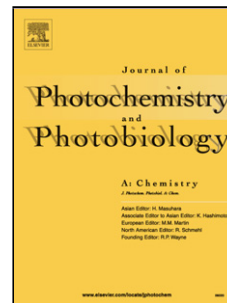


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Excited states interaction with quinones

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Photophysics and photochemistry of porphyrin core PAMAM dendrimers. Excited states interaction with quinones

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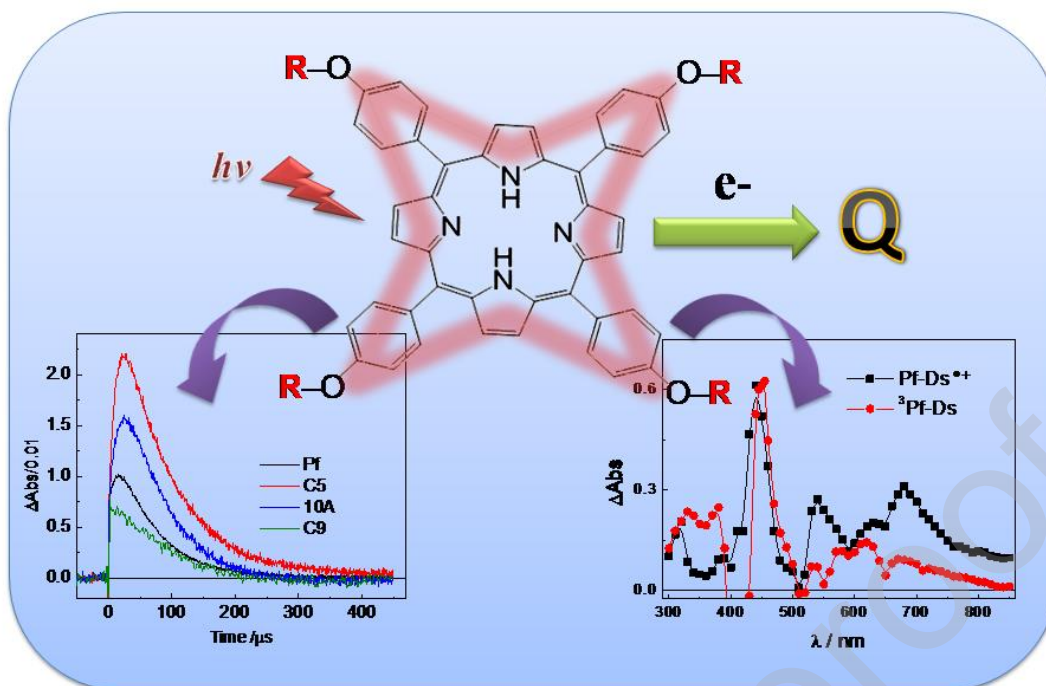
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Graphical abstract



Highlights

- The excited states of porphyrins with PAMAM branches are efficiently quenched by p-benzoquinones.
- The kinetics of the process follows the expectation of electron transfer reactions.
- The charge separation yields are highly dependent of the structure of the dendritic chains and of the benzoquinone derivative.

Abstract

Quenching of excited states of the *meso*-substituted tetraphenyl porphyrins with PAMAM branches, and one with PAMAM generation 1 peripherally-modified with thiazole groups by p-benzoquinones, were studied in DMF solution. Fluorescence lifetime measurements evidence a static component in the quenching process. The dynamic quenching rate constants were close to the diffusional limit except for the case of duroquinone. Apparent association constants of the porphyrin compounds with the

quinones were determined by comparison of static and dynamic measurements of fluorescence quenching. The ground state interaction is very weak with the exception of tetrachlorobenzoquinone. The triplet state decay kinetics and the transient absorption spectra in the presence of the quinones were determined by laser flash photolysis. Triplet quenching rate constants were lower than those of singlet quenching. An electron transfer mechanism was proposed to explain the results. The long-time transient absorption spectra were assigned to the radical cation of the dyes. Relative radical yields were determined and a dependence on the side chains and the quencher was observed.

1. Introduction

The interaction of porphyrins in excited states with quinones is of great interest due to their involving in a number of photobiological processes [1]. A large number of papers have dealt with the subject, and most of these studies were concerned with the interaction of singlet and triplet excited states of metalloporphyrins [2, 3, 4, 5, 6, 7, 8]. Other works investigated the interaction of excited states of free-base and substituted porphyrins with benzoquinone derivatives [9, 10]. These studies showed that the quenching of both singlet and triplet excited states involves an electron transfer from porphyrins to quinones.

