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Light-Induced Electron Transfer in Pyropheophytin−Anthraquinone and Phytochlorin−Anthraquinone Dyads: Influence of Conformational Exchange

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Novel types of donor−acceptor (DA) molecules, consisting of covalently linked pyropheophytin−anthraquinone (PQ and ZnPQ) and phytochlorin−anthraquinone (PCQ and ZnPCQ) dyads and their diastereomers were studied by means of steady-state and time-resolved fluorescence and absorption spectroscopies. Conformational properties were found to play an important role in understanding the observed photochemical behavior of the flexible diastereomers PQ1,2 and ZnPQ1,2 DA dyads. The more compact conformers undergo fast (in a few picoseconds or less) light-induced electron transfer (ET) from the singlet excited state. The most extended conformers, however, possess a separation between the donor and acceptor, which is too long to allow relaxation of the singlet exited state via ET. A fast conformational exchange between the open and folded conformers was observed in a variety of solvents and was found to be crucial for the observed electron-transfer properties of the flexible DA dyads studied. The more rigid DA systems, PCQ and ZnPCQ, exhibited electron-transfer properties that could well be elucidated in the frame of the Marcus theory.

1. Introduction

The need to understand and mimic processes of natural photosynthesis has motivated chemists to synthesize and study different types of porphyrin− and pheophorbide−quinone compounds.[1,2] These molecules can serve as models of the primary light-induced electron transfer (ET) reactions of the natural photosynthesis. Efficient single and multistep intramolecular electron-transfer processes have been observed and investigated. The fundamental principles of the phenomenon from the energetic point of view, the distance and orientation between the donor and the acceptor, and the effect of the solvent have been well established.[3,4] The main synthetic goal has been to construct donor−acceptor (DA) compounds with fixed and known mutual orientations and separations between the donor and acceptor.

When modeling photosynthesis, it is important to create molecular assemblies by combining several functional units capable of performing charge separation. One of the techniques enabling the creation of ordered molecular assemblies is the Langmuir−Blodgett (LB) method.[5] To fulfill the requirements of the LB technique, new types of DA compounds should be synthesized. An important aim in the molecular design is the fabrication of LB monolayers. A good starting point can be natural chlorophyll compounds, which are known to form monolayers on the water−air interface.[6,7] These molecules consist of a chromophore which can act as an electron donor and has a hydrophobic tail, e.g., a phytyl chain, enabling the formation of uniformly ordered layers. The LB films are characterized by the high surface density of the chromophores, and an interchromophore aggregation is one of the problems to be solved when an efficient DA system is designed.[8,9] This is usually achieved by mixing of functional molecules with lipids. A smooth incorporation of the DA molecule into the matrix lipid layer becomes an important requirement. The latter implies that DA systems with a flexible bridge might have an advantage compared to the compounds with a rigid spacer between D and A. It should be noted, however, that flexible bridges make the experimental characterization of the DA compounds more complex. For example, multiexponential fluorescence decays for DA compounds have been observed and explained by the presence of several conformers simultaneously.[10−13] The exchange equilibrium between the conformers was found to be important for the ET reaction from the triplet state.[10,14] The influence of multiple conformers on the photophysical properties of the DA compounds depends on the molecular structure and has to be considered in each particular case.

Recently, six covalently linked pyropheophytin−anthraquinone and phytochlorin−anthraquinone dyads have been synthesized.[15,16] Four of them are pyropheopytin−anthraquinone derivatives. In addition to a spacer group between donor and acceptor, these DA compounds contain a phytyl tail, which makes them suitable for the LB technique.[17] The photochemical properties of these dyads were found to be complicated, since the flexible spacer group between the donor and the acceptor allows a variety of conformers to exist simultaneously. To elucidate the role played by the spacer group, two relatively rigid dyads consisting of comparable ring moieties, but linked with a relatively short chain, were synthesized and chromatographically resolved. We will show that the photochemical properties of these rigid dyads can be treated in the framework of the classic Marcus ET theory.

In this paper, we report a comparative study of the photochemical properties of the two types of DA dyads in order to see the possible effects of the conformational exchange on the

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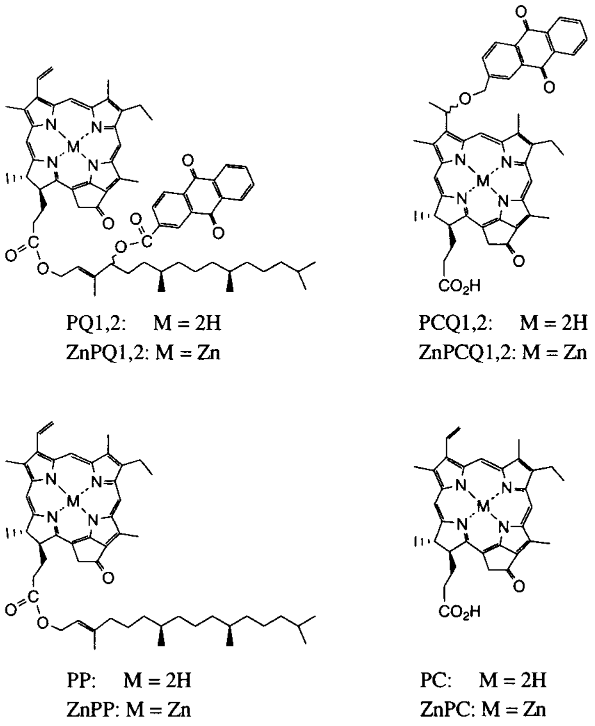

PQ1,2: M = 2H
ZnPQ1,2: M = Zn

PCQ1,2: M = 2H
ZnPCQ1,2: M = Zn

PP: M = 2H
ZnPP: M = Zn

PC: M = 2H
ZnPC: M = Zn

Figure 1. Structures of the compound.

photochemical properties. This kind of knowledge is important for a proper interpretation and understanding of the ET reaction occurring in the DA compounds incorporated into LB films (cf. the accompanying paper[18]).

2. Methods and Materials

The synthesis and complete chromatographic separation of the P4 diastereomers of 13^2-demethoxycarbonyl-P4-oxy-(9,10-anthraquinone-2-carbonyl)−pheophytin *a* (PQ1 and PQ2, Figure 1) and the synthesis of 3^1(*R*,*S*)-[(anthraquinon-2-yl)methoxy]−phytochlorin (PCQ1 and PCQ2, Figure 1) were accomplished as described.[16,19] Although the 3^1(R) and 3^1(S) diastereomers were chromatographically resolved to stereochemical purity, the photochemical properties of the isomers appeared to be very similar, and hence, in this study, we will refer to them as a single compound, PCQ. The reference compounds, 13^2-demethoxycarbonyl−pheophytin *a* (pyroPheo *a*, PP) and 3^1,3^2-didehydrophytochlorin (PC), were prepared from pyroChl *a* as described earlier.[20,21] The zinc(II) insertion into the DA and reference compounds was accomplished according to the standard procedure[22] by refluxing the chloroform solution of the corresponding metal-free derivative with a 5-fold excess of Zn(II) acetate in methanol. The metalation yielded quantitatively the Zn(II) complexes of the pyropheophytin−anthraquinone derivatives (ZnPQ1 and ZnPQ2, Figure 1), those of the phytochlorin−anthraquinone derivatives (ZnPCQ, Figure 1), and those of the reference compounds (ZnPP and ZnPC).

The solvents, toluene (pro analysi grade, Merck), chloroform (HPLC grade, stabilized with 2-methyl-2-butene, Sigma), diethyl ether (pro analysi grade, Merck), cyclohexanol (>99%, J. T. Baker Chemicals B. V., Holland), acetone (for spectroscopy, Merck), methanol (pro analysi grade, Merck), and acetonitrile (HPLC grade, Rathburn), were dried with molecular sieves (BDH Chemicals Ltd., Poole, England), 3 Å (for alcohols and acetonitrile) and 4 Å (for other solvents).

