Photoinduced electron transfer in paraquat inclusion complexes of porphyrin-based receptors

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A series of porphyrins, strapped with aryloxy-substituted polyether chains of various lengths and different substitution patterns, has been photophysically characterised. These molecules act as receptors for bipyridinium dications and their association constants with paraquat in acetonitrile solutions have been determined by absorption and emission spectroscopy; they have been found to be in the range 10^2–10^5. The photophysical characterisation of the complexes has been made in solutions containing more than 95% of associated porphyrin component. A photoinduced electron transfer from the porphyrin excited state to the paraquat guest, responsible for the porphyrin luminescence quenching, takes place with $\tau \ll 20$ ps and is followed by a very fast recombination of the resulting charge-separated state. In only a few cases could the charge-separated state be detected and a lifetime of 20 ps was measured, whereas in most complexes the recombination is faster than 20 ps. In none of the examined complexes was escape from the geminate recombination of the charge-separated state observed.

Introduction

The use of porphyrins as components of photoactive multipartite systems dates back to the early stages of supramolecular chemistry.[1] Since porphyrins or closely related chromophores are widely used by nature to perform key functions in bacterial or green plant photosynthesis, such as charge separation[2] and energy collection,[3] most of their popularity in current research is based on a biomimetic approach in the design of artificial complex systems able to respond to light stimuli and to convert light into other utilisable forms of energy. The robustness of the porphyrin nucleus, its high absorption throughout the visible spectrum, the low redox potentials and the possibility of stacking in higher order aggregates with novel properties, are some of the important peculiarities that have been utilised in such studies.[1,4] In addition, the possibility to fine-tune the redox properties and the excited state energy levels by simple substitution, or different metallation or substitution on the pyrrolic ring, gives these chromophores a versatility that has ensured their place in evolution as well as in chemical research. It should also be mentioned that the strong spectroscopic signals associated with the intermediates of any photoinduced process (radicals and/or excited states) allow a detailed understanding of the mechanism of the photoreaction, and has provided many opportunities for intelligent and creative design of new systems with optimised performances.[1,5–7]

Porphyrinic units have also been included in potential host or guest systems that are able to self-assemble in higher order architectures,[5] as well as in multi-component covalently linked systems[6] or interlocked systems,[7] with the aim of performing useful functions triggered by light absorption, such as energy or electron transfer.

The present report describes the spectroscopic and photophysical characterisation of a series of superstructured porphyrin components and of their complexes with the electron acceptor paraquat (methyl viologen or 4,4′dimethyl-bipyridinium)[8] (Fig. 1) and reports on the photoinduced electron transfer observed in the complexes. As well as the inherent interest in these complexes in their own right as photoinduced electron transfer systems, they also can form the basis for more complex systems where the paraquat unit is incorporated into rotaxane, pseudorotaxane and catenane structures.

Results and discussion

The superstructured porphyrins

The porphyrin-based receptors used in this study are illustrated in Fig. 1. They represent a series of receptors for the paraquat dication PQ^{2+}, but with a systematic variation in design.[8] In **1** and **2** the supra-porphyrin receptor site is provided by flanking *m*-disubstituted aromatic rings with overarching polyether chains, reminiscent of "earmuffs". **1** and **2** differ in the length of the connecting polyether chains, but both of these systems have been shown to bind PQ^{2+} with the bipyridinium rings essentially parallel to the porphyrin plane, and stabilised *inter alia* by edge-to-face interactions with the lateral aromatic rings.[8] The singly-strapped analogue **3** provides a similar geometry for the guest molecule, but the binding is weaker compared to the *bis*-strapped derivatives. In **4**, **5** and **6**, on the other hand, a naphthoquinol or hydroquinol unit is incorporated centrally into the polyether strap; **4** represents a "tighter" strap than the relatively unconstrained analogue **6**, whereas **5** is the hydroquinol equivalent of the naphthoquinol-containing **6**. In all of these cases, it has been shown that the same face-to-face geometry of the guest PQ^{2+} with the porphyrin plane is maintained, with additional stabilisation from the parallel aromatic units of the strap.[8a] Thus in general, all the complexes can be represented by the structure ***n***-PQ^{2+}

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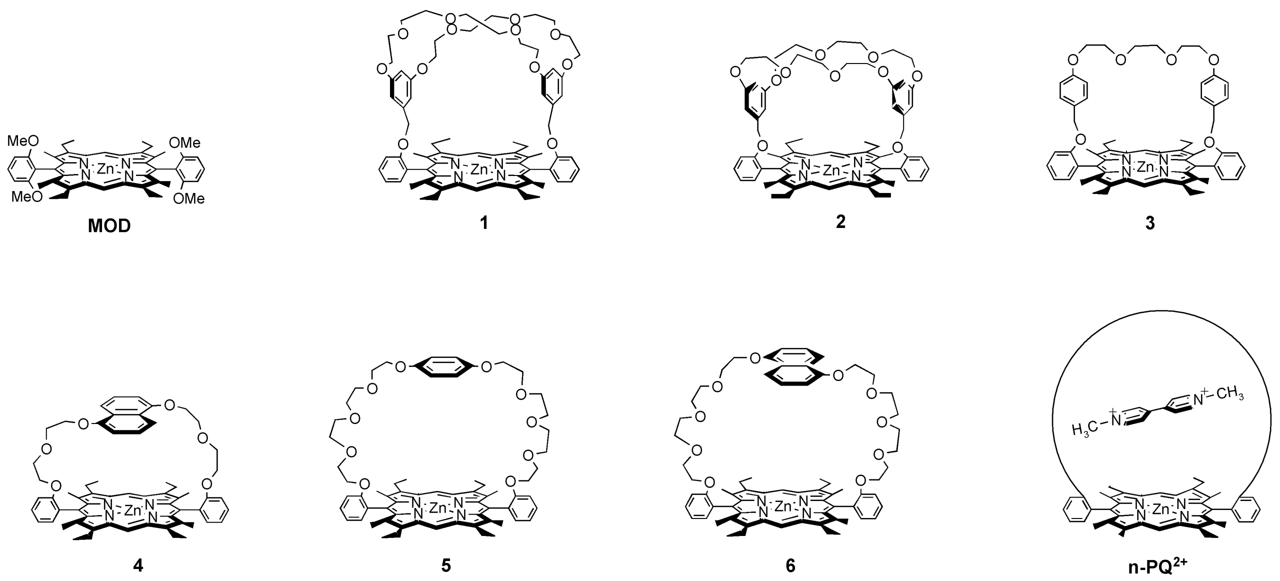

Fig. 1 Schematic formulae of the strapped porphyrins **1**–**6**, the model compound MOD, the guest PQ^{2+} and the generic complex ***n***-PQ^{2+}.

