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Temperature dependence study of pyridine complex formation and emission quenching of copper(II) octaethyl- and tetraphenylporphyrin

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Abstract

Monopyridine-copper(II)-octaethylporphyrin (Cu(OEP)py) and monopyridine-copper(II)-tetraphenylporphyrin (Cu(TPP)py) complexes have been studied. Stability constants in toluene were determined at various temperature ranged between 10 and 60°C from which thermodynamic parameters were determined ($\Delta H_{\mathrm{Cu(OEP)py}} = -19.1 \pm 1.5$ kJ/mol, $\Delta S_{\mathrm{Cu(OEP)py}} = -92.1 \pm 4.1$ J/mol K; $\Delta H_{\mathrm{Cu(TPP)py}} = -16.6 \pm 0.5$ kJ/mol, $\Delta S_{\mathrm{Cu(TPP)py}} = -84.7 \pm 1.5$ J/mol K). Luminescent quenching of Cu(OEP) by pyridine was investigated by steady-state and time resolved technique performed at various temperature (20–60°C) and the thermodynamic parameters of the activated complex were calculated ($\Delta H^{\neq} = 8.3 \pm 1.0$ kJ/mol, $\Delta S^{\neq} = -45.1 \pm 3.2$ J/mol K). ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Porphyrin complexes; Pyridine complexes; Luminescence quenching; Temperature dependence

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1. Introduction

The complex formation studies on reactions between metalloporphyrins and electron donor molecules like nitrogen bases are interesting from both theoretical and experimental point of view [1–4]. The complexes of the same porphyrin ligand with different metal centers show completely different photophysical [5–9] and thus, photochemical behaviour [10,11]. With respect to metal ions Cu(II) [12], VO(II) [13], Hg(II) [1], Zn(II) [1,14] and Cd(II) [1] centered metalloporphyrins form mono- while Ni(II) [12] and Fe(II) [14] porphyrins form bis-pyridine complexes. In contrast Mg(II) [15] porphyrins normally form mono- and bis-pyridine complexes at the same time.

Copper(II) porphyrins are among the most extensively investigated metalloporphyrins. Possessing paramagnetic metal centre (d^9) they exhibit characteristic photophysical properties due to their multiplet electronic structure [16] and sensitivity of the excited state lifetime toward the solvent environment [2,17] and the ligands coordinating to the metal centre along the axis perpendicular to the porphyrin skeleton.

The equilibrium constant of Cu(TPP) with pyridine was determined by Miller and Dorough ($K_{29.9^\circ\mathrm{C}} = 0.05 \pm 0.02$ M^{-1}) [1]. However, the temperature dependence of the stability constant was not measured hence the thermodynamic parameters of the complex have not been determined yet. For the same reason these parameters have not been estimated for the Cu(OEP)-pyridine system either. In order to obtain reliable thermodynamic parameters for (Cu(OEP)py) and (Cu(TPP)py) stepwise stability constants were determined precisely at various temperature. We have also focused attention to obtain activation parameters for quenching of the longer lived trip-quartett excited state.

2. Experimental details

2.1. Materials

Cu(TPP), pyridine and spectral grade toluene were purchased from Aldrich. Cu(OEP) was the generous gift of Prof. McMillin, Purdue University, West Lafayette, IN. Analytic grade ethanol and dichloro-methane were obtained from Reanal. The chlorine impurity in both porphyrins were oxidized by 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) [18,19] in CH_2Cl_2. The porphyrin complexes were separated from DDQ and other impurities on a dry col-

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umn [2,8,20]. For dry-packed chromatography Fluka 507C Al_2O_3 (neutral) filling was used. The eluent was CH_2Cl_2 and CH_2Cl_2/ethanol mixture was used for recrystalization. After recrystalization the porphyrin crystals were filtered and dried under high vacuum (3×10^{-4} mbar) for about 3–4 h.

