<u>Chapter 3.</u> Materials and Film Preparation

3.1 Extended Porphyrazines

In the case of porphyrazine molecules, the central atom(s) in the macrocycle (denoted as 'Me' in Fig. 1) can be for instance a metal (including transition metals, lanthanides, actinides, metalloids) or two hydrogen atoms (for the metal-free porphyrazines).

The metallation of the porphyrazine dianion with a metal that maintains the planarity of the molecule leads to a change of the symmetry from D_{2h} for the metal-free compounds to D_{4h}. For the molecules which contain metals that are not found inside the ring (being situated outside the ligand plane), the symmetry is lowered to C_{4v} [LeL89].

The most often used methods for preparing films from these type of molecules, for both fundamental research and practical applications, are the vacuum sublimation and the Langmuir-Blodgett technique. The vacuum sublimation is utilized for most unsubstituted compounds. The Langmuir-Blodgett method is used for porphyrazine compounds which are regularly substituted at the axial or peripheral positions to make them soluble in volatile organic solvents while remaining insoluble in water.

The morphology of sublimed films is strongly influenced by the sublimation conditions, varying from amorphous to highly crystalline. For example, in the case of phthalocyanine molecules, by suitable choosing the sublimation conditions the so-called α and β crystalline phases can be obtained. The phthalocyanine molecules are positioned in columnar stacks with the ring orientation inclined relative to the axis of the stack, forming a 'herringbone'-like structure (see Fig. 3.1-1). The two crystalline forms differ from each

other by a smaller tilt angle between the axis of the stack and the normal of the phthalocyanine ring for the α phase (26.8°) compared to the β phase (46.8°).
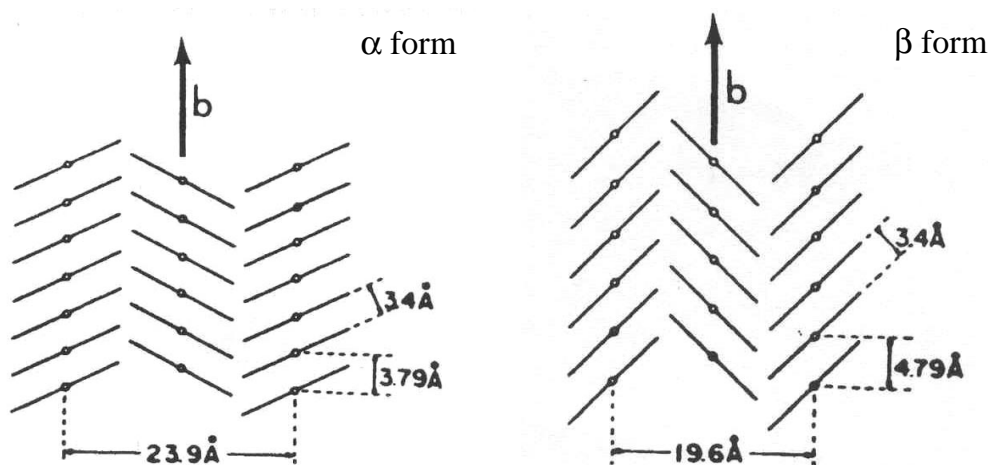

Fig. 3.1-1 Molecular arrangements in copper phthalocyanine crystals of the α form and β form. The data are taken from Ref. [LeL89].

Shorter metal-metal distance and longer interstack distance characterize the α crystal structure in comparison to the β one [LeL89]. Phthalocyanines containing large metal atoms (like Pt or Pb) can deviate from the α and β forms. As determined in the pioneering work of Robertson in 1936, for the β form of most phthalocyanines the monoclinic structure with two molecules per unit cell was confirmed [ZBD97]. For the α form some uncertainty exists in this respect. Tetragonal, orthorhombic and more recently monoclinic structures have been proposed [Gou96] for the α form. In the particular case of PbPc, films deposited at lower substrate temperature were found to be in the monoclinic form while those at high substrate temperature, in the triclinic structure [CKA93].

A significantly smaller amount of comparable studies is found in the literature for naphthalocyanines. For H_2Nc and ZnNc a 'face-to-face, eclipsed' molecular staking with the molecular plane perpendicular on the axis of the stack [YKA93, OCP96] has been determined. The VONc (vanadyl-naphthalocyanine) as well as AlClNc (cloroaluminium naphthalocyanine) molecules were found to have an 'eclipsed, slipped' stacked molecular arrangement, the stacking axis forming an angle with the normal to the molecular plane [YAE90, MNH93, YKA93].

For the Langmuir-Blodgett films, both molecular structure and conditions for film formation and transfer to the substrate influence the morphology. Also, the peripheral groups can influence the LB film morphology. Such a LB film has a layered morphology

in the direction of its thickness, the molecular orientation in one layer being influenced by an adjacent layer or the substrate surface. The ordered domains of the monolayers consist of stacks of cofacially oriented molecules characterized by a dihedral angle between the phthalocyanine ring and monolayer plane and a stack axis orientation [LeL89].

