Hybrid devices such as organic light emitting diodes, solar cells or thin film transistors, based on phthalocyanine (Pc) materials and silicon receive special attention nowadays. PCs have a tendency to form ordered layers, however the growth mode may vary significantly on different substrates [1]. Moreover the first layers near the interface seem to have a structure distinct from the thick films. Consequently the present work was directed towards determining the molecular orientation of phthalocyanine monolayers and thin films using polarization dependent X-ray absorption spectroscopy. The organic materials involved are the copper phthalocyanine (CuPc) and its fluorine derivatives: F₄CuPc and F₁₆CuPc. Hydrogen passivated p-type (111) oriented silicon provided by Siltronic AG with a doping concentration of approximately 1.5x10¹⁵ cm⁻³ was used as the substrate. The passivation process consists of a wet chemical etching in a solution containing HF 40%. After the passivation process the samples were transferred into UHV. All measurements were performed on freshly evaporated organic layers. Their thickness was monitored by a quartz microbalance. The experiments were performed on the MUSTANG spectroscopy chamber at the Russian-German beamline at BESSY II. The NEXAFS spectra were acquired with a PHOIBOS 150 (SPECS) analyzer. The N1s NEXAFS raw data were divided by the spectra of the H-Si(111), background was subtracted and normalized to the absorption step at 425eV photon energy. A series of NEXAFS measurements were performed as a function of thickness and angle of incidence of the synchrotron radiation. Figure 1 displays the CuPc N1s excitation spectra for 2 monolayers a) and CuPc 20 nm b) as a function of the angle of incidence; The lower energy features (398-403 eV) represent the π* resonances, whereas those features above 403 eV are related to the σ* resonances.
angles. This suggests the presence of short range ordering in both cases. This behaviour is similar to F₄CuPc but opposite of F₁₆CuPc which is rather well ordered.

The quantitative analysis of the NEXAFS excitation spectra for CuPc, F₄CuPc and F₁₆CuPc is provided in figure 2. Figure 2 exhibits the normalized resonance intensity of the π* orbitals as a function of the incidence angle of the synchrotron radiation for the three phthalocyanines. The normalized resonance intensity of the π* orbitals is fitted [2] and the average tilt-angle for each case is calculated. The 3-fold symmetry of the silicon substrate is lifted by the surface roughness and as a consequence the model used for the fit contains an azimuthal dependence as well.

Table 1 summarises the results in terms of tilt angles α and azimuthal angles Φ obtained from the fits as well as the average orientation of the molecules. While CuPc and F₄CuPc behave in a similar way in terms of adsorbate geometry with a tilt-angle of the molecular plane higher than 50°, the F₁₆CuPc molecule behaves differently. Regarding the two measured thicknesses it is important to point out the different molecular orientations found in 2 monolayers and in a thin film of 20 nm for each phthalocyanine. This finding confirms previous results for CuPc [3] and represents a new step in describing the F₄CuPc and F₁₆CuPc molecules. The authors acknowledge the BMBF (FK MUSTANG 05KS40C1/3, OS ES3XBA/5) for the financial support and Mike Sperling for his assistance during the beam time.

References