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Supported photosensitizers for the visible light activation of phenols towards oxygen

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Abstract

To circumvent the drawbacks of the homogeneous photosensitization, a series of photosensitizing molecules, mainly porphyrins and phthalocyanines, were supported on aminopropyl silica and/or exchange resins. Their grafting ratios were evaluated and their efficiencies were assayed on the ability to photo-oxidize phenol under $900 \, W/m^2$ visible light. A comparison was done by determining the time necessary to obtain 50% consumption of the substrate. Under these conditions, the meso tetra(4-sulfonatophenyl)porphine displayed the best photocatalytic effect.

1. Introduction

Mechanistic and synthetic studies of photosensitized reactions often encounter difficulties as a result of the insolubility of the photosensitizer. The later, noticeably phthalocyanines in this work, may form dimers or higher aggregates of reduced efficiency [1,2]. It is also necessary to remove the photosensitizer after reaction.

By anchoring the photosensitizer to an insoluble support, one can solve the problem of separation and suppress aggregation. This idea was first proposed by Kautsky [3] and then by Merrifield [4]. Then several ways were investigated to prepare supported molecules.

Immobilization was obtained by adsorption on a solid inorganic support such as silica gel [5,6], alumina, celite, cellulose or more recently Nafion [7]. In solution, if the loading is low, the molecule remains bound to the solid support [6].

Charged molecules can form complexes with the appropriate ion-exchange resin. Rose Bengal, eosin, methylene blue, $Ru(bpy)_3^{2+}$ were attached to acidic cation exchange resins [8]. Recently, several metallated tetrasulfonato phthalocyanines were linked to the basic Amberlite IRA 400 resin [9,10] and phthalocyanines substituted with carboxyl groups were attached to Amberlite IRA 93 [11]. Neutral supports are also involved via chemical reaction with functionalized polymers. Thus Rose Bengal, attached to a chloromethylated styrene–divinylbenzene copolymer [12] was commercialized (sensitox). Metallated porphyrins or phthalocyanines

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were linked to polyacrylonitrile [13]. Several heterogeneous photosensitizers were used immobilized in polyvinyl chloride films, sepharose gel or cellulose acetate [14]. Zinc tetraphenylporphyrine was incorporated into commercially available cellulose acetate hollow fibre membranes. Hematoporphyrin has been included in a polyepoxy resin of the araldite type [15]. Molecules can be chemically bonded to silica previously modified with a sufficiently reactive group which is used in the next step for covalent binding. The amino group is often used for this purpose [16–22]. One can also prepare a silane derivative of the sensitizer which can react with the silica surface to yield the silica bound photocatalyst. The first method is easiest because aminopropyl silica is commercially available. Dicyanoanthracene derivatives were grafted to naked silica [23,24] while metallated phthalocyanines (Fe, Co, Ni) were grafted to aminopropyl silica [25–27].

The aim of the present work was to synthesize oxidative photosensitizers bound to solid supports in order to gain advantages for their separation and efficiency and to observe the consequences on the absorption spectra of the insoluble photosensitizers. Because numerous combinations exist between chromophores, supports and grafting ratios, we selected the phenol photodegradation as a model reaction to compare the photo-oxidative ability of the selected molecules, to well define the better grafting ratio and to explore the possible role of the types of supports.

2. Materials and methods

2.1. General methods

The UV spectra in solvent were recorded using a Cary 50 spectrometer with CH_3CN or THF as solvents. The diffuse reflectance (DRUV) spectra of the solid supported sensitizers were recorded using a Cary 500 spectrometer fitted with a "prying mantice" accessory. Gas chromatography (GC) analyses were performed on a GC 8000 Fisons Instruments chromatograph fitted with a flame ionization detector. A 6 ft × 1/8 in. stainless column packed with 10% OV-101 silicon on chromosorb W-Hp was used with helium as a carrier gas. The chromatograph was coupled with a Spectra Physics data jet integrator. The HPLC separations were performed on a Gilson instrument using $CH_3CN–H_2O$ 1:1 (vol.%) as a mobile phase with a 0.8 ml/min flow rate and a UV detector at 280 nm. The column was a RP 18 Merck, the dimensions of which were 250 mm in length and 4.5 mm external diameter. The CHNS analyses were performed on a Thermo-Finnigan Flash EA 1112 analyzer.

