

# Appendix A

## Analytical tools

### A.1 Details of the MO calculations

The MO calculations are performed with the commercial program HyperChem, release 7.03, Hypercube Inc. on a conventional personal computer. Most calculations were performed with semi-empirical self-consistent-field MO procedures as this methods are about three orders of magnitude less expensive in computation time compared to DFT methods. The molecular structures were determined applying different parameterizations: AM1 (Austin Model 1), PM3 (a reparameterization of AM1) and ZINDO/1 (Zerners non-spectroscopic version of the Intermediate Neglect of Differential Overlap). The molecular geometries were optimized with a conjugate gradient algorithm (Polak-Ribiere). The optimization was stopped if the first derivative of the total energy with respect to the nuclear positions was less than 0.001 kcal/(Å mol) (0.01 kcal/(Å mol) for DTB-Pe-tripod).

Electronic structures were calculated within ZINDO/S (Zerners spectroscopic version of INDO) [243, 244]. The electronic structure of neutral molecules has been found to be rather insensitive on the parameterization used for the structure optimization. For instance, the HOMO eigenvalue for perylene calculated with ZINDO/S for the AM1, PM3 and ZINDO/1 obtained structures differs by less than 25 meV. Closed shell systems (singlet states) are investigated with RHF (spin restricted Hartree-Fock) calculations, open shell systems (doublet and triplet states) with UHV (spin unrestricted Hartree-Fock) calculations.

Excited states for the calculation of electronic absorption spectra, transition dipole moments and oscillator strength were obtained with configuration interaction (CI) calculations performed at the molecular structure of the unexcited molecule (Franck-Condon approximation). In the CI expansion, up to 10 occupied and 10 unoccupied states have been taken into account.

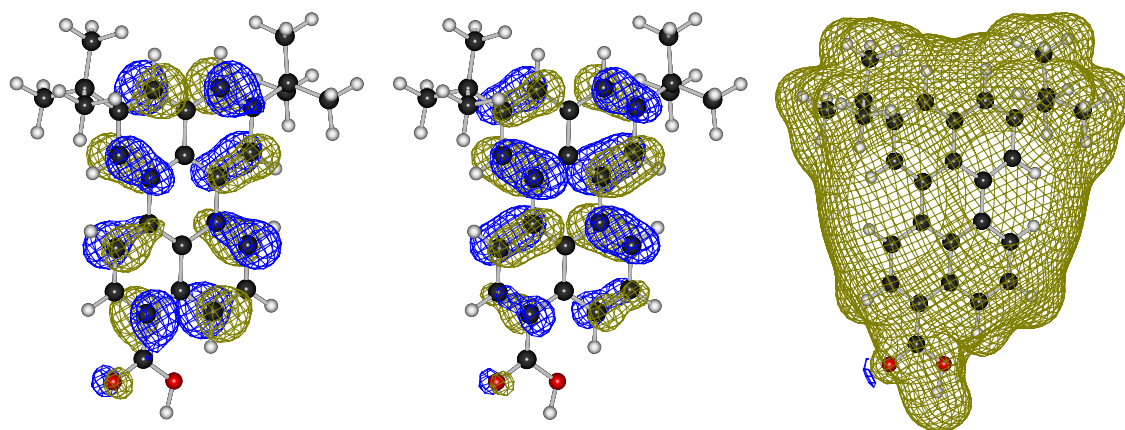


Figure A.1: Oxidized DTB-Pe-COOH (spin unrestricted Hartree-Fock calculation): HOMO [ $E_\alpha = -11.5$  eV] (a), LUMO [ $E_\beta = -5.8$  eV] (b) and electrostatic potential (c).

**Inertial axes.** The three axes (primary, secondary, and tertiary) are associated with the moments of inertia of the molecular system. The primary inertial axis marks the longest distance through the molecule, and the tertiary axis marks the shortest distance, as visualized in Fig. A.2.

