

Magneto-Optical Kerr Effect Spectroscopy—A Sensitive Tool for Investigating the Molecular Orientation in Organic Semiconductor Films

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The detection and control of the molecular growth mode is a key prerequisite for fabricating opto-electronic devices. In this work we present the magneto-optical Kerr effect (MOKE) spectroscopy to be a highly sensitive method for the detection of the molecular orientation. On the example of metal free phthalocyanine (H₂Pc) in thin films, it will be shown that also for diamagnetic molecules a strong magneto-optical response can be expected. The growth mode and thus the intensity of the MOKE signal of H₂Pc is strongly influenced by a templating effect using ultrathin layers of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA). From the MOKE spectra in the energy range from 1.5 to 5.0 eV and the optical constants, the Voigt constant of thin organic films was determined. From the strong in-plane/out-of-plane anisotropy of the optical constants and the value of the Voigt constant the average molecular tilt angle of H₂Pc molecules with respect to the substrate plane can be obtained.

Introduction

A great advantage of implementing molecular systems in hybrid devices is that their properties can be tuned according to the desired application thanks to the large flexibility arising from the carbon chemistry; see, e.g., ref 1. Optical methods have been demonstrated to provide a highly sensitive and rapid way to read and write information.^{2,3} Here it will be shown that the measurement of the magneto-optical response of a molecular film in reflection provides not only access to the intrinsic magneto-optical properties of the material but also a highly sensitive tool to determine the molecular orientation within the film. It should be noted that up to date spectroscopic methods like ellipsometry, IR, Raman, and angular resolved near X-ray absorption fine structure were employed for the determination of the molecular orientation; see, e.g., Zahn et al.⁴ and the references therein.

Magneto-optical studies in the ultraviolet, visible, and near-infrared (UV/vis/near-IR) spectral range of molecular magnetic thin films were so far only performed in transmission, e.g., for M_{1.5}[Cr^{III}(CN)₆]•(H₂O)_n (M = Co(II), Ni(II), Cu(II))⁵ and V(II/III)-containing hexacyanochromate(III) complexes⁶ embedded in an organic matrix. Recently, the first magneto-optical Kerr effect studies of transition metal complexes, namely, CuPc and VOPc, were reported.⁷ These are the only examples of measurements on molecules in reflection, even though MOKE spectroscopy was already successfully used for studies of inorganic ferromagnetic layers,^{8–10} magnetic semiconductors,¹¹ magnetic nanostructures,^{12–14} while single wavelength MOKE is readily applied for reading magneto-optical (MO) disks.¹⁵

In this work the MOKE spectroscopy studies of a pure organic compound, namely metal free phthalocyanine (H₂Pc), will be discussed (Figure 1). Differences in the orientation of H₂Pc

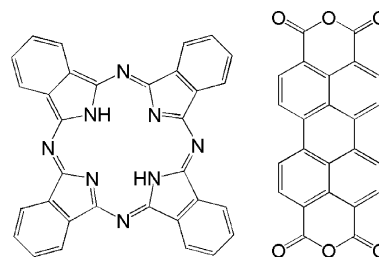


Figure 1. Chemical formula of H₂Pc (left) and PTCDA (right).

molecules were artificially induced by growing H₂Pc on different substrates, namely, Si/SiO₂ and Si/SiO₂/PTCDA, to study the sensitivity of MOKE spectroscopy with regard to the molecular orientation.

The molecules of H₂Pc were used as the model system since they have a good thermal stability and are hence well suited for the controlled deposition of thin films by thermal sublimation in vacuum. On the other hand, the phthalocyanines show semiconducting and photoconducting properties and are often used as active layers in organic based electronic or optoelectronic devices.¹⁶ In view of possible applications in the emerging field of organic-based spintronic devices, their magneto-optical activity in the reflection mode may be of high interest.