2.2. Materials

Acetonitrile (SDS), tetrahydrofuran (SDS) were dried over 4 Å molecular sieves before use. Chloro-2,4,6-trinitrobenzene (gift of S.N.P.E. (France)), 2,4,6-trinitrobenzoic acid (Kodak), phenol (Fluka), tetradecane

(Fluka), zinc phthalocyanine (Fluka), chloro aluminum phthalocyanine (Aldrich), hydroxy aluminum phthalocyanine (Aldrich), sodium meso tetra(4-sulphonatophenyl) porphine (Strem line Chemicals), Dowex 1, Amberlite XAD 8, IRA 96 resins (Fluka) were of commercial origin. The resins were used after washing with water, THF and drying. Aminopropyl silica (Macherey-Nagel – Polygoprep 60-20 NH_2) and silica (Merck 70-230) were dried overnight at 65 °C before use. Tetra(chlorosulphonato) zinc phthalocyanine and tetra(chlorosulphonato) aluminum phthalocyanine were synthesized.

2.3. Photochemical device

The light source was a 150 W tungsten-halogen lamp (Philips type 7158 XHP) housed in a Novamat 130 AF projector. A water filter (Oriel 6117) with 5 cm optical path length was used to stop infrared radiations. A 45° polychromatic reflector (Oriel 66245) was added to irradiate normally to the surface of the heterogeneous solution in a 30 ml Pyrex flask, fitted with a magnetic stirrer.

2.4. Determination of the grafting ratio by C analysis

For the supported photosensitizers adsorbed onto silica, the %C leads directly to the %grafting. With aminopropyl silica it was expressed in mole per 100 g as

$$G = \frac{100(x - y)}{M(y - z)}$$

where M is the molecular weight of the sensitizing molecule $(g\,M^{-1})$, x the %C of aminopropyl silica, y the %C of silica bound photosensitizer, and z the %C of the sensitizing molecule.

2.5. Determination of the bleaching ratio of the supported sensitizers

Diffuse reflectance spectroscopy (DRUV) was used to determine the decrease of chromophore concentration upon irradiation. This was done using the Kubelka-Munk remission function [28]. As in a previous work [29], DRUV spectroscopy aimed to measure the loading of organic chromophores on a solid support. For each sample, several measurements of the reflectance were recorded relative to the naked supports which are non-absorbing in the investigated spectral range. A mean value was used in order to take into account the problems arising from the nonhomogeneity of the surface.

2.6. Method of immobilization

The dye was adsorbed on silica and/or XAD-8 resin (Fluka). Macrocyclic molecules can be adsorbed on these supports without further desorption when suspended in CH_3CN if loading is below 10^{-5} M/100 g silica.

2.6.1. Method starting from silica or aminopropyl silica

In a typical experiment 3 g of silica or aminopropyl silica in suspension in 30 ml CH_3CN or THF was stirred for 3 days in order to wash the silica. The solvent was removed and the support was dried under vacuum at room temperature. The photosensitizer (3×10^{-6} M) was dissolved in 100 ml THF and the absorbance of the solution was measured at the maximum of the Q band near 670 nm for the phthalocyanines or the Soret band near 415 nm for the porphyrins. The solution was mixed with 3 g of silica and was stirred for 7 days. After adjustment to 100 ml the absorbance was measured. The differences in absorbance led to the concentration of the photosensitizer on to 3 g of the support. The solid sensitizer was then filtered and dried under vacuum. We checked the stability of the dye on the support by suspension of an aliquot part in CH_3CN. All the supported photosensitizers were stored in the dark.

2.6.2. Method starting from exchange resins

In a typical experiment, the resin was repeatedly washed with water and then THF. The dried resin (3 g) was immersed under stirring in 100 ml of a THF solution of the photosensitizer for 3 days. Various solutions of different concentrations were used in order to obtain different ratio for fixation on the resin. This was measured using the Beer Lambert relationship at 670 or 415 nm of the solutions as for silica support. The final treatment was the same as for silica support.

2.7. Synthesis of tetra(chlorosulphonato) zinc phthalocyanine

In a flask fitted with a condenser, zinc phthalocyanine (300 mg, 0.519 mmol) was added slowly, at $-18\,^\circ$C, in 5 ml chlorosulfonic acid under stirring. The brown liquid was heated to 78–80 $^\circ$C for 15 min, then diluted in 50 ml acetone at $-18\,^\circ$C (caution). After cooling the deep green solution is again diluted in CH_2Cl_2 until a dark solid separate. The suspension was cooled and the solid was filtered and washed with CH_2Cl_2 and acetone until the washing layer was colorless. The green residue was dried under vacuum and led to 345 mg of crude product. Purified sample was obtained by solvation-precipitation in THF–pentane 50:50 (vol.%). UV–vis (THF) (λ (nm), ε (l mol^{-1} cm^{-1})): 668 (3.1×10^5), 336 (5.1×10^4). IR (KBr, cm^{-1}): 1612, 1518, 1471, 1429, 1333, 1250, 1121, 1079, 1040, 758, 739, 723, 574, 529.

