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Covalently immobilized porphyrins as photooxidation catalysts

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Abstract—Porphyrins covalently linked to aminomethylated Merrifield polymers, by chlorosulfonation activation of the porphyrin nucleus, are able to generate singlet oxygen with an efficiency which is related to the spacer between porphyrin and the polymer backbone. Juglone and ascaridole are efficiently produced in the presence of these supported catalysts.

1. Introduction

Light promoted singlet oxygen reactions are attractive and clean oxidation processes.[1–3] The oxidant is environmentally friendly, allowing for a process following the basic principles of the so-called green chemistry.[4,5]

Requiring light activation, the key element in this process is the presence of a sensitizer molecule that has the role of capturing the radiant energy and passing the energetic surplus to molecular oxygen via the sensitizer triplet state. Sensitizers are organic molecules with good photochemical characteristics, such as conjugated double bonds and aromatic rings, and so they also have some structural weakness relatively to singlet oxygen reactivity and are frequently inactivated in the process. An attempt to circumvent this quenching process is through the immobilization of the sensitizer on a macromolecular framework in order to minimize destructive bimolecular processes.[6] One more advantage of immobilization is to have an heterogeneous catalyst, which allows for an easier separation of products and sensitizer, particularly useful if several cycles are wanted. Another possibility for photooxygenation catalysis is the use of fluorinated solvents in biphasic conditions.[7] In this case the sensitizers are in homogeneous form in the catalytic process and are converted into a heterogeneous form, recovered by extraction at the end of the reaction.

Due to its photochemical characteristics and resistance to degradation, porphyrins are good sensitizers for singlet oxygen generation that are currently used in the non-metallated form under homogeneous conditions.[8] Noteworthy results for immobilized porphyrins were obtained with porphyrins anchored to a soluble PEG matrix[9] and with porphyrins copolymerized with polystyrene polymer.[10] The immobilization of sensitizers was recently reviewed.[11]

Other recent and interesting proposals have appeared, such as immobilization of porphyrins in polymer microchannels,[12] linking fullerenes to amino functionalized silica gel,[13] benzophenone copolymer,[14] polymer sphere-supported *seco*-porphyrazines,[15] porphyrins loaded in polystyrene beads,[16] porphyrin dendrimer structures,[17] and polystyrene nanocontainers doped with porphyrins.[18]

2. Results and discussion

2.1. Synthesis of polymer supported sensitizers

Polystyrene is an attractive and stable structure to graph sensitizers,[19] being supported rose Bengal an example of a commercial product.[20] Also important is the structure of the porphyrin, which can be decisive in the activity of the photosensitizer. Tetra (2,6-dichlorophenyl) porphyrin (TDCPP) **4** (Scheme 2) is one of the most active sensitizers for use in photooxidations.[21,22] The presence of chlorine atoms at the *ortho* positions of the *meso* phenyl groups confers a great resistance to degradation. As far as we know, there has been no attempt to study the behavior of this kind of porphyrin macrocycle covalently linked to polystyrene based polymers as heterogeneous sensitizers.

The strategy for covalently linking porphyrins to the Merrifield polymer involves modification of the polymer structure by reaction with an excess of α,ω-diamines (**1** and **2**)[23] and diamine **3** to obtain the aminoalkylated polymers **AAP1** to **AAP3** (Scheme 1).

Reaction of 1,6-diaminohexane (**1**) in THF at 50 °C with Merrifield polymer (1% cross linked) did not originate significant substitution. Changing the solvent to DMF and the temperature to 70 °C we obtained a light yellow material with 0.35 mmol/g of amine incorporated as shown by elemental analysis. The same strategy was followed with

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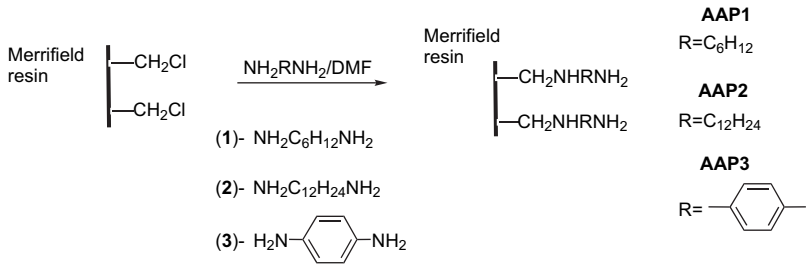


Scheme 1. Sequence of reactions to originate aminoalkylated polymers **AAP1** to **AAP3**.

