

Polyamide Nanofiber Membranes Functionalized with Zinc Phthalocyanines

Annelies Goethals,¹ Tawanda Mugadza,² Yasin Arslanoglu,² Ruphino Zugle,² Edith Antunes,² Stijn W. H. Van Hulle,^{3,4} Tebello Nyokong,² Karen De Clerck¹

¹Department of Textiles, Ghent University, Technologiepark 907, B-9052 Gent, Belgium

²Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

³LIWET, Department of Industrial Biological Sciences, Ghent University, Graaf Karel de Goedelaan 5, B-8500 Kortrijk, Belgium

⁴BIOMATH, Department of Mathematical Modeling, Statistics and Bioinformatics, Ghent University, Coupure Links 653, B-9000 Gent, Belgium

Correspondence to: S. W. H. Van Hulle (E-mail: stijn.vanhulle@ugent)

ABSTRACT: Electrospinning is an efficient method for the production of polyamide nanofiber membranes that are suitable for water filtration. Previous studies have shown that nanofiber membranes have high clean water permeability. The pathogen removal efficiency can be improved by functionalization with (organic) biocides. However, these membranes, like other membranes, are vulnerable to fouling which reduces the filtration efficiency. Therefore the present article investigates the potential of zinc phthalocyanines, which can produce singlet oxygen in the presence of visible light, as a functionalizing agent. The polyamide nanofiber membranes were functionalized with phthalocyanines using both a pre-functionalizing and post-functionalizing method. Only the post-functionalization method shows to result in nanofiber membranes capable of producing singlet oxygen. After 30 min 45% of 1,2-diphenylisobenzofuran (DPBF), used as an oxygen quencher, was removed by reaction with singlet oxygen. This resulted in a removal rate of 0.33 mol DPBF mol⁻¹Zn min⁻¹. During short term leaching tests, phthalocyanines could not be detected. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40486.

KEYWORDS: electrospinning; functionalization of polymers; photochemistry; separation techniques

Received 27 September 2013; accepted 21 January 2014

DOI: 10.1002/app.40486

INTRODUCTION

In recent years, considerable research focusses on the development of nanofiber membranes for water filtration.^{1–5} These nanofiber membranes are mostly produced via electrospinning and have pore sizes usually in the range of 200–400 nm which makes them suited for microfiltration. Electrospinning is a simple, rapid and inexpensive method^{6,7} and is currently in the beginning phase of industrial scale production.⁸ The electrospun nanofiber membranes have unique characteristics such as high porosity, high absorption capacity, high specific surface area and high clean water permeability (CWP) values.^{2,9,10} However, like other membranes, they are prone to the build-up of fouling during the filtration process.

The pathogen removal efficiency and antifouling properties of the nanofiber membranes can be improved by adding functionalizing agents (such as inorganic particles or organic biocides) to the membrane. Previous studies have shown that the pathogen removal of polyamide nanofiber membranes can be significantly

increased by adding nanosilver or organic biocides to the electrospinning solution.² Inorganic nanoparticles with known antibacterial properties, such as silver, copper oxide, zinc oxide, and titanium dioxide, have been incorporated into membrane materials to enhance the antibacterial properties.^{11–16} Different techniques can be used for the functionalization of nanofibers. The nanofibers can be prefunctionalized by adding the functionalizing agents to the spinning solution before electrospinning or the nanofibers can be post-functionalized using a dipcoating or sputtering method.^{2,11}

In addition to these reported functionalizing agents, phthalocyanines (Figure 1) could also be used as a novel and innovative functionalizing agent. Since their discovery over 70 years ago, phthalocyanines and their derivatives have been extensively used as blue, green or cyan colorants (dyes or pigments), for textiles, paper, and inks.¹⁷

Some phthalocyanines, like other photosensitizers, can generate reactive oxygen species (ROS) upon interaction with visible light