The electronic absorption spectra were measured on a Unicam 8700 Series UV/visible spectrophotometer (Unicam Ltd., UK). The solutions prepared for fluorescence studies showed an OD = 0.1 at the λ_{max} of the Soret band ($c \approx 1$ mM; light path of the cuvette $l = 1$ cm). The single photon counting technique (Time Correlated Single Photon Counting Instrument, model 199, from Edinburgh Instruments) was used for time-resolved fluorescence measurements as described elsewhere.[23] The samples were excited by 15 ps pulses at a wavelength of 590 nm. The instrumental response function of the setup was recorded with a scattering solution at the wavelength of the excitation, and it was approximately 120 ps (fwhm). Fluorescence decay curves were recorded in the 630−760 nm wavelength range. To diminish the influence of the scattered excitation, a red cutoff filter was used in front of the monochromator. Normally, decay curves were collected to 10 000 counts at maximum. To study the spectra of the fluorescing components, decays were collected within a constant period (usually 2 min) in the 640−730 nm wavelength range with steps of 5 nm and fitted simultaneously to the sum of exponents in the equation

$$I(t,\lambda) = \sum a_i(\lambda) \exp(-t/\tau_i) \qquad (1)$$

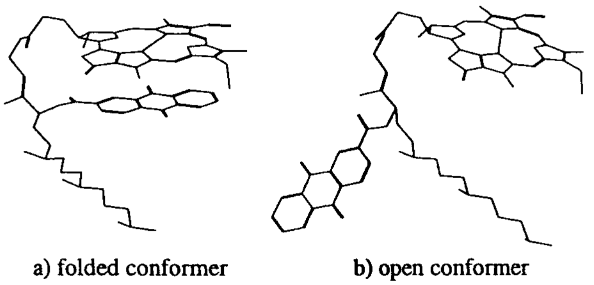
where τ_i is the global lifetime and $a_i(\lambda)$ the local preexponential factor at a particular wavelength. The factors $a_i(\lambda)$ represent so-called decay-associated spectra (DAS), which in the case of the mixture of different noninteracting fluorescing species correspond to the individual spectra of the species.

Studies of fast ET reactions were carried out by means of a fluorescence up-conversion technique generally described by ref 24. Femtosecond pulses were generated by a Ti sapphire laser (model TiF50, Avesta Ltd., Moscow, Russia) pumped by an Ar ion laser (Innova 316P, Coherent Inc.). The sample was excited by the second harmonic centered at approximately 410 nm; the pulse duration was 50 fs, repetition rate 100 MHz, and pulse energy approximately 0.1 nJ. The optically gated fluorescence decay system was from Avesta Ltd. (Moscow, Russia). The sample was placed in a 1 mm rotating cuvette. The fluorescence was mixed with the base radiation (820 nm), and the detection system counted photons at the sum frequency (which corresponds to wavelength of approximately 370 nm for the emission at 670 nm) during 10 s at every delay time. The instrumental response was measured as a correlation function of the base radiation and the second harmonic and was approximately 150 fs (fwhm).

The setup for the transient absorption measurements consisted of a Coumarin 120 dye laser pumped by an eximer laser, a Xe-arc lamp as a source of the monitoring light, two monochromators, a photomultiplier, a digitizer (Tektronix 7912AD), and a controlling PC computer. The time resolution was determined by the excitation pulse duration and was approximately 30 ns. The excitation wavelength was 430 nm and the pulse energy 1 mJ. The transient absorption spectra were recorded in the 360−740 nm wavelength range. The samples prepared for the measurement showed an OD of 0.5 at the λ_{max} of the Soret band ($c \approx 5$ μM, $b = 1$ cm). To estimate relative triplet state yields, the transient curves measured in a microsecond time domain (10−100 μs) were fitted globally to the monoexponential decays for both the DA compounds and the reference compounds and reductions of the signal intensities were estimated over all spectra.

3. Results

3.1. Solution Conformations of the DA Compounds. Since the bridge between the donor and the acceptor moieties



a) folded conformer b) open conformer

Figure 2. Schematic molecular models for the two major conformers of Zn PQ2 (see text for details).

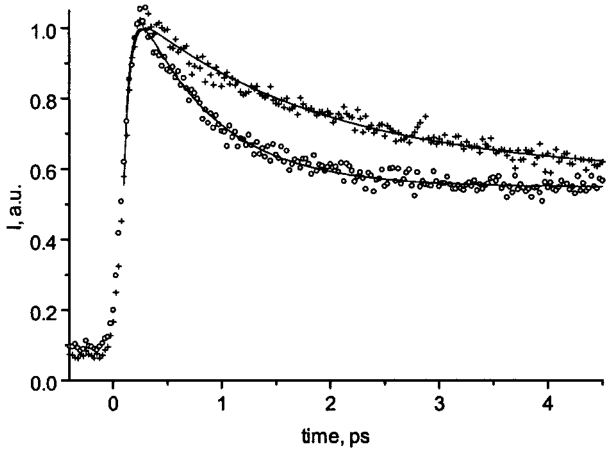


Figure 3. Picosecond fluorescence decay curves for PQ2 in ethanol (+) and in acetonitrile (○). The fittings take into account instrumental response function (~100 fs) and result in lifetimes of 1.8 and 0.7 ps for ethanol and acetonitrile solutions, respectively.

(pheophytin and anthraquinone, respectively) of PQ1,2 and ZnPQ1,2 is flexible, the molecules can exist in solutions as a mixture of the conformers with a variety of the donor−acceptor distances and orientations. Nevertheless, the molecules have dominating types of conformers. It has been found by NMR experiments and by computer molecular modeling[15] that a major part of the ZnPQ1,2 molecules have their phorbin and quinone moieties situated one above the other at an interplanar distance of about 4 Å. This is schematically shown in Figure 2a. This type of conformer is referred to as a folded conformer, and it has the most compact structure and the lowest energy. For the predominating folded conformer of the metal-free PQ1,2 compounds, the distance between the phorbin and anthraquinone planes has been estimated to be between 6 and 8 Å.[15,16] Compared with the folded conformers, a distinctive feature of the open conformers is a large separation between the donor and acceptor moieties. For instance, when the phorbin and anthraquinone rings are on different sides of the phytyl chain, the estimated center-to-center distance can be as large as 20 Å, Figure 2b.

A fast fluorescence decay component is detected in a femto- to picosecond time domain for PQ1,2 and ZnPQ1,2 using a fluorescence up-conversion technique. For PQ1 and PQ2 compounds in solvents of high or moderate polarity (see Figure 3), the time constant for the component is close to 1 ps. After the fast relaxation of fluorescence, there is a long-lived component (lifetime of a few nanoseconds). We suppose that the fast relaxation is due to the quenching of the singlet excited state of the folded conformer via an ET process, whereas the long-lived component corresponds to the decay of the singlet state of the open conformer. In solvents of relatively low dielectric permeability, ET is slower but no correlation between the solvent permeability and the ET rate is observed. In some solvents, e.g., in ethanol, the relaxation of the singlet excited state in a picosecond time domain is multiexponential. A more detailed analysis of the ET process can be made on the basis of NMR experiments discovering conformational states of the compounds in various solvents. In the frame of the present investigation, we attempt to demonstrate that the singlet excited states of the folded conformers of PQ1 and PQ2 undergo ET in a few picoseconds or faster and that the fluorescence decays observed in a subnanosecond time domain (measured using the time-correlated single photon counting technique) represent conformational exchange processes.

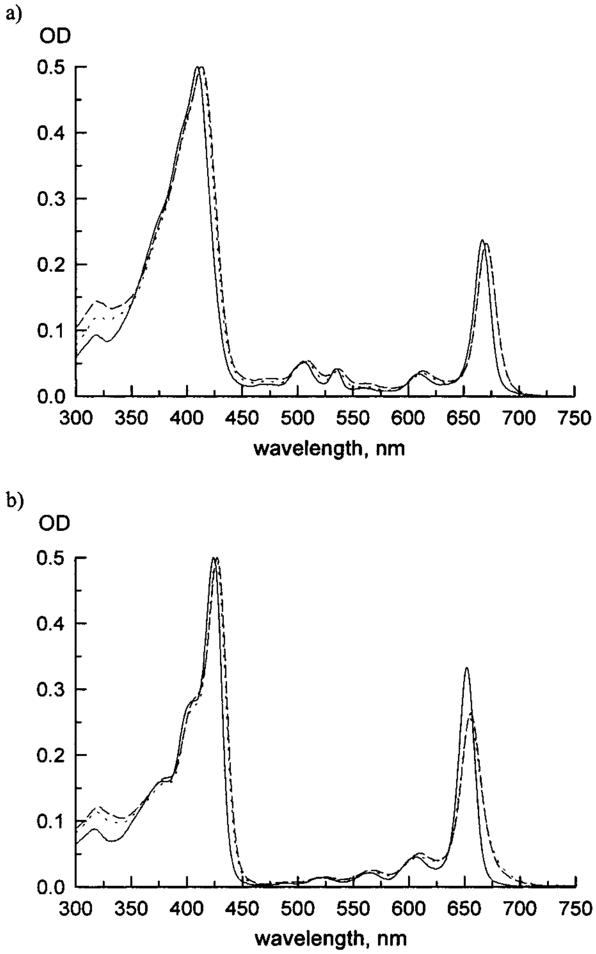


Figure 4. Absorption spectra of (a) PP (solid line), PQ1 (dashed line), and PQ2 (dotted line) and (b) ZnPP (solid line), ZnPQ1 (dashed line) and ZnPQ2 (dotted line) in diethyl ether.