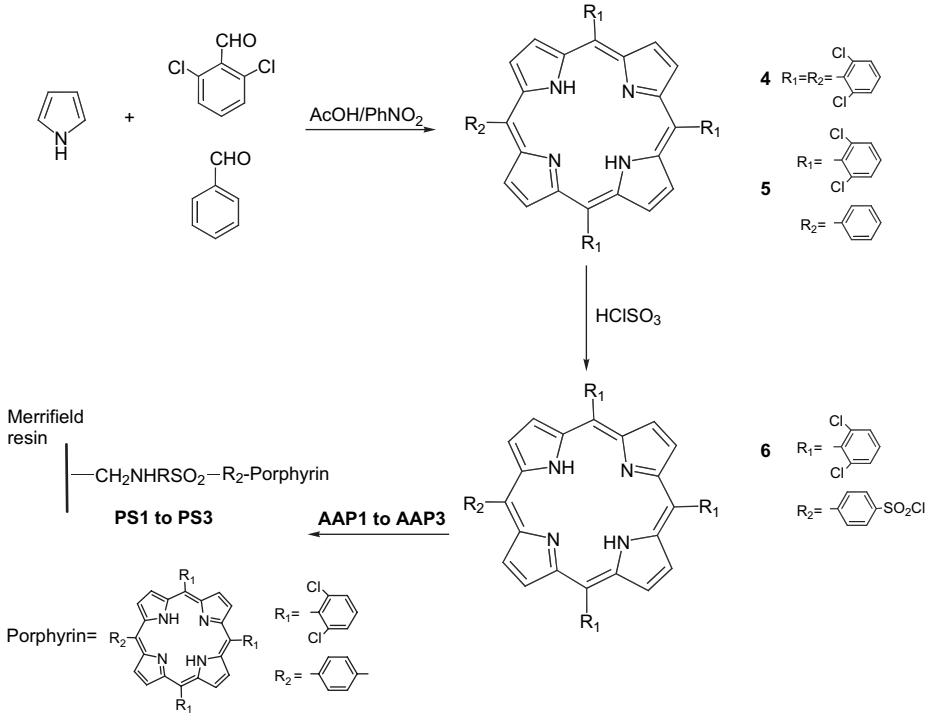
1,12-diaminododecane (**2**) but with 1,4-diaminobenzene (**3**) reaction at room temperature gives a better material with higher incorporation (Table 1).

Different amines originate different incorporation values: 1,6-diaminohexane the lowest and 1,12-diaminododecane the highest value. When we tried higher temperatures for this reaction, darker materials with lower values of incorporation resulted. Taking into account that Merrifield resin presents 1.0–1.5 mmol of chlorine atoms (labeled value) we concluded that about 1/3–1/4 of the groups have been substituted. Infrared spectra of the modified Merrifield resin **AAP1** showed significant differences relatively to the original Merrifield polymer, such as the reduction of the CH_2–Cl band at 1262 cm^{-1} and the appearance of new bands due to the presence of NH_2 groups at 1630 and 1115 cm^{-1}.

