

# Photoinitiated Catalysis in Nafion Membranes Containing Palladium(II) *meso*-Tetrakis(*N*-methyl-4-pyridyl)porphyrin and Iron(III) *meso*-Tetrakis-(2,6-dichlorophenyl)porphyrin for O<sub>2</sub>-Mediated Oxidations of Alkenes

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**Abstract:** Immobilisation of both palladium(II) *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (PdTMPyP<sup>4+</sup>) and iron(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (FeTDCPP<sup>+</sup>) in the same membrane of Nafion creates a new composite system, in which the photo-excited palladium complex induces the O<sub>2</sub>-mediated oxidation of cyclohexene to the corresponding allylic hydroperoxide and the iron porphyrin works as a catalyst for specific oxygenations of cyclohexene and cyclooctene. The role of PdTMPyP<sup>4+</sup> is to induce the photo-activation of O<sub>2</sub> with visible light ( $\lambda > 500$  nm) to generate singlet oxygen (<sup>1</sup>O<sub>2</sub>) by means of energy transfer from the excited triplet state. Consequently, the <sup>1</sup>O<sub>2</sub>-mediated oxidation of cyclohexene to cyclohexenyl hydroperoxide can be realised with a selectivity greater than 90%. Spectroscopic and photophysical

investigations show that the tetracationic palladium porphyrin is mainly fixed to the external part of the Nafion membrane, it is characterised by a triplet-state lifetime significantly higher than that in the solution phase. The monocationic FeTDCPP<sup>+</sup> is able to diffuse into the anionic cavities of Nafion, where it works as a catalyst for O<sub>2</sub>-mediated autooxidation processes that are initiated by the photogenerated hydroperoxides. These processes continue in the dark for many hours giving cyclohex-2-en-1-ol and *trans*-cyclohexane-1,2-diol monoethyl ether as main oxidation products. The presence of this

ether, indirectly, reveals the formation of cyclohexene epoxide which undergoes a nucleophilic attack by ethanol and epoxide opening because of the strong acidic environment inside Nafion. The good photocatalytic efficiency of the oxidation process is demonstrated by an overall quantum yield of 1.1, as well as by a turnover value of  $4.7 \times 10^3$  with respect to the iron porphyrin. When cyclooctene is present as co-substrate, it also undergoes oxygenation. In contrast to what was observed for cyclohexene, cyclooctene epoxide can be accumulated in a significant amount. As far as the stability of the system is concerned, FeTDCPP<sup>+</sup> undergoes about 1% degradation during the process, while the Nafion matrix can be utilised several times without observable modification.

**Keywords:** biomimetic synthesis • heterogeneous catalysis • immobilisation • O-O activation • photo-oxidations

## Introduction

The oxo-functionalization of hydrocarbons is an interesting reaction from the synthetic and industrial points of view.<sup>[1]</sup> Recent research has focused on the employment of molecular oxygen as oxidizing species in order to realise innovative and economically advantageous processes, and, at the same time, move toward a "sustainable chemistry".<sup>[2]</sup> We are interested in

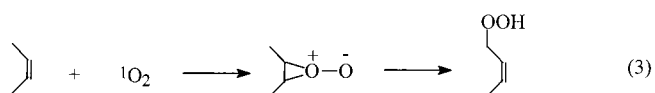
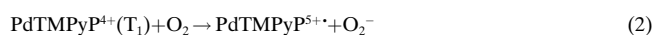
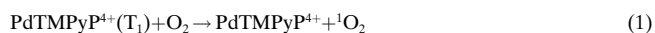
the establishment of composite oxidation photocatalysts, whose peculiar efficiencies and selectivities in oxidation reactions are controlled by the specific functions of their constituents.<sup>[3]</sup> Within this framework, we investigate here a new system based on the use of palladium(II) *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (PdTMPyP<sup>4+</sup>) and iron(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrin (FeTDCPP<sup>+</sup>) supported on Nafion<sup>[4]</sup> membranes. Cyclohexene and cyclooctene have been chosen as representative substrates of unsaturated hydrocarbons, and their selective oxidation by molecular oxygen is one of the current challenges in fine and industrial chemistry.<sup>[1]</sup>

On the basis of pure thermodynamic considerations, most of the organic compounds are not stable with respect to oxidation by O<sub>2</sub>. There are, however, kinetic limitations in this process mainly imposed by the triplet ground state of the O<sub>2</sub> molecule, which is not consistent with the singlet states of

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many organic substrates.  $O_2$  activation can be efficiently achieved by photosensitizers such as PdTMPyP<sup>4+</sup>.<sup>[5]</sup> In particular, this complex is able to transfer energy from its excited triplet state to  $O_2$  to generate singlet oxygen ( $^1O_2$ ) according to Equation (1). Alternatively, the excited state of the palladium porphyrin may activate  $O_2$  through its reduction to the superoxide radical anion ( $O_2^{\cdot-}$ ), as schematised by Equation (2). Part of this paper is concerned with the effects of the Nafion support on the photosensitising properties of PdTMPyP<sup>4+</sup>. Particular attention is devoted to the verification that the photogenerated  $^1O_2$  can react with cycloalkenes to give allylic hydroperoxides, in agreement with the well-known behaviour in the homogeneous phase<sup>[6]</sup> [Eq. (3)]. These allylic hydroperoxides have been widely used as oxidants in hydrocarbon monooxygenations catalysed by iron porphyrins



including FeTDCPP<sup>+</sup>,<sup>[7]</sup> and their presence in the composite system investigated might have, therefore, significant effects on the overall product distribution.

