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Synthesis and photophysical properties of porphyrins containing viologen units for ultrafast molecular photonics†

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Several 5,15-diarylporphyrin derivatives containing viologen units as an electron acceptor for ultrafast intramolecular electron transfer have been synthesized. The fluorescence of the porphyrin–viologen linked systems was appreciably quenched by the attached viologens. In accordance with this, the formation of a charge-separated state was observed upon excitation with a femtosecond (fs) laser at 400 nm. The rate of electron transfer and back transfer was controlled by the different length of alkyl chain spacers between porphyrin and viologen. Attempts to use these porphyrin molecules as a thin film component of ultrafast parallel data processing by guided wave mode geometry were limited by gradual deterioration upon repeated fs laser excitation.

Introduction

Ultrafast optical switching devices based on photoreactions of molecules are expected to have many advantages in the fields of optical data storage and parallel data processing. Most photochromic materials and systems reported so far are based on changes of chemical bonds such as *cis–trans* isomerization or ring formation and opening. Ultrafast photoresponses solely based on photoinduced electron transfer and back reactions have attracted increasing attention because of the wide range of wavelengths, response times, and the extent of changes.

Among the latter systems, supramolecular arrays containing a porphyrin unit as the electron-donating chromophore covalently linked to electron-accepting moieties like quinone or viologen§ *via* a flexible or rigid spacer group play an important role. Tetraarylporphyrins containing one to four viologen units have been extensively investigated.[1–9] The viologen units were found to act as fluorescence quenchers for the excited states of porphyrin, increasing the number of appended viologens led to more effective quenching. The influence of the solvent polarity, mutual orientation and separation distance between the electron donor and the electron acceptor, and types of spacer group on the rate of charge separation and charge recombination has been investigated by means of time-resolved fluorescence spectroscopy and ultrafast flash photolysis techniques. Effects of insertion of different central metal ions into the porphyrin,[9] and of external magnetic fields[5] have also been studied.

Another important group of porphyrin–acceptor complexes investigated in recent years are 5,15-diarylporphyrins with appended acceptors like quinone, pyromellitimide and carotenoid units.[10–22] Besides the above mentioned parameters the influence of the energy gap ($-\Delta G$) between the oxidized and reduced form of the respective ion-pair state and of the temperature on the electron-transfer rates (separation and recombination) have been examined.[14,17] By introduction of a series of electron relay molecules between the initial donor and the ultimate acceptor, leading to a larger spatial separation between donor and acceptor, longer-lived ion-pair states could be formed which could help to clarify the mechanisms of intramolecular electron transfer.[15,16,18,19,21] 5,15-Diarylporphyrins show the Soret band peak at about 400 nm, which is blue-shifted by about 10 nm compared with tetraarylporphyrins. This is an advantage in molecular photonics applications upon excitation with the second harmonics (400 nm) of a typical fs Ti:sapphire laser.

Nagamura *et al.* developed novel materials showing color changes with an extremely broad range in lifetimes of colored species from about 1 picosecond (ps) to infinity due to photoinduced electron transfer and reverse reactions.[23–37] For example, the ion-pair charge transfer (IPCT) complexes of viologens with halides or tetraaryl borates. The red-colored IPCT complex of polymer viologen with iodides showed especially interesting properties such as blue color formation in about 0.2 ps and decay in about 1 ps, transparent and homogeneous thin films by spin-coating, and strong durability against repeated fs laser excitation.[37] Its only one disadvantage is a small molar extinction coefficient at 400 nm. Large extinction coefficients are necessary for use as thin film components with thicknesses of a few hundred nanometeres for ultrafast parallel data processing based on guided wave mode geometry upon fs laser excitation.[38–44]

By contrast the above mentioned diarylporphyrins show a very high molar extinction coefficient at 400 nm (around 137000 M^{-1} cm^{-1}). Therefore the first aim of this work was to synthesize a few 5,15-diarylporphyrins with anionic groups in order to incorporate them into IPCT complexes with polymer viologen. However, the formation of these intermolecular complexes did not succeed presumably due to steric reasons as is discussed in the Supplementary data.† Consequently, intramolecular complexes in which the porphyrin and the viologen units are connected *via* alkyl chain spacers of different lengths have been synthesized. Photoresponsive properties of the porphyrin–viologen complexes have been investigated by excitation with a femtosecond laser at 400 nm and are presented after description of the synthetic routes.