Anal. Calc. for $C_{32}H_{12}N_8O_8S_4Cl_4Zn$: C, 39.54; H, 1.24; N, 11.53; S, 13.20; Cl, 14.74. Found: C, 39.85; H, 1.11; N, 11.37; S, 12.97; Cl, 13.86%.

2.8. Synthesis of tetra(chlorosulphonato) aluminum phthalocyanine

In a flask fitted with a condenser, chloroaluminum phthalocyanine (300 mg, 0.522 mmol) was added slowly, at $-18\,^\circ$C, in 5 ml chlorosulfonic acid under stirring. The brown liquid was heated to 30 $^\circ$C for 15 min, then diluted in 50 ml acetone at $-18\,^\circ$C (caution). After cooling the deep green solution is again diluted in CH_2Cl_2 until a dark solid separate. The suspension was cooled and the solid was filtered and washed with CH_2Cl_2 and acetone until the washing layer was colorless. The green residue was dried under vacuum and led to 380 mg of crude product. Purified sample was obtained by solvation-precipitation in THF–pentane 50:50 (vol.%). UV–vis (THF) (λ (nm), ε (l mol$_{-1}$ cm$_{-1}$)): 670 (1.6×10^5), 638, 606, 336 (5.1×10^4). IR (KBr) (cm^{-1}): 1609, 1501, 1469, 1424, 1334, 1291, 1216 (broad), 1167, 1119, 1064, 903, 880, 763, 734, 591. Anal. Calc. for: $C_{32}H_{12}N_8O_8S_4Cl_5Al$: C, 39.54; H, 1.24; N, 11.53; S, 13.20; Cl, 18.29. Found: C, 38.68; H, 1.26; N, 10.80, S, 13.76; Cl, 18.67%.

2.9. Photochemical oxidation of phenols – general procedure

The supported photosensitizer (150 mg) was suspended in 20 ml of a 5×10^{-4} M phenolic solution in CH_3CN or in H_2O. The solid was maintained in suspension for all the assays using a magnetic stirrer. Oxygen bubbling was maintained for 0.5 h, then the medium was irradiated downward with a parallel beam of visible light (900 W/m^2). In CH_3CN, 2 µl tetradecane were added as an internal standard and the disappearance of the phenol was measured at fixed times by direct GC analysis. In H_2O the decrease in phenol concentration was obtained from the value of the absorbance at 269 nm.

3. Discussion and results

3.1. Grafting ratios

The grafting ratio was measured by elemental analysis and/or absorbance measurement. The results are gathered in Table 1. Qualitative experiments led to the observation that the ability of the supported reactant to play its photosensitizing role needs a grafting ratio upper than 10^{-6} M/100 g (results not shown).

3.2. Efficiencies of the supported photosensitizers for the visible light oxidation of phenols

We chose phenol as a simple pollutant model. The photooxidative properties of the immobilized macrocycles and nitroaromatic compounds were investigated in the same conditions (see experimental procedures). First we checked that phenol was not oxidized with light without photocatalyst. When the support used was able to complex phenol (IRA 67, IRA 96, Amberlite 200, Amberlite XAD 8, Dowex 1) the catalyst was saturated with phenol until constant concentration in solution before light irradiation. To compare the efficiencies of the solid photocatalysts, we determined the time necessary to obtain 50% consumption of phenol in the experimental flask (20 ml; 10^{-4} M phenol; light intensity: 900 W/m^2). The results are gathered in Fig. 1 as histograms.

Table 1
Grafting ratios of the photosensitizers on the supports: M/100 g support

Compound	Support	%Grafting ($\times 10^4$)
AlPcCl	SiNH2	0.18
AlPcCl	SiO2	0.09
AlPcOH	SiO2	0.43
AlPcOH	SiNH2	0.8
AlPcSO2Cl	SiNH2	0.49
Astra Blue	XAD-8	1.42
Chlorophyllin	SiNH2	0.20
CuPcSO2Cl	SiNH2	1.35
Methylene blue	IRC 50	2.08
Porph IX	SiNH2	0.08
PorphSO3H	Dowex 1	1.0
PorphSO3H	IRA 67	1.62
PorphSO3H	IRA 96	1.62
PorphSO3H	SiNH2	0.18
PorphSO3H	XAD-8	0.95
SiPcSO2Cl	SiNH2	0.09
TNB-Cl	IRA 96	6.7
TNB-Cl	SiNH2	6.7
TNB-COOH	Dowex 1	6.15
TNB-COOH	IRA 96	6.15
TNB-COOH	SiNH2	6.15
VB-BO	Amb 200	2.59
ZnPcSO2Cl	SiNH2	0.51