The porphyrazine molecules, which are not doped (most used doping method is oxidation with iodine [HHS98]), form van der Waals-bonded molecular semiconductors. In the case of α or β polymorphic forms of phthalocyanines, it was established that the molecular packing determines a direct π-π interaction between adjacent molecules in the stack but very weak interactions between molecules in adjacent stacks. The interactions between adjacent molecules along the crystal stacks were determined to be essentially of van der Waals type [OrB92].

3.2 Materials

The porphyrazine molecules investigated in this work are sketched in Fig. 3.2-1. For the first three porphyrazines in a given series the substituent denoted R is tert-butyl (C_4H_9 or $C(CH_3)_3$), while for the largest molecule, R is phenyl (C_6H_5). The studied systems are a mixture of several regular isomers, only one of them being represented in Fig. 3.2-1.

The interest was focused on the series of molecules containing a central Cu and Zn atom, respectively. For reference, the first three complexes in a series were also studied in the metal-free form (containing two central hydrogen atoms instead a metal atom). It was not possible to investigate the metal-free compound of the largest molecule in the series because it was found to be unstable during the film preparation process.

The metal-free molecules in each series are labeled according to their increasing size as: tetra(tert-butyl) porphyrazine, tetra(tert-butylbenzo) porphyrazine (or tetra(tert-butyl) phthalocyanine), tetra(tert-butylnaphtho) porphyrazine (or tetra(tert-butyl) naphthalocyanine), and octaphenyl-tetraanthraporphyrazine or octaphenyl-anthracyanine. The scheme is applied to the metal complexes correspondingly (by specifying the metal atom). For example: copper tetra(tert-butyl) porphyrazine, zinc tetra(tert-butylbenzo) porphyrazine or zinc tetra(*tert*-butyl) phthalocyanine, and likewise for the other ones.

For simplicity, the molecules in the series are denoted P0-Me, P1-Me, P2-Me and P3-Me, where P is the symbol for porphyrazine, the numbers 0, 1, 2, 3, represent the number of benzo-units fused to a pyrrole group, and Me indicates the central atom(s) of
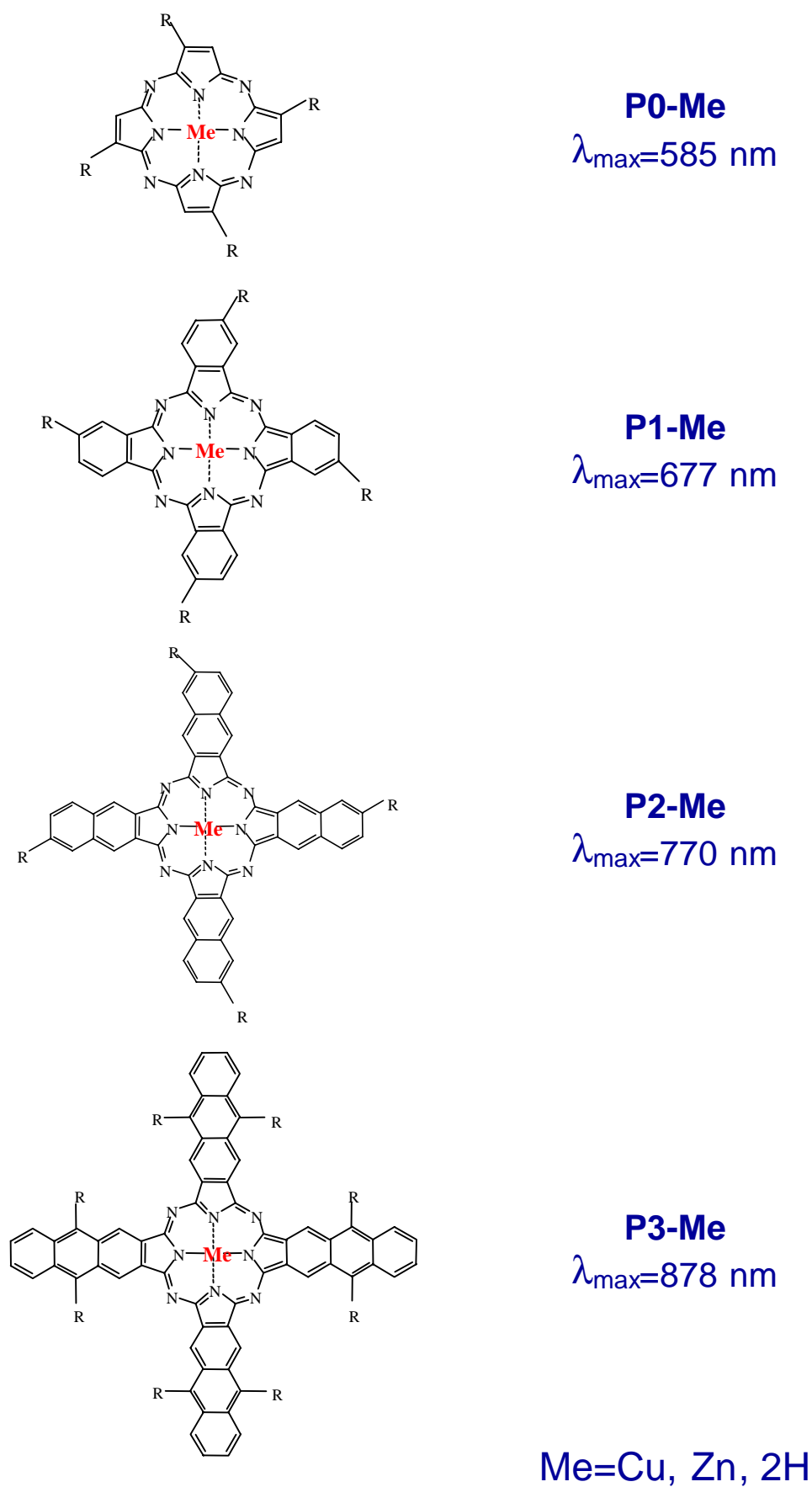
P0-Me
λ_{max}=585 nm

