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PHOTOINDUCED ACTIVATION OF MOLECULAR OXYGEN BY VARIOUS PORPHYRINS, BIS-PORPHYRINS, PHTHALOCYANINES, PYRIDINOPORPHYRAZINS, AND THEIR METAL DERIVATIVES

P. MAILLARD, P. KRAUSZ, C. GIANNOTTI *

Institut de Chimie des Substances Naturelles, CNRS, Gif-sur-Yvette 91190 (France)

and S. GASPARD *

Laboratoire des Pigments Végétaux et Substances Modèles, Ecole Normale Supérieure de St. Cloud, St. Cloud 92210 (France)

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Summary

Aerobic irradiation of tetraphenylporphyrins, phthalocyanines, tetra-t-butylphthalocyanines, tetracarboxylphthalocyanines, tetrapyridinoporphyrazins and some of their metal derivatives with visible light ($\lambda > 420$ nm) give singlet oxygen by energy transfer and oxygen superoxide by electron transfer, but some of their Cu, Zn of Pt derivatives are efficient quenchers for superoxide formation.

Introduction

It is well known that several dyes such as porphyrins and their derivatives can induce the photooxidation of a large variety of organic substrates [1—3], and it has been established that one of the intermediates in these reactions is singlet oxygen produced by energy transfer from the dye triplet state to the oxygen singlet state [4—6]. On the other hand, phthalocyanines are well known to be reactive in the oxidations but their photochemistry has not been much studied. This is certainly due to the lack of solubility of these compounds in the usual solvents. Studies have been made on heteregenous suspensions [7], and it was shown that under irradiation by visible light the metal-free phthalocyanine undergoes an electron transfer and formation of oxygen superoxide. Very recently the formation of oxygen superoxide has been observed

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* Present address I.C.S.N.-C.N.R.S., 91190 Gif-sur-Yvette (France).

with metal-free and metalloporphyrins, which are well known as singlet oxygen photosensitizers [8].

We describe in this paper the photochemical behaviour towards molecular oxygen of several porphyrins, bis-porphyrins, phthalocyanines and pyridinoporphyrazins, with or without complexed metal.

Experimental

The porphyrins and their metal derivatives were prepared by the usual methods [9]. The bis-porphyrins were prepared as described by Little [10]. The syntheses of soluble phthalocyanines and their metallic derivatives have already been reported [11]. The solvents used (acetonitrile, 2,6-lutidine, toluene, dimethyl sulfoxide, pyridine and hexane) were purified by careful distillation. The 2,2′,6,6′-tetramethylpiperidine and the diazabicyclooctane were purchased from Aldrich, and were respectively distilled and sublimed before use. The photochemical and ESR equipments have been described elsewhere [8].

Nomenclature used in this paper. H_2TPP, 5,10,15,20-tetraphenylporphyrin; MTPP, metallo-5,10,15,20-tetraphenylprophyrin; H_2Pc, free phthalocyanine; MPc, metallophthalocyanine (M = Co, Zn, Cu, Pt, Ni); H_2TPPo · C_3p · TPPH_2, 5,10,15-triphenyl-20[2-[3-[*p*-(10,15,20-triphenyl-5-porphinyl)-phenoxy]-propoxy]phenyl]porphyrine; CoTPPo · C_3p · TPPH_2, 5,10,15-triphenyl-20-[2-[3-[*p*-(10,15,20-triphenyl-5-porphinyl)phenoxy]propoxy]phenyl]porphinato(2—)]cobalt(II); CoTPPo · C_3o · TPPCo, 5,10,15-triphenyl-20-[2-[3-[*o*-(10,15,20-triphenyl-5-porphinyl)phenoxy]propoxy]phenyl]porphinato-(2—)]cobalt(II)-cobalt(II) (Fig. 1).

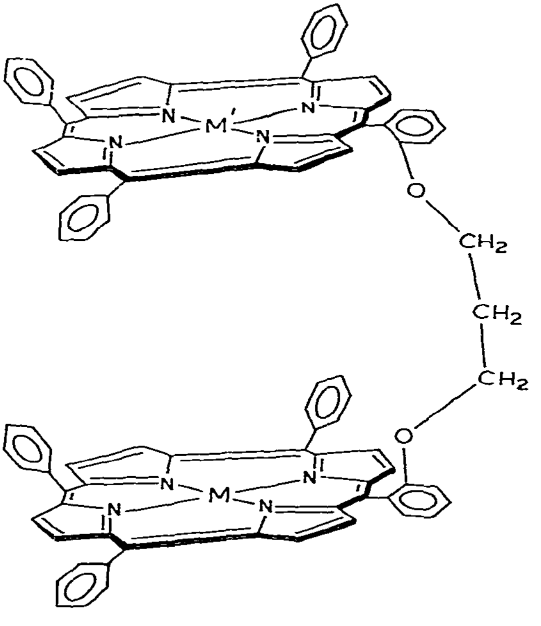

Fig. 1. M = M′ = H_2: H_2TPPo · C_3o · H_2TPP, M = M′ = Co^{II}: CoTPPo · C_3o · TPPCo, M = M′ = Zn: ZnTPPo · C_3o · TPPZn, M = M′ = Cu: CuTPPo · C_3o · TPPCu, M = M′ = Pt: PtTPPo · C_3o · TPPPt.

