CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000375

Unusual Photoinduced Electron Transfer from a Zinc Porphyrin to a Tetrapyridyl Free-Base Porphyrin in a Noncovalent Multiporphyrin Array

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Dedicated to Francesco Barigelletti on the occasion of his retirement

Abstract: Excitation of the peripheral Zn porphyrin units in a noncovalent five-porphyrin array, formed by gable-like zinc(II) bisporphyrins and a central free-base *meso*-tetrakis(4-pyridyl)-porphyrin in a 2:1 ratio, $(\mathbf{ZnP_2})_2$·(**TPyP**), does not lead to a quantitative sensitization of the luminescence of the free-base porphyrin acceptor, even though there is an effective energy transfer. Time resolution of the luminescence evidences a quenching of **TPyP** upon sensitization by the peripheral $\mathbf{ZnP_2}$. The time evolution of the **TPyP** fluorescence in the complex can be described by a bi-exponential fitting with a major component of 180 ps and a minor one of 5 ns, compared to an isolated **TPyP** lifetime of 9.4 ns. The two quenched lifetimes are shown to be correlated to the presence of 2:1 and 1:1 complexes, respectively. No quenching of **TPyP** fluorescence occurs in $(\mathbf{ZnP_2})_2$·(**TPyP**) at 77 K in a rigid solvent for which only an energy-transfer process ($\tau = 150 \pm 10$ ps) from peripheral $\mathbf{ZnP_2}$ to the central **TPyP** is observed. An unusual HOMO–HOMO electron-transfer reaction from $\mathbf{ZnP_2}$ to the excited **TPyP** units, responsible for the observed phenomena, is detected. The resulting charge-separated state, $(\mathbf{ZnP_2})^+{}_2$·$(\mathbf{TPyP})^-$ is found to recombine to the ground state with a lifetime of 11 ns.

Keywords: charge separation · electron transfer · energy transfer · porphyrinoids · supramolecular chemistry

Introduction

Photoinduced processes occurring in noncovalent multiporphyrin arrays have been extensively investigated for their relevance to energy and electron transfer that occurs in natural photosynthetic reaction centers.[1–6] Coordination of a zinc(II) center in a zinc porphyrin by the nitrogen atom of a Lewis base has been one of the most popular motifs in the construction of the assemblies.[7–23] Multiple binding sites and a nearly perfect geometrical matching between partners has been a successful strategy to synthesize associates with very-high stability.[24–27] This is a prerequisite for a photophysical investigation, which generally involves determination at very-low spectroscopic concentrations.

We have recently reported the noncovalent assembly of a three component porphyrin array (Figure 1), resulting from the association of two oblique zinc bis-porphyrins ($\mathbf{ZnP_2}$) around a tetrapyridyl porphyrin (**TPyP**) core.[28] Association was characterized by a high equilibrium constant, of the order of $10^{14}\,\mathrm{M}^{-2}$, which granted a high percentage of association, even in dilute solutions. A preliminary study of the photophysical properties of the arrays has shown that: i) the light energy absorbed by the zinc porphyrin component $\mathbf{ZnP_2}$, which has a fluorescent state energy level of 2.01 eV in the complex, is transferred to the free-base component with an efficiency of 80 %; ii) regardless of the energy transfer, the free-base porphyrin fluorescence (1.93 eV in the complex) was not sensitized, but quenched; iii) a bi-exponential decay of the free-base porphyrin fluorescence with lifetimes of 180 ps ($\approx$75 % of the total decay) and of 5 ns ($\approx$25 % of the total decay),[29] compared to the 9.4 ns lifetime for model **TPyP**, could rationalize the lack of sensitization. To explain the unexpected quenching of the associated

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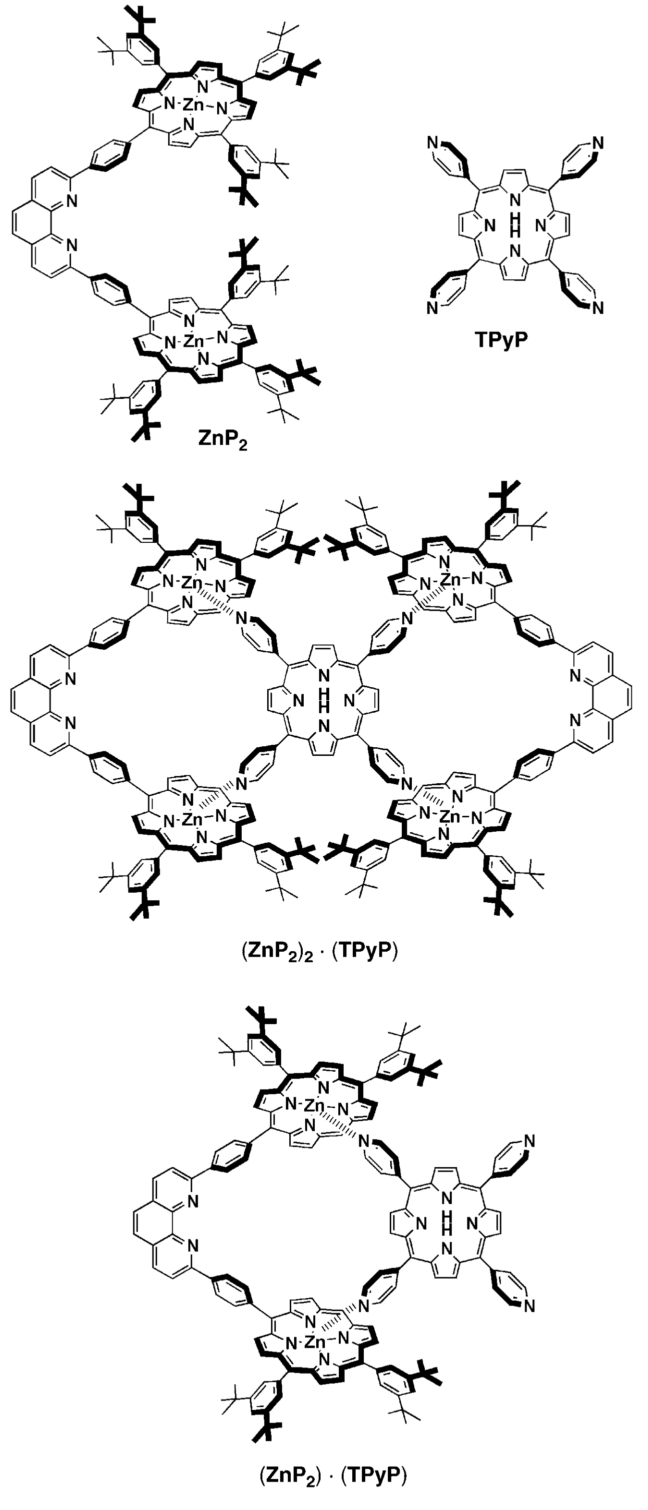