Increasingly, interest is devoted to heterogenisation of metalloporphyrin catalysts since the support makes them easier to handle and recycle than in homogeneous solution. In addition, the support may control some main parameters affecting the reactivity of the reaction intermediates, such as their local concentration, their mobility and the polarity of the reaction environment.<sup>[7a, 8]</sup> Several cationic porphyrins have been successfully immobilised on negatively charged ion-exchange resins.<sup>[9]</sup> In this study the matrix employed is Nafion, a polymeric support comprising a perfluorinated backbone connected to sulfonic groups. Its structure resembles that of a reverse micelle, where the sulfonic head groups are clustered together in polar pockets that are interconnected by short channels within the perfluorocarbon matrix.<sup>[10]</sup>

Nafion has been extensively employed for photophysical and photochemical studies.<sup>[11]</sup> In particular, it is a promising support for oxidative photocatalytic purposes, because it presents a very high affinity for  $O_2$ <sup>[12]</sup> and it is totally transparent to the excitation wavelengths of interest. Some of our preliminary results indicate that this polymeric matrix strongly affects the activity of the photoexcited FeTDCPP<sup>+</sup> in the oxidation of cyclohexene, and the formation of cyclohexene epoxide as reaction intermediate is favoured.<sup>[3a]</sup>

## Results and Discussion

**Heterogenisation of PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> with Nafion membranes:** Either PdTMPyP<sup>4+</sup> or FeTDCPP<sup>+</sup> can be successfully immobilised on Nafion membranes as a consequence of their interaction with the anionic  $\text{SO}_3^-$  groups of the polymeric matrix. According to the procedure described in the Experimental Section, the uptake of 0.3–0.6  $\mu\text{mol}$  of each complex in 1 g of resin, typically, occurred in a few minutes.

Optical microscopy allows us to establish where the metalloporphyrins are mainly located. The edge view of the cross section of the membrane containing PdTMPyP<sup>4+</sup> (PdTMPyP<sup>4+</sup>/Nafion system) reported in Figure 1A shows that the clustering of the complex inside the support is unlikely and that it is mainly fixed in close proximity to the surface of the solid matrix. This is even more evident upon comparison of Figure 1C and Figure 1D, which show that the fluorescence emission of PdTMPyP<sup>4+</sup> is clearly visible on the external part of the Nafion support. These observations are not surprising in view of the strong coulombic attractions between the tetracationic ring of PdTMPyP<sup>4+</sup> and the negatively charged

**Abstract in Italian:** *L'immobilizzazione di palladio(II) meso-tetrakis(N-metil-4-piridil)porfirina (PdTMPyP<sup>4+</sup>) e di ferro(III) meso-tetrakis(2,6-diclorofenil)porfirina (FeTDCPP<sup>+</sup>) sulla stessa membrana di Nafion dà luogo ad un nuovo sistema composto, in cui l'eccitazione fotochimica del complesso di palladio induce l'ossidazione del cicloesene, mediata dall' $O_2$ , al corrispondente allil idroperossido e la ferro porfirina agisce da catalizzatore per specifiche ossigenazioni del cicloesene e del ciclootene.*

*Il ruolo della PdTMPyP<sup>4+</sup> è quello di indurre la fotoattivazione dell' $O_2$  con luce visibile  $\lambda > 500 \text{ nm}$ , generando ossigeno di singoletto ( $^1O_2$ ) attraverso un meccanismo di trasferimento di energia dal suo stato di tripletto eccitato. Una diretta conseguenza di questo processo è l'ossidazione del cicloesene a cicloesenil idroperossido, mediata dall' $^1O_2$  e realizzata con una selettività maggiore del 90%. Studi spettroscopici e fotofisici dimostrano che la palladio porfirina tetracationica è localizzata nella parte esterna della membrana di Nafion, dove è caratterizzata da un tempo di vita del suo stato di tripletto nettamente più alto di quello ottenuto in soluzione omogenea. La FeTDCPP<sup>+</sup> monocationica è capace di diffondere nelle cavità anioniche del Nafion, dove catalizza processi di auto-ossidazione mediati dall' $O_2$ , che sono iniziati dagli idroperossidi fotogenerati. Questi processi continuano al buio per molte ore, dando luogo alla formazione di cicloes-2-en-1-olo e di trans-cicloesan-1,2-diol monoetere come prodotti principali di ossidazione. La presenza di questo etere è un'evidenza indiretta della formazione di cicloesene ossido, il quale, a causa della forte acidità all'interno del Nafion, subisce attacco nucleofilo da parte dell'etanolo con conseguente apertura dell'anello epossidico.*

*La buona efficienza fotocatalitica del processo di ossidazione è dimostrata da un rendimento quantico complessivo di 1.1, e da un valore di turnover di  $4.7 \times 10^3$  rispetto alla ferro porfirina. Quando il ciclootene è presente come co-substrato, anch'esso viene ossidato; tuttavia, al contrario di quanto osservato con il cicloesene, il ciclootene epossido è relativamente stabile e può essere accumulato in quantità significative. Per quanto riguarda la stabilità del sistema, FeTDCPP<sup>+</sup> si degrada solamente di circa l'1% durante l'intero processo, mentre la membrana di Nafion può essere riutilizzata più volte senza subire apprezzabili modifiche.*

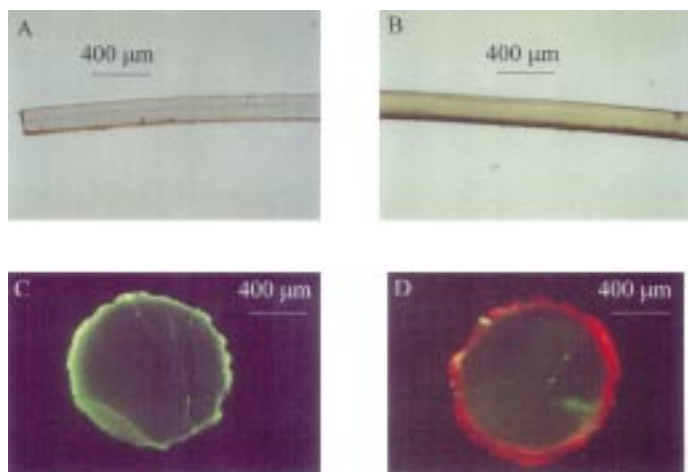


Figure 1. Optical microscopy of Nafion containing PdTMPyP<sup>4+</sup> or FeTDCPP<sup>+</sup>. A) and B): edge views of the cross section of membranes contacted with PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup>, respectively (white light); C) and D): cross sections of an unmodified bead and of a bead contacted with PdTMPyP<sup>4+</sup>, respectively (UV light).

sulfonic groups of the membrane, and this may prevent the diffusion of the complex from the bulk solution to the depth of the polymer.