P1-Me
λ_{max}=677 nm

P2-Me
λ_{max}=770 nm

P3-Me
λ_{max}=878 nm

Me=Cu, Zn, 2H

Fig. 3.2-1 The investigated set of porphyrazine molecules.

Cu, Zn, or 2H. A set of these compounds is similar to that formed by the tetraazaporphyrin (or porphyrazine) (TAP), phthalocyanine (Pc), naphthalocyanine (Nc) and anthracyanine (Ac) (see Fig. 1). The chemical structures of P0-Me and MeTAP, P1-Me and MePc, or P2-Me and MeNc differ by the substitution of a peripheral hydrogen atom with a tert-butyl group on each arm of the molecule. Thus, each of P0-Me, P1-Me and P2-Me molecules has four tert-butyl, $C(CH_3)_3$, groups. The difference between P3-Me and MeAc is the substitution on each arm of the P3-Me molecule of two hydrogen atoms with phenyl, C_6H_5; so this molecule contains eight extra phenyl groups.

The presence of those substituents improves the solubility of the compounds without significantly affecting the absorption spectrum. For example, the introduction of four tert-butyl groups into copper phthalocyanine causes a red shift of the Q-band absorption maximum of only 6 nm as compared to the nonsubstituted compound. This is due to the fact that the influence of a tert-butyl group on the π-system is very low. In the case of phenyl groups in P3-Me, the interaction of the π-electrons of the phenyl rings with the main π-electron system of the molecule is diminished due to the fact that the phenyl groups are twisted out of the macrocyclic porphyrazine plane [AdR79].

The increase in the number of benzo-units causes a shift of the Q-band absorption maximum towards larger wavelengths, indicating a stronger delocalization of the electronic π-electron system [FrM86, FST94, STM98]. The value given below each molecule in Fig. 3.2-1 (585, 677, 770, 878 nm) represents the wavelength of the Q-band absorption maximum obtained for the respective copper compound dissolved in benzene. In the case of the Zn-derivatives the maxima differ only slightly from those of the copper compounds, indicating that the influence of the central metal ion is almost the same. However, the metal-free compounds P0-H_2 and P1-H_2 show a splitting of the Q-band due to the change of the symmetry from D_{4h} to D_{2h} [EdG70].

The P0-Me, P1-Me, P2-Me, and P3-Me compounds were synthesized at the Max Born Institute, Berlin. The unsubstituted CuPc, ZnPc, and H_2Pc were supplementary purified by reprecipitation from concentrated sulfur acid. The copper and zinc complexes of the series P1-Me, P2-Me, P3-Me, as well as the metal-free P1-H_2 and P2-H_2, were prepared according to the previously reported methods [MBL71, FrM86, LeF92]. For the preparation of P0-Cu and P0-Zn, tetra(tert-butyl) porphyrazine (P0-H_2) (Aldrich) was allowed to react with metallo-acetates in pentanol according to the procedure described in [FST94]. The solvents used for spectroscopic purposes were of spectroscopic grade (Merck).

3.3 Preparation of the Films

Most of the films were deposited by sublimation in ultrahigh vacuum (UHV) on a Au(111) single crystal held at room temperature during evaporation. Prior to deposition the Au substrate was cleaned by annealing at 700°C followed by repeated cycles of Ar^+ sputtering (with a typical value for the sample current of 7 μA) and annealing at 750°C.

The film thickness has been monitored by a quartz crystal microbalance. As the density of the substituted compounds was not precisely known, for their respective films the absolute thickness could not be determined precisely. Therefore it was preferred to scale the microbalance indication with the molecule mass in order to achieve the same number of molecules in the film, for all substituted compounds. However, for CuPc and ZnPc, where the densities are known, the film thickness was about 400Å. After preparation the sample was transferred into the analysis chamber for measurements (without breaking the vacuum).

For the compounds partly decomposing during sublimation (P3-Cu and P3-Zn), i.e., where the films produced by UHV sublimation did not only contain intact molecules but also fragments, an alternative preparation mode was used. A wet chemical method, similar to the Langmuir-Blodget technique, was selected. The respective compounds were dissolved in toluene and then the solution formed was put in a recipient containing water. After toluene had evaporated, a uniform layer of molecules was left on the water surface. Afterwards, a gold plated mica wafer was dipped into this recipient and was extracted very slowly, thus part of the molecules found at the water surface would stick to the plate, forming a thin film. The plate was then dried by heating it to about 100°C at 10^{-1} mbar and kept in an Ar atmosphere until transfer into the UHV chamber for measurements. To obtain thicker films, the following method was applied: after the plate was dried, it was again dipped into the recipient for depositing an extra layer of material on the existing film. However, the thickness of the films produced by this method could not be controlled. This was dependent on the thickness of the molecular layer formed at the water surface which in turn, depends on the concentration of the dissolved compound in toluene.

