

A comparative study of water soluble 5,10,15,20-tetrakis(2,6-dichloro-3-sulfo-phenyl)porphyrin and its metal complexes as efficient sensitizers for photodegradation of phenols

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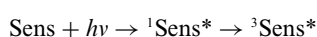
Received 31st May 2005, Accepted 9th June 2005

First published as an Advance Article on the web 28th June 2005

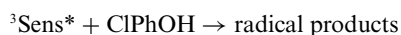
5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfo-phenyl)porphyrin and its tin and zinc complexes were synthesized with high yields and fully characterized. The corresponding water-soluble 5,10,15,20-tetrakis(2,6-dichloro-3-sulfo-phenyl)porphyrins were obtained by hydrolysis with water. An extensive photophysical study of the new water soluble porphyrinic compounds was carried out including absorption and fluorescence spectra, fluorescence quantum yields, triplet absorption spectra, triplet lifetimes, triplet and singlet oxygen quantum yields. These sensitizers were successfully used in the photodegradation of 4-chlorophenol and 2,6-dimethylphenol. A comparison is made of their efficiencies, and some mechanistic considerations are highlighted.

1 Introduction

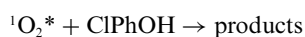
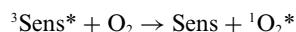
Phenols are major pollutants. Particular concern has been expressed on chlorophenols which are widely used as fungicides, herbicides, wood-protection agents and are also produced in the Kraft bleaching of paper pulp.¹ In addition, other substituted phenols also have negative environmental effects, and serious concerns have been expressed about the levels of these compounds in waste and groundwater. Several methods have been employed to degrade these pollutants.²⁻⁶ Photooxidation appears to be particularly valuable,⁷ and in the last decade much effort has been devoted to the development of new and clean sensitizers that use visible light to degrade these compounds to readily biodegradable photoproducts.⁸⁻¹⁰ Degradation studies of phenols in the presence of different singlet oxygen sensitizers have been reported, and provide important mechanistic information.¹¹⁻¹³ For optimum efficiency, photosensitizers should have as broad UV/visible absorption bands as possible. Porphyrins and phthalocyanines have strong visible absorptions¹⁴ and are particularly good candidates for such photooxidation of phenols.¹⁵⁻¹⁷ Triplet states of these sensitizers are implicated, with reactions going *via* both Type I and Type II mechanisms.¹⁸



Type I mechanism



Type II mechanism



The heavy atom effect induced by the presence of chlorine makes 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin and its metal derivatives particularly good photosensitizers for singlet oxygen production¹⁹⁻²¹ as shown by their use as photooxidants of phenols and naphthols.²² For applications in waste water treatment, soluble derivatives, such as the 3-sulfo-phenyl salts, are particularly valuable, and we have shown that iron 5,10,15,20-tetrakis(2,6-dichloro-3-sulfo-phenyl)porphyrin is a powerful sensitizer for the photooxidation of 4-chlorophenol.¹⁷ The products depend on the presence or absence of oxygen, with the reaction involving both Type I and Type II mechanisms.

To test the role of the metal on these processes, we have extended the study to the free base of this water soluble porphyrin, **1**, and to the newly synthesized zinc, **2**, and tin, **3**, derivatives. Relevant photophysical parameters are presented, reaction products, kinetics and mechanistic details of the photosensitized degradation of 4-chlorophenol (4-CP) and 2,6-dimethylphenol (2,6-DMP) are reported.

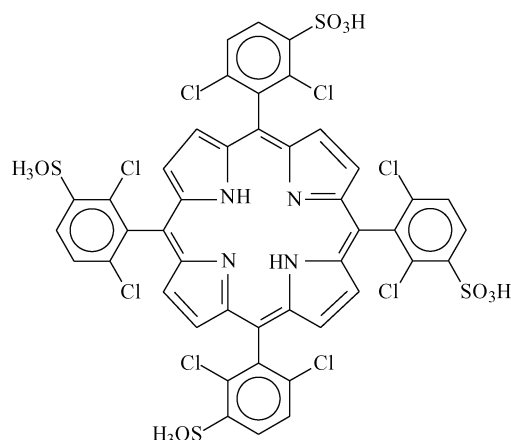
2 Experimental

2.1. Chemicals

4-Chlorophenol (4-CP) (Aldrich) *p*-benzoquinone (BQ) (Aldrich Chem p.a.), *p*-hydroquinone (HQ) (Merck p.a.), 2,6-dimethylphenol (2,6-DMP) (Aldrich), sodium azide (NaN₃), dimethylthiourea (Aldrich) and methanol (HPLC analysis grade, Merck) were used as received. 2,6-Dimethylbenzoquinone (2,6-DBQ) was synthesized using a literature method.⁵ All solvents used in the synthesis of the photosensitizer were purified before use. Solutions were prepared with doubly distilled water, either equilibrated with air or bubbled with nitrogen for 30 min at room temperature.

2.2. Porphyrin and metalloporphyrin synthesis

The synthesis of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin and 5,10,15,20-tetrakis(phenyl)porphyrin (TPP) has been described elsewhere.²³ 5,10,15,20-Tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin (**1**) was synthesized according to our previously described method^{17,23} (Scheme 1).



Scheme 1

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin.

Analysis. Calcd. for $C_{44}H_{18}N_4O_8Cl_{12}S_4$: C, 41.1; H, 1.4; N, 4.4. Found: C, 40.7; H, 1.6; N, 4.3. MS (FAB), $[M^+]$ 1279. 1H NMR ($CDCl_3$), (δ): 8.64 (8 H, s); 8.59 (4 H, d, $J = 8.6$ Hz); 8.05 (4 H, d, $J = 8.6$ Hz); -2.35, (2 H, s).