Table 1. Values for amine incorporation (mmol/g) in Merrifield polymer

Amine	Reaction conditions	Amino-alkylated polymer	Values of amine incorporation (mmol/g)
1,6-Diaminohexane (**1**)	DMF/70 °C/24 h	**AAP1**	0.35
1,12-Diaminododecane (**2**)	DMF/70 °C/24 h	**AAP2**	0.52
1,4-Diaminobenzene (**3**)	DMF/rt/24 h	**AAP3**	0.23

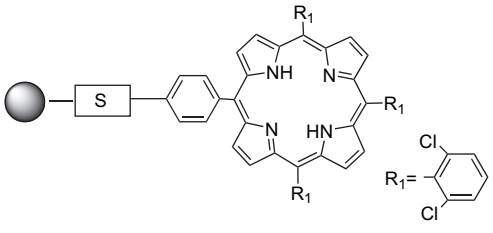
For linking the porphyrin macrocycle to the modified polystyrene derivatives (**AAP1** to **AAP3**) we used the non-symmetric porphyrin **5** obtained from the one-pot mixed aldehyde pyrrol condensation with nitrobenzene as oxidant.[24] Controlled chlorosulfonation of **5** allows the introduction of one single chlorosulfonyl group on the phenyl ring. Differences in reactivity between the phenyl ring and the 2,6-dichlorophenyl ring allow the chlorosulfonation reaction of the mixture of porphyrins **4** and **5** obtained from the one-pot reaction. As only the unsubstituted phenyl ring is chlorosulfonated, any **4** which is present does not react with aminopolymers and can be easily separated from polymer products and recovered at the end. This chlorosulfonation strategy to link the porphyrin macrocycle greatly simplifies the work because it avoids the troublesome isolation of **4** from **5** and allows a new straightforward procedure. Reaction of the chlorosulfonyl derivative **6** with aminopolymers **AAP1** to **AAP3** gives porphyrin attached polymers **PS1** to **PS3** with different spacers between the photosensitive part and the polymer backbone (Scheme 2).



Scheme 2. Sequence of reactions originating supported photosensitizers **PS1** to **PS3**.

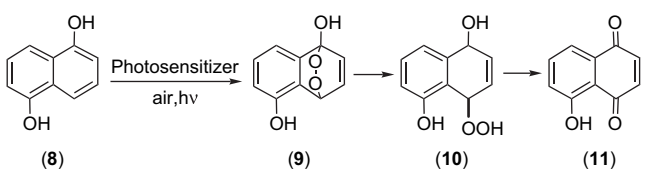
We also tried the chlorosulfonation reaction described above over the mixture of **4** and **5** and reacted the product with commercial aminomethylated polystyrene divinylbenzene copolymer (PSDV-NH_2), obtaining the corresponding porphyrin linked polymer **PS4**. Due to the absence of a spacer, this structure corresponds to a greater proximity of the porphyrin to the polymer backbone. Values for the amount of porphyrin bonding to aminomethylated polymers were calculated from the total nitrogen content of polymers **PS1** to **PS4** and discounting the value of nitrogen corresponding to the initial aminomethylated polymers (Table 2). Polymer **PS2**, with the larger spacer, presents the lowest value for porphyrin incorporation and this can be related to the possibility already suggested[23] that, due to the greater size of the alkylated chain, the two amino groups can react with chloromethyl groups of the polymer, leaving fewer free amino groups to react with chlorosulfonated porphyrins.

Table 2. Values for porphyrin incorporation (mmol/g) in the Merrifield polymer

Polymer-spacer-porphyrin	Values of porphyrin incorporation mmol/g
	
 S=NH$(CH_2)_6$NHSO_2 (**PS1**)	0.21
 S=NH$(CH_2)_{12}$NHSO_2 (**PS2**)	0.06
 S=NHC_6H_4NHSO_2 (**PS3**)	0.11
 NH—SO_2 (**PS4**)	0.06

2.2. Photooxygenation experiments

Naphthoquinones are important structural blocks present in several natural products. One of them, juglone (**11**), is the starting material for several synthetic pathways. Although juglone can be obtained by thermal conditions,[25] photooxygenation of 1,5-dihydroxynaphthalene (**8**) is an attractive route for its synthesis.[26] The mechanism of this reaction seems to involve 1,4-cycloaddition of singlet oxygen, formation of the corresponding 1,4-endo-peroxide (**9**), and decomposition into hydroperoxide (**10**), which oxidizes to juglone (**11**) (Scheme 3).[27,28] Recently described photooxidative approaches use homogeneous sensitizers in conditions of green photochemistry.[29,30]



Scheme 3. Photooxygenation of 1,5-dihydroxynaphthalene (**8**).