Films from Cu-Containing Compounds

For the first three complexes in the series (P0-Cu, P1-Cu, P2-Cu) and for CuPc itself, the films could be prepared by sublimation in UHV. The optimum evaporation temperature was established by performing mass-resolved analyses.

A quadrupole mass spectrometer (QMS) was placed above the quartz crucibles and the mass spectra were recorded at several temperatures. An example of representative mass spectrum for P0-Cu compound is given in Fig. 3.3-1. The peak corresponding to the mass of the molecule is observed at the parent mass of 600 amu. The peak at 300 amu corresponds to the double ionization of the P0-Cu molecule, while the peaks at 585 and 285 amu are assigned to molecular fragments that resulted from the impact of the electrons with the molecules.
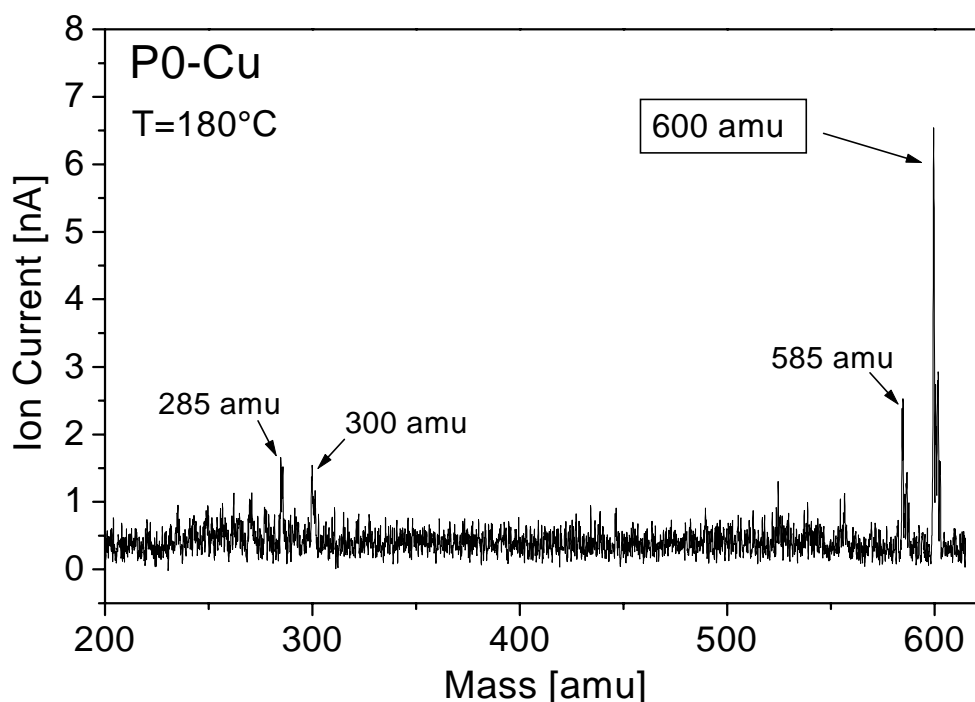

Fig. 3.3-1 QMS spectrum for P0-Cu compound.

The temperatures used for the evaporation of CuPc, P0-Cu, P1-Cu and P2-Cu compounds are shown in Table 3.3-1. As a general trend, the evaporation temperature of these compounds increases with increasing molecular mass. CuPc, P0-Cu, and P1-Cu are stable in a wide range of temperature and the deposition of the films was not a concern. In the case of P2-Cu compound, the deposition time had to be shorter than 20-25 minutes in order to be sure that there is no decomposition of the material during heating.

Compound	CuPc	P0-Cu	P1-Cu	P2-Cu
Evaporation Temperature [°C]	320	180	390	550

Table 3.3-1 Temperatures used for the evaporation of CuPc, P0-Cu, P1-Cu and P2-Cu compounds