The crystal structure of molecular films can be influenced by various parameters such as temperature, pressure, or even the substrate on which the molecules are grown. PTCDA molecules lie flat on a variety of substrates, including, e.g., Si substrates. It was already shown that a PTCDA template layer can favor a flat orientation of the H₂Pc molecules deposited onto it.^{17,18} One reason for this template effect was proposed to be a strong electronic interaction between the π electron systems of the H₂Pc and the PTCDA molecules. This enforced growth mode relaxes gradually with increasing distance from the H₂Pc/PTCDA interface.¹⁸

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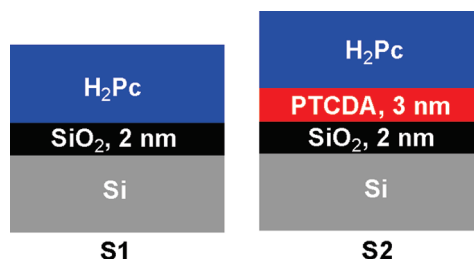


Figure 2. Schematic of the investigated samples.

Experimental Section

The organic layers were produced by organic molecular beam deposition onto Si covered with native oxide and quartz substrates simultaneously. For the sample labeled S1, the H₂Pc was directly grown on Si/SiO₂, and for sample labeled S2, the Si/SiO₂ substrate was covered with 3 nm of PTCDA prior to the H₂Pc deposition; see Figure 2 for a sketch of the sample structures. The H₂Pc and PTCDA layers were deposited with a rate of 0.5 nm/min at a base pressure of 8×10^{-7} mbar. The samples grown on Si/SiO₂ substrates were investigated by means of spectroscopic ellipsometry (SE) and MOKE spectroscopy, while the layers grown on quartz were used for MCD investigations.

Ellipsometry measures the quantities ψ and Δ , which are related to the ratio of the effective Fresnel coefficients r for s- and p-polarized light by the expression $r_p/r_s = \tan \Psi \exp(i\Delta)$. By modeling the data, we determine the thickness and complex dielectric functions of the films. The variable angle spectroscopic ellipsometry (VASE) measurements presented here were performed using an ellipsometer from the company J. A. Woollam Co., Inc.

After transmission of light through a magnetized sample, the change in the state of polarization is described by the complex rotation

$$\Theta_F = \theta_F + i\eta_F \quad (1)$$

It consists of the rotation θ and the ellipticity η , which are the real and the imaginary parts of the Faraday rotation, respectively. The former is called magnetic circular birefringence (MCB) and the latter is known as the magnetic circular dichroism (MCD) effect. For thin films of the thickness d the MCD signal can be calculated according to¹⁹

$$\Theta_F = \theta_F + i\eta_F = \frac{\omega}{2c} \tilde{n} Q d \quad (2)$$

with ω being the angular frequency of the light, c the light velocity, and \tilde{n} the complex index of refraction. The change in the polarization state induced by reflection on a sample in a magnetic field is called magneto-optical Kerr effect (MOKE)^{20,21} and can be described by θ_K and η_K .

The MOKE measurements were carried out ex situ with a homemade setup similar to that described by Herrmann et al.²² It is constructed to detect very small rotation angles of the polarization of about 10^{-3} or even smaller. Taking into account the applied magnetic field that is oriented parallel to the sample normal either in “+B” or in the opposite direction “−B”, the Kerr angle can be determined according to $\Theta_K = (\Theta_{+B} - \Theta_{-B})/2$. The angle of incidence of the light is close to zero (1.3°) and the magnetic field strength applied during the measurements is

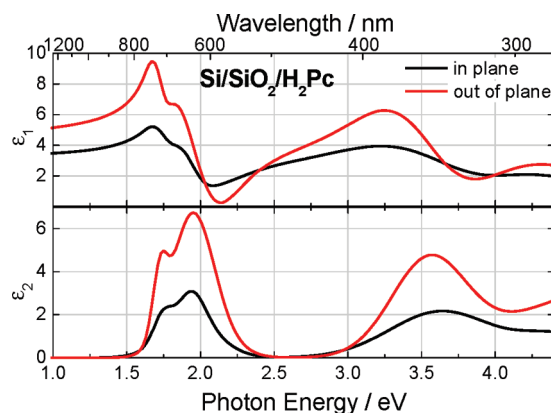


Figure 3. Dielectric function of H₂Pc grown on Si/SiO₂.