Clearly some photocatalysts were inefficient namely: propyl Astra blue, chlorophyllin, tetra(chlorosulfonato) silicon phthalocyanine, Victoria Blue BO. The meso tetra(4-sulphonatophenyl) porphyrin grafted on to aminopropyl sil-

ica or on Dowex 1 was the best one while it was inefficient on the XAD-8 support and exhibited a medium activity on the other supports (IRA 67 and IRA 96). The phthalocyanines AlPcCl and AlPcOH led to good degradation rates but are not so efficient as sulfonated sensitizers in case of long time use because of a greater bleaching ratio. The activity of the phthalocyanines and porphyrins was of the same order than that of the trinitrobenzoic compounds that we early used [30]. Conversely, porphyrines and phthalocyanines bound to modified silica or exchange resins behave as homogeneous compounds and no evidence for aggregation was seen in the DRUV spectra. Thus they are potentially better photocatalysts than monomeric photosensitizers by preventing molecular interaction. Moreover, in general, a covalently bound porphyrin exhibits an enhanced triplet lifetime in comparison with the monomeric photosensitizer [31].

3.3. Bleaching ratios of the supported photosensitizers for the visible light oxidation of phenols

The bleaching ratio was evaluated by DRUV spectroscopy after 7 h irradiation which corresponds to the longest time involved in the assays (Table 2).

As a rule, chlorosulfonated and sulfonated porphyrins or phthalocyanines displayed the better stability under light excitation. This probably originates from a stable binding between the amino group of aminopropylsilica or anionic resins and the sulfonic acid function.
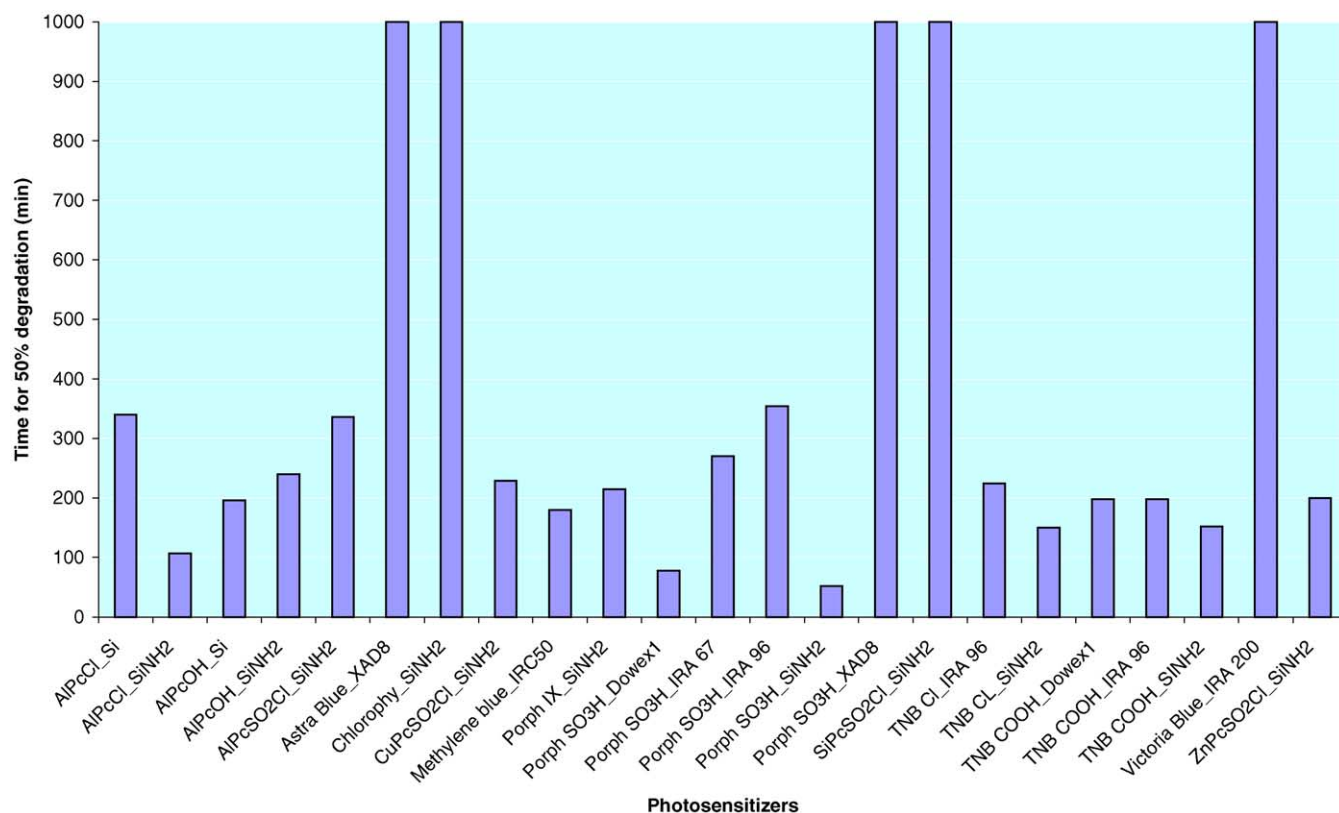

Fig. 1. Comparison of the efficiencies of the immobilized photosensitizers: irradiation time (min) corresponding to 50% phenol degradation; 20 ml, 5×10^{-4} M in CH_3CN; visible light; 900 W/m^2; parallel beam diameter 2 in.

