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Synthesis and photobiocidal properties of cationic porphyrin-grafted paper

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ABSTRACT

We report on the synthesis of cellulose paper bearing a cationic porphyrin, designed for antimicrobial applications. Tricationic porphyrin has been covalently grafted on paper, without previous chemical modification of the cellulosic support, using 1,3,5-triazine derivative as linker. The obtained porphyrin-grafted paper was characterized by infrared (ATR-FTIR), UV–visible and diffuse reflectance UV–vis (DRUV) spectroscopies to confirm the triazine linkage. Thermogravimetric analysis (TGA) was used to investigate thermal properties of grafted paper. Antimicrobial activity of porphyrin–cellulose material was tested under visible light irradiation against *Staphylococcus aureus* and *Escherichia coli*. The two bacterial strains deposited on the resulting photosensitizing filter paper are efficiently killed after illumination.

1. Introduction

Microbial contamination is of great concern in a variety of areas including medical devices, healthcare products, water purification systems, hospitals, dental office equipment, food packaging, food storage, household sanitation, etc. In the last years, major interest has grown in the preparation of materials endowed with antibacterial properties for use in a wide range of fields such as food packaging and transportation, housekeeping, and handling of medical and military items (El-Khouly et al., 2010; Hasmen, Ibrahim, El-Sayed, EL-Husseiny, & El-Enany, 2009; Hou, Zhou, & Wang, 2009; Hsu & Klibanov, 2011; Kenawy, Worley, & Broughton, 2007; Kenawy, 2001; Ngo, Li, Simon, & Garnier, 2011; Tankhiwale & Bajpai, 2009). The need for a control of potentially pathogenic microorganisms in exposed environments has led to the development of antibacterial products.

Antimicrobial surfaces have been obtained by incorporating active agents, currently under study or commercially available, among which can be mentioned quaternary ammonium salts (Lee et al., 2004), N-halamines (Ren, Kocer, Worley, Broughton, & Huang, 2009), guanidine polymers (Kawabata & Taylor, 2007), antibiotics (Cassano et al., 2009), or Ag/TiO_2 nanoparticles (Dastjerdi & Montazer, 2010). However, these agents are not entirely satisfactory because material can loose antibacterial properties in noncovalent systems, release of environmentally hazardous agents, obligation on direct contact between antimicrobial molecules and microorganism, and emergence of antimicrobial resistance.

Our strategy was to develop a new cellulosic material bearing a covalent linker between polymeric surface and new antimicrobial molecules. Indeed, cellulose is an excellent starting material for developing a more sustainable material from renewable resources. So, paper has a visible market-share in hygiene products or in packaging materials. The degradable nature of filter paper makes it an attractive alternative for these uses. Concerning the type of new antimicrobial agents, photosensitizers (PS) such as porphyrins have been intensively studied for their photobactericidal effects in Photodynamic Antimicrobial ChemoTherapy (PACT) (Hamblin & Hassan, 2004; Jori & Spikes, 1984; Nitzan, Balzam-Sudakevitz, & Ashkenazi, 1998; Wainwright, 1998). This treatment involves the use of photosensitive compound which is activated by exposure to visible light (MacDonald & Dougherty, 2001). Although the cellular mechanism of the photodynamic process is not yet fully understood, it is presently admitted that phototoxic effects rely primarily on the formation of singlet oxygen ($^1O_2$) after illumination (DeRosa & Crutchley, 2002; Ochsner, 1997). This highly reactive species is able to react with almost every cellular component, bringing irreversible damages that ultimately lead to cell death (Dolmans, Fukumura, & Jain, 2003; Dougherty, 1987; Soukos, Ximenez-Fyvie, Hamblin, Socransky, & Hasan, 1998). Recent works have shown that porphyrins keep their antimicrobial properties when grafted on carbon nanotubes, nylon fabrics, polyvinylidene fluoride, chitosan or cellulose and that these modified polymers

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can be used alone (nanocrystals) or can be cast into photobactericidal membranes or films (Banerjee, Mondal, Martin, & Kane, 2010; Bozja, Sherrill, Michielsen, & Stojiljkovic, 2003; Cahan, Schwartz, Langzam, & Nitzan, 2011; Feese, Sadeghifar, Gracz, Argyropoulos, & Ghiladi, 2011).

