Novel experimental approach to probing frontier orbitals and HOMO–LUMO gap in π-organometallics

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The research is in a general area of mechanistic organometallic chemistry with particular emphasis on the application of the molecules to electron transport and catalytic reactions. One major thrust is the development of physico-chemistry of highly reactive, promising early-transition metal complexes for comprehensive physical organometallic chemistry. Reactivity originated by a complex interplay of polar, steric, and bond-strength terms and for many cases can be well described in terms of a frontier molecular orbital (FMO) approach. We believe that understanding and predicting chemical reactivity in inorganic and organometallic chemistry can be best achieved, at least, rationally started with use of a FMO approach. A key chemistry problem referred in particular to $(\pi\text{-L})_2MX_2$ family is obtaining reliable experimental or theoretical estimate for electronic structures and relative energies of frontier MOs of complex molecules, if «HOMO–LUMO difference can be due to an energy increase of the filled level, a decrease of the empty level, or both...»

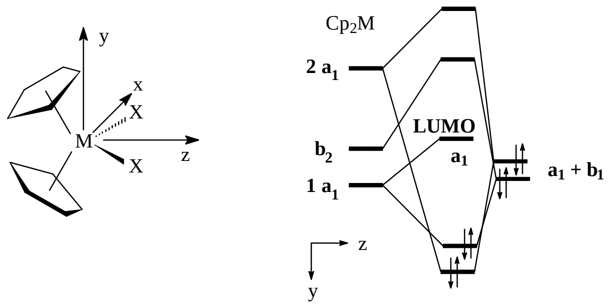

Figure 1. Interaction diagram for $Cp_2M^{IV}X_2$. The indicated orbital occupation corresponds to the bent metallocene fragment Cp_2M (left) and two σ-donor ligands X (right) where X is less electronegative than Cp ligands.

In this report, we focus on generalization regarding ligand-to-metal charge transfer excited states, experimental quantities of the HOMO and LUMO, a trend in the HOMO–LUMO gap, and a division of the electron transition paradigm $E_{h\nu}=a\cdot\Delta E_{\text{redox}}+\sum b_i$ into the strategy of studying d° π-organometallics based on the Ti^{4+}, Zr^{4+}, and Hf^{4+} metal cores.

With use of group 4 bent metallocenes $(\pi\text{-L})_2MX_2$, it is proposed that combination of optical and electrochemical methods can be applied as useful diagnostics to determine in solution «ionization potential», «electron affinity», and HOMO–LUMO gap in organometallic π-complexes. Experimental direct relations between quantities of ground and excited states viz. $E_{h\nu}=a\cdot\Delta E_{\text{redox}}+\sum b_i$ ($E_{h\nu}=E_{\text{LMCT}}$ and E_{em}) are for the first time revealed for *3d–5d* early transition metals (Ti, Zr, and Hf).

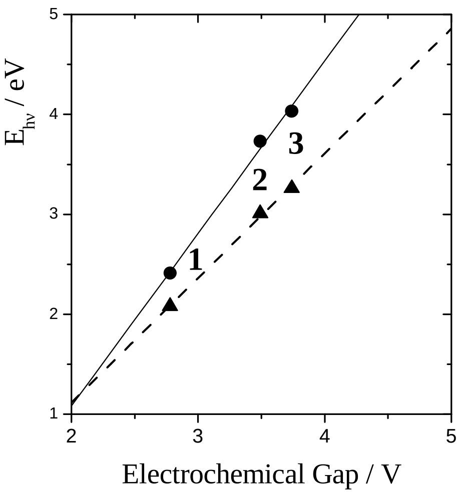

Figure 2. Linear correlations between the electrochemical HOMO-to-LUMO gaps $E_{\text{ox}}–E^\circ_{\text{red}}$ and energies of absorption E_{LMCT} (_______) and emission $E_{\text{em}}(0–0)$ (........) in $Cp_2M^{IV}Cl_2$: M=Ti (**1**), Zr (**2**), Hf (**3**).

The principle correlations are rationalized assuming that the same frontier orbitals are involved in optical and thermal electron-transfer processes. Identity of so called «redox» and «optical» frontier molecular orbitals involved in redox, or electrochemical and optical processes was thus justified. Overall effect of the introduction of a larger sandwich ligand or a bridging group is demonstrated to be progressive reduction of the HOMO–LUMO gap. As important results, unprecedented perturbations introduced in metal-based LUMO *via* methide σ-ligands and the largest HOMO–LUMO gap are for the first time demonstrated for dimethyl complexes. Accordingly, the largest HOMO–LUMO gap is observed for the dimethyl metallocenes, which coincidentally have the highest, both derived electrochemically and spectroscopically, electron transition energy up to 4.5 eV. A key result is inherent accuracy of direct relations $E_{h\nu}$ vs. ΔE_{redox} even upon perturbations introduced in the metal-based LUMO and an apparent change in the localization of the HOMO from a highest orbital provided by $(\pi\text{-L})_2$ onto a highest orbital provided by σ-ligands in $(\pi\text{-L})_2MX_2$.

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