

Photochemical production and characterisation of the radical ions of tetraphenylporphycenes†

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Both the radical anion and radical cation of 2,7,12,17-tetraphenylporphycene and of its palladium(II) complex have been produced by photochemical methods. Their electronic absorption spectrum and decay kinetics have been characterised by global analysis of the time–absorbance–wavelength matrix. The results provide deeper insight on the role of these radical ion species in the photodynamic activity of tetraphenylporphycenes.

Introduction

The novel photosensitisers 2,7,12,17-tetraphenylporphycene (TPPo) and its Pd(II) complex (PdTPPo) have been proposed as candidate drugs for photodynamic therapy (Fig. 1).^{1–3} The study of their photophysics⁴ revealed quite an ideal profile for use in PDT and this was confirmed by the efficient photodynamic inactivation of a wide range of cancer cell lines.^{2,5–7} It is now generally accepted that two general mechanisms can account for the photooxidative damage that leads to cell death. (i) The so-called type-I mechanism which involves the direct reaction of the drug, usually referred to as the photosensitiser, with a biomolecule through electron- or hydrogen-transfer pathways. The radicals or radical ions formed in this primary step readily react with oxygen to produce peroxyradicals, which initiate autooxidation chains eventually leading to cell death. (ii) In the type-II mechanism, energy transfer from the photoexcited sensitiser to oxygen occurs, and the highly reactive, electronically-excited singlet molecular oxygen, O₂(¹Δ_g), is formed, which then reacts with the biomolecules. Factors such as the nature of the sensitiser, the properties of its excited states, *e.g.* energy, lifetime and redox potential, the site of localisation *in vivo*, and the local concentration of target biomolecules and oxygen may be determinant in favouring one mechanism over the other.^{8–11} It is therefore important to establish, for any new sensitiser, its ability to produce both kinds of chemistry.

In the case of TPPo and PdTPPo, the properties of their excited states and their ability to sensitise the formation of O₂(¹Δ_g) have already been documented.⁴ As a means to assess their ability to participate in type-I photodynamic processes, we have studied the photochemical production of their radical anion and cation species and characterised their absorption spectra and kinetics.

The first report on the formation and characterisation of radical ions of porphycenes is by Schlüpmann *et al.*¹² who formed the rad-

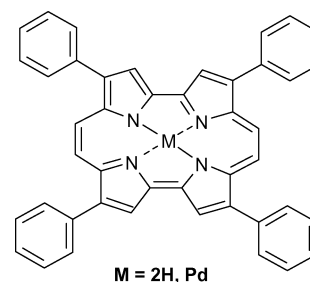


Fig. 1 Chemical structure of TPPo and PdTPPo.

ical anion of the unsubstituted free-base porphycene by reaction with sodium metal and characterised its structure by ESR, ENDOR, and TRIPLE techniques. Later, they extended these studies to some tetraalkyl-derivatives.¹³ Since these pioneering works, further studies on alkyl-substituted porphycenes have been reported using different techniques such as spectroelectrochemistry,^{14–18} pulse- or γ -radiolysis,^{19,20} and Raman spectroscopy.^{21,22} We contribute now the first report for aryl-substituted porphycenes.

Materials and methods

Chemicals

TPPo and PdTPPo were synthesised as described previously.^{1–3} Biphenyl (BP, 99%), benzonitrile (PhCN, 99.9%, HPLC grade), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP, 99.9%) from Aldrich, as well as *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD, 99%) from Sigma were used as received. *N*-methylacridinium hexafluorophosphate (MA⁺) was synthesised by methylation of acridine with methyl iodide in refluxing acetonitrile followed by treatment of the resulting *N*-methylacridinium iodide with silver hexafluorophosphate in methanol.²³ Argon 5.0 was from Abelló-Linde.

Photophysical measurements

Absorption spectra were recorded on a Varian Cary 4 spectrophotometer. Fluorescence quenching measurements were performed with a Spex Fluoromax-2 spectrofluorometer. Radical ions were produced and characterised by nanosecond laser flash photolysis

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† Electronic supplementary information (ESI) available: Time-absorbance–wavelength matrices for TPPo^{•-}, PdTPPo^{•-}, TPPo^{•+} (PhCN), TPPo^{•+} (HFP), PdTPPo^{•+} (PhCN) and PdTPPo^{•+} (HFP). See DOI: 10.1039/b517686g

using an OPO laser (SL OPO, Continuum; 5 ns pulsewidth, 1–10 mJ pulse⁻¹) pumped by a Q-switched Nd-YAG laser (Surelite I-10, Continuum). Photoinduced absorbance changes were monitored with right-angle geometry by an analysing beam produced by a Xe lamp (PTI, 75 W) in combination with a dual-grating monochromator (mod. 101, PTI) coupled to a photomultiplier (Hamamatsu R928, 300–800 nm) or a North Coast EO-817P germanium detector (800–1600 nm). Kinetic analysis of the individual transients was done with the software FitLW developed in our group. Global kinetic analysis of the transient time-absorbance-wavelength matrix was performed with the software Specfit (Spectrum Software Associates). All measurements were carried out in PhCN or in HFP containing 10% PhCN.

