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# Singlet oxygen formation and photostability of *meso*-tetraarylporphyrin derivatives and their copper complexes

José A.S. Cavaleiro [a], Helmut Görner [b], Paula S.S. Lacerda [a], J. Gavin MacDonald [c], Gertraud Mark [b], Maria G.P.M.S. Neves [a], Ronald S. Nohr [c,*], Heinz-Peter Schuchmann [b], Clemens von Sonntag [b,*], Augusto C. Tomé [a]

[a] *Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Max-Planck-Institut für Strahlenchemie, P.O. Box 101365, D-45413 Mülheim, Ruhr, Germany*
[c] *Kimberly-Clark Corporation, Roswell, GA 30076, USA*

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## Abstract

Time-resolved photochemical studies of five porphyrin derivatives and their copper complexes were carried out. Triplet lifetimes (room temperature) were determined under argon, air, and oxygen. The presence of oxygen and copper shortens the triplet lifetimes (argon: in the order of $10^2$ μs) by up to three orders of magnitude. With the copper complexes, $\Phi[O_2(^1\Delta_g)]$ is lower than with the metal-free porphyrins.

The photodegradation, indicated by bleaching, of *meso*-tetraphenylporphyrin and *meso*-tetrakis(pentafluorophenyl)porphyrin under air shows the latter to be more stable than the former, and their copper complexes to be more stable than the porphyrins themselves. With *meso*-tetraphenylporphyrin, the effect depends on the solvent, especially in the absence of oxygen (bleaching is faster in toluene than in benzene). With *meso*-tetraphenylporphyrin in toluene ($\lambda_{irr} = 405$ nm), the quantum yields of bleaching, determined from the rate of fading of the maximum of the Soret band are versus $\sim 1.8 \times 10^{-4}$ (argon) and $\sim 1.1 \times 10^{-5}$ (oxygen). Two rate constants have been roughly estimated: (i) for the H-atom abstraction from toluene by the triplet excited *meso*-tetraphenylporphyrin, in the order of 0.1 dm$^3$ mol$^{-1}$ s$^{-1}$; (ii) for the product-forming reaction of $O_2(^1\Delta_g)$ with *meso*-tetraphenylporphyrin, 40 dm$^3$ mol$^{-1}$ s$^{-1}$.

*Keywords: meso*-Tetraphenylporphyrin; Singlet oxygen; Porphyrin; Photolysis

## 1. Introduction

The interaction of porphyrin derivatives with oxygen under the influence of light, and their photostability, has been a matter of great interest. In fact, the use of these compounds in the field of photodynamic therapy (cf. [1–6]) or as photo-oxidation sensitizers (cf. [7]) dictates a search in the direction of high singlet molecular-oxygen quantum yields $\Phi(^1O_2)$, which implies an efficient intersystem crossing in the photoexcited sensitizer to its triplet state and a long intrinsic lifetime of the latter. Under the conditions prevailing in photodynamic therapy, the long-term photostability or self-destruction [8] of the sensitizer through the attack of $O_2(^1\Delta_g)$ is perhaps not of prime concern. However, various other applications for such compounds, in the presence of light, outside [9–11] the medical domain demand the opposite: the persistence of the porphyrin is critically tied to a minimal challenge by singlet oxygen. A small $\Phi(^1O_2)$, an especial stability toward singlet oxygen, as well as a high intrinsic light stability, are thus desirable characteristics.

With porphyrins, an oxidative attack involving the *meso*-positions [12–15] relies on steric accessibility [16], and one can pose the question whether this vulnerability is further decreased by the introduction of appropriate electron-withdrawing substituents (vulnerability in this sense would be a composite parameter, increasing with both $\Phi(^1O_2)$ and the ease of attack of the macrocycle by $O_2(^1\Delta_g)$). Halogen atoms can be such substituents [7,17]; it has been shown, however, that except for fluorine they increase the quantum yield of singlet oxygen progressively according to their atomic number [18], presumably by facilitation of intersystem crossing from excited singlet to triplet [19]. $\Phi(^1O_2)$ near unity is reported for two chlorine-substituted (in phenyl) *meso*-tetraphenylporphyrins [20]. A similar enhancement of intersystem crossing is

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[*] Corresponding author.

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observed when halogen atoms other than chlorine are substituted directly into the macrocycle; *meso*-substitution by fluorine has the same effect but to a smaller degree [21]. Upon complexation of a porphyrin with some transition metals, the lifetime of the triplet state is drastically reduced. This should also have a positive influence on the intrinsic light stability.

It has been suggested [16] that the robustness of *meso*-tetraphenylporphyrins with respect to oxygenation is not a simple function of electron density in the macrocycle, but that steric conditions may play a decisive role; nevertheless, perfluoroporphyrins are reported to be particularly stable [22,23] against oxidation generally, even in the absence of steric hindrance. In the presence of oxygen, the tetraphenylporphyrin macrocycle was observed to be cleaved at the *meso*-position, provided the phenyl groups were unsubstituted in the *ortho* positions [16] (cf. the relative stability of the *meso*-tetrakis(2,6-dichlorophenyl)porphyrin [7]). The initial step is the addition of singlet oxygen generated in these systems to the double bond involving the *meso* carbon atom [12,16] (in contrast, in the similar macrocycle *meso*-tetrakis(3-hydroxyphenyl)chlorin, hydroxylation of the reduced pyrrolic ring was observed as the most prominent reaction) [24]. The use of fluorine substitution to decrease the electron density in the macrocycle should minimize steric determinants relative to the non-fluorinated prototypes. In this paper, we compare the behavior of some porphyrin derivatives (*meso*-tetraphenylporphyrin **1**, *meso*-tetrakispentafluorophenylporphyrin **2**, *meso*-tetrakis-(4-sulfonatophenyl)porphyrin **3**, naphtho[2,3-b]porphyrin **4**, and the bacteriochlorin **5**) with that of their copper complexes **1-Cu**, **2-Cu**, **3-Cu**, **4-Cu**, and **5-Cu**. We also compare **1** and its copper complex **1-Cu** with their *meso*-tetrakis(pentafluorophenyl) analogs **2** and **2-Cu** with respect to their relative light stability in oxygenated and oxygen-free hydrocarbon solutions.