In order to verify the absence of decomposition products on the sublimed films, control absorption spectroscopy measurements were performed for each candidate. Fig. 3.3-2 shows the absorption spectra of the four copper compounds dissolved in benzene or toluene. The spectra have been normalized to unity and then vertically translated for clarity. Two main bands are observed for each spectrum in Fig. 3.3-2: a strong absorption band (Q band) which shifts systematically to larger wavelengths for increasing ligand size, and a weaker one (Soret band) with the maximum (depending on the molecule) found between 339 and 354 nm [FrM86]. The strong Q band is primarily attributed to the $a_{1u} \rightarrow e_g$ transition (see for example [RoB94, LiS2001]).
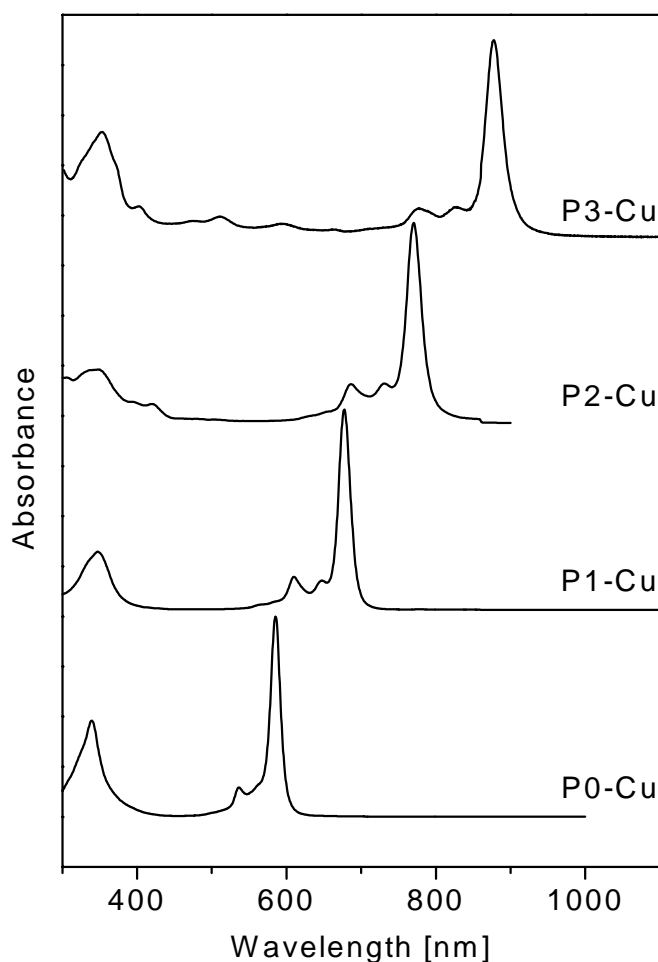

Fig. 3.3-2 Absorption spectra in solution for P0-Cu, P1-Cu, P2-Cu and P3-Cu compounds (also in [FrM86]).

The Soret band partly arises from the $a_{2u} \rightarrow e_g$ excitation [LFE91, LiS2001]; contributions from other transitions, like $n \rightarrow \pi^*$, are also found in this region [RoB94, BRR2002]. The Soret band is more sensitive to the central metal atom than the Q band [STB96,

CWZ2001]. The a_{1u} and a_{2u} are pure ligand orbitals that have the same composition as the HOMO and the HOMO-1 of the metal-free molecule, respectively, while e_g represents the lowest unoccupied (degenerate) molecular orbital of the system. These assignments for the absorption bands are similar in the case of Zn- and 2H-porphyrazines (note, however, the D_{2h} symmetry for the metal-free compounds).

In order to be sure that no decomposition products appear in the sublimation process, the films were prepared by sublimation onto quartz plates prior to measurements. Then the absorption spectra of the films deposited on quartz were measured. Afterwards, the films were dissolved and their absorption spectra, in solution, were taken again. For a film without fragments, the absorption spectrum of the dissolved film is identical with the original spectrum of the compound, in other words with the spectrum prior to evaporation, measured in solution. The absorption spectra of a P2-Cu solid film deposited on quartz, of the same film dissolved in toluene, and of the compound prior to evaporation dissolved in toluene, are shown in Fig. 3.3-3. For clarity, the spectrum of the original compound is vertically translated with respect to the other two spectra.
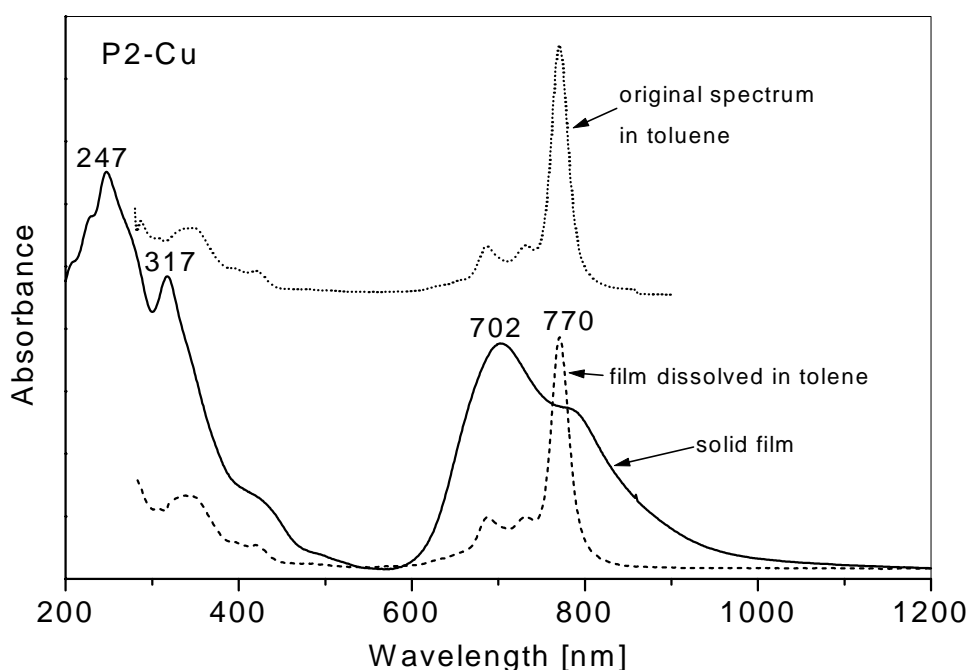

Fig. 3.3-3 Results of absorption measurements for a P2-Cu film deposited on quartz, for the same film dissolved in toluene, and analogous data for P2-Cu prior to evaporation dissolved in toluene.