Preparation of metal complexes.

5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Zn(II). 5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Zn(II) was prepared according to the method of Adler and co-workers.²⁴ 5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrin (50 mg; 0.039 mmol), zinc(II) acetate (0.043 g; 0.195 mmol) in *N,N*-dimethylformamide (15 mL) were stirred at 150 °C for 4 h. The reaction was monitored by UV-visible spectroscopy until the 4 Q bands are transformed into the 2 Q bands typical of the corresponding porphyrin metal complexes. After solvent evaporation the residue was extracted with chloroform and washed (3 times) with water. The solution was dried with $MgSO_4$ and evaporated. The solid was dried, yielding 5,10,15,20-tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Zn(II) (48 mg, 0.035 mmol, 90%). 1H NMR ($CDCl_3$), (δ): 8.62 (8 H, s); 8.57 (4 H, d, $J = 8.6$ Hz); 8.03 (4 H, d, $J = 8.6$ Hz).

5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Sn(IV) chloride. 5,10,15,20-Tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Sn(IV) was prepared according to the method of Whitten and co-workers.²⁵ For this, 5,10,15,20-tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrin (50 mg; 0.039 mmol), tin(II) chloride (0.044 g; 0.195 mmol) were dissolved in pyridine (15 mL) and stirred at 150 °C for 10 h in nitrogen atmosphere. The reaction was monitored by

UV/visible spectroscopy until the 4 Q bands are transformed into the 2 Q bands typical of porphyrin metal complexes. Finally, the reaction was stirred in contact with air for 4 h to promote the oxidation from Sn(II) to Sn(IV). After solvent evaporation the residue was extracted with chloroform and washed (3 times) with water. The solution was dried with $MgSO_4$ and evaporated. The solid was dried, yielding 5,10,15,20-tetrakis(2,6-dichloro-3-chlorosulfophenyl)porphyrinate Sn(II) chloride (46 mg, 0.033 mmol, 85%). 1H NMR ($CDCl_3$), (δ): 8.88 (8 H, s); 8.63 (4 H, d, $J = 7.2$ Hz); 8.07 (4 H, d, $J = 7.2$ Hz).

General method for hydrolysis of chlorosulfonyl compounds to sulfonic acids.

Suspensions of the above chlorosulfonated porphyrin or metalloporphyrins (80 mg) in water were refluxed for 12 h. The resulting solution was concentrated by rotary evaporation and purified using an AMICON-Stirred Ultrafiltration Cell (model 8200). After filtration (3 times) the solutions were concentrated by evaporation and the sulfonic acid porphyrin derivatives precipitated with acetone. The required solids 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin (TDCPPS, **1**), 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinate Zn(II) (ZnTDCPPS **2**), and 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinate Sn(IV) chloride (SnTDCPPS, **3**) were isolated by filtration and dried at 100 °C, yielding 90, 89, and 90%, respectively.

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin, 1. 1H NMR (CD_3OD), (δ): 8.6–9.0 (8 H, m); 8.30–8.50 (4 H, m); 7.90–8.05 (4 H, m); -2.35, (2 H, s).

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinate Zn(II), 2. 1H NMR (CD_3OD), (δ): 8.68–9.0 (8 H, m); 8.53 (4 H, d, $J = 8.4$ Hz); 8.03 (4 H, d, $J = 8.4$ Hz).

5,10,15,20-Tetrakis(2,6-dichloro-3-sulfophenyl)porphyrinate Sn(IV) chloride, 3. 1H NMR (CD_3OD), (δ): 8.87–8.89 (8 H, m); 8.63 (4 H, d, $J = 7.5$ Hz); 8.03 (4 H, d, $J = 7.5$ Hz).

Photophysical data for all the above compounds are presented in Table 1.

2.3. Equipment

1H NMR spectra were recorded on a 300 MHz Bruker-AMX. Mass spectra were obtained through the MS services of the University of Aveiro (Portugal) and University of Wales, Swansea. UV-visible absorption spectra were recorded in quartz cells on a Shimadzu 2100 spectrometer. The molar absorption coefficients were determined using buffered aqueous solutions (KH_2PO_4 -NaOH, pH 7.4).

The fluorescence measurements were made with a SPEX Fluorolog 3-22 spectrofluorimeter, equipped with a 300 W xenon lamp as excitation source. Fluorescence quantum yields were determined for deaerated aqueous solutions of the porphyrins. 5,10,15,20-Tetrakisphenylporphyrin (TPP) in toluene was used as fluorescence standard ($\Phi_F = 0.11$)²⁶ for the determination of the fluorescence quantum yield of TPPS. This was calculated by comparing its spectrally integrated emission to that of the reference solution after correction for the difference in refractive index of toluene and water ($\eta_{\text{toluene}} = 1.49693$ and $\eta_{\text{water}} = 1.332988$).²⁷ The fluorescence quantum yields of the sensitizers **1**, **2** and **3** in deaerated solutions in water were measured relative to

Table 1 Absorption and fluorescence bands, lowest excited singlet energies (E_s) and fluorescence quantum yields of sensitizers **1**, **2** and **3** in aqueous buffer solution (pH 7.4)