For the singlet excited state of the folded conformers of ZnPQ1 and ZnPQ2, the ET takes place faster than in 1 ps for all solvents studied.

The PCQ and ZnPCQ dyads possess less conformational freedom. For these compounds, the donor−acceptor center-to-center distance can be estimated to be approximately 10 Å. The exchange rate for the PCQ conformers should be significantly faster than for the PQ1,2 conformers, since practically any conformation can be achieved after rotation about one or two bonds.

3.2. Steady-State Absorption Spectra. The absorption spectra of PQ1,2 and ZnPQ1,2 and their reference compounds (PP and ZnPP, respectively) are presented in Figure 4. The spectra of the DA compounds are almost identical with the corresponding reference compounds within a 2−3 nm accuracy, but slight differences can be found in the positions of absorption

TABLE 1: Photochemical Parameters for PCQ[b]

solvent	ϵ	τ_1, ns	$k_{et} \times 10^{-9}$, s^{-1}	τ_1/τ_o	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}
diethyl ether	4.34	4.80 ± 0.08	0.06	0.71	0.73	0.43
chloroform[a]	4.81	2.40 ± 0.10	0.2	0.47	0.51	0.23
dichloroethane	10.65	1.50 ± 0.03	0.5	0.25	0.35	0.21
aceton	20.70	1.04 ± 0.02	0.8	0.17	0.22	0.16
methanol	33.62	0.48 ± 0.02	1.9	0.08	0.08	0.08
acetonitrile	37.50	0.70 ± 0.02	1.3	0.11	0.11	0.07

[a] Fluorescence decay of the reference compound was not monoexponential ($\chi^2 \approx 2$); the presence of aggregates in solution is expected. [b] ϵ is the dielectric permeability of the solvent, τ_1 is the fluorescence lifetime, k_{et} is the ET rate constant calculated according to eq 4.2, I_{DA}/I_{ref} is the relative fluorescence yield of the DA compound; I_{DA} is the fluorescence intensity of the DA compound, I_{ref} is the fluorescence intensity of the reference molecule, A_{DA}/A_{ref} is the relative yield of the triplet state.

TABLE 2: Photochemical Parameters for ZnPCQ[b]

solvent	ϵ	τ_1, ns	$k_{et} \times 10^{-9}$, s^{-1}	τ_1/τ_o	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}
diethyl ether[a]	4.34	0.480 ± 0.01	1.8	0.141	0.069	0.067
chloroform[a]	4.81	0.094 ± 0.01	10.3	0.028	0.015	0.022
dichloroethane	10.65	0.066 ± 0.01	14.8	0.021	0.026	0.015
acetone	20.70	0.079 ± 0.01	12.4	0.021	0.036	0.025
methanol	33.62	0.063 ± 0.02	15.6	0.016	0.059	0.025
acetonitrile	37.50	0.062 ± 0.01	15.8	0.016	0.018	0.015

[a] To solve solubility problems, 5% (v/v) of methanol was added. [b] ϵ is dielectric permeability of the solvent, τ_1 is fluorescence lifetime, k_{Et} is ET rate constant calculated according to eq 4.2, I_{DA}/I_{Ref} is relative fluorescence yield of the DA compound; I_{DA} is fluorescence Intensity of the DA compound, I_{Ref} is fluorescence intensity of the reference molecule, A_{DA}/A_{Ref} is relative yield of the triplet state.

maxima. In every solvent studied, the Soret and Q-bands of the PQ1 and PQ2 compounds are shifted to the red. The greatest shift (about 4 nm) was observed in diethyl ether, whereas in other solvents the shifts were 1.5−3 nm. Also a weak red shoulder in the Q-band is observed for the PQ1,2 compounds. A similar red shift (1.5−3 nm) of the absorbance band has been observed for the Zn compounds (the greatest shift of 3 nm was found in diethyl ether). In addition, a reduction in the intensity and a broadening of the Q-band can be clearly seen (Figure 4b).

The absorption spectra of PCQ are shifted to the blue by ca. 2−5 nm relative to the reference compound (PC). ZnPCQ and ZnPC are soluble only in a few solvents. In those solvents, the absorption bands of ZnPCQ are shifted a little to the blue and the Q-band is broadened. Otherwise, the spectra are almost identical with those of the reference compound.

The slight difference in the absorption spectra of the DA and the reference compounds can be explained by the $\pi-\pi$ interaction between the phorbin ring and anthraquinone rings,[13] which can be clearly observed on the basis of ^{1}H NMR $\Delta\delta$ values.[15,16] The different directions of the spectral shifts for PQ1,2 and PCQ indicate different mutual orientations of the donor and acceptor. The most populated folded conformer of PQ1,2 presumably has an almost parallel orientation between the donor and acceptor rings, whereas for PCQ they may be even orthogonal to each other.

3.3. Steady-State Fluorescence Spectra. The fluorescence spectra of PCQ are shifted to the blue relative to the reference compound (PC), being in agreement with the absorption spectral shift. Intensities at the corresponding wavelength maxima for the PCQ and reference compounds were used to compare quenching efficiencies in different solvents. The results are summarized in Table 1. A good correlation between the relative fluorescence efficiencies and solvent polarities (dielectric permeabilities) can be clearly seen, the quenching being stronger for the solvents with higher dielectric permeabilities.

The fluorescence intensity of ZnPCQ is quenched significantly (30−50-fold) in all solvents studied (Table 2), but the fluorescence bands are shifted to the blue compared with ZnPC.

The steady-state fluorescence spectra of the PQ1,2 and ZnPQ1,2 compounds were virtually identical to those of the reference compounds (PP and ZnPP, respectively, Figure 5), despite the red-shift observed in the absorption spectra of the DA compounds relative to the reference compounds. The phenomenon will be discussed in detail on the basis of time-resolved fluorescence measurements.

The relative fluorescence yields of the DA compounds were calculated as the ratio between the intensities of the DA and reference samples at the λ_{max} of the emitted light (Tables 3 and 4). In all solvents studied, the fluorescence intensities of the PQ1,2 and ZnPQ1,2 compounds were quenched as compared with the reference compounds. For both types of the compounds, the fluorescence of the P4(S) diastereomer was quenched stronger than that of the P4(R) diastereomer. Solvents with a wide range of dielectric permeabilities, from 2.38 to 37.5, were used, but practically no solvent dependence of the fluorescence efficiencies were observed. For PQ1,2 in toluene the quenching was, however, somewhat weaker.

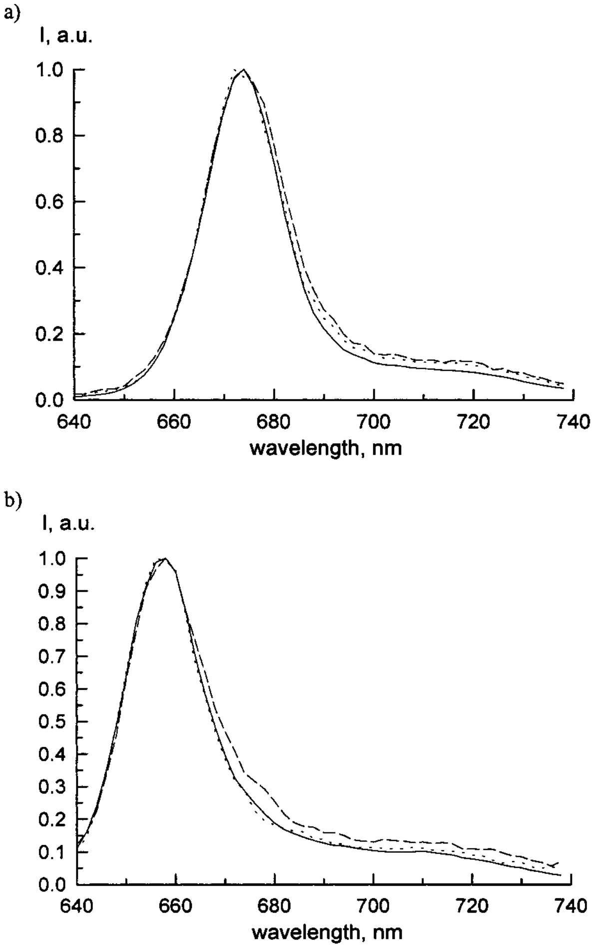


Figure 5. Fluorescence spectra of (a) PP (solid line), PQ1 (dashed line), and PQ2 (dotted line) and (b) ZnPP (solid line), ZnPQ1 (dashed line), and ZnPQ2 (dotted line) in diethyl ether.