Figure 2 provides evidence that heterogenisation with Nafion membranes strongly affects the UV/Vis spectrum of PdTMPyP<sup>4+</sup>. A significant hypsochromic shift of the Soret band of PdTMPyP<sup>4+</sup> (curve B) compared with the spectrum in

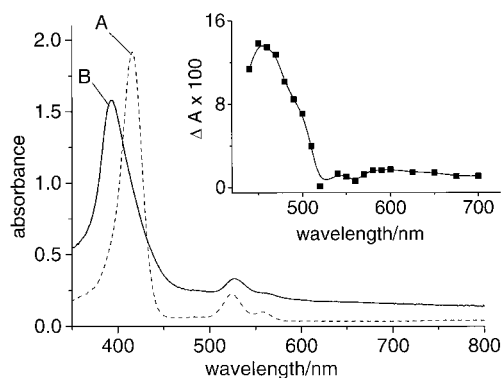


Figure 2. Absorption spectra of PdTMPyP<sup>4+</sup>; A) in aqueous solution; B) in dry membranes of Nafion. Insert: transient absorption spectrum of PdTMPyP<sup>4+</sup> (T<sub>1</sub>) after laser pulse at 532 nm.

water (curve A) is clearly observed. Similar effects of the solid matrix on the UV/Vis spectrum of PdTMPyP<sup>4+</sup> were also observed when the modified membrane was immersed in ethanol, which is the solvent employed in the photocatalytic experiments described below. The spectral changes observed in Figure 2 are well known to accompany the conversion of monomeric porphyrins to face-to-face aggregates.<sup>[13]</sup> Aggregate formation should be favoured because the sulfonic groups of the Nafion surface are expected to screen the positive charges at the periphery of the porphyrin ring, and hence reduce the electrostatic repulsion between the complexes and promote  $\pi$ - $\pi$  interactions.<sup>[14]</sup> The formation of aggregates along the surface of sulfonated polymers was

observed by other authors in the case of cationic iron or manganese porphyrins supported on anionic polymers.<sup>[7a]</sup>

Both the metalloporphyrins PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> can be immobilised simultaneously in Nafion membranes (PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system). The formation of aggregates is unlikely in the case of FeTDCPP<sup>+</sup> because of the presence of the bulky chlorine atoms in the *ortho* positions of the phenyl groups.<sup>[15]</sup> Accordingly, the UV/Vis spectrum of the immobilised iron porphyrin is typical of its monomeric form.

In comparison with PdTMPyP<sup>4+</sup>, FeTDCPP<sup>+</sup> is characterised by a reduced positive charge distributed in a different way. Therefore, its coulombic attraction to the negatively charged sulfonic groups of the membrane is weaker and the iron complex is able to diffuse into the depth of the polymer, where it is expected to be caged inside the large anionic cavities. In line with this statement, Figure 1 B shows that the red-brown FeTDCPP<sup>+</sup> is immobilised, at least in part, inside the depth of the membrane.

#### Photosensitised activation of O<sub>2</sub> with the PdTMPyP<sup>4+</sup>/Nafion system:

The absorption spectrum of the lowest triplet of the palladium porphyrin (PdTMPyP<sup>4+</sup>(T<sub>1</sub>)) can be observed after excitation with a laser pulse at 532 nm under anaerobic conditions and is reported in Figure 2 (insert). Since this spectrum is not noticeably affected by immobilisation of the palladium porphyrin in Nafion, we can compare the decay of the transient absorption at 460 nm of PdTMPyP<sup>4+</sup>(T<sub>1</sub>) dissolved in ethanol with those obtained in membranes of Nafion either immersed in the same alcohol or in the dry state. In all cases, PdTMPyP<sup>4+</sup>(T<sub>1</sub>) decays by first-order kinetics, as exemplified in Figure 3 A for the ethanol swollen membrane.

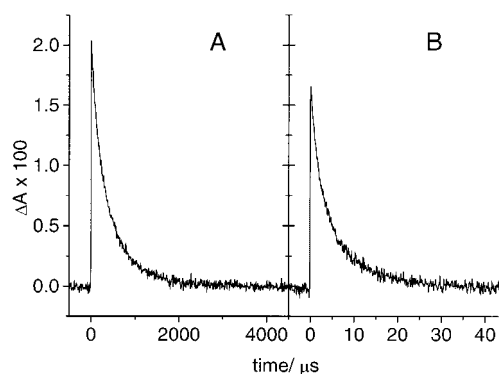


Figure 3. Absorption changes at 460 nm of PdTMPyP<sup>4+</sup> (T<sub>1</sub>) after pulse irradiation at 532 nm of PdTMPyP<sup>4+</sup> immobilized in ethanol swollen Nafion; A) in the absence of oxygen; B) upon O<sub>2</sub> equilibrated conditions.

The respective lifetimes ( $\tau_A$ ) are collected in Table 1. PdTMPyP<sup>4+</sup> supported on Nafion undergoes an enhancement of its excited triplet lifetime compared with the solution-phase, and this indicates that the inhomogeneity of the solid support may reduce the efficiency of thermal-deactivation processes of the excited state.

Table 1 also reports the triplet lifetimes in O<sub>2</sub>-equilibrated media ( $\tau_B$ ), which indicate that the quenching of the excited state of PdTMPyP<sup>4+</sup> by O<sub>2</sub> occurs both in homogeneous solution and in the supported systems. Figure 3 B shows, as an

Table 1. Photophysical properties of PdTMPyP<sup>4+</sup>.