Results

Metal-free tetraphenylprophyrin (H_2TPP) [9], bis(tetraphenyl)porphyrins [10] (H_2TPPo · C_3p · H_2TPP), (H_2TPPp · C_3p · H_2TPP), (H_2TPPo · C_3o · H_2TPP) (Fig. 1), phthalocyanines (H_2Pc), their corresponding metal derivatives [11] (Fig. 1) and also the 4,4′,4″,4‴-metallo-tetra-t-butylphthalocyanine (MPc4T · t-Bu), 4,4′,4″,4‴-tetracarboxyphthalocyanine (MPc4TC) and 4,4′,4″,4‴-tetrapyridinoporphyrazin (MPc4TCaza) [11] in 5×10^{-3} *M*) were irradiated with visible light ($\lambda > 420$ nm) in the aprotic organic solvents benzene, toluene or dimethyl sulfoxide, partly or fully saturated with air or oxygen and containing specific singlet or superoxide oxygen spin traps (5×10^{-2} *M*). We used 2-methylpentene, ergosteryl acetate [13], and 2,2,6,6-tetramethylpiperidine [14, 15] as singlet oxygen quenchers and 5,5′-dimethyl-1-pyrroline *N*-oxide [7,12] as the super oxide spin trap.

TABLE 1

SPECIES DETECTED (The solvent system used is: a, Toluene; b, 30% 2,6-lutidine/70% acetonitrile, c, heterogenous suspension in toluene; d, hexane; e, dimethyl sulfoxide; f, α-chloronaphthalene. The methods used for singlet oxygen or oxygen superoxide detection are: 1,2-methylpentene; 2, ergosteryl-acetate; 3, 5,5-dimethylpyrroline-1-oxide (DMPO); 4, 2,2,6,6-tetramethylpiperidine.)

Excited substrate	$^1O_2$			$O_2^{-\cdot}$		
	Solvent system	Method	Intensity	Solvent system	Method	Intensity
TPP	a, b	1, 2, 4	0.1 weak	b	3	0.6 moderate
TPP/DABCO	b	2	0	b	3	0.5 moderate
H_2Pc	c, f	4	0·6 moder.	b	3	0·5 moderate
H_2TPPo . C_3p · H_2TPP	a	2, 4	0·8 strong	b	3	0·3 weak
H_2TPPo · C_3p · H_2TPP/DABCO	a	2, 4	0 none	b	3	0·3 weak
H_2TPPo · C_3o · TPPH_2	a	4	0·8 strong	b	3	0·2 v. weak
H_2TPPp · C_3p · TPPH_2	a	4	0·8 strong	b	3	0·2 v. weak
H_2TPPo · $(OC_{12}H_{25})_4$	d	4	0·3 weak	b	3	0·2 v. weak
CoTPP	a	2, 4	0·0 none	b	3	0·0 none
CoTPPo · C_3p · TPPH_2	a	2, 4	0·0 none	b	3	0·0 none
CoTPPo · C_3o · TPPCo	a	2, 4	0·0 none	b	3	0·0 none
CoTPPp · C_3p · TPPCo	a	4	0·0 none	b	3	0·0 none
CoPc4Tc b	e	4	0·0 none	e	3	0·0 none
ZnTPP	a	4	0·1 weak	b	3	0·9 strong
ZnTPPo · C_3o · TPPZn	a	4	0·2 weak	b	3	1·0 v. strong
ZnPc4Tc	c, e	2, 4	0·2 weak	b, e	3	0·0 none
ZnPc4T · aza	e	4	0·3 weak	b, e	3	0·0 none
CuTPP	a	4	0·2 weak	b	3	0·0 none
CuPc4T · t-Bu	a	4	0·2 weak	a, b	3	0·1 v. weak
CuTPPo · C_3o · TPPCu	a	4	0·3 weak	b	3	0·0 none
CuPc4T · t-Bu/DABCO	a	4	0·0 none	b	3	0·1 v. weak
PtTPP	a	4	1·0 v. strong	b	3	0·5 moderate
PtTPPo · C_3o · TPPPt	a	4	1·0 v. strong	b	3	0·5 moderate
PtTPP/DABCO	a	4	0·0 none	b	3	0·4 moderate
PtPc4TC	e	4	0·3 weak	e	3	0·0 none
NiTPP	a	4	0·0 none	b	3	0·0 none
NiPc	e	4	0·0 none	e	3	0·0 none
NiPc3T · aza	e	4	0·0 none	e	3	0·0 none