Porph.	Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/M^{-1} \text{cm}^{-1}$)					Fluorescence $\lambda_{\text{max}}/\text{nm}$ 25 °C		$E_s/\text{kJ mol}^{-1}$	Φ_F (degassed)
	$Q_x(0-0)$	$Q_x(1-0)$	$Q_y(0-0)$	$Q_y(1-0)$	B(0-0)	Q(0-0)	Q(0-1)		
TPPS ₄	634 (1100)	554 (3100)	578 (2400)	518 (5800)	413 (2×10^5)	641	697	187.6	5.4×10^{-2}
TDCPPS, 1	640 (380)	584 (1800)	554 (860)	517 (4500)	416 (1×10^5)	643	704	186.5	1.3×10^{-3}
ZnTDCPPS, 2	610 (1200)	558 (5600)	—	—	424 (1.4×10^5)	612	658	195.8	3.5×10^{-3}
SnTDCPPS, 3	592 (470)	556 (4900)	516 (1400)	—	420 (1.2×10^5)	624	649	196.9	1.5×10^{-3}

that of TPPS. All the solutions were adjusted to 0.02 absorbance at the Soret band.

The transient absorption spectra were measured with an Applied Photophysics LKS 60 nanosecond laser flash photolysis kinetic spectrometer, using the third harmonic (355 nm) of a Spectra-Physics Quanta Ray GCR 130–01 Nd:YAG laser for excitation, a Hamamatsu 1P28 photomultiplier and a Hewlett-Packard Infinium oscilloscope (1 GS s^{-1}). Flash photolysis triplet lifetime measurements were made on aerated and argon saturated solutions (*ca.* $1 \times 10^{-5} \text{ M}$), with an absorbance of 0.20 at the excitation wavelength. The triplet–triplet absorption at 460 nm was used for lifetime measurements. All the decays gave good monoexponential fits. The effect of oxygen as quencher of the triplet state of the photosensitizers **1–3** in aqueous solutions was studied in air-equilibrated ($[\text{O}_2] = 2.9 \times 10^{-4} \text{ M}$)²⁷ and deaerated solutions. The effect of 4-CP as a quencher of the excited state of the photosensitizers **1–3** was studied in deaerated solutions.

Room-temperature singlet-oxygen phosphorescence was measured by two independent methods, both using excitation by the third harmonic (355 nm) of a Nd:YAG laser. The absorbance of the sensitizers was adjusted to 0.20 at the excitation wavelength, under conditions such that there were no indications of aggregation of the porphyrins. For the studies carried out in Coimbra, the singlet oxygen emission at 1270 nm was detected by a Hamamatsu R5509-42 photomultiplier, cooled to 193 K in a liquid nitrogen chamber (Products for Research model PC176TSCE005), following laser excitation of aerated D_2O solutions using an adapted Applied Photophysics flash kinetic spectrometer, which allows for the spectral identification of the singlet oxygen phosphorescence and for the measurement of its lifetime in the nanosecond and microsecond range. The modification of the spectrometer involved the interposition of a Melles Griot dielectric mirror (08MLQ005/345), that reflects more than 99.5% of the incident light in the 610–860 nm range, and a Scotch RG665 filter. A 600 line diffraction grating was mounted in the place of the standard diffraction grating of the spectrometer. The filters employed are essential to eliminate from the infrared signal all the first harmonic contributions from the sensitizer emission in the 500–800 nm. To validate this technique, singlet oxygen ($^1\Delta_g$) yields and lifetimes were also obtained at Daresbury using a liquid nitrogen cooled Applied Detector Corporation 403HS Germanium Detector–Amplifier close-coupled to a laser photolysis cell in right-angle geometry. A 1 mm thick, 20 mm diameter piece of AR-coated silicon (II–IV Inc) was placed between the diode and cell to act as cut-off filter below 1100 nm. The 403HS power supply bias voltage was operated at 450 V. The amplifier output was AC coupled to a transient digitizer, as described in detail elsewhere.^{28–30} The quantum yield of singlet oxygen formation was determined by comparison of the initial emission intensity for optically matched solutions at the excitation wavelength of 532 nm using TPPS in D_2O ($A_{532} = 0.20$; $\cong 10^{-5} \text{ M}$, $\Phi_A = 0.64$)³¹ as standard. A reasonable agreement was obtained between the singlet oxygen yields using the two experimental set-ups.

Measurements of triplet yields were carried out by laser flash photolysis on aqueous porphyrin solutions ($7 \times 10^{-6} \text{ M}$) at pH 7.4 using the 355 nm line of a Nd:YAG laser. Triplet state extinction coefficients (ϵ_T) were calculated by the singlet depletion method.⁴⁸ Triplet formation quantum yields (Φ_T) were obtained by the comparative technique using TPPS as standard ($\epsilon_T = 6.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 460 nm, $\Phi_T = 0.61$).^{38,48,49}

Continuous irradiation at 350 nm of aerated solutions of sensitizers **1, 2** and **3**, with 4-CP was carried out using a semi-microreactor, equipped with a mercury lamp. The reaction was monitored both by UV-visible spectroscopy and HPLC analysis. The pH was monitored throughout the irradiation time using a Crison micro-pH 2000 apparatus. For mechanistic studies, an aerated solution of photosensitizer **1** (10^{-4} M) and 4-CP ($5 \times 10^{-4} \text{ M}$) was irradiated at 350 nm in the presence of sodium azide

(10^{-3} M) or thiourea (10^{-3} M). In the case of 2,6-dimethylphenol ($2 \times 10^{-4} \text{ M}$), the determination of the quantum yields at 415 nm was carried out by using a parallel beam obtained from a Schoeffel monochromator connected to a xenon lamp (1600 W). The reactor was a quartz cell of 1 cm path length. The photon flux was evaluated by means of classical ferrioxalate actinometry.³²

