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Water-Soluble Transition-Metal-Phthalocyanines as Singlet Oxygen Photosensitizers in Ene Reactions

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The capability of platinum, palladium and ruthenium sulfophthalocyanines (PtPcS, PdPcS and RuPcS) to act as singlet oxygen [$^1O_2(^1\Delta_g)$] photosensitizers in ene reactions in aqueous medium has been investigated by combining time-resolved and steady-state techniques. Laser flash photolysis experiments with nanosecond time resolution revealed the population of the lowest excited triplet state in the case of PtPcS and PdPcS upon light excitation. In both cases, this transient is effectively quenched by molecular oxygen leading to the formation of $^1O_2(^1\Delta_g)$ with a quantum yield Φ_Δ = 0.24, as unequivocally demonstrated by time-resolved near-infrared luminescence. In contrast, RuPcS did not photosensitize $^1O_2(^1\Delta_g)$, in accordance with the lack of population of the precursor excited triplet state. These metal–sulfophthalocyanines (MPcSs) were further tested in the ene reaction. In line with the photophysical results, PtPcS and PdPcS photosensitized the formation of hydroperoxide by $^1O_2(^1\Delta_g)$ addition to the target α,β-unsaturated carboxylic derivatives whereas RuPcS was totally inactive in this respect. Supporting the MPcSs on Amberlite® apparently made the ene reaction more rapid.

Introduction

Phthalocyanines are an important class of derivatives that are used in several fields.[1] Historically, they have been used as pigments and dyes due to their very high extinction coefficients in the visible region. However, over the last decade, new applications have become very popular, for example, in optoelectronics,[2] new materials[3] and quantum dots.[4] Several metal–phthalocyanines (MPcs) have also been tested as photosensitizers for use in the destruction of tumour cells (photodynamic therapy, PDT).[5]

Indeed, several closed valence shell (i.e., diamagnetic) MPc derivatives are known to be efficient sensitizers for the generation of singlet oxygen on irradiation with visible light.[6] When water-soluble (i.e., sulfonated, Figure 1) MPcs containing Zn or Al are irradiated they are excited to the singlet state (^{1}MPc*), which can undergo intersystem crossing (ISC) to produce the excited triplet state (^{3}MPc*). This ^{3}MPc* can interact with ground-state molecular oxygen, $^3O_2$, to generate singlet oxygen, $^1O_2(^1\Delta_g)$, which can eventually oxidize organic substrates by a type II mechanism[7] (Scheme 1). In contrast, in the presence of a metal with partially filled d orbitals, if the triplet state is populated, it usually has too short a lifetime to interact with molecular oxygen.[8]

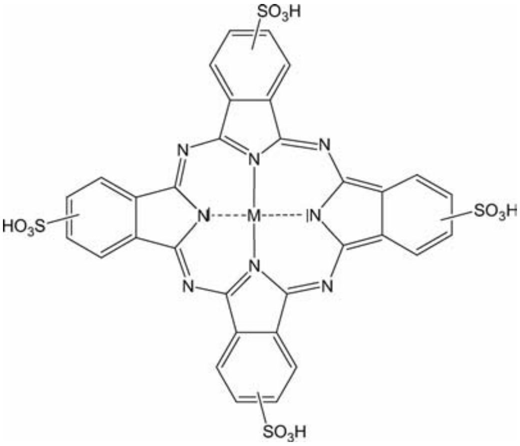
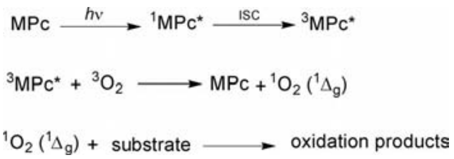


Figure 1. Metal tetrasulfophthalocyanines.



Scheme 1. Reaction pathway leading to a type II mechanism for the oxidation of organic substrates.

