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Covalently immobilized porphyrins on silica modified structures as photooxidation catalysts

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ABSTRACT

Heterogeneous photooxidation catalysts were prepared by the covalent linkage of a porphyrin to aminoalkylated silica particles by chlorosulphonation activation of the porphyrin nucleus. These catalysts were tested in [4+2] cycloaddition and ene reactions promoted by singlet oxygen. Photooxidation of substrates originates high yields of products but with longer reaction times compared to the free porphyrin catalysts. Quenching of singlet oxygen by the silica structure can be the plausible explanation. In the case of the ene reaction with citronellol the supported catalysts originate a distribution of the regioisomeric products which is opposite to that of the homogeneous catalyst.

1. Introduction

Singlet oxygen mediated oxidations are very attractive reactions which make use of clean, accessible and economical reaction conditions [1]. Also very important is that they can give access to very interesting synthetic products, which are very hard to obtain by other methods, as illustrated by the synthesis of artemisin compounds [2], inositols derivatives [3] and natural furan products [4]. Porphyrins are easily accessible compounds which have shown good photosensitizer properties and stability in reaction media, particularly if halogen atoms are present [5]. Their incorporation in heterogeneous matrices is a useful and practical approach to carry out the reaction, since it greatly simplifies the isolation process [6]. However, the structure of the solid matrices can also influence the performance of the photoactive molecule since it is located close to the solid surface. Light, oxygen, and substrate accessibility or quenching effects can also affect the rate of the oxidation reaction [7] and these factors can be influenced by the solid matrix. Silica gel is an inexpensive, available and resistant material for the immobilization of catalysts [8] and recent examples of immobilization of photosensitizers on silica gel have been described [9]. However, one particular aspect of the use of silica as a support for photosensitizers is the possibility of singlet oxygen quenching effects by the silica surface [10]. In previous works we reported the development [6a,11] of a strategy for covalently immobilizing porphyrins, separated from a Merrifield polymer structure by spacers of different lengths. This proved to be a helpful approach since fast kinetics is observed with longer spacers. In this work we extended the same principles of immobilization, using silica as the support and separating the porphyrin from the silica surface by spacers of different length. The effects of different kinds of silica gel and different spacers on photocatalyst activity are evaluated.

2. Experimental

2.1. General

All solvents were purified before use according to literature procedures. α-Terpinene (85% purity), citronellol (95% purity), α-pinene (98% purity), (−)-linalool (95% purity), (3-aminopropyl)-trimethoxysilane (97% purity), (3-glycidyloxypropyl)-trimethoxysilane (98% purity), 1,12-diaminododecane (98% purity), 1,6-diaminohexane, were used as purchased from Aldrich. Silica gel type 60, 35–70 mesh, with particle size of 0.2–0.5 mm was purchased from Fluka; silica gel Davisil®, grade 643, 200–425 mesh, with particle size of 35–70 μm and silica gel, type 9385, 230–400 mesh, with particle size 40–63 μm were purchased from Aldrich. Porphyrin **1** [12] and Porphyrin **2** [6a] were prepared as previously described.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a 400 MHz Bruker spectrometer. *J* values are given in Hertz. Mass spectra were obtained on a HP

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5973 MSD apparatus by electron 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.

2.3. Synthesis of the aminoalkylated silica derivatives ***AAS1*–*AAS5***

2.3.1. Synthesis of ***AAS1*** *[13]*

To a stirred solution of 70 ml dry toluene containing 10% of 3-aminopropylltrimethoxysilane was added 45 g of SiO_2 (silica gel type 60, 35–70 mesh) activated as described [13] at 120 °C. The resulting mixture was refluxed overnight. The amino functionalized silica **AAS1** was isolated by filtration and washed with tetrahydrofuran and methanol, then dried under vacuum for several days. Elemental analysis showed nitrogen content of 0.95%.

2.3.2. Synthesis of ***AAS2*** and ***AAS3*** *[14]*

To a stirred solution of 80 ml dry toluene containing 3.0 mmol of 1,12-diaminohexane, 1.0 mmol of (3-glycidyloxypropyl)-trimethoxysilane was added. The resulting mixture was allowed to react at 80 °C for 24 h. To this solution, 1.5 g of activated SiO_2 (Kieselgel 60, 35–70 mesh) and 5 ml of EtOH were added and the solution was stirred at 80 °C for 24 h. The amino functionalized silica **AAS2** was isolated by filtration and washed with MeOH and EtOH. Then, it was refluxed with EtOH during 1 h, filtered again and dried at 40 °C for several days. The amino functionalized silica **AAS3** was prepared in a similar way to **AAS2**, but using 1,12-diaminododecane instead of 1,6-diaminohexane.

2.3.3. Synthesis of ***AAS4*** and ***AAS5***

AAS4 and **AAS5** were prepared as described for **AAS3**, but using two different samples of silica gel: silica gel Davisil® (200–425 mesh, pore size 150 Å) for **AAS4** and silica gel Kieselgel (230–400 mesh, pore size 60 Å) for **AAS5**.

