

The Role of Charge Transfer Processes in Molecular Chromophores for Non Linear Optics and their Potential in Electron Transfer Processes.

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A relevant theme of our researches, particularly related to the subject of the present meeting, concerns the investigation by photophysical methodologies, of the electron transfer in push-pull architectures involving organometallic or coordination molecular systems.¹ Two of the systems investigated in our laboratory of particular interest are asymmetric metallo porphyrins and Ir(III) and Ru(II) organometallic complexes, linked to strong electron acceptor moieties.

In particular we are actually investigating the theoretical design, synthesis and photophysical characterisation of asymmetric metallo porphyrins mono² and disubstituted³ with donor and/or acceptor groups for applications in second (electrooptical devices) and third order non linear optics (two photon absorption,⁴ optical limiting). Porphyrins are particularly attractive materials because of their chemical and thermal stability and because their photophysical properties can be tuned via suitable structural modifications. Therefore, given their efficiency in the electron transfer processes characterising the photosynthesis, porphyrins may have great potential as sensitisers for light harvesting by the development of solar cells. We have recently shown that specific push-pull porphyrin structures produce a facile and relevant electron transfer process from the HOMO (donor) to the LUMO (acceptor) orbitals.³

Besides, another class of compounds under investigation are cationic and neutral bis-cyclometallated Ir(III) complexes with substituted phenanthrolines. These complexes are of particular interest due to their luminescence⁵ and non linear optical (NLO) properties⁶ easily tuned by an adequate choice of the phenanthroline ligands including a phenanthroline linked to a C₆₀ moiety. In these systems the large NLO properties have been attributed to the significant contribution of rather intense low energy metal to ligand transitions involving a HOMO-LUMO charge transfer from the cyclometallated moiety to the phenanthroline ligand. Recently our attention has been focused also on the synthesis and photophysical characterization of Ru(II) cationic and neutral complexes with a diazafluorene ligand substituted by a C₆₀ moiety. The coordination of a bidentate ligand containing a fullerene moiety to a metal should increase the system solubility, an important factor in the preparation of "bulk heterojunction" cells. In addition, the use of hybrid photoactive materials that combine covalently the polarizable and acceptor properties of the fullerene with the coordination sphere of photoactive metal complexes is attractive due to possible charge transfer processes such as MLCT which may produce an easy photoinduced electron transfer from the metal complex, acting as the system for light harvesting, to the fullerene.

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