The absorption bands of the solid film are broader and slightly shifted in energy with respect to those measured for the compound in solution. This is due to the excitonic coupling between the molecules (the excited state becomes delocalized) [LuV68, YTK86, Roh92]. The absorption spectrum of the dissolved P2-Cu film is similar to the absorption spectrum in solution of the compound prior to evaporation. This indicates that the film deposited on quartz contained only intact molecules. In case of films containing decomposition products, a strong increase of the signal in the (200-300) nm range relative to that of the Q band was noticed.

In addition, for each compound the material left in the quartz oven after film preparation was also examined by measuring the respective absorption spectrum in solution.
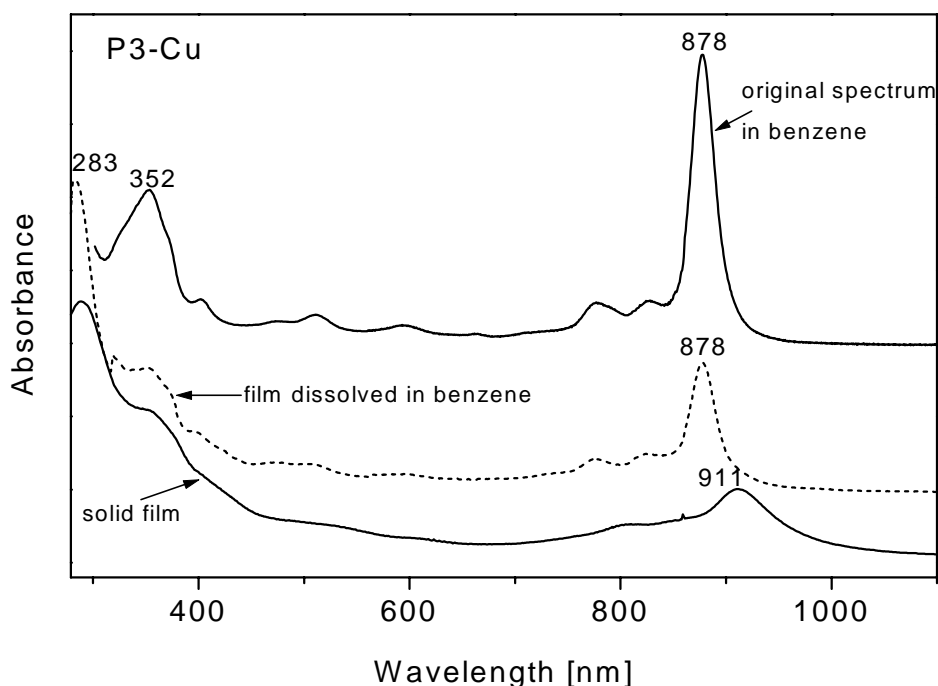

Fig. 3.3-4 Absorption spectrum of a P3-Cu film obtained by sublimation in UHV and deposited on quartz, of the same film dissolved in benzene, and of the P3-Cu compound in benzene prior to evaporation.

In case of the P3-Cu compound it was not possible to obtain a film without fragments by UHV sublimation. The appearance of decomposition products could not be avoided, even for short deposition times. Fig. 3.3-4 displays the absorption spectrum of a P3-Cu film obtained by sublimation on quartz, of the same film dissolved in benzene, and

of the P3-Cu compound dissolved in benzene prior to sublimation. The spectra are not normalized, but the spectrum of the original material in benzene is vertically translated with respect to the other two.

By comparing the two spectra measured in benzene, one can notice the presence of a strong peak at 283 nm in case of the P3-Cu dissolved film. This peak is actually more intense than the characteristic absorption at 878 nm. In addition to that, the intensity ratio between the Q and Soret bands is changed relative to the case of the compound prior to evaporation. These are clear indications of the presence of decomposition products on the film formed during sublimation.
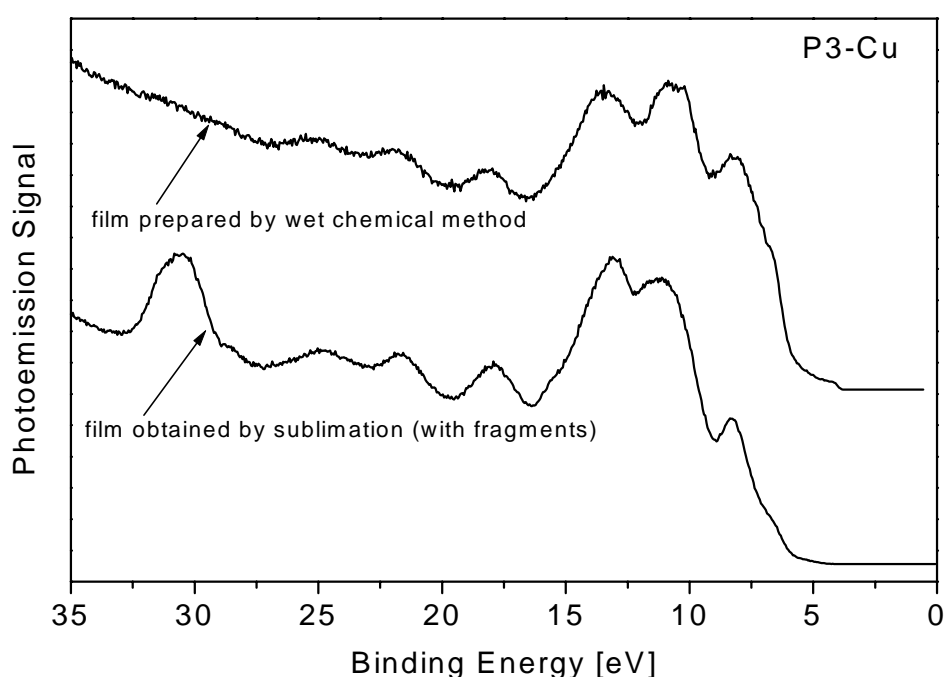
Fig. 3.3-5 The photoemission spectrum of a P3-Cu film obtained by sublimation in UHV and of a P3-Cu film prepared by the wet chemical method. In both cases the excitation energy was 75.8 eV.