Molecules that include benzoquinones in their structure exert various relevant biological activities, for example vitamin K1 in the treatment of people with low levels of prothrombin coagulation protein [11]. Other example is the coenzyme Q, the main function of this molecule is related to the process by which oxygen and nutrients are transformed into energy. Inside the cell there is a complex mechanism to obtain energy, of which Coenzyme Q10 is a fundamental piece. On the other hand, it also acts by protecting cells against exposure to solar radiation and other aggressions caused by free radicals [12]. It forms a protective layer against external aggressions on our skin and organs, preventing them from oxidizing and accumulating damage that ultimately affects their functioning [13]. In the photosynthesis process, quinones and hydroquinones act as electron acceptors. In particular, plastoquinone, an isoprenoid dimethyl benzoquinone, is involved in the electron transport chain in the light-dependent reactions of photosynthesis [14]. Furthermore, special interest in these processes has arisen due to possible applications in systems artificially designed to

mimic photosynthesis [15, 16, 17], photoredox catalysis[18] and photooxidation reactions [19].

Dendrimers are molecules characterized by an inner structure, the core, and a highly branched compact structure of great regularity. These branches may contain a large number of reactive end groups. Several porphyrin-core dendrimers were synthesized and their properties investigated in recent years [20, 21, 22, 23, 24]. The biomedical applications of these compounds are also of interest [25]. In particular the use of dendrimers with porphyrin or phtalocyanine nucleus has been the interest during the last years since these molecules may act as photosensitizers in several biomedical applications [26]. These dendrimers are promising carriers for the design of new photosensitizers since they can enhance the biocompatibility, selectivity and water solubility of the active component. One extra goal in the development of these materials is the possible protection of the porphyrin moiety towards undesirable ground and excited states reactions [27, 28].

Recently, members of our group have synthesized *meso*-substituted tetraphenyl porphyrins with polyamidoamine (PAMAM) dendritic branches, and one with a PAMAM branch derivatized with thiazole moiety, because their metal-binding properties make them suitable as dopants of nylon membranes for water purification [23,24]. In a previous work, we have also studied the photophysical properties of these compounds and the excited states were characterized by means of absorption and fluorescence spectroscopies, and laser flash photolysis [28]. The potential application of these compounds as photosensitizers was assessed by means of singlet oxygen generation via triplet state. In view of the importance of the interaction of porphyrins' excited states with quinones, and considering the effect of dendrimer side chain on the photophysics of the porphyrin nucleus, we now present a study on the excited-states quenching of these compounds by *p*-benzoquinone derivatives. The free-base tetra-(*p*-methoxy)phenyl porphyrin (Pf) corresponding to dendrimer cores was also analyzed for comparison purposes. The structure of the two porphyrin-PAMAM dendrimers of generations 1 (C5) and 2.5 (C9), and of a thiazole derivative (10A) are shown in **Scheme 1**. Benzoquinones are well-known electron acceptors and their interaction with porphyrin excited states has been the subject of several papers [29]. We have chosen *p*-benzoquinones derivatives (**Scheme 2**) of widely different electron acceptor capability in order to explore the excited state reactivity in a photoinduced electron transfer process of the porphyrin-dendrimer compounds (Pf-D). The effect of the dendritic side

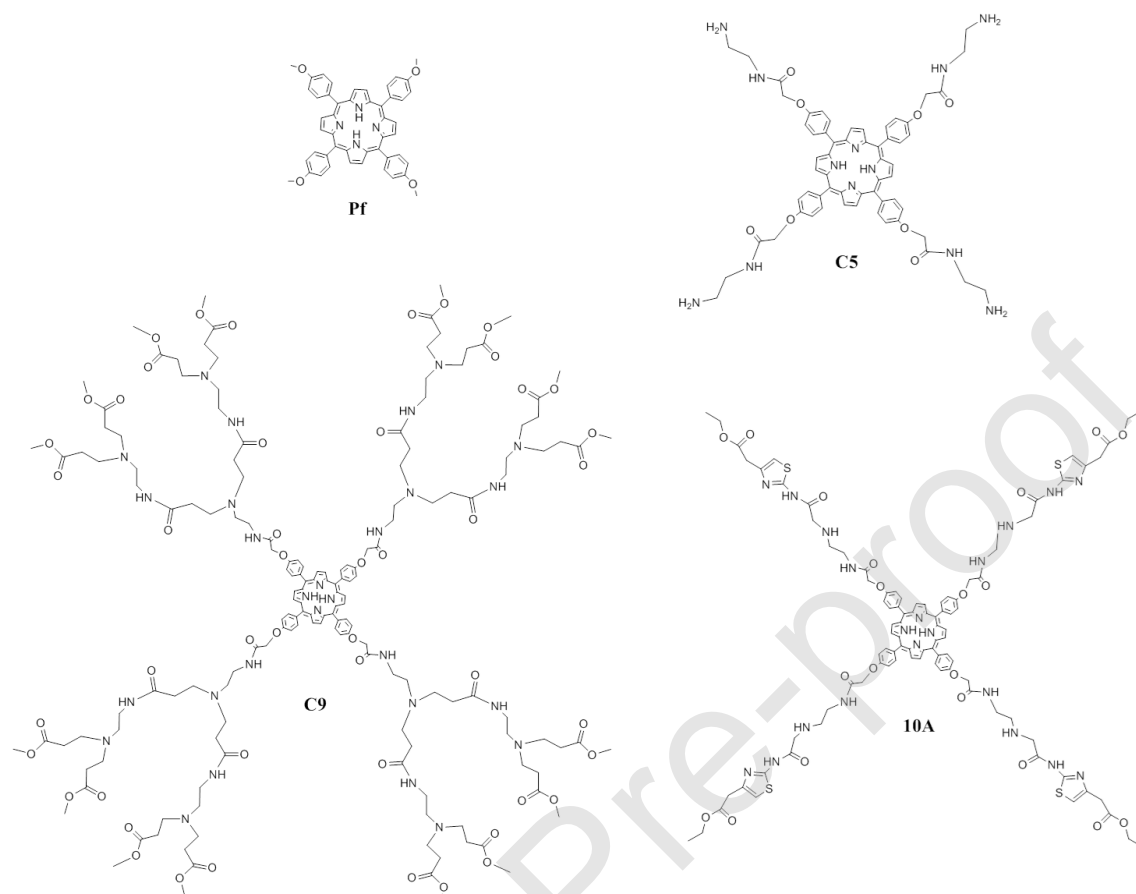
chains on the kinetics of the process and the charge separations yield, was also investigated.