3.4. Subnanosecond Time-Resolved Fluorescence. The fluorescence decay curves of PCQ, ZnPCQ, and PQ1 in several solvents are shown in the nanosecond time domain in Figure 6. In all solvents tested, the fluorescence decay of PCQ can be

TABLE 3: Photochemical Parameters for PQ1 and PQ2[b]

	PQ1						PQ2					
solvent	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}	τ_1, ns[a]	a_1	τ_2, ns[a]	a_2	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}	τ_1, ns[a]	a_1	τ_2, ns[a]	a_2
toluene	0.33	0.40	0.7	0.17	4.7	0.83	0.40	0.50	0.8	0.16	4.8	0.84
diethyl ether	0.14	0.22	1.8	0.50	4.7	0.50	0.19	0.25	1.6	0.50	6.1	0.50
cyclohexanol	0.14	0.12	0.29	0.47	6.2	0.53	0.17	0.13	0.22	0.45	7.1	0.55
acetone	0.14	0.16	2.1	0.81	5.1	0.19	0.18	0.21	1.8	0.62	6.3	0.38
acetonitrile	0.11	0.10	1.9	0.70	5.0	0.30	0.16	0.16	1.5	0.36	6.2	0.64

[a] Lifetime inaccuracy is less than 10%. [b] I_{DA}/I_{Ref} is relative fluorescence yield of the DA compound; I_{DA} is the fluorescence intensity of the DA compound, I_{Ref} is the fluorescence intensity of the reference molecule, A_{DA}/A_{Ref} is the relative yield of the triplet state, τ_1 and τ_2 are fluorescence decay lifetimes, and a_1 and a_2 are relative component amplitudes fitted for decay measured at 675 nm.

TABLE 4: Photochemical Parameters for ZnPQ1 and ZnPQ2[a]

	ZnPQ1						ZnPQ2					
solvent	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}	τ_1, ns[a]	a_1	τ_2, ns[a]	a_2	I_{DA}/I_{Ref}	A_{DA}/A_{Ref}	τ_1, ns[a]	a_1	τ_2, ns[a]	a_2
toluene	0.071	0.022	1.6	0.84	2.8	0.16	0.21	0.12	1.5	0.73	3.2	0.27
diethyl ether	0.056	0.013	1.0	0.89	3.2	0.11	0.11	0.08	0.8	0.60	3.6	0.40
cyclohexanol	0.089	0.013			3.5	1	0.13	0.09			3.8	1
acetone	0.110	0.017	1.0	0.9	2.8	0.1	0.17	0.10	0.9	0.71	3.5	0.29
acetonitrile	0.050	0.016	0.9	0.87	3.0	0.13	0.13	0.12	1.0	0.92	3.8	0.08

[a] Lifetime inaccuracy is less than 10%. [b] I_{DA}/I_{Ref} is the relative fluorescence yield of the DA compound; I_{DA} is the fluorescence intensity of the DA compound, I_{Ref} is the fluorescence intensity of the reference molecule, A_{DA}/A_{Ref} is the relative yield of the triplet state, τ_1 and τ_2 are fluorescence decay lifetimes and a_1 and a_2 are relative component amplitudes fitted for decay measured at 675 nm.

fitted with a two-exponential approximation ($\chi^2 < 1.2$). The lifetimes of the most long-lived component were almost the same as those for the corresponding reference compounds, the relative intensity of the slow component being about 4%, irrespective of solvent and temperature. This slow component was therefore attributed to a small amount of a hydroquinone–phorbin derivative (unable to perform ET) occurring as an impurity in the sample. The lifetime of the fast component was solvent dependent. Qualitatively, an increase in the solvent dielectric permeability results in a decrease of the lifetime. This kind of dependence is typical of fluorescence quenching by intramolecular ET. In general, the quenching means appearance of an additional relaxation channel for the singlet excited state; the rate constant of the new pathway can be calculated from

$$k = (\tau)^{-1} - (\tau_o)^{-1} \tag{2}$$

where τ and τ_o are the fluorescence lifetimes of the DA and reference compounds, respectively.

The Arrhenius plots for the rate, i.e., log(k) vs 1/T, in chloroform, acetone, and acetonitrile are given in Figure 7. The activation energies calculated from the plots are 0.125 eV in acetone and acetonitrile and 0.066 eV in chloroform.

For ZnPCQ, the fluorescence intensity is quenched strongly. Thus, one can expect fast electron transfer to occur. In the time-correlated single-photon fluorescence decay measurements, the observed fast component had a lifetime shorter than 100 ps, which is at the limit of the time resolution of the instrument. Nevertheless, this result is in a qualitative agreement with the steady-state fluorescence measurements (Table 2). On the other hand, fluorescence decays measured by means of the up-conversion technique (100 fs resolution) are in good agreement with those measured using the time-correlated method. For instance, in methanol the observed decay time was 48 ps. It is noteworthy, however, that the up-conversion method requires much higher concentrations of the sample (0.1 mM or higher) and that the weak solubility of the substances significantly reduces the choice of solvents to be tested.

The solubility problem of ZnPCQ results in a rather high value of the weighted square deviation (χ^2) for fittings of the decays in diethyl ether, acetone, and acetonitrile solutions. Therefore, three exponential approximations were used. The fast component was dominating in all cases. The lifetime of the slowest component was approximately the same as the lifetime of the reference compound. The middle-aged component is probably due to the presence of a certain amount of aggregates.

The subnanosecond fluorescence decays of the PQ1,2 and ZnPQ1,2 compounds in the solvents with moderate viscosity may be fitted with the two exponential approximation and reasonable χ^2 values were obtained. The lifetimes are listed in Tables 3 and 4. Short lifetimes were about 1–2 ns, and the long lifetimes were somewhat shorter than those of the corresponding reference compounds.

The temperature dependence of the fluorescence lifetimes was studied in all solvents listed in Tables 3 and 4 in the nanosecond time domain. For all solvents except cyclohexanol, the dependences were not pronounced, as both the lifetimes and the relative intensities of the components were affected by temperature. In all cases, the influence of the temperature variation on the decay parameters correlated well with the temperature dependence of the solvent viscosity.

The fluorescence behavior of the PQ1,2 and ZnPQ1,2 compounds in cyclohexanol (a solvent with high viscosity) differs considerably from that in the other solvents. The fluorescence decays of ZnPQ1,2 were virtually monoexponential (as the fast process is not resolved in the time-correlated measurement) with the lifetimes very close to that of the reference compound (ZnPP). For PQ1,2, a biexponential decay was observed. The fast component had a lifetime of about 200–300 ps, but the slow component had a lifetime identical with that of the reference compound (PP).

Practically no temperature dependence was observed for the fluorescence decays of ZnPQ1,2 in the 20–60 °C temperature range. For PQ1,2, the short-lived component decreased in lifetime with increasing temperature, while the long-lived component maintained the lifetime very close to that of PP. The temperature dependence of the fast component is shown in Figure 7. The activation energy was calculated to be 0.29 ± 0.02 eV for PQ1. For PQ2, the relative intensity of the fast component was smaller and the estimated activation energy was 0.5 ± 0.1 eV.