Results and discussion

Synthesis of porphyrin derivatives

The 5,15-diarylporphyrins without viologen unit were synthesized according to the method of Osuka *et al.*[10] by

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† Electronic supplementary information (ESI) available: details on the preparation of porphyrins **3a**–**3h** and on porphyrin–viologen complexes **5f**–**5h** as well as on transient absorption measurements. See http://www.rsc.org/suppdata/p2/b2/b202991j/

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§ The IUPAC name for viologen is 4,4′-bipyridinium.

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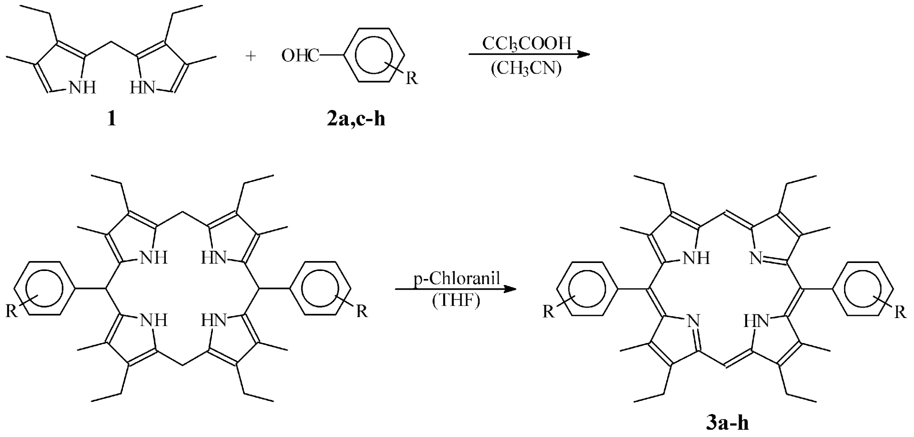


R	a p-COOH	b p-COONa	c p-O(CH$_2$)$_2$Br	d p-O(CH$_2$)$_3$Br
R	e m-O(CH$_2$)$_2$Br	f m-O(CH$_2$)$_3$Br	g m-O(CH$_2$)$_4$Br	h m-O(CH$_2$)$_6$Br

Scheme 1

condensation of the respective substituted benzaldehyde with 3,7-diethyl-2,8-dimethyldipyrromethane **1**. The synthetic route is shown in Scheme 1. The starting materials were reacted with a catalytic amount of trichloroacetic acid in acetonitrile. The porphyrinogen formed after the condensation reaction was oxidized by adding *p*-chloranil¶ in tetrahydrofuran to the reaction mixture. After workup, the yields of the pure diarylporphyrins were between 45 and 65%, which is a little lower than the yields of porphyrins with other electron acceptors obtained by Osuka *et al.*[10]

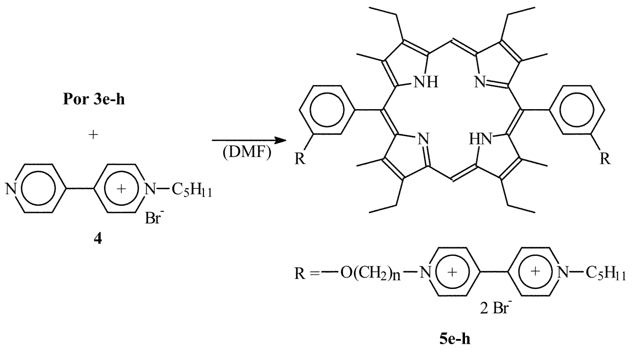
The starting material 3,7-diethyl-2,8-dimethyldipyrromethane **1** was prepared by conventional methods.[45–47] This dipyrromethane could be obtained in good yield in contrast to 2,3,7,8-tetramethyldipyrromethane, which was rather difficult to prepare and gave only very low yields. Another reason for choosing the former dipyrromethane was that the ethyl side chains on the ring of the porphyrins render them more soluble in organic solvents compared to methyl groups.[48,49]

However, the *para*-substituted porphyrins **3a**, **3c** and **3d** turned out to be insoluble or almost insoluble in common solvents like methanol, chloroform, acetone, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), whereas the porphyrins with substituents in the *meta*-position **3e**–**h** could be dissolved in most solvents. The reason for this difference in solubility is probably due to good crystallinity or easy formation of aggregates in the case of the *para*-substituted compounds whereas in the *meta*-substituted diphenylporphyrins these will be sterically less favored. The porphyrin **3a** was rendered soluble by exchange of the carboxy hydrogen with sodium ions, *i.e.* through its transformation into a disodium salt.

