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Harvesting and Electron-Exchange Energy Transfer by d⁰ Metallocene-based Organized Systems

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The present contribution will provide an up-to-date overview of novel experimental and theoretical (derived quantum-chemically) knowledge on photonics of group IV metallocene-based systems, also with respect to their prominent use in catalysis and photoluminescent sensor activity. We have developed photophysical approach to study measurable properties of the frontier MOs of the complexes, estimate orbital nature of rare long-lived ligand-to-metal charge transfer (LMCT) excited states and also supramolecular interactions between basic components of catalytic systems for polymerization: d⁰-metal complexes and unsaturated hydrocarbon substrates in fluid systems. In the similar way, the photophysical approach is highlighted to enable studying fine intermolecular interactions in homogeneous systems with low (catalytic) concentrations of metal complexes that cannot be achieved by other conventional methods.

1. INTRODUCTION

Molecular electronic excited states are of great fundamental and technological importance. In supramolecular photophysics and photochemistry, research has traditionally concentrated on the search for long-lived excited states and utilization of their transformations in light energy conversion, information processing, and photocatalysis. Transition metal complexes are an important class for materials in many areas of science and technology. Studies on simple organometallic systems, those electronic and vibrational transitions can be properly assigned, provide the much needed detailed physico-chemical understanding of relationship between ground electronic state and low-lying excited states with respect to their reactivity, intramolecular bond-splitting mechanisms, electron transfer and energy transfer properties, and so on. In contrast to organic molecules, unambiguous determination of basic characteristics for organotransition metal complex compounds in electronically excited states is rather difficult and remain unresolved for great number of metal-containing systems — the more complex is the molecule or molecular system, the more complicated is the problem. The presence of transition metal ion(s) in molecules/clusters results in partial or complete removal of the multiplicity forbiddance for electronic transitions due to moderate or large spin-orbit coupling of a metal, as well as leads to nonradiative degradation via vibrational interactions owing to high covalence of organometallic bonds and so on. As a result, unlike the well-documented variety of phosphorescent states of organic species, long-lived emissive states of clusters based on organometallic compounds in liquid systems account very limited cases and have not been systematically studied; it is the photochemical properties of late transition metal compounds that have mainly been investigated.

Generally speaking, organometallic complexes/clusters have a variety of low-lying excited states in near-ultraviolet, visible, and near-infrared region. Important is that in coordination compounds, yet radiationless transitions are much more common than radiative transitions. Excitation of electron from a ligand-centered orbital to an orbital, located predominantly on a metal ion, originates ligand-to-metal charge transfer (LMCT) excited state(s). Relatively little knowledge has been gained on photophysics and photochemistry of organometallic complexes having lowest energy ligand-to-metal charge transfer excited states (LMCT) [1−23], unlike metal-to-ligand (MLCT), metal-centered, or ligand-centered excited states based on vast majority of organometallic complexes with metals in low oxidation states. Meanwhile, long-lived LMCT excited states are promising in solar energy conversion and photocatalysis. A very few types of such complexes with metals in high oxidation states have been reported as luminescent, especially in fluid media at room temperature. Throughout recent elegant works, LMCT emissive behavior was elucidated for a very few complexes containing multiply bonded ligands, particularly aromatic π-ligands, and early or middle transition metals in d^0 electronic configuration. Presently, photonics of LMCT excited states based on metal complexes and nanoclusters in multi-component systems represent a challenging area of physico-chemical research.

2. PHOTONICS OF TI, ZR, HF-BASED COMPLEXES

2.1 Frontier molecular orbitals, absorption, and phosphorescence

Recently, we initiated a systematic study on photonics of d^0 group IV metallocenes, possessing rare highly emissive (for Cp_2MCl_2 where $Cp = C_5H_5^-$, $M = Zr(IV)$

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and Hf(IV): Φ_{LUM} = 1 at 77 K), extremely long-lived (τ in the range of milliseconds at 77 K) LMCT excited states (Scheme below) and the electron transfer properties.
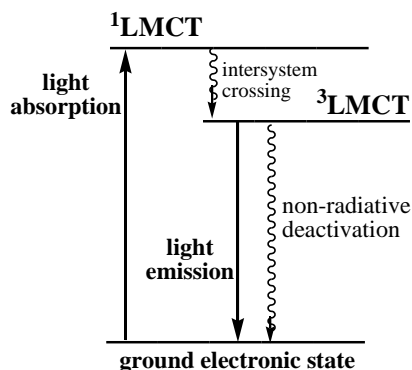