The photostability of the sensitizer and 4-CP or 2,6-DMP was studied. The analysis of degradation products was made using HPLC with an Agilent Technologies chromatography system equipped with a UV-visible 1100 Series variable wavelength detector, G1314 A0 and 1100 Iso pump, G1310–64001, with detection set at 280 nm. A reverse phase column (Zorbax ODS, 4.6 mm \times 250 mm, 5 μm) was used with a mixture of MeOH– H_2O (60 : 40 v/v) as eluent, in isocratic mode with a flow rate of 1 mL min^{-1} . In the case of 2,6-DMP, the kinetic degradation was followed by using a Hewlett-Packard Liquid Chromatography system (HP1050) equipped with a mono-channel UV-visible detector and an automatic injector. The experiments were performed using a reverse phase Merck column (Spherisorb ODS-2, 4.6 mm \times 250 mm, 5 μm) and UV detection at 280 nm. The flow rate was 1.0 mL min^{-1} and the injected volume was 50 μL . The elution was accomplished with water with acetic acid (0.1%) and acetonitrile (60 : 40 v/v).

The formation of the 4-CP photoproducts (benzoquinone (BQ) and hydroquinone (HQ)) and of 2,6 DMP photoproducts (2,6 dimethylbenzoquinone), were monitored against external standards.

3 Results

3.1. Photophysical properties of the sensitizers

The knowledge of the photophysical properties of the water-soluble porphyrins **1, 2** and **3**, is important to establish the mechanism of photodegradation of phenols. We have measured the absorption and emission spectra of these sensitizers under different aqueous conditions, their triplet lifetimes in the presence and absence of oxygen in the presence of 4-chlorophenol. Their singlet-oxygen and triplet quantum yields were also obtained.

It is well established that the concentration of TPPS and the pH of aqueous solutions alters its degree of protonation³³ and of aggregation, and that these have strong effects on the absorption and emission spectra, Φ_T and Φ_A .^{34,35} Although the study of aggregate formation is not the main goal of this work, absorption spectra of all compounds were measured over a very wide range of concentrations (10^{-4} to 10^{-8} M) at pH 7 and no modifications of the spectral shape or extinction coefficients were observed. We note, in particular, the absence of the bands at 489 nm and 710 nm, typical of aggregates with TPPS.³⁴

As shown in Fig. 1, absorption spectra of TDCPPS do show a red shift in the Soret band and transformation of the 4 free base Q bands to 2 on reducing the pH, in agreement with the protonation of the porphyrin nitrogens in acid solution. In the above range of concentrations no modification in the absorptions spectra of TDCPPS were observed, even at pH 2, this is probably due to the lower TDCPPS pK (1.4) than TPPS (4.7) and also due to the presence of bulky *ortho*-chloro groups in the phenyl rings of the porphyrin structure.

The fluorescence spectra of the sensitizers **1, 2** and **3** were measured in buffered aqueous solutions (KH_2PO_4 –NaOH, pH = 7.4, absorbance 0.02 at 413 nm), with excitation wavelength at 413 nm, Fig. 2. The shape and positions of the emission bands 641 and 697 nm of porphyrin **1** are typical of the non-aggregated, free base porphyrins.³³ With the corresponding metalloporphyrins, Zn(II)TDCPPS, **2**, and Sn(IV)TDCPPS, **3**, the shapes of the bands are significantly different from the free base porphyrin TDCPPS, **1**, as predicted theoretically,^{36,37} with the intensity of the (0,0) band lower than the (0,1)

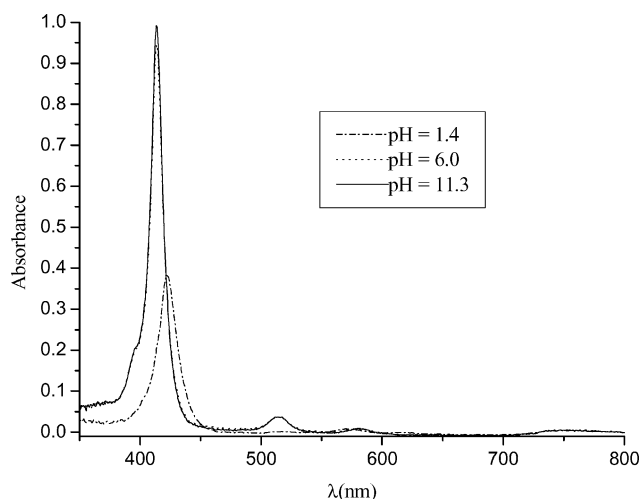


Fig. 1 Absorption spectra of TDCPPS in aqueous solutions (1×10^{-5} M) at pH 1.4, 6.0 and 11.3.

band in the metallated porphyrins, in agreement with the mirror-image relationship with the corresponding absorption spectra. Fluorescence excitation spectra were obtained for all the sensitizers and for TPPS, and the good agreement with the corresponding absorption spectra further confirms the purity of the samples.

