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Electronic Energy Levels of Organic Dyes on Silicon: A Photoelectron Spectroscopy Study of ZnPc, F₁₆ZnPc, and ZnTPP on p-Si(111):H

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Alignment of energy levels and chemical interaction of the organic pigments ZnPc, substituted F₁₆ZnPc, and ZnTPP on H-terminated Si(111) have been deduced from valence band and core level photoelectron spectroscopy with high surface sensitivity for coverage below and in the monolayer region. Hydrogen-terminated Si(111) was prepared in UHV. The dyes have been purified by zone sublimation and were deposited at room temperature by PVD. SXPS taken at the synchrotron BESSY shows physisorption of the dye molecules; chemical shifts indicating strong interactions with the substrate have not been observed. The maxima of the HOMO photoemission of ZnPc, F₁₆ZnPc, and ZnTPP are measured at 0.45, 1.55, and 1.0 eV below the Si valence band maximum. These experimental values are compared to theoretical values and are related to the position of the optical gap, the transport gap, and the redox potentials of the ground and excited state.

1. Introduction

Organic semiconducting pigments exhibit interesting optoelectronic properties as, for example, electroluminescence in organic light-emitting diodes (OLED)¹ and photovoltaic energy conversion in organic solar cells (OSC).² Due to their high absorptivity, organic chromophores are also used as sensitizer monolayers on oxide electrodes as TiO₂³ and ZnO^{4–6} in photoelectrochemical solar cells (PESC). In PESC, nanoporous oxide electrodes are used to increase the effective surface covered with a dye monolayer for light absorption. In OSC, special measures have to be taken for effective charge separation because the optically generated exciton is strongly bound due to low dielectric constants of organic semiconductors. For this purpose, organic–organic⁷ or organic–inorganic⁸ bulk heterojunctions of donor and acceptor phases have been developed. Another factor reducing further the efficiency of OSC is the low conductivity of organic semiconductors.

On the other hand, Si shows exceptional good transport properties for charge carriers but due to the indirect gap lacks in optical absorptivity. Therefore, integration of pigment particles into silicon may lead to composite materials which allow one to combine dye absorptivity and luminescence with Si charge transport. Composites of organic dyes in a microcrystalline silicon matrix may be developed as effective absorber materials for solar cells.⁹ Efficient sensitization may be reached with dyes that allow one to transfer the absorbed solar energy from the excited dye molecules to Si by either injection of electron and hole sequentially or simultaneously as exciton without energy barriers. Recently, energy transfer from an antenna system of dye-loaded zeolyte crystals to Si has been demonstrated.¹⁰ A number of stable molecular structures as, for

example, phthalocyanines, porphyrins, or perylene tetracarboxylic acid diimides allow for the adjustment to the desired optical absorption spectrum. Phthalocyanines and porphyrins appear to be the most attractive candidates for photosensitizers as they absorb throughout the visible region and into the near-IR.^{7,11} A prerequisite for the optoelectronic integration is the knowledge of the energy alignment of the organic frontier orbitals HOMO and LUMO versus the silicon bands as, for example, charge exchange may be controlled thereby. Theoretical calculations and electrochemical measurements show that by substitution of the ligand (unsubstituted, alkyl-substituted, Cl-, or F-substituted) ionization energies may be varied in a broad range while the HOMO–LUMO gap of single molecules is hardly influenced.¹² Variation of the molecular ionization energy by substitution is expected to result in a variation of the line-up of the semiconducting organic film valence and conduction bands versus the silicon substrate bands. Thus, a systematic engineering of band line-up by substitution may be possible. Also, changing the central metal ion results in changes of the ionization energies, while the optical absorption spectrum of single molecules is hardly influenced. Variation of the molecular HOMO–LUMO gap is possible by the change of the molecular structure. In Figure 1a, the molecular structures of metal–phthalocyanine and metal–tetraphenylporphyrin are depicted; in Figure 1b, theoretical ionization energies and affinities for ZnPc and Cl- and F-substituted ZnPc and ZnTPP are displayed.¹²