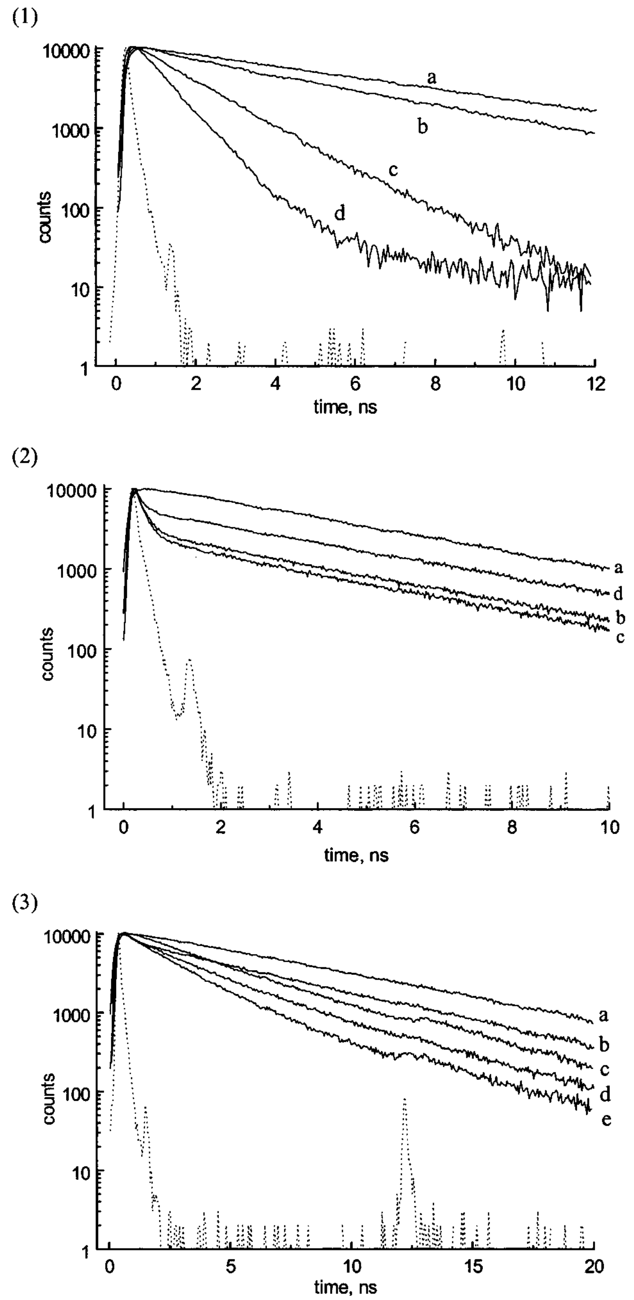


Figure 6. Fluorescence decay curves of (1) PCQ in chloroform (b), acetone (c), and methanol (d); (2) ZnPCQ in chloroform (b), acetone (c), and methanol (d); and (3) PQ1 in diethyl ether (b), cyclohexanol (c), acetone (d) and DMSO (e); curves (a) are decays of the corresponding reference compounds and dashed lines are instrumental response functions. For more details see the text.

3.5. Time-Resolved Fluorescence Spectra. The fluorescence decay curves of PCQ can be fitted globally by two exponentials yielding two decay-associated spectra. The spectrum of the short-lived component is blue-shifted compared to the fluorescence spectrum of the reference compound, which is in agreement with the blue-shift of the absorption spectrum and is attributed to the quenching of the singlet excited state via an intramolecular ET. The spectrum of the long-lived component is virtually identical with the fluorescence spectrum of the reference compound (PC). This emission is attributed to the hydroquinone−pyropheophorbide molecule.

The biexponential decay of fluorescence is an indication of the presence of two fluorescing species. The fluorescence decay curves of PQ1,2 and ZnPQ1,2 in solvents with low and moderate viscosities had practically the same shape at all wavelengths, implying either identical fluorescence spectra for all existing species or an equilibrium between them.

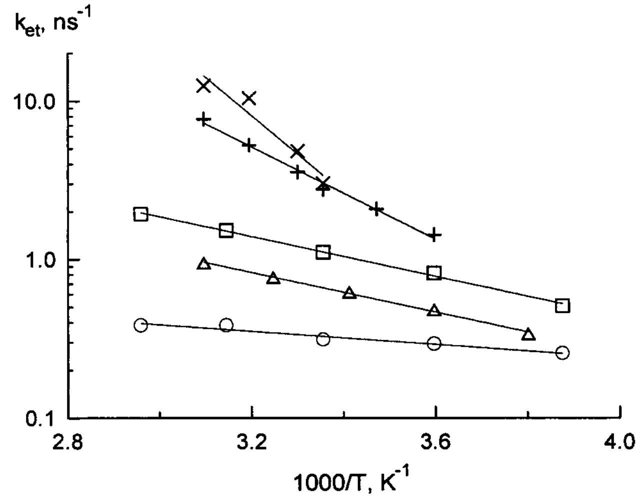


Figure 7. Arrhenius plots of the ET rate constants for PQ1 (+) and PQ2 (×) in cyclohexanol, and PCQ in acetonitrile (□), acetone (△), and chloroform (o).

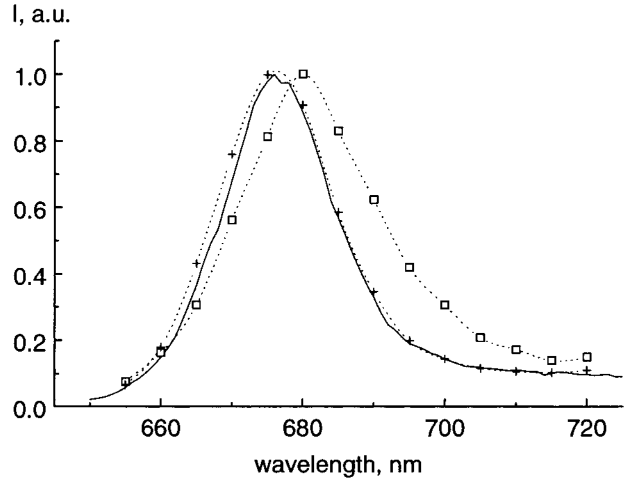


Figure 8. Normalized fluorescence spectra of the fast, 0.29 ns, (□) and the slow, 6.2 ns, (+) components for PQ1 in cyclohexanol, and steady-state fluorescence spectrum for PP (solid line) in cyclohexanol.

For PQ1,2 in cyclohexanol, the fluorescence decays were found to be different at different monitoring wavelengths. The global fitting was done successfully with a two-exponential approximation; the resulting decay-associated spectra are shown in Figure 8 for PQ1 together with the steady-state fluorescence spectrum of PQ1. The spectrum and the lifetime of the long-lived component match well the fluorescence spectrum and the lifetime of the reference compound. The spectrum of the short-lived component is red-shifted compared to that of the long-lived one. The discussion of the other features of the spectra will be presented in section 4.

3.6. Transient Absorption. In the absence of quenchers, the triplet excited state of compounds related to chlorophyll has a lifetime close to 1 ms.[25] Different types of quinones are used as quenchers of the triplet state by means of ET reaction.[26] Transient absorption measurements were carried out in each of the solvents studied in order to determine the relative yields of the triplet state (compared to the reference compounds) and to study the ET reactions. To reduce the oxygen concentration, samples were flushed with nitrogen prior to the measurements. The longest triplet lifetime, close to 0.4 ms, was obtained in

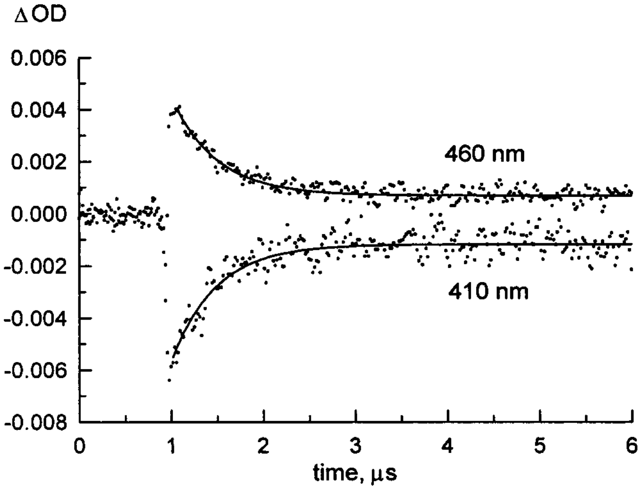


Figure 9. Transient absorption of the ZnPQ1 in cyclohexanol at wavelengths of 410 and 460 nm (dots), solid line represents a monoexponential fit of the data with a lifetime of 540 ns.

cyclohexanol and was the same for all compounds studied. The relative quantum yields of the long-lived triplet states were measured at the excitation energy of about 1 mJ cm^{-2} for the Zn compounds and of about 2 mJ cm^{-2} for the metal-free compounds, thus yielding approximately the same excitation efficiency, 50%, for both types of samples.

The decay of the transient absorption of PCQ was monoexponential and had a differential spectrum characteristic for the triplet state of pyropheophorbide. The relative intensity of the triplet state was obviously solvent dependent. On the qualitative level, the yield of the triplet state decreased with the increasing polarity (dielectric permeability) of the solvent. The values of the relative yield of the triplet state are in agreement with the values of the relative yield of the fluorescence and decrease with the lifetime of fluorescence (Table 1).

The quantum yield of the triplet state of ZnPCQ is rather small due to the efficient electron transfer from the singlet excited state. The accuracy of the measurements were, however, poor (since the absolute absorbances had values less than 0.005), but a qualitative agreement between the fluorescence quenching and the triplet yield reduction can be observed (Table 2).

The differential spectra of the triplet state of PQ1 and PQ2 were similar to those of the reference compound. The decays were almost monoexponential (in a time scale of 20 ns and longer), and the relative yields of the triplet state were reduced to about the same value as those of the fluorescence. Results are summarized in Table 3.