Figure 1. Structures of (**ZnP$_2$**)$_2$·(**TPyP**), of (**ZnP$_2$**)·(**TPyP**) and of the components. In the arrays, two 3,5-di-*tert*-butylphenyl substituents of **ZnP$_2$** are omitted for clarity.

TPyP, a hypothesis related to the occurrence of an electron transfer between the porphyrins or, alternatively, to a change of the intrinsic photophysical parameters of the **TPyP** porphyrin upon complexation, was proposed. In this report we present a series of photophysical investigations apt to verify these hypotheses, we discuss the results and provide evidence for the identification of the unusual deactivation mechanism in this penta-porphyrin array.

Results and Discussion

Luminescence: Absorption and corrected excitation spectra of **ZnP$_2$**, **TPyP**, and of the complex (**ZnP$_2$**)$_2$·(**TPyP**), from a 2:1 stoichiometric mixture of the components, is reported in Figure 2A, and the most relevant photophysical parameters of the system are collected in Table 1.[28] The examination of the excitation spectrum at $\lambda = 730$ nm, for which the emission is exclusively from **TPyP**, allows us to establish that the energy absorbed by the complex is transferred to this moiety with an high efficiency (≈80%).[28] The detected fluorescence yield of **TPyP** in the complex compared to the model alone is reduced to about 20% (inset of Figure 2A, Table 1). Fluorescence from a **ZnP$_2$** solution after increasing additions of **TPyP** is displayed in Figure 2B. The spectra are corrected for the contribution of the direct emission of **TPyP**, determined as fluorescence spectra of **TPyP** solutions

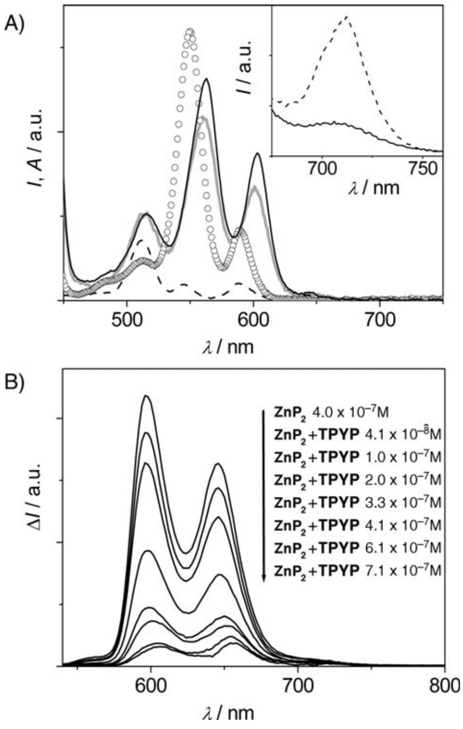

Figure 2. A) Absorption spectrum (——) and arbitrarily scaled corrected excitation spectrum of (**ZnP$_2$**)$_2$·(**TPyP**) measured at $\lambda = 730$ nm (——). The absorption spectra of the components **TPyP** (-----) and **ZnP$_2$** (○) are also shown. In the inset the fluorescence from optically matched **TPyP** (-----) and (**ZnP$_2$**)$_2$·(**TPyP**) (——) solutions, $\lambda_{exc} = 650$ nm. B) Fluorescence of a **ZnP$_2$** solution with increasing amounts of **TPyP**, after subtraction of the direct fluorescence of the corresponding **TPyP** concentration, $\lambda_{exc} = 428$ nm.