(Fig. 1). As a control molecule lacking a receptor site, the simple *o,o′*-dimethoxy derivative MOD (Fig. 1) was utilised.

Ground state absorption. Representative examples of the absorption spectra of the strapped porphyrins and the related model MOD (Fig. 1), are shown in Fig. 2, whereas the absorption data for all compounds are collected in Table 1. The spectra, displaying an intense Soret band at 412–414 nm and Q bands at 542 and 577 nm, are very similar to other closely related zinc(II) 5,15-diaryloctaalkylporphyrins.[7d,e] In the porphyrins **4** and **6**, containing the 1, 5-dioxynaphthalene unit in the strap, the absorption of this unit with bands at 296, 313 and 327 nm is superimposed on the porphyrin absorbance (Fig. 2).

Luminescence. The luminescence properties upon excitation in either the Soret or the Q bands of porphyrins **1**–**6** are essentially identical to those of the model MOD with an emission quantum yield that is the same within experimental error (Table 2 and Fig. 3). The luminescence lifetimes measured by a time-correlated single photon counting apparatus with 1 ns resolution, are reported for MOD and **6** in the insets of Fig. 3 and appear for all compounds in Table 2. The superstructured porphyrins **1**–**6** display a lifetime slightly shorter than the model, with a larger variation detected for compounds **4**–**6**, which have lifetimes shorter by *ca.* 20% than the reference model. The radiative rate constant, $k_r = \phi/\tau$, increases slightly from the model through the series with a maximum value for the compounds containing the dioxyaromatic units **4**–**6** (Table 2). This is indicative of a slight perturbation of the lowest electronic excited state, very likely due to a weak interaction of the porphyrin nucleus with the aromatic units of the strap. It is not surprising that a larger effect is detected for those derivatives bearing an aromatic substituent in the central position of the strap, which allows a face-to-face π-π interaction of the aromatic unit with the porphyrin tetrapyrrolic ring. Clear evidence from NMR solution studies of π-π interactions between the porphyrin and the central aromatic units of the straps in **4**, **5**, and **6** has been previously reported.[8a] No other effects due to the different substitution patterns is detected in the ground and excited state properties of the superstructured porphyrins compared to the model, thus implying that the different components of the system are only weakly interacting, if at all.

The luminescence spectra of the compounds at 77 K in glassy butyronitrile (BuCN), Fig. 4, are very similar for all the compounds and display, in addition to a structured fluorescence band, a strong phosphorescence band around 725–730 nm. It is evident from Fig. 4, where the fluorescence bands have been normalised at 642 nm and reported for MOD, **6**

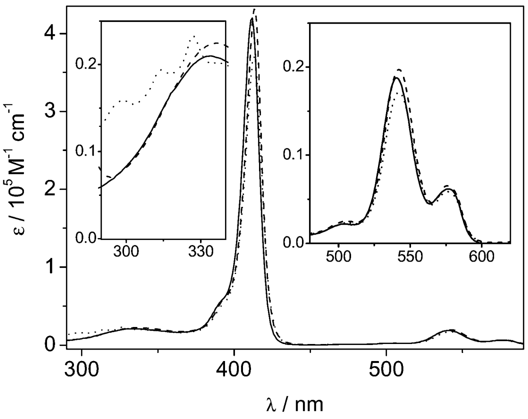

Fig. 2 Absorption spectra in acetonitrile solutions of MOD (—), **2** (---), and **6** (···).

Table 1 Ground state absorption properties of the porphyrins and the complexes at 298 K in acetonitrile solution. The reported charge transfer bands (CT) are from interaction of the paraquat electron acceptor with the porphyrin electron donor

	Soret bands	Q bands	CT bands
	λ_{max}/nm (ε/M^{-1} cm^{-1})	λ_{max}/nm (ε/M^{-1} cm^{-1})	λ_{max}/nm (ε/M^{-1} cm^{-1})
MOD	412 (420 000)	541 (18 800); 577 (6200)	
1	414 (420 000)	543 (18 300); 577 (5700)	
2	413 (430 000)	542 (19 700); 577 (6600)	
3	413 (380 000)	542 (17 200); 577 (5700)	
4	414 (370 000)	542 (17600); 577 (6000)	
5	413 (420 000)	542 (19 000); 577 (6000)	
6	413 (370 000)	542 (17 300); 577 (5700)	
1-PQ^{2+}	418 (314 000)	545 (18 000); 580 (6300)	
2-PQ^{2+}	419 (276 000)	544 (16 700); 578 (6300)	
3-PQ^{2+}	417 (250 000)	543 (17 300); 578 (7000)	
4-PQ^{2+}	420 (224 000)	546 (15 000); 578 (5100)	720 (260)
5-PQ^{2+}	418 (257 000)	544 (17 000); 578 (6700)	720 (230)
6-PQ^{2+}	418 (234 000)	543 (15 000); 578 (5800)	720 (380)

Table 2 Luminescence data in nitrile[a] solutions

		298 K				77 K			
		λ_{max}/ nm	τ/ ns	Φ_{fluo}[b]	k_r/ 10^7 s^{-1}	λ_{max}/ nm	τ/ ns	$\Phi_{fosf(R)}$[c]	E^d/ eV
MOD	^{1}MOD	582	2.6	0.029	1.1	582	3.2		2.13
	^{3}MOD					728	46×10^6	1	1.70
1	^{1}**1**	584	2.3	0.03	1.3	582	2.3		2.13
	^{3}**1**					724	57×10^6	2.1	1.71
2	^{1}**2**	583	2.2	0.030	1.4	580	2.2		2.14
	^{3}**2**					722	59×10^6	2.7	1.72
3	^{1}**3**	584	2.2	0.030	1.4	582	2.3		2.13
	^{3}**3**					724	55×10^6	1.9	1.71
4	^{1}**4**	584	2.1	0.030	1.4	582	2.4		2.13
	^{3}**4**					724	55×10^6	1.9	1.71
5	^{1}**5**	584	2.1	0.030	1.4	582	2.3		2.13
	^{3}**5**					728	70×10^6	1.7	1.70
6	^{1}**6**	584	2.0	0.030	1.5	582	2.2		2.13
	^{3}**6**					726	67×10^6	1.8	1.71