The major problem with the photochemical route is the deactivation of the photosensitizer. In homogeneous medium we have obtained good results for the synthesis of juglone using TDCPP (**4**) as sensitizer.[27] The catalyst stability has been found to be particularly relevant.

We started our studies with the supported photosensitizers **PS1** to **PS4** by trying the juglone photosynthesis in acetonitrile at 30 mM concentration with a catalyst/substrate ratio of 1:100 using air flow and three 50 W halogen lamps. The reactions were followed by UV–visible spectroscopy, by analyzing the increase in the 450 nm absorption band. When an increase was no longer observed, the reaction was stopped and the juglone isolated by chromatography. The blank experiment corresponds to the reaction without photosensitizer (Fig. 1).

Results of Figure 1 show that the activity of supported photosensitizers is dependent on the structure of the spacer between porphyrin and polymer. **PS2** with a C_{12} chain spacer has the greatest activity of the photosensitizers tested, comparable to that of the free porphyrin TDCPP (**4**). **PS1** with a smaller chain spacer gives similar juglone yields, but requiring longer reaction time. **PS3** and **PS4** present much smaller activities. The effects of the length of the spacer on the activity of supported catalysts are documented for thermal oxidations[23,31] and may be related to the characteristics of the catalyst environment. Long spacers allow for an environment more similar to the free catalyst in solution.[23,32] With catalyst **PS2** we tried an experiment with a substrate/catalyst ratio of 600:1 and obtained 58% of product in 15 h.

The nature of the solvent can influence the photooxygenation reactions either due to different oxygen solubility or different lifetimes of singlet oxygen.[33] Changing the solvent from acetonitrile to chloroform, where oxygen singlet has a longer lifetime, originates faster reactions for **PS1** and **PS2** giving about the same juglone yields (Fig. 2). For **PS2** after 3 h 77% isolated yield of juglone is obtained,

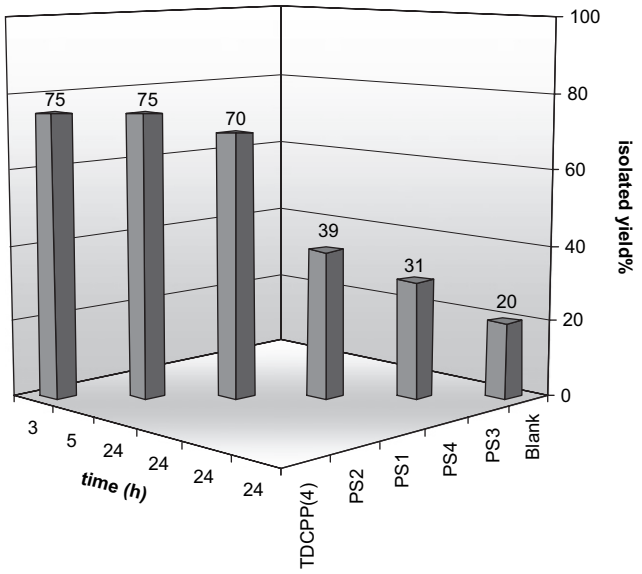


Figure 1. Total reaction time and juglone (**11**) yields for different photosensitizers.