Table 1. Luminescence properties of components and assembly in toluene.[27,28]

	295 K			77 K		
	λ_{max} [nm]	ϕ_{fl}	τ [ns]	λ_{max} [nm]	τ [ns]	E [eV][c]
ZnP_2	597, 648	0.065	2.0	602, 658, 788[a]	2.8	2.06, 1.57[a]
TPyP	645, 712	0.085	9.4	637, 697, 706	10.6	1.95
$(ZnP_2)_2{\cdot}(TPyP)$	616, 650, 712	0.019[b]	0.010,[d] 0.18,[e] 5.0[e]	618, 643, 708	0.160,[d] 11.0[e]	2.01,[d] 1.93[e]

[a] Phosphorescence. [b] Fluorescence yield upon selective excitation of **TPyP** at $\lambda = 646$ nm. [c] Excited-state energy from the luminescence maxima at 77 K. [d] Lifetime/energy level of **ZnP_2** component. [e] Lifetimes/energy level of the **TPyP** component.

at the corresponding concentrations. It is evident that the luminescence of the **ZnP_2** component ($\lambda_{max} = 596$ and 646 nm) decreases upon addition of **TPyP**, but the luminescence of the latter ($\lambda_{max} = 646$ and 712 nm) is not sensitized in spite of the indications derived from the excitation spectra (Figure 2 A). Some explanation of this behavior comes from time-resolved luminescence studies. Figure 3 shows the time profile of the fluorescence detected in the complex at $\lambda = 600 \pm 10$ nm (emission of ^{1}**ZnP_2**) and at $\lambda = 715 \pm 10$ nm (emission of ^{1}**TPyP**) after excitation of the solution with a picosecond laser pulse at $\lambda = 532$ nm.[28] About 90 % of the luminescence of ^{1}**ZnP_2** is quenched with a lifetime of 10 ps, whereas some residual luminescence, owed to uncomplexed ^{1}**ZnP_2**, displays a lifetime of 2 ns. Fluorescence of ^{1}**TPyP** exhibits a bi-exponential behavior, which is mostly quenched (≈75 %), with a lifetime of 180 ps, whereas the residual decay has a nanosecond lifetime. The latter can be better measured with a nanosecond time-correlated single-photon apparatus and is found to be 5 ns, about half that of free **TPyP**, 9.4 ns.

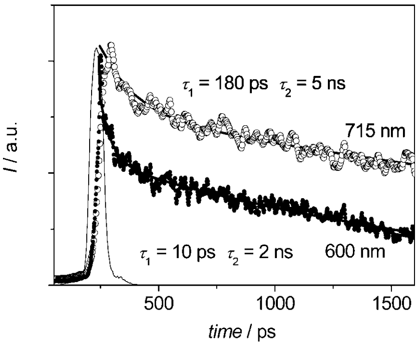

Figure 3. Luminescence profiles and double exponential fitting at the component luminescence maxima in toluene solution of $(ZnP_2)_2{\cdot}(TPyP)$, excitation at $\lambda = 532$ nm (1 mJ, 35 ps pulse). The concentration of components is in a 2:1 ratio.

There are two points that deserve further investigation; one is the origin of the **TPyP** fluorescence quenching, the other is the reason for the bi-exponential behavior. Clearly, whichever is the reason for the quenching, the biphasic behavior is indicative of two different populations of complexes non-equilibrating during the lifetime of the species. One explanation could be that there are two different conformers for the **$(ZnP_2)_2{\cdot}(TPyP)$** stoichiometry. To verify this hypothesis we explored the possibility that **ZnP_2** could complex two *trans* pyridyl positions of **TPyP**. This was done by probing complexation of **ZnP_2** with a 5,15-bis(4′-pyridyl)-10,20-(3,5-di-tert-butylphenyl)-porphyrin, ***trans*DPyP** (Figure 4), but inspection of the results showed that no association occurred. Analysis revealed that the addition of an excess of ***trans*DPyP** to **ZnP_2** does not lead either to the bathochromic shift in the **ZnP_2** absorption bands, typical of the formation of the Zn⋅⋅⋅N axial bond, or to any sizeable quenching or sensitization of the components in the emission spectrum. This indicates that the species do not associate in the concentration range explored for the association of **ZnP_2** with **TPyP** (Figure 4).[28] A likely explanation is the mismatching of the dimensions of the Zn–Zn distance in **ZnP_2**, ≈13.5 Å,[30] and the N–N distance in ***trans*DPyP**, 16 Å . In the present system, this excludes the existence of a conformation for which **ZnP_2** binds two pyridyl residues of **TPyP** *trans* to each other. Another viable possibility to explain the observation of two different populations, is the existence of complexes with different stoichiometries.

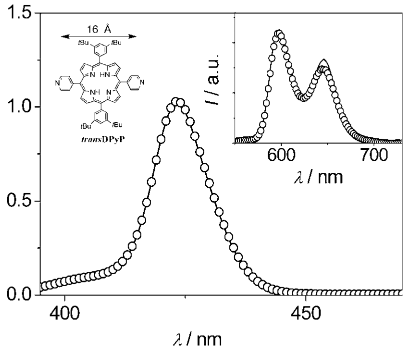

Figure 4. Absorption and luminescence (in the inset, $\lambda_{exc} = 558$ nm) spectra of **ZnP_2** 2.0×10^{-7} M (——) compared with the spectra after addition of ***trans*DPyP** (5×10^{-6} M) and subtraction of the contribution by ***trans*DPyP** itself (○).

To prove this hypothesis we prepared a mixture of **ZnP_2**/**TPyP** in a stoichiometric ratio of 1:1 . In these conditions formation of **$(ZnP_2){\cdot}(TPyP)$** is favored with respect to **$(ZnP_2)_2{\cdot}(TPyP)$**. The association of the first **ZnP_2** has an equilibrium constant of the order of 10^7 M^{-1}, similar to the association of the second **ZnP_2**. This is made possible by a slightly tilted geometry in the 2:1 complex, which allows the entrance of the second coordinating **ZnP_2** without any hindrance by the first one.[28] The time profiles of the luminescence measured in a stoichiometric ratio of 1:1 are reported in Figure 5. A quenched lifetime measured on the **ZnP_2** band is still 10 ps and it accounts for about 90 % of the full decay of the fluorescence of the species. The lifetime measured for the **TPyP** band is still biphasic, but, in this case, less than 30 % of the total decay is described by a lifetime of 180 ps, whereas a large majority (>70 %) is fitted by a