Table 2
Bleaching ratios of the immobilized photosensitizers after 7 h irradiation

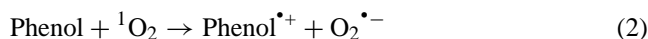| Compound	Support	%Bleaching
AlPcCl	SiNH$_2$	68.3
AlPcCl	SiO$_2$	91.8
AlPcOH	SiO$_2$	85.1
AlPcOH	SiNH$_2$	81.0
AlPcSO$_2$Cl	SiNH$_2$	6.53
Astra Blue	XAD-8	93.5
Chlorophyllin	SiNH$_2$	82.1
CuPcSO$_2$Cl	SiNH$_2$	35.3
Methylene blue	IRC 50	41.4
Porph IX	SiNH$_2$	53.3
PorphSO$_3$H	Dowex 1	19.1
PorphSO$_3$H	IRA 67	20.3
PorphSO$_3$H	IRA 96	25.8
PorphSO$_3$H	SiNH$_2$	72.2
PorphSO$_3$H	XAD-8	76.0
SiPcSO$_2$Cl	SiNH$_2$	18.6
TNB-Cl	IRA 96	22.8
TNB-Cl	SiNH$_2$	98.5
TNB-COOH	Dowex 1	25.7
TNB-COOH	IRA 96	75.4
TNB-COOH	SiNH$_2$	92.5
VB-BO	Amb 200	72.8
ZnPcSO$_2$Cl	SiNH$_2$	25.4

4. Oxidative mechanism

Phthalocyanines and porphyrins have already been described as good oxidizing photosensitizers [32-40] displaying

better properties than classical oxidants such as rose Bengal or methylene blue. Their triplet excited state interacts with $^3O_2$ the solubility of which is 9.1×10^{-3} M in CH$_3$CN and 1.39×10^{-3} M in H$_2$O under 1 atm [41]. Energy transfer generates $^1O_2$ able to oxidize a substrate following a so-called type 2 mechanism.

It was proposed that phenols form exciplexes with $^1O_2$ [42] but as exciplexes dissociate in polar solvents, we discarded this possibility.

The lifetime of $^1O_2$ is 62 µs in CH$_3$CN and 3 µs in H$_2$O [43]. If $^1O_2$ adds on unsaturated bonds or dienes, it does not easily lead to the same reaction with aromatics. Nevertheless, under our conditions, with PorphSO$_3$H_IRA67 as a sensitizer, the addition of histidine, a $^1O_2$ quencher, decreases the rate of the reaction. This result may imply that $^1O_2$ is an oxidizing source in this reaction (Fig. 2).

Photoexcited phthalocyanines and porphyrins may be electron donors or electron acceptors. Depending on the sensitizer, an alternative way could be the $O_2^{\bullet-}$ formation by electron transfer from the photosensitizer to $^3O_2$ (if the excited sensitizer can act as an electron donor (Eq. (1)) or from phenol to $^1O_2$ (Eq. (2)):

$$^3\text{Photosens}^* + {}^3O_2 \rightarrow \text{Photosens}^{\bullet+} + O_2^{\bullet-} \tag{1}$$

$$\text{Phenol} + {}^1O_2 \rightarrow \text{Phenol}^{\bullet+} + O_2^{\bullet-} \tag{2}$$