The transformation of the diarylporphyrins to intermolecular porphyrin–viologen complexes involved severe difficulties, and we were unable to obtain such complexes. Details of synthetic routes with polymer viologen dichloride (PV^{2+} 2Cl$^-$) containing 4,4′-bipyridinium ion as a part of the main chain as well as possible reasons for the unsuccessful preparation are given in the Supplementary data.†

Because of the severe difficulties of preparation of an IPCT complex between 5,15-diarylporphyrin and polymer viologen dichloride we concentrated on the synthesis of molecular arrays in which the porphyrin and the viologen units are connected by alkyl chains of different lengths. The synthesis of similar porphyrin–viologen complexes has been described repeatedly for tetraarylporphyrins in the literature. No reports have been made, however, to the best of our knowledge on diarylporphyrins with linked viologens.

Into the diarylporphyrins **3e**–**h** the viologen unit was introduced by a quarternization reaction with *N*-pentyl-4-(4′-pyridyl)pyridinium bromide **4** (Scheme 2). The respective starting materials were dissolved in DMF and stirred for 3 to 5 days at 80 °C. The *para*-substituted porphyrins **3c** and **3d**, which were almost insoluble in DMF or other common solvents, were not further converted. After work-up, intramolecular porphyrin–viologen complexes in yields between 15 and 23% could be obtained except for porphyrin **3e** with the shortest alkyl chain length (n = 2) probably due to steric hindrance. In the latter case only impure product according to UV–Vis measurements in a very low yield (4.5%) was obtained.



Scheme 2

Spectroscopic and transient absorption measurements

The UV–Vis spectra of the porphyrin–viologen complexes show the viologen band at 265 nm and five bands, which can be attributed to the porphyrin unit, the Soret band at 404 nm and four Q-bands at 504, 537, 572 and 623 nm, respectively. The absorption spectra of porphyrin–viologen linked systems appear to be a superimposition of the individual spectra recorded for the respective diarylporphyrins **3f**–**h** and viologen **4** as shown in Fig. 1 for **5f** as an example. Thus, the appended viologen groups do not perturb the ground state of the porphyrin. Similarly, the fluorescence spectra of the porphyrins without and with intramolecularly appended viologen upon excitation at 576 nm showed the same pattern with bands at 630 and 696 nm, respectively, indicating that the energy level of the first excited singlet state of the porphyrin is not perturbed by the viologens. However, the fluorescence intensity of the

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¶ The IUPAC name for chloranil is tetrachloro-1,4-benzoquinone.

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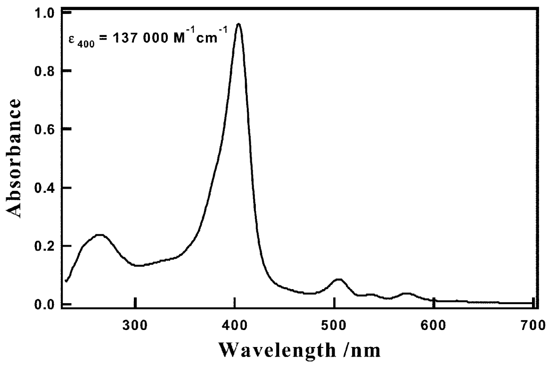

Fig. 1 Absorption spectrum of a methanol solution (6.58 μM) of porphyrin–viologen complex **5f**.