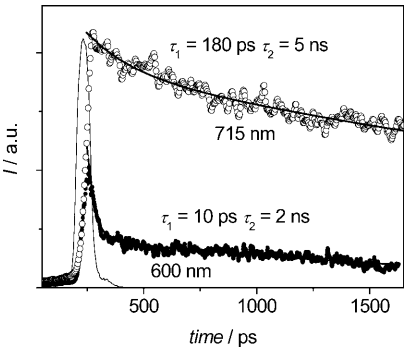

Figure 5. Luminescence profiles and double exponential fitting at the component luminescence maxima in toluene solution of (**ZnP$_2$**)·(**TPyP**), excitation at $\lambda = 532$ nm (1 mJ, 35 ps pulse). The component concentration is in a 1:1 ratio (see text).

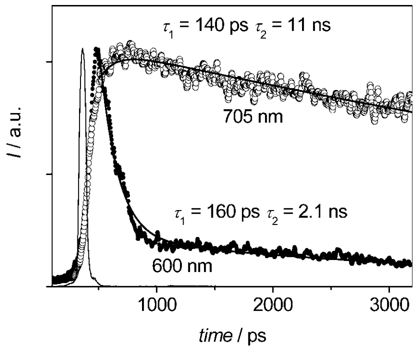

Figure 6. Luminescence profiles and double exponential fitting at the component luminescence maxima in toluene glass at 77 K of the complex (**ZnP$_2$**)$_2$·(**TPyP**), excitation at $\lambda = 532$ nm (1 mJ, 35 ps pulse).

5 ns lifetime. We take this as an indication that in the mixture two complexes are present, one with a 1:1 ratio, the other with a 2:1 ratio and we associate the 5 ns lifetime to the **TPyP** in the 1:1 complex (**ZnP$_2$**)·(**TPyP**), whereas the 180 ps is associated to the **TPyP** lifetime in (**ZnP$_2$**)$_2$·(**TPyP**). Both electronic and steric factors could account for the difference in reactivity between the complexes with different stoichiometry. From an electronic viewpoint, **TPyP** is more electron deficient in the 2:1 complex, compared to the 1:1 complex, and this could have important effects. Additionally, the **TPyP** plane is tilted with respect to the planes containing the phenanthrolines of **ZnP$_2$** in (**ZnP$_2$**)$_2$·(**TPyP**),[28] whereas **TPyP** is most likely coplanar with the phenanthroline plane in the (**ZnP$_2$**)·(**TPyP**) complex, analogous to a formerly characterized complex of **ZnP$_2$** with a *meso*-5,10-bis(4′-pyridyl)-15,20-diphenylporphyrin, **ZnP$_2$**·(***cis*DPyP**).[27] Notably, in the related complex **ZnP$_2$**·(***cis*DPyP**), the luminescence of ***cis*DPyP** was not quenched, but sensitized. In addition to the sensitization of the fluorescence of ***cis*DPyP** detected by steady-state experiments, time resolved experiments showed that the decay of the singlet excited state ^{1}**ZnP$_2$**·(***cis*DPyP**) and the rise of the **ZnP$_2$**·(^{1}***cis*DPyP**) excited state occurred with the same lifetime ($\tau = 50$ ps at room temperature).[27]

To shed more light on the origin of the unexpected quenching of ^{1}**TPyP** in the complexes, we performed a series of experiments. The luminescence decay of **ZnP$_2$** ($\lambda = 600 \pm 10$ nm) and **TPyP** ($\lambda = 705 \pm 10$ nm) components in the 2:1 complex in a toluene glass at 77 K are displayed in Figure 6. These luminescence profiles are different to those at room temperature. ^{1}**ZnP$_2$** decays slightly slower than at room temperature, $\tau = 160$ ps, as expected on the basis of the modest temperature dependence of the energy-transfer process.[31] In ^{1}**TPyP** luminescence a rise can be detected with a lifetime of 140 ps and matches reasonably well to the decay of ^{1}**ZnP$_2$**. This is unambiguous evidence of the occurrence of energy transfer from **ZnP$_2$** to **TPyP** within the complexes at 77 K. Remarkably, one may notice that at this temperature the process is not followed by any quenching of the **TPyP** luminescence, as a lifetime identical to that of free ^{1}**TPyP** at 77 K is measured, 11 ns. We can therefore learn that the room temperature quenching processes of ^{1}**TPyP** with lifetimes of 180 ps and 5 ns are thermally activated processes.

Photoinduced processes: In Figure 7, a schematic energy level diagram of the system is drawn. The singlet excited state energy levels of the complex are derived from the 77 K fluorescence maxima, 2.01 eV and 1.93 eV for the zinc and the free-base component respectively. As no phosphorescence was observed in the complex solution, the levels of the triplets were derived from the phosphorescence maxima of the **ZnP$_2$** component, 1.57 eV, and from a literature value of a tetraaryl free-base porphyrin for **TPyP**, 1.47 eV.[32] We should however take into account also a possible electron-transfer process within the partners. A photoinduced electron-transfer process between a tetraaryl zinc porphyrin and