Reaction media	$\tau_A^{[a]}$ ( $\mu\text{s}$ )	$\tau_B^{[b]}$ ( $\mu\text{s}$ )
EtOH <sup>[c]</sup>	10	0.5
Nafion <sup>[d]</sup>	700	40
Nafion/EtOH <sup>[d]</sup>	400	5

[a] Lifetime of PdTMPyP<sup>4+</sup>(T<sub>1</sub>) in the absence of O<sub>2</sub>. Reported values are  $\pm 5\%$ . [b] Lifetime of PdTMPyP<sup>4+</sup>(T<sub>1</sub>) in the presence of O<sub>2</sub> (760 Torr). Reported values are  $\pm 5\%$ . [c] PdTMPyP<sup>4+</sup> concentration:  $1.7 \times 10^{-5}$  mol dm<sup>-3</sup>.  $\tau_A$  is in good agreement with the value reported in a previous work.<sup>[19]</sup> [d] Amount of PdTMPyP<sup>4+</sup> in Nafion:  $8 \times 10^{-7}$  mol g<sup>-1</sup>.

example, the decay of the transition absorption in the ethanol swollen membrane. The effect of O<sub>2</sub> on the triplet lifetime of the heterogenised PdTMPyP<sup>4+</sup> is more significant in the presence of ethanol than with membranes in the dry state, this is because O<sub>2</sub> diffusivity is known to increase remarkably (about 20 times) in wet Nafion with respect to the dry polymer.<sup>[16]</sup>

As schematised by Equations (1) and (2), the quenching of the palladium porphyrin triplet state by O<sub>2</sub> might give both <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>-•</sup>. To establish that the energy transfer pathway to O<sub>2</sub><sup>1</sup> is prevalent during photoexcitation of the PdTMPyP<sup>4+</sup>/Nafion system under aerobic conditions the following experiments were carried out.

Triethanolamine (TEA) is known to capture the porphyrin radical cation eventually formed as a consequence of the electron transfer reaction 2, and this favours the diffusion of O<sub>2</sub><sup>-•</sup> and leads to the accumulation of detectable H<sub>2</sub>O<sub>2</sub> in the solution bulk.<sup>[11e]</sup> The reductive activation of O<sub>2</sub> during irradiation of the PdTMPyP<sup>4+</sup>/Nafion system can be ruled out since the iodometric analysis after two hours irradiation in the presence of TEA does not reveal the presence of peroxides.

The photogenerated <sup>1</sup>O<sub>2</sub> can be detected by the method of Kraljic and Moshni.<sup>[17]</sup> This species is able to react with imidazole and the imidazole-O<sub>2</sub> adduct oxidises and bleaches *N,N*-dimethyl-4-nitrosoaniline (RNO). Figure 4 shows the

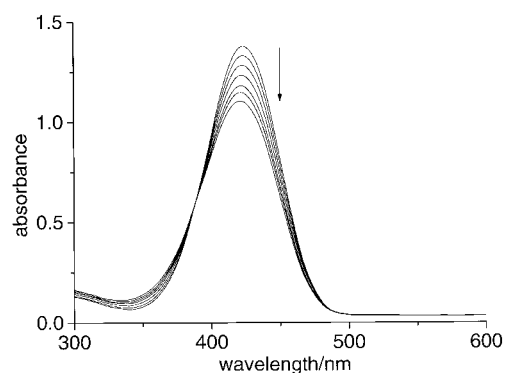


Figure 4. Spectral variations of the solution phase upon irradiation at  $\lambda = 525$  nm of PdTMPyP<sup>4+</sup> immobilized in Nafion membranes (1.5 cm<sup>2</sup>) immersed in oxygenated water solutions (3 mL) of RNO ( $4 \times 10^{-5}$  mol dm<sup>-3</sup>), and imidazole ( $5 \times 10^{-3}$  mol dm<sup>-3</sup>). Irradiation times: 10 min.

spectral variations of RNO upon continuous irradiation of the PdTMPyP<sup>4+</sup>/Nafion system in contact with ethanol containing RNO, imidazole and O<sub>2</sub>. Since RNO is not stable in acidic media, we were forced to use membranes in the sodium form. The absorbance decay at 420 nm can be ascribed to the

oxidation of RNO by <sup>1</sup>O<sub>2</sub>. Also in this case, we did not have any experimental evidence of formation of peroxides derived by the reductive activation of O<sub>2</sub>.

The ability of the photoexcited PdTMPyP<sup>4+</sup>/Nafion system to induce the <sup>1</sup>O<sub>2</sub> mediated oxidation of alkenes has been assessed by using cyclohexene as a representative substrate. Photochemical excitation ( $\lambda > 500$  nm) of the PdTMPyP<sup>4+</sup>/Nafion system in oxygenated mixtures of cyclohexene/ethanol (1:3), results in the oxidation of the alkene to the corresponding allyl hydroperoxide (C<sub>6</sub>H<sub>9</sub>OOH) as the main product (> 90%), with only minor amounts of cyclohex-2-en-1-ol and cyclohex-2-en-1-one. The good selectivity for the production of the hydroperoxide is in agreement with the formation of a peroxirane intermediate as schematised in Equation (3). Irradiation with monochromatic light allowed us to calculate an overall quantum yield for the oxidation of cyclohexene of 0.025 at 525 nm.

As far as the stability of the palladium porphyrin is concerned, it is noteworthy that the modified membranes can be used at least for three subsequent experiments with almost negligible loss of their photochemical activity. In particular, at the end of every photooxidation process, the amount of palladium porphyrin in Nafion is about 5% lower than the initial one. Since there is no evidence of leaching of the catalyst from the resin into the solution, this means that the porphyrin ring undergoes a slow degradation with the formation of small colourless fragments.