2.4. Synthesis of photosensitizers ***PAAS1*–*PAAS5***

The procedure carried out was similar for all five photosensitizers (**PAAS1**–**PAAS5**) [6a]. The procedure for **PAAS1** is described: at room temperature 15 mL of chlorosulphonic acid was added to 213 mg of porphyrin **2**. The solution was stirred for 2 h and then carefully poured over ice in order to precipitate the porphyrin. The precipitate was filtered, dried, dissolved with dichloromethane, and the solution dried with sodium sulphate. The solution was concentrated to 20 mL and 10 mL of pyridine was added followed by 380 mg of the aminoalkylated polymer **AAS1** (the same procedure with **AAS2**, **AAS3**, **AAS4**, **AAS5**). The mixture was stirred overnight at 30 °C, filtered and washed sequentially with dichloromethane, tetrahydrofuran, ethanol, and dichloromethane. Non-bonded porphyrin was eliminated with these washings. After drying the solid at 40 °C, elemental analysis was carried out in order to determine value of porphyrin incorporation.

2.5. Photosynthetic oxidation experiments

2.5.1. General procedure

Photooxidation experiments were carried out at room temperature using a laboratory-built photoreactor consisting of three 50 W halogen lamps. The reactions were carried out in a 100 mL flask equipped with a water condenser and an inlet for air. The solutions were irradiated during the time described with a stream of air continuously flowing into the flask.

2.5.2. α-Terpinene photooxidation

α-Terpinene (4.9 mmol) in 65 mL of chloroform was mixed with the appropriate amount of photosensitizer (9.8×10^{-4} mmol of porphyrin or the equivalent molar amount of supported porphyrin) in order to produce a 1/5000 sensitizer to substrate molar ratio and 203 mg of sodium hydrogenocarbonate were added.

The reaction was monitored by analysing the disappearance of the reagent by GC. The reaction can also be followed by UV–vis spectroscopy at 268 nm. When the reagent was consumed, the reaction mixture was filtered to recover the photosensitizer. The solvent was evaporated, dried by nitrogen flow and the products analysed by NMR spectroscopy.

2.5.2.1. Ascaridole. ^{1}H NMR ($CDCl_3$): δ 0.97 (d, 3H, J = 6.9 Hz, CH_3), 0.98 (d, 3H, d, J = 6.9 Hz, CH_3), 1.31 (s, 3H, CH_3), 1.51–1.56 (m, 2H), 1.85 (sept, 1H, J = 6.9 Hz, isopropyl), 1.97–1.92 (m, 2H), 6.42 (d, 1H, J = 8.6, olefinic CH), 6.53 (d, 1H, J = 8.6 Hz, olefinic CH). MS (EI): m/z M^+ = 168. Spectral data were identical to reported [15].

2.5.2.2. p-Cymene. ^{1}H NMR ($CDCl_3$): δ 1.22 (d, 3H, J = 1.68 Hz, CH_3), 1.24 (d, 3H, J = 1.68 Hz, CH_3), 2.31 (s, 3H, CH_3), 2.87 (sept, H, isopropyl), 7.11 (s, 4H, Ar–H); MS (EI): m/z M^+ = 134. NMR data were identical to those reported [16].

2.5.3. Citronellol photooxidation

Citronellol (**7**) (11.5 mmol) in 154 mL of chloroform was mixed with the appropriate amount of photosensitizer (2.3×10^{-3} mmol of porphyrin or supported porphyrin) to originate a sensitizer to substrate molar ratio of 1/5000. GC was used to monitor the reaction. After filtration of the photosensitizer and evaporation of the solvent, the product was analysed by ^{1}H NMR. The proportion of the two regioisomers thus obtained, (*E*)-7-hydroperoxy-3,7-dimethyloct-5-en-1-ol (**8**) and 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (**9**), was estimated by ^{1}H NMR ([6b,17]).

*2.5.3.1. (E)-7-Hydroperoxy-3,7-dimethyloct-5-en-1-ol (**8**).* ^{1}H NMR ($CDCl_3$): δ 0.87 (d, 3H, J = 6.4 Hz, $CHCH_3$), 1.25–1.71 (m, 5H, CH_2CHCH_2), 3.64 (m, 2H, CH_2OH); 1.29 (s, 6H, $COOH(CH_3)_2$), 5.55 (d, 1H, J = 15.8 Hz, COOHCH=CH), 5.63 (m, 1H, COOHCH=CH).