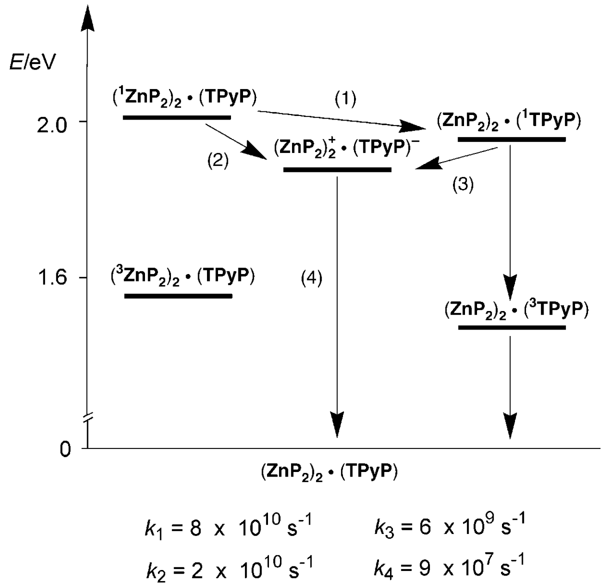

Figure 7. Energy level diagram, photoinduced reaction steps and rate constants in the complex (**ZnP$_2$**)$_2$·(**TPyP**).

a tetraaryl free-base porphyrin leading to the formation of a charge separated (CS) state, characterized by an oxidized zinc porphyrin and a reduced free-base porphyrin, is in general, endoergonic. It has been postulated in a few cases, but not demonstrated.[23,33] The energy of this CS state is at least of the order of 2.1–2.2 eV, slightly higher than the excited states of both porphyrins, conversely the reverse electron transfer, that is, from the free-base porphyrin to the zinc porphyrin, is even more endoergonic with a CS level of the order of 2.3–2.4 eV.[34] Only if the free-base porphyrin electron acceptor has strongly electron withdrawing substituents, has the formation of a CS state characterized by an extra electron on the free-base and a hole on the zinc porphyrin been observed.[35] Pentafluorophenyl substituted free-base porphyrins can be reduced rather easily, at approximately −0.85 V vs SCE, and this makes the formation of the CS state at an energy of approximately 1.6–1.7 eV, thermodynamically feasible by both porphyrin excited states.[35] Returning to the present case of a zinc porphyrin and a tetrapyridyl free-base porphyrin, a few points should be considered. It is well known that if Zn porphyrins are involved in noncovalent bonds with pyridyl residues, they can be more easily oxidized than the uncomplexed counterparts by at least 0.1 V.[36,37] On the other hand, pyridyl substituted porphyrins can be reduced more easily than the corresponding tolyl derivatives: each pyridyl unit accounts for 50 mV anodic shift of the porphyrin redox potential.[38] Therefore, **TPyP** can be reduced at least 0.2 V more easily than the corresponding tetraphenyl analogue, in reasonable agreement with independent determinations, which places the reduction potential of **TPyP** at approximately −1.0 V versus SCE.[39] Therefore, the energy level of a charge separated state corresponding to a reduced **TPyP** and an oxidized $\mathbf{ZnP_2}$ within the complex, $(\mathbf{ZnP_2})_2{}^{+}\cdot(\mathbf{TPyP})^{-}$, would be of the order of 1.7–1.8 eV depending on the solvent, making electron transfer from the excited states of both porphyrins feasible, although with a low driving force.

The fluorescence lifetime of $({}^{1}\mathbf{ZnP_2})_2\cdot(\mathbf{TPyP})$ is 10 ps, from which a rate of fluorescence quenching of $10^{11}\,s^{-1}$ can be calculated, according to the equation $k=1/\tau-1/\tau_0$, in which τ and τ_0 represent the lifetime in the array and in the isolated model, respectively. From inspection of the corrected excitation spectrum of the 2:1 complex (Figure 2), one can derive that excitation of the zinc porphyrin unit to $({}^{1}\mathbf{ZnP_2})_2\cdot(\mathbf{TPyP})$ is followed by an efficient energy transfer to $(\mathbf{ZnP_2})_2\cdot({}^{1}\mathbf{TPyP})$, estimated of the order of 80 % (process (1) in Figure 7).[28] Energy transfer is typical of the zinc porphyrin/free-base porphyrin couple and has been observed before for several noncovalently assembled systems, including the above mentioned $\mathbf{ZnP_2}\cdot$(***cis*DPyP**).[27] The residual 20 % of fluorescence quenching might be ascribable to process (2), a parallel LUMO–LUMO electron transfer from $({}^{1}\mathbf{ZnP_2})_2\cdot(\mathbf{TPyP})$ to the charge separated state $(\mathbf{ZnP_2})_2{}^{+}\cdot(\mathbf{TPyP})^{-}$. This interpretation yields rates of the order of $8\times10^{10}\,s^{-1}$ for the energy-transfer reaction (1), and of the order of $2\times10^{10}\,s^{-1}$ for the electron-transfer reaction (2) at ambient temperature. An estimation of the energy-transfer process (1) between the two porphyrins performed according to the Förster mechanism[40] leads to a rate constant of approximately $6\times10^{10}\,s^{-1}$.[41] Taking into account the associated uncertainties this represents an acceptable agreement with the experimental findings and supports the proposed mechanism. It should however be noticed that, owing to the close proximity of the reactants, an electron-exchange mechanism (Dexter type) might contribute or even be the main mechanism.[42]