Results and discussion

1. Radical anions

Electrochemical studies have shown that up to two electrons can be added to the π -system of TPPo and of PdTPPo.⁴ Radical anions were produced by photoinduced electron transfer from TMPD to the triplet state of the porphycenes in PhCN.

The ground state reduction potential of TPPo and PdTPPo has the same value, -0.73 V vs. SCE in CH_2Cl_2 .⁴ The addition of the triplet energy (1.28 eV for TPPo and 1.31 eV for PdTPPo⁴) to this value yields the reduction potential of the triplet state, $E^0(^3\text{S}/\text{S}^{\cdot-}) = E^0(\text{S}/\text{S}^{\cdot-}) + E_{\text{T}} = 0.55$ V and 0.58 V vs. SCE for ³TPPo and ³PdTPPo, respectively. Thus, electron transfer from TMPD ($E^0(\text{TMPD}^{\cdot+}/\text{TMPD}) = 0.16$ V vs. SCE in PhCN^{24–26}) to the triplet porphycenes is thermodynamically feasible.

In the presence of increasing concentrations of TMPD, the rate of decay of ³TPPo increased linearly according to $k_{\text{obs}} = k_0 + k_{\text{q}} [\text{TMPD}]$ (Fig. 2(A)). Analysis of data in Fig. 2 yields $k_{\text{q}} =$

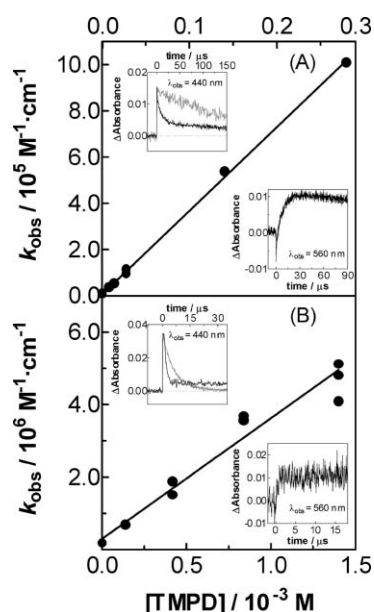


Fig. 2 Increase of the decay rate constant of (A) ³TPPo and (B) ³PdTPPo by TMPD in argon-saturated PhCN. The insets show the absorbance changes in the absence (grey) and in the presence (black) of TMPD. The TMPD concentrations were 28 μM for TPPo and 200 μM for PdTPPo. $\lambda_{\text{exc}} = 532$ nm.

$(3.60 \pm 0.04) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Simultaneously, the formation of a new transient species could be observed, which rose with the same kinetics as those for ³TPPo decay and which is assigned to TPPo^{•-}.

Monitoring the transients at different wavelengths allowed the construction of a time-absorbance-wavelength matrix (see electronic supplementary information, ESI)[†] that yielded, through global analysis, the absorption spectrum and lifetime of TPPo^{•-} (Fig. 3). TPPo^{•-} has a lifetime of 870 μs in argon-saturated benzonitrile. It shows similar bands as the π radical anion of unsubstituted- and tetraalkyl-porphycenes,^{14–19,21,22} *i.e.*, several bands in the 680 to 940 nm range with maximum at 850 nm, and a new band at 560 nm.

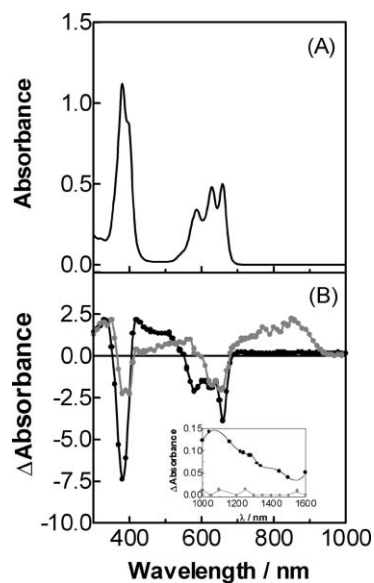


Fig. 3 (A) Ground state spectrum of TPPo. (B) Transient absorption spectrum of ³TPPo (black) and of TPPo^{•-} (grey) as recovered by global analysis of the time-absorbance-wavelength matrix (see ESI).[†] Inset: transient absorption spectrum from 1000–1600 nm. $\lambda_{\text{exc}} = 660$ nm.

