Available online at www.sciencedirect.com
SCIENCE DIRECT®
Dyes and Pigments 58 (2003) 7–18
DYES and PIGMENTS
www.elsevier.com/locate/dyepig

Fluorescence quenching and ESR spectroscopy of metallic porphyrins in the presence of an electron acceptor

Danuta Wróbel*, Jędrzej Łukasiewicz, Henryk Manikowski

Faculty of Technical Physics, Instytute of Physics, Poznan University of Technology, Nieszawska 13A, 60-965, Poznań, Poland

Received 20 August 2002; received in revised form 3 November 2002; accepted 4 February 2003

Abstract

In this paper we determined the optical and ESR properties of metal-free and metal complex tetraphenylporphyrins in the presence of anthraquinone in an isotropic solution of dimethylsulfoxide. Such a system can mimic the electron transfer process between the excited porphyrin dyes and a semiconducting electrode in a photoelectrochemical cell. Dye fluorescence quenching were followed by ESR to determine the origin of an unpaired electron in porphyrins. The Stern–Volmer quenching constants (K_Q), bimolecular quenching rates (k_q) and electron transfer rates (k_{ET}) were determined. The K_Q values changed in the range of 0.5×10^4 to 2.3×10^4 M^{-1} depending on the metal ion incorporated in the porphyrin, k_q changed from 7.0×10^{13} to 1.3×10^{14} M^{-1} s^{-1}. The *g*-values and ΔB were estimated, which showed that the conjugated porphyrin was the origin of the unpaired electron. Both Mg–tetraphenylporphyrin, and Zn–tetraphenylporphyrin showed different photophysical behaviour compared to their Pb–tetraphenylporphyrin and Pt–tetraphenylporphyrin counterparts. The relationship between dye fluorescence quenching and ESR results is discussed.

Keywords: Metallic tetraphenylporphyrin; Electron transfer; Fluorescence quenching; Unpaired electron; Conjugated system; ESR

1. Introduction

The investigation of photoinduced electron transfer is essential in understanding physical processes involving a photoelectrochemical cell (PEC) based on organic dyes. Porphyrins have been extensively studied due to their potential applications in solar energy conversion [1,2]. In a PEC, dyes are used to absorb incident light energy, which leads to electron injection from the excited dye electronic state to the conductive band of a semiconducting electrode.

In such a system, the dye serves as an electron donor and a semiconductor electrode is used as electron acceptor. In our work [1,3,4] and that of other authors [5–7] the photophysical properties of a number of dyes (porphyrins, phthalocyanines, subphthalocyanines) have been studied in an attempt to find correlation between the molecular structure of the dye and its ability to generate a photocurrent in a PEC. We have investigated both the fluorescence and the thermal deactivation of

---

Abbreviations: TPP, tetraphenylporphyrin; M-TPP, metallic tetraphenylporphyrin; DMSO, dimethylsulfloxide; ESR, electron spin resonance; PEC, photoelectrochemical cell; AQ, anthraquinone; ET, electron transfer.

* Corresponding author. Tel.: +48-61-665-3179; fax: +48-61-665-3201.

E-mail address: wrobel@phys.put.poznan.pl (D. Wróbel).

0143-7208/03/$ - see front matter
doi:10.1016/S0143-7208(03)00032-9

the excited state of dye each of which can limit the photovoltaic process and lead to a reduction of the photocurrent intensity. In our recent paper we have indicated the drastic influence which a central metal ion when incorporated in a molecular dye structure can have on the effectiveness of photon-to-electric energy conversion, and the boundary between the electroactive dye layer and the semiconducting electrode in the PEC [1].

Metal-free and metallic porphyrins are characterized by efficient fluorescence emission. Their fluorescence can be strongly quenched by an electron acceptor due to electron transfer. Study of the redox reaction between an electron donor and an acceptor species initiated by incident light can be realized using ESR examination as proposed by Michaeli et al. [8]. Time-resolved ESR spectroscopy of the electron transport reaction has been used for the determination of the excited triplet state generated by laser irradiation [8].

In order to imitate the electron transfer process operating between excited dyes and a semiconducting electrode in a PEC we monitored using fluorescence and ESR so as to determine the correlation between the dye fluorescence quenching behavior and its radical creation.

Photophysical characterization of the electron donor and electron acceptor in a homogenous system is a prerequisite for the better understanding of the effects occurring in the PEC. In the content the fluorescence quenching and electron transfer process in a solution of porphyrins in the presence of quinone were studied. Metal-free and four metallic porphyrins complexed with Zn, Mg, Pt and Pb were chosen for investigation, as their photon-to-current conversion effectiveness in the PEC is known to be strongly affected by the presence of metal in the main molecular core. As was shown in our papers [1–4] Zn- and Mg- dyes are very good compounds for light-to-electric energy conversion, whereas Pb–porphyrin is a poor photoconverter [1].

The mechanism of photovoltage generation in the boundary between an electroactive dye and a semiconducting electrode has been attributed to electron injection in a two-electrode photoelectrochemical cell [9]. However, the major question that remains unsolved is the nature and origin of the electron that is ejected from the dye. This particular matter is described in this paper on the basis of ESR results.

The general idea of this paper was to follow the optical and ESR properties of the metal-free (TPP) and metal-complexed tetraphenylporphyrins (M-TPP) in the presence of quinone in an homogeneous, isotropic system, in order to elucidate the electron-transfer reaction operating between an electroactive dye and a strong electron acceptor.

This paper focused an the advantage of optical and ESR spectroscopies to determine electron transfer behaviour of the porphyrins in the presence of a strong electron acceptor.

2. Experimental

Porphyrins (from Porphyrin System) and anthraquinone (Aldrich) were used without further purification. Five tetraphenylporphyrins (TPP) are used in our experiments: metal free TPP and metal— (Mg, Zn, Pb, Pt) complexed TPP (M-TPP). The molecular structures of porphyrins and anthraquinone (AQ) are presented in Fig. 1. TPP concentration was constant ($C = 10^{-5}$ M) and the AQ concentration changed in the range from 10^{-6} to 10^{-4} M (1×10^{-6}, 5×10^{-6}, 1×10^{-5}, 5×10^{-5} and 1×10^{-4} M). The porphyrins and AQ were dissolved in dimethylsulfoxide (DMSO).