In connection with our research program on PACT (Ringot, Sol, Granet, & Krausz, 2009; Ringot et al., 2011; Sol et al., 2004, 1998) we describe in this article the synthesis of a tricationic photosensitizer and its covalent binding to cellulose paper by using a one-pot grafting strategy using 1,3,5-trichloro-1,3,5-triazine (cyanuric chloride), a highly reactive triazine compound. Chemical attachment of the porphyrinic macrocycle to the cellulosic surface was checked by polymer analysis methods (ATR-FITR, DRUV, UV visible spectrophotometry) and the photobiocidal activity of the modified material was tested against *Escherichia coli* and *Staphylococcus aureus*.

2. Experiments

2.1. Materials

All solvents and reagents were purchased from Aldrich, ACROS or SDS. Pyrrole and dimethylformamide were distilled over CaH_2 under reduced pressure immediately before use. Methylene chloride and chloroform were distilled over P_2O_5, and then over CaH_2. Analytical thin-layer chromatography (TLC) was performed on silica gel (Merck, $60F_{254}$). Merck precoated plates (silica gel 60, 2 mm) were used for preparative thin layer chromatography. Column chromatography was carried out with silica gel (60 ACC, 15–40 μm, Merck). Whatman filter paper (grade 1, 3.5 cm × 3.5 cm squares) was used as cellulose substrate. Light source (LED model Luxéon® Star white Lambertian LXHL-MW1D 5500 K) for photoinactivation system was obtained from Dioptik®, France. *S. aureus* (S2375) and *E. coli* (S2025) were obtained from Institut Pasteur, Paris.

2.2. Analytical methods

All ^{1}H NMR spectra were obtained with a Brücker DPX-400 spectrometer. Elemental analyses were carried out by the "Service Régional de Microanalyse de l'Université Pierre et Marie Curie, Paris". MALDI-TOF mass spectra were recorded with a Voyager Elite (Framingham MA, USA) time-of-flight mass spectrometer equipped with a 337 nm nitrogen laser (VSL 337ND) (Université Pierre et Marie Curie, Paris). It was operated in the reflection-delayed extraction mode at an acceleration voltage of 20 kV. Internal standards (peptides) were used to calibrate the mass scale with the two-point calibration Software version 3.07.1 from PerSeptive Biosystems. One microliter of an acetone solution of matrix (α-cyano-4-hydroxycinnamic acid) and compounds, at concentrations of 0.1 M and 0.01 mM, respectively, were deposited onto the stainless steel sample slide and dried in air. DRUV (diffuse reflectance UV–vis spectroscopy) spectra of porphyrin-modified samples were obtained with a Cary 5000 Varian spectrometer using a 110 mm PTFE integrating sphere. Reflectance spectra were recorded against Teflon standard reflectance spectrum. Each spectrum was recorded in the 350–750 nm range. UV–vis spectra were so recorded on a Specord 210 (Analytik Jena) double-beam spectrophotometer using 10 mm quartz cells. Spectra were realized at appropriate concentration (10^{-5} to 10^{-6} M). ATR-FTIR spectra of unmodified and functionalized samples were recorded with a Varian 800 FT-IR Scinitar Series spectrometer using a single reflection, horizontal ATR accessory. Spectra were collected in the 4000–400 cm^{-1} range and baseline correction was applied using a Varian Scinitar Series software. Thermogravimetric analyses of unmodified and modified samples were carried out using a SETARAM series Setsys 2400 thermogravimetric analyzer under an air atmosphere. Samples (25–30 mg) were heated from room temperature to 500 °C at a rate of 5 °C min^{-1}. Calcined alumina was used as internal standard. Surface morphology of unmodified and functionalized cellulosic samples was examined by SEM using a XL30 Philips scanning microscope. Dried samples were coated with a 17 nm gold–palladium layer using SCD 050, BAL-TEC coating unit accessory. Electron micrographs of samples were recorded at 2000× magnification. All samples were conditioned on disk (diameter 1 cm), purified with acetone at 70 °C for 24 h and dried at 100 °C for 15 min prior to SEM preparations. Quantum yield for $^1O_2$ was determined by direct analysis of the $^1O_2$ near-infrared luminescence at 1270 nm as described in own precedent paper (Ringot et al., 2011).