Likewise, formation of PdTPPo^{•-} was observed with an ET rate constant of $(3.3 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 2(B)). As the ³PdTPPo lifetime, 6.2 μs in benzonitrile, is much shorter than that of TPPo (176 μs),⁴ a higher concentration of TMPD was required to capture the same fraction of excited-state molecules. The lifetime of PdTPPo^{•-} is 330 μs in benzonitrile, somewhat shorter than that of TPPo^{•-}. Fig. 4 shows the transient absorption spectrum of PdTPPo^{•-}, which is markedly different from that of ³PdTPPo. It shows the typical marker bands of the porphycene π -radical (maxima at 560 nm and 830 nm), implying that the reduction occurs at the π -system with no participation of the central metal ion. This is in agreement with the first reduction potential of PdTPPo being almost equal to that of TPPo.⁴

2. Radical cations

Radical cations were formed using the co-sensitisation method.^{28,30–34} Briefly, a photoexcited primary electron acceptor (¹MA⁺ 1 mM, $E(^1\text{MA}^+/\text{MA}^{\cdot+}) = 2.31$ V vs. SCE in CH_2Cl_2 ²⁷) abstracted an electron from the co-sensitiser (BP 0.2 M, $E(\text{BP}^{\cdot+}/\text{BP}) = 1.96$ V vs. SCE in CH_2Cl_2 ²⁸), producing its long-lived radical cation (BP^{•+}). This species subsequently abstracted

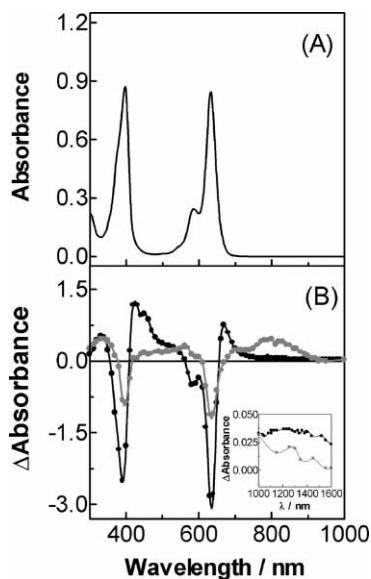
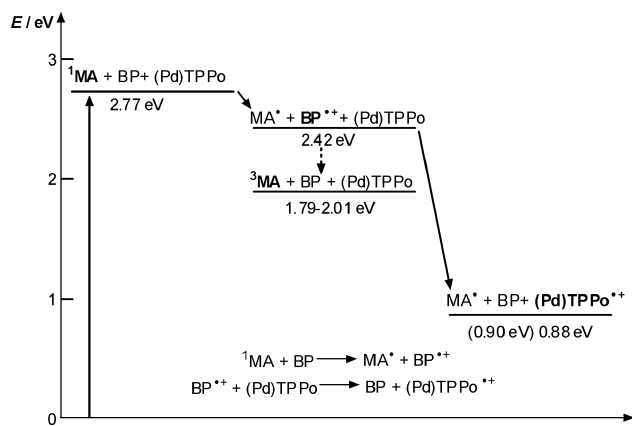


Fig. 4 (A) Ground state spectrum of PdTPPo. (B) Transient absorption spectrum of $^3\text{PdTPPo}$ (black) and of $\text{PdTPPo}^{\bullet-}$ (grey) as recovered by global analysis of the time-absorbance-wavelength matrix (see ESI).† $\lambda_{\text{exc}} = 630$ nm. Inset: transient absorption spectrum from 1000–1600 nm.

an electron from the tetraphenylporphyrines (*ca.* 50 μM , $E(\text{TPPo}/\text{TPPo}^{\bullet+}) = 1.08$ V, $E(\text{PdTPPo}/\text{PdTPPo}^{\bullet+}) = 1.05$ V vs. SCE in CH_2Cl_2)⁴ to yield their radical cations (Scheme 1).