Systematic studies of organic dye ionization energies have been performed in the gas phase,^{13,14} in solution,¹¹ and on layers condensed on metals.^{14–16} Systematic changes of the CuPc ionization energy due to F substitution and partial substitution have been measured on gold.¹⁷ In this paper, we present a systematic study on the HOMO line-up versus the valence band of H-passivated Si(111) as a model system. Using literature values of (i) inverse photoemission, (ii) correction values to deduce the bulk transport gap from UPS–HOMO and inverse photoemission LUMO positions, (iii) exciton binding energies,

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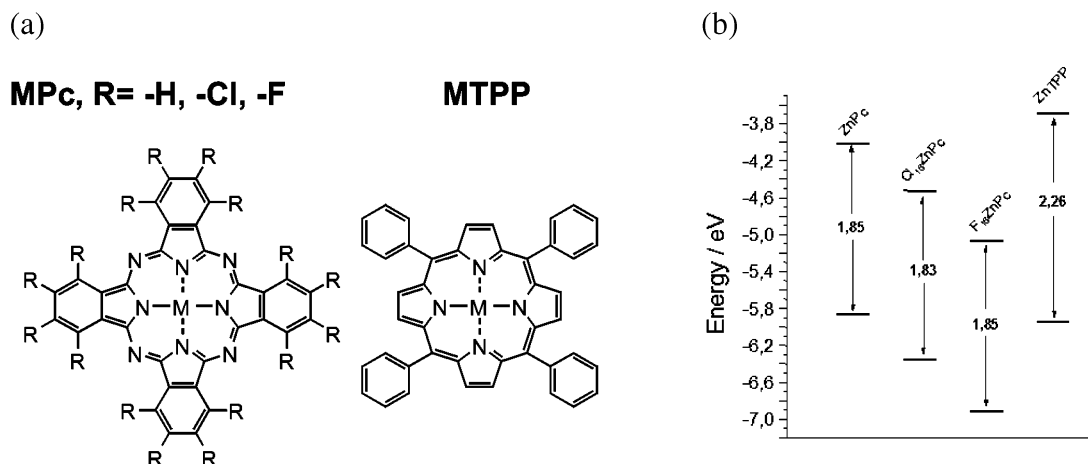


Figure 1. Molecular structure of metal phthalocyanine and metal tetraphenylporphyrin (a) and ionization energies and electron affinities from PM3-MO calculations¹² (b). Substitution of the ligand R=H with, for example, Cl or F allows systematic variation of the ionization energy.

and (iv) optical absorption, estimates of the line-up of the photoemission–inverse photoemission HOMO–LUMO gap, of the bulk transport gap, and of the optical absorption (excitonic) gap are deduced and compared to predictions from electrochemical redox potentials of the ground and excited state of the dye molecules in solution.

2. Experimental Section

The SXPS experiments have been performed at the undulator beam line U49/2 of the BESSY storage ring, which provides photons in the energy range between $h\nu = 90$ and 1400 eV. In addition, the used setup is equipped with a HeI UPS source which was used for the measurement of the valence band spectra. The spectra were obtained using a hemispherical Phoibos 150 (SPECS) energy analyzer of the experimental system SoLiAS (Solid/Liquid Analysis System) permanently operated at BESSY. The emitted photoelectrons were detected in normal emission with an acceptance angle of $\pm 9^\circ$. The base pressure of the analysis chamber is in the lower 10^{-10} mbar range. The Si 2p core levels were measured with 130 eV excitation energy. Binding energies are given relative to the Fermi edge of an Au sample. For the fitting of the core level lines, a polynomial background was removed and mixed Gaussian–Lorentzian line shapes were used. HOMO positions values are given for the peak maxima, not the onset of the emission.

Si(111) wafer samples p-doped with 2×10^{16} B atoms/cm³ (5–10 Ω cm) were used. A thermal oxide was etched away by a 40% HF/sat. $\text{NH}_4\text{F}/\text{H}_2\text{O}$ solution (1:7:70). Resistive direct flash annealing in UHV was performed for formation of the 7×7 reconstruction. Hydrogen was admitted at 400 °C to the 7×7 reconstructed sample via a hot wire source inducing a 1×1 structure.¹⁸ A reverse view LEED system (Omicron) was used for monitoring the surface reconstructions.