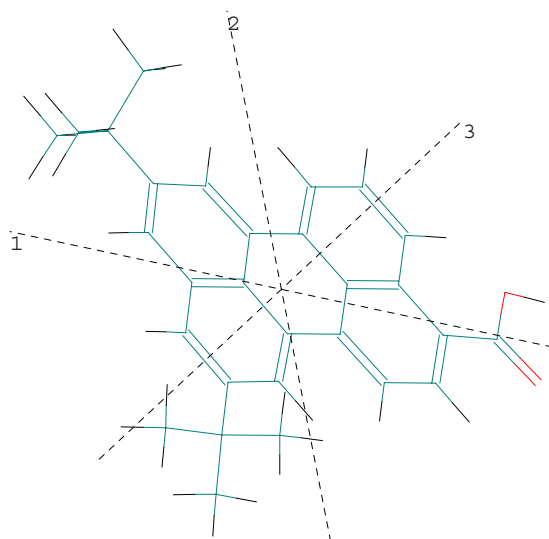


Figure A.2: Definition of the inertial axes considering DTB-Pe-COOH as example.

**Adsorbate-surface bonding geometries.** The adsorption geometries of the DTB-Pe carboxylic, phosphonic, propionic and methyl phosphonic acids (Figs. A.3 and A.4) were modeled by a molecular mechanics (MM) calculation using the MM+ force field with HyperChem. The optimization was performed with the Block-diagonal Newton-Raphson algorithm and was terminated when the gradient of the molecular coordinates fell below  $0.001$  kcal/(Å mol). The  $\text{Ti}_{40}\text{O}_{80}$  anatase cluster is

constructed with the anatase bulk structure [133]. The geometry of the cluster is kept fixed during the MM calculations. Details are given in the figure captions.

