magneto-optical characterization of thin films of functionalized tetraphenylporphyrins

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ABSTRACT

The anisotropic optical constants of vacuum deposited films of H₂TMPP, CuTMPP, and NiTMPP (TMPP = 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin) in the thickness range of 50 to 150 nm were obtained by spectroscopic ellipsometry measurements and subsequent modelling. The angle of the planar molecular backbone with respect to the substrate plane was determined from the degree of optical anisotropy of the optical constants. The resulting angles were compared to those of near edge X-ray absorption fine structure (NEXAFS) spectroscopy on 2 to 5 nm thick films. Gold and natively oxidised silicon were used as substrates. The molecular tilt angle on Si (~38°) was found to be slightly smaller than on gold (~41°) for the thick films. This trend was confirmed by NEXAFS. Magneto-optical Kerr effect spectroscopy was applied in order to obtain the off-diagonal elements of the dielectric tensor under a magnetic field. These results were then used to calculate magnetic circular dichroism spectra for comparison with literature results and the assignment of Faraday terms to the particular absorption features.

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1. Introduction

Porphyrins and their metal complexes rank among the most frequently occurring and most important macrocyclic compounds in nature and are therefore part of many biological and chemical processes like photosynthesis and oxygen transport as well as oxidation and reduction [1]. However, the functionalization of these compounds in order to tailor their properties is still a highly actual research topic, especially as they have gained great interest as active materials in various organic electronic devices, including organic spintronic devices [2,3]. Assembling these compounds as thin films on surfaces in a well-defined way is an important step towards the goal of constructing such devices. In the present work, we investigate the class of 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrins (= TMPP; Fig. 1). This family of molecules is stable against thermal evaporation in vacuum enabling to obtain films of very homogeneous thicknesses with excellent thickness control. In order to estimate the molecular orientation of the molecules on the substrate surface, we used variable angle spectroscopic ellipsometry (VASE) in the UV/Vis spectral range and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. In addition, magneto-optical Kerr effect (MOKE) spectroscopy was conducted to extract information about the energy states involved in the optical transitions of these molecules.

2. Experimental section

Porphyrin H₂TMPP was synthesized by the direct condensation of the appropriate functionalized benzaldehyde with pyrrole in propionic acid under reflux as described Adler et al. [4]. After purification the desired metalloporphyrins MTMPP (M = Cu, Ni) were obtained in a subsequent reaction with the respective metal(II) chloride MCl₂ in dimethylformamide [5]. These molecules were deposited by means of organic molecular beam deposition (OMBD) in a vacuum chamber at a base pressure of 1 · 10⁻⁴ Pa. With acetone, ethanol and distilled water cleaned silicon (111) pieces with a native oxide layer of about 2 nm and silicon pieces covered with a 100 nm thick gold layer were used as substrates. To make the subsequent ellipsometry modelling more reliable, layers of three different thicknesses have been produced and then modelled with the same dielectric function (coupled analysis). The sublimation temperatures of the metalloporphyrins were 300–310 °C, whereas the H₂TMPP already sublimated at 295 °C due to its lower molecular weight. A quartz oscillator placed near the sample was used to control the deposition rate during the process. Typically a deposition rate of 5–7 Hz/min, which corresponds to ~0.5–1 nm/min, was used.

VASE measurements were performed with the M-2000 T-Solar from the J.A. Woollam Company. For analyzing the data, the software “CompleteEASE” was used. Measurements were performed in reflection geometry at three different angles (65°, 70°, and 75° with respect to the substrate normal) and energies between 0.7 and 5.0 eV. The data were modelled using a uniaxial dielectric tensor with the components corresponding to the directions of the film plane different from that

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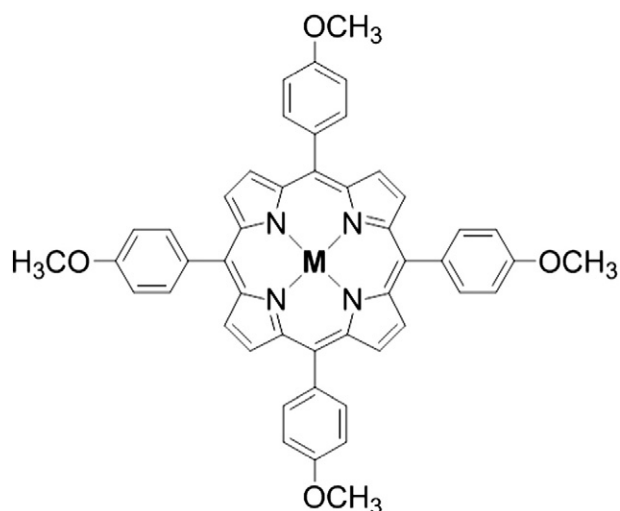


Fig. 1. 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin TMPP (M = 2H, Cu, Ni).

perpendicular to it. However, it was assumed that films of the same material with different film thicknesses possess the same dielectric tensor, and therefore, only the different thickness accounts for the differences in the measured VASE data.

MOKE spectroscopy was used to investigate the absorption behaviour of the TMPPs under influence of an external magnetic field with $B = 1.7$ T.

This experimental technique measures the change in polarization (represented by the complex Kerr angle $\theta_K = \theta_K + i\eta_K$) in a polar reflection geometry. To eliminate the signal related to the optical anisotropy, both field directions perpendicular to the sample were measured and the MOKE spectrum was calculated as their half difference.