TABLE 2

Mixture studied (1/1) (5×10^{-3} *M*)	Solvent system	Species observed with DMPO
TPP/ZnTPP	CH_3CN/lutidine, 7/3	DMPO-$O_2^{-\cdot}$
ZnTPP/CuTPPo · C3o · CuTPP	CH_3CN/lutidine, 7/3	none
ZnTPP/CuTPP	CH_3CN/lutidine, 7/3	none
ZnTPP/ZnPc4TC	DMSO or CH_3CN/lutidine, 7/3	none
ZnTPP/ZnPc4T · aza	DMSO or CH_3CN/lutidine, 7/3	none
ZnTPP/PtPc4TC	DMSO or CH_3CN/lutidine, 7/3	none
ZnTPP/CuPc4T · t-Bu	CH_3CN/lutidine, 7/3	trace of DMPO-$O_2^{-\cdot}$

In Table 1 we have summarized the results obtained. The intensity of the signal coming from the spin-trapped $O_2^{-\cdot}$ superoxide, which is sharply reduced by addition of 10 to 30% of methanol or water, is virtually unaffected by addition of a good $^1\Delta g$ oxygen quencher such as 1,4-diazabicyclooctane (DABCO) [17—19], showing that the formation of oxygen superoxide is not coming from the decomposition of the $^1\Delta g$ oxygen from the direct quenching. The quantum efficiency for trapped radicals could not be precisely determined, but it can be estimated that "strong" signals obtained for the ZnTPP for the $O_2^{-\cdot}$ and $^1O_2$ correspond to an efficiency of approximately 0.1. The data in Table 1 indicate that ZnTPP, PtTPP and PtTPPo · C_3p · PtTPP give oxygen superoxide under photolysis but with ZnPc4TC, ZnPc4T · aza and PtPc4Tc there is no formation of $O_2^{-\cdot}$ while all nickel complexes studied give neither singlet oxygen nor oxygen superoxide. On the other hand, the CuTPP, CuTPPo · C_3o · CuTPP and also the CuPc4T · t-Bu are good photosensitizers for singlet oxygen while (CuOEtP) [17] and copper hematoporphyrin (CuHMP) are not [15]. In addition, CuPc4T · t-Bu gives a trace of the oxygen superoxide. Surprisingly, CoTPPo · C_3p · H_2TPP which has one metal-free porphyrin which should potential catalyse formation of oxygen superoxide or singlet oxygen gives no photo-induced reaction with oxygen.

We also note that the studied metal-free bis-porphyrins H_2TPPo · C_3o · TPPH_2, H_2TPPo · C_3p · H_2TPP and H_2TPPp · C_3p · H_2TPP, have the same type of reactivity as TPP itself. These results are in good agreement with features of the UV visible spectra. In the solvents used there is no shift of the Soret band indicating strong interaction between the two macrocycles. The greater photosensitizer activity of the metal-free bis-TPP than of TPP itself (10/1) could be explained in terms of the absence of any interaction between the two porphyrin macrocycles. The metal free H_2Pc in heteregenous suspension [7] gives rise to oxygen superoxide; we have now shown that under the same conditions the H_2Pc is also a very good singlet oxygen sensitizer. As we have mentioned previously the ZnPcTC, PtPcTC and CuTPP give singlet oxygen but no formation of $O_2^{-\cdot}$ has been detected. The results shown in Table 2 indicate that these compounds are very good quenchers for the oxygen superoxide formed, for example, by the ZnTPP.