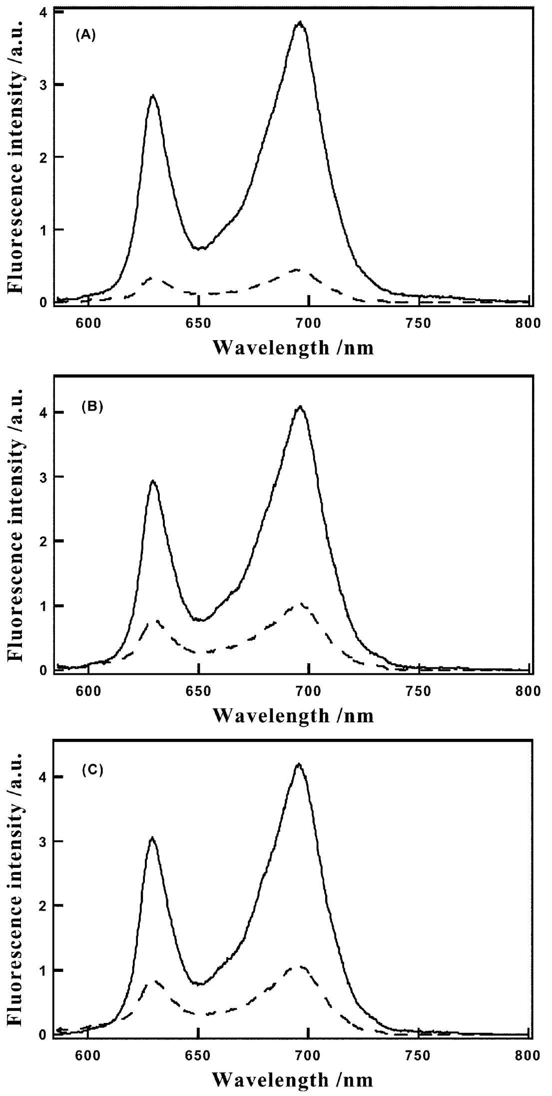

Fig. 2 Fluorescence spectra of porphyrins **3f** (A), **3g** (B) and **3h** (C) (solid lines) and their porphyrin–viologen complexes **5f** (A), **5g** (B) and **5h** (C) (broken lines) in cyclohexanone excited at 575 nm where the absorbance was set at 0.1.

porphyrins **5f–h** was appreciably reduced compared to porphyrins **3f–h** as shown in Fig. 2, clearly indicating that the viologen groups function as efficient quenchers for the excited singlet state of porphyrin. The extent of quenching differs between the porphyrin–viologen complexes depending on the length of connecting alkyl chains. In the case of **5f** the fluorescence quenching is 88% as compared with the porphyrin **3f**, whereas it is 74 and 71% for porphyrins **5g** and **5h**, respectively.

Time-resolved transient absorption spectra of the porphyrin **3f** and of those with a viologen unit **5f**–**5h** dissolved in cyclohexanone have been measured upon excitation with a fs laser at 400 nm. In the case of porphyrin **3f** without appended viologens a strong absorption band at around 450 nm and a smaller one at around 550 nm were observed upon excitation together with transient bleaching of the Q-band as shown in Fig. 3. They can be attributed to the porphyrin excited singlet state. Both bands decayed relatively slowly with a lifetime of more than 1 ns. The electrons in the excited singlet state of porphyrin **3f** without an acceptor may result in the intersystem crossing to the excited triplet state or return to the ground state with fluorescence and heat.

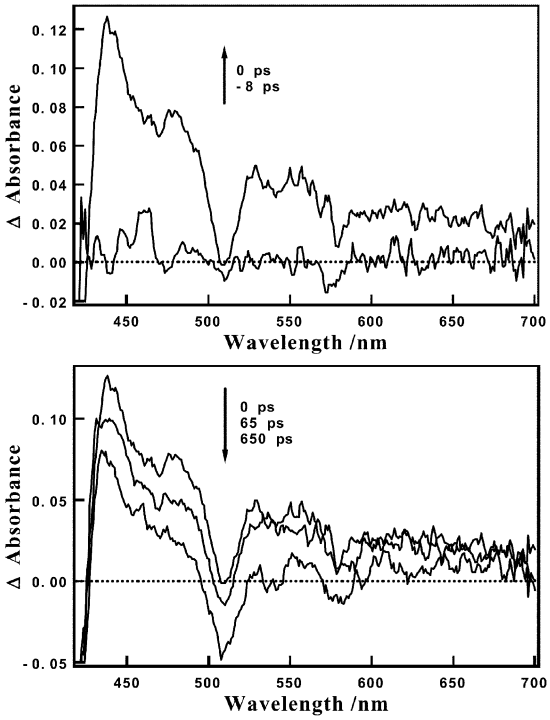

Fig. 3 Transient absorption spectra of porphyrin **3f** in cyclohexanone upon excitation with a fs laser at 400 nm, 60 μJ pulse^{-1}, beam size <1 mm.

