PHOTOPHYISICAL CHARACTERIZATION OF ZINC(II)- AND COPPER(II)- TETRAPHENYL- AND OCTAETHYL- PORPHYRINS, THEIR COMPLEX FORMATION AND QUECHING WITH NITROGEN CONTAINING DONOR MOLECULES

THESES of PhD DISSERTATION

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PRELIMINARIES, INTRODUCTION

Although Soret has found that hemoglobin possesses an intense absorption band at about 400 nm as early as in 1883 and in 1897 Gamgee observed this same thing concerning other porphyrins compounds the start of porphyrin chemistry is dated to the beginning of the XXth century. The nowadays well-known structure of porphyrins constituting of four pyrrol rings was originally proposed by Küster in 1912. This supposition was however objected by Fischer, known as the father of modern porphyrin chemistry, for nearly two decades till in 1929 partially due to Fischer's scientific efforts a porphyrin compound was successfully synthesized from pyrrol thus giving unambiguous evidence of its constitutional structure.

Porphyrin compounds and their metal complexes, the so-called metalloporphyrins, are molecules of general importance for such processes essential for living organisms as photosynthesis (chlorophyll) or O_2-CO_2 metabolism (hemoglobin). Studying, planning and developing porphyrins is an important task even today. Amongst the most significant fields of porphyrin chemistry there are such areas as solar cell preparation, modeling of artificial photosynthesis or killing tumors (Photodynamic Therapy or PDT in brief). This later field of research brought us the idea to investigate the process of equilibration of some metalloporphyrins in the presence of nitrogen containing electron donor molecules.

Copper(II)-tetraphenyl (Cu(TPP)), copper(II)-octaethyl (Cu(OEP)), zinc(II)-tetraphenyl (Zn(TPP)) and zinc(II)-octaethyl (Zn(OEP)) porphyrins were chosen as model compounds. These molecules are known to form only 1:1 adducts with electron donor molecules but due to the difference of the metal center their luminescence properties and the stability of their five-coordinate complexes are significantly different. Equilibrium constants for Zn(TPP) have been published for several donor molecules at various temperatures, while it was determined only at ambient temperature for Cu(TPP) and with pyridine alone. No data was found concerning the chosen ocaethyl porphyrins.

Therefore the main aim of the dissertation was to determine the stability constants of these four porphyrins with nitrogen containing electron donor molecules in toluene at various temperatures ranging between 10 and 60°C by spectrophotometric method from absorption spectra and in case of the zinc(II)-porphyrins also from steady state fluorescent measurements. The special energy structure of copper(II)-porphyrins prompted the determination of their quenching rate constants. Quenching of the luminescent trip-multiplet manifold of copper(II)-porphyrins were carried out at five different temperatures (20-60°C) by two different techniques: (1) steady state luminescence and (2) laser flash photolysis.

THESES

1. The ground and excited state absorption and luminescence of Zn(OEP), Zn(TPP), Cu(OEP) and Cu(TPP) were studied and compared.

1.1 The energy difference between the vibrational levels of the ground (S_0) and excited (S_1) states of four- and five coordinate zinc(II)-porphyrins were determined from absorption and emission spectra. In case of the Cu(II) complexes only the determination of the energy difference between the vibrational levels of the $^2S_1$ state was possible.

1.2 The generally known Jablonski diagramm of zinc(II)- and copper(II)-porphyrins were completed with the energy levels of the five coordinate complex and with those energy decay pathes, which change as a result of the coordination.

2 Luminescence lifetimes of copper(II)-porphyrins were measured in the function of temperature between 10 and 70°C.

2.1 On the basis of calculations and earlier published results the energy difference between the lowest energy trip-multiplet states of Cu(OEP) was found to be half of the value measured for Cu(TPP).

2.2 It was also found that the decay process of the excited state of Cu(TPP) contains one temperature dependent and at least one temeperature independent energy decay process, while the reaction rate of the temperature independent energy decay process of Cu(OEP) is so minute that it can be neglected beside the temperature dependent process.

3. Thermodynamics of the axial ligation of zinc(II)- and copper(II)-porphyrins were studied in the presence of seven different nitrogen containing electron donor molecules at five different temperatures.

3.1 The presence of the following, new complexes in the solution was justified on the basis of the equilibrium measurements: Cu(TPP)3p, Cu(TPP)4p, Cu(OEP)p, Cu(OEP)3p, Cu(OEP)4p, Zn(TPP)2,6Lut, Zn(TPP)An, Zn(TPP)Bn, Zn(OEP)p, Zn(OEP)2p, Zn(OEP)3p, Zn(OEP)4p, Zn(OEP)2,6Lut, Zn(OEP)An, Zn(OEP)Bn.

3.2 Based on the results of MRA and in perfect agreement with literary data 1:1 adduct formation was found in each cases and the possibility of formation of $Zn(P)D_2$ or $Cu(P)D_2$ complexes were unambiguously excluded.

3.3 Equilibrium constants measured for copper(II)-porphyrins were found to be five orders of magnitude smaller than the ones measured in case of zinc(II)-porphyrins.

3.4 Although the value of the equilibrium constant of Zn(TPP) and Zn(OEP) are in the same order of magnitude upon considering the same donor molecule, the Zn(OEP) proved to form less stable complexes as it is indicated by the more negative free energy values.