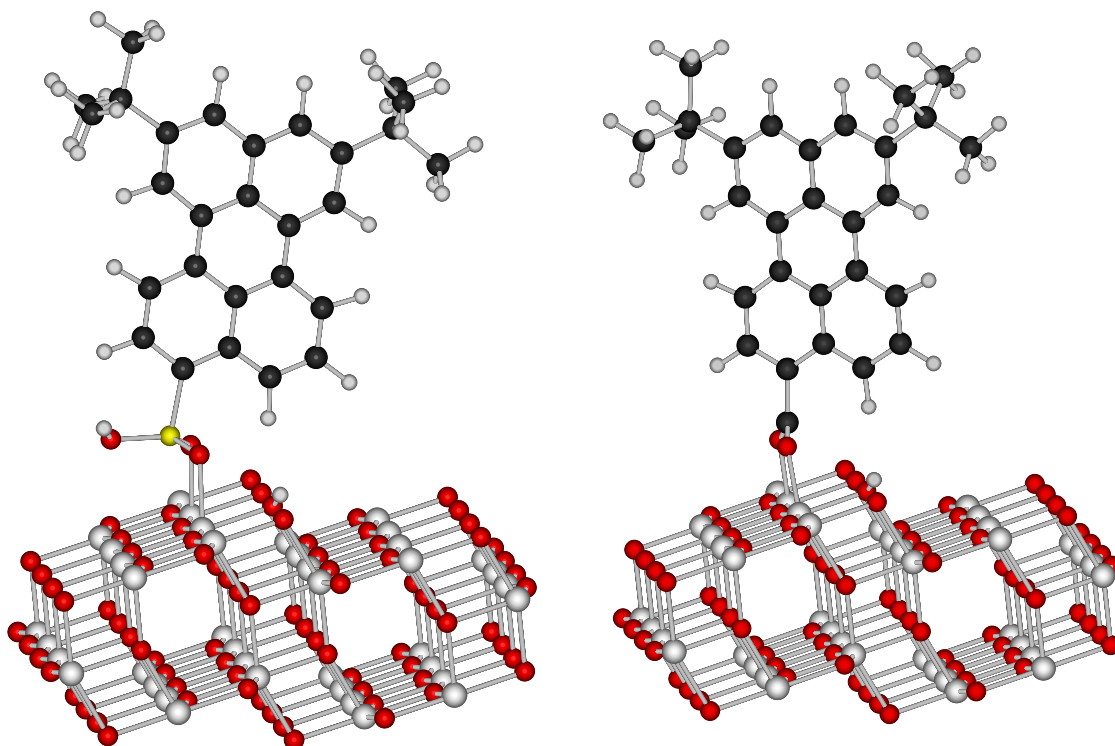


Figure A.3: Molecular mechanics optimized geometries of bi-dentate bonded DTB-Pe-P(O)(OH)<sub>2</sub> (left) and DTB-Pe-COOH (right) on a Ti<sub>40</sub>O<sub>80</sub> anatase cluster with (101) surface (force field: MM+). The geometry of the cluster is not relaxed. The distance between the perylene-carbon linked with the anchor group and the surface-oxygen in-between the binding titanium atoms is 4.25 Å (phosphonic acid) and 4.1 Å (carboxylic acid). Interestingly, with respect to the dye-surface distance the sharp bend in the bringing structure of DTB-Pe-P(O)(OH)<sub>2</sub> compensates for the longer dye-anchor bond of this molecule.

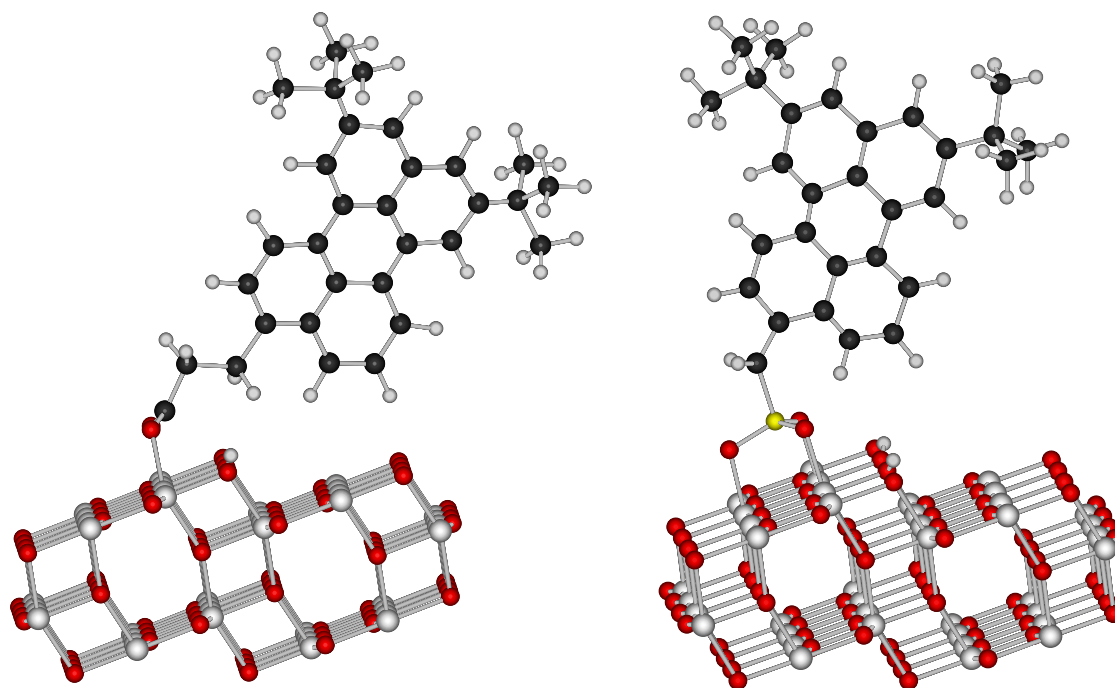


Figure A.4: Molecular mechanics optimized geometries of bi-dentate bonded DTB-Pe-CH<sub>2</sub>-CH<sub>2</sub>-COOH (left) and tri-dentate bonded DTB-Pe-CH<sub>2</sub>-P(O)(OH)<sub>2</sub> (right) (force field: MM+). The system is kept neutral as the dissociated hydrogen is adsorbed at a surface oxygen. Propionic acid: The dye-surface distance for the shown converged geometry exhibits a through-bridge distance of 6.0 Å and a through-space distance of 3.4 Å. According to the molecular mechanics calculations the chromophore does not completely bend back to the surface. Also for a different force field (Amber) the shown geometry appeared as global minimum of the geometry optimization.