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Although MPcs with non-transition metals have been widely investigated for their ability to generate singlet oxygen,[6a,9] very few studies have dealt with transition metals. Recently it was reported that palladium–tetrasulfophthalocyanine (PdPcS) is a highly efficient and stable photosensitizer of singlet oxygen that can degrade chlorophenols and oxidize cyclohexene and sulfides mainly in aqueous media.[10] However, the quantum yields for $^1O_2$ were measured exclusively using dimethylformamide as the solvent.[11]

$^1O_2(^1\Delta_g)$ is a reactive oxygen species[12] that can react with electron-rich derivatives in three different ways: the ene reaction, [2+2] or [4+2] cycloaddition and the oxygenation of compounds with nucleophilic heteroatoms.[13]

Since it was first defined in 1943 by Schenck,[14] the ene reaction has represented a useful method for the diastereoselective oxyfunctionalization of simple organic derivatives.[15] Two alternative mechanisms have been proposed in the past: concerted or stepwise.[16] Other intermediates that are worth a mention include biradicals,[17] zwitterions,[18] exciplexes[19] and perepoxides.[20] A pivotal study that coupled theoretical and experimental data led to the formulation of a two-step, no-intermediate mechanism with a rate-limiting transition state that resembled that of the formation of a perepoxide in the initially proposed stepwise process.[21] However, a large part of the aforementioned literature deals with reactions performed in organic media. Stensaas and co-workers carried out studies in water using α,β-unsaturated derivatives as mechanistic probes and they proposed a perepoxide intermediate that is stabilized by a hydrogen bond with the water solvent.[22] Recently, an interesting overview of the factors controlling the stereoselectivity of the $^1O_2$/alkene ene reaction was published by Alberti and Orfanopoulos.[23]

Our recent interest in the stability and photostability of transition-metal-phthalocyanines,[24] which have also been used as oxidation catalysts,[25] led us to carry out a more complete photochemical investigation. In this contribution we report a photophysical and -chemical study of three metal–tetrasulfophthalocyanines (M = Pt, Pd, Ru) with the aim of rationalizing their photobehaviour in both the homogeneous and heterogeneous phases using Amberlite® as the supporting agent.

Results and Discussion

As indicated above, the population of long-lived ^{3}MPc* is a fundamental pre-requisite to the generation of $^1O_2(^1\Delta_g)$. Laser flash photolysis with nanosecond time resolution is a powerful tool for obtaining spectroscopic and kinetic features of excited triplets of phthalocyanines. Indeed, these transient species show very intense spectral absorption in the visible region and have lifetimes on the microsecond/millisecond timescale. Figure 2 shows the transient absorption spectra obtained upon laser excitation at 532 nm of PtPcS and PdPcS in Ar-saturated solution recorded at different delay times with respect to the initial laser pulse. In both cases the spectra recorded at 0.1 μs show a main band with a maximum at 520 nm. The decay of these bands fits well with monoexponential kinetics with lifetimes of around 190 μs (Figure 2, insets). Furthermore, the time evolution of the absorption does not reveal the formation of any new transient. Experiments carried out in air-equilibrated and oxygen-saturated solutions showed that for both MPcSs the transients observed are effectively quenched by oxygen with a diffusion-controlled bimolecular rate constant ($k_q \approx 2\times10^9$ M^{-1} s^{-1}). On the basis of the literature data, these spectral and kinetic features can be assigned to the lowest excited triplet states of PtPcS and PdPcS.[26] On the other hand, RuPcS did not show any significant transient absorption in the whole of the UV/Vis spectra region. Time-resolved near-infrared luminescence with sub-microsecond time resolution is the most suitable technique for unequivocally demonstrating the generation of $^1O_2(^1\Delta_g)$. Indeed, this species shows a typical luminescence signal at 1.27 μm with a lifetime on the microsecond timescale[27] (see the Exp. Sect. for details). The quantum yields of the singlet oxygen (Φ_Δ) produced by energy transfer from the excited triplet