Scheme 1 Energy diagram showing the cascade of events leading to the formation of $(\text{Pd})\text{TPPo}^{\bullet\bullet+}$ by the co-sensitisation method.^{4,27–29}

In order to ensure a correct assignment of the transient spectra, the photosystem $\text{MA}^{\bullet}/\text{BP}$ was first examined in detail. From the decrease of both the $^1\text{MA}^{\bullet}$ steady-state fluorescence and lifetime (I and τ , respectively, see eqn (1)), we found that BP quenches $^1\text{MA}^{\bullet}$ with a rate constant $k^1_{\text{MA}^{\bullet}, \text{BP}} = 2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 5)

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k^1_{\text{MA}^{\bullet}, \text{BP}} \tau_0 [\text{BP}] \quad (1)$$

where I_0 and τ_0 ($= 42$ ns) are the fluorescence intensity and lifetime, respectively, of $^1\text{MA}^{\bullet}$ in the absence of biphenyl.

Analysis of the time-absorbance-wavelength matrix obtained in solutions containing MA^{\bullet} (1 mM) and BP (0.2 M) photoexcited at 450 nm, where only MA^{\bullet} absorbs, yielded three transient species (Fig. 6) assigned to MA^{\bullet} , $\text{BP}^{\bullet\bullet+}$, and $^3\text{MA}^{\bullet}$ by similarity with their published spectra.^{28,29,35}

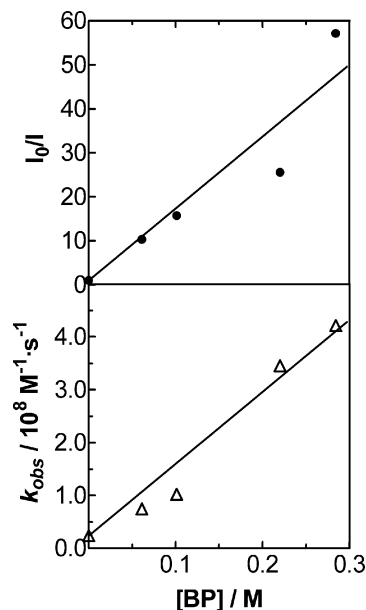


Fig. 5 Quenching of $^1\text{MA}^{\bullet+}$ by BP according to (●) data from the ^1MA steady-state fluorescence ($\lambda_{\text{exc}} = 328$ nm) and, (Δ) data from the ^1MA time-resolved fluorescence ($\lambda_{\text{exc}} = 450$ nm).

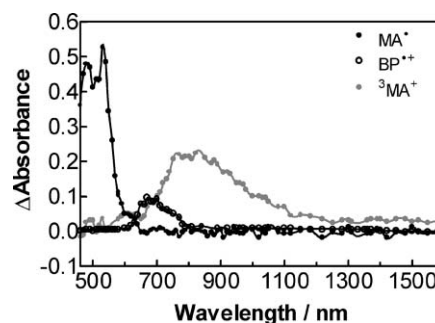


Fig. 6 Transient absorption spectrum in benzonitrile corresponding to MA^{\bullet} , $\text{BP}^{\bullet\bullet+}$ and $^3\text{MA}^{\bullet}$ as recovered by global analysis of the time-absorbance-wavelength matrix. $\lambda_{\text{exc}} = 450$ nm.

In argon-saturated benzonitrile, $\text{BP}^{\bullet\bullet+}$ lives 30 μs , whereas MA^{\bullet} lives several thousands of microseconds and $^3\text{MA}^{\bullet}$ lives 5 μs . When the same system was measured in HFP, a solvent well known to stabilise radical cations,^{36–38} the lifetime of $\text{BP}^{\bullet\bullet+}$ increased 30-fold, up to 1000 μs . Likewise, the lifetime of MA^{\bullet} decreased down to 5 μs , and that of $^3\text{MA}^{\bullet}$ increased ten fold to 50 μs .

When TPPo 38 μM was added to the above photosystem ($\lambda_{\text{exc}} = 455$ nm), quenching of $\text{BP}^{\bullet\bullet+}$ was observed. Under these conditions, less than 10% of 455 nm photons were absorbed by TPPo. From the change of the decay rate of $\text{BP}^{\bullet\bullet+}$ in the presence and absence of TPPo, the reaction rate constant between $\text{BP}^{\bullet\bullet+}$ and TPPo was estimated as $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in PhCN and HFP, respectively. The ensuing $\text{TPPo}^{\bullet\bullet+}$ lived 60 μs in PhCN, increasing up to 3 ms in HFP.