2.2. Methods for data evaluation

For evaluating the experimental data Matrix Rank Analysis (MRA) and PSEQUAD [21] softwares were used. The new algorithm for the application of MRA developed recently [22] is to determine the number of independent absorbing species either in chemically reacting or in equilibrium systems, while PSEQUAD is to calculate equilibrium constants and molar absorption spectra of the species identified in the system from the series of absorption spectra. The lifetime of the short-lived species ($\tau < 30$ ns) have been estimated by Phase Plane deconvolution method [23].

2.3. Instruments

Ground state absorption spectra were recorded on a Carl Zeiss Jena Specord M40 type spectrophotometer which was connected to PC for data storage and acquisition. Steady sate luminescence was detected and stored by a Perkin Elmer LS 50 B-type luminescence spectrometer. Transient absorption and emission measurements were performed as described elsewhere [24,25] with two modifications that the excitation source was a Quantel Brilliant Nd-YAG laser and for the detection of the transient species a Tektronix TDS 684 A 1GHz 5GSample digitizing oscilloscope was used. The Cu(II) complexes were typically excited with 4.5 ns, 355 nm pulses of 30–40 mJ. Samples ($1.07–4.63 \times 10^{-5}$ M) in 1 cm square Hellma quartz cuvettes were deoxygenated by bubbling with argon. The temperature of the samples were controlled by a MLW MK70 type cryostat and a U7 type thermostat connected to the cuvette holder.

3. Results and discussion

3.1. Absorption and emission spectra

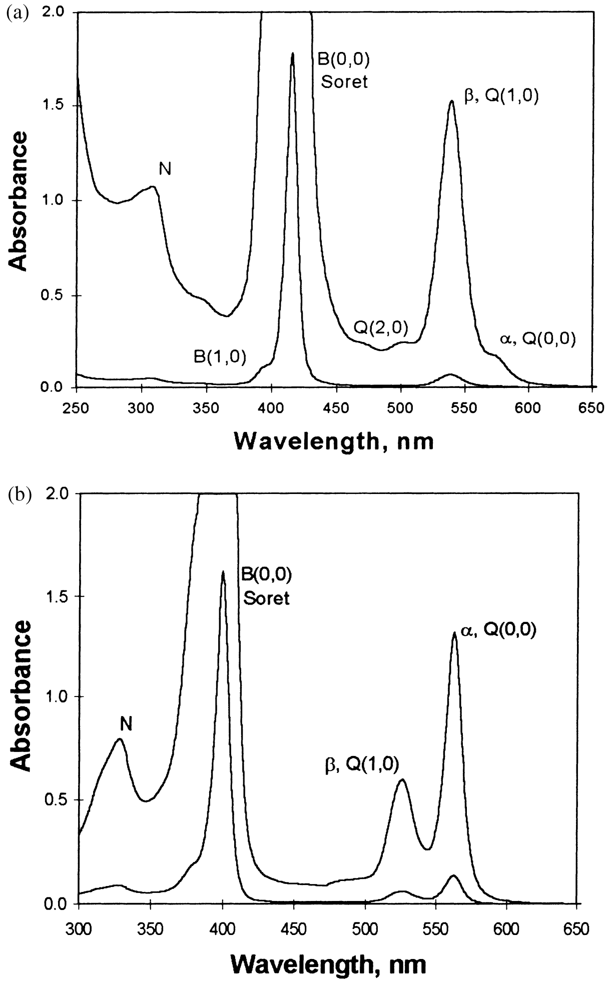

Fig. 1. Ground-state absorption spectrum of (a) CuTPP in CH_2Cl_2 and that of (b) CuOEP in toluene; α is the electronic origin while β is the vibrational overtone; the concentrations of CuTPP are 7.15×10^{-5} M and 3.91×10^{-6} M and the concentrations of CuOEP are 2.75×10^{-5} M and 2.85×10^{-6} M, respectively.