A fast component was found in the transient absorption decays of ZnPQ1 (Figure 9). The lifetime of the fast component varied in different solvents. In cyclohexanol, the lifetime was about 500 ns, in diethyl ether and toluene close to 50 ns and, in acetonitrile and acetone, it was on the level of the time resolution of the setup (20−30 ns). One can note a qualitative correlation between the lifetime and the solvent viscosity. In cyclohexanol, the spectrum of the fast transient component is very close to that of the triplet state. In other solvents, the fast component is too short-lived and can be detected with a reasonable signal-to-noise ratio only at the wavelengths of the maximum signal intensities (420 and 460 nm). Therefore, no reliable conclusions regarding its spectrum can be made. We assume that this fast component corresponds to the transition from the triplet state to the ET state followed by a fast recombination of the charge-separated state. A more detailed discussion is given in section 4.

The long-lived component of ZnPQ1 has a differential spectrum similar to that of the triplet state of the reference compound, and its relative intensity is on the level of 1−2%, which is 3−5 times less than the relative fluorescence yield (Table 4).

The absorption intensity of the fast transient component of ZnPQ2 was too low to be detected reliably. The triplet-state yield is about 10% and is almost independent of the solvent. The differences between the quenching of fluorescence and the quenching of the triplet state are within the experimental accuracy.

4. Discussion

4.1. Kinetic Schemes for PCQ and ZnPCQ. For the light-induced electron transfer in PCQ, the following kinetic model can be drawn:

$$\begin{tikzcd} & h\nu \arrow[d] & \\ D^{+}A^{-} \arrow[d, "k_{cr}"] & D^{s}A \arrow[l, "k_{et}"'] \arrow[r, "k_{isc}"] \arrow[d, "k_{f}"] & D^{t}A \arrow[d, "k_{t}"] \\ DA & DA & DA \end{tikzcd} \qquad (3)$$

where D^s and D^t denote the singlet and triplet excited states, respectively, D$^+$A$^-$ is the charge separated state, k_f, k_{isc}, and k_t are the rate constants for the singlet state decay, intersystem crossing, and the triplet state decay, respectively, and k_{et} and k_{cr} are the rate constants for the light-induced electron transfer and charge recombination, respectively. Based on the experimental results and this model, the electron-transfer rates were calculated according to eq 2 and listed in Table 1 for different solvents.

The scheme predicts a simple dependence between the relative fluorescence yield ($\phi = I_{DA}/I_{Ref}$), the relative triplet-state yield ($\eta = A_{DA}/A_{Ref}$), and the rate constants

$$\phi = \eta = (k_f + k_{isc})/(k_f + k_{isc} + k_{et}) = k_o/(k_o + k_{et}) \qquad (4)$$

where $k_o = k_f + k_{isc}$ is the rate constant of the singlet excited-state decay of the reference compound. These values are summarized in Table 1, and a good matching can be seen.

For ZnPCQ, the same kinetic model (3) can be applied. In this case, $k_{et} \gg k_f + k_{isc}$, and the accuracy is limited by the time resolution of the fluorescence measuring setup and by the presence of about 3−5% of the hydroquinone derivative as impurity. Nevertheless, a good quantitative agreement is obtained (Table 2).

According to the classical theory,[3] the rate constant of ET is given by

$$k_{et} = K \exp(-\Delta G^*/kT) \qquad (5)$$

where ΔG^* is the activation energy for ET and K is a coefficient depending on the nuclear frequency and on the coupling of the initial and final states. The activation energy of the ET reaction is given by the Marcus equation

$$\Delta G^* = (\Delta G^\circ + \lambda)^2/4\lambda \qquad (6)$$

where ΔG° is the difference in the Gibbs free energies of the excited and charge separated states, and λ is the reorganization energy, usually divided into two parts $\lambda = \lambda_{in} + \lambda_{sol}$, the internal reorganization energy of the molecule (λ_{in}) and the medium or solvent reorganization energy (λ_{sol}). The free energy difference can be presented in the form,

$$\Delta G^\circ = E_{ox} - E_{red} - E_{ex} + E_c \quad (7)$$

where E_{ox} is the oxidation potential of the donor, E_{red} is the reduction potential of the acceptor, and E_{ex} is the energy of the excited state. The last term E_c is the energy of the Coulombic interaction

$$E_c = e^2/(4\pi\epsilon_o\epsilon_s r_{da}) \quad (8)$$

where ϵ_s is the static dielectric constant and r_{da} is the donor–acceptor distance. For PCQ, E_c varies from 0.04 eV in acetonitrile to 0.33 eV in diethyl ether ($r_{da} = 10$ Å). E_{red} is the same for the all DA compounds studied above. E_{ex} varies slightly for different compounds (and solvents), as they have different absorption spectra, being in the range of 1.84–1.91 eV. For the same type of compounds, the presence of Zn increases the energy of the excited state by approximately 0.04 eV. The oxidation potentials have been measured for pheophytin *a* and some other chlorophyll derivatives. The difference between the E_{ox} values of the Zn- and metal-free compounds can be estimated to be 0.23 eV.[27] Thus, the ΔG° values should be 0.25–0.27 eV lower for the Zn compounds than for the metal-free compounds.

In the classic approximation, where the donor and the acceptor are spheres in a dielectric continuum, the solvent reorganization energy can be estimated from the equation[3,4]

$$\lambda_{sol} = (1/2r_d + 1/2r_a - 1/r_{da})(1/\epsilon_{op} - 1/\epsilon_s)e^2/4\pi\epsilon_o \quad (9)$$

where r_d and r_a are the effective radii of the donor and acceptor, respectively, and ϵ_{op} is the optical dielectric constant of the solvent. To obtain a quantitative estimation for the λ_{sol}, one has to know the values of r_d and r_a. As a rough approximation, the values $r_d = 7$ Å and $r_a = 3$ Å, can be chosen. In the case of PCQ and ZnPCQ, the DA distance can be estimated from a molecular model to be $r_{da} = 10$ Å. Therefore, we suppose that eq 9 can be used to estimate λ_{sol} for PCQ. For the studied solvents, the extreme values of the solvent reorganization energy are $\lambda_{sol} = 1$ eV in acetonitrile and $\lambda_{sol} = 0.05$ eV in toluene.

According to eq 7, the difference between the ΔG° values for PCQ and ZnPCQ can be calculated from the difference between the E_{ex} and E_{ox} values;[27] thus, we obtain $\Delta E = \Delta G_1^\circ - \Delta G_2^\circ = 0.25$ eV, where subscripts 1 and 2 denote PCQ and ZnPCQ, respectively. The ET rate constants are given by

$$k_{1,2} = K \exp[-(\Delta G_{1,2}^\circ + \lambda)^2/4\lambda kT] \quad (10)$$

Here, it is supposed that the reorganization energy (λ) and the electronic coupling (included in K) are the same for both compounds in the same solvent.

Provided that

$$\Delta G_2^\circ = \Delta G_1^\circ - \Delta E \quad (11)$$

we obtain

$$\begin{aligned} k_2 &= K \exp[-(\Delta G_1^\circ - \Delta E + \lambda)^2/4\lambda kT] \\ &= K \exp[-(\Delta G_1^\circ + \lambda)^2/4\lambda kT] \exp[(\Delta G_1^\circ + \lambda)\Delta E/2\lambda kT - \\ &\qquad \Delta E^2/4\lambda kT] \\ &= k_1 \exp[(\Delta G_1^\circ + \lambda)\Delta E/2\lambda kT - \Delta E^2/4\lambda kT] \quad (12) \end{aligned}$$

and

$$\ln(k_2/k_1) = (\Delta G_1^\circ + \lambda)\Delta E/2\lambda kT - \Delta E^2/4\lambda kT \quad (13)$$

Thus,

$$\Delta G_1^\circ = (2\lambda kT/\Delta E)[\ln(k_2/k_1) + \Delta E^2/4\lambda kT] - \lambda \quad (14)$$

To make a quantitative estimation, we can take the ET rate constants measured in acetone. Thus, $k_1 = 0.8 \times 10^9$ s^{-1}, $k_2 = 12.4 \times 10^9$ s^{-1}, $\lambda = 0.98$ eV (calculated by eq 9), $kT = 0.026$ eV (room temperature), and $\Delta E = 0.25$ eV. Accordingly, $\Delta G_1^\circ = -0.27$ eV for PCQ and $\Delta G_2^\circ = -0.52$ eV for ZnPCQ. For PCQ, the activation energy of ET is, in acetone,

$$\Delta G^* = (\Delta G_1^\circ + \lambda)^2/4\lambda = 0.13 \text{ eV} \quad (15)$$

This is in a good agreement with the activation energy (0.126 eV) calculated by using the Arrhenius equation and the temperature dependence measurements.

The variable part of ΔG_1° is the Coulombic term (E_c) and it depends on the solvent. Using eq 9 one can estimate the ΔG_1° for any solvent. For the most unpolar solvent used, diethyl ether, the energy difference between the excited state and the charge-transfer state is $\Delta G_1^\circ = -0.01$ eV. This small energy difference implies that ET is possible, but it is most likely reversible, being in agreement with the experimental observations (Tables 1 and 3).