2.3. Syntheses

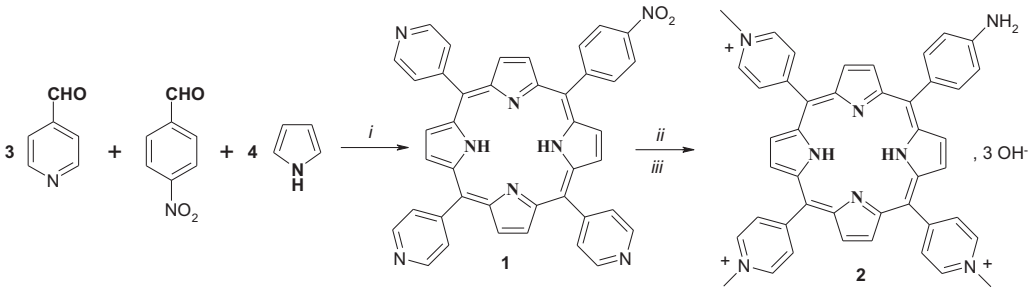
2.3.1. Syntheses of photosensitizers

*2.3.1.1. 5-(4-Nitrophenyl)-10,15,20-(4-pyridyl) porphyrin (**1**).* 2.40 mL of pyridine-4-carbaldehyde (3 equiv.) and 1.28 g of 4-nitrobenzaldehyde (1 equiv.) were added to propionic acid (200 mL). The mixture was heated under reflux with vigorous stirring for 1 h, and then 2.35 mL of freshly distilled pyrrole (4 equiv.) were added. After 1 h, the mixture was cooled and the solvent was evaporated to dryness and the crude product was purified by column and thin-layer chromatography ($CHCl_3$ to $CHCl_3$/EtOH 90/10, v/v) to give 110 mg of compound **1** (7%): R_f: 0.61 ($CHCl_3$/EtOH 90/10), UV–vis ($CHCl_3$) (λ_{max}, nm (ε_M $\times 10^{-3}$ L mol^{-1} cm^{-1})): 416 (390), 512 (17.2), 545 (6.2), 588 (6.4), 642 (2.6). ^{1}H NMR (400.13 MHz, $CDCl_3$,) δ_{ppm}: 9.02 (d, J = 5.1 Hz, 6H, $H_{3,5\text{-pyridyl}}$), 8.82 (m, 6H, $H_{\beta\text{-pyrrolic}}$), 8.77(d, 2H, J = 4.8 HZ, $H_{\beta\text{-pyrrolic}}$), 8.63 (d, 2H, J = 8.7 Hz, $H_{3,5\text{-nitrophenyl}}$), 8.10 (d, J = 5.1 Hz, 6H, $H_{2,6\text{-pyridyl}}$), 8.37 (d, J = 8.7 Hz, 2H, $H_{2,6\text{-nitrophenyl}}$), −2.99 (br s, 2H, NH_{int}), MS (MALDI) m/z for $C_{41}H_{26}N_8O_2$, calcd 662.68, found 663.79 $[M+H]^+$. Microanalysis calcd for $C_{41}H_{26}N_8O_2 \cdot 1/2H_2O$: C, 73.32; H, 4.05; N, 16.69; found C, 73.19; H, 4.09; N, 16.79.