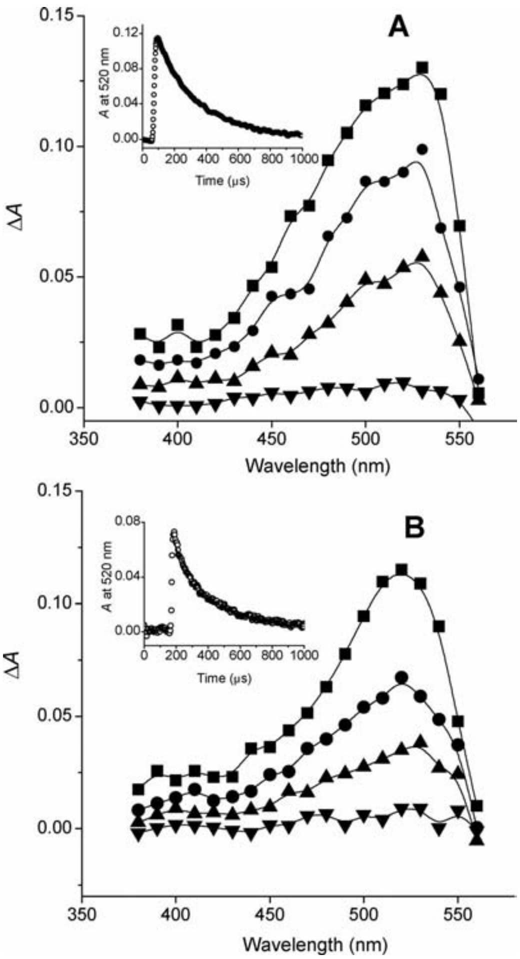


Figure 2. Transient absorption spectra observed upon laser excitation (532 nm) of (A) PdPcS and (B) PtPcS in Ar-saturated aqueous solution at 0.1 (squares), 100 (circles), 300 (triangles, up) and 800 μs (triangles, down) after the laser pulse. $E_{532} \approx 10$ mJ/pulse. Each point is the mean of 10 traces. Insets: decay traces monitored at 520 nm and the related monoexponential fitting.

state of PtPcS and PdPcS to molecular oxygen were determined in partially deuterated water (30% D_2O) solution using tetrakis(4-sulfonatophenyl)porphyrin (TPPS) as the reference compound. The luminescence intensity at zero time of the time-dependent signal (see the Exp. Sect.) was plotted as a function of the laser intensity at different molar ratios.[28] Because all of the solutions were optically matched at the excitation wavelength, the values of Φ_Δ for the phthalocyanines can be obtained directly from the different slopes, π, of the straight lines produced from Equation (1) in which a value of $\Phi_\Delta^{(TPPS)} = 0.6$ was assumed for TPPS, in accord with the literature.[28] The results are shown in Figure 3, together with a typical luminescence decay trace for $^1O_2(^1\Delta_g)$.

$$\Phi_\Delta^{(Pcs)} = \Phi_\Delta^{(TPPS)}\pi^{(Pcs)}/\pi^{(TPPS)} \quad (1)$$

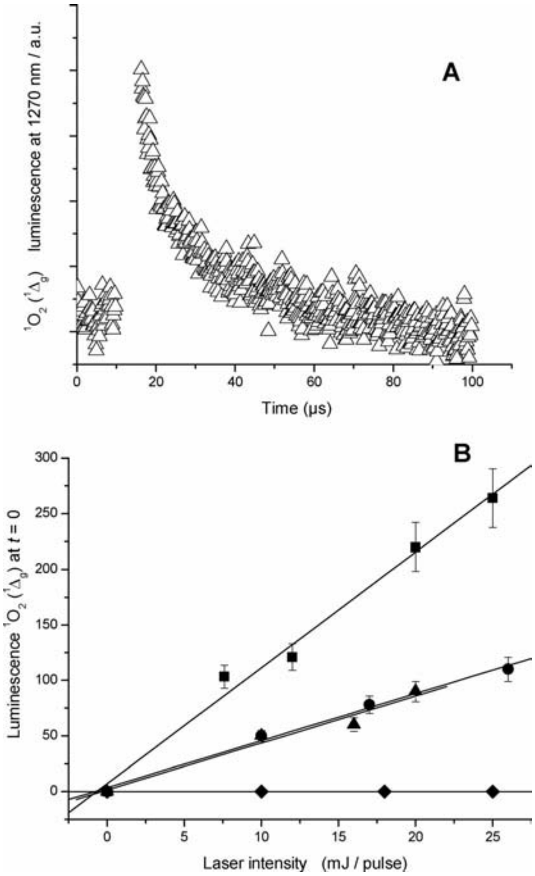


Figure 3. (A) Representative decay kinetics of $^1O_2(^1\Delta_g)$ monitored at 1270 nm and (B) dependence of the luminescence intensity of $^1O_2(^1\Delta_g)$ at $t = 0$ for optically matched solutions of TPPS (squares), PtPcS (circles), PdPcS (triangles) and RuPcS (diamonds). Each point is the mean of 10 traces.

