

# Temperature and solvent dependent charge transfer in self-organized porphyrin-quinone compounds

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## Abstract

Porphyrin chromophores form self-assembled triads or tetrads via Zn complexation by pyridine when functional groups are tailored in an appropriate way. Photoinduced energy and electron transfer within the assemblies depend strongly on temperature and solvent polarity. This is merely a consequence of the stability of the assemblies.

## 1. INTRODUCTION

Supramolecular chemistry has provided us with concepts (ref. 1) how to organize molecular assemblies via self-organization or self-assembling. One of the basic ideas is to form assemblies while only slightly changing the electronic properties of the individual molecular components but influencing interactions among the individual components considerably. Due to these interactions one might observe e.g. photoinduced excitation energy or charge transfer. The complexation will be achieved by weak intermolecular forces such as electrostatic forces in case of molecular ions (ref. 2), hydrogen bonding (ref. 3) or ligand formation (ref. 4). The intermolecular interactions will only slightly change the static molecular properties and are often hardly visible in the conventional optical spectra. Due to the weak binding forces environmental conditions influence critically the self-organization process. In case of self-organization in solvents the two basic influences that have to be matched carefully are solvent polarity and temperature.

Recently, we reported on the formation of porphyrin-quinone tetrads (ref. 4) shown in Fig. 1 which show both electron and excitation energy transfer (ref. 5). In this communication we like to concentrate on some aspects which are imposed by solvent polarity and temperature.

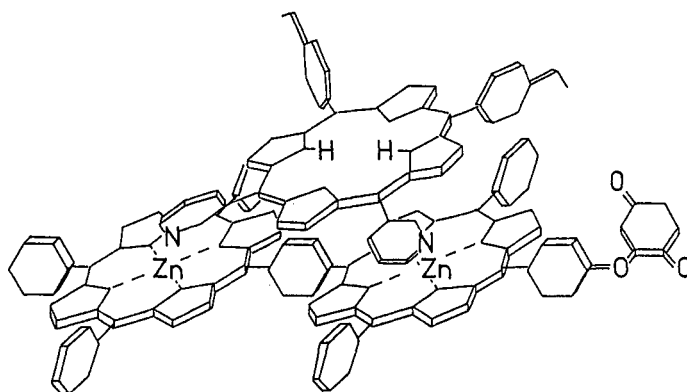


Fig. 1 Schematic scheme of a self-organized assembly.

## 2. EXPERIMENTAL

The synthesis of porphyrin dimers will be published in a forthcoming paper.  $10^{-5}$  molar solutions of tetraphenyl-zinc porphyrine-quinone dimers (ZnPDQ) and free base bi(1,4-ethyl-phenyl)-bipyridine porphyrin monomers (2Pyr-H<sub>2</sub>P) have been dissolved in a 1:1 molar ratio in spectroscopic grade cyclohexane after extensive thin layer chromatography of the individual components. Despite this careful sample preparation we always observe spurious amounts of variant porphyrin components. Complexation of porphyrins with pyridine has also been performed in spectroscopic grade solvents.

Absorption and fluorescence spectra have been measured in Shimadzu UV240 and RF340 spectrometers using variable temperature units. Time-resolved spectra are obtained with a recently described (ref. 6) synchronously pumped dye laser system with an overall time response of 40-50 ps.

## 3. RESULTS AND DISCUSSION

It is a widely known phenomena that the d-orbitals of central metals in porphyrins can be complexed by nitrogen or oxygen due to the presence of lonepair orbitals. Typical ligand molecules are pyridine, pyrazine, dioxane or piperidine. In case of Zn as a central atom complexation results in a red shift of the absorption and emission bands in the order of a few nm. The effect of complexation depends strongly on the solvent. In some solvents complexation already takes place with the solvent itself. Table 1 collects some data for the fluorescence origins in various solvents.

TABLE 1 Influence of complexation by pyridine on the fluorescence origin ( $F_{00}$ ) of ZnP

Solvent	$F_{00}/\text{nm}$	$F_{00}/\text{nm}$ (with pyridine)
cyclohexane	595	608
toluene	599	612
MTHF	602	607
CH <sub>2</sub> Cl <sub>2</sub>	598	612
DMF	607	611
acetonitrile	606	612

Complexation obviously results in a rearrangement of the  $\pi$ -electron distribution of the porphyrin ring. Additionally, complexation is accompanied by changes in the structure of the porphyrin as is obvious from the Frank-Condon envelope of the ZnP absorption and emission spectra. Fig. 2 compares the correspondent spectra in cyclohexane both for ZnP and pyridine complexed ZnP. Two effects are evident. In the uncomplexed ZnP absorption spectrum the intensity ratio of the two Q-bands (which are assigned to the absorption origin and a vibrational line) is very much in favour of the vibrational band. Upon excitation to the first excited singlet state the fluorescence origin increases in intensity with respect to the vibrational band. This is accompanied by a slight Stokes shift and a change in the energy separation of the vibrational band with respect to the correspondent origin. Such observations indicate that ZnP changes the equilibrium conformation upon optical excitation. Time resolved fluorescence experiments indicate that such changes occur on a time scale of 100-200 ps (ref. 7).