*2.3.1.2. 5-(4-Aminophenyl)-10,15, 20-tri(4-N-methylpyridinium) porphyrin (**2**).* To a solution of **1** (76 mg, 0.1 mmol, 1 equiv.) in anhydrous DMF (10 mL), an excess of iodomethane (62 μL, 1 mmol, 10 equiv.) was added under argon atmosphere. The mixture was kept at room temperature with magnetic stirring for 24 h. After precipitation with diethyl ether and filtration, the corresponding cationic nitro porphyrin was obtained with 94% yield (87 mg). To a solution of cationic nitro porphyrin (71 mg, 80 μmol, 1 equiv.) in H_2O (10 mL), a solution of $SnCl_2$ (54 mg, 240 μmol, 3 equiv.) in 10 mL 37% HCl was added. Acetic acid (10 mL) was added to make a homogeneous solution and the resulting mixture was heated at 70–80 °C, overnight under stirring. Reaction was stopped by neutralization with 1 M NaOH (100 mL). The mixture was washed with water (2× 100 mL), dried on $MgSO_4$ and filtered. 54 mg of porphyrin **2**, purple solid, were obtained (90%). TLC ($CHCl_3$/MeOH/H_2O: 5/4/1): R_f = 0.12; UV–visible (H_2O) (λ_{max}, nm (ε_M $\times 10^{-3}$ L mol^{-1} cm^{-1})): 424 (10.4); 518 (4.3); 552 (4.0); 589 (3.9); 644 (3.6); ^{1}H NMR (400.13 MHz, DMSO d_6): δ_{ppm} = 9.51 (s, broad, 6H, $H_{3,5\text{-pyridyl}}$); 9.10 (m, 8H, $H_{\beta\text{-pyrrolic}}$); 9,00 (d, J = 4.4 Hz, 6H, $H_{2,6\text{-pyridyl}}$); 7.90 (d, J = 8.3 Hz, 2H,$H_{2,6\text{-aminophenyl}}$), 7.04 (d, J = 8.3 Hz, 2H,$H_{3,5\text{-aminophenyl}}$); 4.74 (s, 9H, N_{CH_3}); −3.06 (br s, 2H, $NH_{int.}$); MS (MALDI) m/z for $C_{44}H_{40}N_8O_3$, calcd 728.82, found 575.57 $[M-3OH]^+$. Microanalysis calcd for $C_{44}H_{40}N_8O_3 \cdot H_2O$: C, 70.75; H, 5.40; N, 15.01; found C, 70.27; H, 5.13; N, 14.82.

2.3.2. Grafting of filter paper by photosensitizers

As shown in Scheme 2, porphyrin **2** (43 mg, 58 μmol, 1 equiv.) in THF (10 mL) was cooled at 0 °C, and then cyanuric chloride (11 mg, 58 μmol, 1 equiv.) and *N*,*N*-diisopropyl ethylamine DIPEA (12 μL, 70 μmol, 1.2 equiv.) were added. The mixture was stirred for 30 min



Scheme 1. Synthetic route of tricationic aminoporphyrin **2**: (*i*) propionic acid, reflux, 2H; (*ii*) CH_3I excess, DMF, 24H; (*iii*) $SnCl_2$, HCl, 70–80 °C, 18 h, and then NaOH.

and then was left to reach room temperature. Then, 3.5 cm × 3.5 cm squares of Whatman filter paper grade 1, previously soaked in 0.5 M NaOH during 24 h, were introduced in this solution. After 24 h of grafting reaction, modified surfaces were washed with water (80 °C) and DMF under reflux during 24 h then dried at 100 °C for 1 h.