Table 1
Absorption and emission data of copper porphyrins in toluene at 25°C

	Absorption			Emission	
Porphyrin	λ_{max} nm	ε, M^{-1} cm^{-1}	τ, ns	λ_{max} nm	τ, ns
Cu(TPP)	417 ± 1	457,000 ± 3000	31 ± 2	807[a]	30[a]
	539 ± 1	21,400 ± 100			29[d]
	575 ± 2 sh.	2200 ± 100			
Cu(OEP)	399 ± 1	345,000 ± 4000	97 ± 9	690 ± 3[b], [687[a]]	97 ± 5
	526 ± 1	21,000 ± 200		725 ± 5[b], [732[a]]	115[a]
	563 ± 1	48,000 ± 500			110[c]
					105[d]

[a] Data was taken from [27].
[b] Data obtained using uncorrected emission spectrum.
[c] Measured in methylene chloride at room temperature, [28].
[d] Measured in toluene at room temperature, [18].

The visible absorption spectra of Cu(TPP) in CH_2Cl_2 and Cu(OEP) in toluene are demonstrated on Fig. 1. The absorption band structures are quite similar as it is expected since those are mainly deriving from the porphyrin skeleton. The suitable absorption bands of Cu(OEP) appear at higher energy than that of Cu(TPP). Assignments are given according to J.R. Platt [26] and the fine structure of B and Q bands are also designated on Fig. 1. It is interesting to note that the intensity of Q(1,0) band is stronger than that of Q(0,0) for Cu(TPP) while the ratio of the Q-band is reversed in the case of Cu(OEP). Uncorrected emission spectra of Cu(OEP) at room temperature in toluene at various pyridine concentrations indicating vibrational structure of the ground state are presented in Fig. 2(a). Characteristic data of the absorption and emission spectra are listed in Table 1. along with the

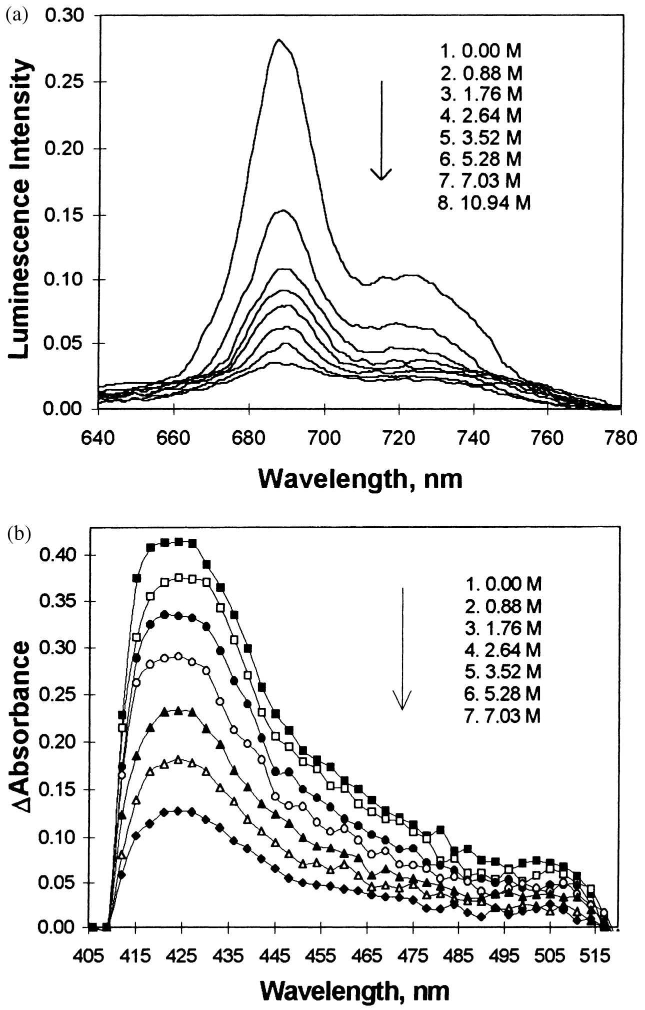

Fig. 2. Uncorrected emission spectra at 20°C -the excitation and emission slits were at 10 nm, each spectra is a result of the average of 17 scans and the excitation wavelength was (a) 563 nm and transient absorption spectra of CuOEP at (b) 30°C in toluene at various pyridine concentrations. The value of pyridine concentrations are multiplied with 10^2.

lifetime of transient species derived from transient absorption and emission measurements in toluene at 25°C. Transient absorption and emission signals were found to be monoexponential. The lifetimes determined for the longer-lived excited species are in good agreement with data taken from literature [18,27,28].