The interaction of ground and singlet-excited states of Pf-D with the quinones was characterized by absorption and fluorescence spectroscopies. The triplet-excited states of the molecules in the presence of quinone derivatives were analyzed by means of laser flash photolysis, which allows assessing the spectral and kinetic features of transient species formed after light absorption. The triplet state of Pf-D was quenched by quinones and the kinetics and spectral data confirm that the quenching process is a one-electron oxidation of the porphyrin.

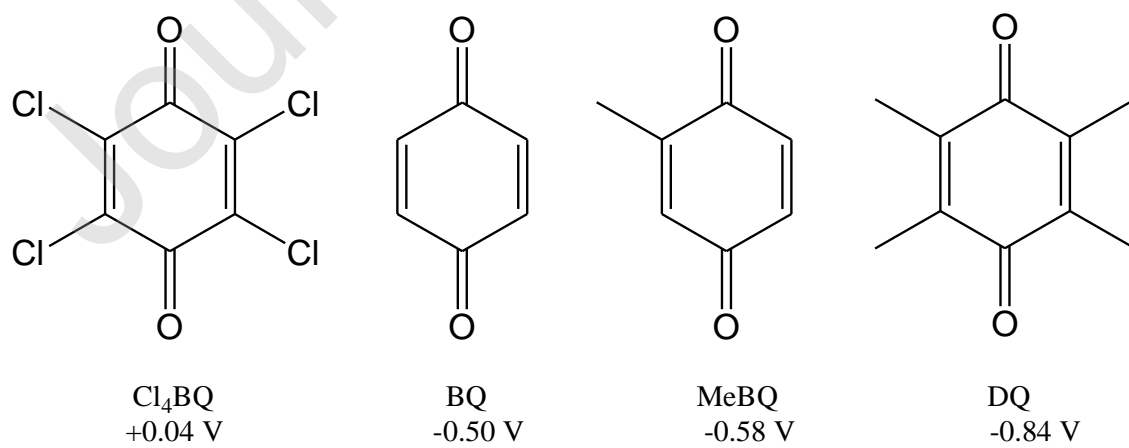
2. Experimental

The porphyrin-PAMAM dendrimers of generations 1 (C5) and 2.5 (C9), a thiazole PAMAM derivative (10A) and the free-base tetra-(*p*-methoxy)phenyl porphyrin (Pf) were synthesized according to previously reported methods and used without further purification[23,24]. *p*-Benzoquinone (BQ), *p*-toluquinone (MeBQ), duroquinone (DQ), tetrachloro 1,4-benzoquinone (chloranil, Cl₄BQ), from Aldrich, were purified by sublimation before using.

All experiments were carried out in dimethylformamide (DMF) from Sintorgan (HPLC grade). The absorption spectra and fluorescence measurements were obtained on a diode array equipment Hewlett Packard 6453E and a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer respectively. Fluorescence lifetime measurements were carried out with the time correlated single photon counting technique using an Edinburgh Instruments OB-900 equipment. The mathematical analysis of the decay was performed with the software provided by Edinburgh Instruments. All fluorescence determinations were carried out at room temperature, 25 ± 1 °C, in air equilibrated DMF solutions. Spectra of transients and triplet states quenching were obtained by laser flash photolysis at 532 nm. The experimental setup has been described elsewhere [30]. For laser flash photolysis experiments, solutions were de-oxygenated by bubbling with solvent saturated high purity argon. The temperature of the laser flash photolysis measurements was controlled at 25 ± 1 °C.



Scheme 1: Structures of porphyrin-dendrimer compounds



Scheme 1: Structures of p-benzoquinones compounds

3. Results and discussion

Fluorescence quenching

When excited in the Q bands Pf and the three Pf-D present typical porphyrin fluorescence with maxima at 658 and 715 nm in DMF [27]. Fluorescence lifetimes are in the order of 10-12 ns with independence of the dendrimer chain. The fluorescence intensity and lifetime are quenched by benzoquinones without changes of the spectral shape. This is shown in **Figure 1** for the case of quenching by Cl₄BQ. Also there was not any appreciable effect on the Pf-D absorption spectra, in the region of the Q bands, for the concentration range of the quinones employed.