In the transient absorption spectra of porphyrin–viologen complex **5f** the build-up of an absorption band with a maximum at around 620 nm can be clearly observed within 1.5 ps, which was slightly delayed compared to the transient absorption of the porphyrin excited singlet bands at 450 and 550 nm as shown in Fig. 4. This new band at 620 nm was unambiguously assigned to the formation of viologen radical cations.[35,37] The formation of these radical ions undoubtedly results from the electron transfer from the excited singlet state of the donor porphyrin unit to the acceptor viologen moiety. These results correspond well to the most efficient fluorescence quenching in **5f** as mentioned above.

Fig. 5 shows transient absorption spectra for the porphyrin–viologen complex linked by a hexamethylene unit **5h**. The peak at about 620 nm attributed to the viologen radical cations was observed after a slight delay in a similar manner as for **5f**. It should be noted that its yield is lower than that observed for **5f** in Fig. 4, clearly indicating the effect of the length of the connecting alkyl chains on photoinduced intramolecular electron transfer.

The porphyrin–viologen complex linked by a tetramethylene unit **5g** showed a slightly peculiar transient absorption as shown in Fig. 6. The relative yield of viologen radical cations was the lowest among the three porphyrin–viologen systems studied although the fluorescence quenching was slightly larger than for **5h**. It is interesting that fluorescence quenching in **5g** did not result in the formation of charge-separated species. It might be ascribed to the unfavorable conformation of viologen units

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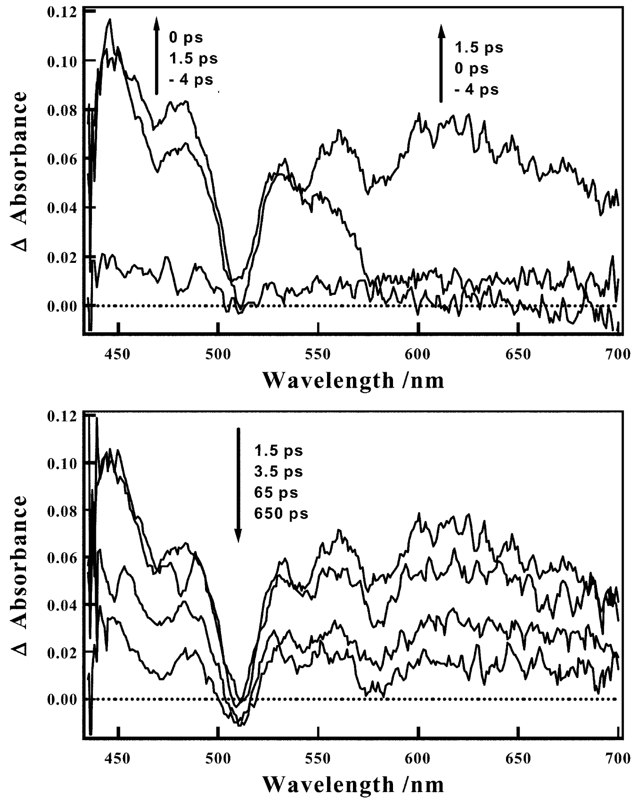

Fig. 4 Transient absorption spectra of porphyrin–viologen complex **5f** in cyclohexanone upon excitation with a fs laser at 400 nm, 90 µJ pulse^{-1}, beam size <1 mm.