The zinc(II) complex of phthalocyanine (ZnPc) was prepared by the reaction of sublimed phthalonitrile and zinc(II) acetate (99.99%, Aldrich) in dry *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) under reflux.¹⁹ The isolated product was washed with water and then treated with methanol in a Soxhlet apparatus. The zinc(II) complex of hexadecafluorophthalocyanine (F_{16}ZnPc) was obtained by heating a 4:1 mixture of sublimed tetrafluorophthalonitrile in zinc(II) acetate (99.99%, Aldrich) in a vacuum-sealed glass tube for 1 h at 180 °C.²⁰ The resulting dark blue powder was treated in a Soxhlet apparatus with water and light petroleum (bp 100–

120 °C) to remove inorganic and organic contaminations. The zinc(II) complex of meso-tetraphenylporphyrin (ZnTPP) was used as received (Aldrich). The metal complexes were purified by zone sublimation at 10^{-7} – 10^{-6} mbar: ZnPc at 370 °C, F_{16}ZnPc at 350 °C, and ZnTPP at 260 °C.

The dyes have been evaporated from Al_2O_3 crucibles onto the Si samples at room temperature. For each dye a separate source was used, one source mounted to the UHV preparation chamber at a time. ZnPc, F_{16}ZnPc , and ZnTPP have been evaporated at 280, 300, and 190 °C at a deposition rate of 1–10 Å/min after degassing at lower temperature (150 °C). The temperature was measured with a thermocouple mounted to the crucible. At room temperature, ZnPc adsorbs onto Si(111):H in the α modification as detected with differential reflection spectroscopy in a separate experiment not displayed here. Flash annealing and hydrogen termination have been carried out in one UHV chamber and dye deposition was carried out in a separate chamber. Both chambers are integrated to the analysis chamber. The nominal thickness of the adsorbed dye layers has been deduced from the attenuation of the Si 2p emission measured at 130 eV excitation energy. Exponential damping and a mean free path of $\lambda = 6$ Å were assumed for the Si 2p electrons with a kinetic energy of 30 eV in the organic material.²¹ Energy levels of dye molecules in the gas phase have been calculated using the Hyperchem program. The calculation method PM3, next lowest state, RHF approximation was employed.

3. Experimental Results

As at higher coverage the substrate valence band maximum cannot be identified in the valence band spectra, it has to be deduced from the binding energy difference between the Si 2p core level and the valence band maximum of the clean H-terminated substrate using 98.8 eV for $E_{\text{VBM}} - E_{\text{Si}2\text{p}3/2}$.²¹ A good fit to the Si 2p core levels of the clean substrate is achieved with two doublets shifted by 0.23 eV assigned to the bulk species and the H-terminated surface species at higher binding energy. Binding energies of the Si 2p $3/2$ bulk component $E_{\text{Si}2\text{p}3/2}$ have been measured at 99.5, 99.3, and 99.45 eV for the clean p-doped samples used for ZnPc, F_{16}ZnPc , and ZnTPP adsorption, respectively. The line widths of the bulk and H-terminated surface component were 0.3 and 0.2 eV. Because the Si 2p $3/2$ binding energy can vary for extremely p- to extremely n-doped samples between 98.8 and 99.9 eV, the measured values correspond to mid-gap or slight n positions of

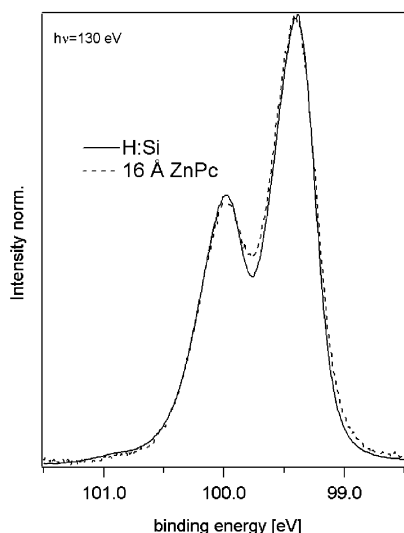


Figure 2. Si 2p core levels measured with 130 eV excitation energy of a H-terminated substrate and samples covered with 16 Å ZnPc. Minor changes of the line shape indicate physisorption of the dye molecules. Similar spectra have been obtained for F₁₆ZnPc and ZnTPP.