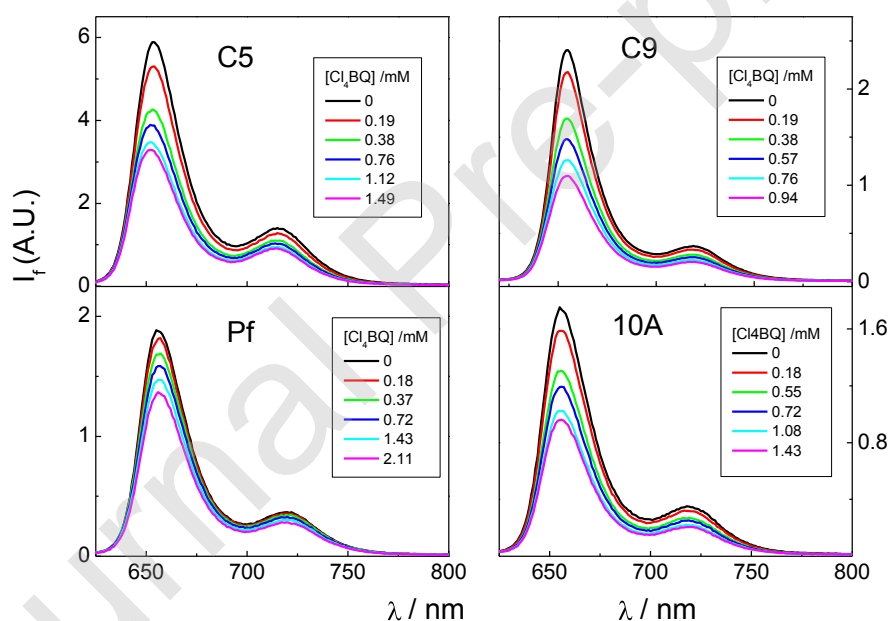


Figure 1: Fluorescence emission spectra of PF-Ds in DMF in the presence of chloranil (Cl₄BQ)

Singlet quenching rate constants, 1k_q , were determined from fluorescence lifetime measurements according to eqn. (1)

$$\tau^0 / \tau = 1 + k_q \tau^0 [Q] \quad (1)$$

where τ_0 and τ stand for the fluorescence lifetime in the absence and the presence of the quinone Q , respectively. Rate constants are collected in Table 1.

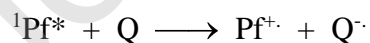
Table 1: Singlet quenching rate constants measured by fluorescence lifetime in units of $10^9 \text{ M}^{-1}\text{s}^{-1}$

Pf-D/Q	Cl ₄ BQ (+0.04) ^(a)	BQ (-0.50) ^(a)	MeBQ (-0.58) ^(a)	DQ (-0.84) ^(a)
Pf	6.2	5.9	5.3	3.6
C5	3.9	4.5	4.4	2.4
C9	4.9	5.7	4.8	2.8
10A	4.7	5.6	4.7	2.6

Estimated error in rate constants $\pm 5 \%$

(a) Reduction potential in volts in acetonitrile vs SCE from refs (31, 32)

The values for Cl₄BQ, BQ and MeBQ are in the diffusional limit of DMF, while those for DQ are lower by a factor of two. This reflects the more negative reduction potential of DQ. An approximate estimation of the Gibbs energy change for an electron transfer quenching process shows that for the first three quinones the reaction



is exergonic by more than -0.3 eV, while for DQ it is nearly termoneutral. Therefore, the lower values for the quenching rate constants by DQ are in line with an electron transfer reaction from the singlet excited state to the quinone.

Quenching experiments were also carried out by measurements of static fluorescence intensity in the absence (I^0) and the presence (I) of the quinone Q. Plots of I^0/I are linear, with a higher slope than the corresponding τ^0/τ plot, and in some cases an upward curvature is observed.

In **Figure 2** an example of I^0/I plots and corresponding lifetime measurements in the form of τ^0/τ are shown for the case of 10A quenched by p-benzoquinone. It can be seen that static measurements fall on a straight line with a higher slope than dynamic measurements. The difference in slopes is an indication of a static component in the quenching mechanism. It is well-known that, if dynamic and static quenching occurs simultaneously, the intensity measurement of the quenching process is described by the following equation [33,34]

$$I^0 / I = 1 + \left(k_q \tau^0 + K_{as} \right) [Q] + k_q \tau^0 K_{as} [Q]^2 \quad (2)$$

where K_{as} is the apparent association constant of a non-fluorescent 1:1 ground state complex. At low quencher concentrations and weak ground state association, the contribution of the third term in eqn. (2) is very low (in the case of Fig. 1 it can be estimated as less than 5 % to the value of I^0/I). In this case eqn. (2) reduces to