The absorption spectra were received using a Specord SP40 (Carl-Zeiss) in the range of 300–800 nm. Steady-state fluorescence spectra were obtained in the wavelength region corresponding to the Soret band absorption and collected in the range of 500–800 nm using a Hitachi F 4500. Optical measurements were obtained in a quartz cuvette (1 mm and 1 cm for absorption and fluorescence measurements, respectively). The natural lifetimes of the dyes in DMSO were estimated on the basis of the absorption and fluorescence spectra as proposed in [10] using Eq. (1):

$$\frac{1}{\tau_N} = 2.88 \times 10^{-9} \times n^2 \frac{\int_\lambda \frac{F(\lambda)}{\lambda^2} \mathrm{d}\lambda}{\int_\lambda F(\lambda)\lambda \mathrm{d}\lambda} \int_\lambda \frac{\varepsilon(\lambda)}{\lambda} \mathrm{d}\lambda, \qquad (1)$$

where n is refractive index of the sample and $\varepsilon(\lambda)$ and $F(\lambda)$ are the areas under the absorption and fluorescence spectra, respectively.

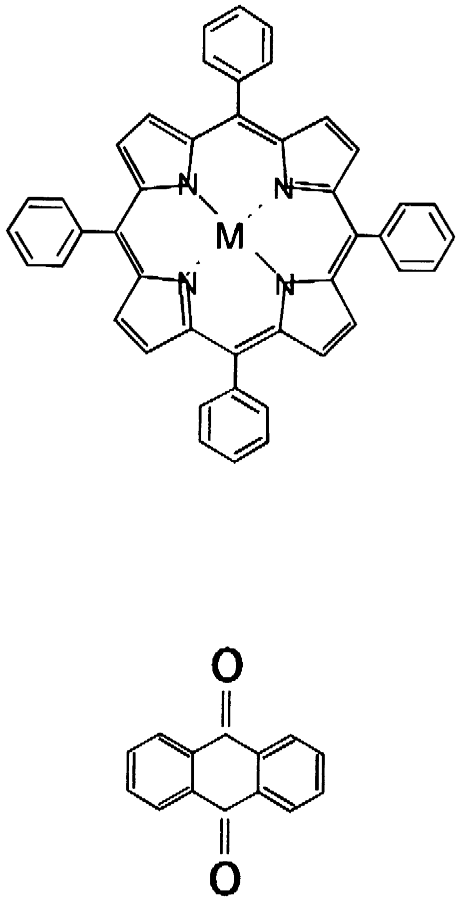

Fig.1. The molecular structure of the porphyrins and AQ used in experiment.

The fluorescence quantum yield (Φ) and average fluorescence lifetimes of the porphyrins in DMSO were evaluated with respect to coumarin in ethanol ($\Phi_R = 0.85$) [11] using Eqns (2) and (3):

$$\Phi = \Phi_R \frac{F_D}{F_R} \frac{A_R}{A_D} \frac{n^2}{n_R^2}, \tag{2}$$

$$\Phi = \frac{\tau_0}{\tau_N}, \tag{3}$$

where F_R and F_D are the fluorescence intensities of coumarin and dye, respectively, A_R and A_D the absorbance of the coumarin and dye, respectively, n and n_R the refractive indices of the dye in DMSO and coumarin in ethanol, respectively and τ_N and τ_0 are the natural and average fluorescence lifetimes, respectively.

The Stern–Volmer equation [Eq. (4)] was used for the analysis of fluorescence quenching by an external quencher [12,13]:

$$\frac{F_0}{F} = 1 + K_Q[Q], \tag{4}$$

where F_o and F are dye fluorescence intensities in the absence/presence of the quencher Q and K_Q is the Stern–Volmer quenching constant.

The bimolecular quenching rate k_q was calculated using Eq. (5) [14]:

$$K_Q = \tau_0 k_q, \tag{5}$$

where τ_o is the fluorescence lifetime of the dye in the absence of a quencher.

ESR was performed using a Radiopan SE/X-2540 spectrometr. Samples in DMSO solution were placed in a flat ESR cell and centered in the minimum electric field inside a RCX 660A resonator operating in TM_{110} mode. In a front wall of the resonator there was a window of 8 mm in diameter equipped with the optical system facilitating illumination of the sample during the ESR experiment. The ESR signals were measured in both the dark and under illumination with the white light from a halogen 150 W projector. The light intensity was stabilized and it was of 41.5 mW/cm^2.

Calculation of the photoinduced electron transport rate, k_{ET}, can be achieved by using Eq. (6) [15]:

$$k_{ET} = \frac{1}{\tau_F} - \frac{1}{\tau_0}, \tag{6}$$

where τ_F and τ_o are the fluorescence lifetimes of the porphyrins with and without an external quencher, respectively.

3. Results

3.1. Absorption

Fig. 2 shows the absorption spectra of the dyes in the presence of AQ of different concentration.