Transient absorption spectra determined by laser flash photolysis measurements are depicted in Fig. 3. The absorption band of the excited porphyrins - peaking at 475 nm for the Cu(TPP) and 425 nm for the Cu(OEP), respectively-are at least three times stronger than the Q-band bleaching and nearly the same as the B-band bleaching, which suggest that its molar extinction coefficient is in the order of 10^5. In addition their lifetimes are relatively long (~30 ns for Cu(TPP) and ~100 ns for Cu(OEP)), hence the excited state molecules are assigned as equilibrated trip-doublet (^{2}T) and trip-quartet (^{4}T) [2,16–18,28]. The energy gap between the emitting ^{2}T and ^{4}T is about 200 cm^{-1} for the OEP and 700 cm^{-1} for the TPP complex [17]. In such a coupled system the decay rate of the excited species depends on the decay rate of both states (^{2}T and ^{4}T) and the equilibrium constant. The large molar extinction coefficient of the transient absorption is attributed to a spin and symmetry allowed transition to a higher energy state.

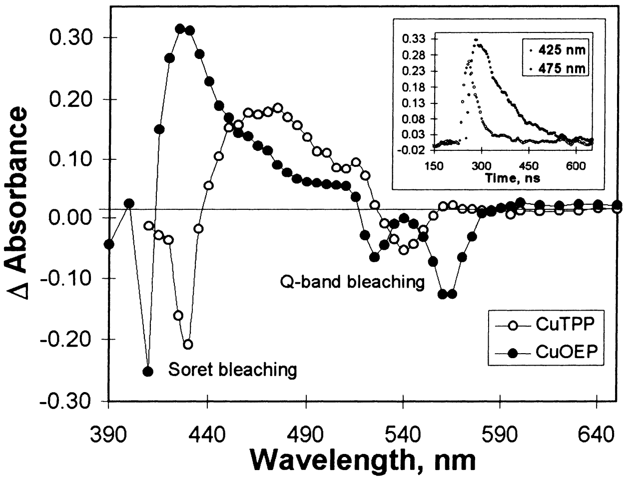

Fig. 3. Transient absorption spectra of CuTPP (4.1 × 10^{-5} M) and CuOEP (4.63 × 10^{-5} M) in toluene at ambient temperature, detected 20 ns after the laser pulse of 355 nm.

3.2. Stability constants of the mono-pyridine complexes

The stability constants were determined by photometric method. The optical changes of the ground-state absorption spectra were followed within the Q region between 460–660 nm. Fig. 4. shows the spectral changes in (a) Cu(TPP)-pyridine and (b) Cu(OEP)-pyridine systems at 20°C. In case of Cu(TPP) when the concentration of pyridine is increased, a red shift of the spectrum occurs along with the decrease of the Q(1,0) and the increase of the Q(0,0) band. However, no shifting of the Q(0,0) band was observed apparently in the case of Cu(OEP) while besides its considerable decrease a slight broadening is obvious as the spectra are possesing isobestic points at 553 and 569 nm. The absorbance of the Q(1,0) band is the same within experimental error but besides its broadening this band shows a weak shift towards smaller energies. Matrix rank analysis (MRA) of the spectra performed on data obtained at various temperatures resulted in two linearly independent absorbing species for both systems, which is a confirmation and in perfect agreement with previous findings [1] that only the copper(II) porphyrin and its monopyridine complex absorb light though no further (bis-pyridine) complex is at present.