Fig. 1 – Schematic representation for photophysics of Cp_2MCl_2 and related d^0 (half-)metallocene complexes

It is reasonable to conclude that in Cp_2MCl_2 and related d^0 (half-)metallocene complexes, ultra-fast dissipation of the excess energy follows a sequence of elementary stages: vibrational relaxation to equilibrium geometry followed by internal conversion, change of the spin multiplicity (intersystem crossing) and so on, eventually producing long-lived, thermally-equilibrated, emissive triplet excited state(s): ^{3}LMCT. Excitation into either first or second transition results in the same long-lived luminescent LMCT excited states. It is assumed that intersystem crossing to the lowest triplet state occurs with quantum efficiency 100%, at least, in representative group IV metal triad complexes Cp_2MCl_2. [14-15] The energy trend of the emission along the representative triad Cp_2MCl_2 is in line with the $\pi(Cp^-) \rightarrow d(M)$ absorption energies. The Zr and Hf isostructural complexes exhibit strong blue/green luminescence upon photoexcitation, in contrast to red emission in titanocene, in both solid state at room and low temperatures and in frozen solutions. Importantly, emission from the representative metallocene complexes Cp_2MCl_2 originates from spin-forbidden triplet excited states: $^3A_1 \rightarrow \,^1B_2$.

The equal maximal quantum yields (Φ_{LUM} = 1.0) in very closely related molecules Cp_2ZrCl_2 and Cp_2HfCl_2 dramatically surpass that (Φ_{LUM} = 0.09) in smaller molecule Cp_2TiCl_2. The experimental lifetime (λ_{exc} = 337 nm) of $T_1 \rightarrow S_0$ transitions in the isostructural triad depends strictly on the metal nature, e.g. in the isostructural complexes Cp_2MCl_2: 2 ms (*Zr*); ca. 0.8 ms (*Ti*), and 0.3 ms (*Hf*, the shortest one) in glassy solutions at 77 K. It should be stressed that the emission quantum yields (Φ_{LUM}) and excited-state lifetimes (τ) in the group 4 organometallics are among the highest known for metal-containing compounds.

It is instructive to merge further photophysical and electrochemical observations into one conceptual framework (Figs. 2−4). The individual first oxidation and reduction potentials and the difference thereof (electrochemical gap *G*) can be related to inherent thermodynamic and kinetic quantities within the structurally-related d^0 organometallic series.
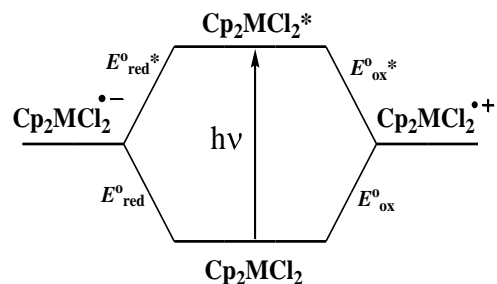

Fig. 2 – Schematic representation for the one-electron reduction and oxidation of the representative group IV metallocene triad Cp_2MCl_2 (M = Ti, Zr, Hf) in their ground and the LMCT emissive state.
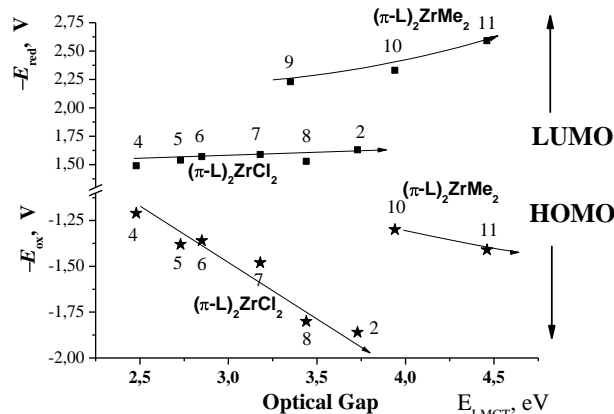

