

## **The Influence of Anchor and Bridge Groups on Ultrafast Heterogeneous Electron Transfer**

The dynamics of heterogeneous electron transfer are investigated by using several spectroscopic techniques. The system under study is the perylene chromophore chemically attached via different bridge-anchor groups to the surface of nano-structured  $\text{TiO}_2$  anatase. The energies of relevant electronic levels at the interface are determined by UPS and XPS, and the system is found to be in the so-called "wide band limit", in which the electron transfer rate is mainly controlled by the interfacial electronic coupling. The kinetics of the forward and the backward interfacial electron transfer are studied by pump-probe spectroscopy with sub-20 fs laser pulses. The electron injection from perylene directly bound to the surface with a carboxylic group occurs with a time constant of 13 fs. The exchange of the anchor group by a phosphonic acid as well as the insertion of electronically saturated ( $\text{sp}^3$ -hybridized) molecular units in-between the chromophore and the anchor groups systematically decelerates the electron injection. The trend observed in the forward electron injection is reflected in the kinetics of the initial backward transfer (recombination). In contrast, a conjugated bridge is found to function as a "molecular wire" with respect to electron injection but as a  $\text{sp}^3$ -hybridized analog with respect to recombination. The observed differences in the injection times for different bridge-anchor groups can be explained in terms of the molecular structures: the excited state wave functions of the isolated dyes, obtained by semi-empirical calculations, can predict qualitative trends for the interfacial electronic interaction and thus for the injection time. A rate equation model is applied for the extraction of the time constants. The validity of this model for the extraction of population kinetics on the time scale of electronic dephasing processes is verified by comparison with an optical Bloch equations model.