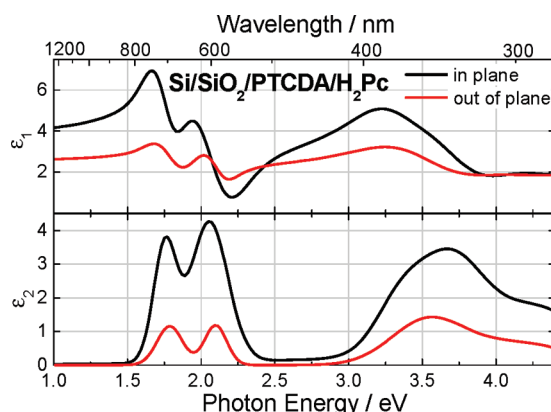


Figure 4. Dielectric function of H₂Pc grown on Si/SiO₂/PTCDA, in the region close to the H₂Pc/PTCDA interface.

0.35 T. The sign of the MOKE spectra is defined as in ref 22 following a sign convention often used in the literature.

The MCD spectra were obtained using a home-built instrument consisting of a JASCO J-715 spectropolarimeter and an Oxford Instruments SPECTROMAG magnetocryostat. The spectra were recorded for the organic films grown on quartz glass. The measuring procedure is analogous to the MOKE measurements whereas MCD measurements were performed in transmission.

Results and Discussion

Spectroscopic Ellipsometry Studies. Figures 3 and 4 show the Kramers–Kronig consistent dielectric functions of H₂Pc grown on Si/SiO₂ (S1) and Si/SiO₂/PTCDA (S2), respectively. They were derived from the VASE spectra recorded for three angles of incidence ($\Phi = 65^\circ, 70^\circ$, and 75°) shown in Figure s1 of the Supporting Information. Selected fit parameters are summarized in Table s1 and s2 (Supporting Information).

The dielectric function can be significantly influenced by the molecular orientation. Due to the strong correlation between the dielectric function and the film thickness in the modeling of the VASE data, it is useful to investigate several samples having the same dielectric function and different thickness and fit their experimental spectra simultaneously. Therefore two samples having different thicknesses, namely 45 nm (S1–45 and S2–45) and 97 nm (S1–97 and S2–97), were prepared for each system. The dielectric functions are described by the Cauchy equation $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$, where A , B , and C are fit parameters and λ is the wavelength of light, in the range from 1.0 to 1.4 eV, and by a sum of Gauss oscillators in the absorbing spectral range from 1.4 to 4.4 eV.

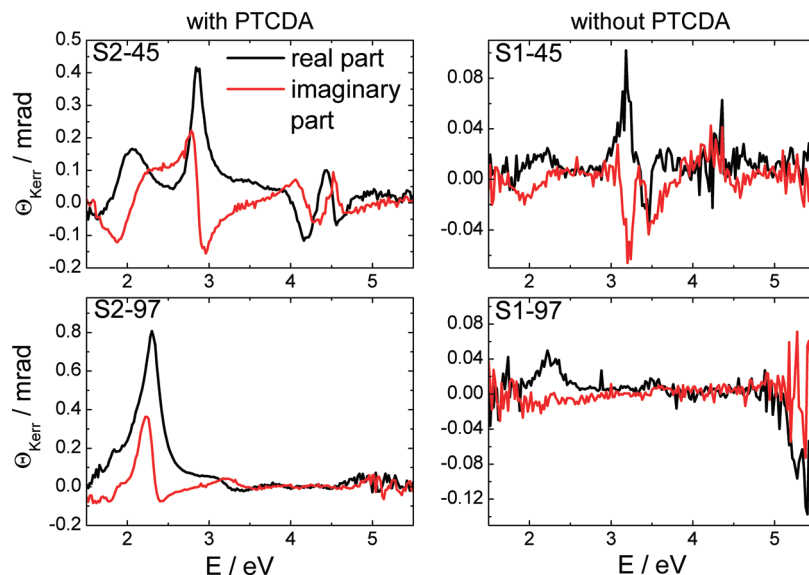


Figure 5. MOKE spectra of four different H₂Pc samples with different film thicknesses grown on Si/SiO₂/PTCDA (left) and Si/SiO₂ (right).