Fig. 3 – Tendency (V *vs*. SCE) in the first reduction potential ("the LUMO energy in solution") and the first oxidation potential ("the HOMO energy in solution") with changes in energy of the first LMCT absorption band maximum obtained experimentally for the nine structurally related zirconocenes. The complexes appear in the order: *2* – Cp_2ZrCl_2, *4* – $Ph_2C(CpFlu)ZrCl_2$, *5* – $Me_2SiInd_2ZrCl_2$, *6* – *rac*-$(CH_2)_2Ind_2ZrCl_2$, *7* – Ind_2ZrCl_2, *8* – $Me_2SiCp_2ZrCl_2$, *9* – *rac*-$(CH_2)_2Ind_2ZrMe_2$, *10* – Ind_2ZrMe_2, *11* – Cp_2ZrMe_2

In the recent studies, a first experimental evidence and theoretical justification for the existence of a linear correlation between energies of the electrochemical gap (difference of the redox potentials) and optical gap (absorption and luminescence energies) between the frontier MOs was revealed for a class of π-complexes using group IV metal complexes $(π-L)_2MX_2$ as an instructive example (Figs. 4, 5), viz.: $\Delta E(optical) = a\Delta E(redox) + \sum b_i$.
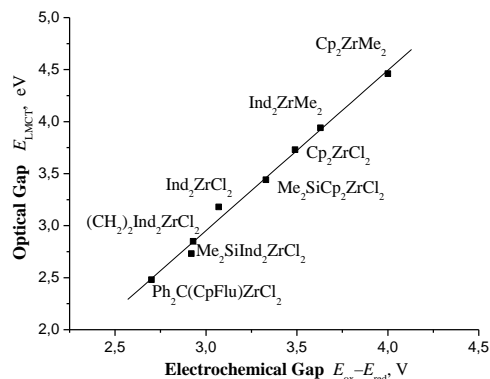

Fig. 4 – Variation of energy of the lowest LMCT absorption band maximum with the difference between the first oxidation and reduction potentials $E_{ox}-E°_{red}$ obtained for d^0 zirconocenes
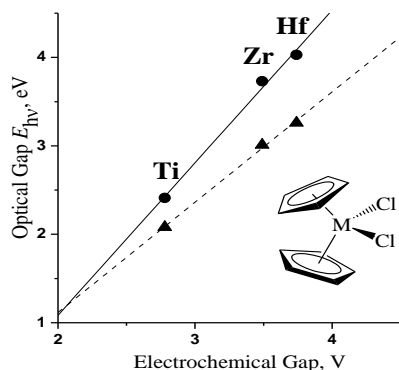
Fig. 5 – Linear correlations between energies of the electrochemical gap $E_{ox} - E°_{red}$ and energies of the HOMO–LUMO absorption maximum E_{LMCT} (........) and energies of 0–0' electronic transition obtained from emission spectra $E_{em}(0-0)$ (........) in Cp_2MCl_2: M=Ti, Zr, and Hf

Such an approach produces a practical basis for unraveling relation between the properties of individual metallocene precursors (for active catalysts), the structure of organometallic catalytic species and their anticipated/actual catalytic functions in multi-component catalytic (and other, e.g. photocensor [22-23]) systems.

2.2 Electron-exchange resonant energy transfer

We have developed first photophysical approach to estimate orbital nature of rare long-lived ligand-to-metal charge transfer excited states and also coordinative interaction of basic components of catalytic systems for polymerization: metallocene complexes and unsaturated hydrocarbon substrates. Energy transfer mechanism was recently employed to study chemical interactions at low, close to catalytic concentrations (which cannot be achieved with conventional techniques, such as NMR) between Zr(IV) and Hf(IV) π-complexes (as highly-emissive energy donors) and unsaturated hydrocarbons (as non-phosphorescent triplet energy acceptors). In these highly organized systems, chromophores Cp_2MCl_2 (M = Zr and Hf) can be selectively photoexcited. The long-lived state energy of Zr or Hf was revealed to be nonradiatively transferred to unsaturated hydrocarbons, resulting in emission quenching of the metallocene (the efficiency of intermolecular triplet energy transfer was examined by steady-state luminescence spectroscopy at low temperature) (Figure 6).