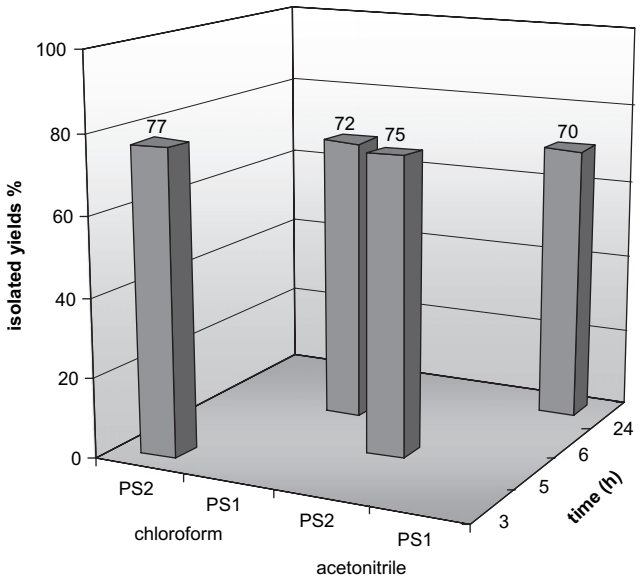


Figure 2. Comparative values in chloroform and acetonitrile of juglone (**11**) yield for photosensitizers **PS1** and **PS2**.

which shows that this supported sensitizer is superior to supported rose Bengal.[26]

The possibility of easy recycling is the major advantage of supported catalysts. Using chloroform as solvent we tried catalyst **PS2** in three cycles of photooxygenations (Fig. 3). The catalyst is simply filtered, washed, dried, and used with a new substrate batch. We observed a gradual increase of time required to finish the reaction and a decrease in the final yield of isolated juglone. As we never observed leaching of the catalyst, this inactivation means that the link to the polymer structure was not affected. One possibility is the destruction of the porphyrin and consequent loss to solution in a form not detectable by visible spectroscopy. However, elemental analysis for **PS2** after recycling shows only a 10% decrease of the nitrogen content, which shows that the observed inactivation is not related to a massive degradation of the macrocycle.

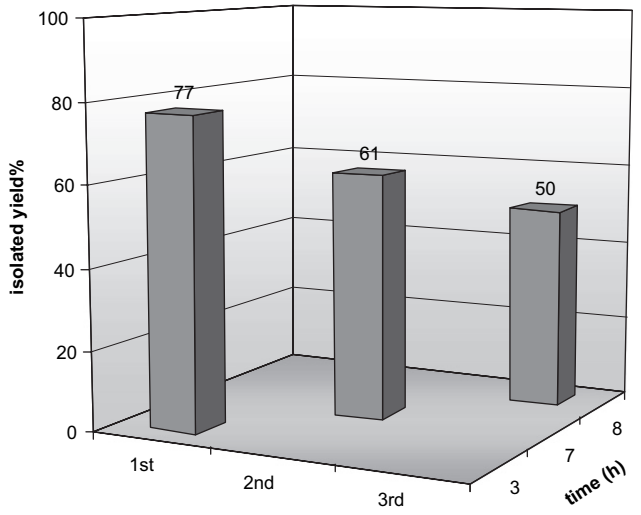
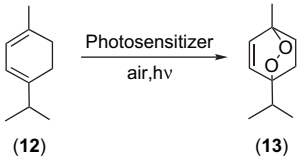


Figure 3. Total reaction time and juglone (**11**) yields for three consecutive reactions with **PS2**.

Photooxygenation of α-terpinene (**12**) to originate ascaridole (**13**) was also studied (Scheme 4).[34]



Scheme 4. Photooxygenation of α-terpinene (**12**).

We used the same photooxidative system as before with chloroform as solvent, but with a sensitizer/substrate ratio of 1:600. The reaction was followed by analyzing the disappearance of **12** by GC. For supported catalysts the polymer was filtered at the end of the reaction and the solvent evaporated. NMR analysis showed that the main product is the endoperoxide **13**, which is confirmed by GC/MS analysis. The results with **PS1**, **PS2**, and TDCPP (**4**) are shown in Figure 4.

