

**Photoinduced electron transfer in triarylmethane lactones.
Photophysics-structure relationship**

Ewelina Karolak-Solarska

This thesis presents results of a study on the structure–property relationships in a class of donor acceptor (D–A) molecules, triarylmethane lactones (LTAM). By introducing systematic structural and orientational modifications the effect on the photoinduced electron transfer processes was investigated. For this purpose, a series of triarylmethane lactones was designed, synthesized and characterized by spectroscopic methods.

In LTAM molecules, separation of the electron donating moiety from the electron accepting one by an sp^3 carbon atom allows in the ground state for preservation of individual photophysical properties of the structural subunits. On the excited state level, the tetrahedral carbon link in combination with a C–heteroatom bond serves as an effective channel for intramolecular electronic communication and enables strong electronic coupling resulting in an ultrafast and efficient ET with formation of an intramolecular exciplex of a radical ion pair structure. Based on the study of LTAM with two (D–D–A triad) or with one (D–A dyad) D moieties it was found that not only the primary ET process occurs in close analogy in both molecules, but also the deactivation paths of the CT states are virtually the same in triads and dyads. Hence, in symmetric D–D–A triads only one D group is actively involved in the charge separation (CS) process. Both, dyads and triads form CT triplet states in excited state deactivation. The work explored the effect of structural modifications resulting in changing the reduction potential of the acceptor subunit in LTAM of the D–D–(DA) type. The rate and yield of the ET process in these molecules are strongly solvent dependent, since the solvation dynamics generally controls the energy and availability of the excited states. Special attention was paid to the effect of mutual orientation of the D and A subunits on the excited state processes in spiro–derivatives of LTAM. The presence of spiroconjugation between D and A was demonstrated and its effect on the photophysics described. Almost equal energies of the D and A subunits result in inversion of nearly degenerated excited states and fluorescence switching as a function of solvent polarity and temperature. Moreover, the rigid spiro–structure affects not only the energetics, but it opens new deactivation pathways for the initially excited molecule. It was shown that a vibronically hot molecule can undergo a lactone ring–opening reaction with formation of a short–lived (on the ps time scale) zwitterionic species. It was also found that minor modifications of the structural subunits of LTAM result in significant changes in energies of the lowest excited states, and consequently in the involvement of the primary ET in a sequence of processes, enabling manipulation of the CS reaction, and even molecular engineering, especially because these simple D–A systems display dual fluorescence. The question of exploiting dual fluorescence in white light generation in derivatives of crystal violet lactone (CVL) was addressed. Using two CVL analogues, it was shown that dual emission is a general property of the D–D–(DA) structures built on an sp^3 carbon atom.