Using the PSEQUAD program developed to determine the stability constants of equilibrium systems [21,29] the stability constants of 1 : 1 copper(II) porphyrin -pyridin, Cu(P)py, complexes have been calculated. The program solves the mass balance equations of the equilibrium system and evaluates the equilibrium concentration of species and their sta-

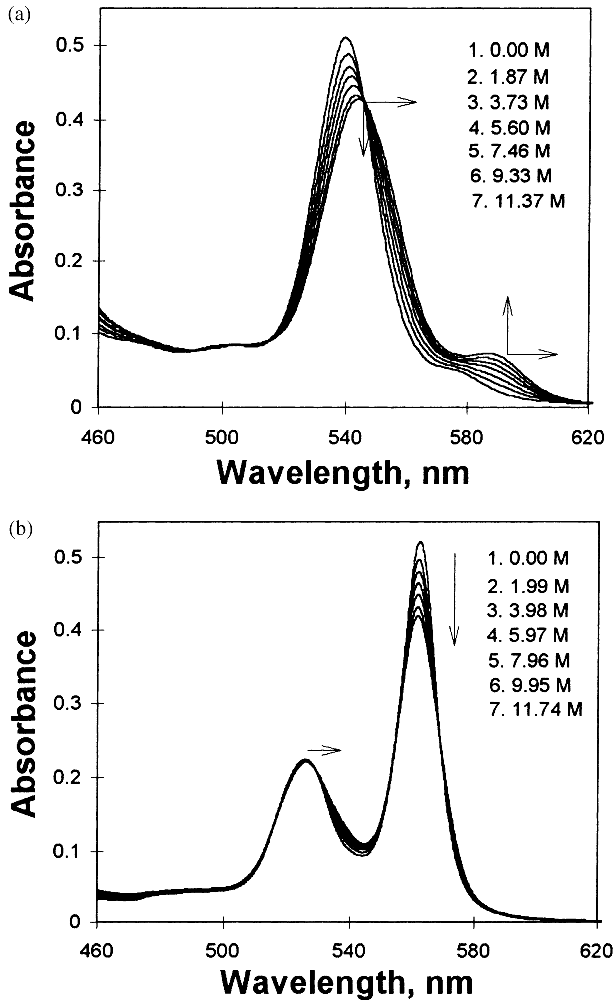

Fig. 4. Photometric titration of CuTPP (a) (2.36×10^{-5} M) and CuOEP (b) (1.07×10^{-5} M) with pyridine at 20°C.

bility constants and molar absorbancies for the investigated spectral range.

It also gives the error of the calculated data. The basic equations related to our systems are given as:

$$C_{\mathrm{Cu(P)}} = [\mathrm{Cu(P)}] + K[\mathrm{Cu(P)}][\mathrm{py}] \tag{1}$$

$$C_{\mathrm{py}} = [\mathrm{py}] + K[\mathrm{Cu(P)}][\mathrm{py}] \tag{2}$$

$$D_\lambda = \mathrm{l}(\varepsilon_{\lambda,\mathrm{Cu(P)}}[\mathrm{Cu(P)}] + \varepsilon_{\lambda,\mathrm{Cu(P)py}}K[\mathrm{Cu(P)}][\mathrm{py}]) \tag{3}$$

where $C_{\mathrm{Cu(P)}}$ is the analytical concentration of the copper(II) porphyrin complex, C_{py} is the analytical concentration of the pyridine, [Cu(P)] is the equlibrium concentration of copper(II) porphyrin complex, [py] is the equlibrium concentration of the pyridine, K is the stability constant of Cu(P)py complex, D_λ is the absorbance measured at wavelength λ, l is the optical path length of the cuvette, $\varepsilon_{\lambda,\mathrm{Cu(P)}}$ is the molar extinction coefficient of copper(II) porphyrin at wavelength λ and $\varepsilon_{\lambda,\mathrm{Cu(P)py}}$ is the molar extinction coefficient of the copper(II) porphyrin -pyridine complex.