A comparison between the described results and those obtained in analogous experiments carried out with dissolved PdTMPyP<sup>4+</sup> in homogeneous solutions indicates that heterogenisation with Nafion membranes does not affect significantly the photosensitising properties of PdTMPyP<sup>4+</sup> in terms of both the mechanism for O<sub>2</sub> activation and the oxidation quantum yield. On the other hand, the solid matrix has a positive effect on the stability of PdTMPyP<sup>4+</sup>. In fact the equivalents of produced hydroperoxide per equivalent of consumed porphyrin in the heterogeneous system are about  $4 \times 10^3$ , and about four times higher than those obtained in the homogeneous phase.

**Photocatalytic properties of the PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system:** The photocatalytic properties of the PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system have been assessed by irradiation with light of wavelength higher than 500 nm. Under these conditions PdTMPyP<sup>4+</sup> is the photochemically active species of the composite system, since the well-known redox photoactivity of FeTDCPP<sup>+</sup> can be induced only with wavelengths lower than 400 nm.<sup>[3]</sup>

The results so far discussed provide evidence that irradiation of the PdTMPyP<sup>4+</sup>/Nafion system in the presence of cyclohexene and O<sub>2</sub> leads to the formation of C<sub>6</sub>H<sub>9</sub>OOH. Interestingly, curve A of Figure 5 shows that the formation of this hydroperoxide continues in the dark for many hours after irradiation of Nafion membranes containing both PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> for 240 min. Curves B and C indicate that this thermal process does not occur in the absence of FeTDCPP<sup>+</sup> or upon irradiation of a mixture of PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> in homogeneous solution.

These findings are a clear indication that the iron-porphyrin complex inside Nafion works as a catalyst for O<sub>2</sub>-

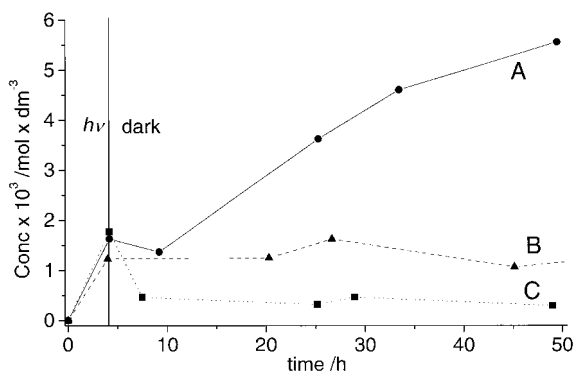
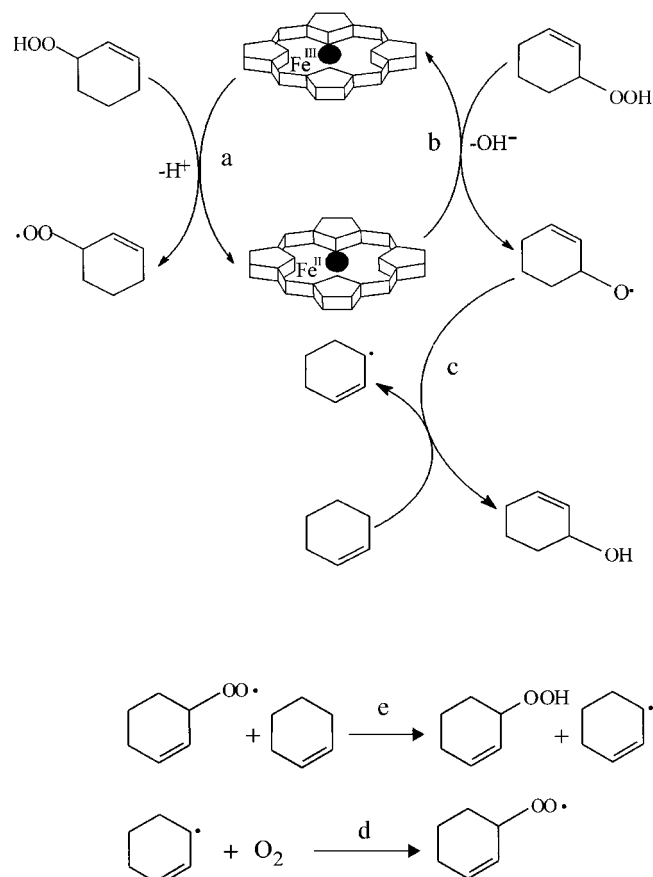


Figure 5. Variation of the  $C_6H_9OOH$  concentration as during 240 min irradiation ( $\lambda > 500$  nm) and 46 h in the dark; A) PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system (membranes of 1.5 cm<sup>2</sup>) in a ethanol/cyclohexene (3:1; 3 mL) mixed solvent; B) PdTMPyP<sup>4+</sup>/Nafion system in the same mixed solvent; C) PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> dissolved in the same mixed solvent acidified with  $CF_3SO_3H$  ( $2 \times 10^{-2}$  mol dm<sup>-3</sup>).

mediated autooxidation processes, which are initiated by the photochemically obtained  $C_6H_9OOH$ . On the basis of literature data, it is plausible that inhomogeneity effects and high oxygen concentration inside the polymeric matrix may favour the reaction of the allyl hydroperoxide with the porphyrin complex both in its ferric and ferrous form according to Scheme 1 (steps a,b).<sup>[7h]</sup> The so obtained radical intermediates  $C_6H_9O\cdot$  and  $C_6H_9OO\cdot$ , in turn, are able to initiate chain



Scheme 1. Thermal catalysis by FeTDCPP<sup>+</sup> in Nafion initiated by allyl hydroperoxides.

autooxidation processes that would account for the accumulation of  $C_6H_9OOH$  (steps c, d, e).

Table 2 reports the nature and yields of all the oxidation products of cyclohexene after 240 min irradiation followed by 95 h in the dark (Table 2, entry 2). It is evident that, in addition to  $C_6H_9OOH$ , the catalytic activity of FeTDCPP<sup>+</sup> yields other products, whose formation already begins during the first 240 minutes irradiation (Table 2, entry 1). In particular, cyclohex-2-en-1-ol and *trans*-cyclohexane-1,2-diol monoethyl ether represented about the 80% of the overall oxidised cyclohexene. It has been possible to verify that the thermal oxidation process carried on for at least another three days, and induced a further increase (70%) of the oxidation products.