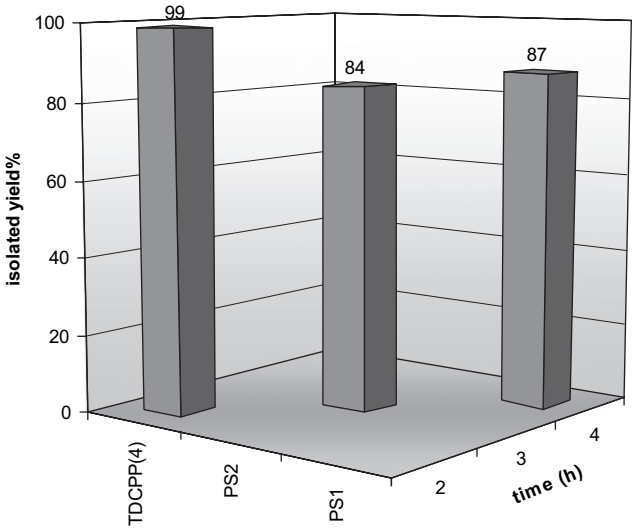


Figure 4. Isolated yield of ascaridole (**13**) and total reaction time for α-terpinene (**12**) photooxidation with **PS1** and **PS2**.

From Figure 4 we conclude that **PS2** is again more active than **PS1** and less active than the free sensitizer **4**, but with the advantage of the easy procedure to isolate the product. For **PS2** about 10% of another compound is detected by GC/MS and corresponds to the same percentage for small signals seen in the NMR spectrum. This compound is already present in the reagent and was identified as *p*-cymene. In the case of **PS1** the amount of this product increases to 30% (by NMR), which may be explained by the competitive oxidation of α-terpinene by oxygen when oxygenation by singlet oxygen is a slower process.

The problem of inactivation of the sensitizers in reutilization experiments was once again studied with this substrate. Oelgemoller suggested[26] that the production of acid from photooxidation reactions in chloroform may be one explanation for sensitizer inactivation. In our case even though not promoting sensitizer destruction, acid may originate protonation of the porphyrins, which may present lower

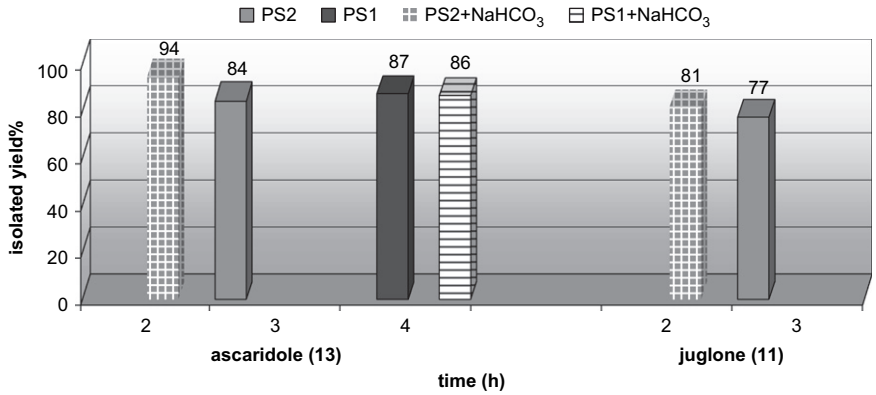


Figure 5. Comparative yields of ascaridole (**13**) and juglone (**11**) for reactions with photosensitizers **PS1** and **PS2** in the presence and absence of $NaHCO_3$.

values for singlet oxygen quantum yields as positively charged dyes.[35] To circumvent this possibility we repeated the photooxidation of α-terpinene (**12**) and 1,5-dihydroxynaphthalene (**8**) in the presence of solid sodium hydrogen carbonate (Fig. 5).

From Figure 5 we conclude that the presence of sodium hydrogen carbonate decreases reaction time of the photooxygenations, possibly by avoiding the formation of porphyrin cations and this may be the major deactivation pathway for these supported catalysts. The effect of the base is more pronounced in the case of **PS2** than in **PS1**. This beneficial effect of the base addition is more pronounced in reutilization experiments. Sensitizer **PS2** in α-terpinene photooxygenations shows small values of activity loss after three consecutive reactions (Fig. 6), which is a promising characteristic to be explored in future studies.