the surface Fermi levels, indicating that the H-termination has not been perfect and the surface Fermi level is pinned by some remaining Si dangling bonds.

In the course of dye molecule deposition, the substrate emission is increasingly damped. Only minor changes occurred in the line shapes of the substrate Si 2p emission as demonstrated for ZnPc in Figure 2. The Si 2p core level emission of the freshly H-terminated substrate and the substrate covered with a nominal coverage of 16 Å of ZnPc are displayed. The spectra have been normalized in intensity and in energy to the fresh sample emission. For the Si 2p emission of the ZnPc covered sample, a good fit is still achieved with the same components; only the line width of the surface component has been increased by 100 meV. The absence of chemically shifted components is a clear indication that the deposited dye molecules are physisorbed

without forming chemical bonds with the substrate surface atoms. Similar spectra are obtained in the case of F₁₆ZnPc, indicating that substitution by F does not result in increased reactivity. Also, ZnTPP was found to be physisorbed.

Si 2p spectra of samples covered with 16 Å of ZnPc, 12 Å of F₁₆ZnPc, and 14 Å of ZnTPP are displayed in Figure 3a; the respective HeI valence band spectra are displayed in Figure 3b. By referring to the energetic position of $E_F - (E_{VBM} - E_{Si2p3/2}) = E_F - 98.8$ eV in Figure 3a, the substrate valence band maximum position below the Fermi level can be directly deduced from the bulk peak position as indicated. Due to adsorption of dye molecules, the binding energy of the Si 2p core levels is changed, indicating charge transfer. This translates to a Fermi level shift induced in the Si-surface. In the case of ZnPc, the surface Fermi level is shifted toward the conduction band by 150 meV and by 200 meV in the case of ZnTPP, while F₁₆ZnPc induces a shift toward the valence band by 100 meV. The values are given for the respective highest measured coverages, while in Figure 4 the development of the Si 2p 3/2 binding energy in the course of ZnPc, F₁₆ZnPc, and ZnTPP deposition is displayed. Clearly the electron-donating character of ZnPc has been changed to electron-accepting character by F substitution.

The spectral shapes of the HeI valence band spectra of ZnPc and F₁₆ZnPc (Figure 3b) agree well with spectra measured in the gas phase and on Au.¹⁴ A polynomial background has been subtracted from the displayed valence band spectra, taking account of the secondary electrons. The respective HOMO maxima are found at 1.15, 2.05, and 1.65 eV below the Fermi level. Taking the valence band maximum at bulk Si 2p 3/2 as 98.8 eV and the HOMO position from the valence band spectra displayed in Figure 3b, the Si(111):H–HOMO offsets as measured with photoelectron spectroscopy for ZnPc, F₁₆ZnPc, and ZnTPP are 0.45, 1.55, and 1.0 eV, respectively.

4. Discussion

The main objective of this contribution is the experimental determination of the alignment of energy levels and the