An alternative procedure for preparing the P3-Cu films was the wet chemical method (similar to the LB technique) previously described in this chapter. For checking its suitability in the case of this Cu complex, the method was first applied for the preparation of a P2-Cu film. The photoemission spectrum of the P2-Cu film obtained in this way was compared with the photoemission spectrum of a P2-Cu film prepared by sublimation in UHV. Since the spectra turned out to be similar, as will be shown in Chapter 5, it was

concluded that this method is also appropriate for preparing P3-Cu films. It is worth to note at this point that the photoemission spectra of the valence region, at several photon energies, of a P2-Cu film obtained by sublimation in UHV and kept in air for about 20 minutes were found to be identical to those of a film unexposed to air.

The photoemission spectrum of a P3-Cu film obtained by sublimation is compared with that of a P3-Cu film prepared by the wet chemical method in Fig. 3.3-5. Most of the features are similar but a strong peak found at a binding energy of about 31 eV is present in the photoemission spectrum of the sublimed film without having any correspondent feature in the spectrum of the other film. Under these circumstances, this peak was determined to be caused by the molecular fragments present in the evaporated film. The nature of the decomposition products was not investigated in these experiments.

Films from Zn-Containing Compounds

Similarly to the case of Cu containing molecules, films from P0-Zn, P1-Zn, P2-Zn compounds, and ZnPc could be prepared by UHV sublimation. The temperatures used for the evaporation of these materials are roughly similar to those used for the copper compounds and are listed in Table 3.3-2.

Compound	ZnPc	P0-Zn	P1-Zn	P2-Zn
Evaporation Temperature [°C]	390	195	400	500

Table 3.3-2 Temperatures used for the evaporation of ZnPc, P0-Zn, P1-Zn, and P2-Zn compounds.

The verification of the films produced by sublimation and of the materials left in the ovens after deposition was done in the same way as described for the case of the Cu compounds. Fig. 3.3-6 displays the absorption spectra measured for a P2-Zn film obtained by sublimation in UHV on a quartz plate, for the same film dissolved in dioxane, and for P2-Zn dissolved in dioxane prior to sublimation. The original spectrum measured in dioxane is vertically translated for better comparison. The comparison of the data indicates that the film deposited on the quartz contained only intact molecules; with the absorption spectrum of the dissolved film being identical with the spectrum of the material before sublimation.

Similarly to the case of copper compounds, the preparation of P3-Zn films requires a wet chemical technique. Initially, a P1-Zn film was prepared by the same wet chemical method as used for P3-Cu. Its photoemission spectrum was then compared with that of a P1-Zn film obtained by sublimation. As opposed to the case of the copper compounds, the

spectra of the films of the Zn complexes obtained in these two ways, do show significant differences. A more detailed discussion of the P3-Zn spectrum will be presented in Chapter 6.
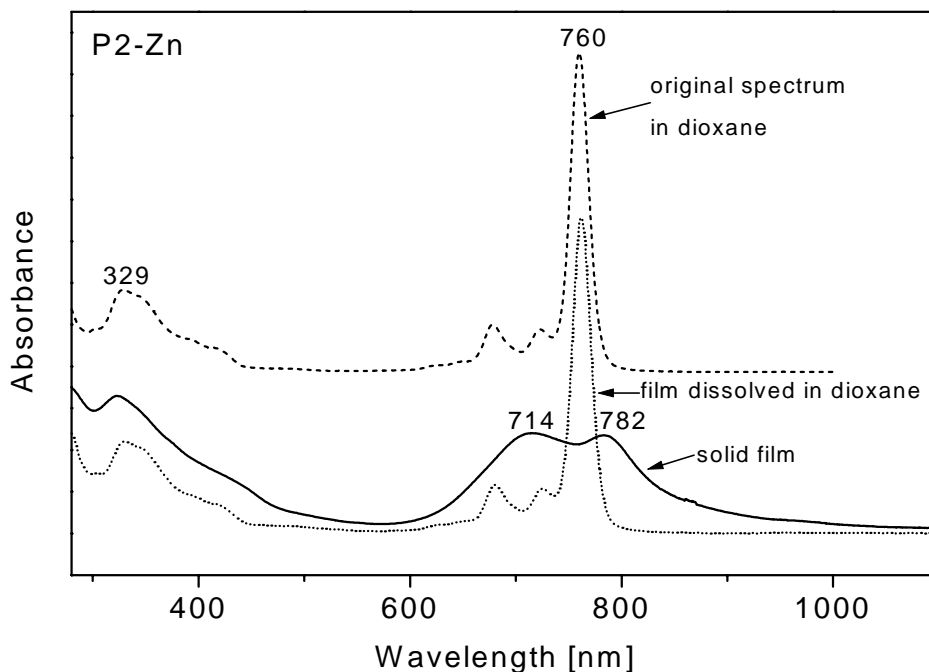