Table 2
Stability constants, K_t, for the pyridine complexes of Cu(TPP) and Cu(OEP) at 10–60°C, and the thermodynamic parameters of the complex formation

t (°C)	Cu(TPP)py $K_t(\times10^2)$	Cu(OEP)py $K_t(\times10^2)$
10	4.19 ± 0.14	4.98 ± 0.36
20	3.45 ± 0.08	3.87 ± 0.27
30	2.92 ± 0.09	3.21 ± 0.39
40	2.07 ± 0.07	2.49 ± 0.26
50	1.80 ± 0.08	1.76 ± 0.20
60	1.51 ± 0.09	
ΔS	-84.7 ± 1.5 kJ/mol K	-92.1 ± 4.1 kJ/mol K
ΔH	-16.6 ± 0.5 kJ/mol	-19.1 ± 1.5 kJ/mol
ΔG	8.7 kJ/mol	8.3 kJ/mol

The stability constants determined at various temperatures are given in Table 2. The figures are very similar for both penta-coordinated complexes, however, the formation of Cu(OEP)py is less endothermic than that of Cu(TPP)py. It is interesting to note that the spectral changes in Cu(OEP)-pyridine system were so minute at 60°C that PSEQUAD was not able to calculate a reasonable K value at this temperature. Fig. 5. presents the calculated ground-state absorption spectra of the five coordinate copper(II) complexes. Comparing these spectra of pyridine complexes rather different features can be observed. Besides the red shift of Q(1,0) and Q(0,0) bands of Cu(TPP)py a considerable increase in the intensity of Q(0,0) band is also at present. On the other hand the formation of Cu(OEP)py results in the same splitting ($\Delta E\cong380\,\mathrm{cm}^{-1}$) of the Q(1,0) and the Q(0,0) bands shifted very slightly to longer wavelengths (Fig. 5b) which can be interpreted by the Jahn-Teller distortion of the ground or the excited state molecule.

3.3. Temperature dependence of excited state quenching

The quenching of the longer-lived excited state by pyridine was performed by three different methods; luminescence intensity, luminescence lifetime and transient absorption measurements for Cu(OEP). A series of uncorrected emission spectra of Cu(OEP) at room temperature in toluene at various concentration of pyridine are presented in Fig. 2(a). The MRA calculations gave only one luminescent species. Analysis of the transient absorption spectra detected at various quencher concentration resulted in the same conclusion, Fig. 2(b). It is in good agreement with the earlier observations according to which only the four-coordinate excited Cu(OEP) is luminescent and has an absorption peaking at 425 nm, while the penta-coordinate excited species go back to the ground-state through a doublet quenching state (^{2}PQ) in a non-radiative decay [18,27,30]. The data was evaluated using the well-known Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{\mathrm{SV}}[Q] \tag{4}$$