According to the laser flash photolysis experiments, both PtPcS and PdPcS photosensitized the formation of $^1O_2(^1\Delta_g)$ with $\Phi_\Delta = 0.24$ in both cases. In contrast, no $^1O_2(^1\Delta_g)$ generation was observed for RuPcS, in agreement with the absence of signal from the excited triplet state. The value of Φ_Δ found for PtPcS and PdPcS is lower than those reported for similar metal–phthalocyanines in DMF solution,[11] which can be attributed to a partial aggregation of the photosensitizers in the aqueous medium. Indeed, for both PtPcS and PdPcS the visible spectra in water solution showed clear deviations from the Lambert–Beer law at about 2 μM (Figure 4). It is well known that an aggregation phenomenon commonly leads to the self-quenching effects that preclude the photogeneration of $^1O_2(^1\Delta_g)$.[29]

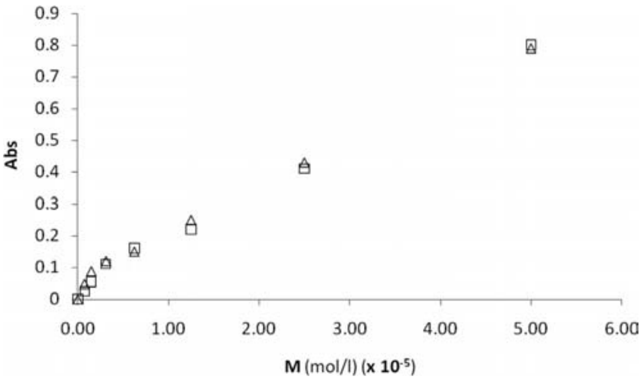


Figure 4. Absorbances recorded at several concentrations of metal–phthalocyanines: PdPcS (squares) and PtPcS (triangles).

This hypothesis is well supported by the spectroscopic data summarized in Table 1. Indeed, in the aqueous medium, the positions of the Q-band absorption maxima of both PtPcS and PdPcS are significantly blue-shifted in comparison with those found in DMF solution in which the MPcSs are present in their monomeric forms.[30]

Table 1. Maximum absorption signals of the Q bands of PtPcS and PdPcS in water, DMF, and when supported on Amberlite® (solid-state spectra).

	Q-band maximum absorption [nm]		
	Water	DMF	Amberlite-supported
PtPcS	603	651	656
PdPcS	590	662	663

We then studied the photostability of the MPcSs by irradiating PtPcS, PdPcS and RuPcS in air-equilibrated water solutions in the presence of 0.1 M NaOH. Both the Pt and Pd derivatives were very stable even after 5 d of continuous irradiation. In contrast, RuPcS showed around 20% degradation after irradiation for 1 d and around 50% degradation after 5 d, as confirmed by the dramatic changes in the steady-state absorption spectra. To support the idea of the involvement of aggregation in this photostability behaviour, we also irradiated (visible light) the MPcSs in the presence and absence of Triton X-100, a well-known agent that is used to monomerize MPcSs in aqueous media. Indeed, the solutions containing the surfactant showed greater bleaching than in the absence of Triton X-100. After 5 d of irradiation, the PdPcS/surfactant system showed a decrease in the Q-band attenuated by 60%, 35% Q-band attenuation was seen for the PtPcS/surfactant system, and RuPcS showed the same degradation trend without the surfactant. These findings strongly suggest that in the aggregated forms seen above, the MPcSs are stable in the presence of $^1O_2(^1\Delta_g)$

and that the bleaching observed in the case of RuPcS should be due to a photodegradation mechanism that is not type II. There are potentially several reasons for the relatively good photostability of PtPcS and PdPcS, and we believe that the aggregation, which tends to hinder the oxidation by $^1O_2(^1\Delta_g)$, is one of these. As expected for the solvent used (D_2O), the lifetime of $^1O_2(^1\Delta_g)$ (ca. 20 µs) is in good agreement with the hypothesis of aggregation contributing to the photostability, which reduces the role of singlet oxygen in oxidation processes with the photosensitizers.