[a] Acetonitrile at 298 K and butyronitrile at 77 K; butyronitrile is used since it forms transparent matrices. [b] Fluorescence quantum yield upon excitation at 413 nm and at 542 nm, see experimental section for details. [c] Relative phosphorescence yield. [d] Energy derived from the emission band maximum at 77 K.

and **2**, that the phosphorescence yield is increasing in this order. The phosphorescence lifetimes were measured in glassy butyronitrile upon excitation at 532 nm with a Nd-YAG laser (18 ps pulse duration) and these appear in Table 2. Since the triplet lifetimes do not parallel the observed increase in phosphorescence yield (Table 2), it can be deduced that either the triplet yields or the radiative rate constants are different for the different compounds. The fluorescence lifetime measured at 77 K (Table 2) is slightly higher than the one measured at 298 K only in the case of MOD, while for the other derivatives the lifetimes are essentially temperature independent.

Transient absorption. Typically for each of the compounds, the difference absorption spectrum measured at the end of a 35 ps pulse in acetonitrile solutions is characterised by an intense absorbance with maximum around 460–480 nm with the stimulated emission bands at 584 and 634 nm overlaying the bleaching of the ground state absorption due to the Q bands at 540 nm and 577 nm. Two representative cases, MOD and **2**, are shown in Fig. 5. The spectra appear slightly different in shape but it should be recalled that this is due to differences in ground state spectra, as a result of the absorbances of MOD and **2** at 532 nm being respectively 0.17 and 0.5. The evolution within the time window of this equipment (*ca.* 3 ns) does not allow us to follow the complete intersystem crossing from the singlet excited state to the triplet excited state of the porphyrins; nonetheless the spectrum with 3 ns delay in Fig. 5 (bold line) already shows the characteristics of the triplet absorbance. It displays a band shifted to wavelength shorter than the singlet excited state, the bleaching of bands due to the ground state absorbance and the disappearance of the stimulated emission bands. The time evolution of the singlet spectrum registered at 510 nm can be fitted by an exponential decay characterised by a lifetime (insets of Fig. 5 and Table 3) that is, in each case, in agreement with the excited singlet state lifetime derived from luminescence decay (Table 2).

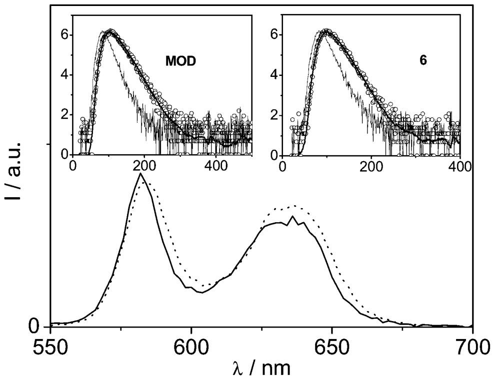

Fig. 3 Emission spectra in acetonitrile solutions of optically matched solutions excited at 413 nm: MOD (—), and **6** (···). In the insets are given the logarithmic plots of the fluorescence decay of the samples upon excitation at 337 nm, emission at 590 nm: experimental data and fitted function. The instrumental function is also shown as a thin line.

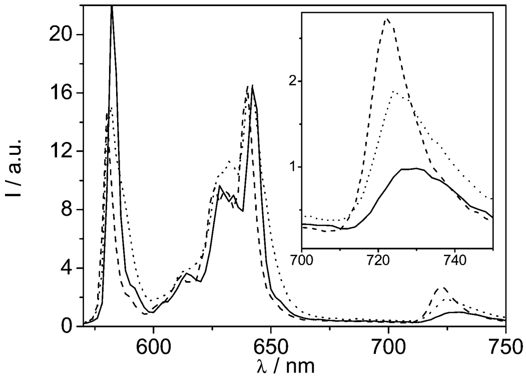

Fig. 4 Luminescence spectra at 77 K in butyronitrile solutions for MOD (—), **2** (---), and **6** (···). The spectra are normalised at the 642 nm maximum, which was preferred to normalisation in the 583 maximum, more liable to re-absorption. In the inset the phosphorescence bands are expanded.

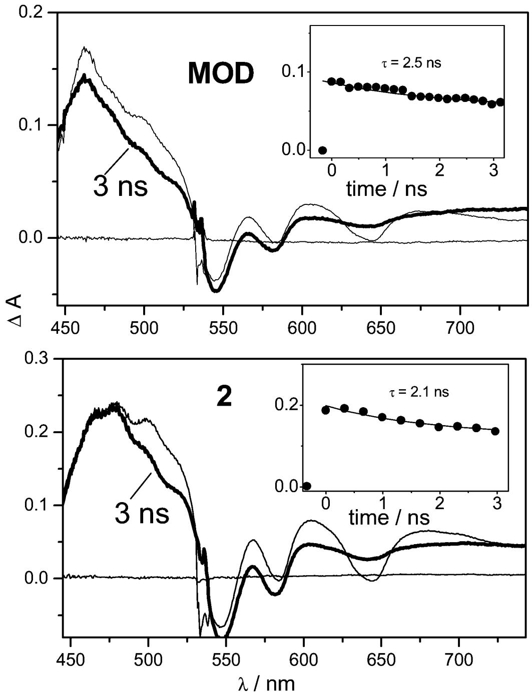

Fig. 5 Transient absorption difference detected in acetonitrile solutions of MOD (upper panel) and **2** (lower panel) at the end of a 35 ps laser pulse (532 nm, 3 mJ per pulse) (thin line) and 3 ns after the pulse (bold line); the baseline is also shown. The absorbance of the solution at 532 nm was 0.17 for MOD and 0.5 for **2**. In the insets the decay of the absorbance at 510 nm is shown with fit to a single exponential.

