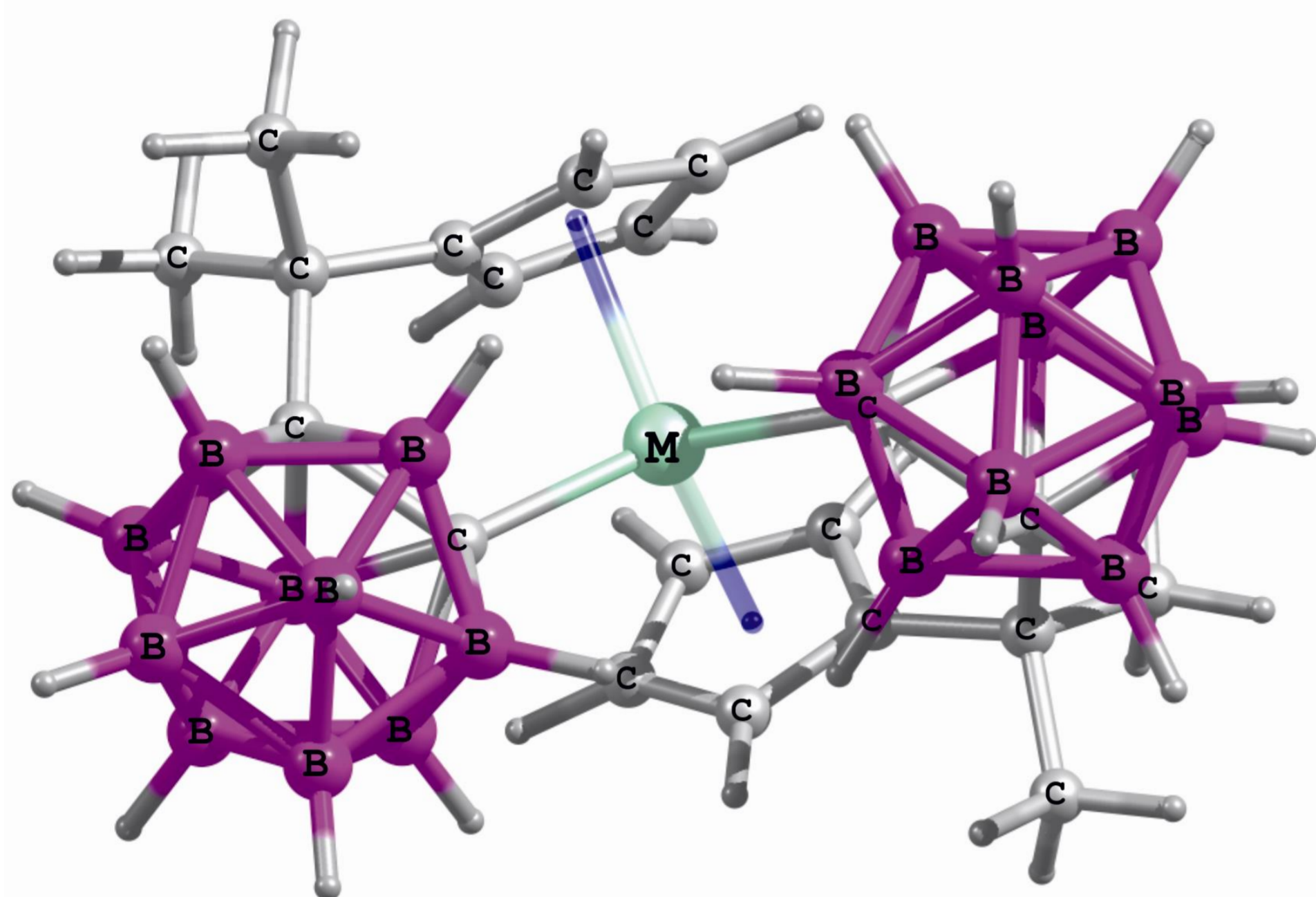


# LMCT states of sophisticated group 4 metallocene dicarboranyls

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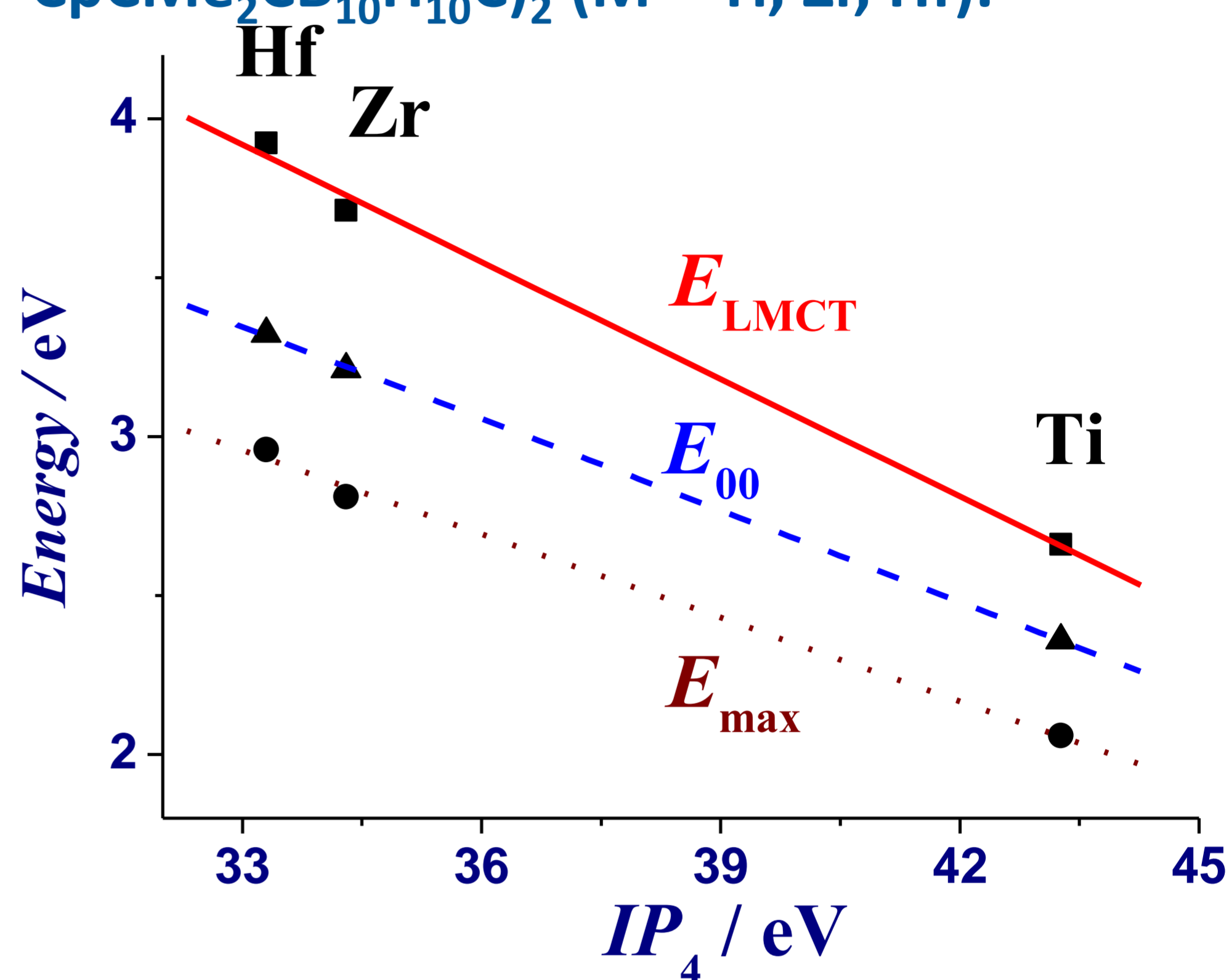
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Presently, *photophysical and quantum-chemical methods* were applied to study the orbital nature and extremely rare *ligand-to-metal charge transfer (LMCT) excited states based on non-classical organometallics*: structurally-complex  $d^0$  metallocenes, bearing polyhedral boron-containing  $\sigma$ -ligands  $M(\eta^5:\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$  ( $M = \text{Ti, Zr, Hf}$ ).