Ene reactions were performed by using tiglic acid and cyclohex-1-ene-1-carboxylic acid as model compounds. The reactions were carried out in both homogeneous and heterogeneous phases. The formation of hydroperoxide and its corresponding alcohol derivative was monitored by NMR upon irradiation with visible light of an alkaline D_2O solution of these α,β-unsaturated acids (10 mM) in the presence of the MPcS (0.1, 0.025 mM). For the heterogeneous reactions, the MPcS complexes were supported on Amberlite® anion-exchange resin (1%, w/w). In the homogeneous phase and for both tiglic acid (Figure 5) and cyclohex-1-ene-1-carboxylic acid (Figure 6), the mass balances (conversion of reactants vs. yield of products) were strictly respected.

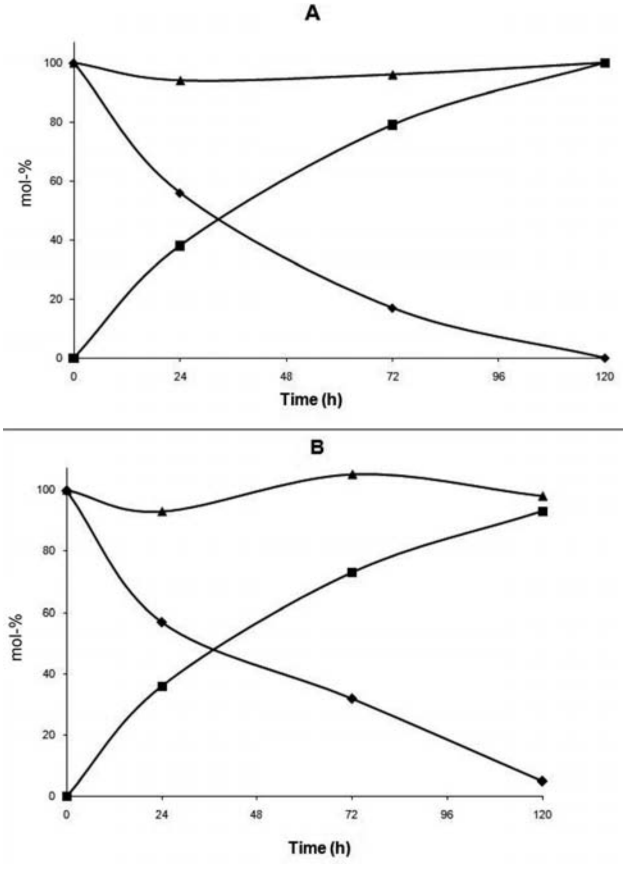


Figure 5. Photobehaviour in the homogeneous phase with (A) PtPcS and (B) PdPcS in the ene reaction with tiglic acid, showing tiglic acid concentrations (circles), yields of alcohol + hydroperoxide (major products, ***a*** + ***a′***; squares) and the mass balance (triangles).