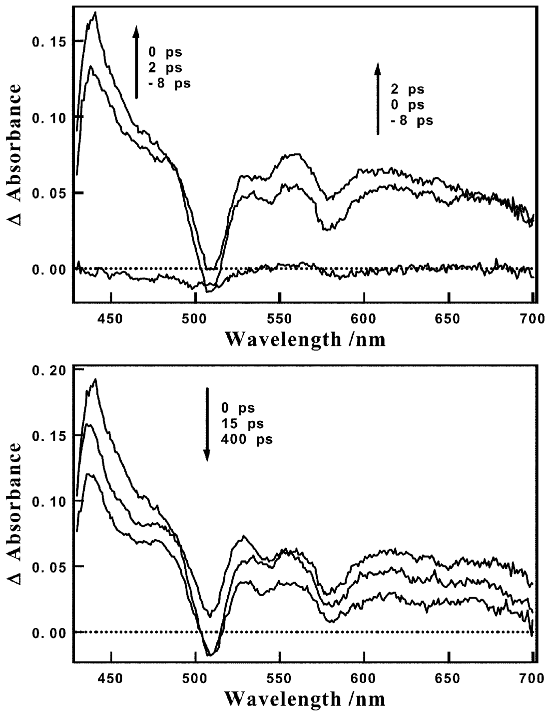

Fig. 5 Transient absorption spectra of porphyrin–viologen complex **5h** in cyclohexanone upon excitation with a fs laser at 400 nm, 120 µJ pulse^{-1}, beam size <1 mm.

relative to the porphyrin ring under the tetramethylene bridge. The porphyrin–viologen complex linked by a hexamethylene unit seems to have more freedom to form favorable conformations compared with tetramethylene bridges.

Fig. 7 shows the time profiles of transient absorption of the complex **5f** at 450 nm and 620 nm attributable to the formation and decay of the porphyrin excited singlet state and of the

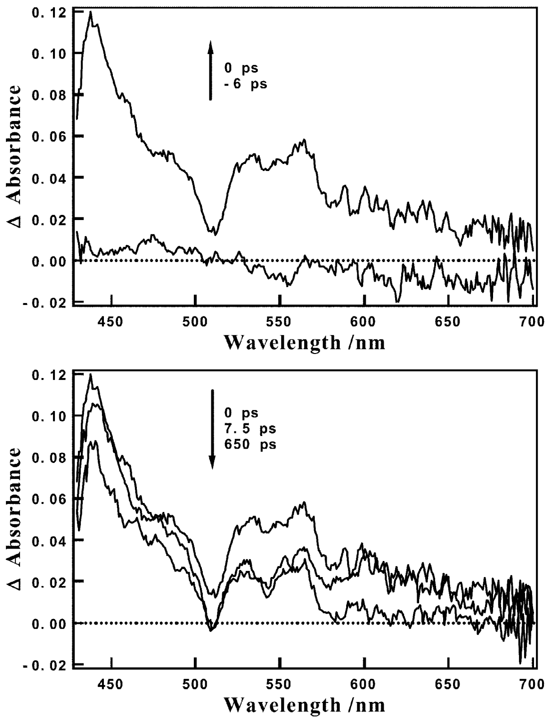

Fig. 6 Transient absorption spectra of porphyrin–viologen complex **5g** in cyclohexanone upon excitation with a fs laser at 400 nm, 100 µJ pulse^{-1}, beam size <1 mm.

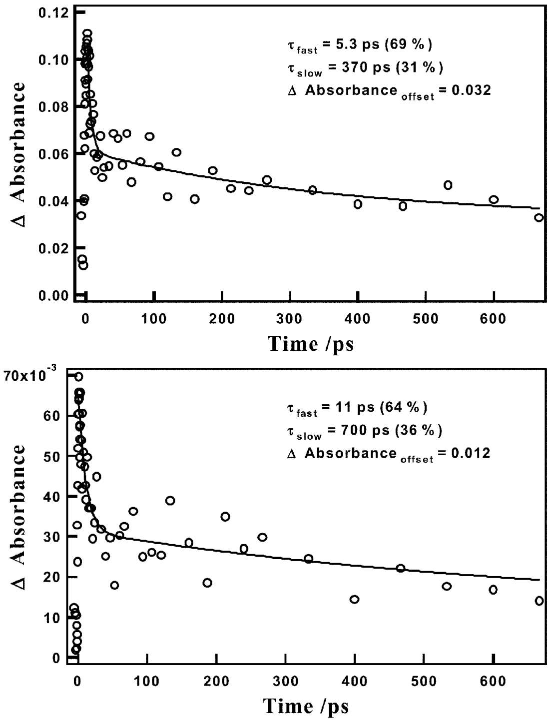

Fig. 7 Time profiles of transient absorption of porphyrin–viologen complex **5f** at 450 nm (upper graph) and 620 nm (lower graph).