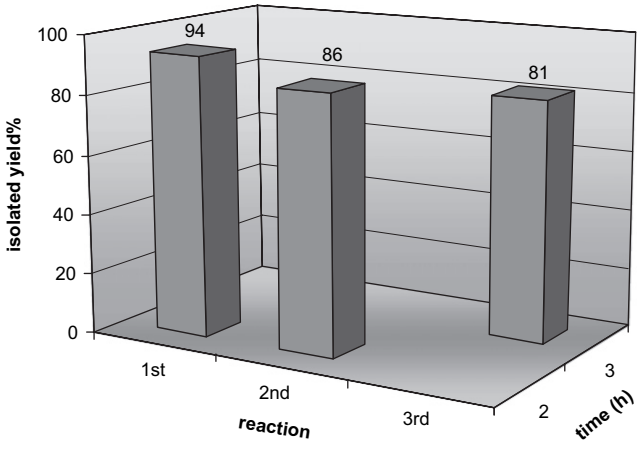


Figure 6. Total reaction time and ascaridole (**13**) yields for three consecutive reactions with **PS2** as photosensitizer in the presence of sodium hydrogen carbonate.

3. Conclusion

Porphyrins can be easily and selectively chlorosulfonated and covalently linked to the Merrifield polymer. Selected spacers can also be easily intercalated between the porphyrin nucleus and the polymer, with a C_{12} carbon chain as spacer being the most convenient to make a good sensitizer for oxygen singlet oxidations. The presence of sodium hydrogen carbonate in the reaction medium increases the efficiency of the system, possibly by avoiding the formation of cationic porphyrinic species.

4. Experimental

4.1. Materials and methods

All solvents were purified before use according to the literature procedures. 1,5-Dihydroxynaphthalene, α-terpinene, and aminomethylated polystyrene divinylbenzene copolymer were used as purchased from Aldrich. Porphyrin **4** was obtained as described in the literature.[24]

4.2. Instrumentation

^{1}H NMR spectra were recorded on a 300 MHz Bruker-AMX spectrometer. *J* values are given in Hertz. Mass spectra were obtained on a HP 5973 MSD apparatus by electronic impact at 70 eV. Elemental analysis was carried out using a Fisons Instruments EA1108-CHNS-0 apparatus. Absorption spectra were measured on a Hitachi U-2001 spectrometer. Gas chromatography was carried out using a Supelcowax (30 m× 0.25 mm) capillary column on a Hewlett-Packard 5890A instrument with a Hewlett-Packard 3396A integrator. GC analysis was run at 80 °C (5 min)/20 °C min^{-1}/200 °C (20 min); detector temperature 250 °C, injector temperature 220 °C.

4.3. Synthesis of porphyrin 5[24]

To a solution of 7.0 g (40 mmol) of 2,6-dichlorobenzaldehyde, 0.85 g (8.0 mmol) of benzaldehyde in 100 mL of acetic acid, 8 mL of acetic anhydride and 25 mL of nitrobenzene at 120 °C, and 3.5 mL (50 mmol) of pyrrole were slowly added. The reaction was maintained at this temperature for 2 h. After cooling, 275 mg of a mixture of porphyrins **4** and **5** was obtained. By NMR the mixture contains about 13% of porphyrin **4** and 72% of porphyrin **5**.

4.4. Synthesis of aminoalkylated polymers AAP1 to AAP3

To a mixture of 3.0 g of Merrifield polymer in 25 mL of DMF, 1.5 g of amine (**1**–**3**) was added. The mixture was

placed at 70 °C for 24 h (room temperature for amine **3**). After cooling the mixture was poured in 150 mL of water, filtered, and washed with water, methanol, dichloromethane, and methanol again. The residue was dried in an oven under vacuum. Elemental analysis of this product gives the incorporation of the amino alkyl chain in the polymer structure.