Literature data on the fluorescence quantum yield (Φ_F) of TPPS show a wide scatter, with values ranging from $\Phi_F = 0.060 \pm 0.005$ to 0.16.^{26,38,31} Such a variation, which may be a consequence of both pH effects and aggregation, has prompted us to make a reliable determination of the fluorescence quantum yield of TPPS using TPP in toluene ($\Phi_F = 0.11$)²⁶ as standard. The fluorescence quantum yield of TPPS was obtained by comparison between the integrated emission spectra of TPPS and the reference solution, after correcting for differences in the absorbance of the solutions and refractive index of the solvents. We obtained $\Phi_F = 0.054 \pm 0.005$, in very good agreement with Braslavsky and Gensch³⁸ who used tetrapropylporphycene in toluene as standard. It is worth noting that some of the other reported Φ_F values are not accompanied by the description of the specific conditions of the experiment, such as pH and buffer, which may have significant effects on quantum yields, and it is important to emphasize that we observed significant differences in the emission intensity of TPPS as a function of properties of the solution. For example, we observed rather disperse values when we adjust the pH to 7 by adding few drops of a concentrated solution of NaOH, while when the pH was adjusted with NaHCO_3 , a total quenching of the fluorescence was observed. With the phosphate buffer system mentioned above, we obtained reproducible fluorescence quantum yields using freshly prepared solutions at pH 7.4, and recommend this to be used as standard for this compound.

This TPPS (*ca.* 10^{-7} M) solution buffered at pH 7.4, was used as the reference for the determination of the fluorescence quantum yields of **1**, **2** and **3** in aqueous solutions and the data are presented in Table 1. Although there is a significant difference between Φ_F for TPPS and the corresponding *o*-chlorinated porphyrin, TDCPPS, **1**, the central metal did not have any significant effect on. This is consistent with photophysical measurements on other *o*-halogenated porphyrins, where Φ_F was found to decrease in the presence of halogen atoms in the *o*-positions of the phenyl ring, but was rather insensitive to the effect of the central metal²⁰ reflecting the importance of through-space interactions on the heavy atom effect.

The triplet-triplet absorption spectra of the sensitizers were obtained by laser flash photolysis, and show a common band with a maximum at 460 nm, typical of porphyrinic compounds, Fig. 3. No other transient species were observed.

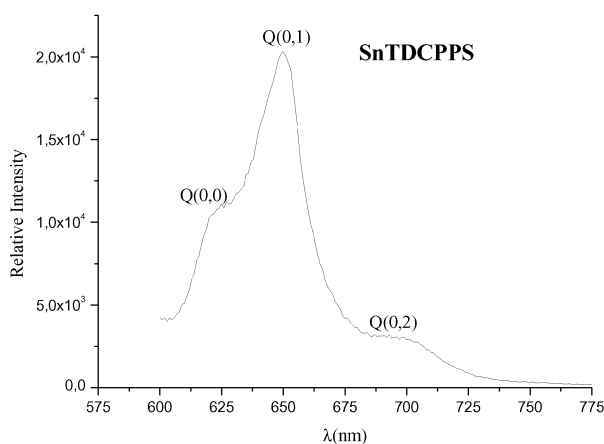
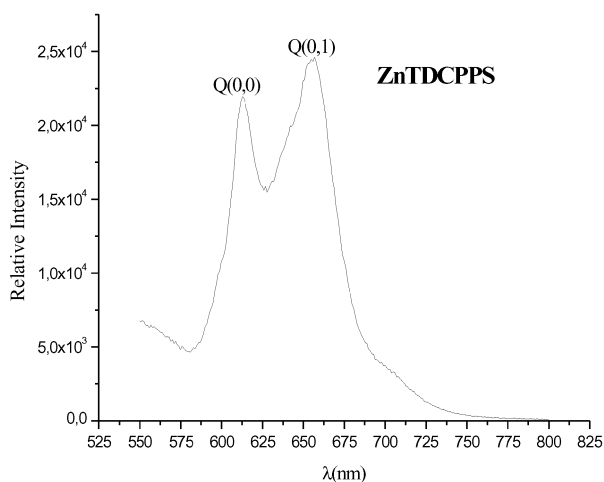
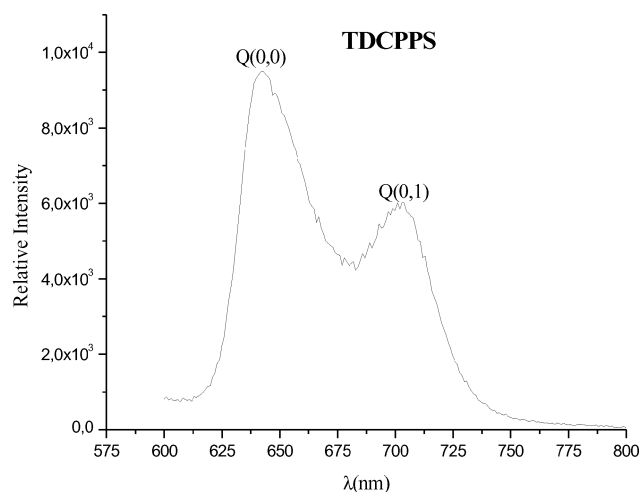


Fig. 2 Fluorescence spectra of sensitizers TDCPPS, ZnTDCPPS, SnTDCPPS in aqueous solutions.

The triplet-state lifetimes of porphyrin **1** and metalloporphyrins **2** and **3** in aqueous solutions, pH = 7.4 excited at 355 nm ($A_{355} = 0.20$) were measured at 460 nm under air and argon atmospheres, and from these the bimolecular rate constants (k_q) for the quenching of the triplet states of sensitizers by molecular oxygen ($^3\text{O}_2$) were calculated using the concentration of oxygen in water (2.9×10^{-4} M),²⁷

$$k_q = (1/\tau_{\text{O}_2} - 1/\tau_{\text{N}_2})/[\text{O}_2]$$

Table 2 presents the values obtained for lifetimes and rate constants. Following the classical work of Porter and co-workers³⁹ it is believed that when sufficiently exothermic triplet-triplet energy transfers to molecular oxygen occur, k_q

Table 2 Triplet lifetimes in aerated and deaerated aqueous solutions, with respective oxygen quenching rate constants, triplet and singlet oxygen quantum yields