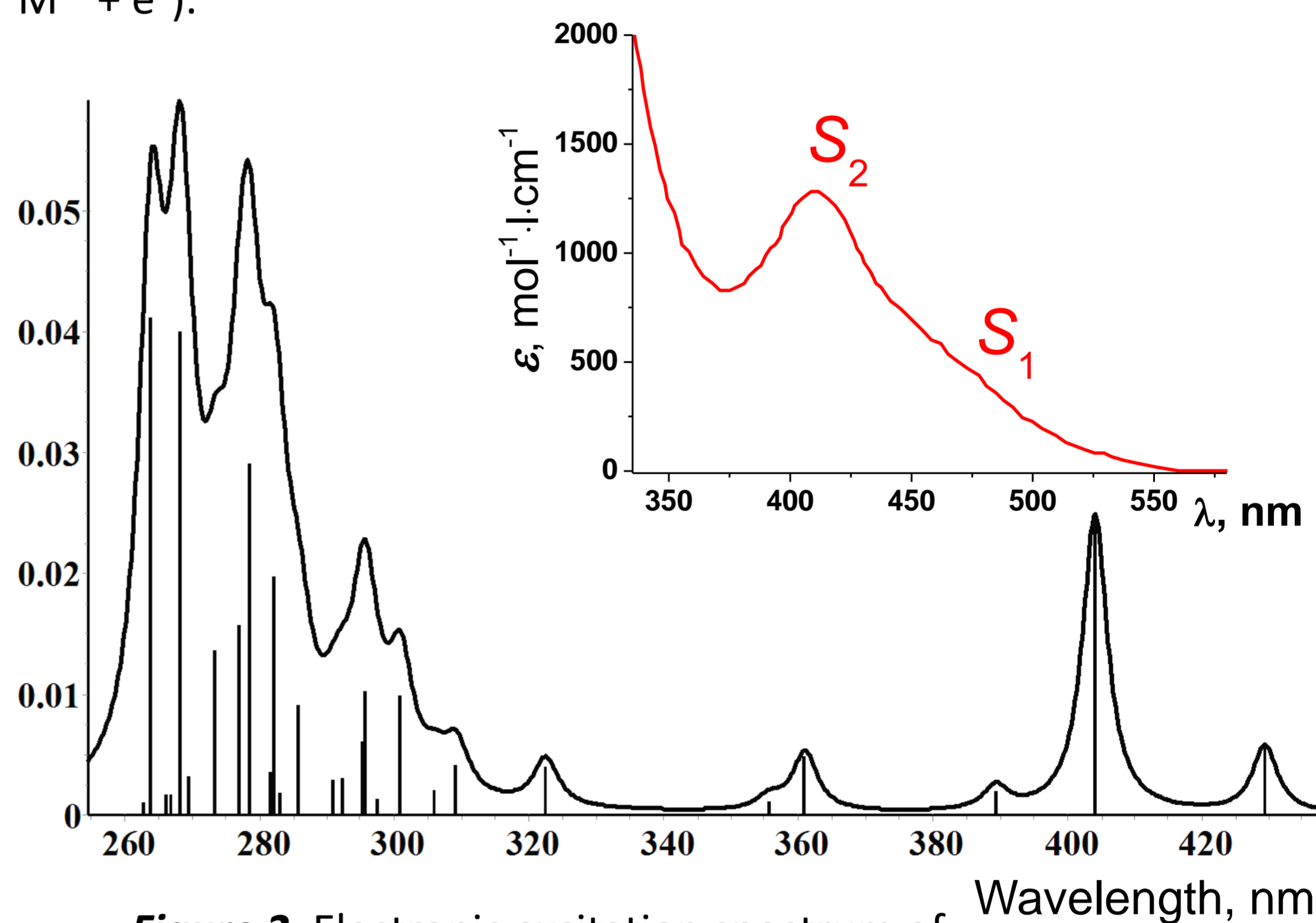


We have conducted a lasting study on molecular photonics of group 4 metallocene complexes, having rare  $^3\text{LMCT}$  excited states. The group 4 metallocenes, bearing carboranyl ligands, were revealed to possess emissive LMCT states in fluids (Fig. 1). The electronic excitation spectra (Fig. 2) were first simulated.