4,4′-bipyridinium radical cations, respectively. They showed a very rapid rise in less than 1 ps, which was almost the same as the time resolution of our fs Ti:sapphire laser measurement system with a regenerative amplifier. A similar extremely rapid formation of 4,4′-bipyridinium radical ions was observed for polymer viologen salts with iodide (I$^-$) ions in methanol solution[37] and tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB$^-$) ions in DME and DMSO,[35] respectively. These results demonstrate that the charge-separated 4,4′-bipyridinium radical cations were formed directly upon charge transfer excitation because of the nature of IPCT absorption bands

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according to which the electrons correlated with the IPCT band are transferred partially at the ground state and completely at the excited state.

The decay of both time profiles was fitted by the sum of two exponentials

$$I_{\mathrm{A}}(t) = A_0 + A_1 \exp\left({}^{-t}\!/_{\tau_1}\right) + A_2 \exp\left({}^{-t}\!/_{\tau_2}\right) \tag{1}$$

yielding lifetimes of a fast component (τ_1) and of a slower one (τ_2) with the relative amplitudes A_1 and A_2, respectively. For the decay curve of the porphyrin **5f** excited singlet state, values of τ_1 = 5.3 ps and τ_2 = 370 ps with fractions of 69% and 31% were obtained, respectively. The decay of viologen radical cations yields lifetimes of 11 ps (64%) and 700 ps (36%) for the fast and the slow component, respectively.

Double exponential decay behavior has often been documented. In most cases it is ascribed to different conformers of the molecular arrays in which the donor and acceptor units are held at different separation distances, to competing intramolecular and intermolecular electron transfer between donor and acceptor, or to different orientation of the molecules in the respective solvent, particularly in polar solvents. In order to get some idea of the origin of the decay, we have studied the fluorescence and transient absorption behavior for a mixture of porphyrin **3f** and polymer viologen dichloride containing 4,4′-bipyridinium ion in the same molar ratio as in the porphyrin–viologen linked system **5f** under the same conditions. In these mixtures, no fluorescence quenching of the porphyrin **3f** was observed, nor was the formation of viologen radical cations in transient absorption measurements observed. The transient absorption results for the mixture are very similar to those of porphyrin **3f** alone indicating that no intermolecular electron transfer between the porphyrin and the viologen moiety takes place. These results most probably exclude the contribution of intermolecular interactions to the double exponential decay. A different orientation of the molecule caused by the polarity of solvent can also be excluded in the nonpolar solvent cyclohexanone, therefore the double exponential decay behavior probably results from different conformers of the porphyrin–viologen complexes.

The time profiles of the porphyrin excited singlet band (at 450 nm) and of the viologen radical cation band (at 620 nm) for the porphyrin–viologen complex **5h** are shown in Fig. 8. They show a similar rapid rise as for **5f** but the decay was appreciably slower. Fitting the decay time profiles by the sum of two exponentials according to eqn. (1) yields lifetimes of τ_1 = 8.9 ps (81%) and τ_2 = 80 ps (19%) for the porphyrin excited singlet band, and of τ_1 = 2.1 ps (10%) and τ_2 = 82 ps (90%) for the viologen radical cation band. The relatively higher value for a very long-lived component (Δ Absorbance$_{\text{offset}}$) at 620 nm compared to the porphyrin–viologen complex **5f** strongly suggests that there are much slower decay components with lifetimes probably in the ns timescale. The slower decay of the band at 620 nm indicates that a longer-lived charge-separated state is formed to a greater extent in the case of porphyrin–viologen complex **5h** compared to **5f**. This is clearly due to a longer separation distance between the donor porphyrin and the acceptor viologen units. Thus, by inserting alkyl chain spacers of different lengths between porphyrin and viologen the rate of electron transfer and back transfer can be controlled.