Fig. 2 also demonstrates that complexation of ZnP with pyridine effects the ZnP optical spectrum. In absorption the 0-0 band is drastically increased with respect to the vibrational band. In case of fluorescence the origin becomes even stronger than the vibrational band. Comparing the Frank Condon envelope of ZnP with the one of H<sub>2</sub>P we have to assume that in the complexed form of ZnP in the excited state has a structure similar to H<sub>2</sub>P.

Turning now to those complexed forms which are indicated in Fig. 1, the following strategy in order to form reasonably well organized complexes has to be followed. Based on the idea that complexation happens via a close contact of Zn d-orbitals and N lone pair orbitals Zn-Zn distances have to be

matched with those of N-N distances of the substituted pyridine rings. Depending whether the ZnPD is in a linear or twisted form Zn-Zn becomes about  $11.5\text{\AA}$  or  $9\text{\AA}$ , whereas N-N amounts to  $12\text{-}14\text{\AA}$  in the linear or to  $8\text{-}12\text{\AA}$  in the with respect to  $\text{H}_2\text{P}$  twisted substitution of pyridine rings. The distances are somewhat loosely defined due to the remaining flexibility of the phenyl substituents. As we have shown elsewhere in detail (ref. 5) only proper matching of both distances results in the formation of stable twofold coordinated complexes. The spectral shifts are indistinguishable from pyridine complexation and are predominantly obvious in the vibrational band of the ZnP absorption, because the absorption origin is masked by the strong  $\text{H}_2\text{P}$  bands. As we have outlined (ref. 5) the ZnP fluorescence is dramatically decreased due to fast energy transfer from ZnP to the energetically lower lying  $\text{H}_2\text{P}$ . The times scale of this process is below 10 ps (ref. 7).

Fig. 3 shows the effect of complexation on the Soret bands of ZnPD. In case of complexation with  $2\text{Pyr-H}_2\text{P}$  the latter absorption has been subtracted in order to reduce spectral disturbances due to the  $2\text{Pyr-H}_2\text{P}$  absorption which is almost not altered by complexation. The upper spectrum shows a splitting of the ZnPD Soret band present in the dimeric form which is due to excitonic coupling of the two covalently linked ZnP monomers. This splitting is reduced in case of complexation by pyridine and is considerably increased in case of complexation by  $2\text{Pyr-H}_2\text{P}$ . Qualitatively this behaviour can be understood in the sense that the latter complexation forces the ZnP dimers to be more coplanar as a consequence of the two-fold coordination. A quantitative description is beyond the scope of the present communication but has been discussed recently in a similar context (ref. 8).

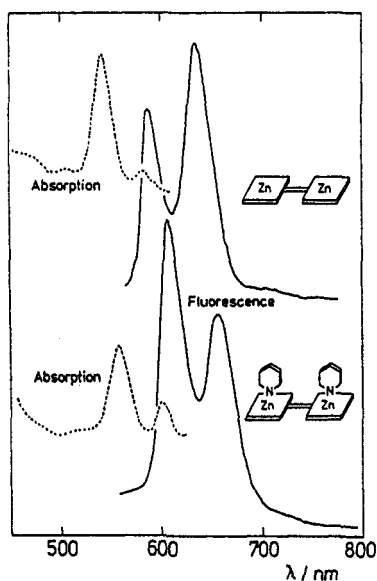


Fig. 2 Absorption and fluorescence emission spectra of ZnPD in cyclohexane. The bottom spectrum shows the influence of complexation by pyridine.

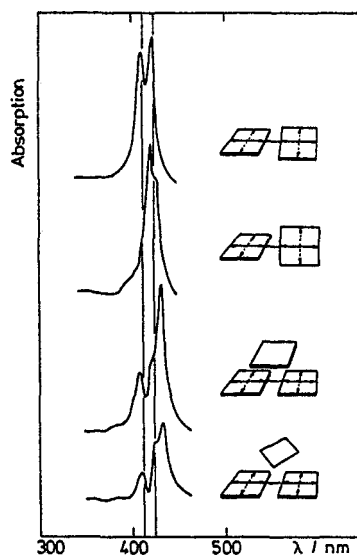


Fig. 3 Soret band spectra of ZnPD in cyclohexane. The kind of complexation is indicated in the figure.

Complexes of the kind depicted in Fig. 1 are only weakly bound complexes. Upon addition of a stronger complex former such as pyridine they are destroyed again. Also the increase of temperature will have influence on the stability of the complex. Fig. 4 shows the fluorescence of an equimolar mixture of ZnPD and  $2\text{Pyr-H}_2\text{P}$  as a function of temperature. Raising the temperature from 295 K to 365 K results in an increase and spectral shift of the ZnPD fluorescence. According to a titration experiment at 295 K the complexation constant amounts to  $1.4 \cdot 10^6$  l/mol which corresponds to a situation where about 70% of the ZnPD molecules are in the complexed form. This reduces to about 10% at 365 K.