2.4. Grafting ratio

The molar grafting ratio (%) of porphyrin-grafted paper was calculated by two methods. Firstly, it was assessed by the difference between initial porphyrin amount in the grafting reaction and unreacted porphyrin present at the end of the grafting reaction, assuming that this difference represented the amount of porphyrin actually bound to each cotton sample, according to the following formula:

$$\text{grafting ratio}\,(\%) = \left[1 - \frac{(A_{\text{Soret}}/\varepsilon_{\text{Soret}}) \times V \times d}{n_{\text{initial}}}\right] \times 100$$

where "A_{Soret}" is the Soret band absorbance of porphyrin–triazine compound corresponding to the free photosensitizer in a solution consisting, for each cotton sample, of the final reacting solution mixed with the various washings operated after the grafting reaction, "$\varepsilon_{\text{Soret}}$" is the Soret band molar absorption coefficient of the free photosensitizer, "V" is the volume of prepared solution for obtaining absorbance value between 0 and 1, "d" is the dilution factor done for UV–vis measurement and "n_{initial}" is the initial amount of photosensitizer (mol) present before initiating the grafting reaction. In parallel, percentage of grafting was also determined by dissolution of paper. So, grafted paper (25.2 mg) was finely crushed and suspended in 26.9 mL of water. 2.5 g of NaOH was then added, and the mixture was shaken at room temperature until complete dissolution of NaOH. The suspension was cooled and held at −20 °C until it was frozen. Allowed to thaw at room temperature, the solid turned into a gel-like mass (Isogai & Atalla, 1998). Water (20.6 mL) was then added and a colored cellulose–porphyrin solution appeared after gentle shaking. The optical density of solution was recorded at the Soret band absorbance.

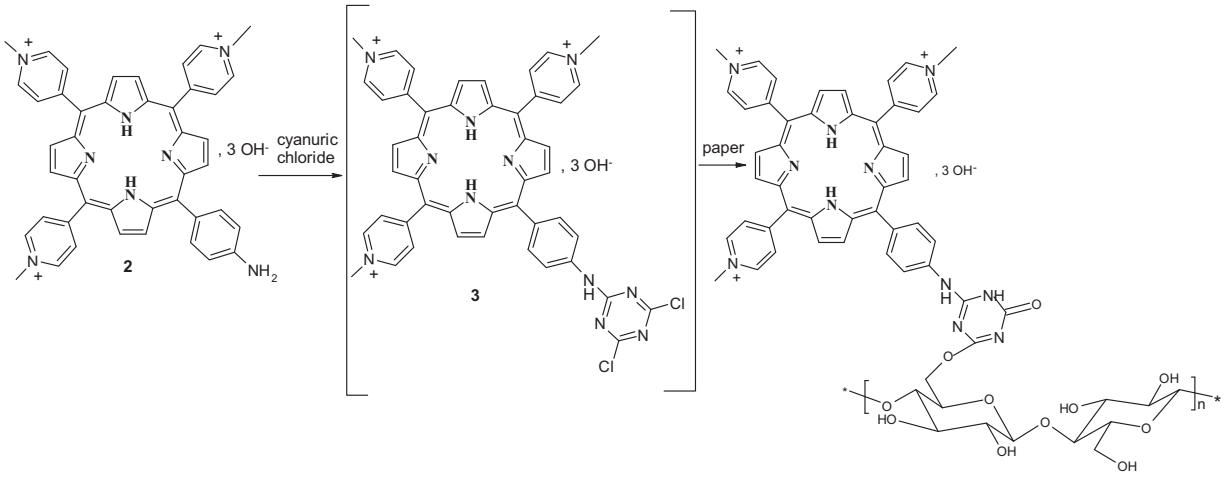
2.5. Antibacterial activity of photosensitizing paper

2.5.1. Growth conditions of bacterial cells

S. aureus (Gram +) and *E. coli* (Gram −) were inoculated into tryptic soy broth (pancreatic casein extract 17 g/L, soy flour papaic digest 3 g/L, dextrose 2.5 g/L, NaCl 5 g/L, and K_2HPO_4 2.5 g/L) and incubated at 37 °C overnight under aerobic conditions. The mother cultures were further diluted to give a working suspension containing approximately 10^5 CFU/mL.