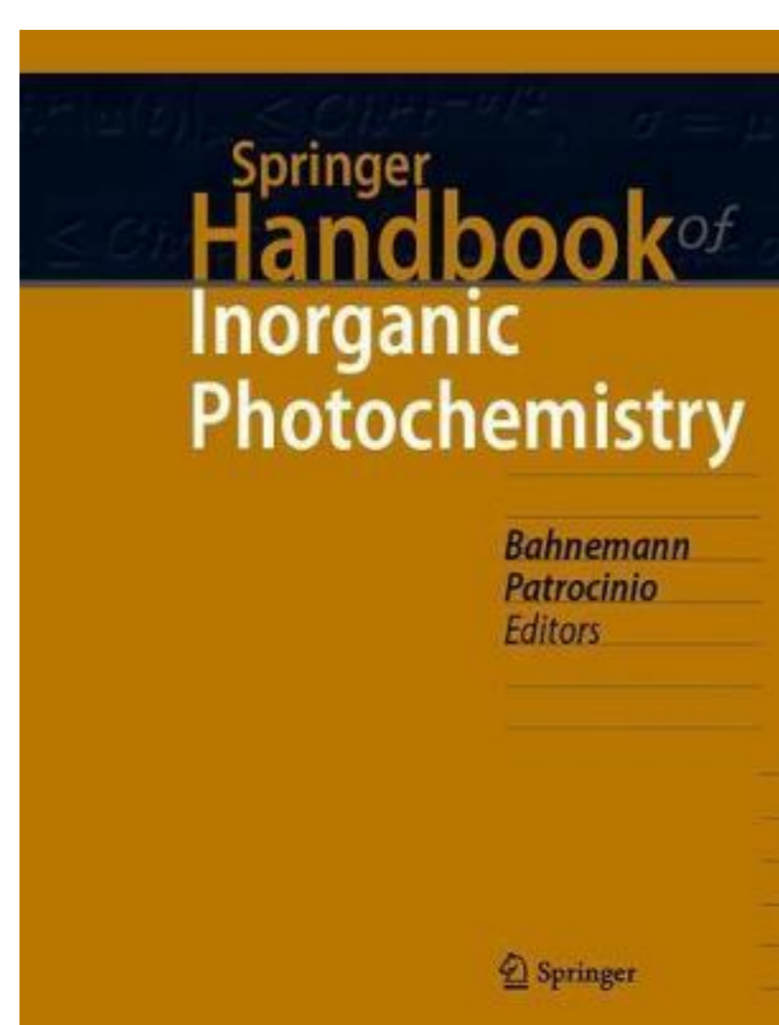
A good agreement of the results of theoretical (TDDFT) and photophysical studies was obtained (the energy and the oscillator strength, etc.), accounting for the unusual change in the nature of LMCT states and the dipole moment of  $(\eta^5\text{-RCp})_2\text{MX}_2$  when replacing  $\sigma$ -ligands. The electric dipole moment  $\mu_g$  increases multiple times on going from dimethyl (1.5–1.9 D) to dicarboranyl (10–11D) complexes. Applying photophysical methods and the calculations, we demonstrate that despite the presence of metal – carbon  $\sigma$ -bonds, structurally complex  $d^0$  metallocene dicarboranyls  $M(\eta^5:\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$ , in contrast to dimethyl counterparts  $\text{Cp}_2\text{MMe}_2$ , possess LMCT states with charge transfer predominantly from the aromatic  $\pi$ -ligands to the metal, a high dipole moment, and photoluminescent properties, making them similar to the dichloride analogs  $\text{Cp}_2\text{MCl}_2$  which lack the M–C  $\sigma$ -bonds.



**Figure 1.** Linear correlations of energies of the first absorption maximum ( $E_{\text{LMCT}}$ ), 0-0 transition ( $E_{00}$ ), and emission maximum ( $E_{\text{max}}$ ) in  $M(\eta^5:\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$  with  $IP_4$  of the metals ( $M^{3+} = M^{4+} + e^-$ ).



**Figure 2.** Electronic excitation spectrum of  $\text{Ti}(\eta^5:\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$  in gas (TDDFT/B3LYP/DGDZVP). The inset shows the experimental spectrum.



G. Loukova,  
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