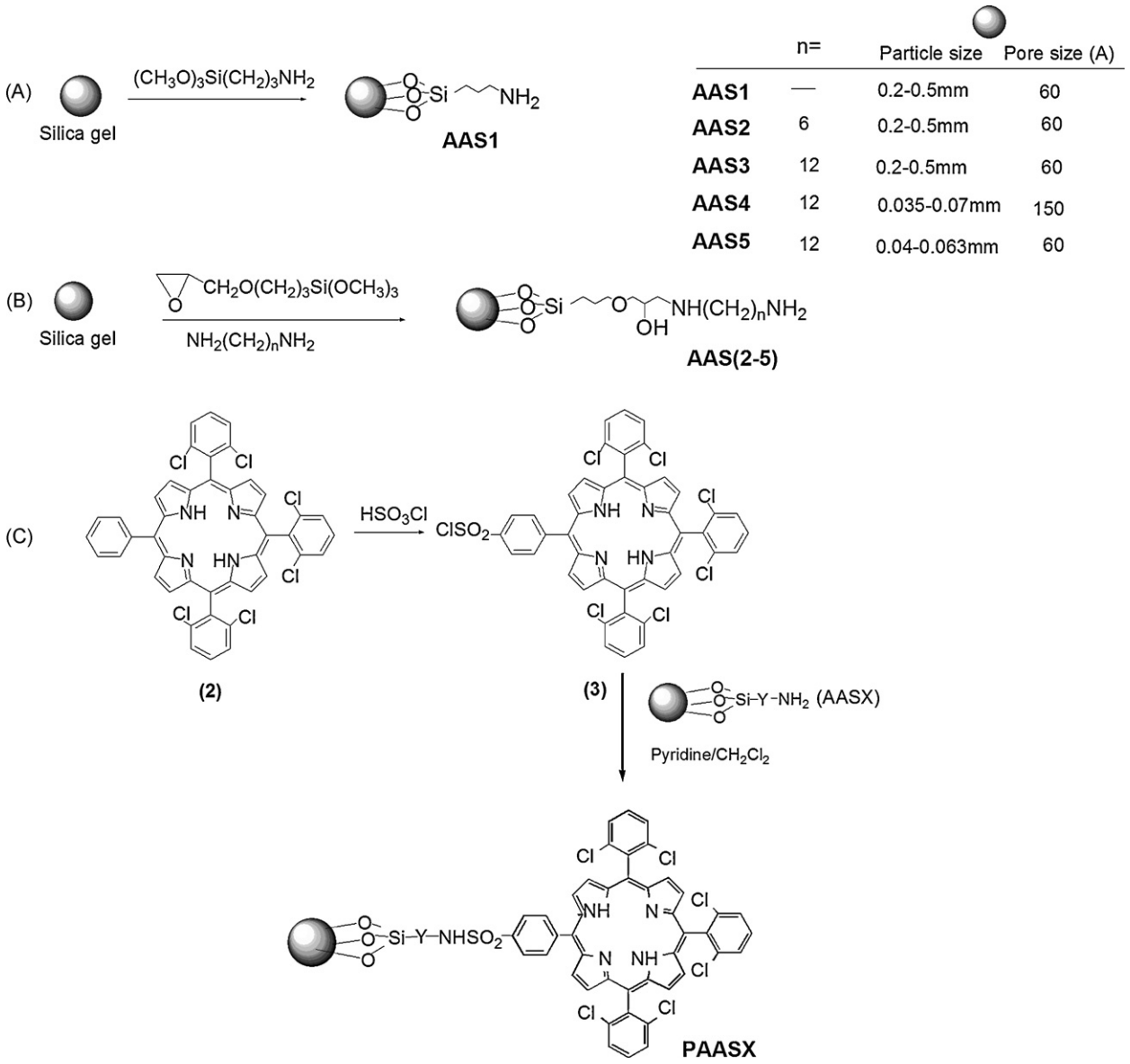
*2.5.3.2. 6-Hydroperoxy-3,7-dimethyloct-7-en-1-ol (**9**).* ^{1}H NMR ($CDCl_3$): δ 0.85 (d, 3H, J = 6.5 Hz, $CHCH_3$), 1.25–1.71 (m, 5H, CH_2CHCH_2), 3.64 (m, 2H, CH_2OH), 1.65 (s, 3H, C_qCH_3), 1.95 (m, 2H, $COOHCH_2$), 4.24 (m, 1H, CHOOH), 4.95 (s, 2H, C_q=CH_2). The proportion of the two regioisomers (**8**) and (**9**) was estimated by ^{1}H NMR as follows:

$$\%\ \text{for}\ (\mathbf{8}) = \frac{[(\text{area}\ \delta_{H5.55} + \text{area}\ \delta_{H5.68})/2]}{[(\text{area}\ \delta_{H5.55} + \text{area}\ \delta_{H5.68})/2 + (\text{area}\ \delta_{H} = 4.95)/2]} \times 100$$

2.5.4. Linalool photooxidation

The substrate (11.5 mmol) in 154 mL of chloroform was mixed with the appropriate amount of photosensitizer (2.3×10^{-3} mmol of porphyrin or supported porphyrin) to originate a sensitizer to substrate molar ratio of 1/5000. GC was used to monitor the reaction until disappearance of the reagent. After filtration of the photosensitizer and evaporation of the solvent, the isolated product was analysed by ^{1}H NMR [18].