$$I^0 / I = 1 + \left(k_q \tau^0 + K_{as} \right) [Q] \quad (3)$$

From the difference of the slopes in equation (1) and (3), the apparent association constant can be obtained. A similar approach was used by T. Chaudhuri et al. to determine association constants of meso-tetra-2-chlorophenylporphyrin with fullerenes and chloranils in toluene [35]. When an appreciable upward curvature was observed, the values of K_{as} were determined by a second order polynomial fitting of the I^0/I vs. $[Q]$ plots using eqn. (2). Examples of an upward curvature in the static SV plots are shown in **Figures 3** and **4**. The values of the apparent association constants are collected in Table 2. It can be observed that there are important differences in the magnitude of the interaction. From the values in the table, it can be concluded that for MBA and DQ the interaction is very weak- In the case of Cl₄BQ and BQ when the

interaction is more important, it is favored when the porphyrin nucleus is substituted by the dendrimers chains. It is interesting to note that the association constants for Cl₄BQ with C9 and 10A are of the same order than those determined for the interaction of chloranils with meso-tetra-2-chlorophenylporphyrin [35]. In any case, the interaction is not affecting the electronic distribution in the porphyrin ring since there are not apparent differences in the position and intensity of the Q bands in the absence and the presence of the quinone. These results are similar to those reported by Harriman et al. [9] for the fluorescence quenching by BQ of free-base meso-tetratolyl porphyrin (H₂TTP) in DMF. The authors also found that the addition of BQ quenches the fluorescence of H₂TTP without any effect on its absorption spectrum. Moreover, the association constants of BQ and H₂TTP are of the same order of magnitude that those found in our case. From Table 2 it can be seen that the values of K_{as} for a given Pf-D are in the order Cl₄BQ > BQ > MeBQ > DQ. This is the same order of the reduction potentials in Table 1 and it can be concluded that some type of electron donor-acceptor contribution is operative in the interaction. It can also be observed that the interaction is more favorable when the porphyrin nucleus is surrounded by the dendrimer chains.

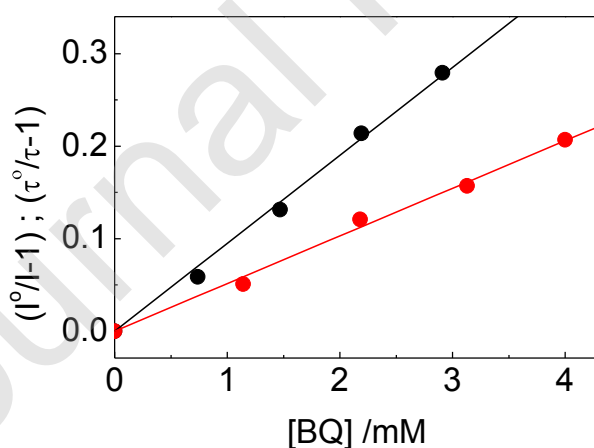


Figure 2: Stern-Volmer plots for the fluorescence quenching of 10A by p-benzoquinone. Lifetime measurements (red) and fluorescence intensity (black).

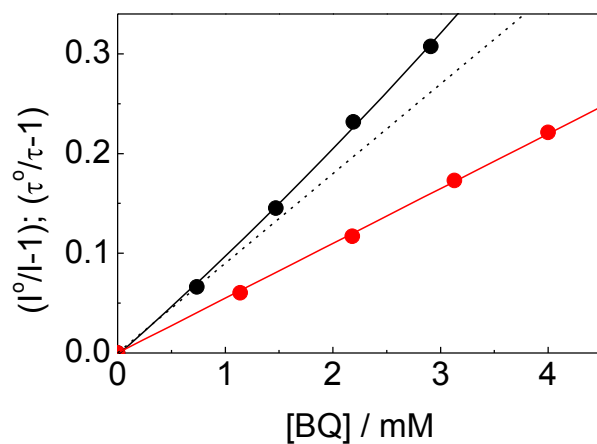


Figure 3: Stern-Volmer plots for the fluorescence quenching of C9 by p-benzoquinone. Lifetime measurements (red) and fluorescence intensity (black). The dotted line is the linear extrapolation of the initial values of fluorescence intensity measurements. The solid line (black) is the fitting according to eqn. (2)

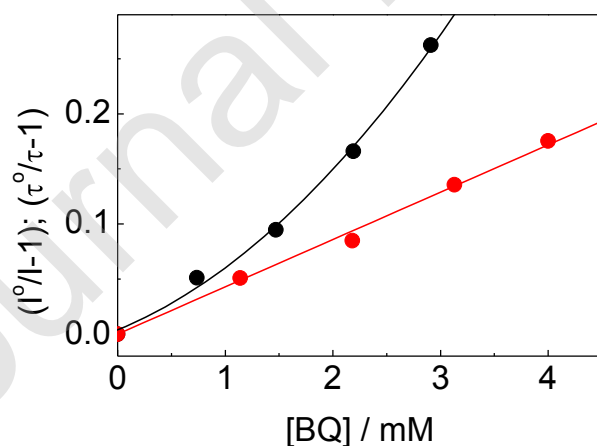


Figure 4: Stern-Volmer plots for the fluorescence quenching of C5 by p-benzoquinone. Lifetime measurements (red) and fluorescence intensity (black).