2.5.2. Photodynamic treatment

Unmodified and porphyrinic filter paper sample were purified with acetone at 70 °C for 24 h, dried at 100 °C for 15 min and autoclaved at 120 °C for 15 min before antibacterial assessment. Sterile photosensitizing filter paper disks (0.5 cm diameter) impregnated with 30 μL of bacterial inoculum at a cell density of approximately 10^5 CFU/mL were deposited on sterile Petri dishes, and then incubated at 37 °C for 24 h under white light irradiation in wet atmosphere as described previously. Each sample was removed and transferred into 1 mL of extraction solution: Triton X-100, 0.5% (v/v) for *S. aureus* and 0.05% (v/v) for *E. coli*. After 30 min of gentle stirring at room temperature, serial dilutions of these suspensions were performed. Aliquots (100 μL) of diluted samples were then spread on tryptic soy agar plates. After incubation at 37 °C for 24 h, *plates were counted* to determine total *colony*-forming units (CFU) per mL



Scheme 2. Synthetic route to photoantimicrobial filter paper.

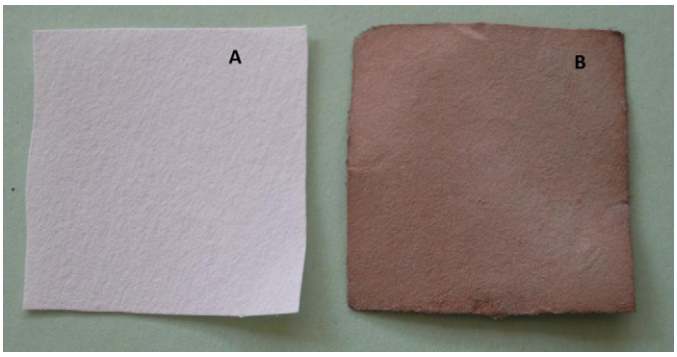


Fig. 1. Photographs of (A) filter paper; (B) filter paper after reaction with aminoporphyrin **2** and cyanuric chloride.

of undiluted suspension. Each test was done in triplicate and was conducted along with necessary controls: a sample was processed immediately after bacterial impregnation ($t = 0$), another one was incubated at 37 °C for 24 h in the dark; unmodified filter papers were also processed in the same conditions (24 h at 37 °C in the dark and under white light irradiation).

3. Results and discussion

As shown in Scheme 1, 5-(4-nitrophenyl)-10,15,20-tripyridylporphyrin **1** was prepared according to classical porphyrin synthesis methods (Meng et al., 1994), by condensation of 4-nitrobenzaldehyde, pyridine-4-carbaldehyde and pyrrole in propionic acid. Methylation by iodomethane, followed by reduction with $SnCl_2$/HCl, led to the final cationic compound **2**. Methylation and reduction resulted in good yield (overall 85%). All compounds and intermediates were characterized by ^{1}H NMR, UV–visible, mass spectroscopies. Also quantum yield for $^1O_2$ production of compound **2** was found to be equal to 0.82.

Grafting reaction was ruled out in one pot. In a first step, compound **2** reacted with cyanuric chloride at 0 °C, leading to the porphyrin–triazine derivative **3** which is not isolated (Scheme 2). Then, alkali-treated paper was introduced in the porphyrin–triazine reaction mixture as described above (see Section 2.3). Paper filter samples were removed, thoroughly washed with water, and then immersed in hot DMF (24 h, 120 °C). This washing cycle was repeated until disappearance of any trace of free porphyrin in washing solutions (UV-titration at 420 nm). After drying at 100 °C, the resulting paper samples gained a reddish-brown tint (Fig. 1).