NEXAFS measurements were performed at the RGL-station (Russian-German beamline) of the Helmholtz-Zentrum Berlin. The total electron yield of the N K-edge was collected at 4 incidence angles. Consequently, the current of a gold mesh inserted in the beam in front of the sample was measured and used for data normalization. All measurements were performed in ultra-high vacuum conditions with a base pressure of $5.0 \cdot 10^{-8}$ Pa.

The samples were prepared by OMBD in a separated chamber and transferred into the analysis chamber without breaking the vacuum. The sublimation temperature was between 280 °C and 310 °C, depending on the molecule. Using a low deposition rate of 0.05 nm/min, films with thicknesses from 0.5 nm to 5.0 nm were produced.

3. Results and discussion

3.1. Optical investigations

Exemplarily, the measured ellipsometric parameters (Ψ and Δ) as a function of photon energy are presented for H_2 TMPP in Fig. 2 by continuous lines. These data were first modelled using a Cauchy-fit in a non-absorbing energy range of the spectrum (0.7–1.75 eV) for thickness determination. Then a general oscillator model was developed for the whole spectrum to simulate a dielectric function ϵ , which describes the measured data best. Therefore, the imaginary part of ϵ has been described with Gaussian oscillators resulting in a Kramers–Kronig consistent model for this material. The results of the numerical fit with the uniaxial anisotropic model are shown by the dotted lines in Fig. 2.

The imaginary part of the optical constants determined from the VASE data fitting is shown in Fig. 3 for all three measured porphyrin complexes.

The extinction coefficient spectra show a low intensity Q band in the visible energy range and a high intensity B band (or Soret band) in the ultraviolet energy range. This shape of the absorption spectrum is

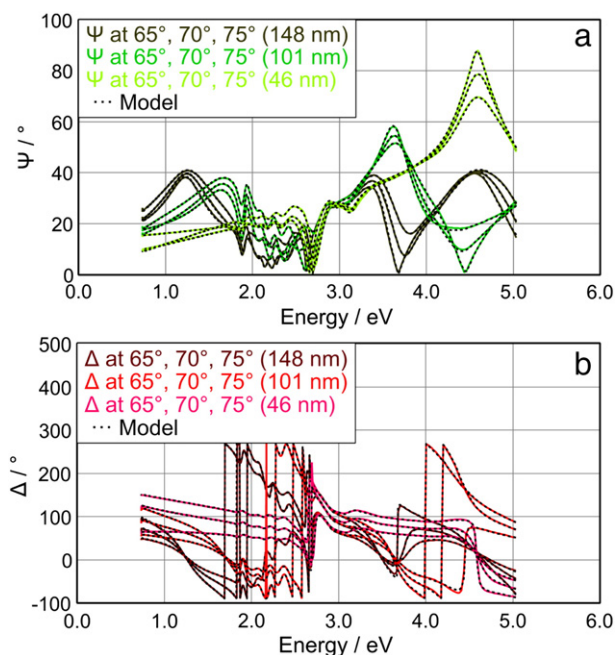


Fig. 2. VASE data (a) Psi (Ψ) and (b) Delta (Δ) at three different incident angles (65°, 70° and 75°) for thin films of H_2 TMPP. Dotted line shows the developed model. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

typical for porphyrins [6]. Similar to the phthalocyanines, in the metal porphyrins, the Q band is usually split in two peaks due to a vibrational progression [7]. The larger number of peaks present in the Q band of the H_2 TMPP as compared to the metal TMPPs can be explained, similar to other porphyrin families, by a splitting of the Q band of free base porphyrins from two (in metalloporphyrins) into four peaks (in metal free porphyrins) due to a symmetry reduction which removes the orbital degeneracy of involved energy states [1,8].

All porphyrin films exhibit an anisotropic absorption behaviour reflected by the difference of in- and out of plane absorption intensity (see Fig. 3).

This anisotropy of the extinction coefficient k gained from the modelled VASE data can be used to determine the tilt angle α of the molecules with respect to the substrate [9]. The degree of anisotropy A_{out}/A_{in} was determined by integrating k over energy in the area of the Q band (H_2 TMPP: 1.8–2.5 eV, CuTMPP: 2.0–2.4 eV, NiTMPP: 2.1–2.5 eV; see Fig. 4).

In the study of Edwards et al. [10], the peak at 1.7 eV was observed to rise during an absorption measurement run, leading to the conclusion that the exposure to the measurement beam yields a decomposition of the material. This conclusion is supported by the fact that this peak does not follow the degree of anisotropy of the rest of the spectrum. In our case, the relative intensity of this peak is very low, indicating that the content of decomposition products is small enough to leave the shape of the Q band intact. Therefore, our model should still give reasonable results.

Eq. (1), which is used to calculate the molecular tilt angle with respect to the substrate plane α [9,11], gives an average value for the measured area on the sample.

$$\alpha = \arccos \sqrt{\frac{2 - A_{out}/A_{in}}{2 + A_{out}/A_{in}}} \quad (1)$$

One assumes that the geometry of the porphyrin macrocycle is planar leading to a maximum of in-plane absorption, when the molecules are parallel oriented to the surface (molecule normal perpendicular to the substrate, $\alpha = 0^\circ$) and a maximum of out of plane absorption in

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