4.5. Synthesis of polymeric photosensitizers PS1 to PS4

At room temperature 15 mL of chlorosulfonic acid was added to 150 mg of a mixture of porphyrins **4** and **5**. The solution was stirred for 2 h and then carefully poured over ice in order to precipitate the porphyrins. The precipitate was filtered, dried, dissolved with dichloromethane, and the solution dried with sodium sulfate. The solution was concentrated to 30 mL, 1 mL of pyridine was added followed by 300 mg of the aminoalkylated polymers **AAP1** (**AAP2**, **AAP3** or PSDV-NH_2). The mixture was stirred overnight at 30 °C, filtered, and washed with dichloromethane, tetrahydrofuran, methanol, and dichloromethane again. Non-bonding porphyrin was eliminated with these washings. After drying the solid under vacuum elemental analysis was carried out in order to determine porphyrin incorporation.

4.6. Photosynthetic oxidation experiments

4.6.1. General photooxidation procedure. Photooxidation experiments were carried out at room temperature using a laboratory-built photoreactor consisting of three 50 W lamps. The reactions were carried out in a 100 mL flask equipped with a water condenser (an ice condenser in the case of the substrate α-terpinene) and an entrance for air. The solutions were irradiated with a stream of air continuously flowing into the flask.

4.6.1.1. 1,5-Dihydroxynaphthalene photooxidation. The substrate (96 mg) in acetonitrile (20 mL) was mixed with an amount of photosensitizer (porphyrin or supported porphyrins) in order to originate the proper molar ratio of sensitizer to substrate. The evolution of the reaction was monitored by UV–vis spectroscopy at 416 nm. The reaction mixtures were filtered to recover the sensitizer and the solvent evaporated. The residue was chromatographed on a silica gel column using CH_2Cl_2 as an eluent to give juglone (5-hydroxy-1,4-naphthoquinone) as the product.

This reaction was also carried out in the presence of $CHCl_3$ (14 mL), using acetonitrile (6 mL) only to dissolve the substrate. In the experiment made in the presence of base, 60 mg of sodium hydrogen carbonate was added.

5-Hydroxy-1,4-naphthoquinone: Yellow brownish solid, ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=7.28 (1H, d, *J* 2.50, H-naph.), 7.30 (1H, d, *J* 2.50, H-naph.), 7.61–7.68 (3H, m, H-naph.), 11.9 ppm (1H, s, OH); MS (EI, 70 eV): *m*/*z*= 174 (M^+, 100%), 146 (19%), 118 (28%), 92 (24%), 63 (19%). Spectral data were identical to those reported.[27]

4.6.1.2. α-Terpinene photooxidation. The substrate in $CHCl_3$ was mixed with the appropriate amount of photosensitizer in order to originate the proper molar ratio of sensitizer to substrate. The evolution of the reaction was monitored by analyzing the disappearance of the reagent using GC. The reaction evolution can also be followed by UV–vis spectroscopy at 268 nm. When the reagent was consumed the reaction mixture was filtered to recover the sensitizer. The solvent was evaporated, dried by nitrogen flow, and analyzed by NMR spectroscopy. In the experiment made in the presence of base, 60 mg of sodium hydrogen carbonate was initially added.

Ascaridole: colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=0.97 (3H, d, *J* 6.90, CH_3), 0.98 (3H, d, *J* 6.9, CH_3), 1.31 (3H, s, CH_3), 1.51–1.56 (2H, m), 1.85 (H, sept, *J* 6.90, isopropyl), 1.97–1.92 (2H, m), 6.42 (H, d, *J* 8.58, olefinic CH), 6.53 ppm (H, d, *J* 8.58, olefinic CH); MS (EI, 70 eV): *m*/*z*=168 (M^+, 1%), 150 (7%), 134 (32%), 119 (100%), 107 (33%), 91 (37%). Spectral data were identical to those reported.[36]

p-Cymene: ^{1}H NMR (300 MHz, $CDCl_3$): δ_H=1.22 (3H, d, *J* 1.68, CH_3), 1.24 (3H, d, *J* 1.68, CH_3), 2.31 (3H, s, CH_3), 2.87 (H, sept, isopropyl), 7.11 (4H, s, Ar-H); MS (EI, 70 eV): *m*/*z*=134 (M^+, 29%), 119 (100%), 115 (6%), 103 (6%), 91 (17%), 77 (5%). NMR data were identical to those reported.[37]

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