The distinct difference in the offset values of Δ Absorbance in the decay curves at 450 nm for porphyrin–viologen complexes **5f** and **5h** clearly indicates that a longer-lived species must have formed in different amounts in each complex. The ratios of the maximum value of Δ Absorbance and its offset value are 0.29 and 0.48 for **5f** and **5h**, respectively. The residual absorption at around 450 nm can be assigned to the porphyrin excited triplet state,[13,16] which is produced by intersystem crossing from the excited singlet state competing with charge separation between the porphyrin excited singlet state and viologen. The rise in absorption at 450 nm due to the formation of porphyrin excited triplet state does not affect the fast decay component of porphyrin excited singlet state in Figs. 7 and 8, whereas the slow decay component is clearly affected by it. The different amount of porphyrin excited triplet state formed in the complexes **5f** and **5h**, again, is due to the different length of alkyl chain spacers. In the porphyrin–viologen complex **5f** linked by a trimethylene unit a relatively small amount of porphyrin excited triplet state is formed, as most electrons of the porphyrin excited singlet state are transferred to the viologen unit resulting in a high quantum yield of charge-separated species. In complex **5h** linked by a hexamethylene unit, however, a lower portion of electrons in the porphyrin excited singlet state is transferred to the viologen units due to the longer separation distance between porphyrin and viologen and, consequently, a higher amount of electrons results in the intersystem crossing to the porphyrin excited triplet state compared to complex **5f**. These results correspond well to the lower quantum yield of viologen radical band in **5h** as well as to the lower fluorescence quenching of **5h** compared to **5f** as mentioned above.

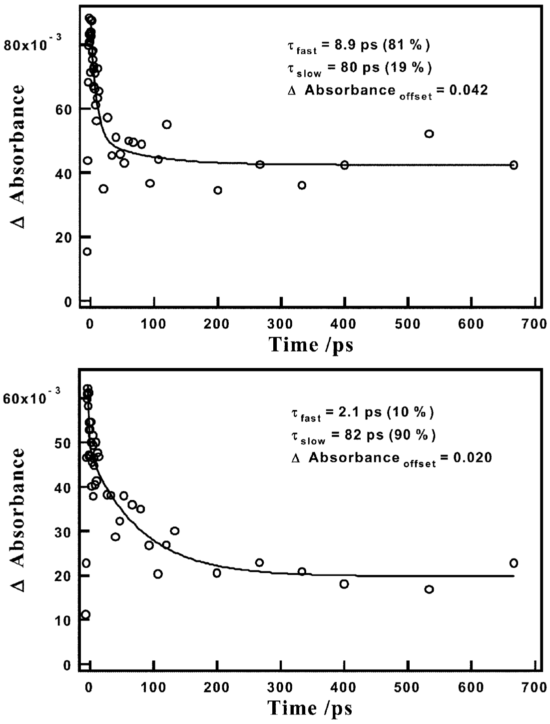

Fig. 8 Time profiles of transient absorption of porphyrin–viologen complex **5h** at 450 nm (upper graph) and 620 nm (lower graph).

In order to use photoresponsive materials as a component of ultrafast parallel data processing by guided wave mode geometry upon fs laser excitation they have to be immobilized in a thin film.[38–44] By casting a cyclohexanone solution of the porphyrin–viologen complex **5f** onto a glass slide followed by drying *in vacuo* at room temperature a transparent cast film could be obtained. By excitation of this cast film with the fs laser at 400 nm, however, no transient absorption signal could be obtained. Instead, the photoexcited point on the cast film showed persistent bleaching. This indicates that the porphyrin unit in the complex deteriorated by photoexcitation with the fs laser at 400 nm in the solid film. In solution, transient absorption could be observed because the solution was stirred. However, the absorption spectrum of **5f** in solution after many laser shots showed a slight decrease in the intensity of the absorption band maxima compared to the spectrum before excitation indicating the bleaching due to deterioration of porphyrin–viologen complex during repeated laser excitation at 400 nm. A similar decrease was observed for **3f**, **5g** and **5h** after laser

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excitation. This is partly because of higher excitation energy at 400 nm, which results in the second excited singlet state of porphyrins.[50,51]

In summary, ultrafast absorption changes could be observed particularly in the porphyrin–viologen complex **5f** where the porphyrin and the viologen units are separated by a relatively short trimethylene chain. The rate of electron transfer can be controlled by the length of the alkyl chain spacers. However, porphyrin–viologen complexes are not applicable as a thin film component of ultrafast parallel data processing by guided wave mode geometry upon fs laser excitation because the porphyrin unit is gradually deteriorated by repeated laser shots. More stable photoresponsive materials with similar ultrafast photoresponses as observed in our porphyrin–viologen complexes have to be found. One promising candidate may be complexes between phthalocyanine and viologen, which is under investigation.

Experimental

Details on the preparation of porphyrins **3a**–**3h** and on porphyrin–viologen complexes **5f**–**5h** as well as on transient absorption measurements are given in the Supplementary data.†

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