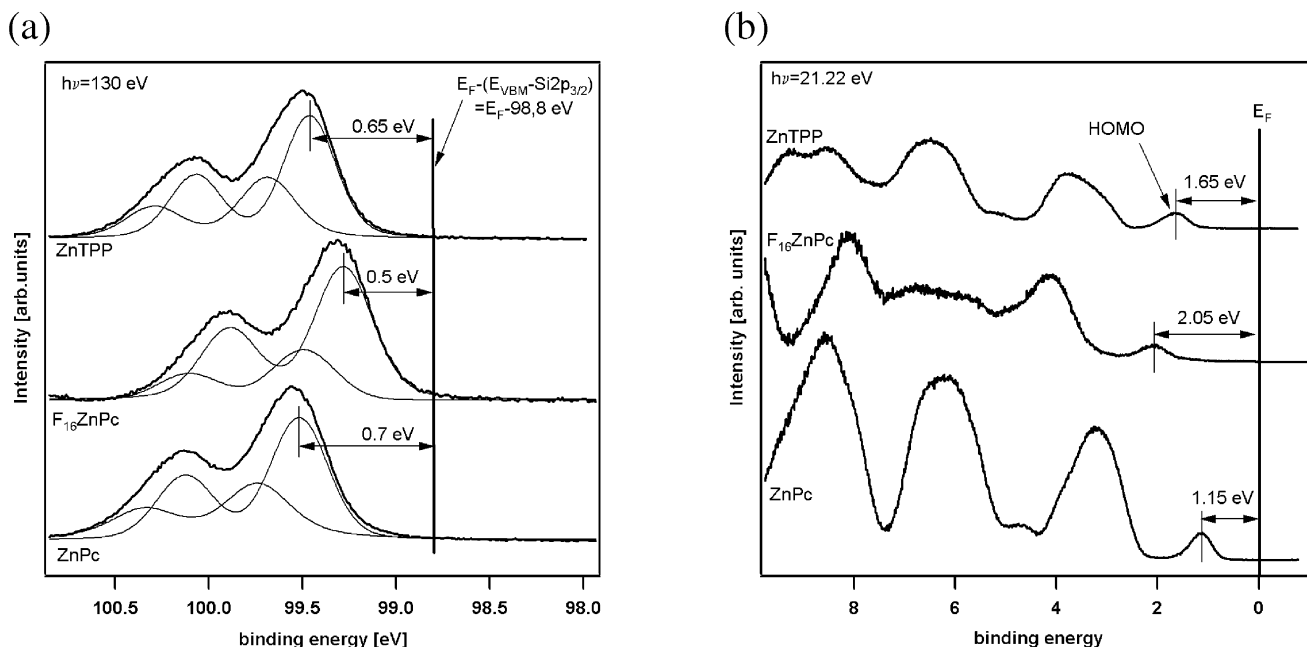


Figure 3. (a) Si 2p core levels of H-terminated Si(111) covered with 16 Å of ZnPc, 12 Å of F₁₆ZnPc, and 14 Å of ZnTPP. The energetic difference of the Si 2p 3/2 bulk component to the mark at $E_F - (E_{VBM} - E_{Si2p3/2}) = E_F - 98.8$ eV gives a direct reading of the valence band maximum position below the Fermi level as indicated. (b) He I valence band spectra of ZnPc, F₁₆ZnPc, and ZnTPP on Si(111):H. The HOMO peak positions are indicated. The secondary electron background has been removed.

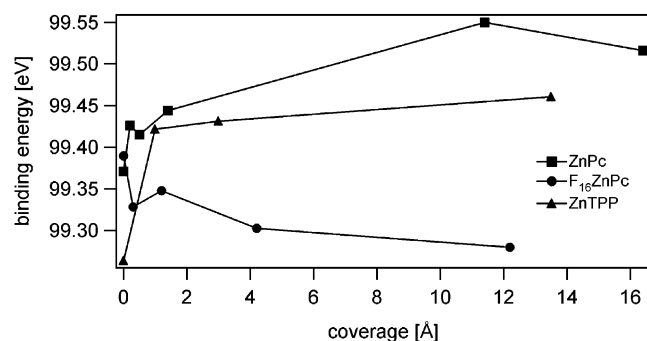


Figure 4. Si 2p 3/2 binding energy in the course of ZnPc, ZnTPP, and F₁₆ZnPc adsorption. Increasing binding energy corresponds to raising of the substrate surface Fermi level due to electron donation by the adsorbate. By F substitution, the electron-donating character of ZnPc has been changed to electron-accepting character.