If the sensitizer acts as an electron acceptor, an electron transfer from phenol may also be assumed (Eq. (3)), followed by
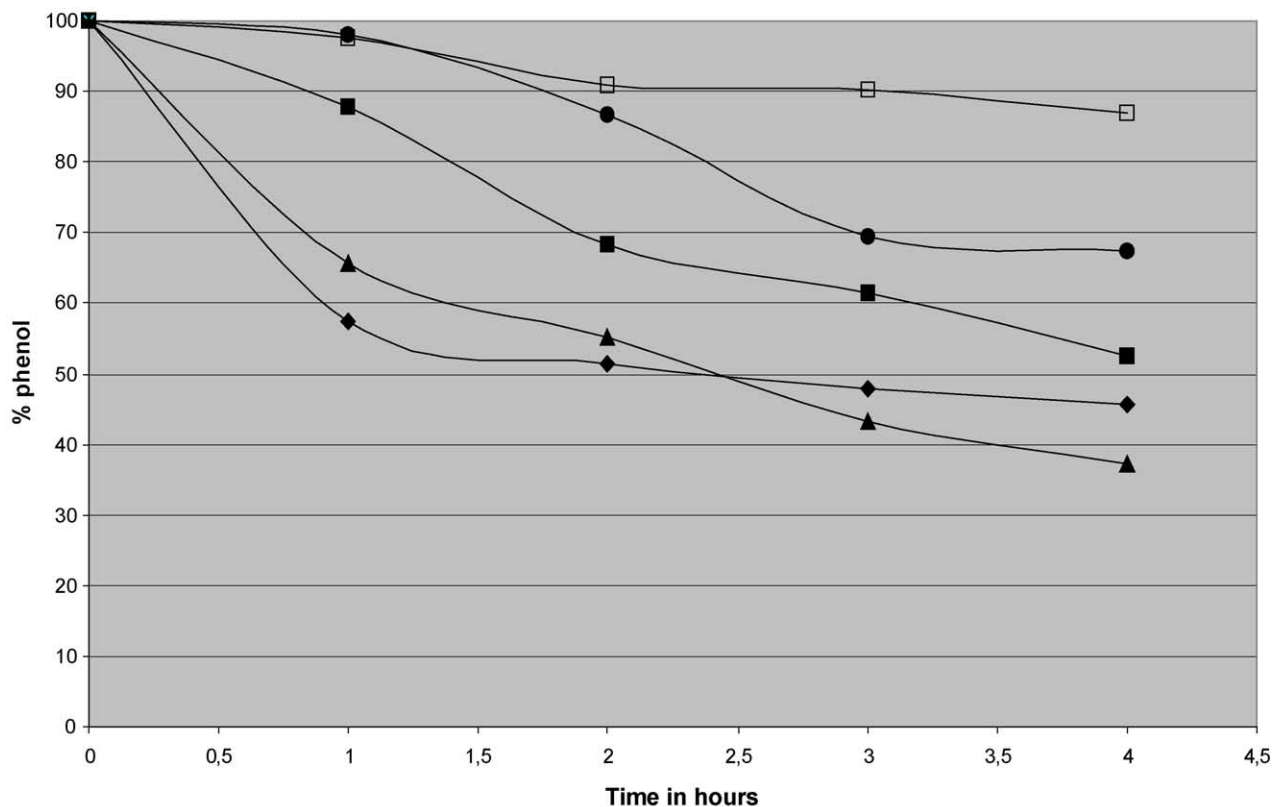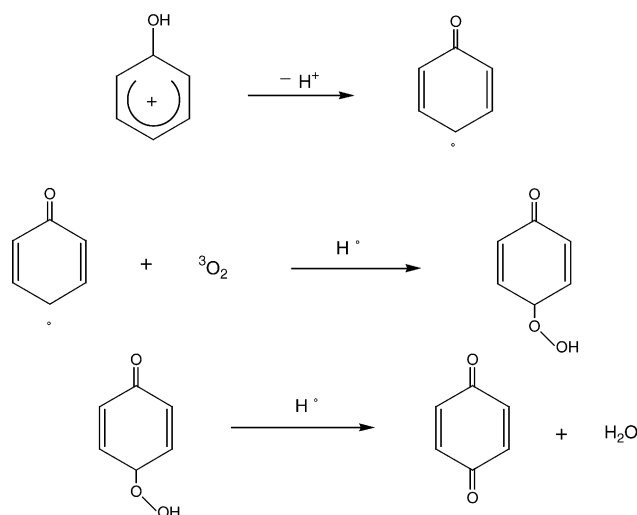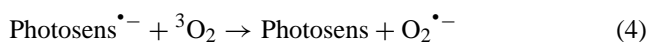

Fig. 2. Comparison of the phenol disappearance rate in presence of additives (2.5×10^{-4} M): (■) none; (●) histidine; (♦) H$_2$O$_2$; (□) NaHSO$_3$; (▲) K$_2$S$_2$O$_8$. PorphSO3H/IRA 67 photosensitizer: 5×10^{-4} M in 20 ml H$_2$O; visible light; 900 W/m^2; parallel beam diameter 2 in.