The absorption spectra are the superposition of the individual spectra of the porphyrins and

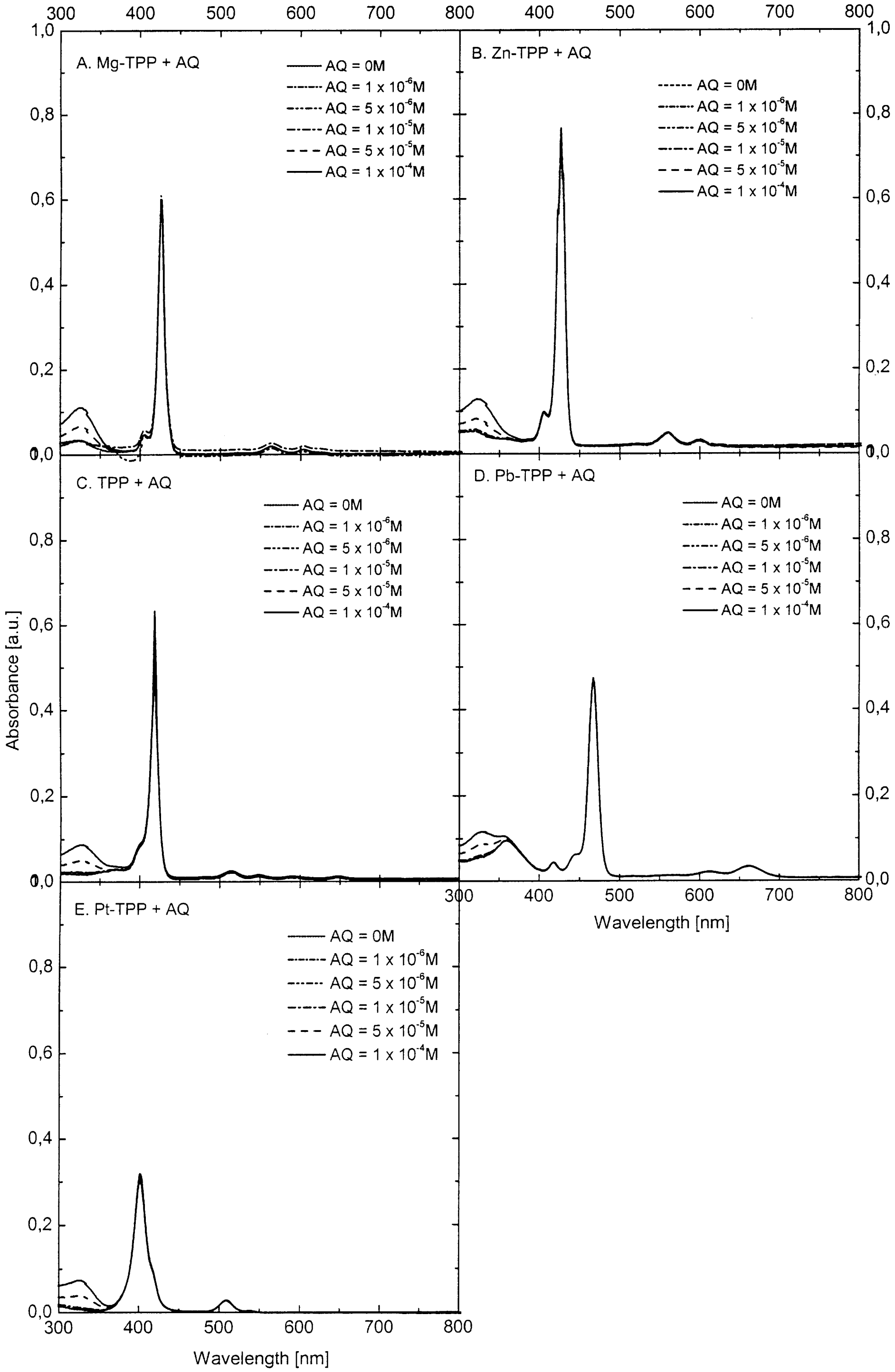

Fig. 2. The absorption spectra of the dyes in DMSO in the presence of AQ (A: Mg–TPP, B: Zn–TPP, C: TPP, D: Pb–TPP, E: Pt–TPP).

quinone. At a wavelength greater than 350 nm the absorption of AQ was negligible and the spectra in the range from 350 to 800 nm can be assigned to those of the porphyrin. Thus, in the visible region, the typical absorption patterns of metal-free TPP (Fig. 2C) and M-TPP (Fig. 2A,B,D,E) are observed with an intensive Soret band (401–467 nm depending on dye). The intensities of the remaining bands (500–700nm) were very low and these bands are named "Q bands" in the literature [16]. The shape of the spectra and the band positions are in accordance with literature [16] and indicate the existence of the monomeric dye. The relative shift in the Soret band position of Mg-TPP can be attributed to the presence of a metal ion in the porphyrin structure [16]. The shift of the electronic absorption spectra (the Soret band) is closely connected to the electronegativity of the incorporated metal which strongly affects the π-electron system [16]. The only remarkable exception among the absorption dye spectra is the Pb–TPP spectrum whose main absorbance was at a longer wavelength (467 nm) with respect to the remaining Me-TPP's (401–427 nm). A similar observation was reported in our previous paper [**1**] in which dyes were dissolved in polyvinyl–alcohol–DMSO. At this point it seems important to note the particularly high molar absorption coefficient obtained for Mg–TPP and Zn–TPP. Such an observation confirms previous results [1] and is essential with respect to the very high effectiveness of the dyes in conversion of photon energy to electric energy in the PEC [2]. In contrast Pb–TPP was found to be a rather poor photoconverter [1]. The absorption band at 327 nm can be assigned to AQ and its intensity increases in accordance with increasing concentration.

The absorption spectra do not show any significant change in shape and band position with respect to those of the monomeric dye forms. A red and/or blue shift is usually observed when an aggregated dye or complex species are formed; this was not the case in this work. Thus, in light of the absorption spectra obtained we can claim the existence of the monomeric, non-complexed forms of TPP or M–TPP in the samples even upon treatment with AQ. The exception was Pb–TPP for which the absorption band at 419 nm was assigned to the monomeric dye; the strong band at about 467 nm could be designated to another species in which a charge–transfer process is involved [17].

3.2. Fluorescence quenching

All porphyrins show more or less intensive fluorescence and the spectra exhibit two bands in the range of 600–714 nm depending on dye; the fluorescence intensity declines upon successive addition of AQ (Fig. 3). The observed decrease in the fluorescence intensity is due to quenching of the excited state of the porphyrins in the presence of AQ. In our case we can neglect concentration quenching by the porphyrin dyes because of the low concentration used and the absence of dye aggregates. Thus, we have every reason to believe that the observed quenching of the TPP and Mg–TPP excited states can be attributed to an electron transfer process. The electron-donating porphyrin dyes and AQ due to its electron acceptor feature are involved in this process.