## 2. Experimental

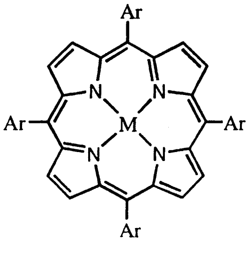
Compounds **1** ($C_{44}H_{30}N_4$), **1-Cu** ($CuC_{44}H_{28}N_4$), **2** ($C_{44}H_{10}F_{20}N_4$), and **3** ($Na_4C_{44}H_{26}N_4O_{12}S_4$) were obtained from Aldrich. Compounds **2-Cu** ($CuC_{44}H_8F_{20}N_4$), and **3-Cu** ($CuNa_4C_{44}H_{24}N_4O_{12}S_4$) were prepared by metallation of the corresponding free bases with copper acetate [25]. The naphthoporphyrin **4** ($C_{52}H_{34}N_4$) and the bacteriochlorin **5** ($C_{60}H_{26}F_{20}N_4$) were prepared by Diels–Alder reactions of the porphyrins **1** and **2** with *ortho*-benzoquinodimethane [26]. Compounds **4-Cu** ($CuC_{52}H_{32}N_4$), and **5-Cu** ($CuC_{60}H_{24}F_{20}N_4$) were obtained by metallation of the corresponding free porphyrin derivatives with copper acetate [27].

### 2.1. Time-resolved spectroscopy

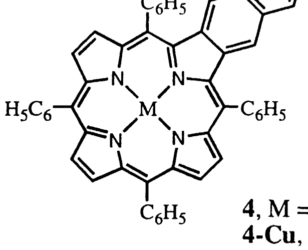
Laser-flash photolysis measurements were carried out using the second harmonic of a neodymium laser ($\lambda_{exc}$ = 530 nm, pulse width: 15 ns), and in some cases an excimer laser ($\lambda_{exc}$ = 308 nm, pulse width: 20 ns). For fast and slow detection, transient digitizers (Tektronix, 7912AD and 390AD) were used. Data handling was done by computer (Archimedes 540). Phosphorescence of $O_2(^1\Delta_g)$ at 1269 nm was detected after the pulse, using a cooled Ge detector (North Coast, EO 817FP), a silicon filter, and an interference filter together with an amplifier (Comlinear, CLC-103) as described elsewhere [28,29].

### 2.2. Photodegradation experiments

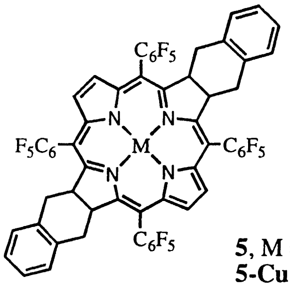
The *meso*-tetraphenylphorphyrins **1** and **1-Cu** and the *meso*-tetrakis(pentafluorophenyl) analogs **2** and **2-Cu** were dissolved in benzene to a concentration of $1 \times 10^{-4}$ mol dm$^{-3}$ which implies total absorption in the



**1**, Ar = $C_6H_5$, M = 2 H
**1-Cu**, Ar = $C_6H_5$, M = Cu
**2**, Ar = $C_6F_5$, M = 2 H
**2-Cu**, Ar = $C_6F_5$, M = Cu
**3**, Ar = $C_6H_4$-4-$SO_3Na$, M = 2 H
**3-Cu**, Ar = $C_6H_4$-4-$SO_3Na$, M = Cu



**4**, M = 2 H
**4-Cu**, M = Cu



**5**, M = 2 H
**5-Cu**, M = Cu

maximum of the band near 400 nm, and irradiated in Teflon-stoppered 1 mm quartz cuvettes with the visible-range light of a 1000 W Hanovia xenon–mercury lamp (400 nm cut-off filter GG 400, Schott (Mainz, Germany); heat filter 4 mm KG5, Schott). The solutions were left aerated: cells that could not be made completely airtight under the circumstances had to be used in these relatively high-light intensity experiments owing to limitations of space in this particular irradiation set-up. The photodegradation experiments were carried out under conditions of identical optical density. The decrease of the absorbance (measured in the maximum of one of the absorption bands in the 500–600 nm region; the measurements were done at room temperature) was followed as a function of time. In most cases, the degree of bleaching did not exceed 5%.

Photodegradation experiments were also done with an irradiation arrangement that allowed the use of airtight cells [30], where the solutions (the porphyrins **1**, **1-Cu**, and **2** in benzene and toluene in the micromolar concentration range) could be purged with argon or saturated with oxygen. These experiments were carried out using the filtered light (400 nm cut-off filter GG 400, Schott) of a Philips HPK 125 W lamp housed in a water-cooled quartz well. Moreover, a band filter (PIL 1/405, Schott, $\lambda_{max} = 405$ nm, half-width: 18 nm) which isolates the 405 nm line of the medium-pressure Hg lamp and transmits in the wavelength range of the Soret bands of these compounds, was used to estimate the quantum yields $\Phi_b$ of bleaching of the Soret band. The light intensity was determined by ferrioxalate actinometry [31,32]. Further, a 455 nm cut-off filter (GG 455, Schott) was also used to estimate the proportion of photobleaching of **1** through absorption in the wavelength region of the Q-bands, compared to the total visible range.