In the case of the methyl-phosphonic acid with tri-dentate bonding of the anchor group(right), the geometry is more defined. The through-bond distance between the perylene-carbon linked to the bridge group and the local surface plane defined by the three binding surface-Ti atoms is 5.1 Å, the through-space distance is 4.1 Å.

## A.2 Details of the UPS and XPS measurements

Stationary ultraviolet photoemission spectra were recorded with a hemispherical analyzer (VSW HAS 100) in a separate UHV chamber. A commercial He-UV-discharge lamp emitting 21.22 eV photons was used for excitation of the samples. The spectra were measured normal to the surface without angular resolution. The pass energy of the analyzer was 2 eV. The UPS setup provides an energy resolution of about 100 meV. A detailed description of the setup can be found elsewhere [100]. The sample has been biased with -2.00 V (-4.00 eV for the determination of the secondary edge) and heated to 360 K during the UPS measurements. Due to the limited conductivity of the nanostructured anatase films, charging of the samples during the UPS measurement is usually a problem. One solution is the usage of thinner films, however, this alters the preparation procedure. It was observed that the strong temperature dependence of the conductivity of nano-structured anatase [177] can be utilized to overcome the charging problem. Heating the samples to about 370 K is sufficient to prevent charging of the 2  $\mu\text{m}$  thick films for the given UPS setup. Comparing the optical absorption before and after the UPS measurement reveals only a slight reduction of the absorbance, but no spectral changes.

The onset of the desorption or decomposition of the adsorbates was found to be above 450 K for DTB-Pe-CH=CH-COOH by increasing slowly the temperature and monitoring the C 1s peak via XPS and the partial pressure of possible decomposition products by a mass spectrometer. This observation is in agreement with the high thermal stability of up to 670 K observed for other perylene derivatives exhibiting substituted groups [245]. Recently, it has been observed that the reactivity of carboxylic acids on anatase depends on the preparation conditions [246]. Adsorbates on fully oxidized surfaces, which is also a realistic situation for the nano-structured films, did not desorb below 750 K.

Table A.1 summarizes the fit parameters of the XPS measurements for all investigated perylene derivatives. The column labeled "burned" denotes the sample mentioned above, which was heated above the decomposition temperature of the adsorbate. The observed spread in the peak positions as well in the peak shapes between different perylene derivatives is within the spread of the parameters for repeated measurements with the same dye. The same statement holds for the position of the HOMO and HOMO-1/3 peaks obtained from UPS measurements. Thus, the alignment of the molecular levels with respect to the semiconductor states are independent of the bridge-anchor group (inclusive tripod).

	pure TiO <sub>2</sub>	carboxylic	burned	propionic	acrylic	tripod	phosphonic	methyl-phosphonic
O 1s BE [eV]	530.71	530.72	530.75	530.66	530.74	530.70	530.65	530.69
O 1s FWHM [eV]	1.66	1.65	1.68	1.65	1.54	1.59	1.73	1.67
O 1s asymm	-0.09	-0.13	-0.09	-0.09	-0.10	-0.21	-0.17	-0.15
O 1s G/L	0.60	0.65	0.57	0.58	0.63	0.81	0.66	0.66
Ti 2p <sub>3/2</sub> BE [eV]	459.37	459.39	459.41	459.31	459.39	459.35	459.29	459.32
2p <sub>1/2</sub> - 2p <sub>3/2</sub> [eV]	5.77	5.76	5.73	5.75	5.76	5.70	5.77	5.77
FWHM Ti 2p <sub>3/2</sub> [eV]	1.47	1.44	1.46	1.47	1.45	1.39	1.46	1.43
C 1s BE without asym [eV]	285.07	285.01	284.76	284.83	284.86	285.16	284.90	285.06
C 1s FWHM [eV]	1.95	1.73	1.77	1.77	1.71	1.561	1.74	1.82
O 1s BE - Ti 2p <sub>3/2</sub> BE [eV]	71.34	71.33	71.36	71.35	71.35	71.35	71.36	71.39
O 1s BE - C 1s BE [eV]	245.64	245.71	245.99	245.83	245.88	245.54	245.75	245.63
Ti 2p <sub>3/2</sub> BE - C 1s BE [eV]	174.30	174.38	174.65	174.48	174.53	174.19	174.39	174.26
C 1s BE with asym [eV]	285.03	284.99	284.72	284.81	284.84	285.14	284.95	285.02
C 1s FWHM [eV]	1.95	1.73	1.78	1.77	1.71	1.56	1.73	1.82
C 1s asymm	-0.08	-0.07	-0.09	-0.04	-0.05	-0.06	-0.11	-0.09
C 1s G/L	0.35	0.42	0.58	0.37	0.53	0.51	-0.11	0.44
O 1s BE - C 1s BE [eV]	245.68	245.73	246.03	245.85	245.90	245.56	245.70	245.67
Ti 2p <sub>3/2</sub> BE - C 1s BE [eV]	174.34	174.40	174.69	174.50	174.55	174.21	174.34	174.30