*2.5.4.1. 7-Hydroperoxy-3,7-dimethyloct-2,5-dien-1-ol (**12**).* ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 3H), 1.32 (s, 6H), 2.26 (dd, 1H, J = 13.6, 7.1 Hz); 2.31 (dd, 1H, J = 13.6, 6.3 Hz), 5.06 (dd, 1H, J = 10.6, 1.2 Hz),



	n=	Particle size	Pore size (A)
AAS1	—	0.2-0.5mm	60
AAS2	6	0.2-0.5mm	60
AAS3	12	0.2-0.5mm	60
AAS4	12	0.035-0.07mm	150
AAS5	12	0.04-0.063mm	60

Scheme 1. Synthesis of the aminoalquilated silicas (**AAS1**–**AAS5**) and the photooxidation catalysts (**PAAS1**–**PAAS5**).

5.19 (dd, 1H, J = 17.2, 1.2 Hz), 5.61 (d, 1H, J = 16.0 Hz), 5.68 (ddd, 1H, J = 15.8, 7.2, 6.3 Hz), 5.91 (dd, 1H, J = 17.2, 10.6 Hz)

*2.5.4.2. 6-Hydroperoxy-3,7-dimethyloct-1,7-dien-1-ol (**13**).* ^{1}H NMR ($CDCl_3$): δ 1.27 (bs, 3H), 1.66–1.49 (m, 4H), 1.70 (bs, 3H), 4.28 (m, 1H), 4.99 (m, 2H), 5.05 (dd, 1H, J = 10.8, 1.1 Hz), 5.19 (dd, 1H, J = 17.4, 1.1 Hz), 5.20 (dd, 1H, J = 17.4, 1.1 Hz), 5.86 (dd, 1H, J = 17.3, 10.6 Hz), 5.85 (dd, 1H, J = 17.3, 10.8 Hz). The proportion of the two regioisomers obtained, (*E*)-7-hydroperoxy-3,7-dimethyloct-2,5-dien-1-ol (**12**) and 6-hydroperoxy-3,7-dimethyloct-1,7-dien-1-ol (**13**) was estimated by ^{1}H NMR as follows [18]

$$\%\,\text{for}\,(\mathbf{12}) = \frac{[(\text{area}\,\delta_{H2.31} + \text{area}\,\delta_{H2.26})/2]}{[(\text{area}\,\delta_{H4.28}) + (\text{area}\,\delta_{H2.31} + \text{area}\,\delta_{H2.26})/2]} \times 100$$

3. Results and discussion

3.1. Synthesis of silica supported photosensitizers *PAAS1*–*PAAS5*

The preparation of supported photosensitizers is indicated in Scheme 1. The first step is the modification of the silica surface by two reaction types for introducing different spacers. **AAS1** was prepared following the reaction with 3-(aminopropyl)trimetoxysilane (A) [13]. In order to prepare the modified silica supports **AAS2**–**AAS5** we adapted the procedure described by Louloudi and co-workers [14] using 3-(glycidyloxypropyl)-trimethoxysilane and 1,6-hexanediamine or 1,12-dodecanediamine (B). We selected two particle sizes and two pore volumes in order to examine if these structural parameters influence the porphyrin loading and the photooxidation process.