Sensitizer	$\tau_{O_2}/\mu\text{s}$	$\tau_{N_2}/\mu\text{s}$	$k_q(O_2)/M^{-1} s^{-1}$	$\epsilon^*_T/M^{-1} cm^{-1}$	ϕ_{Δ}^a	ϕ_{Δ}^b	ϕ_T^c	S_{Δ}
TDCPPS, 1	4.21 ± 0.06	397.4 ± 3.5	8.39×10^8	6.2×10^4	0.73 ± 0.10	0.76 ± 0.11	0.88	0.83
ZnTDCPPS, 2	7.93 ± 0.09	368.7 ± 6.4	4.41×10^8	6.5×10^4	0.51 ± 0.07	0.59 ± 0.09	0.92	0.55
SnTDCPPS, 3	10.46 ± 0.09	432.4 ± 14.0	3.33×10^8	6.2×10^4	0.51 ± 0.12	0.46 ± 0.07	0.83	0.61

^a Obtained in Coimbra using infrared photomultiplier as detector. ^b Obtained in Daresbury using a germanium photodiode. ^c Estimated error 15%.

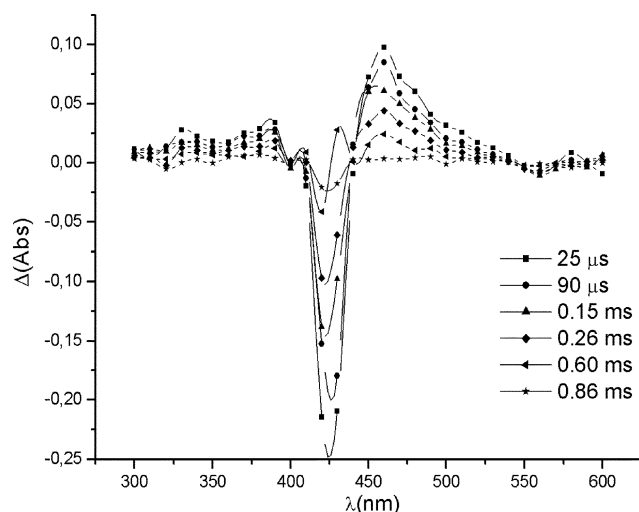
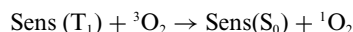


Fig. 3 Transient absorption spectra observed following laser flash photolysis at 355 nm of an argon-saturated solution of sensitizer **2** in water.

attains the statistical limit of one ninth of the diffusion rate constant (k_{diff}).



Taking $k_{diff} = 9.8 \times 10^9 M^{-1} s^{-1}$ in water, the quenching rate constants obtained in this work are lower than expected for this mechanism ($1.0 \times 10^9 M^{-1} s^{-1}$). A similar effect has already been observed for the quenching of *o*-chlorinated porphyrins, chlorins and bacterichlorins by oxygen in toluene solutions.^{19,40,41} The oxygen quenching rate constants measured for the chloro-sulfonated porphyrins in aqueous solution in this work are in very good agreement with the rates measured for the analogous chlorinated porphyrins in toluene^{19,40} $k_q(\text{TDCPPS}) = 8.4 \times 10^8$ vs. $k_q(\text{TDCPP}) = 8.6 \times 10^8 M^{-1} s^{-1}$ and $k_q(\text{ZnTDCPPS}) = 4.4 \times 10^8$ vs. $k_q(\text{ZnTDCPP}) = 6.2 \times 10^8 M^{-1} s^{-1}$, which is consistent with the expectation that the sulfonic groups do not contribute to the Franck–Condon factors associated with energy transfer. The triplet state quenching mechanism was further explored using room-temperature, time-resolved singlet oxygen phosphorescence measurements, as described below.

3.2. Singlet oxygen emission

Singlet oxygen quantum yields following laser excitation of sensitizer solutions can be obtained from the comparison of singlet oxygen phosphorescence intensity at 1270 nm with that of an optically matched reference sensitizer. For TPPS in water at pH 7, the literature ϕ_{Δ} values, 0.62–0.64, are identical within the experimental error,^{31,35,42–44} and we have used the value³¹ of 0.64 for this sensitizer in deuterated water at pH 7.4. Two independent detection systems were used, with data from that in Coimbra using an infrared photomultiplier, which had not previously been verified for this type of measurements, compared with those of a well-established set-up using a germanium diode. In the studies using the infrared sensitive photomultiplier, the decays of the singlet oxygen emissions were measured at 1270 nm with the reference and with our sensitizers, with matched absorbances at

the excitation wavelength, and were extrapolated to time-zero at a given laser intensity.

Different laser intensities were employed and the quantum yields were obtained from the ratios of the slopes obtained with different sensitizers and TPPS as standard. The singlet oxygen quantum yields of sensitizers **1**, **2** and **3** in D_2O solutions are reported in Table 2.

Measurements were also made using a germanium diode detector, and are also given in Table 2. Reasonable agreement is observed between results using the two detectors, validating the infrared photomultiplier system. It can be noted that absolute uncertainties in measurements of singlet oxygen quantum yields range typically between $\pm 7\%$ and $\pm 15\%$,⁴² and the differences between our results using the independent set-ups are well within these limits.

3.3. Phenol photodegradation

Photodegradation kinetics of 4-CP and 2,6-dimethylphenol were studied with sensitizers **1**, **2** and **3** by following the changes in the absorption spectra with the irradiation time or HPLC. The absorption spectrum of 4-CP is in the wavelength range between 240 and 300 nm with a maximum at 280 nm, and during irradiation, the most important changes were observed in this region, with a significant decrease in the band at 280 nm and a concomitant increase in absorption in the region between 240–265 nm.