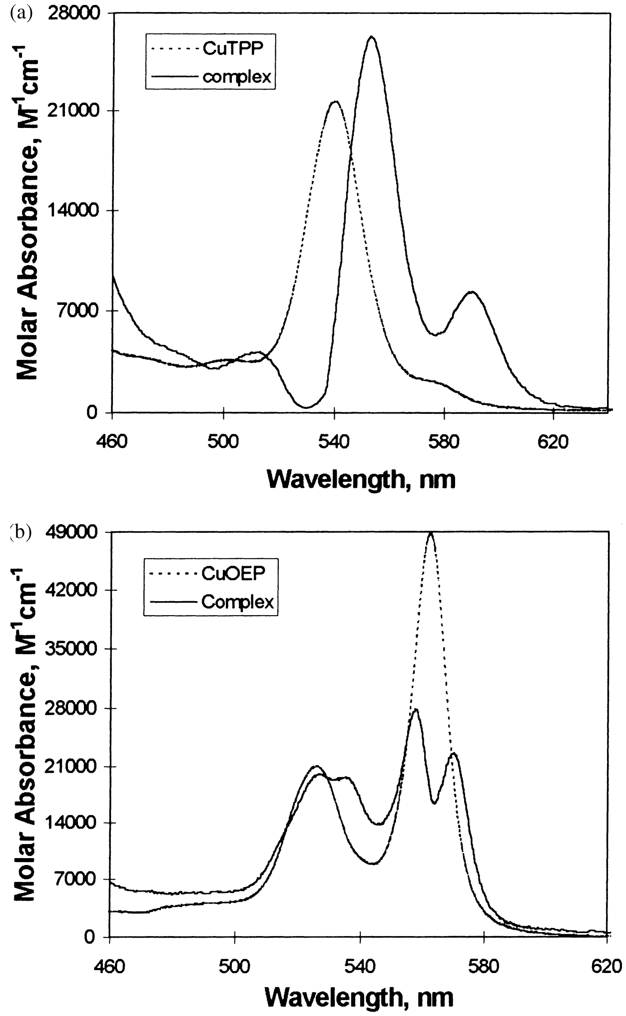

Fig. 5. Calculated ground-state absorption spectra of (a) CuTPP and (b) CuOEP monpyridine complexes at 20°C.

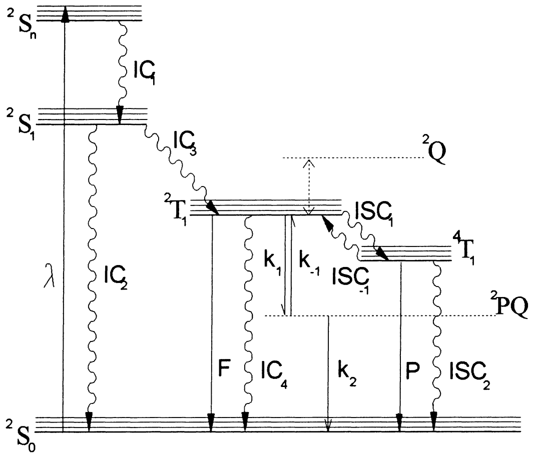

Fig. 6. General Jablonski representation of copper(II) porphyrins. The assignments are: λ is for the excitation wavelength needed to be used to excite a certain Cu(P) complex, IC is for Internal Conversion, ISC is for Intersystem Crossing, P is for phosphorence and F is for fluorescence. Dotted line and dual representation of the doublett quenching state is due to the concept that besides lying at different energy levels in case of different porphyrins at the four-coordinate (^{2}Q) state [17] upon the formation of the penta-coordinate species the quenching state drops in energy closer to or below the $^2T_1/^4T_1$ manifold (^{2}PQ) as the axial ligand binding of a σ-donor molecule to excited Cu(P) perturbs the molecular orbital of these porphyrins [2,27,28].

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \tag{5}$$

$$K_{SV} = k_q\tau_0 \tag{6}$$

where [Q] is the concentration of the quencher, I_0 is the luminescence intensity when $[Q]=0$, τ_0 is the lifetime of the excited state molecule when $[Q]=0$ and K_{SV} is the Stern-Volmer constant.

The results of quenching studies are summarized in Table 3. The rate coefficients for quenching of the longer-lived Cu(OEP) excited state as well as the activation parameters estimated using rate coefficients measured at various temperature and determined by different methods are almost identical and show good agreement with previously published data. The figures clearly indicate that activation is controlled by both enthalpy and entropy. Because the energy gap between ^{4}T and ^{2}T is very small (~200 cm^{-1} for the *Cu(OEP) complex) these states can be regarded as equally populated excited states at ambient temperature [17]. The free energy of activation is about 2000 cm^{-1} for the five-coordinate excited species. The *Cu(OEP)py complex can decay rapidly to the ground state via non-radiative process and it is reasonable to assume that its $\nu=0$ vibration level lies near to its luminescent states. Therefore we can conclude that the quenching occurs according to the following kinetic scheme:

$$^{2/4}\mathrm{T} + \mathrm{py} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^2\mathrm{PQ} \tag{7}$$

$$^2\mathrm{PQ} \xrightarrow{k_2} \text{Ground state } (^2S) \tag{8}$$

Fig. 6 gives the Jablonski representation of copper(II) porphyrins [9,17,18]. In general, when the steady-state approximation for $^{2/4}$T is used k_q related to the constants in the scheme by

$$k_q = k_1\left[\frac{k_2}{k_{-1}+k_2}\right] \tag{9}$$

Note that k_1 and k_{-1} are the rate constants describing the formation of the penta-coordinate ^{2}PQ state and its reverse process and k_2 is the sum of rate constants leading to the deactivation of the ^{2}PQ state.