The evaluation of $\Phi_b$ is based on the expression (1), by following the decrease of the absorbance *A* as a function of time. The term *F*(*t*), evaluated graphically for a sequence of irradiation times, takes into account the fact that the experiment is carried out under conditions of non-negligible absorbance. The slope of the plot of $\log(A/A_0)$ versus $F(t)$ is proportional to $\Phi_b$ ($\varepsilon$, decadic molar absorption coefficient at the wavelength of irradiation, in this case, the 405 nm line of the medium-pressure Hg lamp, *l* is the optical pathlength, $I_0$ the incident light intensity).

$$\log\left(\frac{A}{A_0}\right) = \frac{\Phi_b \varepsilon l I_0}{2.3} \int \frac{1-10^{-A}}{A}\,\mathrm{d}t = \frac{\Phi_b \varepsilon l I_0}{2.3} F(t) \qquad (1)$$

## 3. Results and discussion

### 3.1. Time-resolved spectroscopy

The metal-free porphyrins studied as well as their Cu(II)-complexes can be excited at 530 or 308 nm. The triplet states of **1**, **2**, **4**, and **5** in toluene or dichloromethane are characterized by absorption spectra taken in the range from 360 to 700 nm. As an example, Fig. 1 shows the behavior of **2** in air-saturated dichloromethane, and **2-Cu** in the absence of oxygen.

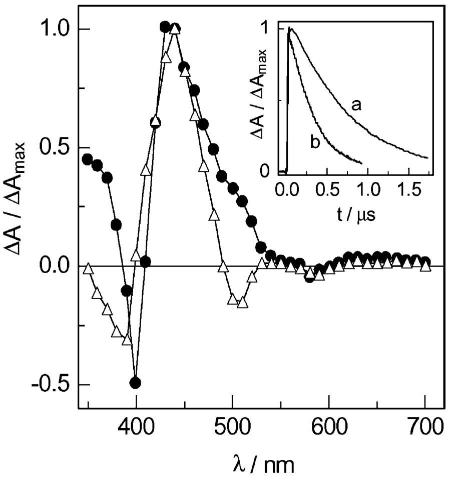


Fig. 1. *T–T* absorption spectra (normalized) of **2** (△) and **2-Cu** (●) in dichloromethane ($\lambda_{exc} = 308$ nm). Inset: triplet decay at 440 nm ((a) **2**, under air; (b) **2-Cu**, under argon).

The triplet is formed within the time of the laser pulse ($\lambda_{exc} = 530$ nm) and then decays to a level that reveals a small amount of ground-state bleaching (e.g. for **2** at 390, 505, and 580 nm). The *T–T* absorption maximum, $\lambda_{max}$, differs slightly from compound to compound. Interestingly, however, the presence or absence of copper in a particular porphyrin makes little difference to the general appearance of the spectrum. In the presence of oxygen, the decay follows a first-order law (cf. trace (a), inset in Fig. 1); this is essentially the same also under argon at low laser intensities; the lifetimes given in Table 1 refer to these lower-intensity conditions. The triplet lifetimes in oxygen-, air-, and argon-saturated solution $\tau_T(O_2)$, $\tau_T$(air), and $\tau_T$(Ar) are listed in Table 1.

In the copper complexes **1-Cu**, **2-Cu**, and **5-Cu**, $\tau_T$(Ar) is much shorter than in the copper-free compounds, i.e. by about three orders of magnitude, but can still be determined where the lifetime is longer than the duration of the laser pulse (~12 ns). Fig. 1 shows the *T–T* absorption spectrum of **2-Cu**, measured in argon-saturated dichloromethane; here, the minima of spectral bleaching are red-shifted to 400 and 585 nm and $\tau_T(\mathrm{Ar}) = 200$ ns (Table 1). The effect of copper on the triplet lifetime is similar to that of certain further transition metals such as cobalt, manganese, iron, or nickel, in contrast to the situation with others, e.g. magnesium and zinc (both redox-inactive) which have hardly any effect on the triplet lifetimes (cf. [39,40]). It is worth noting in this context that substitution by bromine is reported to counteract the intersystem–crossing-accelerating effect of the metal atom [41]. The *T–T* absorption spectra of the copper complexes are essentially the same as those of the respective porphyrins alone (Fig. 1, cf. Table 1). For **3-Cu**, **4-Cu**, and **5-Cu**, the triplet lifetimes are comparable with the duration of the laser

Table 1
*T–T* absorption maxima, triplet lifetimes in the presence and absence of $O_2$, and quantum yields of singlet oxygen formation[a] at room temperature