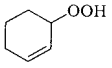
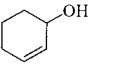

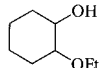

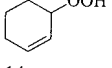
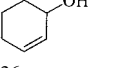

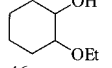

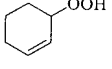
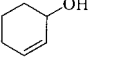

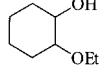

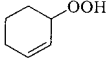
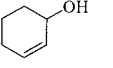

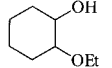

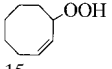
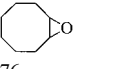





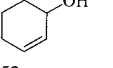

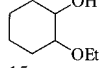
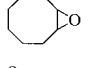
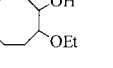
The presence of *trans*-cyclohexane-1,2-diol monoethyl ether among the products indirectly reveals the formation of cyclohexene epoxide which, in the strong acidic environment inside Nafion, undergoes a nucleophilic attack by ethanol, and leads to the epoxide opening. This is confirmed by the observation that the epoxide in acidic solution undergoes the same nucleophilic attack with the formation of the same product during the photochemical oxidation.

The good photocatalytic efficiency of the PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system is demonstrated by an overall quantum yield for the oxidation of cyclohexene of 1.1 at 525 nm, that is, about forty times higher than that obtained during irradiation of PdTMPyP<sup>4+</sup>/Nafion (see before) and a turnover value (moles of oxidised cyclohexene per mole of FeTDCPP<sup>+</sup> immobilised) of  $4.7 \times 10^3$ , which corresponds to a reaction rate of 0.8 turnover min<sup>-1</sup>. Another important issue is the catalyst stability. In this respect, we note that the Nafion matrix can be utilised at least three times without any appreciable modification and that FeTDCPP<sup>+</sup> undergoes only 1% degradation to colourless fragments during the process. PdTMPyP<sup>4+</sup> is less stable than FeTDCPP<sup>+</sup> and about 30% PdTMPyP<sup>4+</sup> was lost during the entire catalytic experiment.

The described processes take place because the optimum conditions have been found, the conditions are related to the peculiar reactivity of both the photogenerated intermediates and the organic substrates inside the solid matrix. For example, with *tert*-butyl hydroperoxide as initiator of the catalytic oxidation of cyclohexene instead of the photogenerated allyl hydroperoxide the reaction yields are reduced by ten times. We also showed that the effect of the Nafion matrix is not just of providing an acidic environment. In fact, entries 3 and 4 of Table 2 show that although irradiation of mixtures of PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> dissolved in EtOH acidified with trifluoromethanesulfonic acid give the same oxidation products as the heterogeneous system, no subsequent oxidation process in the dark is initiated.

The PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system significantly improves the photocatalytic properties of the previously investigated FeTDCPP<sup>+</sup>/Nafion photocatalyst<sup>[3a]</sup> since 1) it is activated by visible light instead of ultraviolet wavelengths; 2) as a consequence of its significant activity in the dark, it presents a quantum yield value for the oxygenation of cyclohexene about two orders of magnitude higher; 3) its catalytic rate in terms of turnover min<sup>-1</sup> is about four times higher.

Table 2. Photoinduced catalytic oxygenation of cyclohexene and cyclooctene by the PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system.<sup>[a]</sup>

Entry	System	Substrate	Product distribution [%]						Total turnover <sup>[b]</sup>
1	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> / Nafion <sup>[c]</sup> + <i>hν</i>		 71	 13	 9	 7			340
2	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> / Nafion <sup>[c]</sup> + <i>hν</i> + dark		 14	 36	 4	 46			4700
3	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> solution <sup>[d]</sup> + <i>hν</i>		 65	 7	 11	 17			370
4	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> / solution <sup>[d]</sup> + <i>hν</i> + dark		 38	 11	 6	 45			360
5	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> / Nafion <sup>[c]</sup> + <i>hν</i> + dark		 15	 76	 9	 9	 6		210
6	PdTMPyP <sup>4+</sup> /FeTDCPP <sup>+</sup> / Nafion <sup>[c]</sup> + <i>hν</i> + dark	 	ROOH 7	 52	 11	 15	 9	 6	6100

[a] The composite system (Nafion membranes of 1.5 cm<sup>2</sup> containing both the porphyrins immersed in mixtures of alkene/ethanol 1/3) has been photoirradiated for four hours at  $\lambda > 500$  nm in the presence of 760 Torr of O<sub>2</sub>. In some cases irradiation was followed by 95 h of thermal catalysis in the dark. [b] Moles of oxidized alkenes per mole of FeTDCPP<sup>+</sup> which was present at the beginning of the process. [c] 0.06 ± 0.01 g of Nafion contained 3.0 ± 0.3 × 10<sup>-7</sup> mol g<sup>-1</sup> of PdTMPyP<sup>4+</sup> and 6.0 ± 0.6 × 10<sup>-7</sup> mol g<sup>-1</sup> of FeTDCPP<sup>+</sup>. [d] Initial concentration of PdTMPyP<sup>4+</sup>: 6.5 ± 0.5 × 10<sup>-6</sup> mol dm<sup>-3</sup>. Initial concentration of FeTDCPP<sup>+</sup>: 1.3 ± 0.1 × 10<sup>-6</sup> mol dm<sup>-3</sup>. The solutions were acidified with CF<sub>3</sub>SO<sub>3</sub>H (2 × 10<sup>-2</sup> mol dm<sup>-3</sup>).

The metalloporphyrin-catalysed oxygenation of alkenes by alkyl hydroperoxides has been extensively investigated in the last two decades.<sup>[7a,b]</sup> The factors that control the competition between the proposed mechanisms are strongly connected to the specific properties of the reaction environment and are still the object of much-discussed investigation by different research groups.<sup>[7c-h]</sup> Two reaction pathways are commonly proposed, neither of which can be ruled out in the photocatalytic system investigated here. 1) A free-radical mechanism initiated by the homolytic cleavage of the peroxidic O–O bond by the iron–porphyrin catalyst generates iron(IV)–oxo porphyrin and alkoxy radicals. 2) The formation of a monooxygenating iron(V)–oxo porphyrin as a consequence of the heterolytic cleavage of the O–O bond.