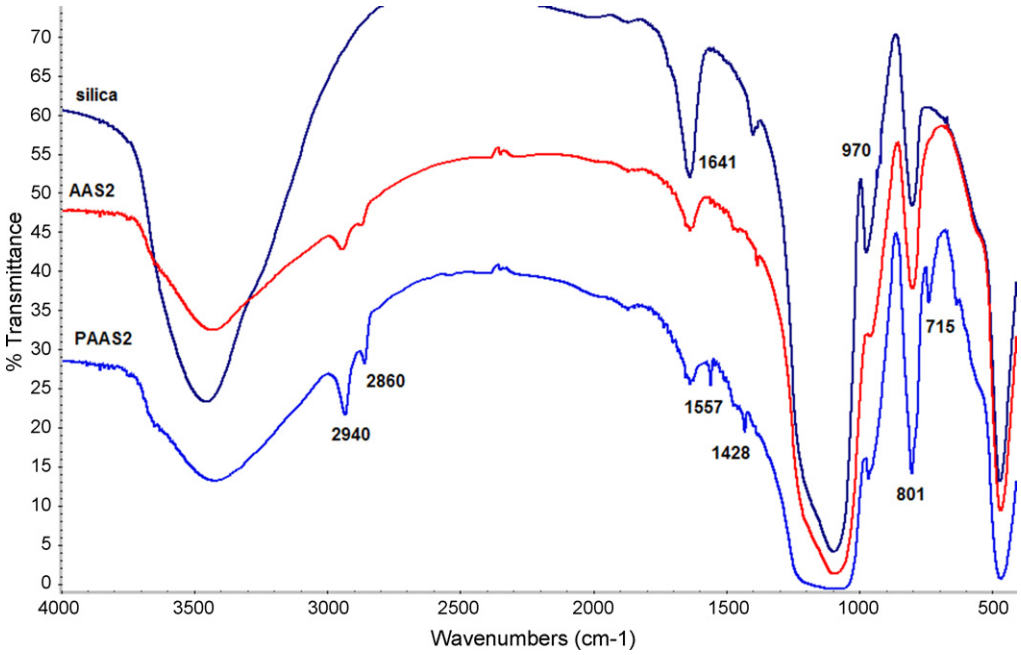


Fig. 1. Comparative FTIR spectra of silica, **AAS2** and **PAAS2**.

The incorporation of the organic parts into the silica structure can be monitored by analysing the FTIR spectra of the different compounds (Fig. 1). The infrared spectrum of the silica gel shows the typical Si–O lattice vibrations: a strong and broad band at 1094 cm^{-1} with a shoulder at 1200 cm^{-1}; a strong band at 470 cm^{-1} and a medium intensity band at 801 cm^{-1}. Furthermore, a very broad band centred a 3450 cm^{-1} with medium intensity due to the O–H stretching vibrations assigned to isolated surface SiO–H groups is observed. A band at 1641 cm^{-1} is attributed to the H–O–H bending vibrations of adsorbed water [13,19]. Upon amine functionalization (**AAS2**) a decrease in the intensity of the very broad band at 3450 cm^{-1} is observed, indicating that the reaction between the isolated silanol groups and the aminosilane derivate took place. Additionally the presence of characteristic CH_2 stretching bands at 2940 cm^{-1} and 2860 cm^{-1} confirm the reaction. A weak band at 1428 cm^{-1} in the spectrum of **AAS2** can also be correlated with the presence of CH_2 groups [20]. Similar trends are observed in the case of the aminoalkylated silica derivatives **AAS1** and **AAS3**–**AAS5**. The UV–vis spectra of *meso*-tetra(2,6-dichlorophenyl)porphyrin in solution, **PAAS2** and **PAAS3** as suspensions in dichloromethane are presented in Fig. 2. Spectra of supported photosensitizes shows the Soret band at 418 nm almost at the same position as the free porphyrin but have a much broader bands with lower relative intensity. The characteristic and less intense Q bands of free porphyrin at 514 and 589 nm are red shifted to 520 and 595 nm respectively. Curiously the very small Q band of the free porphyrin at 645 nm occurs at 667 nm and is relatively much more intense in the case of the supported photosensitizers.

Elemental analysis of the nitrogen content gives values of loadings for the amino groups for the different aminoalkylated silicas (Table 1). The values for the incorporation of amines depend on the aminosilane derivative, (3-aminopropyl)-trimethoxysilane incorporating more effectively than (3-glycidyloxypropyl)-trimethoxysilane, which is expected due to the easier reaction process (A versus B, Scheme 1).

The synthesis of the supported photosensitizers **PAAS1**–**PAAS5** was carried out by using conditions for the selective chlorosulphonation of the non-symmetrical porphyrin **2** and the reaction of the chlorosulphonyl derivative 3 [6a] with the terminal amino groups of modified silica supports (**AAS1**–**AAS5**) (C, Scheme 1). The FTIR spectrum of the supported photosensitizer **PAAS2** (Fig. 1) shows new bands at 1557 cm^{-1}, and 715 cm^{-1} and changes in the band at 801 cm^{-1}, which already appears in the spectrum of the free

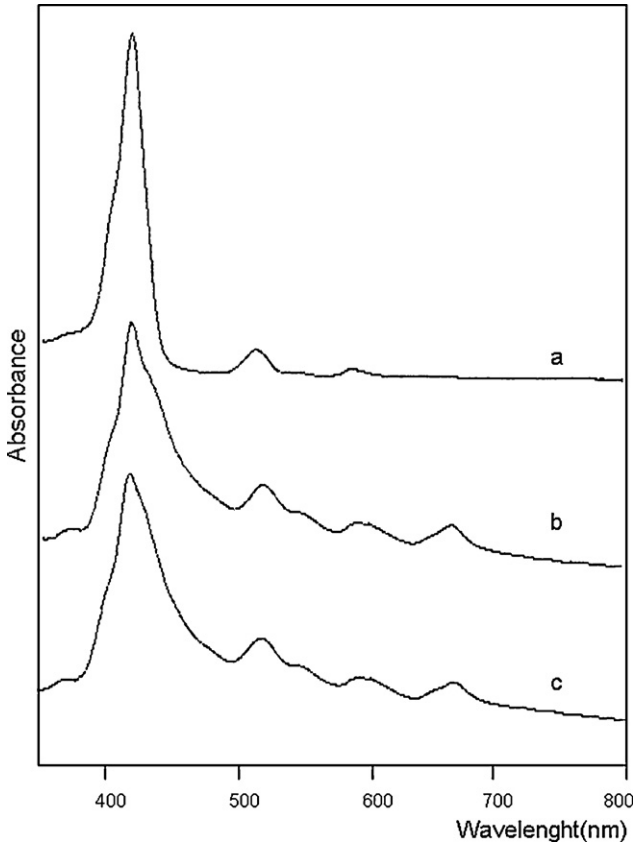
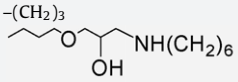
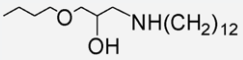
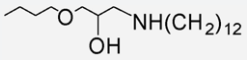
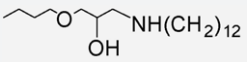


