From solution to solid state: energy- and electron-transfer in complex materials

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Summary

The interaction of different types of chemical entities such as transition metal complexes, luminescent organic chromophores and noble metals can lead to the development of complex materials with special properties that are more than the sum of the individual components. For the research described in this Thesis, it is aimed at the development of multicomponent systems and their interaction with light. Besides intrinsic photophysical properties of the separate compounds (e.g. absorption, emission, ...), light can, in suitably designed assemblies, induce directional processes such as energy and electron transfer.

This Thesis presents the synthesis, characterization and optical properties of these complex materials in solution or as solid. After a brief introduction to the general phenomena occurring upon light excitation of a molecule, the background of the energy- and electron-transfer processes is described. As pyrene is one of the main organic chromophores used in this work, an exemplification of molecules that contain this moiety and show energy and/or electron transfer is given (Chapter 1). Detailed spectroscopic investigations as well as synthetic procedures of many different types of photoactive systems are described in Chapter 2 to Chapter 7. Finally, Chapter 8 presents the instrumentation characteristics and the conditions used for the measurements presented in this work.

In Chapter 2, a molecular wire composed of a ruthenium trisbipyridine moiety covalently linked via a diethynylene-benzene spacer to a pyrene unit is described. Upon excitation of the metal complex the pyrene triplet state emission is observed at room temperature under strict deaerated conditions. Time resolved studies also evidenced a relatively slow forward triplet state equilibration rate, in the order of $2 \times 10^5 \, \text{s}^{-1}$ (5 μs), and an even slower back energy transfer rate, $3.3 \times 10^4 \, \text{s}^{-1}$, still faster than the intrinsic decay time of the pyrene (200 μs).

Chapter 3 presents the effect of meta vs para conjugation on the energy transfer processes in ruthenium-oligophenylene-osmium systems, by comparing meta substituted oligophenylene bridges to para-substituted ones. A superexchange mechanism is proposed.

The synthesis and the behaviour of a system in which pyrene is covalently bound to a terpyridyl unit in its neutral form, its zinc complex and its protonated form are described in Chapter 4. For these molecules, an electron transfer process was shown to occur forming the radical cation of the pyrene and the radical anion of the terpyridine upon excitation. The transient absorption spectroscopy of these molecules reveals a deactivation process to a long-lived triplet state that we have attributed to the pyrene.
Chapter 5 is focused on the Non Linear Optical (NLO) properties of functionalized metal complexes. After a brief introduction on NLO phenomena, the synthesis and the photophysical characterization of ruthenium bisterpyridine complexes in which one terpyridine unit is substituted with electron-acceptors or electron-donors is given. The photophysical properties reveal the involvement in the Metal to Ligand Charge Transfer (MLCT) excited state of the ligand that is acceptor-functionalized. When electron donor groups are attached to one of the ligands, the unsubstituted terpyridine ligand seems to be involved in the MLCT excited state. These results as well as the presence of an Intra Ligand Charge Transfer (ILCT) state were used in order to explain the experimental NLO results. We demonstrate that the addition of low-lying CT states to the usual MLCT levels of ruthenium bisterpyridine systems can increase the hyperpolarizability (β-value). Also increasing the distance between metal complex and electron donor or acceptor by addition of phenylene bridging units increases the NLO response.

Chapter 6 focusses on metal surfaces and ruthenium trisbipyridine complexes that possess one (or two) aliphatic tail(s) terminated by thiol functions. The complexes were study in solution as well as anchored to the metallic surface. Indeed, after attachment, only a weak emission was found (τ ≈ 6 ns, k ≈ 2 x 10^8 s⁻¹) due to the strong queching of the metal substrate. Furthermore, the investigation of the assembly on the surface revealed a low coverage value. Such conclusions were resulted from the electrochemical characterization as well as the confocal microscopy images.

Finally, in Chapter 7, the preparation of gold nanoparticles “templated” by sulfur containing dendrimers is reported. It is shown that the generation of the dendrimers as well as the position of the sulfur atoms in the dendritic structure leads to different formation and reactivity of the particles. Considering the size, it is suggested that one small nanoparticle (d= 1.8 nm) could be stabilized by just one dendrimer. For sulfur containing molecules that do not contain the dendritic structure, no formation or stabilization of gold nanoparticles was observed.