The HPLC analysis against standards of the reaction mixture of all the systems after 7 h of irradiation indicated that the main photoproducts were *p*-benzoquinone and *p*-hydroquinone with 4-CP and mainly 2,6-dimethylbenzoquinone (2,6-DBQ) with 2,6-DMP. With longer irradiation time several secondary photoproducts were formed, but these have not yet been identified.

Despite of the overlapping of absorption spectrum of 4-CP and the main photoproducts bands, *p*-benzoquinone ($\lambda = 245$ nm) and *p*-hydroquinone ($\lambda = 288$ nm), it was possible to carry out a spectral deconvolution in order to separate the absorbances of the reagents and the photoproducts as described in ref. 45. This was done with the program SPECPEAK, version 2.0 assuming Gaussian band shapes. The most interesting Gaussian bands from the point of view of their physical meaning are at 245, 280, and 286 nm. As anticipated, the height of the Gaussian band at 280 nm (attributed to 4-CP absorption) decreases exponentially with the irradiation time while those of *p*-benzoquinone and *p*-hydroquinone (measured at 245 and 286 nm respectively) increase. The exponential decay of the Gaussian band at 280 nm for the system 4-CP ($5 \times 10^{-4} M$) using TDCPPS ($10^{-4} M$) as sensitizer, follows first order kinetics. The calculated rate constants for all the systems studied, using different sensitizers, are collected in Table 3.

To corroborate these calculations, the same deconvolution treatment was done for the system 4-CP sensitized by FeTDCPPS and the kinetic constant $k = 1.2 \times 10^{-4} s^{-1}$ was obtained. This is in agreement with the value ($k = 9.5 \times 10^{-5} s^{-1}$) obtained by HPLC analysis.¹⁷

In order to design more efficient photosensitizers for the oxidation of phenols, it is important to understand the mechanism involved in the reactions described above. Four different

Table 3 Kinetic constants for sensitized photodegradation reaction of 4-CP obtained from the exponential decrease of Gaussian band at 280 nm deconvoluted as described in ref. 45

Porphyrin	$k(4\text{-CP})/\text{s}^{-1}$
TDCPPS, 1	2.7×10^{-5}
ZnTDCPPS, 2	3.7×10^{-4}
SnTDCPPS, 3	1.3×10^{-3}

Table 4 Quenching constants of triplet state of sensitizers 1, 2 and 3 by 4-CP in argon saturated aqueous solutions

Sensitizer	$k_q(4\text{-CP})/\text{M}^{-1} \text{s}^{-1}$
TDCPPS, 1	$\leq 10^6$
ZnTDCPPS, 2	1.9×10^7
SnTDCPPS, 3	2.2×10^7

processes have been followed: (i) singlet oxygen formation with all the photosensitizers 1, 2 and 3, Table 2; (ii) laser flash photolysis studies of sensitizer triplet state decay in the presence and absence of oxygen, Table 2; (iii) laser flash photolysis of the sensitizer triplet states in the presence of phenols, Table 4; (iv) photolysis of 4-CP using sensitizer 1, with radical and oxygen singlet traps, Fig. 4.

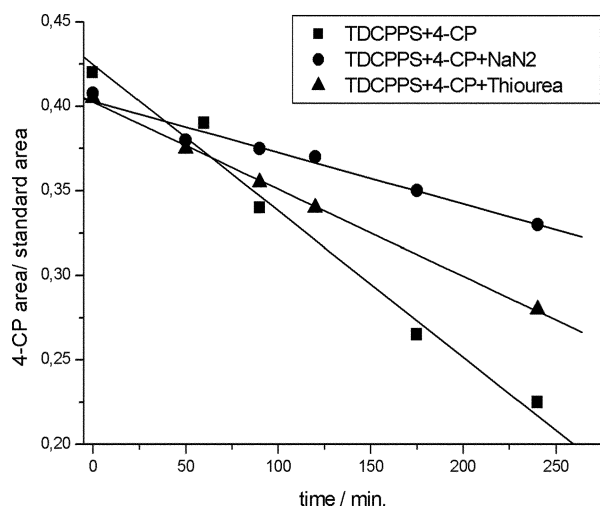


Fig. 4 HPLC, kinetic studies of TDCPPS sensitized photodegradation of 4-CP in aqueous solution in the presence of sodium azide and thiourea using 2,4-dichlorophenol as external standard.

To evaluate the quenching of the triplet state of the sensitizers by phenols, 4-chlorophenol was taken as a model compound, and flash photolysis experiments were carried out with excitation at 355 nm of aqueous solutions deaerated with argon with different 4-CP concentrations ($2.1\text{--}8.4 \times 10^{-3}$ M). The relevant second order quenching rate constants are presented in Table 4.