Qualitatively behavior of the PCQ is similar to that of the porphyrin–anthraquinone (PAQ) dyad reported by Cormier and co-workers.[28] The ET reaction is not favorable in solvents with a dielectric permeability lower than 4, but it dominates in relaxation of the singlet excited state in solvents with permeability higher than 5. Quantitatively, our results are in agreement with the classical Marcus theory, making it different from the data reported for the PAQ dyad which had a shorter donor–acceptor distance.

4.2. Singlet Excited States of PQ1,2 and ZnPQ1,2. The PQ and ZnPQ compounds are composed of donor and acceptor groups comparable with those in PCQ and ZnPCQ. Nevertheless, their apparent photophysical behaviors are quite different. A key property of the PQ systems is the coexistence of various conformers. Different orientations and distances between the donor and acceptor moieties can affect the ET rate and, therefore, result in multiexponential fluorescence decays with particular lifetimes corresponding to the quenching of the singlet excited states of particular conformers by ET.[10–13] Another effect of the conformational variation is due to the exchange between conformers during the lifetime of the singlet excited state, which seems to be the case for PQ1,2 and ZnPQ1,2 in solvents with a low or moderate viscosity.

It has been demonstrated earlier[16] that two main types of conformers exist for the PQ compounds. There are folded conformers undergoing fast (in a few picoseconds) light-induced ET, which is not detectable with the time-correlated single photon counting technique. The lifetime of the singlet excited state for the open conformers is almost the same as for the reference compound in solvents of high viscosity, e.g., cyclohexanol, where the conformational exchange rate is slow. In solvents of low viscosity, the excited open conformer can convert to the folded one and thus perform ET. Here the rate-limiting process is the conformer transformation, and it is observed in the nanosecond time domain. The influence of the exchange between conformers on the apparent fluorescence lifetimes is the subject of the following discussion.

Two basic types of conformers will be considered: the folded ones, which perform ET, and the open ones, which do not undergo ET. The equilibrium between them depends on the solvent and temperature, and can be denoted by the equation

$$\mathrm{DA} \underset{k_{\mathrm{of}}}{\overset{k_{\mathrm{fo}}}{\rightleftharpoons}} \text{D-A} \tag{16}$$

where DA represents the folded conformer and D-A the open one. k_{fo} and k_{of} are the rate constants of the transformations. The conformational exchange rate depends on the solvent viscosity. The viscosity of cyclohexanol is relatively high (68 cp), and the conformational exchange should be hence much slower than the relaxation rate of the singlet excited state via fluorescence, intersystem crossing, and nonradiative relaxation. In cyclohexanol the exchange between the conformers can be neglected in the time scale of a few nanoseconds. Thus, after excitation, there are two possible independent relaxation pathways, one for the folded conformers,

$$\begin{tikzcd} \mathrm{D^+A^-} \arrow[d, "k_{\mathrm{f}}"] & \mathrm{D^sA} \arrow[l, "k_{\mathrm{et}}"'] \arrow[r, "k_{\mathrm{isc}}"] & \mathrm{D^tA} \\ \mathrm{DA} & & \end{tikzcd} \qquad (17)$$

and another for the open conformers,

$$\begin{tikzcd} \mathrm{D^s\text{-}A} \arrow[d, "k_{\mathrm{f}}"] \arrow[r, "k_{\mathrm{isc}}"] & \mathrm{D^t\text{-}A} \\ \mathrm{D\text{-}A} & \end{tikzcd} \qquad (18)$$

Here, $\mathrm{D^+A^-}$ is a charge-separated state and $\mathrm{D^tA}$ and $\mathrm{D^t\text{-}A}$ represent the triplet states of the folded and open conformers, respectively. In the fluorescence decay measurements, one would expect to observe a biexponential decay with the lifetimes given by the equations

$$\tau_1 = (k_{\mathrm{et}} + k_{\mathrm{isc}} + k_{\mathrm{f}})^{-1} \tag{19}$$

and

$$\tau_2 = (k_{\mathrm{isc}} + k_{\mathrm{f}})^{-1} = k_{\mathrm{o}}^{-1} = \tau_{\mathrm{o}} \tag{20}$$

The latter lifetime (τ_2) is the observed fluorescence lifetime for the open conformer, i.e., the singlet excited state lifetime in the absence of electron transfer, and should be the same as the lifetime of the reference compound (τ_0). The first lifetime (τ_1) is the observed fluorescence lifetime for the folded conformer and reflects the effect of the light-induced electron transfer. The rate constant of the electron transfer can be calculated from the equation

$$k_{\mathrm{et}} = (\tau_1)^{-1} - (\tau_2)^{-1} \tag{21}$$

The fluorescence decays of the PQ1 and PQ2 have been found to fit well to two exponentials. The longer lifetime of PQ2 is exactly the same as that of the reference compound (PP). The longer lifetime of PQ1 is somewhat shorter but still very close to the lifetime of the reference compound. Thus, the electron-transfer rates can be, estimated to be in cyclohexanol, $3.3 \times 10^9\ \mathrm{s}^{-1}$ for PQ1 and $4.4 \times 10^9\ \mathrm{s}^{-1}$ for PQ2.

If the solution contains two noninteracting molecular species, the decay-associated spectra should represent the fluorescence spectra of the species, in the present case the open and folded conformers. The decay-associated spectra are presented in Figure 8 for PQ1 together with the fluorescence spectrum of the reference compound. The slow component, representing the fluorescence spectrum of the open conformer, matches well the fluorescence spectrum of the reference compound. The decay-associated spectrum of the fast component is attributed to the folded conformer. The spectrum $\lambda_{\max}$ is shifted to the red by ca. 5 nm, and it is about 5 nm broader compared to the spectrum of the reference compound.

From the data presented in Table 3, one can estimate that, in cyclohexanol, 90% of PQ1 molecules are in the form of folded conformers, whereas the contribution of the folded conformers in the steady-state fluorescence spectra is ca. 25%. Therefore, the absorption spectrum is mainly due to the folded conformers, and the observed red shift, relative to PP, is a consequence of weak $\pi-\pi$ interactions between the donor and acceptor moieties. The steady-state fluorescence, however, is mainly determined by the open conformers, spectroscopically similar to the reference compound. This results in a good coincidence of the steady-state fluorescence spectra in Figure 5.

The fluorescence decays of ZnPQ1 and ZnPQ2 were almost monoexponential in cyclohexanol. The fluorescence lifetimes for ZnPQ2 and ZnPP were equal, and the lifetime for ZnPQ1 was very close to that of the reference compound. Nevertheless, the fluorescence intensities of ZnPQ1 and ZnPQ2 were quenched, compared to the reference compound (ZnPP), to the levels of 0.09 and 0.13, respectively. The electron-transfer rates were too fast to be measured by the single photon counting technique ($k_{\mathrm{et}} \gg k_{\mathrm{isc}} + k_{\mathrm{f}}$). Thus, only the ratio of the concentrations of the folded to open conformers can be estimated to be 10:1 for ZnPQ1 and 6.7:1 for ZnPQ2.

In solutions with low viscosity, the conformational exchange, eq 16, might mix the two decay pathways represented by eqs 17 and 18. As a first approximation, one may consider the conformer exchange in the excited state only. The scheme for the singlet excited-state relaxation is

$$\begin{tikzcd} & \mathrm{D^tA} & & \\ \mathrm{D^+A^-} & \mathrm{D^sA} \arrow[l, "k_{\mathrm{et}}"'] \arrow[u, "k_{\mathrm{isc}}"'] \arrow[d, "k_{\mathrm{f}}"] \arrow[r, shift left, "k_{\mathrm{fo}}"] & \mathrm{D^s\text{-}A} \arrow[l, shift left, "k_{\mathrm{of}}"] \arrow[r, "k_{\mathrm{isc}}"] \arrow[d, "k_{\mathrm{f}}"] & \mathrm{D^t\text{-}A} \\ & \mathrm{DA} & \mathrm{D\text{-}A} & \end{tikzcd} \qquad (22)$$

A two-exponential decay could be expected for the fluorescence decay of this system.