The bonding of porphyrin to cellulose was confirmed by diffuse reflectance UV–vis (DRUV) (Fig. 2), UV–visible spectrophotometer and attenuated total reflectance Fourier transform infrared (ATR-FTIR). So, amount of grafted photosensitizer (μmol/mg of paper simple) was evaluated using UV–visible titration by two methods (see Section 2). Results have showed a grafting yield of 55% (0.03 μmol/mg of paper simple) which was similar with grafting yield of different porphyrins on cotton fabrics (Ringot et al., 2011). ATR-FTIR spectrum of native paper displays the classical peaks at 3340 cm^{-1} (OH stretching), 1325 and 1045 cm^{-1} (C—O stretching). Spectrum of modified paper displays 1636 and 1562 cm^{-1} peaks (amide stretching), which attests of the presence of a bond corresponding to the amide function (substitution of the last chlorine atom on the 1,3,5-triazine ring by the hydroxyl group after treatment of filter paper with NaOH). Moreover, presence of peaks in the 900–800 cm^{-1} zone has been assigned to a deformation vibration band of bound aromatic macrocycle (—C=C—) and intense 1352 cm^{-1} signal corresponds to stretching vibration of the iminium form (—C=N$^+$ pyridinium).

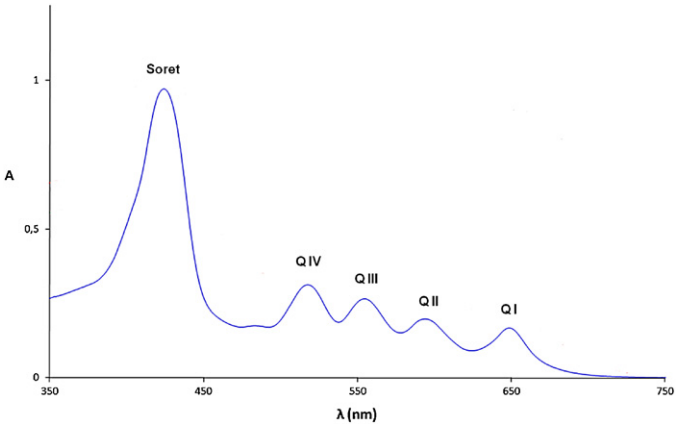


Fig. 2. DRUV spectrum (350–750 nm) of porphyrin grafted paper.

Thermogravimetric analysis (TGA) was used to investigate thermal properties of grafted paper. The thermogravimetric curves for the untreated (solid line) and grafted (dotted line) filter paper are shown in Fig. 3. These two curves present a similar initial weight loss which can be attributed to a water loss (dehydration phenomenon). At high temperature, the two samples loose a great amount of weight in the stage of decomposition (300–350 °C). Then above 350 °C, a relative slow thermal degradation of the sample residues is observed. Moreover, between 350 and 400 °C, the grafted paper shows a weight loss that is more important compared to the untreated paper due to the decomposition of photosensitizers and the removal of linker groups. Nevertheless, we can notice that the starting material and the derivatized paper present quasi-similar thermal stabilities and by comparing with other results, this comportment strongly supports the linkage of organic molecules on cellulosic moiety (de Bergamasco, Zanin, & de Moraes, 2007; Ringot et al., 2011).

Surfaces of unmodified and porphyrin-grafted papers were examined by scanning electron microscopy (SEM) (Fig. 4). Photomicrographs did not show visible difference between the two samples. These observations indicate that porphyrin grafting did not affect fiber morphology.

Photodynamic activity of modified filter paper was evaluated against *S. aureus* and *E. coli*, used as models of Gram-positive and Gram-negative bacteria, respectively. Experimental results are reported in Fig. 5. First of all, it appears necessary to justify the different controls. Untreated filter paper sample (in darkness or irradiated) and modified filter paper sample (in darkness), all of them permit bacterial growth of 4 or 2 log units (for *S. aureus* and

