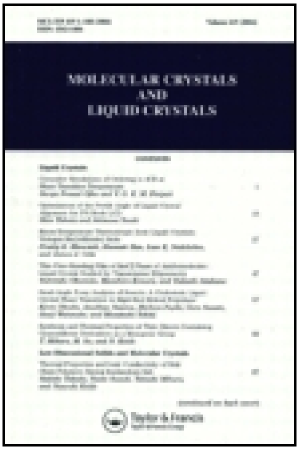

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PHOTOINDUCED CHARGE AND PROTON TRANSFER IN SELFORGANIZED PORPHYRIN-COMPLEXES AND CYCLODEXTRIN INCLUSION COMPOUNDS

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Abstract The impact of selforganization on photophysical properties of organic compounds has been investigated. Due to this mechanism, the rate constant of the intermolecular charge transfer in porphyrin–quinone complexes is increased and the equilibration of different tautomers of HBO is influenced by cyclodextrin moieties in liquid solution.

INTRODUCTION

Photoinduced electron or proton transfer are in many cases the (fast) primary steps in complex chemical reactions. To mimic such reactions model compounds have been synthesized[1], which enable a microscopic description of reaction pathways as long as energetics and structural relationships are well characterized. This approach though it has its merits with respect to the detailed knowledge about the system is limited because of the restricted variation of its functionality and the tedious replacement of individual components. An alternative approach has been provided by the concepts of supramolecular chemistry[2] which makes use of the selforganization of individual functional units. We have investigated the influence of two basically different selforganization mechanisms on electron and proton transfer reactions. In the first case, we have made use of the capability of central atoms in porphyrins to ligate aromatic nitrogen heterocycles in a non–polar environment. In the second example we have investigated the influence of the inclusion of 2–(2'–hydroxyphenyl)benzoxazole (HBO) into various cyclodextrins in polar solvents upon photoinduced intramolecular proton transfer.

ELECTRON TRANSFER IN SELFORGANIZED PORPHYRIN–QUINONES

Recently we have shown that electron transfer between tetraphenylporphyrins and quinones (Q) can be induced by photoexcitation in case that Q is covalently linked to either free base (H_2P) or zinc (ZnP) porphyrins.[3] Extending the porphyrin monomers to homo or hetero dimers results in a drastic influence upon charge transfer rates.[4] To increase the number of involved chromophores we have made use of selforganization. The Zn atoms in the center of the porphyrin ring offer the possibility to coordinate suitable ligands. As shown in Fig. 1, we have replaced two of the phenyl rings of H_2P by pyridine. As is already known[5], pyridine is in suitable solvents a strong ligand for ZnP. In our case the two nitrogen atoms have approximately the same distance (12–14 Å) as the two central Zn atoms (11.5 Å) in the ZnP dimer. When using the unpolar solvent cyclohexane both zinc atoms are coordinated by pyridine as is evident from typical red shifts of about 10–15 nm in absorption and emission experiments.[5] If using only one pyridine ring the complexation is much less pronounced and the correspondent equilibrium constant drops by about 2 orders of magnitude. However, from this result it is not yet proven whether the complexation really occurs within one and the same ZnP dimer. This can be checked by a variation of the N–N and Zn–Zn distance, respectively. Reducing the Zn–Zn distance to about 9 Å for a gable form (*m*–position at the connecting phenyl ring) of the ZnP dimer the complexation is less pronounced, as can be seen in Fig. 2.

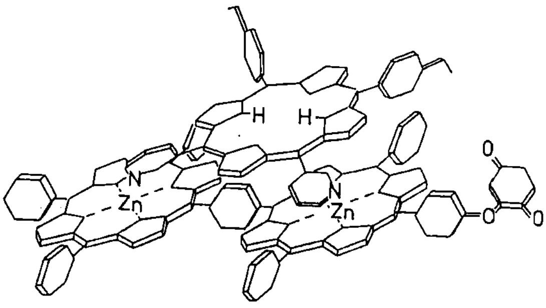

FIGURE 1 Schematic arrangement of a selforganized aggregate using the with respect to the 2 pyridins twisted H_2P form.