The LUMO–LUMO electron transfer, Figure 7 reaction (2), is slower than the energy-transfer reaction, owing to the higher reorganization energy associated with electron transfer compared to energy transfer and can compete only to a low extent.[43] Once $(\mathbf{ZnP_2})_2\cdot({}^{1}\mathbf{TPyP})$ is formed, it decays with a lifetime of 180 ps; the 5 ns lifetime has in fact been assigned to deactivation in the 1:1 complex of $(\mathbf{ZnP_2})\cdot({}^{1}\mathbf{TPyP})$. It is not our aim to study in detail the latter complex, but we can reasonably postulate that the 5 ns lifetime is owed to the same type of reactivity, in the different electronic environment of the $(\mathbf{ZnP_2})\cdot(\mathbf{TPyP})$ complex. The reaction depleting $(\mathbf{ZnP_2})_2\cdot({}^{1}\mathbf{TPyP})$, as well as $(\mathbf{ZnP_2})\cdot({}^{1}\mathbf{TPyP})$, can be a HOMO–HOMO electron transfer, reaction (3), to form the charge separated state $(\mathbf{ZnP_2})_2{}^{+}\cdot(\mathbf{TPyP})^{-}$ (Figure 7). An electron-transfer quenching mechanism of ${}^{1}\mathbf{TPyP}$ by a Zn porphyrin was formerly proposed in a complex between a cyclic Zn tetraporphyrin coordinated though four Zn−N bonds to a central **TPyP**, but more details are lacking and no evidence was provided.[33] The electron-transfer hypothesis would also agree with the observed behavior at 77 K (Figure 6) for which the deactivation processes of $(\mathbf{ZnP_2})_2\cdot({}^{1}\mathbf{TPyP})$ are blocked and only energy transfer from the Zn porphyrin to the free-base porphyrin occurs. The energy level of charge-separated state is strongly destabilized by solvent rigidification and a slight exergonic electron transfer at ambient temperature would become endoergonic at 77 K and could no longer take place.[44] We cannot however rule out the possibility that the observed quenching of **TPyP** at room temperature is owed to a perturbation of its electronic states, caused either by distortion/constraints or by electronic perturbations in the congested environment. This might introduce important changes in intrinsic photophysical parameters of **TPyP** as internal conversion, intersystem crossing or radiative decays, affecting the luminescence properties of the complexed **TPyP.** A similar interpretation was put forward to explain the incomplete sensitization of a central free-base porphyrin in a star-shaped pentaporphyrin with four zinc porphyrins at the periphery. The units were connected by flexible nucleosidic linkers, which allowed close approach and strong electronic interaction of the reactants.[45]

Time-resolved absorption: To shed light into the dynamics of the excited states and the possible deactivation steps, transient-absorption spectroscopy in the nano- and picosecond time regimes were performed. The detection of ionic species, either $\mathbf{ZnP_2}^{+}$or $\mathbf{TPyP}^{-}$ would support the hypothesis of electron transfer. The oxidized zinc porphyrin radical is quite well characterized and exhibits a sharp maximum at $\lambda = 409$ nm ($\varepsilon \approx 1.9 \times 10^5\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), a shoulder around $\lambda = 460$–470 nm ($\varepsilon \approx 4 \times 10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) and a broad structureless feature ($\varepsilon \approx 1 \times 10^4\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) in the region around $\lambda = 500$–700 nm.[46] In the wavelength range above $\lambda = 450$ nm, accessible to the picosecond experiment, the $\lambda = 460$–470 nm shoulder is generally distorted by ground-state absorption and the ΔA spectrum displays a band with an apparent maximum around $\lambda = 480$–490 nm.[34] Unfortunately the characterization of the zinc porphyrin radical cation is not so trivial, owing to the extensive overlap with the singlet and triplet excited state absorption bands of both **ZnP_2** and **TPyP** in the same spectral region. The end of pulse spectrum and the 3.5 ns spectrum from a pump and probe experiment with ps resolution and excitation at $\lambda = 532$ nm (mostly **ZnP_2** is excited, ≈70%) are displayed in Figure 8. The time evolution at $\lambda = 490$ nm is reported in the inset and shows a modest rise with a lifetime of 160 ps followed by a slower growth for which precise determination is precluded by the time window of the experiment (3.5 ns), but which might be of the order of several nanoseconds (<10 ns, see below). The measured 160 ps is coincident within error to the shortest (180 ps), and the several nanosecond lifetime is compatible with the longest (5 ns) fluorescence lifetime measured for the decay of **^{1}TPyP** by luminescence spectroscopy and assigned to **(ZnP_2)$_2$·(^{1}TPyP)** and **(ZnP_2)·(^{1}TPyP)**, respectively. The spectral changes are fully consistent with the formation of an oxidized zinc porphyrin radical, **ZnP_2^{+}**, indicative of the formation of a CS state within both the 1:1 and the 2:1 assemblies. The data from a nanosecond flash-photolysis experiment are more clear (Figure 9). No rise at $\lambda = 490$ nm is detected, confirming a lifetime lower than 10 ns (the time resolution for this experiment) for the slow rising part detected in the picosecond experiment. The end of pulse absorption spectrum and a spectrum taken with 100 ns delay with respect to the laser pulse are displayed in Figure 9A. The difference between the end of pulse and the 100 ns spectra is reported in Figure 9B: It displays a band centered around $\lambda = 480$ nm, bleaching bands at $\lambda = 560$ and 600 nm and a lower absorbance up to the NIR regions. In the region around $\lambda = 650$–750 nm there is an interference by the emission of residual free **TPyP**, which, though weak, overshadows the absorbance at short times. The absorption decays with a lifetime of 11 ns, inset, and its spectrum is fully compatible with the spectrum of an oxidized zinc porphyrin confirming the results of the picosecond experiment. Conversely, the spectrum registered at 100 ns (see Figure 9A) has a maximum around $\lambda = 470$ nm and evolves slowly, with a lifetime of approximately 300 microseconds in air purged solutions (Figure 10). The lifetime is strongly affected by the presence of oxygen, being reduced to 550 ns in air equilibrated solutions. A reaction rate with oxygen $k_{\mathrm{ox}} = 1.1 \times 10^9\,\mathrm{M}^{-1}\mathrm{s}^{-1}$ can be calculated, consistent with a porphyrin triplet nature for the long-lived intermediate. A comparison with the results of a flash-photolysis experiment on solutions of the models **TPyP** and **ZnP_2** in toluene, Figure 10, should be taken with some caution, given the interference with ground state absorption below $\lambda = 500$ nm, but they allow to identify the long lived product/s in the complex as a mixture of the two triplets, very likely a **(ZnP_2)$_2$·(^{3}TPyP)** and some free **$^3ZnP_2$**. In the array the triplet state localized on **TPyP**, **(ZnP_2)$_2$·(^{3}TPyP)**, is the lowest excited state (Figure 7) and the light energy, which is not used for charge separation, is expected to be funneled into this state. Comparison of ΔA in the region out of the ground state absorption (Figure 10) allows a rough calculation of the triplet yield in the com-