The fluorescence quenching data, obtained with AQ as the external quencher of the porphyrin dye's fluorescence, were analyzed using the Stern–Volmer equation [Eq. (4)]. The results are shown in Fig. 4A–E for the metallic-free TPP and the M–TPP. The linear character of the Stern–Volmer plots indicates typical homogeneous dynamic quenching of the TPP dyes by AQ. From the slopes of the Stern–Volmer plots, the Stern–Volmer quenching constants K_Q were estimated and found to range from 0.5×10^4 to 2.3×10^4 M^{-1}. These values were similar to those obtained for Zn–tetrasulfophenylporphyrin quenched by colloidal TiO_2 which was found to be 1.5×10^4 M^{-1} [18]. From Eq. (5) the molecular quenching rate constants k_q were calculated. The k_q results, together with the fluorescence dye parameters (fluorescence lifetimes, fluorescence quantum yields etc.), are summarized in Table 1. The k_q values for the metallic-free TPP and M–TPP (Mg, Zn, Pb, Pt) were in the order of magnitude ranging from 10^{13} to 10^{14} M^{-1} s^{-1}. These values differ from those previously obtained for haematoporphyrin (HP) and protoporphyrin (PP) in small phosphate unilamellar vesicles (10^9–10^{11} M^{-1} s^{-1}) [14]. The fact that the k_q values obtained were higher than

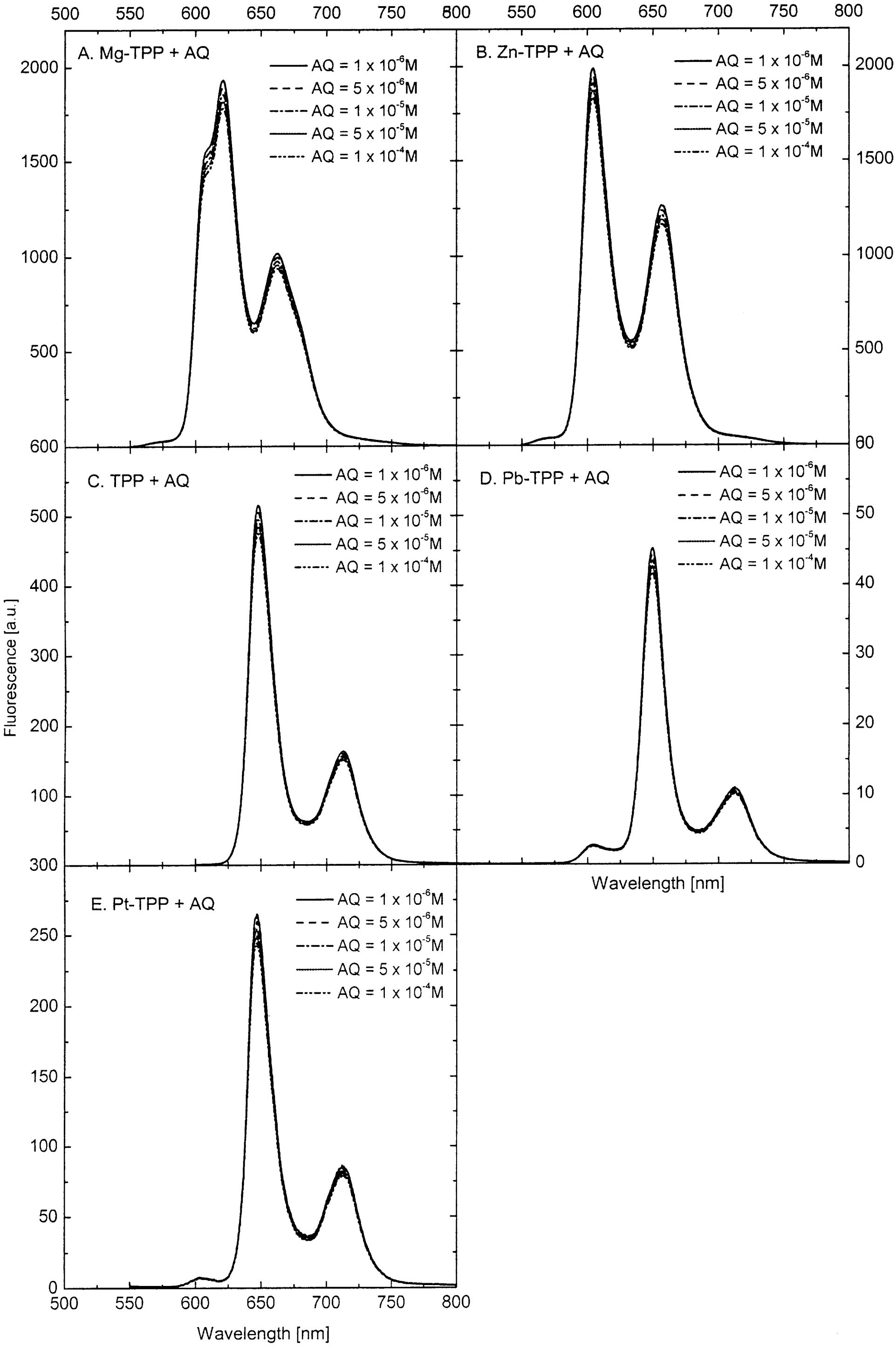

Fig. 3. The fluorescence spectra of the dyes in DMSO in the presence of AQ (A: Mg–TPP, B: Zn–TPP, C: TPP, D: Pb–TPP, E: Pt–TPP).