Entry 5 of Table 2 shows that the PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion system in the presence of O<sub>2</sub> and light was also able to induce the oxygenation of cyclooctene. In contrast to what is observed for cyclohexene, cyclooctene epoxide is relatively stable and can be accumulated in a significant amount. However, the catalytic oxidation of cyclooctene is twenty times lower than that of cyclohexene, probably because of its low reactivity especially towards allylic hydrogen-atom abstraction, which is a key step in the overall oxidation process as shown in Scheme 1. The fundamental role of cyclohexene in the oxidation mechanism is demonstrated by entry 6 of Table 2, this shows that when the experiments are carried out in the presence of cyclohexene as a cosubstrate, cyclooctene is oxidised to a greater extent and the total turnover increases up to 6.1 × 10<sup>3</sup>.

## Conclusion

The composite photocatalyst investigated shows a peculiar activity that is the result of specific roles of all of its components: PdTMPyP<sup>4+</sup>, FeTDCPP<sup>+</sup>, and the Nafion matrix.

The catalytic process is photoinitiated by PdTMPyP<sup>4+</sup>. This complex is mainly fixed near the surface of the polymer matrix, where it undergoes a pronounced enhancement of the lifetime of its triplet excited state compared with that of the porphyrin in solution-phase. The role of PdTMPyP<sup>4+</sup> is to induce the photoactivation of O<sub>2</sub> with visible light ( $\lambda > 500$  nm), to generate singlet oxygen (<sup>1</sup>O<sub>2</sub>) by energy transfer from its triplet state. As a consequence, the <sup>1</sup>O<sub>2</sub>-mediated oxidation of cyclohexene to cyclohexenyl hydroperoxide can be realised with a selectivity higher than 90%.

The catalytic oxidation of alkenes by alkyl hydroperoxides generated in situ from molecular oxygen at room temperature and atmospheric pressure is very attractive from the synthetic and industrial points of view. This is achieved by FeTDCPP<sup>+</sup> which works as a catalyst for O<sub>2</sub>-mediated autooxidation processes of cyclohexene and cyclooctene with turnover values higher than 4 × 10<sup>3</sup>. Nafion is a very versatile support for applied synthetic purposes. The isolation of the iron porphyrins within the solid support causes a significant thermal activity that continues in the dark for many hours after the initial photoactivation.

Further experiments are in progress in our laboratory to investigate the possibility that other unsaturated hydrocarbons can be successfully oxidised with good selectivity by the photoexcited PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion photocatalyst. Moreover, the possibility that this system may be employed in

large-scale experiments on the use of membrane photo-reactors should be urgently investigated in view of further developments in applied organic synthesis.

## Experimental Section

**Materials:** The palladium complex [PdTMPyP]Cl<sub>4</sub> was synthesized by the modified method proposed by Pasternack and co-workers.<sup>[18]</sup> The initial metal-free porphyrin [H<sub>2</sub>TMPyP](C<sub>7</sub>H<sub>7</sub>SO<sub>3</sub>)<sub>4</sub> (Aldrich) was transformed to the chloride form by flow of an aqueous solution through a column with Dowex 1 × 8–100 anionite (the Cl<sup>-</sup> form). A mixture of [H<sub>2</sub>TMPyP]Cl<sub>4</sub> and Na<sub>2</sub>PdCl<sub>4</sub> was refluxed for one hour. The resulting cationic metalloporphyrin was precipitated by sodium tetrafluoroborate and then transformed to the chloride form using an anion-exchange resin.<sup>[19]</sup> The purity of the obtained metalloporphyrin was checked by thin-layer chromatography and by NMR and optical spectra. Nafion 117 is a DuPont product (about 178 μm thick and 1100 of equivalent weight). Cyclohexene and cyclooctene (Fluka) were distilled before use. All other chemicals were spectroscopic grade products (Aldrich and Fluka) and were used without further purification.

[FeTDCPP]Cl was kindly supplied by Drs. D. Mansuy and P. Battioni of the University René Descartes of Paris.

**Apparatus:** The employed photomicroscope was Zeiss, model Axiophot, equipped with a reflected fluorescence condenser and a mercury vapour lamp, HBO 50W, with BP 436/10 exciter and LP 470 barrier filters.

Gas chromatographic analyses were carried out on a DANI 8521 gas chromatograph, equipped with a flame ionization detector, using columns packed with Carbowax 20M 5% on Chromosorb W-AW. UV/Vis absorption spectra were recorded by a Kontron, model Uvikon 940, spectrophotometer, and emission spectra by a Fluoro Max-2 fluorimeter from ISA instruments. Continuous irradiations were performed with a xenon mercury lamp by Oriel, with a thermostable cell holder (26 ± 1 °C). A glass cut-off filter selected excitation wavelengths over 500 nm.

Photoexcitation at 525 nm, where the palladium porphyrin presents an absorption maximum was performed using a monochromator. The light intensity was measured by the ferrioxalate actinometric method.<sup>[20]</sup> All irradiations were carried out in a spectrophotometric quartz cell of one cm path length. Deaerated samples were prepared by a vacuum line, equipped with diffusive pump. When necessary irradiations were carried out under an atmosphere of oxygen.