The formation of complexes has been studied without the covalently linked Q, in which case the ZnP fluorescence is quenched due to fast energy transfer within 10 ps from ZnP to H_2P.[5] In the presence of Q, however, both the fluorescence of ZnP and H_2P are quenched. This is due to fast electron transfer from ZnP or H_2P to Q. Without complexation the dimeric form of ZnP exhibits an electron transfer time of 240 ps, much slower than the energy transfer from ZnP to H_2P. The complex without Q has a fluorescence lifetime of the H_2P component of about 8 ns, which is shortened to about 500 ps in the Q–substituted form. We have performed the

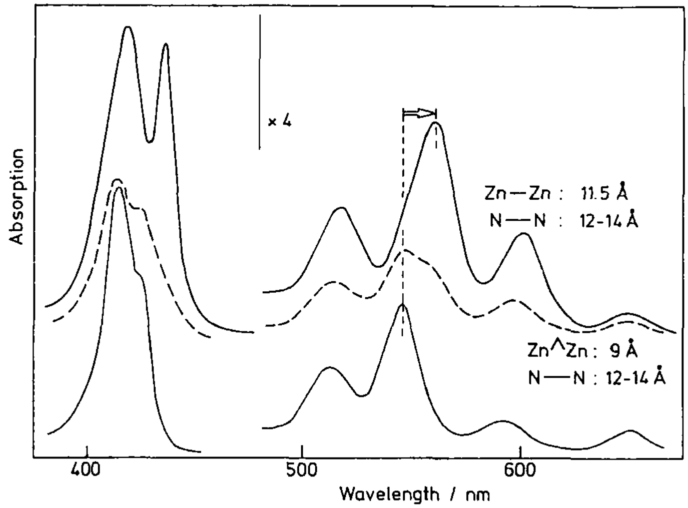

FIGURE 2 Q- and Soret-band absorption of complexed porphyrins without quinone for two different combinations of Zn-Zn and N-N arrangements. The arrow indicates the spectral shift upon complexation. The lower spectrum is a superposition of an equimolar H_2P and (ZnP-ZnP) mixture.

experiments using a linear arrangement of the two pyridin substituents and a twisted one shown in Fig. 1. The results are collected in Table 1.

TABLE 1 Electron transfer times at 300 K.

Compound	H_2P-Q distance	Transfer time
(ZnP-ZnPQ)-(2Pyr-H_2P)	17.5 Å	500 ps
(ZnP-ZnPQ)∧(2Pyr-H_2P)	20.5 Å	670 ps
H_2PQ	10.6 Å	1400 ps
ZnP-ZnPQ	10.6 Å	240 ps

The comparison of different combinations of porphyrins and quinones clearly demonstrates that when exciting ZnP energy is transfered to H_2P in a time shorter than 10 ps. But even in the with respect to Q remote localization of excitation energy electron transfer to Q is still possible. Table 1 provides a comparison of the relevant electron transfer times which have been corrected for the intrinsic H_2P fluorescence lifetime. Also included is the center-to-center distance from H_2P to Q in the various situations. As it is evident electron transfer in the complex is despite the larger distance much faster as compared to the covalently linked form. Additionally, the complexed forms show only a minor change in transfer times upon changes in distance. From this we conclude that the spatially intermediate ZnP dimer mediates the electron transfer from H_2P to Q. Electron transfer from ZnP to Q is expected to be faster as compared to H_2P because of the increased driving force of the redoxpotential.[6] Whether ZnP mediates the electron transfer via a thermal activation of excitation energy from H_2P to ZnP or via superexchange as observed in porphyrin–quinone heterodimers[4] is presently an open question and will be further investigated varying the temperature. In conclusion, adjusting temperature and solvent selforganization via ligand formation provides effective means to form aggregates with a competition of energy and electron transfer and optimizes electron transfer rates for a given electron donor chromophore.