| Porphyrin | Solvent | $\lambda_{max}$ (nm) | $\tau_T(O_2)$ (ns) | $\tau_T$(air) (ns) | $\tau_T$(Ar) (μs) | $\Phi(^1O_2)^b$ under $O_2$ | $\Phi(^1O_2)^b$ under air |
|---|---|---|---|---|---|---|---|
| **1** | $CH_2Cl_2$ | 440 | 100 | 400 | 50 | 0.6 | |
| | Toluene | 440 | 70, 200,[c] 400[d] | 350 | >20, >10[c] | 0.6, 0.67,[c] 0.68[d] | 0.6 |
| **1-Cu** | $CH_2Cl_2$ | 470 | 23 | 33 | 0.04, 0.037[e] | 0.3 | 0.08 |
| | Toluene | 470 | 18, 16[c] | 25 | 0.028, 0.018[c] | 0.15, 0.03[c] | <0.1 |
| **2** | $CH_2Cl_2$ | 440 | 140 | 600 | 100 | 0.8 | 0.8 |
| | Toluene | 440 | 110 | 530 | >20 | 0.6 | 0.6 |
| **2-Cu** | $CH_2Cl_2$ | 440 | 40 | 80 | 0.20 | 0.5 | |
| | Toluene | 450 | 60 | 70 | 0.09 | 0.3 | 0.1 |
| **3** | $CH_3CN$[f] | | | 1800[g] | 400[h] | ≈0.5 | ≈0.5, 0.62,[g] 0.61[i] |
| **3-Cu** | $CH_3CN$[f] | | | | | <0.05 | |
| | $D_2O$[j] | 440 | <20 | | <0.02 | <0.04 | <0.01[k] |
| **4** | $CH_2Cl_2$ | 470 | 90 | 500 | 80 | 0.6 | 0.6 |
| | Toluene | 465 | 55 | 300 | >20 | 0.6 | 0.6 |
| **4-Cu** | $CH_2Cl_2$ | 470 | <20 | <20 | <0.02 | 0.05 | <0.02 |
| | Toluene | 470 | <10 | 12 | 0.014 | 0.2 | 0.1 |
| **5** | $CH_2Cl_2$ | 420 | 80 | 400 | 60 | 0.6 | 0.6 |
| | Toluene | | 60 | | >20 | 0.6 | 0.6 |
| **5-Cu** | $CH_2Cl_2$ | <440 | <20 | <20 | 0.03 | <0.02 | |
| | Toluene | | <10 | 12 | 0.015 | <0.02 | |

[a] $\lambda_{exc} = 530$ nm, except in the $\Phi(^1O_2)$-determination experiments done in toluene and acetonitrile, where $\lambda_{exc} = 308$ nm.
[b] $A_{530} = 0.2$, and $A_{308} = 0.8$.
[c] See [33].
[d] See [18].
[e] See [34].
[f] Acetonitrile:$D_2O$ = 99:1.
[g] Aqueous solution [35].
[h] Aqueous solution [36].
[i] Aqueous solution [37].
[j] 99% $D_2O$.
[k] Aqueous solution [38].

pulse, i.e. any effect of oxygen on its decay is barely observable, even though the triplet-quenching by oxygen is fast, the rate constants being in the order of $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$, i.e. almost diffusion-controlled [40,42,43]. Otherwise, the properties are comparable. When the compounds, dissolved in dichloromethane or toluene, were excited at 308 nm, the results were similar; the somewhat longer pulse duration of the 308 nm laser (20 ns) places slightly narrower constraints on the measurement of fast decays in this time range.

The $\Phi(^1O_2)$ could be determined for compounds **1**, **2**, **4**, **5**, and **1-Cu**, **2-Cu**, **4-Cu**; estimates are given for **3** and **3-Cu.** The lifetime $\tau_\Delta$ of $^1O_2$ in dichloromethane was obtained from its first-order decay, observed at 1269 nm, and found to be 100 μs; note that a small dependence of the kinetics on the laser intensity gives rise to a slightly faster decay above an intensity of 2 MW cm$^{-2}$. The phosphorescence of $^1O_2$ is overlapped by an intense peak (overall scatter) which, however, ceases to distort the kinetics beyond ca. 10 μs. The assignment is supported by the absence of the signal under argon.

In the copper-free systems, $\Phi(^1O_2)$ is found to be quite high, in agreement with [39]. In oxygen-saturated solutions, $\Phi(^1O_2)$ values were obtained from the signal at 10 μs, using optically matched solutions ($A_{530} = 0.3$). In order to obtain absolute values, **1** in dichloromethane was used as a reference, assuming $\Phi(^1O_2) = 0.6$ at oxygen saturation; literature values for **1** are reported at 0.50–0.55 (chloroform, air-saturated), 0.70 (toluene, air-saturated), 0.88 (toluene, oxygen-saturated) [39], and 0.63 (benzene, oxygen-saturated) [44]. For **3** (insoluble in organic solvents), $\Phi(^1O_2)$ is 0.42–0.76 ($D_2O$, in the presence of oxygen) [39]. In general, values are higher with oxygen that with air saturation.

With the copper complexes $\Phi(^1O_2)$ are found to be lower than with the metal-free porphyrins (Table 1); for **1-Cu**, $\Phi(^1O_2)$ is found to be smaller than 0.01 (carbon tetrachloride, air-saturated) [39].

The copper-free compounds show the same $\Phi(^1O_2)$ in both air- and oxygen-saturated dichloromethane, whereas for **1-Cu**, **4-Cu**, and most clearly for **2-Cu**, $\Phi(^1O_2)$ increases on saturating with oxygen compared to air. The fact that with

**4-Cu** $\Phi(^1O_2)$ is so low is in agreement with the short triplet lifetime even under argon. In the case of **5-Cu**, the reason for the failure to detect any singlet oxygen is not obvious; there may be quenching without $^1O_2$ formation, or insufficient sensitivity. A comparison of **5-Cu** with **4-Cu** in toluene, where $\tau_\Delta$ is about 28 μs reveals that $^1O_2$ would have been detected in the latter case even though the triplet lifetimes in the presence and absence of oxygen are practically the same for **5-Cu** and **4-Cu**. Regarding **3**, $^1O_2$ could equally not be detected with **3-Cu**, even though the copper-free **3** shows a relatively high $\Phi(^1O_2)$ of about 0.5. For **3** and **3-Cu** in acetonitrile with 1% $D_2O$, the life-time $\tau_\Delta$ of $^1O_2$ is about 65 μs. Polar and hydrogen-bonding solvents that are required to dissolve ionic compounds such as **3** and **3-Cu** can give rise to additional effects upon photoexcitation, e.g. to a change in the extent of hydrogen bonding [35] and photoionization [45] which in the presence of oxygen will lead to the formation of superoxide $O_2^{\bullet -}$, and so in systems containing transition metal ions via Fenton-type reactions, eventually of OH radicals [46].