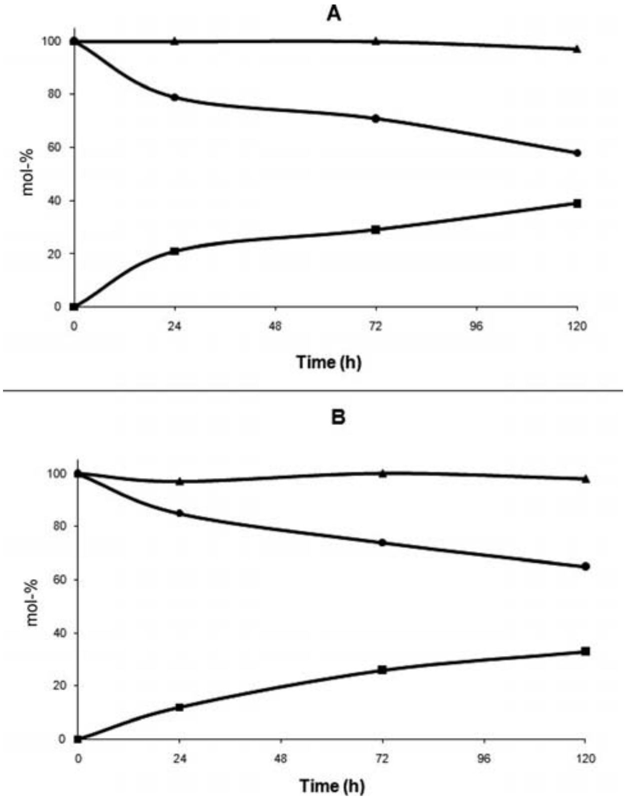


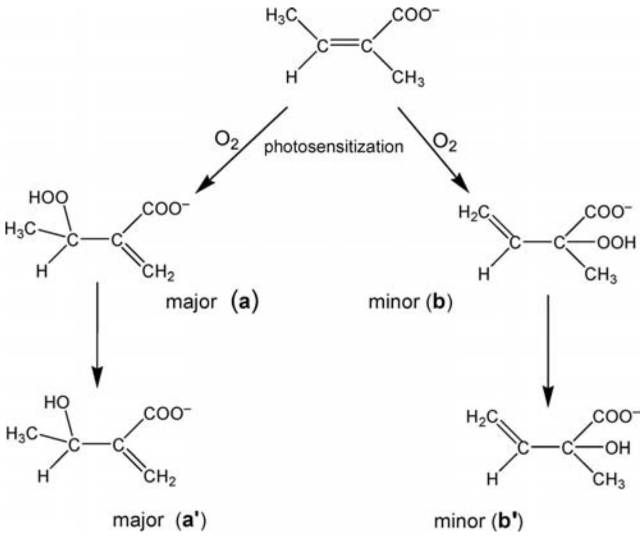
Figure 6. Photobehaviour in the homogeneous phase of (A) PtPcS and (B) PdPcS in the ene reaction with cyclohex-1-ene-1-carboxylic acid, showing cyclohex-1-ene-1-carboxylic acid concentrations (circles), yields of alcohol + hydroperoxide (major isomer; squares) and the mass balance (triangles).

Of the two potential isomers, only one was detected (Scheme 2, **a** and **a′**), in good agreement with the results published by Stensaas et al., who reported a maximum yield of only 5% of the **b** derivative (Scheme 2).[22b] After 5 d, PtPcS triggered quantitative conversion of tiglic acid, whereas with PdPcS a small amount (<5%) of the unreacted reagent was still detectable; RuPcS was totally inactive.

Cyclohex-1-ene-1-carboxylic acid showed significantly lower conversion rates (PtPcS, 37%; PdPcS, 32%; after 120 h). Again, RuPcS was not active.

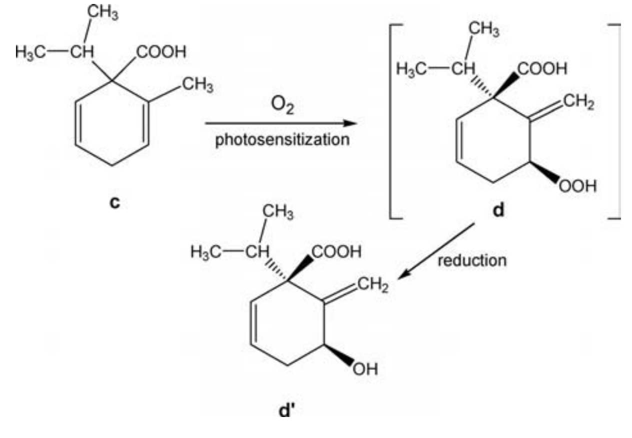
Experiments were also performed at a lower temperature, 0 °C rather than 35 °C (see the Exp. Sect.). For the reactions performed at 0 °C, hydroperoxide **a** was the only product after 24 h. At the higher temperature (35 °C), it is likely that the disproportion of hydroperoxide **a** was very fast as the alcohol derivative **a′** was the main reaction product, at least after prolonged irradiation.

To investigate the regiochemistry of the reactions, we synthesized 2-methyl-1-(1-methylethyl)cyclohexa-2,5-diene-1-carboxylic acid (**c**), which has previously been used in ene reactions performed with chemically or photochemically generated $^1O_2(^1\Delta_g)$.[31] Upon irradiation under the same conditions as described above and in the presence of both PtPcS and PdPcS, only one stable product was detected (see Scheme 3), which appears to be the same product as pre-



Scheme 2. Oxidation of tiglic acid photosensitized by $^1O_2(^1\Delta_g)$.

viously reported[31a] with the carboxy and hydroxy groups mutually *cis*-oriented in the cyclohexenyl ring. In the presence of RuPcS, no reaction was observed even after irradiation for five days.



Scheme 3. Oxidation of 2-methyl-1-(1-methylethyl)cyclohexa-2,5-diene-1-carboxylic acid photosensitized by $^1O_2(^1\Delta_g)$.