Fig. 2. Comparative UV–vis spectra of a solution of the free porphyrin H_2TDCPP (a) and dichloromethane suspensions of **PAAS2** (b) and **PAAS3** (c). Scales adjusted to give approximately equivalent absorptions of the Soret peak at 418 nm.

Table 1
Values for amino groups and porphyrin incorporation (mmol/g) for photosensitizers **PAAS1**–**PAAS5**.

Aminoalkylated silica	Values of amino incorporation (mmol/g)	Supported photosensitizer	Si—Y—NHSO$_2$Porphyrin Y=	Values of porphyrin incorporation (mmol/g)[a]
AAS1	0.68	**PAAS1**	–(CH$_2$)$_3$	0.040
AAS2	0.38	**PAAS2**		0.142
AAS3	0.31	**PAAS3**		0.115
AAS4	0.29	**PAAS4**		0.158
AAS5	0.33	**PAAS5**		0.151

[a] Value obtained by subtracting the value for the corresponding amino modified silicas (**AAS1**–**AAS5**).

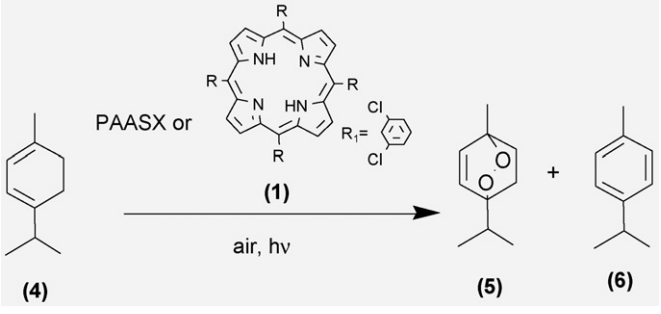
porphyrin. Elemental analysis of the products indicates the values for porphyrin incorporation into the solid support (Table 1). For **PAAS2**–**PAAS5** the values for incorporation have the same magnitude. No significant differences were observed, in spite of the different particle size of the silica structures. Comparatively, these values are greater than the ones we observed when the same porphyrin was linked to the Merrifield modified polymers [11]. However, from the values of the amino incorporation and porphyrin incorporation, we can envisage that only 50% or less of the terminal amino groups reacted with the porphyrin. In the case of **PAAS1** we observed a great decrease in the value of porphyrin incorporation in spite of the high value for the amino incorporation. Our explanation is that the proximity of the silica structure to the terminal amino group somehow hinders the access of the chlorosulphonated derivative and originates less incorporation of the porphyrin. A similar situation was already observed by us with Merrifield structures [6a].

3.2. Photooxygenation experiments

Evaluations of the photoactivitiy of the different photosensitizers were carried out using α-terpinene (**4**) as substrate with sensitizer to substrate ratios of 1:600 and 1:5000. The major product is the [4+2]-cycloadduct ascaridole (**5**) [15] and *p*-cymene (**6**) is the minor product resulting from the air oxidation of α-terpinene. For comparison a reaction with the free porphyrin (**1**) was carried out (Table 2).

Results from Table 1 show that photosensitizers **PAAS1**–**PAAS5** are active catalysts for singlet oxygen generation but with a lower activity than the free porphyrin **1**, which can be partially attributed to the silica structure. The result of entry 3 shows that silica significantly slow down the homogeneous catalytic process; it seems that the quenching effects by hydroxyl groups at the silica surface may be operating [10]. For supported photosensitizers, especially for high substrate to catalyst ratios, the amount of non-singlet oxi-

Table 2
Results for the photooxidation of α-terpinene using porphyrin **1** or **PAAS1**–**PAAS5** as sensitizers.