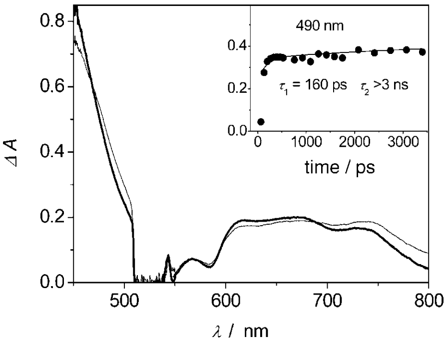

Figure 8. Transient-absorption spectra of a toluene solution of **(ZnP_2)$_2$·(TPyP)** after $\lambda = 532$ nm excitation (3 mJ, 35 ps pulse) at the end of pulse (thick line) and at 3.5 ns after laser pulse (thin line). In the inset the time profile at $\lambda = 490$ nm and the biexponential fitting are displayed.

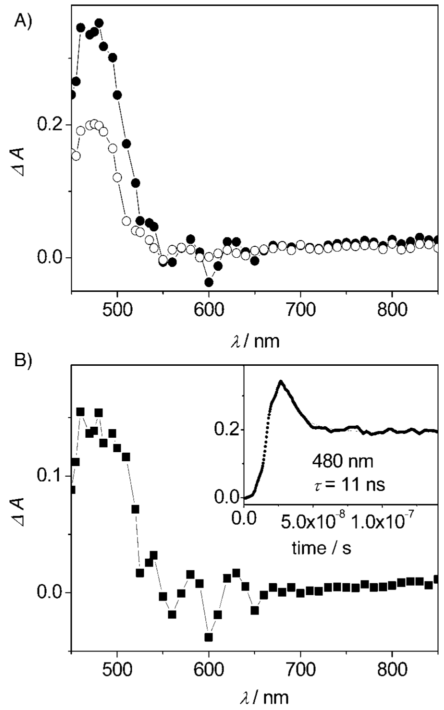

Figure 9. A) Transient-absorption spectra of an air-free toluene solution of **(ZnP_2)$_2$·(TPyP)** after $\lambda = 532$ nm excitation (3 mJ, 18 ns pulse) at the end of pulse (full circles) and at 100 ns after the laser pulse (empty circles). B) Difference of the transient absorbance spectra reported in A). In the inset the decay of the species and the exponential fitting are reported.

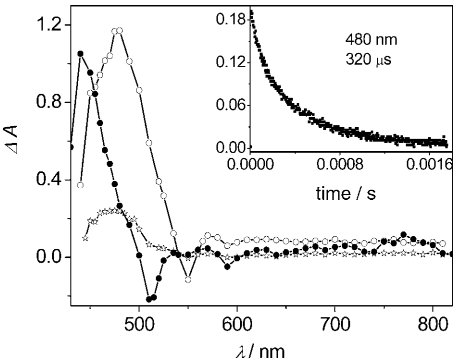

Figure 10. Transient-absorption spectra of an air-free toluene solution of (**ZnP$_2$**)$_2$·(**TPyP**) after 532 nm excitation (3 mJ, 18 ns pulse) at 100 ns after the laser pulse (stars) compared to optically matched solutions of **TPyP** (full circles) and **ZnP$_2$** (open circles). In the inset the decay of the (**ZnP$_2$**)$_2$·(**TPyP**) spectrum at 480 nm is displayed.

plex, which is of the order of 10–20 % with respect to the **TPyP** model. This yield can be fully accounted for by the intersystem crossing in conditions of reduced efficiency, owing to competition with electron transfer, reaction (3).[47] This agreement proves that no other step forming the triplet excited state is active and is a clear indication that recombination of the CS state occurs to the ground state, and not to the triplet state. This is not unexpected in the present system for which the relatively short lifetime of the CS state is not favorable to the occurrence of a spin-flip, required to change the multiplicity of the originally formed singlet CS state.

Evidence for the existence of a charge separated state in (**ZnP$_2$**)$_2$·(**TPyP**), which is formed by a reaction with a 170 ± 10 ps lifetime (average of luminescence and transient absorption data) and decays with a lifetime of 11 ns has been provided. This supports the electron transfer mechanism, reaction (3), able to explain the quenching of the central **TPyP** in the complex, after a sensitization from the **ZnP$_2$** component has occurred. The additional quenched luminescence lifetime of 5 ns is assigned to the same electron transfer within the 1:1 complex (**ZnP$_2$**)·(**TPyP**), which is present as a minor component in the mixture with a stoichiometric ratio of 2:1. The difference in reactivity of the two complexes is the result of the more electron deficient nature of **TPyP** when involved in the three-component, 2:1 assembly, than in the 1:1 complex. The consequent more favorable driving force for electron-transfer reaction in (**ZnP$_2$**)$_2$·(**TPyP**) than in (**ZnP$_2$**)·(**TPyP**) induces a faster electron transfer in the former (1/170 ps) than in the latter (1/5 ns).