A significant difference was observed between rate constants for reaction of 4-CP with the free base porphyrin and with the metalloporphyrins, indicating the importance of the central metal on the mechanism of photodegradation. The expected reaction involves electron transfer from chlorophenol to the

excited porphyrin, as suggested for 4-CP and FeTDCPPS by the observation of dimeric products.¹⁷ The above differences probably reflect variations in the oxidation potential of the excited triplet state of the porphyrins. Since the triplet state of TDCPPS, 1, is not significantly quenched by 4-CP, this sensitizer was selected to study the effect of the singlet oxygen scavenger sodium azide and the radical trap thiourea on the photodegradation rate. Two groups of experiments were carried out on aerated aqueous solutions of TDCPPS (10^{-4} M) and 4-CP (5×10^{-4} M) irradiated at 350 nm. The first was made in the presence of sodium azide (10^{-3} M), while for the second thiourea (10^{-3} M) was added. Aliquots from the irradiated solutions were analysed following various times of irradiation by HPLC. Data are compared with those under similar conditions in the absence of scavengers. In all cases the decrease of the concentration of 4-CP follows good first order kinetics, with rate constants $k(\text{TDCPPS}) = 8.47 \times 10^{-4} \text{ s}^{-1}$, $k(\text{NaN}_3) = 2.44 \times 10^{-4} \text{ s}^{-1}$, $k(\text{thiourea}) = 4.60 \times 10^{-4} \text{ s}^{-1}$.

From the overall results, and the fact that the rates are slower in the presence of either scavenger when compared to the system without scavenger, it is possible to conclude that both Type I and Type II mechanisms are involved. However, from the relative rate constants in the presence of NaN_3 and thiourea (singlet oxygen and radical trap respectively) with sensitizer 1, it seems probable that the main mechanism involves singlet oxygen. This is in agreement with kinetic data on triplet quenching by 4-CP, Table 4, and singlet oxygen quantum yields, Table 2. In contrast, with sensitizers 2 and 3 the main mechanism seems to involve electron transfer, since higher rate constants of the triplet quenching by 4-CP are observed, which is in agreement with the lower singlet oxygen quantum yield efficiency (S_A , Table 2).

As in our previous study with FeTDCPPS,¹⁷ the two mechanisms occur in parallel, but their relative importance is strongly dependent upon the particular porphyrin used. The fact that with sensitizers 2 and 3 the direct reaction between the triplet state and 4-CP is more efficient than with the free base (Tables 2 and 4) is in agreement with the lower triplet and singlet oxygen quantum yield observed for these metalloporphyrins.

The quantum yields of photodegradation of 2,6-DMP were measured with sensitizers 1, 2 and 3 under continuous excitation at 415 nm, Table 5.

In all the cases, the role played by molecular oxygen in the degradation mechanism of 2,6-DMP is highlighted by the fact that the quantum yield of 2,6-DMP disappearance decreases when oxygen free solutions were used. Such an observation could be due to the formation of singlet oxygen as already shown for 4-CP. This result was further confirmed by using NaN_3 as singlet oxygen scavenger. However, it is clear from the facts that substantial degradation of 2,6-DMP was also observed in deaerated solution, and that the quantum yields of this are comparable to those in the presence of azide ion that two pathways in parallel are involved in the photodegradation: singlet oxygen and electron transfer process.

It is interesting to note that 2,6-dimethylbenzoquinone (2,6-DBQ) was the main product observed in all systems. However, this only accounted for roughly 50% of 2,6-DMP conversion. As previously reported on degradation *via* radical processes,^{5,17} the formation of dimeric and oligomeric products may explain these observations.

Table 5 Quantum yields for disappearance of 2,6-DMP (1×10^{-3} M) from aqueous solutions in the presence of sensitizers 1, 2 and 3 under different experimental conditions. These were determined at about 10% conversion of 2,6-DMP

Conditions	TDCPPS, 1	ZnTDCPPS, 2	SnTDCPPS, 3
Aerated solution	1.5×10^{-2}	8.0×10^{-2}	3.8×10^{-2}
Deaerated solution	3.5×10^{-3}	2.5×10^{-2}	1.5×10^{-2}
Oxygenated solution	1.3×10^{-2}	8.5×10^{-2}	4.0×10^{-2}
Aerated solution in the presence of NaN_3 (1.0×10^{-3} M)	3.4×10^{-3}	1.0×10^{-2}	1.0×10^{-2}

Conclusions

The results of this study show that 5,10,15,20-tetrakis(2,6-dichloro-3-sulfophenyl)porphyrin and its tin, and zinc complexes are efficient photosensitizers for the degradation of phenols in aqueous solutions. In all cases, the porphyrins sensitize singlet oxygen formation, leading to the possibility of a Type II degradation mechanism, probably proceeding via 2 + 4 cycloaddition to form the endoperoxide, followed by formation of *p*-benzoquinone and hydroquinone. Some hydroquinone may also be formed on direct photolysis of benzoquinone.⁴⁶ It is possible that there is also formation of some hydroperoxide, and we note that metallophthalocyanines photosensitize the breakdown of these to form hydroxyl, alkoxy or peroxy free radicals.⁴⁷ This is also likely to be the case with these metalloporphyrins.

However, the flash photolysis results reported here and in a previous study¹⁷ show this occurs in parallel with electron transfer from chlorophenols to metalloporphyrins, to produce phenoxyl radicals. This will lead to formation of benzoquinone derivatives and oligomeric species. The relative importance of the two parallel pathways is strongly dependent on the porphyrin used.

In contrast to other water soluble porphyrins, these chloro-substituted derivatives show little tendency to aggregate under the conditions studied and are excellent candidates for sensitizing photodegradation of phenols with visible light. This work is being extended to a study of the photodegradation under environmental conditions using immobilized porphyrins.

Acknowledgements

The authors thank FCT, FEDER, POCTI, the Universidad de Burgos and GRICES-CNRS for financial support. Singlet oxygen measurements experiments at the Free Radical Research Facility in the Synchrotron Radiation Department of the CLRC Daresbury Laboratory, Warrington, UK, were carried out with the support of the European Commission through the "Improving Human Potential" Transnational Access to Major Research Infrastructures Contract HPRI-CT-2002-00183.

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