Entry	Photosensitizer	$R = n_{ph}/n_{terp}$[a]	Time (h)	**5** (%)[b]
1	**1**	1/600	1.5	93 (7)
2	**1**	1/5000	2.3	96 (4)
3	**1**[c]	1/5000	5	98 (2)
4	**PAAS1**	1/600	5	94 (6)
5	**PAAS1**	1/5000	8.5	90 (10)
6	**PAAS2**	1/5000	7.5	76 (24)
7	**PAAS3**	1/600	5.5	97 (3)
8	**PAAS3**	1/5000	7.5	86 (14)
11	**PAAS4**	1/5000	10.5	77 (23)
12	**PAAS5**	1/5000	13	76 (24)

[a] Photosensitizer/α-terpinene ratio.
[b] Isolated yield of **5**. In parenthesis, the amount of formed *p*-cymene (**6**). Determined by ^{1}H NMR of the reaction mixture after filtration the catalyst and solvent removal taking into account that 5% of *p*-cymene exist in the initial reagent.
[c] 8 mg of silica is added to the homogeneous solution.

Table 3
Reutilization experiments with **PAAS1**–**PAAS3** in the photooxidation of α-terpinene.[a].

	Photosensitizer	Time (h)	**5** (%)[b]
	PAAS1	8.5	90 (10)
1st Reutilization	**PAAS1**	8.5	78 (22)
2nd Reutilization	**PAAS1**	12.5	50 (50)
	PAAS2	7.5	76 (24)
1st Reutilization	**PAAS2**	9.5	67 (34)
2nd Reutilization	**PAAS2**	16	42 (58)
	PAAS3	7.5	86 (14)
1st Reutilization	**PAAS3**	11.5	83 (17)
2nd Reutilization	**PAAS3**	11.5	85 (15)

[a] Photosensitizer/α-terpinene ratio: 1/5000.
[b] Isolated yield of **5**. In parenthesis, the amount of formed *p*-cymene (**6**). Determined by ^{1}H NMR of the reaction mixture after filtration the catalyst and solvent removal taking into account that 5% of *p*-cymene exist in the initial reagent.

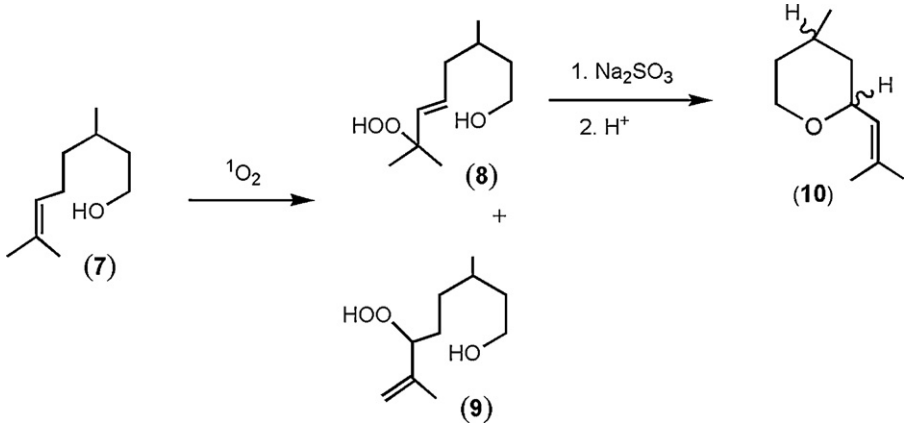
dation product is increased. Among the photosensitizers we do not observe a clear relationship between the length of the spacer (**PAAS1**–**PAAS3**) and the activity of the photocatalysts as observed for Merrifield based photosensitizers [6a]. Even with the longer spacer chain, silica deactivating effects are operating. The photosensitizer with the C3 chain spacer presents very similar activity to photosensitizers with C6 or C12 chain spacers. Another observation is that changing to a smaller silica particle size originates photosensitizers (**PAAS4**, **PAAS5**) with lower activities possibly because a more efficient quenching effect occurs, due to the relative surface increase of silica [10c].

The ability of the different supported catalysts in reusing experiments was attempted in the photooxidation of terpinene, photosensitizers were separated by filtration and tried in a new reaction (Table 3). For all the **PAAS1** and **PAAS2** time for reaction completion increases from first to second reutilization which indicate a progressive deactivation of the catalyst. Also the amount of *p*-cymene (not derived from singlet oxygen oxidation) gradually increases. Photosensitizer **PAAS3** which was the most active show to be the most resistant structure to reutilization as showed by the small increase of reaction time but maintaining the selectivity for ascaridole (**5**).

The photooxidation of citronellol (**7**) originates 2 regioisomeric hidroperoxydes (**8** and **9**) resulting from the ene reaction [6b] (Scheme 2). Compound **8** can be reduced to the corresponding alcohol and by acid-mediated cyclization furnishes a diastereomeric mixture of rose oxide (**10**), which is a valuable compound in perfumery [21]. It is also possible that by using acid treatment compound **9** can be transformed to **10** [22].