Table 3 Absorption properties of the excited states at 298 K in air-free acetonitrile, and reaction with oxygen

	State	$\lambda_{\max}$[a]/nm	τ[b]/ns	k_{ox}[c]/10^9 s^{-1}
MOD	^{1}MOD	460	2.5	
	^{3}MOD	450	54×10^3	1.4
1	^{1}1	460	2.2	
	^{3}1	450	56×10^3	1.6
2	^{1}2	470	2.1	
	^{3}2	450	65×10^3	1.4
3	^{1}3	460	–[d]	
	^{3}3	450	60×10^3	1.7
4	^{1}4	470	1.9	
	^{3}4	450	74×10^3	1.5
5	^{1}5	480	2.1	
	^{3}5	450	63×10^3	1.6
6	^{1}6	480	1.9	
	^{3}6	450	41×10^3	1.5

[a] The position of the apparent maximum is in part determined by the ground state absorbance. [b] Determined at 510 nm and 3 mJ per pulse for the singlet, and at 450 nm and 0.1 mJ per pulse for the triplet. [c] See experimental for details. [d] The solubility is too low, bad signal-to-noise ratio.

The triplet properties can be better studied by means of a flash-photolysis apparatus with nanosecond resolution and a wider time window. The triplet spectra measured at 20 ns after the laser pulse are reported in Fig. 6 for MOD and **5**. The maximum of the absorbance is at 450 nm with a broad, less intense absorption extending up to 800 nm, which is superimposed on the bleaching features of the ground state Q bands (540 and 580 nm), in full agreement with typical Zn porphyrin triplet spectra.[4b,5] The lifetime of the triplet is measured in air-free solutions and with reduced laser intensity, to prevent a second-order decay component due to triplet-triplet annihilation, and is satisfactorily fitted by a single exponential, as shown in the inset of Fig. 6 for **5**. The triplet lifetimes measured for the samples at 298 K in acetonitrile are reported in Table 3.

There has recently been some interest in the photophysical properties of *meso*-5,15-diaryloctaalkylporphyrins, where the substitution pattern does not induce severe out-of-plane distortion as in more heavily substituted porphyrins, but nonetheless gives rise to a planar and a slightly non-planar conformation separated by a modest barrier.[9] While the singlet excited states of the *meso*-diaryloctaalkylporphyrin, and therefore the ground state absorption and emission properties, are essentially identical to those of normal aryl or alkyl porphyrins, the triplet state properties are significantly altered with respect to normal porphyrins.[9a] In particular the triplet lifetime at 298 K is significantly shortened, from hundreds of microseconds to few microseconds, and a thermally activated conversion of a primary triplet state to a secondary species, presumably a different triplet, has been recently identified.[9b] These effects have been correlated to torsional librations of the phenyl substituent around the single C–C bond leading to a non-planar conformation of the porphyrin macrocycle. This slightly distorted conformation could be at the origin of the secondary triplet and of an enhancement in the non-radiative decay rate of the triplet to the ground state, responsible for the lifetime shortening.[9a] In agreement with this interpretation, bulky substituents in the ortho position of the phenyl ring should prevent rotation and result in normal behaviour. The present samples are indeed *meso*-diaryloctaalkylporphyrins with bulky substituents in the ortho positions,that is the dimethoxy groups in the model MOD and the ether substituents in **1**–**6**, and so on the basis of the proposed model these should not display any anomalous behaviour. While we observe for the triplet lifetime at 298 K a modest reduction with respect to common Zn(II) porphyrins, from several hundred microseconds to *ca.* 50 μs (Table 3), we do not observe any activated conversion of the triplet state to a different intermediate, in agreement with the proposed mechanism. In fact, the time profile of the absorbance of ^{3}MOD at 460 nm on an expanded time scale does not show any change, whereas the time profile of the triplet state of Zn(II) 5,15-*bis*(3′,5′-di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin,[7d,7e] Fig. 7, clearly shows a conversion from the triplet originally formed to a different intermediate. The behaviour of the other samples is identical to that of MOD and is consistent with the existence of only one triplet species, which decays to the ground state without further reaction.

The superstructured porphyrin-PQ^{2+} complexes

Complexation. The complexation of PQ^{2+} by these and other related porphyrin-based systems has been previously studied in detail by NMR methods in mixed solvents.[8a] Compound **2** and structurally analogous porphyrins with a shorter strap than in **5** and **6** (with triethylene glycol linkages on each side of the central aromatic moeity instead of tetraethylene glycol units as in the present case) have been the object of previous photophysical studies in acetonitrile solutions.[7b,10]

In this study we have measured the association constants of the full series with paraquat in acetonitrile by making use of absorption and fluorescence spectroscopy over a wide concentration range. The photophysical properties of the complexes

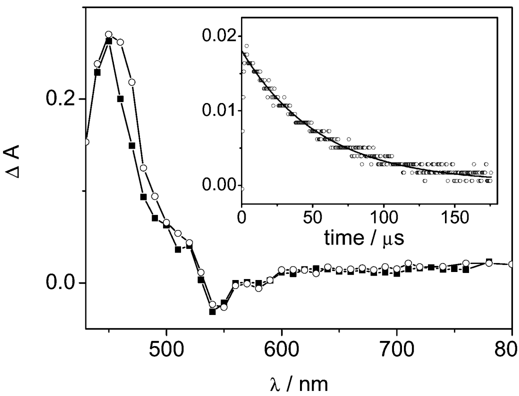

Fig. 6 Transient absorption difference detected in acetonitrile solutions of MOD (■) and **5** (○) at the end of a 18 ns laser pulse (532 nm, 1.5 mJ per pulse). The absorbance of the solution at 532 nm was 0.17 for MOD and 0.19 for **5**. In the inset the decay of the triplet at 450 nm in air-free solutions and with 0.1 mJ per pulse is shown for compound **5**, with the fit to a single exponential.