In the limit that $k_2 \gg k_{-1}$ $k_q = k_1$ and the parameters determined by the measured rate coefficients characterize the irreversible $^{2/4}\mathrm{T} + \mathrm{py} \rightarrow {}^2\mathrm{PQ}$ process. On the other hand in the limit that $k_2 \ll k_{-1}$ $^{2/4}$T and ^{2}PQ are in equilibrium hence $\Delta H^{\neq}$ can be a negative value when the bond between the copper centre of the excited complex and the nitrogen atom of pyridine is relatively strong. The positive activation

Table 3
Rate constants for quenching of Cu(OEP) by pyridine in toluene at 20–60°C and the thermodynamic parameters of the activated complex

t(°C)	k_q, $M^{-1}\,s^{-1}$, (Steady state luminescence)[a]	k_q, $M^{-1}\,s^{-1}$ (Laser flash photolysis)[b]		
20	9.56×10^{8}	9.31×10^{8}	9.29×10^{8}[c]	9.1×10^{8}[d]
30	1.12×10^{9}	1.03×10^{9}	1.06×10^{9}[c]	
40	1.33×10^{9}	1.23×10^{9}		
50	1.45×10^{9}	1.42×10^{9}		
60	1.56×10^{9}	1.54×10^{9}		
$\Delta S^{\neq}$	-46.9 ± 2.5 Jk/mol K	-45.1 ± 3.2 kJ/mol K		
$\Delta H^{\neq}$	7.6 ± 0.7 kJ/mol	8.3 ± 1.0 kJ/mol		
$\Delta G^{\neq}$	21.6 kJ/mol	21.7 kJ/mol		

[a] Calculated according to Eqs. (4) and (6).
[b] Calculated according to Eqs. (5) and (6).
[c] Calculated from transient absorption decay, detected at 425 nm.
[d] Measured in toluene at 25°C, [27].

enthalpy and the negative activation entropy can be regarded as the confirmation of the $k_2 \gg k_{-1}$ limit.

4. Conclusions

The absorption spectra of the ground and excited state of Cu(TPP) and Cu(OEP) as well as the luminescence properties of Cu(OEP) were investigated at various temperatures and were compared.

Although the stability constants of the pyidine complexes are larger in most cases for the Cu(OEP)-pyridine system than for the Cu(TPP)py complex these differences are so small that it is reasonable to conclude that the stability of the Cu(TPP)py and Cu(OEP)py complexes are practically the same. Based on the results of MRA and statistical considerations the existance of a Cu(TPP)py$_2$ or Cu(OEP)py$_2$ bis-pyridine complex can be excluded. The more negative ΔS and ΔH values for Cu(OEP)py formation than that of the Cu(TPP)py formation has been regarded as an indication of a considerable structural transformation caused by the coordination of the pyridine ligand to the metal centre of Cu(OEP). Hence it is reasonable to assume that the formation of Cu(OEP)py can enhance the distortion via Jahn–Teller effect which leads to the splitting of the Q(1,0) and the Q(0,0) bands revealed for the first time. An other interpretation of the doubled spectrum in Fig. 5(b) was suggested by the referee. According to this besides the nitrogen-to-copper bound a π-stacked adduct is also formed. In this case an equilibrium between the two associated complexes is expected thus it is hard to assign their absorption bands experimentally.

The temperature dependent quenching studies indicated a moderate activation barrier for the formation of the doublet penta-coordinate quenching state (^{2}PQ) and a moderately negative activation entropy. This result is consistent with the reasonable assumption that the formation of the penta-coordinate species needs small structural change from the excited state ($^{2/4}$T) of the Cu(OEP). The quenching is efficient because the formation of the ^{2}PQ state is followed by a very fast spin-allowed transition to the ground state.

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