Discussion

The energy transfer involved in the formation of singlet oxygen comes from the triplet state of the photosensitizer (Fig. 2) [16]. The difference between

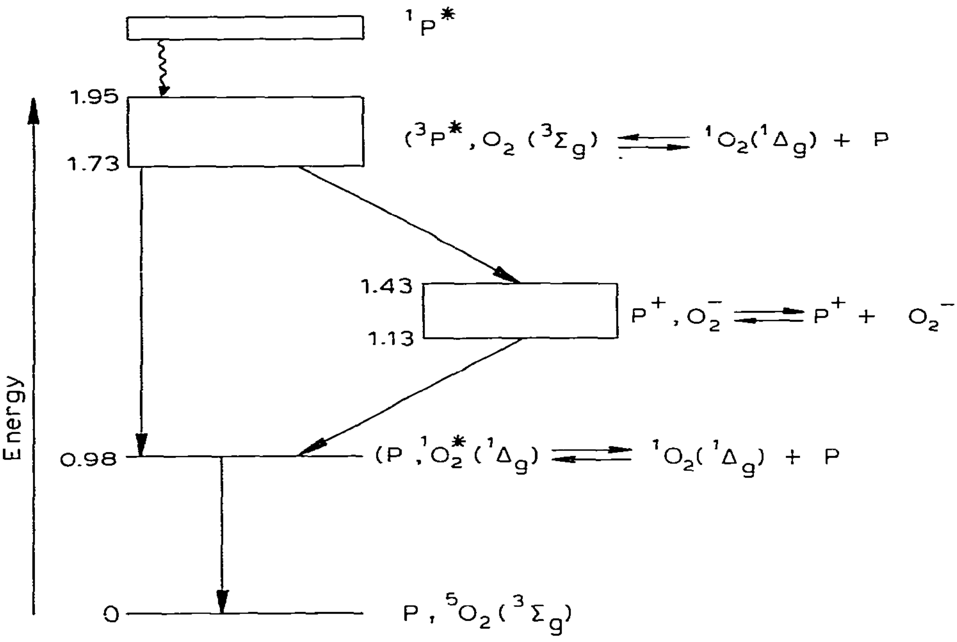

Fig. 2. Energy relationships for porphyrin and metalloporphyrins—oxygen couples. Energies (in volts) are from ref. 8.

the dye which photosensitizes the ground state $^3\Sigma g O_2$ to $1\Delta g O_2$ and the one which does not, originates either in the energy levels of the triplet states or in the life time of the triplet states. The triplet state energy level of the donating compound must be above the oxygen singlet state energy level. The increase in the triplet state energy level, or the increase in the life time of these excited states, due to the nature of the macrocyclic ring, could explain why the CuTPP, CuTPPo · C_3o · CuTPP and CuPc4T · t-Bu under visible light irradiation give singlet oxygen, while the CuHMP and the CuOEtP do not. Gouterman and al. [20] have demonstrated that in the case of the copper porphyrin and copper octaalkylporphyrins (CuOAlP) the spectrum is essentially due to a triplet doublet; on the other hand, the luminescent spectrum of the CuTPP is essentially due to a quartet state.

Thus CuTPP must be a better singlet oxygen photosensitizer than CuOAlP. In the case of CuPc4T · t-Bu and of CuTPPo · C_3o · CuTPP we can postulate that the energy level of the triplet quartet is similar to the level of the CuTPP which must be involved in the photosensitizing properties of these compounds towards singlet oxygen formation. In confirmation of this point, it has been shown that the quantum yield of the CuPc triplet state formation (>0.7 is quite large [20]).

The Co^{II} and Ni^{II} complexes give no singlet oxygen and this could be attributed to the fact that they are not luminescent. $\emptyset p < 0.0005$ [21]. On the other hand the Zn and Pt complexes have good phosphorescent emission quantum yields (0.2—0.9) and are fairly good singlet oxygen photosensitizers [21].

It has recently been shown that singlet oxygen sensitizers can produce oxygen superoxide by electron transfer [7,8,22]. The experiments on the studied compounds show that those compounds which give no singlet oxygen also give no oxygen superoxide. Following the mechanism already described [8] (Fig. 2) the triplet energy level of the (P^*O_2) complex is between the $^1\Sigma g$ and $^1\Delta g$ oxygen singlet energy level. A compound which has a smaller energy level $^3P^*$ than the oxygen $^1\Delta g$ singlet state cannot give any singlet oxygen and therefore cannot transfer one electron and produce $O_2^{-\bullet}$. This must be the case for cobalt and nickel complexes.

For the zinc and platinum phthalocyanines and copper porphyrins (or bisporphyrins), it seems that a more complex process is involved. These compounds can induce singlet oxygen formation but cannot give oxygen superoxide. We have shown that they are quenchers for ZnTPP oxygen superoxide formation (Table 2). Two mechanisms can account for these results: either a very fast decomposition of the superoxide anion $O_2^{-\bullet}$ or quenching of the electron transfer from the donor to the oxygen. In the case of CuTPP we have shown that quenching of the electron transfer [23] is involved. On the other hand the reactions with zinc and platinum phthalocyanines look similar to those already described for FeTPP [24] and superoxyde dismutase [25,26]. A study of this problem is in progress.

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