Regioisomer **8** is the preferable compound for large scale process for rose oxide production [23] therefore it would be very useful if a process could originate some preference for this isomer. In the case of the ene reaction of allylic alcohols, hydrogen bonds in the substrate are determinant for the regio- and diastereoselectivity [24]. In the case of citronellol photooxidation, examples in the literature show that with different reaction conditions **8** or **9** can predominate or be produced in near equal amounts [6b,11,23,25]. Our expectation was that hydroxyl groups of the silica surface could establish hydrogen interactions with **7** and influence the regioselectivity of the products. The results of the photooxidation of citronellol with silica supported photosensitizers **PAAS1**–**PAAS5** are shown in Table 4.

From Table 4 we can observe that supported photocatalysts originate a high level of conversion of citronellol into hydroperoxides **8** and **9**. From the isolated products, **9** was found to have predomi-

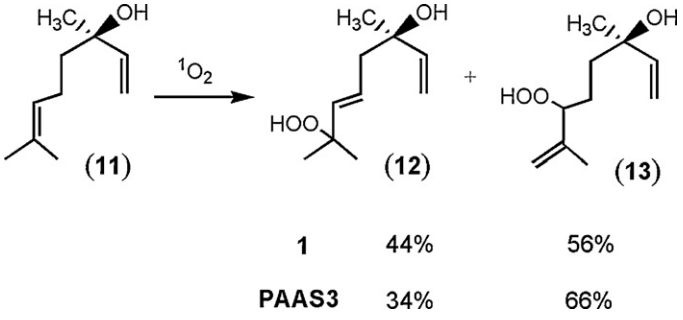


Scheme 2. Products from the singlet oxygen oxidation of citronellol (**7**) and reactions to originate rose oxide (**10**).

Table 4
Results for the photooxidation of citronellol using porphyrin **1** or **PAAS1**–**PAAS5** as sensitizers.

Entry	Photosensitizer	$R = n_{ph}/n_{terp}$[a]	Time (h)	Isolated yield (%)	**8**/**9** (%)[b]
1	**1**	1/600	1.5	99	49/51
2	**1**	1/5000	4	97	48/52
3	**1**	1/5000[c]	5	99	53/47
4	**PAAS1**	1/600	9	95	47/53
5	**PAAS1**	1/5000	45	99	34/66
6	**PAAS2**	1/5000	59	99	36/64
7	**PAAS3**	1/600	28	99	44/56
8	**PAAS3**	1/5000	44	99	35/65
9	**PAAS3**	1/5000[c]	47	99	45/55
10	**PAAS4**	1/5000	47	98	40/60
11	**PAAS5**	1/5000	71	99	39/61

[a] Photosensitizer/α-terpinene ratio.
[b] % of **8** and **9** in reaction mixture by ^{1}H NMR after filtration the catalyst and solvent removal.
[c] CCl_4 was the reaction solvent.



Scheme 3. Relative yields of products from the singlet oxygen oxidation of linalool (**11**) using porphyrin **1** and **PAAS3** as sensitizers.

nance over the regioisomer **8**, depending on the reaction conditions. In solution with porphyrin **1** (entries 1 and 2) a slight excess of **9** over **8** is observed, in agreement with the expected regioselectivity for a trisubstituted double bond [26], but unlike other systems where **8** is the predominant isomer [23,25a,c]. Changing the reaction solvent to carbon tetrachloride (entry 3) increases the amount regioisomer **8** as the major product, as observed by others [25a]. Supported photosensitizers, however, show a preference for regioisomer **9** which is evident in the 1/5000 ratio (entries 5, 6, 8–11). The preference for **9** was already observed in polystyrene supported photosensitizer photooxidation systems [11,25d], but in the case of our silica supported photosensitizers this preference is more obvious. Again, changing the solvent for carbon tetrachloride originates an increase of the regioisomer **8** relatively to the reaction carried out in chloroform (compare entries 8 and 9). The reason for this increment may possibly be related to the primary hydroxyl group on citronellol which may help to fix this substrate to the silica surface and somehow favor regioselectivity for product **9**. The effect of the hydroxyl group on the regioselectivity with this kind of supported photosensitizers is also observed in the case of linalool (**11**). The photooxidation of **11** with the silica supported photosensitizer **PAAS3** favors the formation of the hydroperoxide **13** relatively to the photooxidation with the free photosensitizer **1** (Scheme 3).

4. Conclusion

We have achieved the synthesis of heterogeneous silica supported photooxidation catalysts by chlorosulphonation of porphyrins and reaction with aminomodified silica supports. The photooxidation of α-terpinene (**4**) with these heterogeneous catalysts gives the [4+2] cyclic product ascaridole with high yields but reaction times are much longer than using the non-supported porphyrin **1**. Photooxidation of citronellol (**7**) with supported catalysts also gives high yields of products derived from the ene reaction and shows a preference for regioisomer **9** which is substantially different from the photooxidation with homogeneous catalysts which favor regioisomer **8**.

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