TABLE 1: Values of the Angle between the Molecular Plane of H₂Pc and the Substrate Plane Calculated from SE Investigations^a

H ₂ Pc layers	angle α /deg from SE	$\cos(\alpha)$	normalized cosine	normalized Q magnitude	angle α /deg from MOKE
S1-45	82 ± 6	0.14 ± 0.07	0.16 ± 0.08	0.12 ± 0.03	81 ± 2
S2-45	29 ± 6	0.87 ± 0.03	1.00 ± 0.03	1.00 ± 0.03	29 ± 4

^a The magnitude of the Q constant was determined at 2.23 eV. The normalization was done with respect to S2-45. The angle in the last column was calculated from $\arccos(Q)$.

Additionally, the surface roughness was included in the model, described as a mixture of 50% material and 50% voids.²⁵ Modeling the samples with H₂Pc on a PTCDA thin film required a more sophisticated model because of the template effect of PTCDA on phthalocyanine films grown on top. This model assumes that the H₂Pc molecules at the H₂Pc/PTCDA interface adopt a flat orientation and allows a relaxation of the molecular orientation of H₂Pc with increasing film thickness up to a distance from the interface of more than about 30 nm. The outermost part of the H₂Pc film was consequently modeled using a uniaxial anisotropic dielectric function of H₂Pc as obtained from the layers grown directly on SiO₂, plus surface roughness. For the transition region a graded layer with Bruggeman effective medium approximation in 10 steps was used. At the interface to PTCDA a uniaxial anisotropic mathematical model for the unknown dielectric function was applied.

The dielectric function determined for H₂Pc on SiO₂ implies a large tilt angle α of the molecular plane with respect to the substrate plane, as the out-of-plane component is stronger than the in-plane component (cf. Figure 3), indicating that the coupling between the transition dipoles and the component of the electric field vector perpendicular to the sample plane is stronger than the coupling to the component of the electric field vector parallel to the sample plane. Since the transition dipoles corresponding to the bands centered around 2.0 eV and around 3.5 eV lie within the molecular plane, this implies that the molecular plane adopts a tilt angle α larger than 54°. In the case of H₂Pc grown on PTCDA the in-plane component of the dielectric function is significantly stronger than its out-of-plane component (cf. Figure 4), indicating a small tilt angle α . It has to be stressed, however, that this model holds only for the first nanometers of H₂Pc in the vicinity of the H₂Pc/PTCDA interface. For higher film thicknesses the molecules tilt upward into an alignment imposed by their bulk crystal structure.

It was previously shown¹⁷ that the orientation of the molecules with respect to the substrate plane can be estimated from the ratio of the out-of-plane and the in-plane component of the optical constant k in the spectral range of the optical transition between 1.5 and 2.4 eV (Q-band). To estimate the molecular tilt angle α with respect to the substrate plane from the anisotropy of the dielectric function, a few assumptions are made regarding the properties of the H₂Pc films:

- the absorbance is proportional to the \cos^2 of the transition dipole moment,
- the molecular orientation is isotropic in the azimuthal plane
- the single molecule can be considered to have disk symmetry in absorption since the Q-band of H₂Pc originates from two nearly degenerated optical transitions with transition dipoles lying within the molecular plane.