Amberlite-supported MPcSs were also used to photooxidize tiglic acid and cyclohexenecarboxylic acid in alkaline D_2O solution. The product distributions in the presence of PtPcS and PdPcS were exactly the same as those seen in the homogeneous phase, although they were formed with around five-fold higher rates of conversion. In fact, for example, 5 d were necessary for the quantitative transformation of tiglic acid under homogeneous conditions in comparison with only one day necessary under heterogeneous conditions. RuPcS showed negligible reactivity with the alcohol yields never exceeding 10% and the hydroperoxide derivative never detected.

The enhanced reactivity observed for PtPcS and PdPcS can be attributed to a lower level of stacking of the photosensitizers induced by the Amberlite. Heterogenization might indeed significantly reduce the aggregation level of the phthalocyanine derivatives, making the photosensitization process more efficient as a result of the increase in the monomeric form, which is the most active in photogenerating $^1O_2(^1\Delta_g)$. Indeed, the solid-state visible spectra of these Amberlite-supported phthalocyanines showed the Q bands to be redshifted to 656 nm with PtPcS and to 663 nm with PdPcS. Of note, these values are perfectly superimposable on the Q bands recorded in DMF in which MPcSs are preferentially present in their monomeric forms[30] (see Table 1).

Conclusions

The photobleaching of phthalocyanines is crucial for application in photodynamic therapy and $^1O_2(^1\Delta_g)$ has often been indicated as being at least partially responsible for the self-bleaching of zinc and aluminium tetrasulfonated phthalocyanines. Indeed, it is commonly accepted in the literature that the photobleaching mechanism of phthalocyanines is complex and that there is often an association with several other kinds of degradative pathways.[32] In our case, good photostability of PtPcS and PdPcS was observed, together with moderate but significant $^1O_2(^1\Delta_g)$ quantum yields. The aggregation of MPcSs in water solution is shown to be involved, although this would appear not to be the only pathway. Note also, for example, that the data in the literature is mainly on AlPc and ZnPc, and metallation by other transition metals alters the π system and therefore their redox properties. Indeed, aggregation of the photosensitizer reduces the concentration of the monomeric active form in the photogeneration of $^1O_2(^1\Delta_g)$, although, on the other hand, this can limit the autoxidation processes mediated by this transient species. Thus, the systems reported herein offer a useful compromise between photostability and $^1O_2(^1\Delta_g)$ quantum yield. The synthetic point of view must also be taken into consideration because the two photosensitizers PtPcS and PdPcS can be used efficiently in both homogeneous and heterogeneous phases to functionalize α,β-unsaturated carboxylic acids by the well-known ene reaction.

Experimental Section

Materials: Tiglic acid, cyclohex-1-ene-1-carboxylic acid, (anthracene-9,10-diyl)bis(methylmalonate), Triton X-100 and Amberlite IRA-900 were purchased from Sigma–Aldrich. Deuterated water (99.8%) was purchased from Armar Chemicals. Ultrapure water was produced by a Millipore Milli-Q plus 185 apparatus. 1-Methylethyl-2-methylcyclohexa-2,5-dienecarboxylic acid was synthesized following the literature procedure.[33] PtPcS, PdPcS and RuPcS were prepared by template synthesis following previously reported general procedures for the synthesis of MPcS.[34] For their characterization, see the publications of d′Alessandro[24] and Nicastro[25] and their co-workers. The Amberlite-supported MPcSs were prepared as indicated in the literature:[35] Amberlite IRA-900 (1 g) was added to a solution of the MPcS (10 mg) in H_2O/CH_3CN (40 mL, 1:1) and the mixture was stirred at room temperature for 48 h. At the end of reaction, the solution was colourless and the phthalocyanine B and Q bands were no longer observed in the UV/Vis spectrum.

Photochemical Experiments in the Homogeneous Phase: Water (or D_2O; 10 mL) containing the MPcS (0.5, 0.1, 0.025 mM) was basified to pH 13 by the addition of NaOH pellets. A GLP 22 Crison pH-meter was used to measure the pH of the solutions at room temperature, with the calibration performed by using Crison standard buffer calibration solutions of pH 7.0 and 9.0. The carboxylic acids (10 mM) were added and the solutions were irradiated with visible light for up to 5 days. The reactions were carried out inside a photoreactor chamber at a temperature of about 35 °C in open quartz test-tubes. Experiments at 0 °C were carried out by using a cryostat apparatus. Aliquots (1 mL) were sampled and the reaction mixtures were analysed by UV/Vis and ^1H and ^{13}C NMR spectroscopy.

