Ligand-to-metal charge transfer excited states in organometallics

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Organometallic compounds are an important class of materials in many areas of science and technology. Most organometallic compounds dissipate excitation energy very rapidly in nonradiative fashion, and only a small fraction have excited states with moderate lifetimes, from which luminescence typically can occur. One of the key problems in photophysics and photochemistry of organometallic complexes is the assignment and characterization of their higher-lying and lower-lying excited states. Most organometallic complexes possess metals in low oxidation states; so far in UV-vis spectrum, low-energy metal-to-ligand charge transfer (MLCT) transitions dominate.

Ligand-to-metal charge transfer (LMCT) excited states play an important role in the photophysics and photochemistry of metal complexes, however, knowledge on photophysical properties of complexes having pure LMCT excited states, unlike MLCT, metal-centered, ligand-centered or other excited states, accounts almost silent observations. LMCT excited states of organometallic compounds are the extremely rare and much less studied type of electronically excited states. [1-5] Perhaps, only early-transition metal complexes in high oxidation states exhibit readily identifiable LMCT excited states. The examples to be discussed will illustrate the rich variety of photophysical and photochemical behavior, exhibited by organometallic species in their pure LMCT excited states. Principle emphasis will be given to investigations on solvatochromism, relation between LMCT transition energies and differences in oxidation and reduction potentials, relation between emission quantum efficiency and lifetime, electron-exchange (Dexter) resonant energy transfer, and photolysis of organometallic compounds in their LMCT excited states.

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