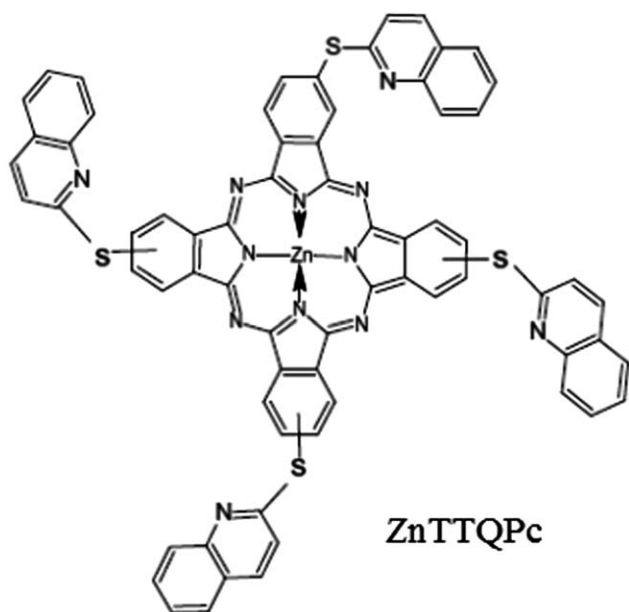


Figure 1. Molecular structure of ZnTTQPc.¹⁷

of suitable wavelength in the presence of ground state molecular oxygen. Whether the phthalocyanines can produce ROS or not mainly depends on their structure. They can differ from each other in chemical properties that may be tuned by modifying the central metal/semi-metal atom and the number and type of side chains.¹⁸ The central metal plays a crucial role in the photobiological activity influencing the triplet yield and the triplet lifetime of the compound and the introduction of polar substituents on the side chains which modify the overall balance of polarity. Thus, also influencing the solubility of the phthalocyanines.¹⁹

The main ROS of phthalocyanines is singlet oxygen (1O_2), a metastable excited state of ground state molecular oxygen 3O_2 , which is most often produced by energy transfer from an electronically excited triplet state of the sensitizer molecule to the ground state 3O_2 . Singlet oxygen is highly cytotoxic and is capable of killing cells and microorganisms. This effect has been used in photodynamic therapy (PDT) to effectively kill tumor cells in the treatment of cancer.^{20–24} Most studies focus on water-soluble phthalocyanines since solubility in the blood stream is necessary if they should be used for PDT, however this is unwanted for use as a functionalizing agent in membranes.

PDT has also been used against bacterial infections, yeasts, parasites and fungi.^{25,26} In several studies, phthalocyanines appeared to be effective inhibitors of various gram-negative and gram-positive bacteria.^{27–29} Another advantage is that the adaptability of microorganisms to the singlet oxygen and other reactive oxygen forms is highly improbable. Therefore it could offer an alternative for chlorination which does lead to the rise of resistant pathogens. The application of photosensitizers, both porphyrins and phthalocyanines, in water treatment has so far been limited to several specific purposes such as the removal of chemical pollution in water^{30,31} or the removal of algae.³² However singlet oxygen is not selective and is toxic to all living cells

in the water. As such, singlet oxygen can be harmful towards the environment and release of phthalocyanines into water should be avoided as much as possible. For this reason, the use of immobilized phthalocyanines in water treatment would be more suited. Especially in filtration applications where there is limited access to electricity, but visible light is abundantly present (e.g., in some third world countries), the electrospun nanofiber membranes functionalized with phthalocyanines can have great potential.^{33–35}

The use of phthalocyanines as a functionalizing agent for electrospun nanofiber membrane material is still very limited. Phthalocyanines have been immobilized on electrospun nanofiber membranes such as reinforced chitosan membranes by using a post-functionalization method³³ and also polyurethane nanofabrics have been functionalized with zinc photosensitizers³⁴ or zinc phthalocyanines.³⁶ In this study, it will be investigated whether the zinc phthalocyanines can be incorporated into a uniform polyamide 6 nanofiber membrane and whether they have potential to improve the membranes properties. First, filtration properties (clean water permeability and pathogen removal efficiency) of the non-functionalized membrane are characterized. Then different pre-functionalization and post-functionalization methods will be compared. Preliminary experiments had shown that the non-reinforced PA nanofiber membranes could not tolerate an aggressive method (including the use of NaOH) as used by Bonnett et al.,³³ however the same methods that have been used for functionalizing membranes with Ag as described by Decostere et al.,¹ can be used. The singlet oxygen production of the two different functionalization methods will be compared by studying the degradation of an oxygen quencher. It will be demonstrated that the prefunctionalized membranes perform better in terms of diphenylisobenzofuran (DPBF) removal, which indicates better singlet oxygen production. As such this study aims at demonstrating the proof-of-principle of the functioning of electrospun nanofiber membranes functionalized with phthalocyanines.

EXPERIMENTAL

Materials

Polyamide 6, acetic acid, formic acid were purchased at Sigma-Aldrich. *N,N*-dimethylformamide (DMF), chloroform, (tetrahydrofuran (THF), were purchased from SAARCHEM; 1,2-diphenylisobenzofuran (DPBF) was purchased from Aldrich.