Under these assumptions the angle α is calculated using the following dependence on the area below the Q-band in the in plane (A_{in}) and out of plane (A_{oop}) components of $k \cdot \omega$:

$$\alpha = \arccos \sqrt{\frac{2A_{in} - A_{oop}}{2A_{in} + A_{oop}}} \quad (3)$$

The angles $\alpha_{S1-45} = 82 \pm 6^\circ$ and $\alpha_{S2-45} = 29 \pm 6^\circ$ were determined for H₂Pc grown on Si/SiO₂ (S1-45) and Si/SiO₂/PTCDA (S2-45), respectively.

Magneto-Optical Kerr Effect Investigations. The MOKE spectra measured on the samples with PTCDA (S2-45 and S2-97) and without PTCDA (S1-45 and S1-97) are shown in Figure 5. The main spectral features shift toward lower energies with increasing film thickness—an indication that they are strongly influenced by interference effects.

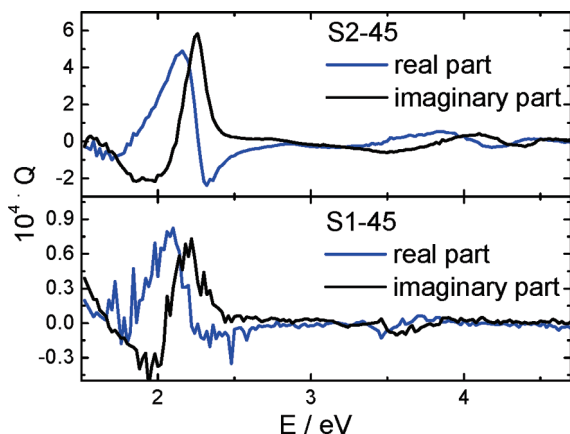


Figure 6. Voigt spectra of H₂Pc grown on Si/SiO₂ and on Si/SiO₂/PTCDA.

Calculation of the Voigt Constant. The Voigt constant Q can be obtained from the MOKE spectra recorded in polar MOKE geometry, a method that has already been applied to ferromagnetic films with thicknesses well below the penetration depth of the light where the Voigt constant lies in the order of magnitude of 10^{-2} .²² Since thin films of organic semiconductors are expected to have a very low Voigt constant, in the order of 10^{-5} , the magneto-optical investigations are commonly performed in transmission, by means of MCD, taking advantage of the higher sensitivity of this method compared to measurements in reflection.

A general model for the determination of the Voigt constant of thin films was proposed by Zak et al.²³ In the present case some simplifications can be done thanks to the polar measurement geometry.⁷

The investigated samples can be modeled as three layer systems. The incident light comes from the air side represented by a layer with infinite thickness and the refractive index $n_A = 1$. The second layer is the organic film with the thickness d and optical constants known from ellipsometry investigations. Below this film lies the silicon substrate whose effective optical constants also were determined by ellipsometry. Due to its low thickness (3 nm), the contribution of the PTCDA layer to the MOKE signal of the samples S2 can be neglected.

The numerical calculations were performed using the Matlab software. The contribution of the optical anisotropy of the sample which can be measured by means of reflection anisotropy spectroscopy was neglected herein because this part is eliminated by processing the difference between two measurements at opposite magnetic field directions.

Determination of the Molecular Orientation. The Voigt spectra, i.e., the energy dispersion of the Q values, of the samples S1-45 and S2-45 are shown in Figure 6. The interference effects present in the MOKE spectra are removed in the Voigt spectra—a fact that provides the first validation of the model outlined in the previous section. The model was further checked by inserting the calculated Q values and the optical constants into the eq 2 to obtain the MCD spectrum. In Figure 7 the MCD ellipticity calculated from the Voigt spectra is compared with the experimental results obtained for a 46 nm thick sample at $B = 0.35$ T. Good agreement in the shape and the magnitude of the calculated and experimental MCD spectra is found, which provides an independent proof of the proposed model. However, some minor differences in the signal height and small spectral shifts are apparent. This can be due to slight structural differences in the organic films grown on the quartz