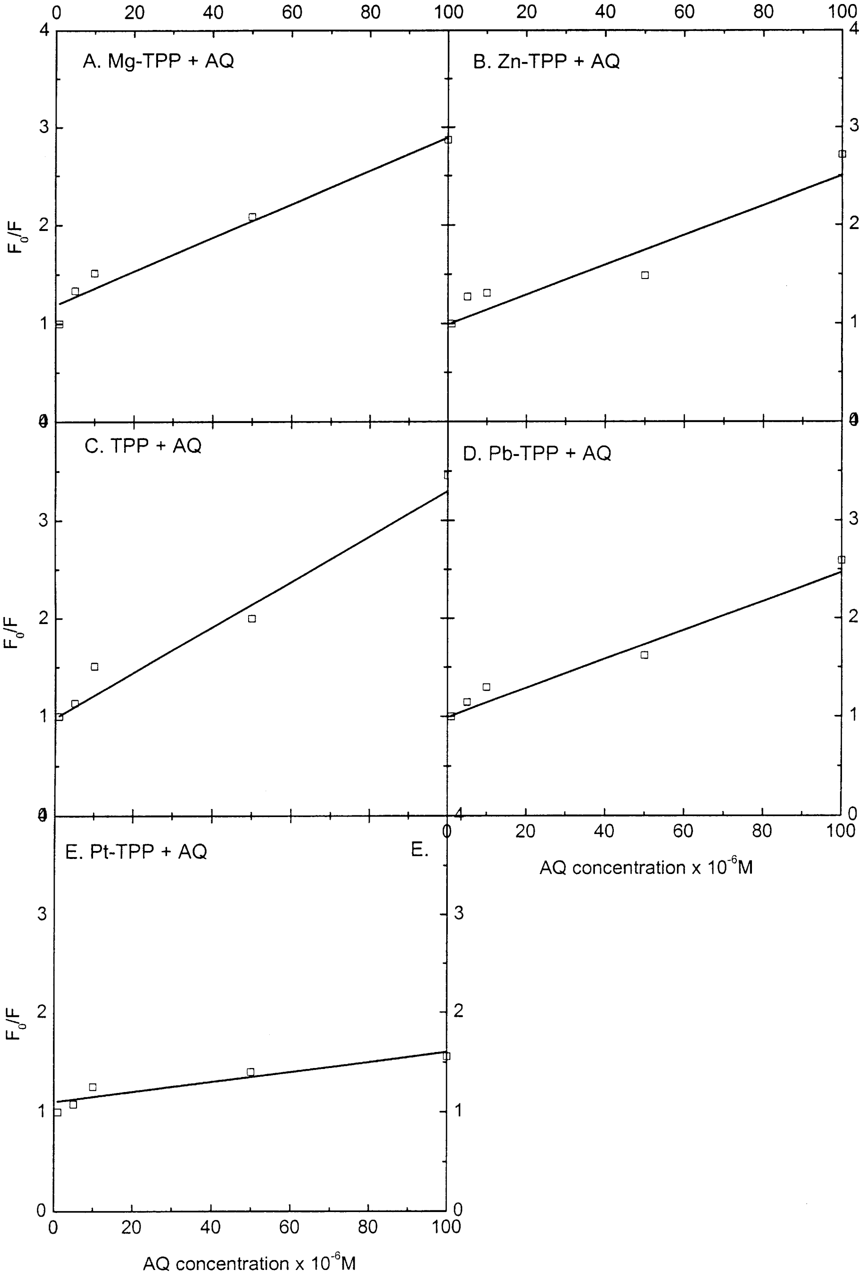

Fig. 4. The Stern–Volmer relation for the porphyrins/AQ in DMSO (A: Mg–TPP, B: Zn–TPP, C: TPP, D: Pb–TPP, E: Pt–TPP).

those for HP and PP in [**14**] can be explained in terms of the difference in the physical parameters (viscosity, density, polarity, refractive index, etc.) of DMSO and liposomes. The lowest k_q values were obtained for Mg–TPP and Zn–TPP (0.7×10^{13} and 0.9×10^{13} M^{-1} s^{-1}, respectively) whereas Pb–TPP is characterized by very fast quenching by AQ ($k_q = 1.3\times10^{14}$).

If we suppose that the observed fluorescence quenching of the excited singlet states of TPP and

Table 1
Fluorescence parameters for porphyrins in DMSO

Dye	τ_N (ns)	τ_0 (ns)	τ_F (ns)	Φ	K_Q (M^{-1})	k_q (M^{-1} s^{-1})	k_{ET} (s^{-1})
TPP	16.3	0.33	0.30	0.02	$(2.3\pm0.3)\times10^4$	$(7.0\pm0.3)\times10^{13}$	$(0.30\pm0.02)\times10^9$
Mg–TPP	31.8	2.54	1.11	0.08	$(1.7\pm0.2)\times10^4$	$(0.7\pm0.1)\times10^{13}$	$(0.50\pm0.02)\times10^9$
Zn–TPP	25.1	1.76	1.07	0.07	$(1.5\pm0.3)\times10^4$	$(0.9\pm0.1)\times10^{13}$	$(0.36\pm0.03)\times10^9$
Pb–TPP	6.2	0.12	0.08	0.02	$(1.5\pm0.2)\times10^4$	$(1.3\pm0.1)\times10^{14}$	$(4.17\pm0.05)\times10^9$
Pt–TPP	17.5	0.35	–	0.02	$(0.5\pm0.1)\times10^4$	$(1.4\pm0.1)\times10^{13}$	–

τ_N—natural fluorescence lifetime, τ_0—average fluorescence lifetime in the absence of AQ, τ_F—average fluorescence lifetime in the presence of AQ. $\Delta\tau_N = \pm0.1$(ns), $\Delta\tau_F = \pm0.1$(ns), $\Delta\tau_0 = \pm0.1$(ns). Φ—quantum yield of fluorescence with respect to coumarine (in the absence of AQ); $\Delta\Phi = \pm0.001$. K_Q—Stern–Volmer constant. k_q—quenching constant. k_{ET}—electron transfer rate from porphyrin to AQ.

M–TPP was due to electron transfer to AQ, the electron transfer rate constant can be calculated [Eqn. (6)]. The data are shown in Table 1. The k_{ET} values were similar to those found in [15] for a covalently linked porphyrin-quinone system.