Scheme 1.

the possible formation of superoxide anion (Eq. (4)):

$$^3\text{Photosens}^* + \text{Phenol} \rightarrow \text{Photosens}^{\bullet-} + \text{Phenol}^{\bullet+} \qquad (3)$$

$$\text{Photosens}^{\bullet-} + {}^3\text{O}_2 \rightarrow \text{Photosens} + \text{O}_2^{\bullet-} \qquad (4)$$

Thus, in polar solvents the phenol radical cation can be formed. It is strongly acidic and readily deprotonates leading to a radical which is the source of the 1,4-benzoquinone as the first oxidation product (Scheme 1). This could be evidenced by UV spectroscopy: the disappearance of the phenol band at 269 nm corresponds to the formation of the benzoquinone band at 240 nm with an isobestic point at 262 nm (result not shown).

The reactivity of $\text{O}_2^{\bullet-}$ is well known [44]. The pK_a of $\text{O}_2^{\bullet-}$ in aprotic medium was estimated to be 24. This value corresponds to a strong basicity which imply that in CH_3CN the oxygen superoxide is able to deprotonate phenol leading to phenol anion and $\text{HO}_2^{\bullet}$ (Scheme 2).

$\text{HO}_2^{\bullet}$ disproportionates (Eq. (5)) and generates H_2O_2 which is probably one of the possible oxidative species as its addition in the medium increases the photo-oxidation rate (Fig. 2):
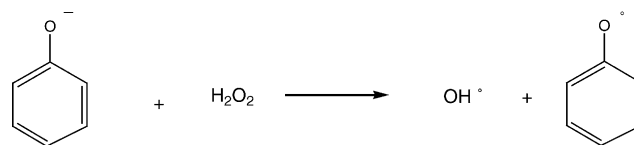
$$2\text{HO}_2^{\bullet} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \qquad (5)$$

An other possible oxidative species is $\text{HO}^{\bullet}$ which could be formed by electron transfer from phenol anion to H_2O_2 leading also to phenol radical (Scheme 3).

In water, an electron donor such as NaHSO_3, added in the medium, competes with the electron donor and decreases
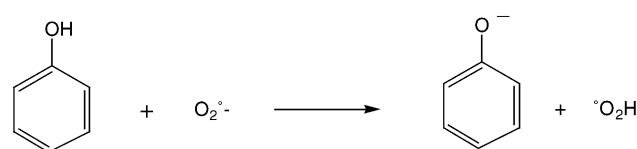
Scheme 2.

Scheme 3.

the oxidation rate. Conversely $\text{K}_2\text{S}_2\text{O}_8$, an electron acceptor, increases it.

In water, $\text{HO}^{\bullet}$ is strongly oxidative. Its reducing potential is 2.07 V at pH 7 and 1.89 V at pH 10. [44].

5. Conclusion

This study confirms that immobilized photosensitizers display several properties which differ from classical soluble photosensitizers. On the whole, the DRUV spectra of the grafted photosensitizer are close to the absorption spectra of the homogeneous ones but, in some cases, bonding to the support inhibits the chromophore, resulting in a loss of the photosensitizing efficiency. Moreover, the amount of the photosensitizer on the support must be kept at a low level, in order to prevent self-quenching or non-accessibility of the substrate.

Finally, the support is an important part of the reagent as outline in the case of the sulphonated porphyrin. It is responsible for the stability of the chromophore, the accessibility of the reagent and the solvent compatibility of the system.

References

[1] O. Valdesaguilera, D.C. Neckers, Acc. Chem. Res. 22 (1989) 171.
[2] D. Xu, D.C. Neckers, J. Photochem. Photobiol. A: Chem. 40 (1987) 361.
[3] H. Kautsky, Trans. Faraday Soc. 35 (1939) 216.
[4] R.B. Merrifield, J. Am. Chem. Soc. 85 (1963) 2149.
[5] R. Nilson, D.R. Kearns, Photochem. Photobiol. 19 (1974) 181.
[6] J. Prekumar, R. Ramaraj, J. Photochem. Photobiol. A: Chem. 110 (1998) 53.
[7] H. Kautsky, Trans. Faraday Soc. 35 (1939) 3795.
[8] J. Mosinger, K. Losinska, T. Abrhamova, S. Veiserova, Z. Micka, I. Nemcova, B. Mosinger, Anal. Lett. 33 (2000) 1091.
[9] S.L. Buell, J.N. Demas, J. Phys. Chem. 87 (1983) 4675.
[10] R. Gerdes, O. Bartels, G. Schneider, D. Wöhrle, G. Schulz-Ekloff, Polym. Adv. Technol. 12 (2001) 152.
[11] O. Bartels, D. Worhle, R. Gerdes, G. Schneider, G. Schulz-Ekloff, J. Inform. Record. 25 (2000) 251.
[12] J. Paczkowski, D.C. Neckers, Macromolecules 18 (1985) 1245.
[13] S.N. Gupta, L. Thijs, D.C. Neckers, Macromolecules 13 (1980) 1037.
[14] D. Faust, K.H. Funken, G. Horneck, B. Milow, J. Ortner, M. Sattleger, M. Schäfer, C. Schmitz, Solar Energy 65 (1999) 71.
[15] A.P. Schaap, A.L. Thayer, E.C. Blossey, D.C. Neckers, J. Am. Chem. Soc. 97 (1975) 3741.
[16] E. Krogh, P. Wan, Top. Curr. Chem. 156 (1990) 93.
[17] L. Nondek, J. Malek, J. Chromatogr. 155 (1978) 187.
[18] C.H. Lochmüller, R.R. Ryall, C.W. Amoss, J. Chromatogr. 178 (1979) 298.