Nanosecond flash photolysis transient absorption spectra were measured by irradiation of the sample with 6–8 ns (fwhm) of a Continuum Surelight Nd:YAG laser (10 Hz repetition rate) and using a pulsed Xe-lamp as probe light perpendicular to the laser beam. The excitation wavelength was obtained by frequency doubling (532 nm). The 150 W Xe lamp was equipped with an Applied Photophysics Model 408 power supply and an Applied Photophysics Model 410 pulsing unit (giving pulses of 0.5 ms). The Nafion membranes were sandwiched between two glass slides and the orientation of the films was 45° with respect to the laser and probe light. The scatter light was reflected to the probe light. Using suitable pre- and post- cutoff and bandpass filters we were able to measure kinetic traces without any artifacts from scattering. The light was collected in a LDC Analytical monochromator, detected by a R928 PMT (Hamamatsu), and recorded on LeCroy 9360 (600 MHz) oscilloscope. The absorption transients were plotted as  $\Delta A = \log(I_0/I_t)$  versus time, where  $I_0$  was the monitoring light intensity prior to the laser pulse and  $I_t$  was the observed signal at delay time  $t$ .

### Procedures

**Immobilisation of PdTMPyP<sup>4+</sup> and of FeTDCPP<sup>+</sup> in Nafion:** The membrane of Nafion was cleaned by boiling it for about 30 min in nitric acid (3 mol dm<sup>-3</sup>) washed in water and finally dried. Nafion in sodium form was obtained by placing the purified membrane in contact with a NaOH aqueous solution (1 mol dm<sup>-3</sup>) for 30 min. The composite system PdTMPyP<sup>4+</sup>/FeTDCPP<sup>+</sup>/Nafion was obtained by swelling a membrane of Nafion in a mixture of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (10/1 v/v) containing the iron porphyrin (1 × 10<sup>-4</sup> mol dm<sup>-3</sup>) for 1–2 min. Once the polymer had absorbed FeTDCPP<sup>+</sup>, it was then soaked in H<sub>2</sub>O/CH<sub>3</sub>OH (3:1 v/v) with PdTMPyP<sup>4+</sup> (1 × 10<sup>-4</sup> mol dm<sup>-3</sup>) for about 20 min. When necessary, Nafion

membranes only with the palladium porphyrin were prepared. The amounts of metalloporphyrins immobilised in the membrane were determined following their absorbance decrease in the solution phase. Typically, a membrane of 1.5 cm<sup>2</sup> contained about 4–8 × 10<sup>-7</sup> moles of each complex per gram of Nafion.

**Photosensitisation experiments:** Nafion of 1.5 cm<sup>2</sup> in the sodium form containing PdTMPyP<sup>4+</sup> were immersed in solutions of *N,N*-dimethyl-4-nitrosoaniline (RNO, 4 × 10<sup>-5</sup> mol dm<sup>-3</sup>) and imidazole (5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) each in ethanol (3 mL) inside a fluorimetric cell. After reaching equilibration (six hours), the whole system was irradiated at  $\lambda > 500$  nm. The oxidation of RNO was followed by its typical absorbance decrease at 420 nm ( $\epsilon = 28100 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ).<sup>[17, 21]</sup> The absorption of the solution phase was read at 90° to avoid interference of the soaked membrane. A comparison with the photoreactivity of PdTMPyP<sup>4+</sup> in homogeneous solutions was carried out by irradiation of the palladium complex (about 1 × 10<sup>-5</sup> mol dm<sup>-3</sup>) dissolved in ethanol in the presence of RNO (4 × 10<sup>-5</sup> mol dm<sup>-3</sup>) and imidazole (5 × 10<sup>-3</sup> mol dm<sup>-3</sup>). To dissolve the complex completely, PdTMPyP<sup>4+</sup> was diluted in ethanol from a concentrated water solution. Oxidation of RNO was never observed when blank experiments were run in the dark. Moreover no photochemical process occurred in the absence of palladium porphyrin.

In analogous experiments, membranes of Nafion containing PdTMPyP<sup>4+</sup> were immersed in aqueous solutions of triethanolamine (TEA, 0.1 mol dm<sup>-3</sup>) and HCl (0.1 mol dm<sup>-3</sup>) and irradiated at  $\lambda > 500$  nm. After 2 h irradiation, the eventual formation of H<sub>2</sub>O<sub>2</sub> was tested iodometrically, by measurement of the absorbance value owing to I<sub>3</sub><sup>-</sup> at 351 nm ( $\epsilon = 26400 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ ), and comparison with a blank experiment.<sup>[11c]</sup> Similar irradiations were also carried out in the homogeneous phase, dissolving the palladium complex (about 1 × 10<sup>-5</sup> mol dm<sup>-3</sup>) in aqueous solutions containing TEA (0.1 mol dm<sup>-3</sup>) and HCl (0.1 mol dm<sup>-3</sup>).

**Photocatalytic experiments:** Photooxidation of cyclohexene and cyclooctene was performed by irradiation at  $\lambda > 500$  nm of Nafion membranes of 1.5 cm<sup>2</sup> containing PdTMPyP<sup>4+</sup> alone or both PdTMPyP<sup>4+</sup> and FeTDCPP<sup>+</sup> immersed in mixtures of alkene/ethanol 1/3. The experiments were carried out under static conditions in a 3 mL fluorimetric cell. Analogous experiments were carried out by irradiation of homogeneous solutions of the metalloporphyrins in the same mixed solvent acidified with CF<sub>3</sub>SO<sub>3</sub>H (2 × 10<sup>-2</sup> mol dm<sup>-3</sup>). UV absorption spectra were measured before and after the irradiation to estimate the amount of porphyrin destroyed. A quantitative comparison between the photoinduced catalytic properties of the metalloporphyrins in homogeneous solution and in the heterogeneous system was possible because the amounts of PdTMPyP<sup>4+</sup> were chosen so its absorption of the incident light was the same for both the systems. Blank experiments were carried out in order to verify that no oxidation of the alkenes was observed without photochemical excitation of PdTMPyP<sup>4+</sup>. The determination of hydroperoxides was performed by a spectrophotometric standard method reported in the literature.<sup>[22]</sup> The analysis of the other products was carried out by gas-chromatographic techniques following the procedure previously reported.<sup>[21]</sup>

## Acknowledgement

This research was supported by MURST (PRIN) and C.N.R. (project 95/95–5 %).

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Received: February 12, 2001 [F3069]