TAUTOMERIZATION OF HBO IN α-CYCLODEXTRIN

The photophysics of excited–state intramolecular proton transfer compounds such as HBO has been investigated recently by several groups.[7–9] After excitation into the first excited singlet–state, HBO undergoes intramolecular proton transfer from the hydroxyl group to the nitrogene atom (see Fig. 3). As a result, a dual fluorescence is observed: the shorter–wavelength emission is attributed to enol–fluorescence (from the excited E_{cis}) and the longer–wavelength emission to keto–fluorescence (from the excited K_{cis}). In the electronic ground–state other tautomers are predicted.[7] In our investigation, the trans–keto tautomer K_{tr} (see Fig. 3) must be taken into account.

We investigated the aggregation of HBO with α-Cyclodextrin (α-CD) in DMSO via optical spectroscopy. The absorption, fluorescence–excitation, and fluorescence spectra are shown in Fig. 3 a–c for comparison without α-CD and with a high concentration of α-CD (about a factor of 100 higher than the HBO concentration). The absorption and fluorescence excitation spectra consist of three distinguishable bands: band A, maximum at 295 nm, band B (332 nm), and band C (380 nm). Band C, which is rather small in absorption, has higher intensity in fluorescence–excitation. That means that the fluorescence intensity of C at 500 nm is higher than that of A and B, which have rather the same intensity in absorption and fluorescence–excitation. The fluorescence spectra depend strongly on excitation wavelength. With $\lambda_{ex} = 320\,\mathrm{nm}$ two bands can be observed, band X at 365 nm and band Y at 480 nm. With $\lambda_{ex} = 375\,\mathrm{nm}$ only one band Z at 440 nm can be observed. We make the following assignment. A and B are mainly absorption bands of E_{cis}. C and a part of A are bands of K_{tr}. Band X corresponds to fluorescence from the excited E_{cis}, band Y from the excited K_{cis}, and Z from the excited K_{tr}. Band C, X, and Z are not observed in non–polar solvents. That means, firstly, that K_{tr} is stabilized in DMSO due to hydrogen bonds to the solvent and, secondly, that