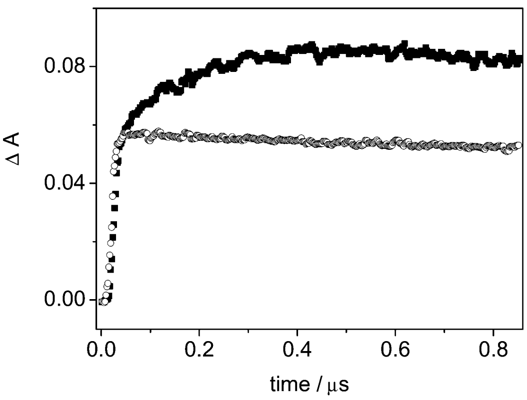

Fig. 7 Normalised transient absorption difference in acetonitrile solutions detected at 470 nm for **4** (○) and Zn(II) 5,15-bis(3′,5′-di-*tert*-butylphenyl)-2,8,12,18-tetrahexyl-3,7,13,17-tetramethylporphyrin (■). See text for details.

and the electron transfer processes have been determined in acetonitrile solutions containing *at least* 95%[11] of the complexed species. This allows us to unambiguously determine the properties of the components in the complex with no (or little) interference from uncomplexed units freely diffusing in the solution and with their reaction products, which could have compromised previous studies.[10]

Ground state absorption. The absorption spectra of the porphyrins display an important change upon addition of PQ^{2+}; in Fig. 8 the absorption spectra of a few representative cases of complexes corresponding to $>95\%$ complexation are reported.[11] The spectra of all complexes display absorption bands shifted to lower energy and with lower epsilon than the component porphyrins (Table 1). On the low energy side of the porphyrinic Q bands, a broad shoulder is detected for the complexes of compounds **4**–**6**, with a maximum around 720 nm and molar absorption coefficients of the order of a few hundreds. Due to the low solubility of the strapped porphyrins the above figures are to be considered only as indicative values. The band, which is absent in the complexes of **1**–**3** (Table 1, inset of Fig. 8), is assigned to a charge transfer (CT) interaction of the PQ^{2+} unit with the porphyrin, which is effective only when the strap contains hydroquinol or naphthoquinol aromatic units parallel to the porphyrin. While it would be tempting to ascribe this fact to different orientations that the guest can assume, parallel to the porphyrin plane in the complexes of **4**–**6**, or perpendicular to such a plane in the case of the **1**–**3**, previous NMR and solid state structural studies have indicated that the guest is parallel to the porphyrin in all these cases,[8a] at least under the more concentrated solution conditions of the NMR measurements. If geometry has to be excluded, the reason for the different behaviour has to be assigned to another characteristic of the two series of hosts, namely **1**–**3** and **4**–**6**, which could be due to a different structural rigidity or different solvation properties. In contrast, the CT bands deriving from the interaction between the aromatic units of the superstructure and the PQ^{2+} can be seen in the region around 450–520 nm[12] in all the complexes.

The absorbance changes (ΔA), defined as the difference between the spectra calculated on the basis of the molar absorption coefficients of paraquat and porphyrins in acetonitrile, and the spectra actually observed, are reported for a constant concentration of porphyrin and varying concentrations of PQ^{2+} in Fig. 9. The ΔA changes for each porphyrin-PQ^{2+} system can be treated according to either a Benesi–Hildebrand[13,14] (inset of Fig. 9) or a Wilcox[15,16] treatment, to derive the association constants. The association constants for all complexes, calculated from the ground state absorption signals, are reported in Table 4 and are in good agreement with values obtained by NMR titrations in different mixed-solvent systems.[8a]

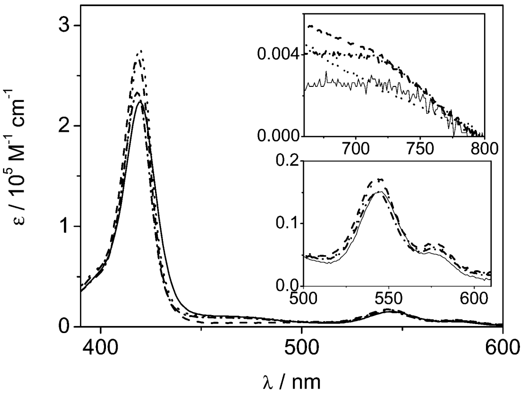

Fig. 8 Absorption spectra in toluene solutions of the complexes **1**-PQ^{2+} (···), **4**-PQ^{2+} (—), **5**-PQ^{2+} (---), and **6**-PQ^{2+} (–·–). The spectra were taken at $>95\%$ concentration of complex. In the insets the Q and the CT band regions are expanded.

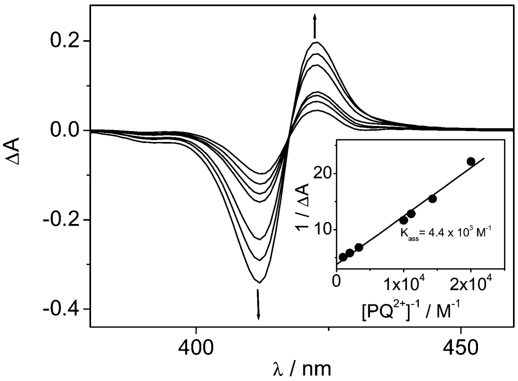

Fig. 9 Difference between the absorption spectra of the components and of the mixtures of **6** and PQ^{2+} illustrating the formation of the complex **6**-PQ^{2+}. The determination is performed at constant concentration of **6** (2×10^{-6} M) and at concentrations of PQ^{2+} ranging from 5×10^{-5} to 10^{-3} M. In the inset the absorbance at 423 nm is treated by the Benesi–Hildebrand formalism to derive the association constant.

Luminescence. The porphyrin luminescence is quenched in the complexes of porphyrins **1**–**6** upon addition of PQ^{2+}, as expected on the basis of the occurrence of a fast electron transfer from the Zn(II) porphyrin electron donor to the PQ^{2+} electron acceptor unit within the complexes. In Fig. 10 the quenching of the luminescence for **3** and **2** upon addition of increasing amounts of PQ^{2+} is shown. Addition of PQ^{2+} to the reference compound MOD did not result in any appreciable change in the luminescence yield up to a concentration of $PQ^{2+} = 5 \times 10^{-2}$ M, the highest concentration of guest used in the present experiments, indicating that diffusional quenching has no effect under the present conditions. The quenching of the luminescence can be used to derive the association constants and in the inset the change in emission intensity at 634 nm is fitted for **3** according to the Benesi–Hildebrand equation[13,14] [Fig. 10(a)] whereas that of **2** is fitted by the Wilcox equation[15,16] [Fig. 10(b)]. The association constants derived from the change in the luminescence intensities of the complexes are reported in Table 4.