Fig. 7 shows the transient absorption spectra in both solvents. Broad absorption bands can be observed in the 460–570 nm region and above 700 nm, with maxima at 530 and 820 nm. Transient absorption below 460 nm was dominated by the intense photobleaching of the MA^{\bullet} ground state. Again, these spectral changes are consistent with the results on the unsubstituted

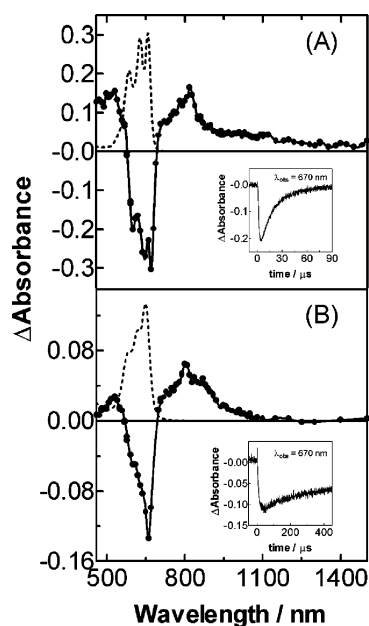


Fig. 7 Transient absorption spectra of TPPo^{**} in (A) PhCN and (B) HFP, as recovered by global analysis of the time-absorbance-wavelength matrix (see ESI).† The ground state absorption spectrum is shown in dotted line. Insets: transient absorbance at 670 nm, $\lambda_{exc} = 455$ nm.

porphyrine and its tetraalkyl derivatives.^{15,16,18,20} Global analysis of the time-absorbance-wavelength matrix using the kinetic system in Scheme 1 (see ESI)† showed the presence of MA^{*}, BP^{**} and TPPo^{**}. Interestingly, the signal corresponding to ³MA was absent, suggesting that this species was formed, in the absence of TPPo, by charge recombination of the MA^{*}-BP^{**} pair.

In HFP, TPPo^{**} shows a visible absorption band centred at 530 nm and a NIR band with maximum at 800 nm, 20 nm hypsochromically shifted relative to that in PhCN. A similar shift is also observed in the absorption spectrum of the ground state and can be attributed to the ability of the protic solvents to form hydrogen bonds with the lone pairs of the nitrogen in the macrocycle, thus lowering the energy of the π -state without modifying that of the π^* -state.³⁹

In a parallel experiment, a solution containing MA⁺ (1 mM), BP (0.2 M) and PdTPPo (50 μ M) in PhCN and HFP was irradiated at 450 nm to produce PdTPPo^{**}. The results of PdTPPo were similar to those for TPPo (Fig. 8): the rate constant for quenching of BP^{**} by PdTPPo was $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in PhCN and HFP, respectively; the lifetime of PdTPPo^{**} was 28 μ s in PhCN and up to 1.5 ms in HFP. PdTPPo^{**} showed a visible band, extending from 460 to 570 nm, and a broad NIR band peaking at 820 nm which shifted to 810 nm in HFP. A very similar pattern is found in tetraalkylmetalloporphyrines.^{15,16,18,20}

Conclusions

This work establishes the characteristics of the radical forms of a tetraarylporphyrine, TPPo, and its Pd(II) complex. Spectroscopically, they follow the π -radical pattern found in alkyl-substituted porphyrines: both the radical anions and the radical cations absorb at longer wavelengths than the triplet states. These spectral signatures should allow us to gain deeper insight on the

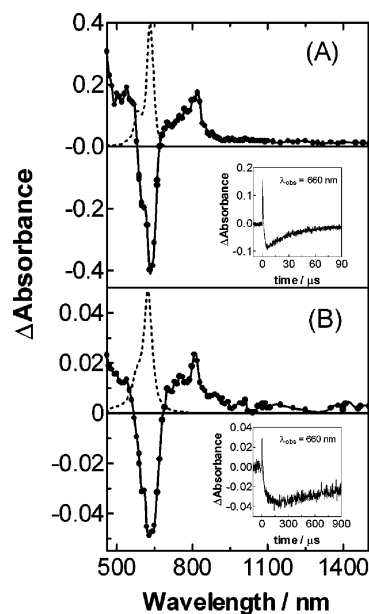


Fig. 8 Transient absorption spectra of PdTPPo^{**} in (A) PhCN and (B) HFP, as recovered by global analysis of the time-absorbance-wavelength matrix (see ESI).† Ground state absorption spectra are shown in dotted line. Insets: transient absorbance at 660 nm showing the initial formation of BP^{**} (positive absorbance, see Fig. 6) and the PdTPPo ground state bleaching and recovery as the PdTPPo^{**} species is formed and decays, respectively, $\lambda_{exc} = 450$ nm.

role of type-I processes in the photodynamic activity of TPPo and PdTPPo.

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