Table 2. Apparent association constant (M^{-1}) for the interaction of ground state Pf-D compounds with p-benzoquinones

	Cl ₄ BQ	BQ	MeBQ	DQ
Pf	117	36	10	7
C5	880	46	7	6
C9	1200	79	17	5
10A	1390	55	13	6

Triplet state interaction

When laser flash excited at 532 nm in DMF, Pf-D compounds present the typical porphyrin T-T absorption spectrum with maxima at ca. 450 nm [36, 37]. The triplet decays in several hundreds of microseconds. In the presence of quinones the triplet decays faster (**Figure 5**) and a new differential spectrum appears in the long time. The latter may be attributed to the porphyrin radical cation [38, 39], with apparent maxima at 440, 540 and 680 nm, **Figure 6**.

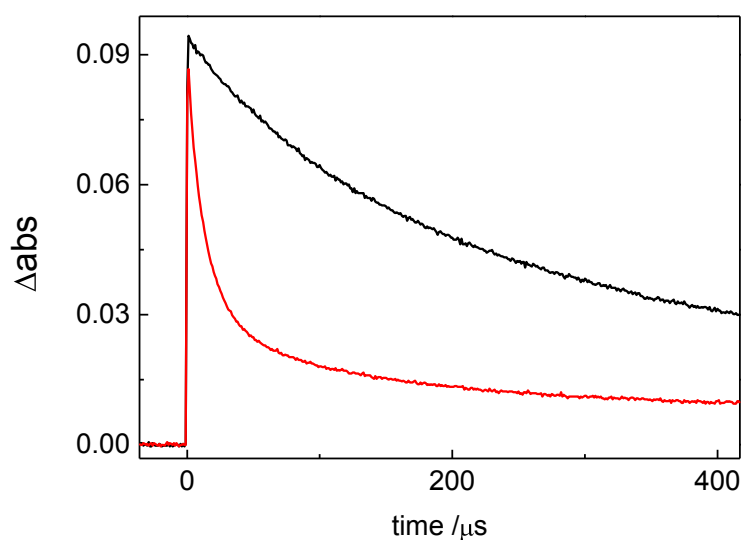


Figure 5: Decay of transient absorption at 470 nm of 10A after the laser pulse at 532 nm in the absence (black) and the presence (red) of Cl₄BQ 5.6×10^{-5} M

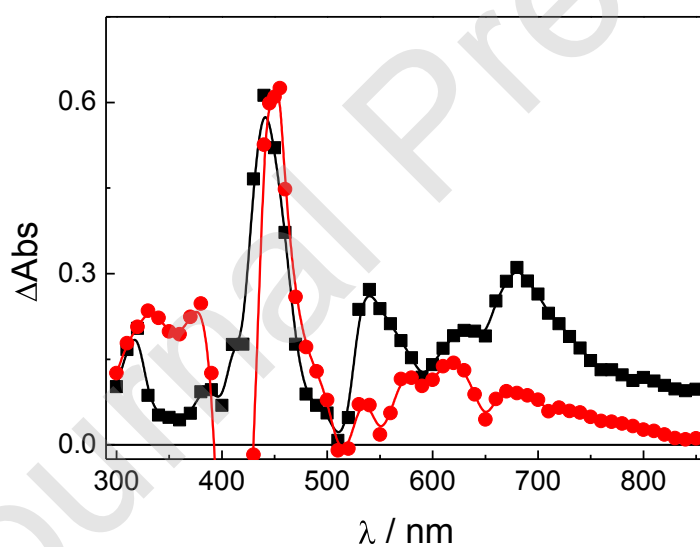
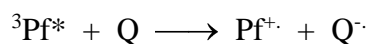


Figure 6: Transient absorption spectrum at 5 μ s after the laser pulse of Pf in the absence (red) and the presence (black) of BQ 1.5 mM. The spectra are normalized at the maximum ca. 450 nm

Accordingly, the triplet quenching process may be explained in terms of the electron transfer reaction



Bimolecular triplet quenching rate constants were determined from laser flash photolysis experiments by two different procedures. The triplet decay at the maximum absorption, 470 nm, as a function of quinone concentration was adjusted by a bi-exponential function (**Figure 5**). The shorter time corresponds to the triplet decay in the presence of the quinone and the longer time to the decay of the radical cation of the porphyrin. The latter, although a minor component, contributes to the absorption at the monitoring wavelength. The triplet decay lifetime determined in this way were used to evaluate the rate constants from the slopes of plots according to eqn. (4).

$${}^3\tau^{-1} = {}^3\tau_o^{-1} + {}^3k_q [Q] \quad (4)$$

where ${}^3\tau_o$ and ${}^3\tau$ stand for the triplet lifetime in the absence and the presence of the quinone Q , respectively. A representative plot according to eqn. (4) is shown in **Figure 7**. In some cases rate constant were also determined from the multi-parameter non-linear fitting of the growth and decay of the absorption of the radical at 550 nm.