Conclusion

Energy transfer within a noncovalent five-porphyrin assembly (**ZnP$_2$**)$_2$·(**TPyP**) containing four peripheral zinc porphyrin donors and a tetrapyridyl free-base porphyrin acceptor does not lead to quantitative sensitization of the luminescence of the free-base porphyrin acceptor, but conversely a quenching of the latter luminescence is detected. This is an unusual outcome for this couple, which is a typical donor–acceptor pair for energy-transfer reactions, and some similar phenomena have been reported in a few cases involving the tetrapyridyl free-base porphyrin as an energy acceptor, however they have never been clearly addressed.[23,33]

We have performed an in-depth investigation by time-resolved spectroscopic techniques of the photoinduced processes in the system and have provided evidences for the occurrence of electron transfer from the zinc porphyrin components to the free-base component upon excitation of the latter within the complex (HOMO–HOMO electron transfer). Excitation of the zinc porphyrin component leads predominantly to energy transfer to the free-base component, but also to a parallel, less efficient, LUMO–LUMO electron transfer. The unusual electron-transfer process in this donor–acceptor couple is made possible by the easier oxidation of zinc porphyrin when involved in coordination bonds with pyridyl residues and by the more facile reduction of tetrapyridyl free-base porphyrin with respect to the tetraaryl or the dipyridyl homologue. The higher electron deficiency of **TPyP** when involved in the (**ZnP$_2$**)$_2$·(**TPyP**) complex is very likely responsible for promoting the process in comparison to the 1:1 complex (**ZnP$_2$**)·(**TPyP**), which displays a lower rate.

This is, to our knowledge, the first unequivocal detection of an electron-transfer process from a Zn porphyrin to a free-base porphyrin with the exclusion of pentafluorophenyl substituted free-base porphyrins. In view of this the pair, which is a typical couple used for energy transfer investigations, should be regarded with some caution.

Experimental Section

All experiments were conducted in toluene solutions and the solvent used was spectroscopic grade toluene (C. Erba). Details on the preparation of the complexes and characterization of association parameters have been reported previously.[28,48] Absorption spectra were recorded by using a Perkin–Elmer Lambda 9 spectrophotometer and emission spectra, uncorrected if not otherwise specified, were detected by using a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier. Luminescence quantum yields were evaluated from the area of the luminescence spectra, corrected for the photomultiplier response, with reference to TPP (5,10,15,20-tetraphenyl-porphyrin) in aerated toluene ($\Phi_{fl} = 0.11$).[49] Experiments at 77 K made use of quartz capillary tubes immersed in liquid nitrogen contained in a home-made quartz dewar. Except otherwise specified experiments were conducted in a 2:1 molecular ratio of **ZnP$_2$**:**TPyP**. Fluorescence lifetimes in the nanosecond range were detected by an IBH time correlated single photon counting apparatus with excitation at $\lambda = 560$ nm. Luminescence lifetimes in the picosecond range were determined by an apparatus based on a Nd:YAG laser (Continuum PY62–10) with a 35 ps pulse duration, 532 nm, 1.5 mJ per pulse and a Streak Camera (Hamamtsu C1587 equipped with M1952). Solutions with absorbance of approximately 0.2–0.3 at the exciting wavelength were used. The luminescence signals from 1000 laser shots were averaged and the time profile was measured from the streak image in a wavelength range of approximately 20 nm around the selected wavelength. The resolution time after deconvolution is 10 ps.[20] Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd-YAG laser (Continuum PY62/10, 35 ps pulse, 532 nm, 3 mJ). Solutions with absorbance of approximately 0.4–0.5 at the exciting wavelength were used. A broad band interference filter (K3 Balzers, maximized transmission at $\lambda = 500$ nm) was placed on the white continuum analyzing light to enhance the ratio of the wavelength component below $\lambda = 520$ nm in comparison with longer wavelength. More details on the apparatus can be found elsewhere.[50] Laser flash photolysis in the nanosecond range was performed by using a Nd-YAG laser (18 ns pulse, 532 nm, 3 mJ) and an apparatus previously described.[51] The samples with absorbances in the range 0.1–0.4 were bubbled with Ar for approximately 15 min and sealed in home made 10 mm optical cells. For the calculation of the reactivity with oxygen a solubility of oxygen in air saturated toluene of 1.8×10^{-3} M was taken.

Estimated errors are 10 % on exponential lifetimes or 20 % for more complex kinetic models, 20 % on quantum yields, 20 % on molar absorption coefficients and 3 nm on emission and absorption peaks. Computation of the integral overlap and of the rate for the energy-transfer processes according to Förster mechanism were performed with the use of Matlab 5.2.[52] Working temperature, if not otherwise specified, was 295 ± 2 K.

Acknowledgements

Financial support from Italian CNR (Project PM-P04-010 MACOL) is gratefully acknowledged. We thank Elisabetta Iengo (University of Trieste) for a gift of 5,15-bis(4′-pyridyl)-10,20-(3,5-di-tert-butylphenyl)-porphyrin. We acknowledge the French Ministry of Education for a fellowship (M.B.) and COSTD31 for support.

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Received: February 11, 2010