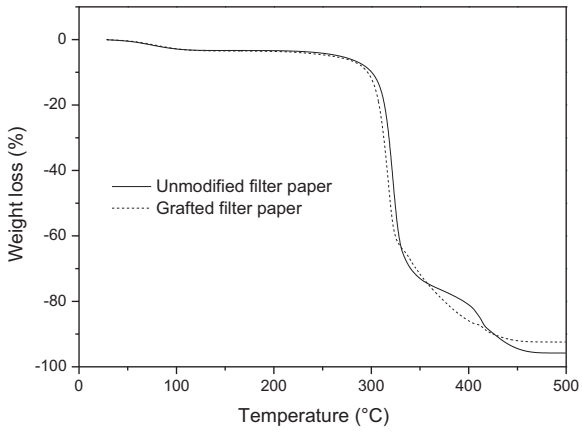


Fig. 3. TGA thermograms of filter paper before and after grafting.

Fig. 4. SEM photomicrographs (20 μm scale) of unmodified filter paper (a) and porphyrin grafted paper (b).

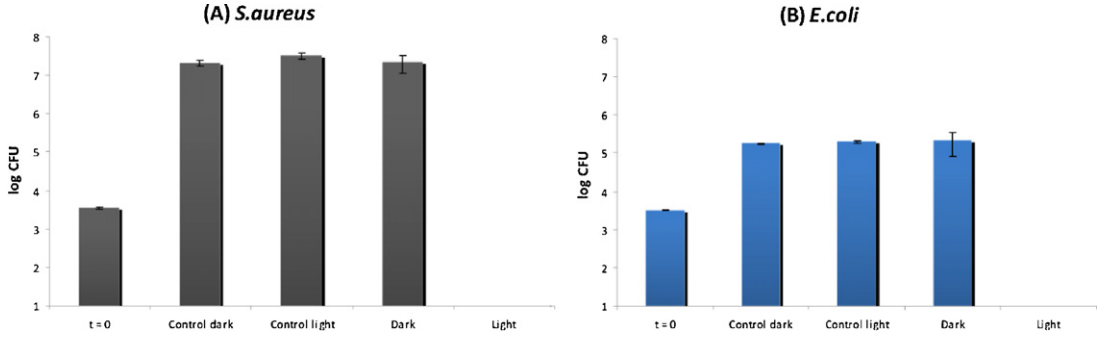


Fig. 5. Bacterial counts ($\log_{10}$ CFU) of (A) *S. aureus* and (B) *E. coli*.

E. coli, respectively) compared with reference ($t = 0$, CFU number initially present on paper squares). These controls demonstrate that either chemical modification of filter paper alone or light dose (9.5 J/cm^2) alone has no influence on bacterial growth. Furthermore, these three controls allowed us to discriminate between bacteriostatic or bactericidal properties of the photosensitizing paper.

Experimental data show that paper bearing photosensitizer exerts a strong photobactericidal effect against the two bacterial strains. Indeed, after a 24 h exposure to light totalling a fluence of 9.5 J/cm^2, no surviving bacteria, either *S. aureus* or *E. coli*, could be detected on grafted filter paper. Owing to the insoluble and immobilized character of the photosensitizer, mechanistic interpretations of these experiments must take into account the generation of a reactive species, such as singlet oxygen, on the material surface (Bonnet, Krysteva, Lalov, & Artarsky, 2006), followed by its diffusion and eventual interaction with target cells. Midden and co-workers have already shown that such photoinhibition is due to the type II photochemical process implying singlet oxygen ($^1O_2$) that ultimately damages the cell envelope since the photosensitizer does not penetrate bacterial cells (Dahl et al., 1987).

From these preliminary results, we can conclude that the tested surface has an excellent photoactivity against Gram positive and Gram negative bacteria.

4. Conclusion

In the present study, photosensitizing filter paper was successfully prepared by grafting a cationic porphyrin on cellulose using cyanuric chloride as linking agent. This strategy avoids preliminary chemical modification of the cellulosic material which appears very interesting for further industrial applications. This functionalized cellulose sample displayed a strong photoantibacterial activity against *S. aureus* and *E. coli*. So, this surface could be efficiently used in biomedical areas to prevent bacterial infections.

Acknowledgments

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