Inspection of the results in Table 1 suggests that the triplet lifetimes and singlet oxygen quantum yields are not greatly affected by the perfluorination of the *meso*-phenyl groups (**1** versus **2**, and **1-Cu** versus **2-Cu**), though the $\tau_T$(Ar) values of the pentafluorophenyl-bearing copper complex **2-Cu** appear to be longer than those of **1-Cu** by a factor of three to five (Table 1), which is partly reflected in the apparently slightly larger $\Phi(^1O_2)$ values of **2-Cu**. Partially fluorine-substituted *meso*-tetraphenylporphyrins which additionally carry an electron-donating substituent ($-OCH_3$) on phenyl show no discernible trend when compared with the fluorine-free compound [18]. A remarkable dependence of the triplet lifetime of *meso*-phenylated porphyrins on the size of the substituents in the phenyl ring and in the pyrrole β-position has been observed [47]. At room temperature in the absence of substituents or in the presence of *small* substituents (low restriction to phenyl rotation), but also in the case of bulky substituents (rotation blocked), these lifetimes are in the order of 1 ms [47]. In the case of substituents of intermediate size, the triplet lifetimes are observed to decrease by up to about two orders of magnitude [47]. This is attributed to a distortion of the macrocycle symmetry when the substituents "squeeze through" upon the hindered rotation of the phenyl group. Efficient non-radiative deactivation via a second triplet state has been linked to the conformational flexibility induced by *meso*-diaryl substitution in zinc porphyrins [48], the overall triplet lifetime being in the order of a few microseconds.

### 3.2. Photodegradation

#### 3.2.1. Xenon-lamp set-up

The progress of the degradation was determined from the decrease of the highest of the Q peaks in the optical spectra of **1** (Fig. 2), **1-Cu** (Fig. 3), **2** and **2-Cu** (Fig. 4). Absorption spectra of **1** [49–52] and **1-Cu** [49,51] have been reported in the literature.

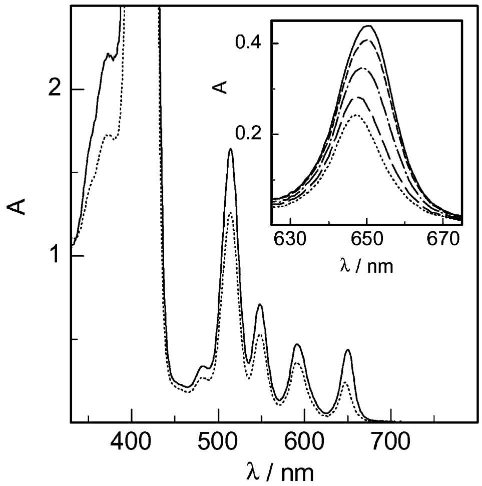


Fig. 2. Absorption spectrum of **1** in benzene ($10^{-4}$ mol dm$^{-3}$, aerated) and its evolution under irradiation (Hanovia xenon lamp, 1000 W). Traces are: (—) before irradiation, and (· · ·) after 1 h irradiation. The rate of photodegradation in the experiments is monitored by the decline of the peak at 515 nm. Inset: decrease of the first Q peak, near 650 nm, occurs with a clear blue-shift of the maximum (see text).

These spectra deserve some comment. The metal-free porphyrins **1** and **2** show four Q peaks in the wavelength range from 500 to 650 nm, as expected [53], even though in the fluoro-substituted **2**, the first (640 nm) and the third (540 nm) of these peaks are comparatively small. Their number is less in **1-Cu** (one peak plus shoulder) and **2-Cu** (two) [53]. The evolution of the spectra with irradiation time brings on a general decrease of the absorption, not just in the peaks (cf. Fig. 2). The disparately larger decrease, with a blue-shift, of the maximum of the first Q peak (650 nm) [51] of **1** seen in Fig. 2 suggests the presence of a *meso*-tetraphenylchlorin impurity which is oxidized to the porphyrin under these conditions.

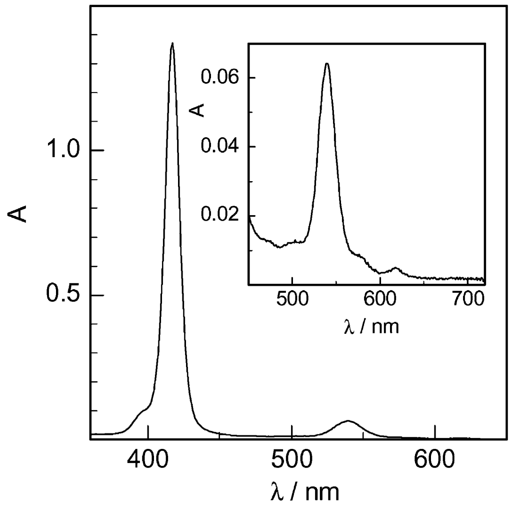


Fig. 3. Absorption spectrum of **1-Cu** in benzene ($2 \times 10^{-6}$ mol dm$^{-3}$).