In **Figure 8** the absorption profile at 550 nm after the laser pulse of C5 is shown for different concentrations of MeBQ. In the absence of the quinone the absorption corresponds to the T-T transition. As the concentration of MeBQ increases the absorption of the radical cation of the porphyrin core follows a growth and decay profile which can be adjusted with four parameters. These parameters corresponds to the initial T-T absorption, the final absorbance of the radical, the growth rate constant, assigned to the triplet quenching, and the radical decay rate constant. The agreement of the two procedures is fair, considering the uncertainty of the multi-parameter method.

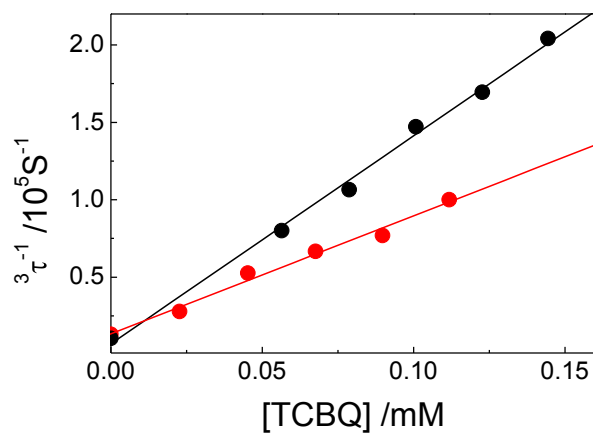


Figure 7: Reciprocal of the short time component of the decay at 450 nm for the triplet quenching of 10A (black) and C9 (red) by Cl4BQ.

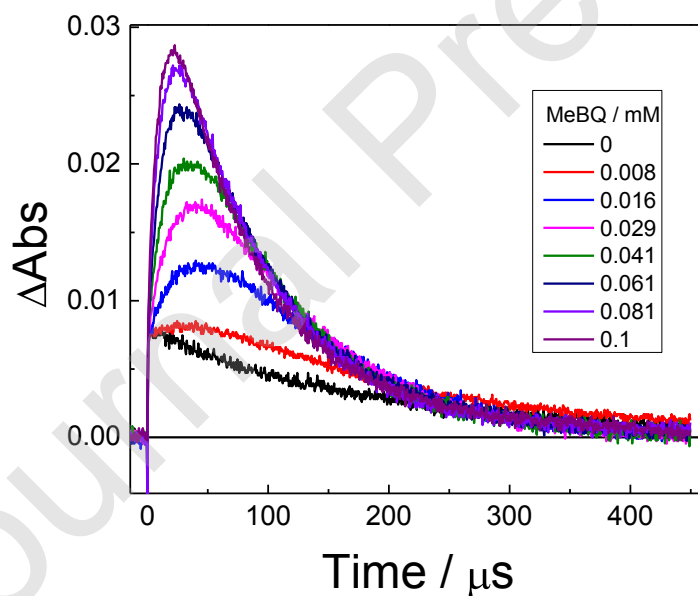


Figure 8: Transient absorption at 550 nm of C5 as a function of MeBQ concentration.

The values in Table 3 are lower than those for singlet quenching, as expected for a triplet mediated electron transfer process. It can be seen that the values reach a limit

(ca. $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) which is below the expectation of the theoretical value for diffusional rate constant in DMF ($7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$). This is not surprising since it was previously reported that triplet state diffusional limit for an electron transfer process fall below the values of singlet state mediated process [40].

Table 3: Triplet quenching rate constants measured by laser flash photolysis in units of $10^9 \text{ M}^{-1}\text{s}^{-1}$

Dendrimer/Q	Cl ₄ BQ	BQ	MeBQ	DQ
Pf	2.2	1.6	0.2	0.001
C5	1.9	1.0	0.9	(a)
C9	1.0	2.2	0.45	(a)
10A	1.4	2.8	0.6	(a)

(a) Too low to be measured.

Estimated error in rate constants $\pm 10 \%$

Radical yield

The triplet quenching reaction results in the formation of radical ions according to eqn, (4). The spectrum after triplet decay in the presence of quinones present two new absorption bands at 550 and 700 nm, as exemplified in **Figure 6**, that may be ascribed to the radical cation of the porphyrin moiety. In all cases the absorption at 550 nm, due to the radical cation, shows an initial growth followed by decay in the long time. The radical yield in the triplet quenching process may be estimated from this transient absorption.

The results show an important difference among the Pf-D compounds. In **Figure 9** it is shown the absorption profiles of the radical cation of the different porphyrin-dendrimer compounds for the triplet quenching by MeBQ. The absorption at 532 nm,

the laser pulse, was matched for all the solutions. The quinone concentration was such that more than 90 % of triplets were intercepted before their decay in all cases.