Fig. 3.3-6 Absorption spectrum of a P2-Zn film deposited on quartz by sublimation in UHV, of the same film dissolved in dioxane and of the P2-Zn compound in dioxane prior evaporation.

After photoemission measurements, these P1-Zn and P3-Zn films prepared by the wet chemical method were dissolved in toluene and their absorption spectra were measured. The absorption spectra also differ noticeably from those of their respective starting materials; thus indicating a transformation of these compounds. One possible cause of the transformation may be the formation of radicals. It is worth mentioning that ZnPc and ZnNc can easily form cation radicals [ToT96]. Therefore, care had to be taken in examining the photoemission measurements done on P3-Zn.

Films from Metal-Free Compounds

Films of metal-free compounds were prepared by sublimation in UHV of P0-H_2, P1-H_2, P2-H_2, and H_2Pc. Similar to the case of molecules containing central metal atoms, P0-H_2, P1-H_2, and H_2Pc films were obtained without difficulty; only for P_2-H_2 the appearance of molecular fragments was observed for longer deposition times. Thus, the deposition time was kept below 20 minutes and the evaporation temperature around 500 °C

for P2-H_2 films. Table 3.3-3 shows the evaporation temperatures used for the preparation of films of the metal-free compounds. The values are similar to those used for the metal containing compounds.

Compound	H$_2$Pc	P0-H$_2$	P1-H$_2$	P2-H$_2$
Evaporation Temperature [°C]	380	180	350	500

Table 3.3-3 Temperatures used for the evaporation of H$_2$Pc, P0-H$_2$, P1-H$_2$ and P2-H$_2$ compounds.

In order to verify that the sublimed films contained only intact molecules, the absorption spectrum of the dissolved film and the absorption spectrum (in solution) of the compound prior to sublimation were again compared. As an example, Fig. 3.3-7 displays the absorption spectrum of a dissolved P2-H_2 film from the Au(111) crystal and of the P2-H_2 compound in benzene prior to evaporation. The spectra are vertically displaced with respect to each other. The two curves are similar; hence no material decomposition occurred during sublimation.

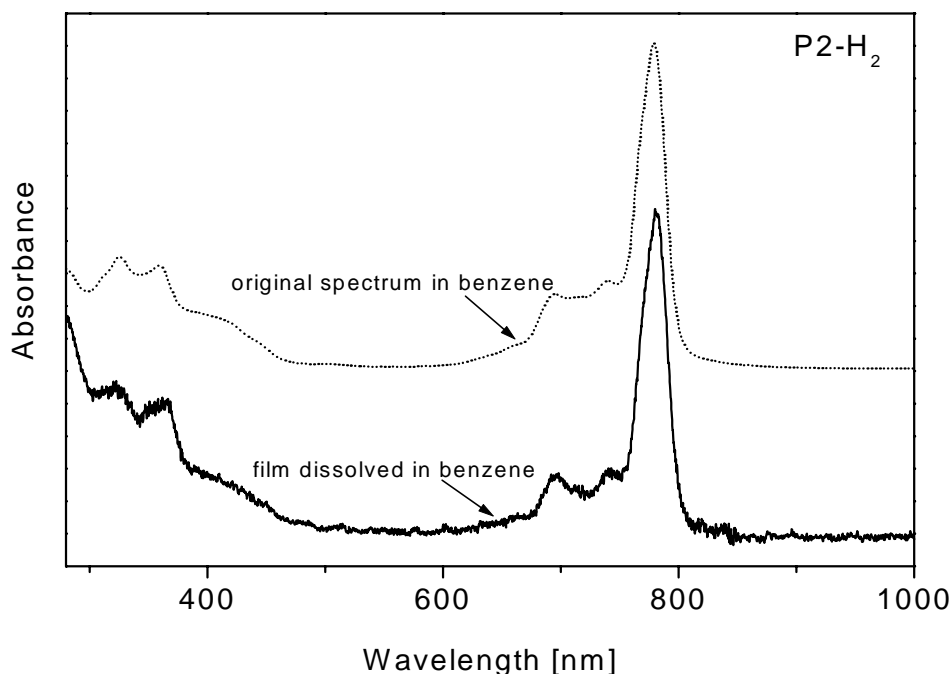As previously mentioned, films from P3-H_2 compounds could not be prepared.

Fig. 3.3-7 Absorption spectra of a dissolved P2-H_2 film from the Au(111) crystal surface and of the P2-H_2 compound in benzene prior evaporation.