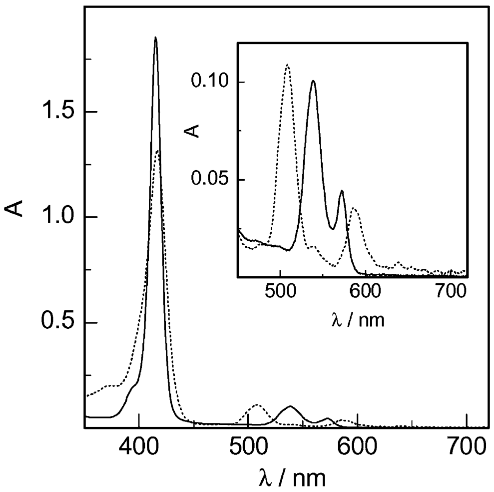


Fig. 4. Absorption spectra of **2** (···) and **2-Cu** (—) in benzene ($4 \times 10^{-6}$ mol dm$^{-3}$).

Relative rates of the degradation in benzene are shown in Fig. 5, the aim here being to arrive at a rough comparison of the stabilities of these compounds towards unfiltered visible light under conditions (hydrocarbon solvents) that are considered to approximate certain applications (organic polymeric matrix, no exclusion of air), where porphyrins may be used as stabilizers [10,11]. Similar results regarding the bleaching were obtained with **1** in toluene.

It is seen from Fig. 5 that in the cases investigated, the photostability of the copper complexes exceeds those of the free porphyrins, and that the fluorinated systems are more stable than the unsubstituted ones. This behavior parallels the relative stabilities of these ligands in metal complexes when used as catalysts in oxygenation reactions [54–56]. A similar trend has been reported for porphyrins fluorinated in the macrocycle [22,57].

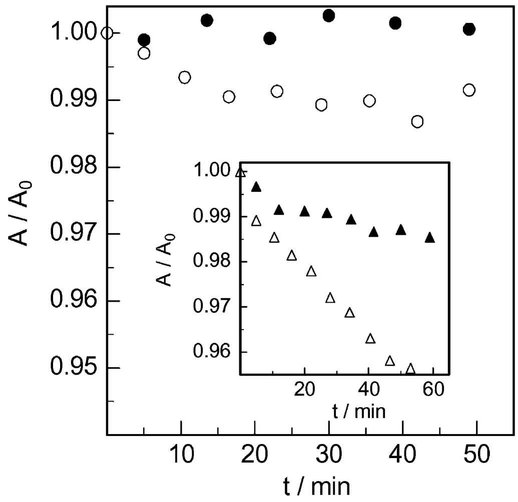


Fig. 5. Bleaching (at λ of maximum of highest Q peak) of **2** (○) and **2-Cu** (●). Inset: **1** (△) and **1-Cu** (▲) ($4 \times 10^{-6}$ molar in benzene, not anoxic), 1000 W (Hanovia) xenon lamp, wavelength range above 400 nm.

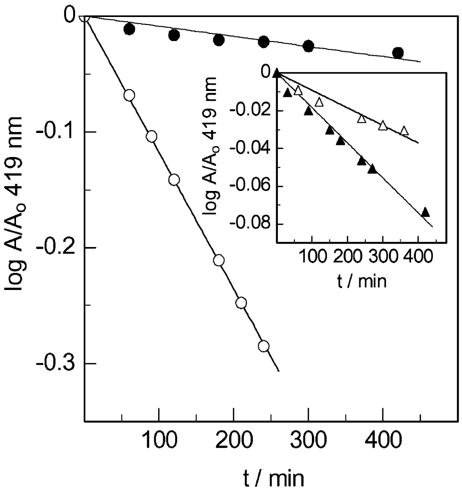


Fig. 6. Rate of bleaching (at λ of maximum of Soret band, near 419 nm) of **1** ($4 \times 10^{-6}$ mol dm$^{-3}$) in toluene (○, △) and benzene (●, ▲). Gas conditions: main-frame, argon, and in inset, oxygen. Visible light of a 125 W HPK lamp (Philips), wavelength above 400 nm.

As the presence of the copper ion reduces the triplet lifetime and thereby to some extent the $\Phi(^1O_2)$ (Table 1), the fact that the copper complexes **1-Cu** and **2-Cu** are more photostable than the corresponding metal-free porphyrins, is in line with the hypothesis that in the presence of oxygen much of the photodecomposition is mediated by singlet oxygen [12,14,16] (although much of the singlet oxygen is expected to be de-excited unproductively [58] by the dye, given that the quenching rate constants regarding these compounds with singlet oxygen are reported to be largely at $10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ and above [59]).

### 3.2.2. HPK-lamp set-up

The results of these experiments show that the rate of photodegradation is indeed dependent on the state of oxygenation of the matrix. Moreover, the chemical nature of the medium plays an important role especially in the absence of oxygen (it has been reported that degradation is accelerated in chlorinated media) [60]. The degradation under argon is much more efficient in toluene than in benzene. This is shown in Fig. 6. A protective effect of oxygen, clearly apparent from Fig. 6 compared to the toluene/argon case (○), is explained by the deexcitation of the porphyrin triplet state by $O_2$, in competition with reactions that would otherwise lead to chromophore loss; the rate constants for this process are close to $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ [18,42,43].

Regarding compound **1**, in contrast to the situation in the presence of oxygen, where the degradation appears largely linked to outright bleaching (Fig. 2) over the spectral range between 400 and 700 nm, there is considerable spectral change (decrease of peaks, filling in of troughs) when the photolysis is carried out in the absence of oxygen (Fig. 7) which indicates that the chemistry is different in the two cases.