Time-resolved luminescence experiments with 20 ps resolution in acetonitrile solutions of complexes containing $>95\%$ complex,[11] indicate that in all cases the quenching of the porphyrin, that is the electron transfer process from the singlet excited state of the porphyrin to the PQ^{2+} electron acceptor, hereafter called charge separation (CS), occurs with rates faster than the resolution of our experiments. The luminescence time profiles of the complexes, in fact, can be fitted with lifetimes of *ca* 2 ns, and account for *ca.* 3–5% of the total signal of the porphyrin without PQ^{2+}. Thus, the residual luminescence is assigned to the presence of some uncomplexed porphyrin. In Fig. 11 are reported the luminescence results of steady state

Table 4 Association constants K_{ass} in acetonitrile determined by ground state absorbance and emission spectroscopic techniques

	K_{ass}/M^{-1}	
	Absorbance	Emission
MOD-PQ^{2+}	< 10	< 10
1-PQ^{2+}	7×10^4	8×10^4
2-PQ^{2+}	1.4×10^5	1.4×10^5
3-PQ^{2+}	5×10^2	6×10^2
4-PQ^{2+}	3×10^4	2.5×10^4
5-PQ^{2+}	3×10^2	5×10^2
6-PQ^{2+}	4.5×10^3	4×10^3

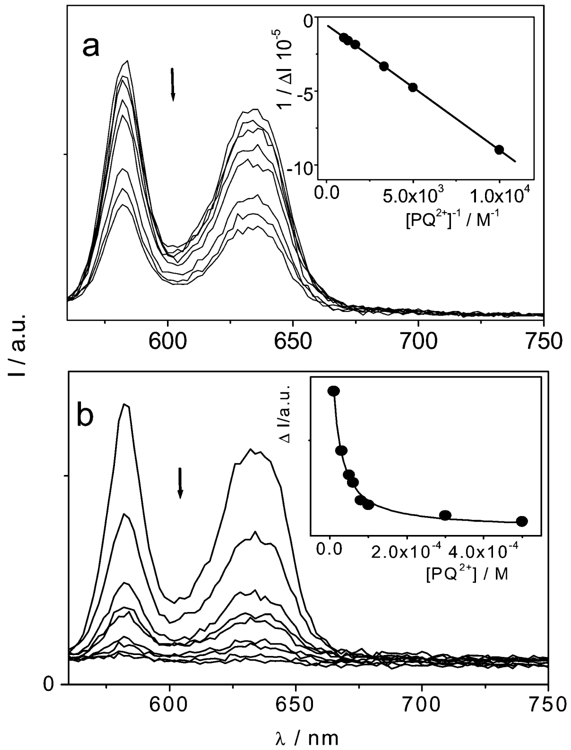

Fig. 10 Quenching of the luminescence for toluene solutions of (a) **3** (1.7×10^{-6} M) and (b) **2** (1.4×10^{-6} M) upon addition of increasing amounts of PQ^{2+}. In the insets the luminescence quenching at 634 nm according to a (a) Benesi–Hildebrand plot or a (b) Wilcox equation is shown. See text for details.

and time-resolved experiments for porphyrin **6** and complex **6**-PQ^{2+}.

Time-resolved absorption. The charge-separated (CS) state formed upon electron transfer from the porphyrin to the PQ^{2+} within the complex is characterised by a porphyrin cation and a reduced paraquat radical. The former displays a characteristic absorption band around 670 nm[17] and the latter has, in addition to a strong band at 390 nm, a broader absorbance at 600 nm.[18] These characteristics make the transient absorption technique quite convenient for the determination of the CS state properties. In Fig. 12 are shown a few representative cases of absorption spectra detected in the complexes, compared with the host spectra under the same experimental conditions, upon excitation with a 35 ps laser pulse at 532 nm.

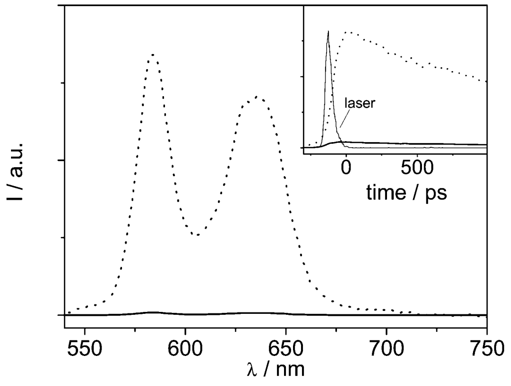

Fig. 11 Luminescence at 298 K in acetonitrile solutions of **6** (···) and of **6**-PQ^{2+} (—), obtained by addition of 5×10^{-3} M PQ^{2+} to the solution of **6**. This corresponds to a $> 95\%$ complexation of porphyrin . In the inset the time-resolved signal at 585 nm for **6** (···) and **6**-PQ^{2+} (—) is reported with the laser profile.

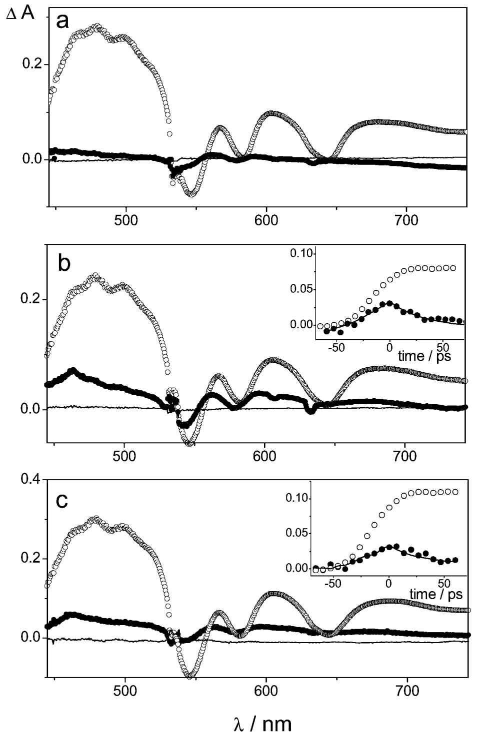

Fig. 12 Transient absorption signal detected upon excitation by a 35 ps pulse (532 nm, 3 mJ per pulse) of porphyrins **2** (a), **5** (b) and **6** (c) as open circles (○). As full circles (●) are reported the spectra during the pulse of **2**-PQ^{2+} (a),**5**-PQ^{2+} (b) and **6**-PQ^{2+} (c), obtained by addition of PQ^{2+} to the above porphyrins. The porphyrin complexation is $> 95\%$. In the insets are shown the time profiles at 600 nm of the complexes (●) superimposed with the one of the porphyrin (○).