Fig. 5 shows as a function of temperature the fluorescence of an equimolar solution of ZnPDQ and 2Pyr-H<sub>2</sub>P. In this case the ZnPD fluorescence is strongly quenched at all temperatures. At high temperatures the fluorescence is quenched due to electron transfer from ZnPD to Q on a time scale of 136 ps (ref. 9) and at low temperatures due to energy transfer from ZnPD to 2Pyr-H<sub>2</sub>P. But contrary to the situation of the temperature behaviour of the complex shown in Fig. 4, no isobestic point is observed but instead the H<sub>2</sub>P fluorescence is also going down following complexation. This is due to long-range electron transfer from 2Pyr-H<sub>2</sub>P to Q (ref. 4) which occurs within 500 ps (refs. 5, 10).

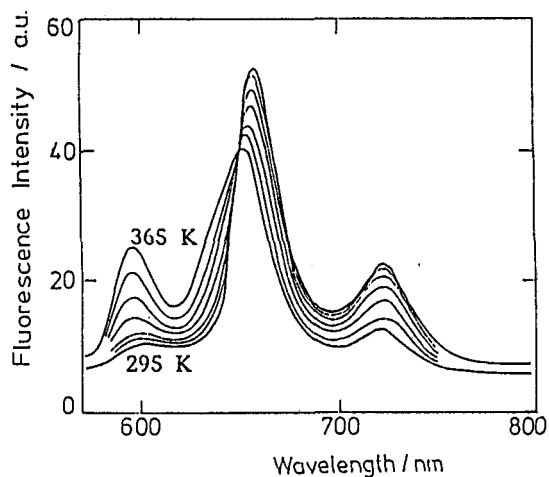


Fig. 4 Temperature dependence of the fluorescence of the complex form of ZnPD (twisted) with 2Pyr-H<sub>2</sub>P in cyclohexane.

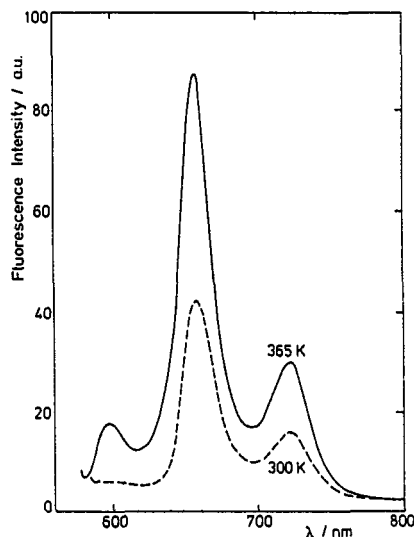


Fig. 5 Temperature dependence of the fluorescence of ZnPDQ-2Pyr-H<sub>2</sub>P in cyclohexane.

This effect is also evident when inspecting temperature dependent 2Pyr-H<sub>2</sub>P fluorescence decays in Fig. 6. For comparison the pure H<sub>2</sub>P fluorescence decay is also depicted. At all temperatures the decay is biexponential. The long component always equals, the H<sub>2</sub>P fluorescence lifetime of 8.5 ns. The short component is in the order of 500 ps. Upon decreasing the temperature from 365 K to 295 K the time scale does not change considerably but the relative amplitudes do. At 295 K the short component determined by electron transfer from 2Pyr-H<sub>2</sub>P to Q is the dominant component.

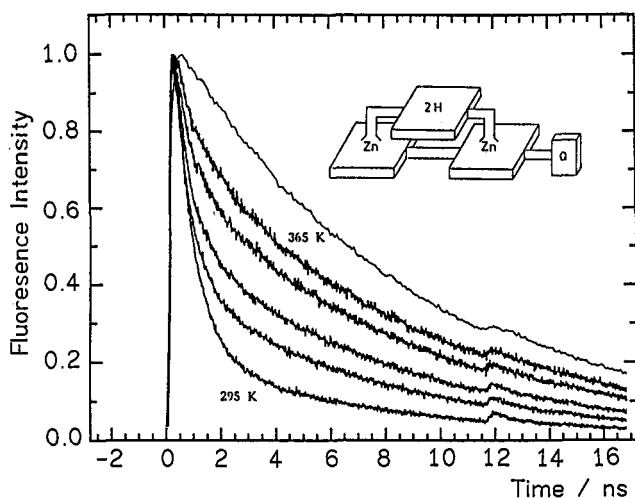


Fig. 6 Temperature dependent fluorescence decay of ZnPDQ-2Pyr-H<sub>2</sub>P in cyclohexane. The spectrum at the top shows the decay of H<sub>2</sub>P.

#### 4. CONCLUSION

We have shown that solvent and temperature influence the stability of self-organized complexes considerably. This has a pronounced impact on the electron and energy transfer kinetics within the self-assembled tetrad. A temperature change from 295 K to 365 K will completely break up the complexes and purely intramolecular kinetics are observed. The presently discussed examples of self-organized assemblies demonstrate the capability of the concepts of supramolecular chemistry in the case of photoinduced transfer processes. Further work on these and other systems (ref. 11) is under way to form more extended but still well-defined assemblies enabling vectorial energy and electron transfer processes.

#### Acknowledgement

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