3.3. ESR spectroscopy

Alternation in the ESR signal provides information about the interaction of the porphyrins with electron-accepting molecules, in this case, AQ. The rise in the ESR signal was dependent on AQ concentration and also depended on the kind of metal in the TPP structure. This is illustrated in Fig. 5 which shows the steady-state ESR results for both the metal-free and metallic porphyrins. No ESR signal was observed for the individual dyes and AQ dissolved in DMSO either in the dark or during illumination. The largest changes in the ESR amplitudes were observed for Mg–TPP and Zn–TPP (Fig. 5) and a particularly large change was found for the dye with a high concentration of AQ (5×10^{-5} and 1×10^{-4} M). On the other hand, a modest alternation was obtained for Pb–TPP, even in the sample of highest AQ concentration. For TPP, Pt–TPP and Pb–TPP, the ESR signals were similar to each other in value for identical irradiation conditions and at the same AQ concentration.

The ESR parameters are shown in Table 2. The g-values were in the range of 2.0043–2.0046 ($\pm$0.0001) for all dyes investigated, these being slightly higher than those obtained for porphyrin-like dyes in the literature [15]. The difference can be attributed to the presence of the AQ molecules.

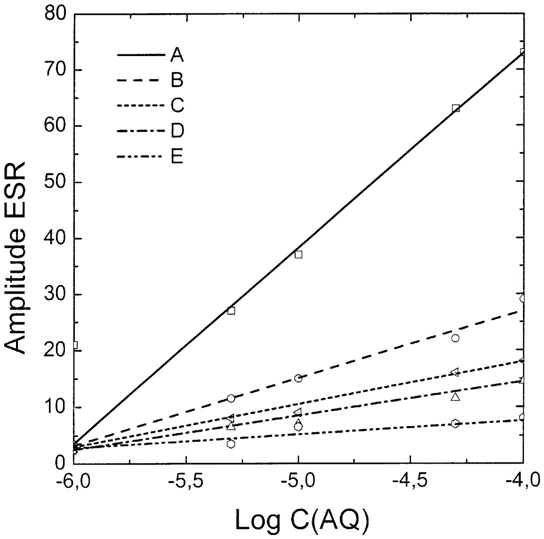

Fig. 5. The ESR signal as a function of AQ concentration upon illumination (A: Mg–TPP, B: Zn–TPP, C: Pt–TPP, D: TPP, E: Pb–TPP). Porphyrin concentration— 10^{-5} M; AQ concentrations— 1×10^{-4}, 5×10^{-4}, 1×10^{-5}, 5×10^{-5}, 1×10^{-6} M (in log scale).

Table 2
ESR parameters for porphyrins and AQ mixture and relative changes in ESR signal (R) for porphyrins in the presence of AQ [with respect to the TPP with AQ (1 μM)]

Dye	R	ΔB (mT)	g
TPP	1	0.28 ± 0.02	2.0046 ± 0.0001
Mg–TPP	29	0.35 ± 0.02	2.0043 ± 0.0001
Zn–TPP	12	0.35 ± 0.02	2.0045 ± 0.0001
Pb–TPP	3	0.32 ± 0.02	2.0044 ± 0.0001
Pt–TPP	7	0.33 ± 0.02	2.0046 ± 0.0001

The most stable dyes were metal-free TPP and Pb–TPP since their unpaired electron concentrations were smallest. For that reason we estimated the relative unpaired electrons in the individual dye in the presence of AQ with respect to the sample of TPP with AQ (10^{-6} M) as a standard. The "free radical" appears predominantly in the metallic porphyrin. The strong ESR signals observed for Mg–TPP and Zn–TPP indicate that the amount of unpaired electrons ("free radicals") was large and increases with increase in AQ concentration. The significant increase in the number of unpaired electrons upon illumination obtained for Mg–TPP and Zn–TPP indicates their very good electron-donating character.

4. Discussion

The general idea of this paper was to find a relationship between dye fluorescence quenching and free radical creation using ESR spectroscopy.

Some authors suggest that a central metal ion is a prerequisite for a good photosensitizer [15]. In our previous work we showed that the electroactivity of a dye and thus its ability to generate current induced by light depends strongly on the dye's molecular structure and the type of metal incorporated in the molecular skeleton. A previous study [1,2] of porphyrins and phthalocyanines showed how Mg, Zn, Pt, Pb and other metals influence photovoltaic effects [19]. Pb–TPP exhibited the worst ability for photoconversion of the investigated dyes [19]. Metal-free TPP and Pt–TPP were also rather poor photoconverters [1]. In contrast, Mg–TPP, Zn–TPP [1] and their chemical analogues [3] were found to be perfect photoconverters. Metal incorporation enhanced the ability of the dye for photoconversion due to π-electron delocalization [3]. The broken π-bands in the free phthalocyanine matrix were suggested as the origin of the unpaired electrons [20].

The appearance of an ESR signal in the case of TPP in the presence of AQ confirms our earlier suggestion as to the origin of the unpaired electrons [1]. As we discussed in a previous paper [2], the free electron transferred to AQ may have come from the π-electron of the conjugated porphine ring system and not from the metal. Evidence for the origin of the electrons in the TPP dye was also provided when the value of the line width ΔB and g-value for the dyes investigated in this paper were compared with those obtained for the metal free porphyrin-like molecules [20] whose molecular skeleton is very similar to the porphyrin molecular structure. The increase in number of the unpaired electrons in Mg–TPP and Zn–TPP (with respect to metal-free TPP) implies a positive influence of the metal on the electron-donating character of the metallic porphyrins due to changes in π-electron delocalization.

In a fluorescence the electron transfer process occurs almost immediately after light absorption i.e. in the lifetime of the excited singlet state of the dye molecules in nearly 10^{-9} s. Thus, in a fluorescence experiment we observe only those dye molecules which do not interact with AQ and do not fall thermally to the ground state. The remaining dyes, which transferred electrons to AQ, were not observed in this experiment.