The signal for the complex is essentially zero in most cases, as shown in Fig. 12(a) for **2**-PQ^{2+}. Only in **5**-PQ^{2+} and **6**-PQ^{2+} can very weak absorbances with maxima at 600 and 670 nm be detected [Fig. 12(b,c)]. The signal, ascribable to the charge-separated state, is formed and decays within the pulse duration, as can be seen from the insets of Fig. 12(b) for **5**-PQ^{2+} and of Fig. 12(c) for **6**-PQ^{2+}, where the time decay of the absorbance of the CS state is shown together with the formation of the porphyrin singlet, instantaneous with the pulse. After correction of the signal for the instrumental response a lifetime of the order of 20 ps for the CS state in **5**-PQ^{2+} and **6**-PQ^{2+} can be derived. In all other cases no transient is detected after or during the pulse, indicating that the CS state has an even shorter lifetime and does not accumulate during the pulse. As can be clearly seen, no residual absorbance ascribable to escape from the recombination is present in any case. In addition, no singlet or triplet absorbance remains in the complex, except a few percentage assigned to the uncomplexed porphyrin ($< 5\%$). In agreement, nanosecond flash-photolysis experiments on the complexes at $> 95\%$ complexation do not indicate any residual absorption except the few percentage coming from the inter-system crossing of the uncomplexed porphyrin. In the complexed porphyrins, inter-system crossing is, in fact, precluded by fast deactivation of the excited singlet state *via* electron transfer to the paraquat.

The present finding, which indicates complete recombination of the CS state in the complexes within a few tens of picoseconds in the most favourable cases, is in contrast with a previous report performed on the complex **2**-PQ^{2+} and compounds related to **5** and **6**, but with a shorter strap in conditions of incomplete complexation.[7b,10] In these reports, experiments with nanosecond resolution led the authors to the conclusion that the reduced radical PQ^{2+} could escape the geminate recombination and freely diffuse in solution, leading to a diffusion-controlled, slow recombination of the CS state. It appears very likely that in those cases the spectroscopic properties of the solutions were dominated by uncomplexed porphyrins and by diffusive effects, which led to an interpretation different from the present case.

Electron transfer in the complexes

A schematic energy level diagram for the generic complex ***n***-PQ^{2+} is drawn in Fig. 13. The singlet and triplet excited state localised on the porphyrin components, essentially identical in all cases, can be derived from the spectroscopic data of Table 2 and are respectively 2.13 eV for ^{1}***n***-PQ^{2+} and 1.71 eV for ^{3}n ***n***-PQ^{2+}. The redox potentials for PQ^{2+} and the porphyrinic components, necessary to assign the energy level of the charge-separated state, can be derived from the literature. On the basis of the reported value of +0.63 V for the first oxidation of a zinc *meso*-diaryloctaalkylporphyrin in butyronitrile[7d] and of −0.43 V for the first monoelectronic reduction potential of PQ^{2+} in acetonitrile,[19] a value of *ca.* 1.1 eV can be derived for the charge-separated state corresponding to the oxidation of the strapped porphyrin and the reduction of the paraquat unit in the complex, that is ***n***$^+$-PQ$^+$. We will assume an identical value for the charge-separated state of all complexes. Small changes in such values, namely increase of the oxidation potential of the porphyrin and decrease (more negative) of the reduction potential of the paraquat, are expected because of the CT interaction taking place between the porphyrinic component and the paraquat unit within the complexes. Such effects are expected to be very small compared to the overall energy involved in the reaction and, in view of the approximate type of approach, they will not be considered. The ΔG^0 of the electron transfer reaction from the singlet excited state of the porphyrin unit to the paraquat acceptor is extremely high, of the order of −1.05 eV and a similar value ($\Delta G^0 = -1.1$ eV) applies to the recombination reaction to the ground state. Given the close similarity of the thermodynamic parameters for all complexes, the differences can be ascribed to structural differences.

Several types of weak interactions contribute to the formation of the complexes, including C–H–O, π–π and electrostatic interactions between the ether oxygens of the strap and the positive nitrogens of the guest,[8] but in the case of complexes **4**-PQ^{2+}, **5**-PQ^{2+} and **6**-PQ^{2+}, a large contribution has to be ascribed to the CT interactions between the paraquat unit and the dimethoxy aromatic component of the strap. This would position the guest close to the aromatic component of the strap, in order to maximise such an interaction, and further from the porphyrin electron donor than in the other cases, **1**-PQ^{2+}, **2**-PQ^{2+} and **3**-PQ^{2+}, where such an interaction involves aromatic units located closer to the porphyrin plane (Fig. 1). This type of reasoning is valid for the complexes containing the longer strap **5**-PQ^{2+} and **6**-PQ^{2+}, but not for complex **4**-PQ^{2+} where the strap is rather tight and no real spatial separation of the paraquat from the porphyrin can occur. We are unable to detect any postulated effect of the distance between reacting partners on the rate of charge separation in the different complexes because of instrumental limitations. In all cases the reaction is faster than the 20 ps resolution, and we can only derive a lower limit of 5×10^{10} s^{-1} for the rate constant. In contrast, as far as the charge recombination reaction is concerned, we can detect in complexes **5**-PQ^{2+} and **6**-PQ^{2+} a charge-separated state whose recombination reaction rate (5×10^{10} s^{-1}) is slower than for all other cases. It should be noted that the rate of CR in this situation is considerably lower than that measured for a contact ion pair between an anionic porphyrin and a paraquat acceptor with a similar driving force, $k \sim 10^{12}$ s^{-1}.[20] The difference should reflect the looser type of interaction in the present case, resulting in a larger spatial separation of the reacting partners, especially in **5**-PQ^{2+} and **6**-PQ^{2+}, which causes a retardation of the recombination reaction.