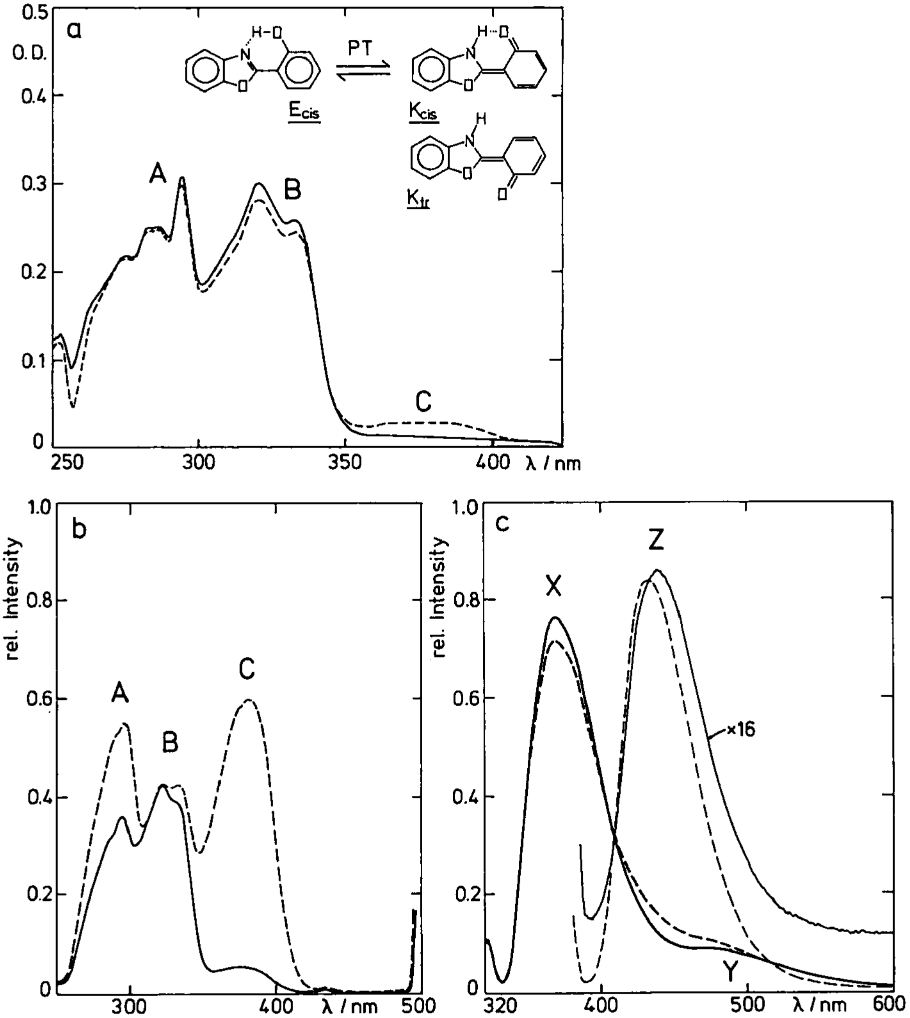

FIGURE 3 Spectra of HBO in DMSO without (———) and with α–CD (– – –) at room temperature. (a) absorption, (b) fluorescence–excitation with $\lambda_{em} = 500\,\mathrm{nm}$, (c) fluorescence with $\lambda_{ex} = 320\,\mathrm{nm}$ (——— , – – –) and $\lambda_{ex} = 375\,\mathrm{nm}$ (——— , – – –).

in the excited state E_{cis} is stabilized, too. The spectra of the solutions with high α–CD–concentrations differ significantly from those of pure DMSO solutions. The main differences are as follows. (i) Band A increases in the fluorescence-excitation spectrum by 50%. (ii) Band B decreases by 10%. (iii) Band C is shifted to the red (bathochromic) and increases by a factor of 10. (iv) Band Z is shifted to the blue (hypsochromic) and increases by a factor of 16.

Two main aspects of HBO are of interest in our experiments, firstly, the equilibrium of different tautomers in the ground-state, and secondly, the influence of the inclusion in α-CD on the PT-reaction. Firstly, the isosbestic points at 295 nm and 340 nm in the absorption spectra show that there is an equilibrium between E_{cis} and K_{tr}, the latter more stabilized in α-CD. Additionaly, the differences concerning bands C and Z can be explained with either a change in equilibrium of two bands or a spectral shift of one band. From the shape of the bands and a shift of the fluorescence band at different excitation wavelengths ($\lambda_{ex} = 375\,\mathrm{nm}$ and $\lambda_{ex} = 400\,\mathrm{nm}$, the latter not shown in Fig. 3), we conclude that **two** tautomers of HBO with different emission wavelengths absorb around 380 nm, say $K_{tr}(1)$ at 375 nm and $K_{tr}(2)$ at 385 nm, with fluorescence bands at 440nm ($K_{tr}(2)$) and 430 nm ($K_{tr}(2)$). In α-CD, $K_{tr}(2)$, the one with the smaller Stokes-shift, is more stabilized. From our experiments follows, secondly, that the PT-reaction is **not** influenced by the α-CD-environment, because the intensity ratio of enol- and keto-fluorescence is nearly constant. The differences concerning E_{cis} (increase of band A in fluorescence-excitation and changes in fluorescence bands X and Y) are due to the increasing concentration of K_{tr} and decreasing concentration of E_{cis}.

An open question is how the equilibrium reaction between E_{cis} and K_{tr} takes place, because it consists of both a PT-reaction and a rotation around a C-C bond (see Fig. 3). Either an intermediate twisted tautomer can play a role[8] or a bimolecular reaction $E_{cis} + E_{cis} \rightarrow K_{tr} + K_{tr}$ takes place[9].

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