On the basis of the fluorescence quenching parameters which describe the primary processes occurring in 10^{-9} s in porphyrins and ESR results (the final stage of the electron transfer reaction from the porphyrins to AQ) we can draw some conclusions concerning the processes occurring in the timescale between ns and μs.

Zn–TPP and Mg–TPP were the most interesting dyes from the point of view of the conversion of light energy to electric energy (they are the best photoconverters). Also, Pb–TPP and Pt–TPP due to their poor (or almost none in the case of Pb–TPP) photoconversion can be the objects of our discussion.

In the light of the estimated fluorescence quenching constants obtained for metal-free TPP and M–TPP (Table 1) we can divide the porphyrin dyes investigated into two groups: the first group comprises of dye with fluorescence quenching constants of the order of about 7.0×10^{13}–1.3×10^{14} M^{-1} s^{-1} (TPP, Pb–TPP) and the second group (Mg–TPP and Zn–TPP) with a k_q value of the order of 10^{13} M^{-1} s^{-1}. The k_q values indicate the faster quenching of TPP, Pb–TPP and Pt–TPP in the presence of AQ than those of Mg–TPP and Zn–TPP. These results seem to be in contradiction with the ESR results which show that the largest changes in ESR signals occurred for Mg–TPP and Zn–TPP. The large changes in the Mg–TPP and Zn–TPP ESR responses in the presence of AQ and upon illumination indicate a high concentration of the porphyrin with an unpaired electron when compared to the ESR responses of the remaining investigated dyes. Such disaccord in the fluorescence quenching results (k_q) and the ESR responses could be explained by means of the differences in the rates of the processes occurring in the time range from ns (fluorescence) and μs (ESR).

One of the deactivation process of the excited singlet/triplet states is thermal relaxation as shown in our [2] and other papers [21] by means of photoacoustic/photothermal studies. The decreasing lifetimes of the porphyrin dyes in the presence of AQ was closely connected to electron transport to AQ and thermal deactivation.

Moreover, the electron transfer reaction is always accompanied by a charge recombination process. On the basis of the delayed luminescence examination of some porphyrins [22] we showed that the recombination of the charges is a process which is responsible for the delayed deactivation of the excited state of the dye when a triplet state is involved.

The fluorescence and ESR experiments reveel that the charge recombination process is, however, supposed to proceed at different rates for the first dye group (TPP, Pb–TPP) and the second group (Mg–TPP, Zn–TPP). Since Mg–TPP and Zn–TPP were characterized by the lowest k_q (when compared to the k_q of the remaining dyes) on the one hand and the highest ESR signals, we can suggest that a charge recombination process was slower than the charge recombination in the remaining dyes (TPP, Pb–TPP, Pt–TPP). This conclusion can be supported by previous photovoltaic/photocurrent observation on dyes which were embedded in a photoelectrochemical cell [1,2]. The slow charge recombination processes for Zn–TPP and Mg–TPP compounds could explain their high ability for photocurrent generation. As mentioned above, Pb–TPP is a bad photoconverter [1,2]; its high k_q and low ESR signal in the presence of AQ and its poor ability for conversion of photon energy to electric energy could indicate its fast charge recombination occurring in the electron donor-acceptor chain.

Confirmation of the difference in the charge recombination processes in Mg–TPP and Zn–TPP on the one hand and the remaining dyes (TPP, Pb–TPP, Pt–TPP) on the other, is secured when we take into consideration the lifetimes, fluorescence quenching rate constants as well the rate constants of electron transport, k_{ET}, together with the ESR signal results of the investigated dyes; Mg–TPP and Zn–TPP were characterized by longest lifetimes compared to the remaining dyes. This result implies that the dyes could interact with the quinone quencher for a long time in the nanosecond time range. Their fluorescence was quenched rather slowly ($k_q = 0.7–0.9 \times 10^{13}$ M^{-1} s^{-1}, $k_{ET} = 0.36–0.50 \times 10^9$ s^{-1}) when the estimated parameters are compared with those obtained for Pb–TPP ($k_q = 1.3 \times 10^{14}$ M^{-1} s^{-1}, $k_{ET} = 4.1 \times 10^9$ s^{-1}).

There still remains discussion as to the participation of the excited singlet or triplet states of the dye molecules in the electron transfer reaction [23,24]. For example, several articles report the electron-donating character of the singlet excited states of phthalocyanines with respect to methylviologene [23,25]. In contrast, some authors claim that in the good photosensitizers, the triplet state must be involved in the process [24].

The long lifetimes could also indicate an intensive, intersystem crossing transition which could lead to a high population of the dye triplet state (unpublished data— will be the subject of a forthcoming paper). Since we observed high ESR signals for Mg–TPP and Zn–TPP as the final stage of the electron transport between the dyes and AQ, the recombination process either with in singlet or the triplet state, was a slow process. The Pb–TPP dye was very sensitive for triplet state generation due to spin-orbit coupling in the presence of the heavy atom [24]. Its rapid fluorescence quenching ($k_q = 1.3 \times 10^{14}$ M^{-1} s^{-1}, $k_{ET} = 4.1 \times 10^9$ s^{-1}) could then be due to quenching by AQ and also to the effective intersystem crossing of the triplet state. The low ESR amplitude of Pb–TPP thus indicates the fast charge recombination occuring in the electron donor-acceptor chain with participation of both the singlet and triplet states (unpublished data).

Our results presented in this paper support our photovoltage/photocurrent observation obtained for a PEC based on porphyrin dyes [1,2]. The high ability of Zn–TPP and Mg–TPP to generate photocurrent can be explained not only by the dye structure as indicated previously [19] but also by a slow charge recombination process. In contrast rapid charge recombination in Pb–TPP could be the reason for its poor photoconversion behavior in the PEC.

Results of both fluorescence quenching and ESR explain a difference in photocurrent generation in a photoelectrochemical cell between metal-free porphyrin and its metallic analogues [1,2]. This study seems to be essential for understanding and the improvement of photoconversion in the PEC based on organic materials.