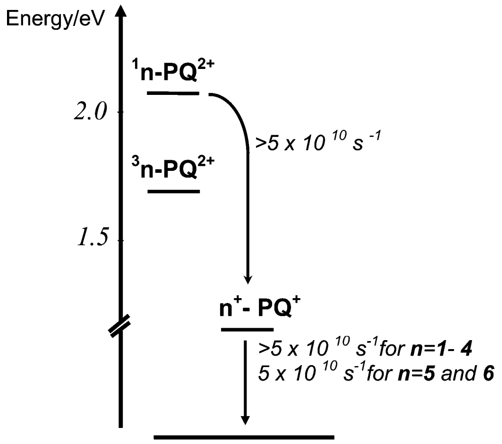

Fig. 13 Schematic energy level diagram for the generic complex ***n***-PQ^{2+} and pertinent rate constants.

Conclusions

We have determined the photophysical and spectroscopic properties of a series of porphyrins with appended superstructures, which are able to bind the electron donor paraquat. The association constants have been determined in acetonitrile by absorption and emission spectroscopy. Solutions containing > 95% of porphyrin in the associated form have been used to characterise the photoinduced processes in the complexes. Electron transfer from the excited state of the porphyrinic component has been evidenced in the complexes and a lower limit of 5×10^{10} s^{-1} has been set for this reaction rate constant. The formation of a charge-separated state has been detected in a few cases and the charge recombination rate constant determined to be 5×10^{10} s^{-1}. The slower rates in the charge recombination reaction have been correlated to the dimensions and internal structure of the receptor site. Moreover, it has been shown that the previously postulated escape of the reduced guest from the complex to freely diffuse in solution, with a consequent dramatic increase of the charge-separated state lifetime, does not occur in these types of complexes.

Experimental

The synthesis and characterisation of the porphyrin and complexes has been reported and discussed previously.[8]

The solvents used were Spectroscopic Grade (C. Erba). Titration experiments for the determination of association constants were performed using a constant concentration of host ***n*** and variable concentrations of guest PQ^{2+}. Precise aliquots of PQ^{2+} solutions were vacuum dried, in some cases PQ^{2+} was directly weighted, then dissolved in a solution of ***n***, to ensure a constant concentration of porphyrin during the titration. Absorption spectra were recorded with a Perkin–Elmer Lambda 9 spectrophotometer and emission spectra, uncorrected if not otherwise specified, were detected by a Spex Fluorolog II spectrofluorimeter equipped with a Hamamatsu R928 photomultiplier. In titration experiments excitation was performed at the isosbestic point of the complexed and uncoplexed porphyrin spectra. Relative luminescence intensities were evaluated from the area (on an energy scale) of the luminescence spectra corrected for the photomultiplier response. Luminescence quantum yields ϕ for the components were obtained with reference to a standard, Zn(II) 5,10,15,20-*tetrakis*-(3′,5′-di-*tert*-butylphenyl)porphyrin, in toluene with $\phi = 0.08$.[5f]

Phosphorescence lifetimes were determined by exciting the sample, dipped in liquid nitrogen, with a Nd-YAG laser (532 nm, 18 ns pulse duration, 2 mJ per pulse); the emitted light was selected at right angles by coloured glass filters and an IR absorbing filter (700 nm $< \lambda <$ 900 nm) and was detected by the same set up as in the flash-photolysis system (see below). Fluorescence lifetimes longer than 1 ns were detected by an IBH time-correlated single photon counting apparatus with excitation at 337 nm. Luminescence lifetimes shorter than one nanosecond were determined by an apparatus based on a Nd:YAG laser (Continuum PY62–10) with a 35 ps pulse, 532 nm, 1 mJ per pulse and a streak camera.[21] In a typical experiment, the luminescence signals from 1000 laser shots were averaged and the time profile was measured from the streak image in a wavelength range of *ca.* 20 nm around the selected wavelength. Spectra in a selected time window were also acquired from the streak image, consisting of a rectangular matrix of 480 points (wavelength) times 512 points (time). The fitting of the luminescence decays were performed by standard iterative nonlinear programs taking into consideration the instrumental response.

Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd-YAG laser (35 ps pulse, 532 nm, 2–4 mJ) and an OMA detector.[22] The instrumental response profile was obtained by measuring the buildup of the absorption of the porphyrin singlet at 600 nm. T-T absorption spectra and lifetimes were determined by a laser flash photolysis apparatus based on a Nd:YAG laser (JK Lasers) delivering 532 nm pulses of 18 ns.[23] The energy used was of 1.5 mJ for the determination of the spectra and the reaction rate with oxygen, whereas it was 0.1 mJ per pulse for the triplet lifetime determinations, to prevent undesired second-order reactions. Experiments on triplets were conducted in home-made, 10 mm optical path cuvettes, bubbled with argon for 5 min. The oxygen quenching reaction rate constant , k_q , was determined from the equation: $k = k_0 + k_q[O_2]$, by measuring the rate constant, k, for three independent concentrations of dissolved oxygen. The oxygen solubility in air-equilibrated acetonitrile was taken to be 1.9×10^{-3} mol l^{-1}.[24] Experiments at 77 K made use of quartz capillary tubes immersed in liquid nitrogen contained in a home-made quartz dewar. Estimated errors are 10% on lifetimes, 20% on quantum yields and 30% on association constants.

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16 The equation[15] has the expression: $\Delta\mathrm{Obs} = (\Delta\mathrm{Obs}_{\max}/2S_0)\{K_{\mathrm{dis}} + X + S_0 - [(K_{\mathrm{dis}} + X + S_0)^2 - 4XS_0]^{1/2}$. Obs stand for any observable, absorbance or emission intensity in the present case, S_0 is the constant concentration of the host, X is the variable concentration of guest, $\Delta\mathrm{Obs}_{\max}$ is the maximum variation of the observable and $K_{\mathrm{dis}} = 1/K_{\mathrm{ass}}$.

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