comparison to calculated ionization and affinity potentials and electrochemical redox potentials. After the HOMO positions have been experimentally determined, we can deduce the LUMO positions using results from inverse photoemission spectroscopy on metallic samples. Yet the HOMO–LUMO gap as measured with surface sensitive UPS and inverse photoemission IPES on organic films appears larger than the electronically relevant transport gap E_t . A correction value for deducing bulk HOMO/LUMO positions from UPS/IPES has to be applied. Following the arguments given by Hill et al.,²³ the difference is due to the smaller polarization at the surface versus the bulk (approximately 0.6 eV) and to vibrational excitation in UPS/IPES which tend to shift both of the measured HOMO and LUMO peaks away from the Fermi level to the Frank Condon maxima (approximately 0.2 eV).²³ For comparison with electrochemically and photoelectrochemically determined redox potentials of the ground and excited state of the dye molecules in solution, the positions of the transport gap E_t and the optical (excitonic) absorption gap E_{opt} are important. While $E^{UPS/IPES}$ and E_t are given by states of positive and negative ions, E_{opt} is given by states of the neutral molecule. In Figure 5, we have tentatively

depicted the line-up of the UPS–IPES gap $E^{UPS/IPES}$, the transport gap E_t , and the optical absorption HOMO–LUMO gap E_{opt} of ZnPc, F₁₆ZnPc, and ZnTPP. For lack of detailed data, E_t and E_{opt} are placed symmetrically versus $E^{UPS/IPES}$, assuming the same correction values for deducing bulk HOMO/LUMO positions from UPS/IPES for electrons and holes²³ and the same stabilization energy for each exciton partner due to coulomb interaction. While the Q-band absorption of dissolved ZnPc and F₁₆ZnPc molecules is narrow (fwhm = 20 meV) with a maximum at almost the same energy (1.82 and 1.81 eV), the absorption of deposited films is broad (fwhm = 450 and 670 meV) with two maxima at 1.75 and 2.00 eV for ZnPc and 1.52 and 1.90 eV for F₁₆ZnPc.²⁰ Because due to instrumental broadening and averaging over different surroundings the line width of UPS and especially IPES is broad as compared to optical spectra, we use in Figure 5 a mean value for the optical absorption gap of 1.8 eV for both phthalocyanine films, ignoring any details of the absorption spectra. Similarly, we use an optical absorption gap of 2.2 eV for ZnTPP films as measured for dissolved molecules.²⁴ The phthalocyanine UPS–HOMO peak offsets relative to the Si VB show a 1.1 eV shift to higher binding energy due to F substitution. This value agrees well with the PM3-MO calculated ionization shift of 1.07 eV.^{12,14} While in the gas phase 0.9 eV and on gold a value of 0.56 eV for the stabilization of the HOMO due to F substitution was measured with UPS, a difference of 0.7 eV was found for the redox potential of the first oxidation of ZnPc in DMF and F₁₆-ZnPc in CH₂Cl₂ solution.¹⁴ As in the MO calculations, the UPS–HOMO position of adsorbed ZnTPP is found below the HOMO of ZnPc. Yet while the experimental difference is 0.55 eV, the calculated value for the free molecules is 0.1 eV only.

With the experimental ZnPc HOMO^{UPS} value of 0.45 eV below the VBM, we find the LUMO^{IPES} at 1.45 eV above the CBM by using $E^{UPS/IPES} = 3.0$ eV as measured on gold.²⁵ With $E_{opt} = 1.8$ eV and placed symmetrical to $E^{UPS/IPES}$ in Figure 5, the HOMO^{opt} is found 0.15 eV above the VBM and the LUMO^{opt} is 0.85 eV above the CBM. Using an exciton binding energy value of 0.6 eV as determined for CuPc,²⁵ we tentatively