Photochemical Experiments in the Heterogeneous Phase: Water (or D_2O; 5 mL) containing the Amberlite-supported MPcS (31.25 mg, 1% w/w) was basified to pH 13 by the addition of NaOH pellets. The carboxylic acids (10 mM) were added and the solutions were irradiated with visible light for up to 5 days under continuous stirring. The reactions were carried out inside a photoreactor chamber at a temperature of about 35 °C in quartz test-tubes. Aliquots (1 mL) were sampled and filtered, and the reaction mixtures were analysed by UV/Vis and ^1H and ^{13}C NMR spectroscopy. Experiments in the presence of ADMA (0.01 mM) were conducted in 50 mM phosphate buffer at pH 7.2, sampling the reaction mixture at 1, 3, 5 and 7 min. Analyses were performed by spectrophotometry, following the decrease in the absorbance at 379 nm.

Steady-State Irradiation: A photochemical multi-ray apparatus (Helios Italquartz, Milano, Italy) equipped with 10 visible-light lamps (15 W each, λ = 450–600 nm), was used to irradiate the water solutions. These lamps (length 47 cm, diameter 2 cm) were fixed in a special lamp-holder with IP 44 protection and were equipped with a special aluminium reflector to increase their radiation power.

Laser Flash Photolysis: All of the samples were excited with the second harmonic of a Nd:YAG Continuum Surelite II-10 laser (532 nm, 6 ns, ca. 5 mJ) using quartz cells with a path length of 1.0 cm. The excited solutions were analysed with a Luzchem Research mLFP1-11 apparatus with an orthogonal pump/probe configuration. The probe source was a ceramic xenon lamp coupled to quartz fibre optic cables. The laser pulse and the mLFP1-11 system were synchronized by a Tektronix TDS 3032 digitizer operating in pre-trigger mode. The signals from a compact Hamamatsu photomultiplier were initially captured by the digitizer and then transferred to a personal computer controlled by Luzchem Research software operating in the National Instruments LabView 5.1 environment. For experiments in the absence of oxygen, the solutions were deoxygenated by bubbling with a vigorous and constant flux of pure argon (previously saturated with solvent). In all of these experiments, the solutions were renewed after each laser shot (in a flow cell of 1 cm optical path), to prevent probable auto-oxidation processes. The sample temperature was 295 ± 2 K. The energy of the laser pulse was measured at each shot with a SPHD25 Scientech pyroelectric meter.

Singlet Oxygen Detection: Photogeneration of $^1O_2(^1\Delta_g)$ upon laser excitation of the photosensitizer was monitored by luminescence measurements in air-saturated deuterated water. We used D_2O because it extends the lifetime of singlet oxygen compared with in water. The near-IR luminescence of singlet oxygen at 1.27 µm resulting from the forbidden transition $^3\Sigma_g^- \leftarrow {}^1\Delta_g$ was observed; this was probed orthogonally to the exciting beam with a pre-amplified (low impedance) Ge photodiode (Hamamatsu EI-P, 300 ns resolution) maintained at –196 °C and coupled to a long-pass silicon filter (>1.1 µm) and an interference filter (1.27 µm). Pure signals of $^1O_2(^1\Delta_g)$ were obtained as differences between signals in air- and Ar-saturated solutions. The temporal profile of the luminescence was fitted to a single-exponential decay function with the exclusion of the initial portion of the plot, which was affected by scattered excitation light, fluorescence and the formation profile of singlet oxygen itself. The initial luminescences were extrapolated from the curve-fitting.

Analysis: NMR measurements were performed with a Bruker Avance 300 MHz spectrometer equipped with a 5 mm BBO probe (30–300 MHz). Water suppression was determined using a presaturation sequence with a composite pulse (zgcppr; Bruker sequence). A co-axial capillary tube containing a 30 mM solution of [2,2,3,3-D_4]3-(trimethylsilyl)propionic acid was used as reference and for the lock procedure, as the sodium salt in water (D_2O). The UV/Vis spectra were recorded with a 6505 UV/Vis Jenway spectrophotometer.

Acknowledgments

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