

Chapter 5

Summary

The heterogeneous electron transfer from different perylene derivatives into nanostructured TiO₂ anatase under UHV conditions was systematically investigated by time-resolved pump-probe spectroscopy. The perylene molecule was shown to be a very beneficial chromophore for the study of ET processes as the absorption spectra of the involved electronic states allow for directly keeping track of the ET process via the pump-probe signals.

UHV conditions offer two obvious advantages for the investigation. First, the complicated energetic influence and response behavior of a solvent environment was avoided. Secondly, tools of surface science like UPS and XPS could be applied and the energetic positions of the adsorbate states relative to the semiconductor were determined by direct experiments carried out at the same interface that was investigated with transient absorption measurements. From UPS data the energy of the perylene ground state could be determined at 1.9 eV below the Fermi level, which coincides with the conduction band minimum (CBM) for illuminated samples. In combination with the electronic excitation energy, the position of the photoexcited state could be estimated to be around 800 meV above the CBM. As the reorganization energy of the electron injection is significantly smaller, the perylene-anatase system represents an heterogeneous ET system in the "wide band limit" [7, 70]. In this regime the ET rate depends only on the electronic coupling and the density of acceptor states in the semiconductor.

The electronic coupling between the adsorbate and the surface was systematically varied by exchanging the bridge-anchor groups, which provide the chemical linkage to the surface. Electron injection from the perylene chromophore directly bound to the surface via a carboxylic group occurs with a time constant of 13 fs. The exchange of this particular anchor group by a phosphonic acid group decelerates the electron transfer by a factor of two. As the density of the acceptor states is independent of the adsorbate, the change in the ET rate could be assigned solely to differences in

the strength of the electronic coupling. The differences in the electronic interaction were found to be reflected in the absorption spectra of the adsorbed dyes.

The adsorption geometries of the perylene chromophore with the carboxylic and the phosphonic acid anchor on an ideal anatase cluster were modeled by molecular mechanics calculations. For both these anchors the distance between the perylene body and the surface was found to be virtually identical. The experimentally observed differences in the electronic coupling mediated by the anchor groups could be rationalized by semi-empirical MO calculations for the free dyes. The extension of the excited wave functions onto the anchor group provides a qualitative measure of the electronic coupling to the surface. The differences between the carboxylic and the phosphonic acid anchors were ascribed to the different local symmetry of the anchor groups.

The insertion of one and two methylene groups in-between the chromophore and the phosphonic acid and the carboxylic acid anchors was found to reduce the ET rate by a factor of two and four, respectively. The differences in the injection kinetics were found to be mirrored by the kinetics of the recombination within the first picosecond for these electronically saturated bridge-anchor groups.

A significantly different behavior was observed for DTB-Pe-CH=CH-COOH, i.e. an sp^2 -hybridized bridge group. The forward injection from this chromophore occurs on the same time scale as from DTB-Pe-COOH, whereas the recombination kinetics resembles that of DTB-Pe-CH₂-CH₂-COOH. This qualitative difference compared to the symmetry of the saturated bridge-anchor groups could be explained by the different localization of the donor wave function for the injection and the acceptor wave function for the recombination reaction. It is emphasized here that such a behavior reflects the basic principle of a molecular diode.

The results on the injection times for perylene attached to carboxylic, acrylic, and propionic acids were compared to recent DFT cluster calculations of P. Persson and M. Lundqvist. The trend in the injection times agrees well between theory and experiment, the absolute values differ by a factor of two.

A qualitative different time scale of up to several picoseconds for the electron injection was observed for the perylene tripod chromophore. However, the electron injection was found to be multi-exponential with a fast component below 50 fs. This behavior was ascribed to inhomogeneities of the surface-binding of the molecule and to possible nonideal arrangements of the 25 Å molecule in the nano-structured film with about 100 Å mean pore diameter. Associating the longest observed time constant of about 3 ps with electron injection from ideally bound molecules, the distance dependence parameter β was estimated to 0.9/Å for non-adiabatic ET.

The time constants were obtained from the pump-probe signals by rate equation

fit models. The validity of the rate equation model for the extraction of ultrafast population relaxation times in the order of the pulse duration and the electronic dephasing was carefully examined by a comparison with an optical Bloch equations model of two incoherently coupled two-level systems. The differences in the cation absorption signal between the rate model and the Bloch model were found to be mainly a shift in time, whereas the temporal shape of both signals showed a fair agreement. Therefore, the rate equation model was found to provide a rather good description if time-zero is allowed to be a free fit parameter.

In order to time-resolve electronic processes on the 10 fs-time scale, the experimental prerequisite was the generation of sufficiently short laser pulses. The adaptation of the NOPA scheme to the pulse energy available from a high repetition rate laser system was a major improvement. It was achieved in a collaboration with E. Riedle's group, LMU Munich. The NOPA was shown to provide significantly shorter pulses and higher pulse energies compared to the collinear amplification scheme used before. Short pump pulses around 435 nm suitable for the excitation of perylene were generated by operating the NOPA in the NIR and frequency-doubling the output. In this way, sub-15 fs pulses with sufficient pulse energy were achieved in the spectral range between 420 and 450 nm.

Another experimental development was the design and the construction of an UHV chamber, which allows the introduction of gases and liquids at a high purity grade.

The microscopic properties of nano-structured metal oxides are known to be sensitive to details of the preparation procedure. The reliable investigation of such systems required the investigation of a large number of samples. Therefore, more than 100 samples were studied by time-resolved spectroscopy.

One outer parameter affecting the ET kinetics within the nano-structured anatase films is the choice of the glass substrate. Sodium diffuses from the substrate into the anatase films from glasses with a high sodium oxide content (soda-lime glass or $\text{SnO}_2\text{:F}$ on soda-lime glass). In the presence of sodium the electronic as well as the chemical coupling of the sensitizers is weakened, most likely due to the formation of a saline complex by the carboxylate group and Na^+ . As this effect is also observed for the conducting glass used in DSSC's, the reduction of the sodium concentration in the anatase film might improve the long-term stability due to a reduction of the cell degradation caused by dye detachment.

This thesis provides a microscopic picture of interfacial ET under UHV conditions. The observed differences between the systematically varied adsorbates are explained in terms of the different molecular wave functions. As long as one can predict the trend in the electron injection times with the stationary molecular electronic structure of the free molecule, the system can be regarded as being in the non-adiabatic limit. Future investigations based on the findings and results of this thesis

can address the effects of coherences, both vibrational as well as electronic (in the adiabatic limit), on the ET process. The study of these effects should provide interesting details of the electron injection dynamics.