Acknowledgements

This paper is supported by the State Committee for Scientific Research, grant No. 5 P03B 146 20 (D.W, J.Ł) and by Poznan University of Technology, grant- TB 62-176/02-DS (H.M).

References

[1] Wróbel D, Łukasiewicz J., Goc J., Waszkowiak A., Ion RM. Photocurrent generation in an electrochemical cell with substituted metalloporphyrins. Journal of Molecular Structure 2000;555:407–17.

[2] Wróbel D, Goc J, Ion RM. Photovoltaic and spectral properties of tetraphenyloporphyrin and metallotetraphenyloporphyrin dyes. Journal of Molecular Structure 1998;450:239–46.

[3] Wróbel D, Boguta A, Ion RM. Photovoltaic effects in metal-free and substituted metallic sulfophtalocyanines in the photochemical cell. Journal of Molecular Structure 2001;595:127–38.

[4] Wróbel D, Boguta A, Ion RM. Mixtures of synthetic organic dyes in a photoelectrochemical cell. Journal of Photochemistry and Photobiology A: Chemistry 2001;138: 7–22.

[5] Wöhrle D, Kreienhoop L, Schlettwein D. Phthalocyanines and related macrocycles in organic photovoltaic junctions. In: Leznoff Lever, editor. Phthalocyanine—properties and applications. New York: VCH-Publishers; 1996. p. 219–84.

[6] Mayer JP, Schlettwein D, Wöhrle D, Jeager NI. Charge transport in thin films of molecular semiconductor as investigated by measurements of thermoelectric power and electrical conductivity. Thin Solid Films 1995;258:317–24.

[7] Naito H, Kishimoto K, Nagase T. Transient photoconductivity study of localized-state distributions in metallophthalocyanines. Thin Solid Films 1998;331:82–8.

[8] Michaeli S, Hugerat M, Levanon H, Bernitz M, Natt A, Neumann R. Control of porphyrin orientation in thermotropic liquid crystals by molecular design—a time resolved EPR study. J Am Chem Soc 1992;114:3612–5.

[9] Ptak A, Der A, Toth-Boconadi R, Naser NS, Fr^{1}ckowiak D. Photocurrent kinetics (in the microsecond time range) of chlorophyll a, chlorophyll b and stilbazolium merocyanine solution in nematic liquid crystal located in an electrochemical cell. J Photochem Photobiol A Chemistry 1997;104:133–9.

[10] Van Zandvoort MAMJ, Wróbel D, Lettinga P, Van Ginkel G, Levine YK. Chlorophylls in polymers. State of chlorophyll in unstretched polymer systems. Photochem Photobiol 1994;62:279–89.

[11] Fletcher AN, Bliss DE, Kauffman JM. Lasing and fluorescent characteristics of nine, new, flashlamp—pumpable, coumarin dyes in ethanl and ethanol:water. Optics Communications 1983;47:57–61.

[12] Moan J, Kvam E, Hoving E, Berg K. In: Riklis E, editor. Photobiology. New York: Plenum; 1991, p. 821.

[13] Fessenden RW, Kamat PV. Rate constants for charge injection from excited sensitizer into SnO2, ZnO, and TiO2 semiconductor nanocrystallites. J Phys Chem 1995; 99:12902–6.

[14] Ricchelli F, Gobbo S. Porphyrins as fluorescent probes for monitoring phase transitions of lipid domains in biological membranes. Factors influencing the microenvironment of haematoporphyrin and protoporphyrin in liposomes. Journal of Photocherm and Photobiol B: Biology 1995;29: 65–70.

[15] Zimmermann J, von Gersdorff J, Kurreck H, Roeder B. Determination of the electron transfer parameters of covalently linked porphyrin-quinone with mesogenic substituents—optical spectroscopic studies in solution. Journal of Photochem and Photobiol B:Biology 1997;40:209–17.

[16] Vernon LP, Seely GR. The chlorophylls. New York, London: Academic Press; 1996.

[17] Gouterman M. In: Dolphin D. The porphyrins, vol. III. New York: Academic Press; 1978.

[18] Haifang M, Huihua D, Hongwu L, Yaochun S, Zuhong L, Huijun X. Photosensitization of TiO_2 semiconductor with porphyrin. Journal of Photochem and Photobiol A: Chemistry 1998;114:209–12.

[19] Wróbel D, Boguta A. Porphyrins and phthalocyanines—correlation of molecular structure and photoactivity, molecular low dimensional and nanostructured materials for advanced applications. In: Graja A, Agronovich VM, Kajzar F, editors. NATO Sciences Series Volume. Kluwer Publ.; 2002. p. 71–80.

[20] Assour JM, Harrison SE. On the origin of unpaired electrons in metal-free phtalocyanine. The Journal of Physical Chemistry 1964;68:872–8.

[21] Wróbel D, Hany¿ I, Planner A, Dudkowiak A, Sarna T. Energy deactivation pathways of porphyrins and dopa melanin in polyvinyl alcohol systems. J Photochem and Photobiol 1998;47:165–72.

[22] Wróbel D, Hanyż I, Bartkowiak R, Ion RM. Fluorescence and time-resolved delayed luminescence of porphyrins in organic solvents and polymer matrices. J Fluorescence 1998;8(3):191–8.

[23] Ohtani H, Kobayashi T, Tanno T, Yamada A, Wöhrle D, Ohno T. Efficient photoreduction of methylviologen by metallophthalocyanine as sensitizer. Photochem Photobiol 1986;44:125–30.

[24] Azenha EG, Serra AC, Pineiro M, Pereira MM, de Melo JS, Arnaut LG, et al. Heavy-atom effects on metalloporphyrins and polyhalogenated porphyrins. Chemical Physics 2002;280:177–90.

[25] Tanno T, Wöhrle D, Kaneko M, Yamada A. Ber. Bunsennnges. Rapid photoreduction of methyl viologen with visible light using methal-phthalocyanines as sensitizers. Phys Chem 1980;84:1032–4.