Table A.1: Fit parameters of the XPS spectra for all investigated perylene derivatives. The peak positions are given as binding energies (relative to the Fermi level). The column denoted "burned" is a DTR-Pe-CH=CH-COOH sample, which has been heated up to 630 K under UHV conditions. The dye was completely decomposed (and eventually partially desorbed) by this treatment and appeared sooty. The O 1s and Ti 2p are fitted with asymmetric peak functions, as outlined in section 3.4.3. The C 1s peaks are fitted with both symmetric and asymmetric peaks, the according fit parameters are given in the upper and lower half of the table, respectively.

## A.3 Further analytical tools

### A.3.1 Single photon counting (SPC)

The principle of time-correlated SPC is to obtain the fluorescence decay by recording less than one emitted photon per excitation pulse. The experiments have been performed at an excitation rate of 150 kHz and a detection rate of about 2 kHz. The data was averaged with an Ortec ADC. The response function of the setup was determined by the jitter of the electronics. The decay curves have been fitted by mono-exponential decays convoluted with the response function.

All chromophores except DTB-Pe-COOH were dissolved in dried toluene with concentrations below  $10^{-5}$  mol/l. DTB-Pe-COOH was dissolved in 3:1 (vol.) toluene:methanol to prevent dimerization via the carboxylic group. The transition was pumped with a pulse of approximately 150 fs duration centered at 400 nm.

### A.3.2 Stationary absorption and emission spectroscopy

Linear absorption spectra are recorded with Bruins Instruments Omega 10 and 20 UV-VIS-NIR spectrometer with a slit width of 0.5 mm. The emission spectra are taken with a Spex FluoroMax spectrometer with a bandpass of 4 nm. The dye concentrations were below  $10^{-5}$  mol/l for the absorption measurements and below  $10^{-6}$  mol/l for the emission scans.

### A.3.3 FT-IR spectroscopy

The IR spectra were recorded with a Bruker Equinox IFS55 spectrometer equipped with a diamond ATR unit. The sensitized and unsensitized anatase samples have been prepared as described above, and then brought into UHV over night to evaporate the solvent from the nano-porous film. After this the anatase films were scratched off the glass substrate on the ATR crystal in the nitrogen flooded spectrometer.

### A.3.4 Raman spectroscopy

Raman spectra were recorded with a Bruker IFS 66v/S spectrometer with a Bruker FRA 106/S Raman module. The samples were excited with 200 mW of 1064 nm light (Nd:YAG). The signal was recorded with a resolution of  $4\text{ cm}^{-1}$  in backscattering geometry with a liquid-N<sub>2</sub> cooled Ge-D416 detector.

### **A.3.5 Transmission electron microscopy (TEM)**

TEM images were obtained with a Philips CM12 transmission electron microscope with a maximum electron energy of 120 keV. The achievable lateral resolution is 2.0 Å. Electron transparent samples of the temperature-treated colloidal anatase films were obtained by scratching of the film from the glass substrate. The fragments have been investigated on a gold grid.

### **A.3.6 Scanning electron microscopy (SEM)**

SEM images were taken with a LEO 1530 Gemini microscope by use of an In-Lens detector. Low acceleration voltages between 2 and 5 kV were applied to avoid charging of the samples.



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