A very fast electron transfer can be assumed for the folded conformer in the case of the Zn(II) derivatives. Thus, the scheme can be simplified as follows:

$$\begin{tikzcd} \mathrm{D^+A^-} & \mathrm{D^sA} \arrow[l, "k_{\mathrm{et}}"'] \arrow[d, "k_{\mathrm{f}}"] & \mathrm{D^s\text{-}A} \arrow[l, "k_{\mathrm{fo}}"'] \arrow[r, "k_{\mathrm{isc}}"] \arrow[d, "k_{\mathrm{f}}"] & \mathrm{D^t\text{-}A} \\ & \mathrm{DA} & \mathrm{D\text{-}A} & \end{tikzcd} \qquad (23)$$

where only the electron-transfer reaction has been taken into account for the folded conformer ($k_{\mathrm{et}} \gg k_{\mathrm{isc}}$, k_{f} and k_{of}). The fluorescence decay should be monoexponential with a lifetime, $\tau = (k_{\mathrm{isc}} + k_{\mathrm{f}} + k_{\mathrm{of}})^{-1}$. Nevertheless, in all solvents tested, cyclohexanol being an exception, biexponential decays were observed. The explanation could be that PQ1,2 have many degrees of conformational freedom. The energetically most preferable state, the folded conformer, has been observed by the ^{1}H NMR technique[15,16] and confirmed by the femtosecond up-conversion fluorescence decay measurements. The presence of the open conformer is deduced from the observation of the component with a rather long fluorescence lifetime, while the steady-state fluorescence intensity was reduced significantly.

The molecular modeling[15] provides a set of possible conformations for the open conformers with almost equal energies. Some of them can transform to folded conformers through a one-step rotation about a covalent bond, some of them need two or more sequential rotations to form a folded conformer. The different initial conformational states need dissimilar rotation times to transform to the folded conformer, resulting in a multiexponential decay of fluorescence.

The open conformers have fluorescence spectra similar to those of the reference compound, since there is no interaction between the donor and acceptor moieties. Thus, different types of open conformers cannot be distinguished directly from the fluorescence spectra. The folded conformers have no contribution to the steady-state fluorescence spectra, since they undergo extremely fast ET. For this reason, the steady-state fluorescence spectra of PQ1,2 and their reference compound are almost identical (Figure 5). On the contrary, the absorption spectra of PQ1,2 and ZnPQ1,2 are determined mainly by the folded conformers, as they are dominating in all solvents studied.

The relative fractions of the folded and open conformers depend on the particular compound. From the results obtained by the steady-state fluorescence quenching experiments, one can conclude that the PQ1 and ZnPQ1 diastereomers have a higher population of the folded conformers compared to the PQ2 and ZnPQ2 diastereomers, and that the Zn compounds have higher relative concentrations of the folded conformers than the corresponding metal-free derivatives.

The relative energies of the individual states, included in the ET process as E_{ox}, E_{red}, and E_{ex}, should be the same for PQ1,2 and PCQ and for ZnPQ1,2 and ZnPCQ compounds, respectively. This arises from the similarity of the donor and acceptor moieties in the DA molecules. The differences lie in the reorganization (λ) and Coulombic (E_{c}) energies, being a result of different geometries of the DA compounds. The short donor−acceptor separation for the PQ compounds makes the continuum approximation unacceptable, and eqs 8 and 9 have to be developed in order to take into account the sizes and mutual orientations of the donor and acceptor moieties, as well as the arrangement of the solvent molecules. Internal reorganization energies might be important in the energetic balance of the PQ1,2 compounds. Particularly, in the case of the flexible bridge, the electrostatic interaction may change the molecular conformation.

The decrease in the donor−acceptor separation usually results in a faster electron transfer. The ET rates for PQ1,2 were determined in several solvents and found to be about 5 times those for PCQ in the same environments. This observation is in agreement with the estimated DA distances of ca. 7 and 10 Å for PQ and PCQ, respectively. This also indicates that, in the present case, the ET takes place through the space rather than through bonds.

4.3. Triplet States of ZnPQ. No transient absorptions of charge-separated states were observed in the time scale of 20 ns or longer, implying that the lifetime of the charge-separated states should be shorter than 20 ns. This is in agreement with many previous studies on one-step electron-transfer reactions (for a review see ref 1).

If the triplet excited state can process ET, one should observe either a decrease in the triplet state lifetimes or a reduction in the triplet state yield. The values of the relative triplet state yields for PQ1,2 are in agreement with the fluorescence reduction (Table 3). The triplet state lifetimes of PQ1,2 are about the same as for the reference compounds. Thus, it can be concluded that ET reactions do not take place from the triplet excited states of PQ1,2 in any of the studied solvents.

The relaxations of the triplet states of ZnPQ1 and partially of ZnPQ2 were at least biexponential, and the yields of the long-lived triplet states were reduced compared to the singlet state quenching. The energy level (relative to the ground state) of the triplet state for chlorophyll *a* is close to 1.3 eV;[29] the energy of the ET state for ZnPCQ is 1.39 eV (in acetone). Thus, for the ZnPCQ the ET state is about 0.09 eV higher in energy than the triplet state. This is quite a small value, and the energy of the ET state for ZnPQ can be even lower than that of triplet state, because of the shorter distance between the donor and the acceptor than for ZnPCQ. One experimental evidence for the lower energy can be seen from the fact that for metal-free PQ dyads ET takes place even in unpolar solvent, e.g., in toluene ($\epsilon = 2.379$), whereas for PCQ ET was observed only in solvents with the permeability $\epsilon > 4.3$. Therefore, the triplet state of ZnPQ1 most likely processes ET. The folded conformers, however, undergo fast ET ($k_{\mathrm{et}} \gg k_{\mathrm{o}}$), and cannot form a triplet state. The mechanism of the triplet state formation should involve open conformers. Thus, the scheme (23) can be completed as follows:

$$\begin{tikzcd}
\mathrm{D^{+}A^{-}} \arrow[d, "k_{\mathrm{cr}}"] & \mathrm{D^{s}A} \arrow[l, "k_{\mathrm{et}}"'] & \mathrm{D^{s}\text{-}A} \arrow[l, "k_{\mathrm{fo}}"'] \arrow[r, "k_{\mathrm{isc}}"] \arrow[d, "k_{\mathrm{f}}"] & \mathrm{D^{t}\text{-}A} \arrow[r, "k_{\mathrm{of}}"] \arrow[d, "k_{\mathrm{t}}"] & \mathrm{D^{t}A} \arrow[r, "k'_{\mathrm{et}}"] \arrow[d, "k_{\mathrm{t}}"] & \mathrm{D^{+}A^{-}} \arrow[d, "k'_{\mathrm{cr}}"] \\
\mathrm{DA} & & \mathrm{D\text{-}A} & \mathrm{D\text{-}A} & \mathrm{DA} & \mathrm{DA}
\end{tikzcd} \qquad (24)$$

where k'_{et} and k'_{cr} are the rate constants of the electron transfer and charge recombination from the triplet state and k_{t} is the rate constant of the triplet state relaxation, e.g., in cyclohexanol $2.5 \times 10^{3}\ \mathrm{s}^{-1}$. The observed fast component in the transient absorption decay correlates well with the solvent viscosity but not with the dielectric permeability. Therefore, in the sequence, $\mathrm{D^{t}\text{-}A} \rightarrow \mathrm{D^{t}A} \rightarrow \mathrm{D^{+}A^{-}} \rightarrow \mathrm{DA}$, the slowest step is $\mathrm{D^{t}\text{-}A} \rightarrow \mathrm{D^{t}A}$, $k_{\mathrm{of}} \ll k'_{\mathrm{et}}, k'_{\mathrm{cr}}$. For this reason, only the open-to-folded transformation was taken into account in the scheme. As soon as the open conformer is transformed into the folded one, it processes fast electron transfer and recombines to the ground state.

Because of the low triplet yields of the DA compounds, the signal-to-noise ratios were not higher than 20 in the nanosecond time domain. Only monoexponential fittings were reasonable, resulting in the following lifetimes for the triplet state of the open conformer, ca. 540 ns in cyclohexanol, 30−50 ns in toluene and diethyl ether, and less than 20 ns in acetone and acetonitrile. The conformational exchange time of 540 ns is long enough to be neglected in the fluorescence measurements and, hence, the system can be regarded as a mixture of the noninteracting stable conformers, as proposed in section 4.2.

5. Conclusions

Two types of model DA dyads have been studied. One type is represented by the compounds with a relatively short and rigid bridge between the donor and the acceptor groups (PCQ and ZnPCQ). It was shown that the electron transfer properties of these rigid DA compounds can be described in terms of the classical Marcus theory. The rates and energy parameters for the photoinduced ET of these DA compounds were determined. Another type of DA compounds (PQ1,2 and ZnPQ1,2) is characterized by a relative long and flexible bridge between the donor and acceptor. They can perform fast photoinduced ET, which is, however, completely determined by the exchange rates and equilibrium populations of the conformers. The folded conformers predominate in all solvents and undergo extremely fast electron transfer from the singlet excited state. The compounds retain the phytyl tail and are, hence, good candidates for studying photoinduced electron transfer in solid LB films.[18]

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