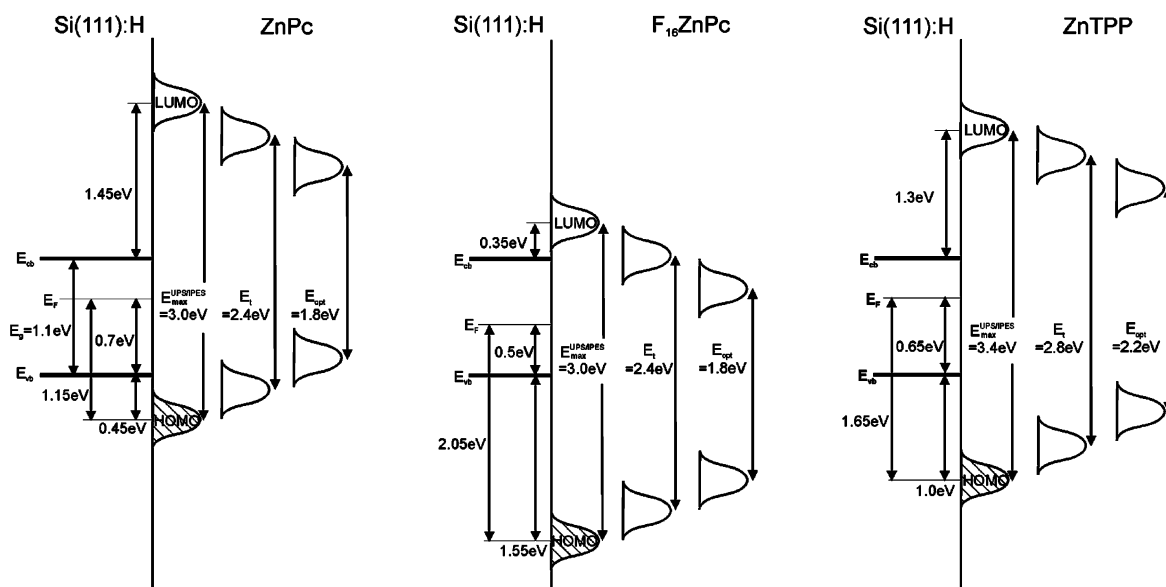


Figure 5. HOMO position of ZnPc, F₁₆ZnPc, and ZnTPP on Si(111):H as determined experimentally (hatched HOMO peak). In addition, the ZnPc LUMO is sketched, using the HOMO–LUMO gap as measured with photoemission and inverse photoemission on gold.²³ The bulk transport gap and the optical (excitonic) gap are indicated, where 0.3 eV both for electron and for hole relaxation and a 0.6 eV exciton binding energy have been taken as determined for CuPc.²⁵ Using the optical gap of F₁₆ZnPc²⁰ and ZnTPP²⁴ and the same values for exciton binding energy and correction values for deducing bulk HOMO/LUMO positions from UPS/IPES as for ZnPc, the HOMO–LUMO gaps $E^{UPS/IPES}$, E_t , and E_{opt} have been sketched for these dyes also. While $E^{UPS/IPES}$ and E_t are given by states of positive and negative ions, E_{opt} is given by states of the neutral molecule.

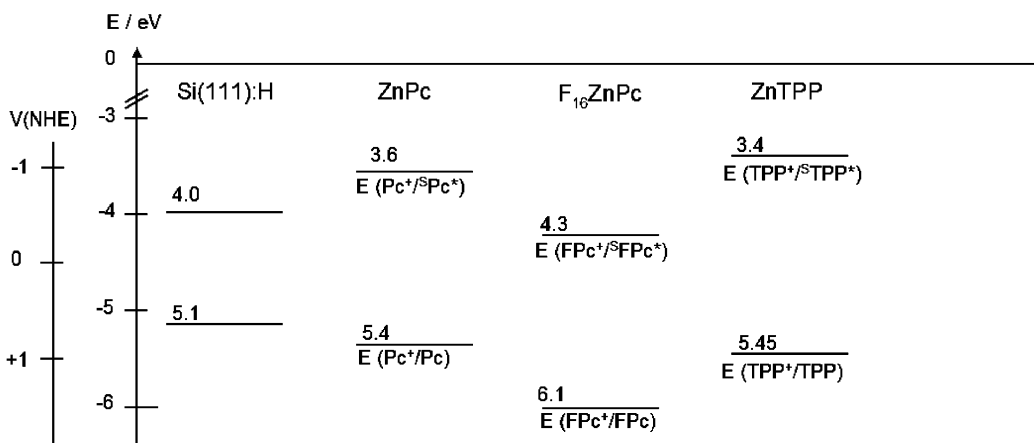


Figure 6. Band line-up as predicted from electrochemical measurements of dye oxidation potentials of ground and excited state versus electron affinity and ionization potentials of Si(111):H.