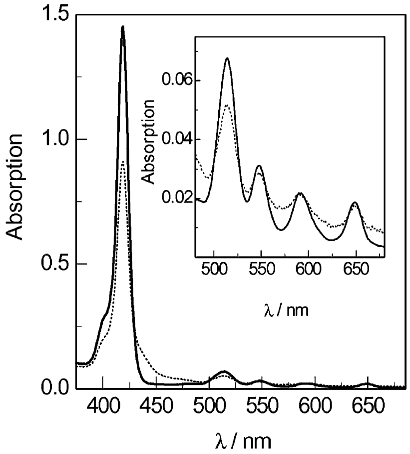


Fig. 7. Spectral change in the anoxic photodegradation of **1** ($4 \times 10^{-6}$ mol dm$^{-3}$) in toluene over an irradiation period of 240 min. Philips 125 W HPK lamp, wavelength range above 400 nm.

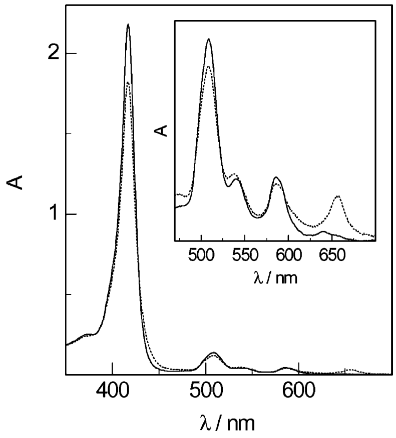


Fig. 8. Spectral change in the anoxic photodegradation of **2** ($4 \times 10^{-6}$ mol dm$^{-3}$ in toluene) over an irradiation period of 330 min. Philips 125 W HPK lamp, wavelength range above 400 nm.

Remarkably, in the case of **2** (also in argon-saturated toluene) the evolution of the spectrum appears different from **1**. The absorbance at the first Q band (near 650 nm) increases as the irradiation progresses (the heights of the other bands decrease, Fig. 8). This is thought to be due to the reduction of **2** to the corresponding chlorin (for instance, in *meso*-tetrakis(2,6-difluorophenyl)chlorin, as well as in some chlorinated analogues, the absorption coefficients in this '650' band are larger than those of the corresponding porphyrins by about one order of magnitude [20]). In another context, it has been shown that **2** is reduced quite easily [61].

The quantum yield of bleaching of **1** in argon-saturated toluene has been determined at $\Phi_b = 1.8 \times 10^{-4}$ (based on a Fe(II) quantum yield of the ferrioxalate actinometer of 1.14 [32] over the wavelength range of the band filter which is centered on 405 nm). This value for $\Phi_b$ has then been assumed to also hold for the irradiation condition referred to in Fig. 6. On the basis of the slope of the "argon" line (○) in Fig. 6, the quantum yields that apply to the other situations referred to in the Fig. 6, i.e. aerated solutions of **1** (not shown), and data for **1-Cu** (not shown), were then estimated from such data by the Rule of Three (Table 2).

Using a 455 nm cut-off filter, it was found that the bleaching of **1** in argon-saturated toluene proceeded at a rate that was about 1/7 of the rate observed with the 400 nm cut-off filter, under otherwise equal conditions. This implies that most of the photolytic effect is induced by the absorption of the light into the Soret band.

The results obtained with toluene (Fig. 6) indicate that the presence of oxygen can have a positive influence on the photostability under certain conditions. This depends on the relative importance of several elementary reactions that contribute to the photodestruction of the porphyrin (products Q, Q′, R, and S; reactions 4, 5, 7, and 10).

$$\mathrm{P} \rightarrow \mathrm{P}^* \tag{2}$$

$$\mathrm{P}^* \rightarrow \mathrm{P} \tag{3}$$

$$\mathrm{P}^* \rightarrow \mathrm{Q} \tag{4}$$

$$\mathrm{P}^* + \mathrm{M} \rightarrow \mathrm{Q}' \tag{5}$$

$$\mathrm{P}^* + \mathrm{O}_2 \rightarrow \mathrm{P} + \mathrm{O}_2^* \tag{6}$$

$$\mathrm{P}^* + \mathrm{O}_2 \rightarrow \mathrm{R} \tag{7}$$

$$\mathrm{O}_2^* \rightarrow \mathrm{O}_2 \tag{8}$$

$$\mathrm{O}_2^* + \mathrm{P} \rightarrow \mathrm{O}_2 + \mathrm{P} \tag{9}$$

$$\mathrm{O}_2^* + \mathrm{P} \rightarrow \mathrm{S} \tag{10}$$

Oxygen de-excites (reactions 6 and 7) the triplet-state of the porphyrin, P*, which would otherwise lead to chromophore loss (reactions 4 and 5); depending on the size of the rate constant for reaction 5 will the protective effect or the destructive effect caused by the presence of oxygen relative to its absence, predominate. Thus, with benzene, $k_5$ is smaller

Table 2
Initial quantum yields $\Phi_b$ of bleaching (determined in the maximum of the Soret band) of *meso*-tetraphenylporphyrin **1** and its copper complex **1-Cu** in benzene or toluene in the absence and presence of oxygen

| Gassing condition | **1** in benzene | **1** in toluene | **1-Cu** in benzene | **1-Cu** in toluene |
|---|---|---|---|---|
| Argon | $\sim 1.2 \times 10^{-5}$ | $18.0 \times 10^{-5}$ | $\sim 0.7 \times 10^{-5}$ | $\sim 0.6 \times 10^{-5}$ |
| Air | $\sim 1.4 \times 10^{-5}$ | $\sim 0.8 \times 10^{-5}$ | n.d. | n.d. |
| Oxygen | $\sim 2.6 \times 10^{-5}$ | $\sim 1.1 \times 10^{-5}$ | $\sim 1 \times 10^{-5}$ | $\sim 1.5 \times 10^{-5}$ |

than with toluene (reaction 5 can be viewed as an H-atom abstraction from the solvent molecule M by triplet-state $P^*$). It can be shown that both contrasting results, shown in Fig. 6, are qualitatively explained under the assumption, guided by the literature [43–59], of reasonable values for the rate constants for the reactions grouped together in Scheme 1.