Perhaps, the most unexpected significant result is a linear relation between values of the critical radius of sphere for electron-exchange resonant energy transfer [5], where actual electron-exchange interaction can occur, and a number of carbon atoms in linear α-olefins (having $E_T \sim 25000$ cm^{-1}), viz. R_0 (Å) = −2.47 + 1.35n (obtained with the use of hafnocene systems [$Cp_2HfCl_2 + C_nH_{2n}$ + alkane] at 77 K). This correlation suggests coordinative interactions, in the ground electronic state, between an unsaturated hydrocarbon and a d^0 metal in a metallocene. Arrangement of the unsaturated quencher around the d^0 metal core was shown to dramatically affect the triplet energy-transfer efficiency and coordinative interaction in solution. d^0 Organotransition metal complexes are thus coordinated (via inner- and outer-sphere modes) with alkenes and dienes via combination of two or more types of more
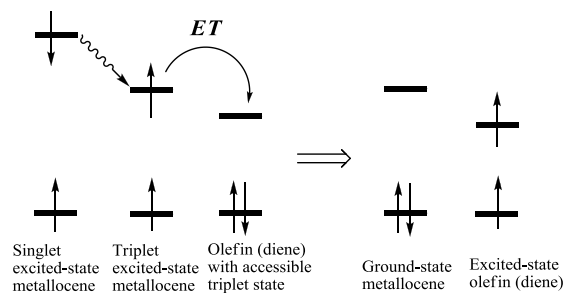

Fig. 6 – Schematic representation for non-radiative (resonant) triplet energy transfer from d^0 metallocenes to energy traps (unsaturated hydrocarbons here) via electron-exchange mechanism

or less pronounced noncovalent interactions: metal – ligand coordinative bonds, aromatic π—π-stacking, and so on. These findings provide a new example of resonant triplet energy transfer use for studying intermolecular interactions, in particular, the first example of systematic study of coordination between unsaturated hydrocarbons and d^0 metal complexes with the energy transfer approach.

In summary, a combined photophysical and theoretical approach made it possible to carry out study of the phenomenon of monomer coordination in practical catalytic or near-practical conditions, that may be of crucial importance for understanding mechanism and prediction of a multistage catalytic process of unsaturated compounds polymerization with organometallic complexes, particularly, d^0 metal complexes.

3. CONCLUSIVE REMARKS

A representative organometallic family, possessing promising LMCT states, is group IV metallocene complexes. Notably, early-transition metal bent metallocene have been a cornerstone in the development of modern coordination organometallic chemistry and catalysis and continue to be a focus of chemical and structural studies giving fresh insights into reactivity, structural preferences, and bonding requirements and even in medical chemistry. Intensive studies made it possible for us and others to determine energetic and orbital characteristics for organometallic complex compounds and their organized systems based on early-transition metals, triplet nature of their lowest excited states, supramolecular and specific (donor – acceptor) interactions of the metal complexes at rather low concentrations (10^{-6}–10^{-5} mol l^{-1}) with unsaturated compounds and a solvent. It was revealed that independent electrochemical and optical estimates provide consistent data on the trends in the frontier MO energies and the energy gap in d^0 metal complexes. Consequently, the combination of electrochemical and photophysical methods can be applied as useful diagnostics to determine in solution «ionization potential» and «electron affinity» (relative energies of frontier MOs measured as reduction and oxidation potentials) and the HOMO–LUMO energy gap in complex molecules clusters based on group IV metals (Ti, Zr, Hf).

The amazing diversity of bent sandwich complexes of early transition metals makes their study extremely exciting. There is still great scope for novel chemical, catalytic, photophysical, electrochemical, and structur-

al investigations of these organometallic molecules and systems based on them. A photophysical approach made it possible to reveal and begin an experimental study of the phenomenon of monomer coordination in practical catalytic or near-practical conditions that may be of crucial importance for understanding mechanism and prediction of a multistage catalytic process of unsaturated compounds polymerization with organometallic complexes, particularly, d^0 metal complexes. A photophysical approach offers possibilities of a direct study of real multi-component systems including catalytic ones, which have found wide applications in fundamental science and technology.

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