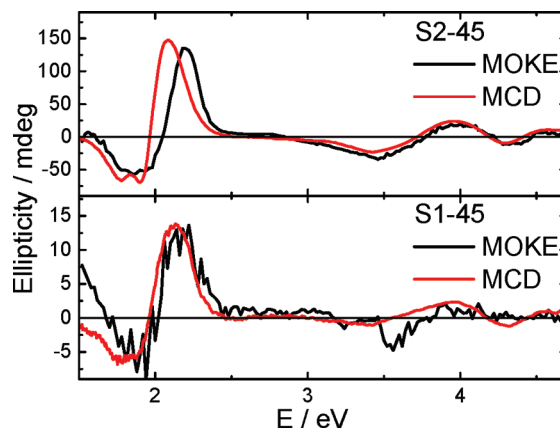


Figure 7. Ellipticity derived from MOKE and MCD spectra for H₂Pc grown on Si/SiO₂ with (S2-45) and without PTCDA (S1-45) as interlayer.

and silicon substrates for MCD and MOKE investigations, respectively.

The spectrum of the Q parameter in Figure 6 of the sample S1-45 shows significantly less intensity (almost by a factor of 10) than that of the sample S2-45, cf., e.g., the value for Q at 2.23 eV. The same trend was observed for the ellipticity.

The influence of the molecular orientation on the magneto-optical response has already been used in ref 24 to explain MCD results. There it was suggested that 2D transitions polarized in the molecular plane, such as the almost degenerated Q-band transitions of the phthalocyanines, produce a maximum MCD signal for light incident normal to the molecular plane and zero signal for light propagating within the molecular plane. Thus for light incident normal to the sample surface, perfectly lying molecules would yield a maximum MCD signal while standing molecules would give no signal. This hypothesis also holds for the Voigt constant, even though the exact angular dependence may differ from the case of the MCD signal because of the fact that the refractive index \tilde{n} , which is angular dependent, enters as a factor between Q and the MCD ellipticity, cf. eq 2.

Assuming a cosine dependence of the magnitude of Q on the molecular tilt angle α and taking one tilt angle as known from the SE results, e.g., for the sample S2-45, the value of α for the sample S1-45 can be calculated from the magnitude of Q . The result ($81 \pm 2^\circ$) compares well with that extracted from the SE measurements ($82 \pm 6^\circ$, cf. Table 1), and lies within the error limits of SE. The absolute error value in determining the molecular tilt angle from SE especially for small $\cos(\alpha)$ is higher than for the MOKE investigations, since eq 3 is only a rough estimate for the determination of α by means of SE when the angle becomes small. Therefore the MOKE measurements may provide a more accurate tool to determine the molecular orientation.

Summary and Conclusions

MOKE spectroscopy in the energy range from 1.5 to 5.0 eV was demonstrated to be a highly sensitive tool for the detection of the molecular orientation of diamagnetic organic semiconductors with layer thicknesses in the range of tens of nanometers deposited onto opaque substrates. The growth mode of H₂Pc was found to be strongly influenced by the templating effect of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA), leading to a small tilt angle of the H₂Pc molecules upon deposition in high vacuum.

Using a three-layer model and the knowledge of the optical constants of the film as well as of the substrate, the film

thickness, and the MOKE spectra, the Voigt constants of the H₂Pc films were extracted.

For the example of H₂Pc it was shown that the magnitude of the Voigt constant in the visible spectral range can be exploited to estimate the tilt angle of the molecular plane with respect to the substrate plane. The highest intensity of the Voigt constant was observed in the spectral range of the π – π^* transitions and in the case when the H₂Pc molecules adopt a small tilt angle with respect to the substrate.

The MOKE spectroscopy was shown to be more sensitive regarding the orientation of the molecules with respect to the substrate than SE. This provides an important contribution to the field of organic semiconductor physics in which the molecular orientation is of great importance.

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Supporting Information Available: Figure of ellipsometric angles, tables of film thickness, and surface roughness values and of Gaussian oscillators. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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