[19] W.E. Hammers, A.G.M. Theenwes, W.K. Brederode, C.L. de Ligny, J. Chromatogr. 243 (1982) 321.

[20] L. Nondek, R. Ponec, J. Chromatogr. 294 (1984) 2434.

[21] M. Verzele, N. Van de Velde, Chromatographia 20 (1985) 239.

[22] C.H. Lochmüller, C.W. Amoss, J. Chromatogr. 108 (1975) 85.

[23] N. Soggiu, H. Cardy, J.L. Habib Jiwan, I. Leray, J.Ph. Soumillion, S. Lacombe, J. Photochem. Photobiol. A: Chem. 124 (1999) 1.

[24] S. Lacombe, H. Cardy, M. Simon, A. Khoukh, J.Ph. Soumillion, M. Ayadim, Photochem. Photobiol. Sci. 1 (2002) 347.

[25] S. Tamagaki, E. Liesner, D.C. Neckers, J. Org. Chem. 45 (1980) 1573.

[26] H. Fischer, G. Schulz-Ekloff, D. Worhle, Chem. Eng. Technol. 20 (1997) 624.

[27] M. Mifune, M. Onoda, T. Takatsuki, T. Kanai, A. Iwado, N. Motohashi, J. Haginaka, Y. Saito, Chem. Pharm. Bull. 47 (1999) 346.

[28] A.A. Christy, O.M. Kvalheim, R.A. Velapoldi, Vib. Spectrosc. 9 (1995) 19, and references cited.

[29] S. Lacombe, H. Cardy, N. Soggiu, S. Blanc, J.L. Habib-Jiwan, J.P. Soumillion, Micropor. Mesopor. Mater. 46 (2001) 311.

[30] M. Julliard, C. Legris, M. Chanon, J. Photochem. Photobiol. A: Chem. 61 (1991) 137.

[31] A.A. Gorman, I.R. Gould, I. Hamblett, M.C. Standen, J. Am. Chem. Soc. 106 (1984) 6956.

[32] S. Mangematin, A.B. Sorokin, J. Porphyrins Phthalocyanines 5 (2001) 674.

[33] G. Schneider, D. Wöhrle, W. Schulz-Ekloff, Photochem. Photobiol. 60 (1994) 33.

[34] W. Spiller, D. Wöhrle, G. Schulz-Ekloff, W.T. Ford, G. Schneider, J. Stark, J. Photochem. Photobiol. A: Chem. 95 (1996) 161.

[35] M. Ronge, R.V. Bensasson, E.J. Land, R. Pariente, Photochem. Photobiol. 47 (1988) 485.

[36] J.R. Wagner, H. Ali, P. Langlois, N. Brasseur, J.E. Van Lier, Photochem. Photobiol. 45 (1987) 587.

[37] T.P.A. Devasagayam, A.R. Sundquist, P.D. Maskio, S. Kaiser, H. Sies, J. Photochem. Photobiol. B: Biol. 9 (1991) 105.

[38] X.F. Zhang, H.-J. Xu, J. Photochem. Photobiol. B: Biol. 24 (1994) 109.

[39] R. Langlois, H. Ali, N. Brasseur, J.R. Wagner, J.E. Van Lier, Photochem. Photobiol. 44 (1986) 117.

[40] G. Ferraudi, G.A. Argüello, H. Ali, J.E. Van Lier, Photochem. Photobiol. 47 (1988) 657.

[41] S.L. Murov, I. Carmichael, G.L. Hug (Eds.), Handbook of Photochemistry, 2nd ed., Marcel Dekker, New York, 1993, p. 289.

[42] J.-L. Ravanat, M. Berger, J. Benard, R. Langlois, R. Ouellet, J.E. Van Lier, J. Cadet, Photochem. Photobiol. 55 (1992) 809.

[43] C.S. Foote, E.L. Clennan, in: C.S. Foote, J.S. Valentine, R. Greenberg, J.L. Liebman (Eds.), Active Oxygen in Chemistry, Blackie, London, 1995, p. 106.

[44] B.H.J. Bielski, Photochem. Photobiol. 28 (1978) 645.