place the transport gap E_t and find the HOMO^t at 0.15 eV below the VBM and the LUMO^t at 1.15 eV above the CBM. For lack of specific correction values for deducing bulk HOMO/LUMO positions from UPS/IPES for electrons and holes and exciton binding energies in the literature, we use the same values we used for ZnPc also for F₁₆ZnPc and ZnTPP. The obtained line-up positions of $E^{\text{UPS/IPES}}$, E_t , and E_{opt} are summarized in Figure 5.

For comparison, we show in Figure 6 a prediction of the line-up as given by electrochemical redox potentials of the ground and excited singlet state and Si(111):H affinity and ionization potential on a common vacuum scale using 4.5 eV for adjusting the NHE redox scale to vacuum. The oxidation potentials of the ground and excited states V_{ox} and V_{ox}^* of ZnPc have been measured at +0.92 and -0.91 V, and those of ZnTPP have been measured at +0.95 and -1.1 V.¹¹ For F₁₆ZnPc, only V_{ox} is known at +1.6 V.²⁶ In Figure 6, we used the same difference of 1.83 V between V_{ox} and V_{ox}^* for F₁₆ZnPc as is known for ZnPc. Assuming that in V_{ox} the stabilization due to solvation is included and assuming that this stabilization is similar to the extramolecular polarization in the organic film, it is expected that V_{ox} coincides with HOMO^t. This coincidence is nearly found for ZnPc, but for F₁₆ZnPc and ZnTPP our deduced HOMO^t is found at an approximately 0.3 eV lower position. The reason may be found in the many estimates and approximations we had to make to deduce the HOMO^t energies and, in addition, specific interface dipoles due to electrochemical double layers not considered in Figure 6.

5. Summary and Conclusion

Three dyes, ZnPc, F₁₆ZnPc, and ZnTPP, have been deposited in UHV onto UHV prepared p-Si(111):H at room temperature and analyzed with 130 eV PES and He I UPS. Si(111):H has proven to be an ideal nonreactive substrate as indicated by almost unaffected line shapes of the Si 2p core level emission. While ZnPc and ZnTPP show electron-donating character moving the pinning position of the substrate by 150 and 200 meV toward the conduction band, F₁₆ZnPc shows electron-accepting character moving the pinning position by 100 meV toward the valence band. From the measurements, the UPS–HOMO maximum line-up can directly be found at 0.45, 1.55, and 1.0 eV below the Si valence band. Using estimates from literature values for the optical gaps, the exciton binding energies, and correction values for deducing bulk HOMO/LUMO positions from UPS/IPES energies, we conclude on the positions of the optical gap and the electron and hole transport

gaps referring to the energy band positions of H-terminated silicon. Considering energetic barriers from the obtained line-up, electron and hole injection from the dye to the semiconductor is energetically favored for ZnPc and ZnTPP, while electron injection from the Si conduction band to F₁₆ZnPc is favored. For ZnTPP, also exciton injection from the dye to the semiconductor is barrier-free, while for ZnPc, the exciton bound hole has to overcome a small barrier of 0.15 eV.

For organic semiconductor materials, the position of the HOMO and LUMO depends strongly on the respective environment (bulk, surface, interface, solution, gas phase). Different measurement methods (UPS/IPES, I–V, electrochemical) will result in different values. Specific measurements and considerations will be needed to conclude from experimentally determined values on the specific HOMO/LUMO positions in a specific application. It is evident that a more detailed experimental determination of the dye energy level positions and their alignment to the substrate levels is needed for systematically changed environments (adsorbed monomolecular dyes, dye films, dyes in solvation shells).

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