Regarding the behavior of porphyrin **1**, rough estimates may be made regarding the values for the rate constants $k_5$ of the reactive quenching of $P^*$ by toluene (1) and of $k_{10}$ of the $^1O_2$ chemical quenching by P (2).

1. Considering that under argon, $\Phi_b$ is about 20 times larger in toluene than in benzene, one may use the expression $\Phi_b \sim \Phi_5 = k_5\,[M]/(1/\tau_T(Ar) + k_5[M])$. Putting [M] at $10\,\mathrm{mol\,dm^{-3}}$, $\tau_T(Ar)$ at $2 \times 10^{-5}$ s (Table 1), and $\Phi_b$ at $1.8 \times 10^{-4}$ (Table 2), one obtains a value in the order of $0.1\,\mathrm{dm\,mol^{-1}\,s^{-1}}$ for $k_5$.
2. Since $\Phi_{10} = k_{10}[P]/(k_8 + k_9[P] + k_{10}[P])$, and if $\Phi_{10}$ is set equal to $10^{-5}$, $k_8$ to $10^4\,\mathrm{dm\,mol^{-1}\,s^{-1}}$ [59], $k_9 + k_{10}$ to $10^7\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ [59], and [P] to $4 \times 10^{-6}\,\mathrm{mol\,dm^{-3}}$, $k_{10}$ is obtained at $40\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$. This value can be smaller depending on the relative importance of the contributions by reactions 4, 5, and 7, but may be larger depending on how well $\Phi_b$ reflects the decomposition quantum yield of the porphyrin.

Similar bleaching experiments to **1** have been done with **1-Cu**. In argon-saturated toluene, $\Phi_b$ is roughly estimated at $6 \times 10^{-6}$, as the scatter of the data has precluded a more accurate evaluation. The value for the oxygenated situation lies in the same range. So do the values for the benzene solutions (Table 2). The fact that in argon-saturated toluene the rate of bleaching of **1-Cu** is so much slower than that of **1** is in support of the importance of reaction 5 in the copper-free porphyrin while the fast rate of triplet quenching (Table 1) competes favorably with reaction 5 in **1-Cu**. Nevertheless, in the presence of oxygen, $^1O_2$ is still formed in the case of **1-Cu** (cf. Table 1) and could enhance the degradation of the latter (Table 2).

The bleaching efficiency (in the Soret band maximum) of the pentafluorophenyl compound **2** in argon-saturated toluene has been compared to that of **1**, from which it emerges that under these conditions the quantum yields of bleaching are similar (under argon, the rate of **2** is about 75% of the rate of **1**, data not shown), as might already have been expected from the similarity of the triplet lifetimes under argon (Table 1). The apparently greater stability of **2** in the presence of oxygen, compared to **1** (Fig. 5), may be a case of steric protection of the *meso*-position against attack by $^1O_2$ [7,16], or it may be caused by the electron-withdrawing substituents [17,22].

While the chemistry of the reaction of singlet oxygen with porphyrins has begun to be worked out [12–14,16], the chemistry behind that part of the bleaching which is not mediated by oxygen is largely unclear at this stage. The fact that the copper complexes appear more stable than the metal-free porphyrins suggests that a macrocycle-excited state not a metal-centered excited state is involved in this irreversible change.

Various different light-induced modes of reaction are reported in the literature. In coordinating solvents, with Cu(II) porphyrins in the excited state the tendency to bind an axial ligand increases [62], while in other metalloporphyrin systems the reverse, i.e. the photodissociation of (axial) ligands [42,63] has been reported [64]. In such systems, the axial ligand itself may also be cleaved, as in $PMn\text{–}ONO_2 \rightarrow PMn\text{=}O + NO_2$ [65]. The photodissociation of a macrocyclic-*N*-to-metal bond one expects to be very highly reversible, however. In the presence of electron acceptors other than oxygen (or electron donors), electron transfer is reported to take place with the formation of the porphyrin $\pi$ radical cation (or anion) [60,66–68].The rotation, in *meso*-tetraphenylporphyrins, of the phenyl group around its bond (leading to atropisomerization in the case of asymmetrically substituted phenyl groups) is induced by irradiation as the rotational barrier is lowered upon excitation [69].

In the absence of triplet quenching by oxygen, H-atom abstraction from a donor by the porphyrin triplet can lead to photoreduction, which can give rise to the chlorin and, in the metal-free porphyrin, also to the phlorin (5,22-dihydroporphyrin) [15]. This reaction is expected to be slow if the solvent is the sole H-atom donor unless its C–H bonds are quite weak. It is conceivable that in the absence of oxygen, charge transfer occurs between excited and ground-state porphyrin molecules, or any other reactive additive or solvent impurity, with disproportionation/recombination reactions [70] and proton transfer followed by a cascade of reduction steps giving rise to various porphyrin derivatives which are reduced to a greater or lesser degree. This would explain the progressive smearing-out of the absorption spectrum (Fig. 7) upon irradiation.

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