

Theoretical description of photochemical properties of palladium(II) complexes with tetrapyrrole ligands

The topic of the dissertation focuses on two complexes of the palladium(II) ion, respectively with the corrin ligand $[Pd(II)HM-CN-corr]^+$ and with the porphyrin $[Pd(II)porr]$. Due to the large size of the molecular structures of the tested compounds, the methods based on DFT (Density Functional Theory) and TD-DFT (Time Dependent-Density Functional Theory) were used to effectively carry out the research on the basis of calculations. In the first area, the aim of the research was the detailed characterization of the complex electronic structure of the ground state and low-lying, electronic excited states, taking into account the differences and similarities resulting from the presence of the corrin and porphyrin rings. The results of the calculations for the $[Pd(II)HM-CN-corr]^+$ complex, using the hybrid and gradient functionals, show differences both in terms of energy and the nature of low-lying excited singlet states, while the simulated absorption bands show better agreement with the experimental data in the case of the BP86 gradient functional. In the case of the $[Pd(II)porr]$ complex, the lowest excited singlet state, according to the calculation results, is the result of an electronic transition within the orbitals of the porphyrin ring. The description of the electronic structure of low-lying excited states for this complex is practically independent of the type used in the functional calculations, and similarly to $[Pd(II)HM-CN-corr]^+$, the calculated excitation energies show better agreement with the experimental data in the case of using the BP86 gradient functional. The second thematic part of the dissertation describes the mechanism of luminescence processes for the $[Pd(II)HM-CN-corr]^+$ complex. The analysis of the individual energy surfaces of the excited states allowed to propose a coherent photophysical mechanism, which in the case of the studied complex allowed to explain the occurrence of the phenomena of fluorescence and phosphorescence. In the proposed mechanism, the deformation of the equatorial coordination sphere of palladium is responsible for the effective interaction of S_1/T , which leads to an increase in the spin-orbital coupling between the lowest excited singlet state and the triplet state, which opens an effective path to phosphorescence. It is highly probable that the proposed S_1/T intersystem crossing mechanism (ISC – Inter-System Crossing) may be of a more general nature and apply to the entire group of complexes with the macrocyclic tetrapyrrole ligand. The third area of issues discussed in the dissertation concerns the interactions in the palladium(II)porphyrin-molecular oxygen system. On the basis of the obtained results, the mechanism and energetics of the process of transforming oxygen to the singlet state in the presence of the porphyrin palladium (II) complex were characterized. The conducted studies did not clearly indicate the preferred direction of the reaction and to a large extent suggest the possibility of coexistence of the oxidation process of the porphyrin ring and the dissociation process leading to the formation of a singlet oxygen molecule.