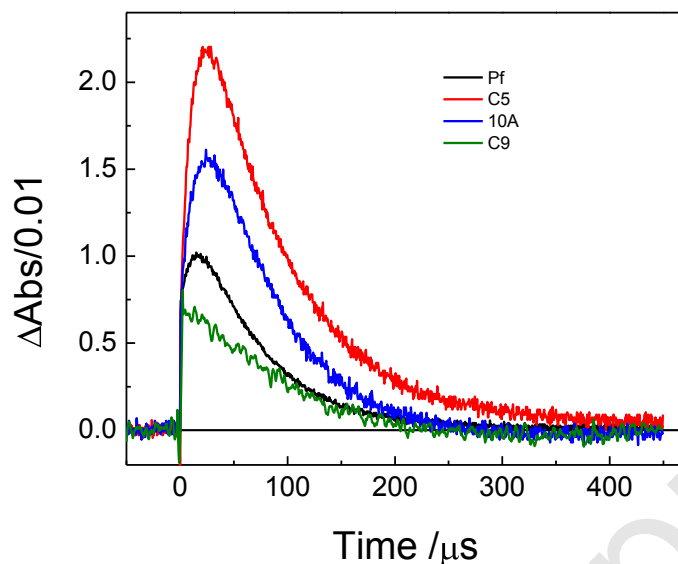


Figure 9: Transient absorption at 550 nm in the quenching of porphyrin-dendrimers by MeBQ in DMF.

An evaluation of radical quantum yield requires knowledge of the triplet and radical absorption coefficients at the measuring wavelength [41]. Unfortunately, it is very difficult to evaluate these quantities due the overlap of the absorption spectra of the transient species with the ground state absorption. Therefore, relative radical yields were estimated from the absorption profiles similar to those shown in **Figure 9**, and they are given in **Table 4**. They are presented relative to the yield of C5-BQ pair and they are based on the assumption that the absorption coefficient of the four porphyrins is the same.

A rough estimation of the radical quantum yield can be made on the assumption that the T-T absorption coefficient at 450 nm of the Pf-D compounds is of the order of $6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This is based on comparison with the data for tetraphenyl and tetrahydroxyphenyl porphyrins in different solvents [35]. The absorption of the cation radical is much lower, an absorption coefficient of the order of $1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ in the range 550-700 nm may be estimated from the data of tetratolyl and tetraphenyl porphyrins and metalloporphyrins [37,42]. Using these values together with the initial

triplet absorption at 450 nm and the estimated final radical absorption, an efficiency of the charge separation reaction close to unity results for the case of C5-BQ pair.

It is remarkable the large differences in the yield depending on the structure of the dendrimer chains appended to the porphyrin ring, although even higher differences are observed when the different quinones are compared. Considering the different Pf-D compounds, the order of radical yield may be established as $C5 > 10A > C9$ for the triplet quenching by BQ and MeBQ. This is made clearer in Fig. 8. The yield for DQ could not be measured due to the very low triplet quenching that makes necessary a high concentration of the quinone that precludes a clean observation of the triplet reaction not contaminated with the singlet process.

The yield is a consequence of the competition between the separation rate of the initial radical pair and their back recombination. These processes are in turn dependent on the initial separation distance in the radical pair and the energetic of the process, viz. the free energy of the radical pair, plus the coulomb energy of the opposite charges. For Cl₄BQ the yield is low and practically independent of the porphyrin derivative. For this compound the radical pair initially formed is expected to be the lower in energy, due to the energetics of the quenching process. Therefore, the back recombination to ground state should be more competitive with the radical separation. In addition, the separation rate may be affected by the structural features of the side chains.

In summary, the excited states of Pf-D compounds are efficiently quenched by p-benzoquinones. A ground state interaction was observed, which was important only in the case of chloranil. The association constants could be determined from the analysis of the singlet quenching process based on fluorescence intensity measurements. The values are of the same order than those reported for the ground state interaction of porphyrins with other quinones. This is an indication that the interaction with the quinones is mainly with the porphyrin nucleus and not with the dendritic side chains. Fluorescence lifetime measurements allowed the measurement of bimolecular rate constant for dynamic quenching. The kinetics of the process follows the expectation of electron transfer reactions, with values close to the diffusional limit except for duroquinone. It may be assessed that the side chains do not preclude the excited state interaction with the quencher. Triplet state quenching rate constants are lower than those of the singlet state, as expected for a photoinduced electron transfer process. It was of particular interest to determine the charge separation yield in the reaction of triplet quenching. In this case a notable dependence on the structure of the dendritic chains and on the

benzoquinone derivative was observed. The yield depends of several factors, including the separation distance, the energetics and the structure of the side chain.

Table 4: Relative Radical Yields in the triplet quenching of Pf-Ds by p-benzoquinones in DMF

	Cl ₄ BQ	BQ	MeBQ
Pf		0.84	0.22
C5	0.27	1	0.5
C9	0.27	0.66	0.20
10A	0.22	0.84	0.36

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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