3.5 However the equilibrium constants of Cu(OEP)D complexes were found to be somewhat larger than that of Cu(TPP)D if we consider the small values of equilibrium constants with comparatively high relative error it is reasonable to conclude that the stability of these complexes are practically the same.

3.6 The formation of Cu(OEP)D involved more negative ΔS and ΔH values than that the formation of Cu(TPP)D, which finding is attributed to the indication of a considerable structural reorganization due to the coordination of the fifth-ligand to the metal centre of Cu(OEP). Thus we suggest that the splitting of the α and the β bands stems from the distortion via Jahn-Teller effect enhanced by the formation of Cu(OEP)D.

3.7 It was clearly demonstrated in case of all the four porphyrins that steric hindrance (2-picoline, 2,6-lutidine) led to the decrease, while positive inductive effect (3-picoline, 4-picoline) to the increase of complex stability.

3.8 In case of zinc(II)-porphyrins free energy of the excited state complexes ($\Delta G^{\circ *}$) were calculated from the measured values of the ground state free energy (ΔG°) and the fluorescence maxima of the (0-0) transition of the four- and five-coordinate complexes and were found to be 20-40 % more negative than the ΔG° values.

3.9 Stability constants of the excited state equilibrium systems (K*) were calculated from the $\Delta G^{\circ *}$ values by the help of equation: $\Delta G^{\circ *} = -RT\ln K^*$. These estimated K* values were given as one order of magnitude larger than the measured ground state K values. However within experimental error the same K values were obtained from both absorption and luminescence measurements. This seemingly contradictory finding can be explained with the relatively short lifetime of the excited singlet porphyrin ($\tau_{F1} \sim 2.7$ ns) on the basis of which it is quite reasonable to say that no matter how large the excited state stability constant is there is practically no time for the equilibrium process to set and only the luminescence of the four- and five-coordinate species, equilibrated in the ground state, is detected.

4. Quenching of both copper(II)-porphyrins were studied with the presence of all the seven Lewis bases at different temperatures.

4.1 As the temperature dependent quenching measurements have justified the activation barrier for the *Cu(OEP)D molecule is bigger than that of *Cu(TPP).

4.2 $\Delta G^{\neq}$ values calculated for both porphyrins clearly demonstrate the steric effect of methyl group(s) whereas the activation free energy is not sensitive to positive inductive effect.

4.3 As temperature dependent quenching investigations revealed the formation of the ^{2}PQ state is incident to a moderately negative activation entropy and a moderate activation barrier ($\Delta G^{\neq}$), which result is in agreement with the reasonable assumption that for the formation of the penta-coordinate complex small structural reorganization is needed from the $^{2/4}$T excited state of Cu(P). When the ^{2}PQ state is formed a very fast spin-allowed transition to the ground state follows, which accounts for the efficient quenching.

Publications

1. G. Szintay, A. Horváth, G. Grampp
   „Temperature dependence study of pyridine complex formation and emission quenching of copper(II) octaethyl- and tetraphenylporphyrin"
   J. Photochem. & Photobiol. A: Chem., 126 (1999) 83-89

2. G. Szintay, A. Horváth
   „Temperature dependence study of five-coordinate complex formation of zinc(II) octaethyl and tetraphenylporphyrin"
   Inorganica Chimica Acta , 310 (2000) 175-182

3. G. Szintay, A. Horváth
   „Five-coordinate complex formation and luminescence quenching study of copper(II) porphyrins"
   Inorganica Chimica Acta , 324 (2001) 278-285

4. Szintay G., Horváth A.
   „Cink(II)- és Réz(II)- oktaetil és tetrafenil porfirinek fotofizikai sajátságainak összehasonlítása és nitrogén bázisokkal képzett komplexeinek jellemzése"
   Magyar Kémiai Folyóirat, 108, 10 (2002) 455-465

Oral presentations, posters

1. Szintay G., Horváth A.:
   Oral presentation: „A réz(II)-tetrafenil-porfirin és a réz(II)-oktaetil-porfirin fotofizikai és fotokémiai tulajdonságainak összehasonlítása"
   MKE XXXIII. Komplexkémiai Kollokviuma, Paks, 1998. május 27-29.

2. Szintay G., Horváth A.:
   Oral presentation: „Cink(II) és réz(II) porfirin komplexek fotofizikai és fotokémiai sajátságai"
   MKEKE XXXIV. Komplexkémiai Kollokviuma, Tata, 1999. Május 19-21.

3. Szintay Gergely:
   Oral presentation: „Réz(II) porfirinek fotofizikája és lumineszcenciájuk kioltása nitrogén bázisokkal"
   MTA Reakciókinetikai és fotokémia Munkabizottság ülése, Balatonalmádi, 2000. április 28-29

4. G. Szintay, A. Horváth
   Poster: „Temperature dependence study of five coordinate complex formation and quenching of metalloporphyrins in the presence of nitrogen bases"
   XVIII. IUPAC Symposium on Photochemistry, Dresden, Germany, July 22-27, 2000

5. G. Szintay, A. Horváth
   Poster: „Five-coordinate complex formation and luminescence quenching study of copper(II) and zinc(II) porphyrins in the presence of nitrogen bases"
   14th International Symposium on the Photochemistry and Photophysics of Coordination Compounds, Veszprém, Hungary July 7-12, 2001