Equipment

The viscosity of the electrospinning solution was measured using a Brookfield viscometer LVDV-II, the conductivity was measured with a CDM210 conductivity meter (Radiometer Analytical) and the surface tension was determined using a Wilhelmy plate method. Scanning electron microscope (Jeol Quanta 200 F FE) was used to verify the absence of beads and drops and to determine the average fiber diameter of the nanofiber membranes out of 50 measurements. The surface area of the nanofiber membranes was analyzed using Micromeritics ASAP 2020 Physisorption Analyzer. The clean water permeability and pathogen removal efficiency of the nonfunctionalized nanofiber membrane were determined using a flow through system as described in Decostere et al.¹ and Daels et al.² The clean water

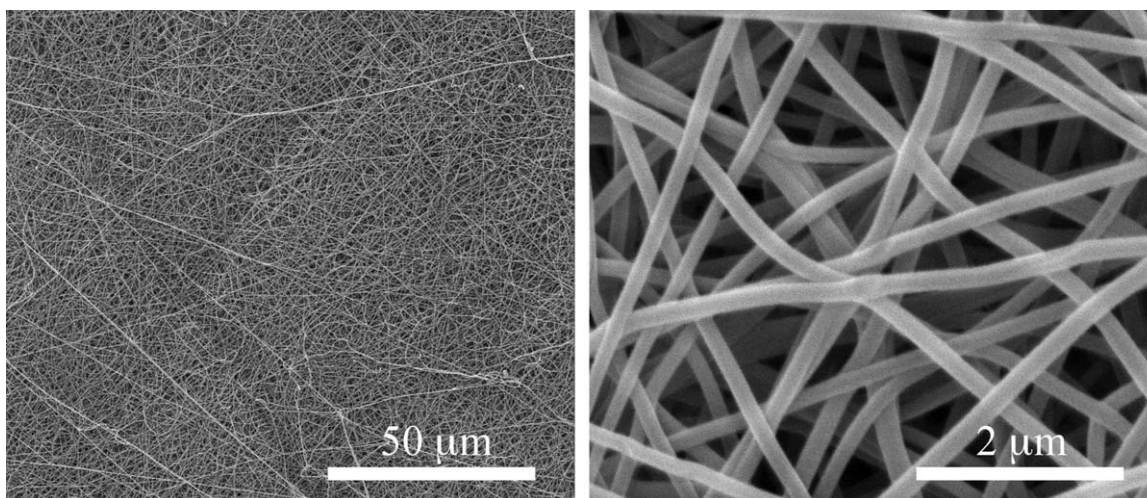


Figure 2. SEM images of non-functionalized PA nanofiber membrane.

permeability was determined by measuring the flux at different trans-membrane pressures. The pathogen removal efficiency was determined by filtering 100 mL of water inoculated with $6 \text{ Log}_{10} \text{ CFU}/100 \text{ mL}$ *E. coli*. Further, the culturable microorganisms were enumerated by inoculation in a nutrient agar culture medium at 37°C for 24 h.

UV-vis absorption spectra were recorded on a Cary 500 Vis/NIR spectrophotometer. A measurement path length of 1 cm was used.

Preparation of the Polyamide Nanofiber Membranes

The membranes were prepared by nozzle electrospinning as described in De Vrieze et al.⁷ The standard setup for nozzle electrospinning consisted of a syringe with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector. An electric field was applied across a polyamide 6 formic acid/acetic acid solution and a collector plate. As the solution jet travels, it is bend and/or split by the electric forces while the solvent evaporates. This mechanism led to the formation of nanofibers which were attracted to the grounded collecting plate. Both single nozzle⁷ and multi nozzle² setups were used to produce the membranes.

The post-functionalization was performed on pieces of one large polyamide nanofiber membrane ($100 \times 40 \text{ cm}^2$) which was produced on a 10-nozzle setup using a 16 wt% 50/50v% formic acid/acetic acid solution under steady state conditions (in terms of e.g., voltage difference between syringe tip and collector).^{7,37} These steady state conditions guarantee that the membrane structure is free of drops and beads.³⁷ The speed of the collector was set so that the grammage of the membrane is constant at 15 g m^{-2} , which guarantees a uniform thickness of the whole membrane. SEM images (Figure 2) show that the result is indeed a defect-free nanofiber membrane.

Preparation and Incorporation of Photosensitizers

The synthesis of ZnTTQPc ((4)-tetra[2-thioquinoline]phthalocyaninato zinc(II)) is performed according to Erdogmus and Nyokong.³⁸ The molecular structure of the complexes are shown in Figure 1.

Prefunctionalization was achieved by adding ZnTTQPc to the 16 wt % polyamide 6, 50/50 v/v% formic acid/acetic acid solution. This solution is electrospun into a membrane using the single nozzle setup as described above. This membrane is further denoted as membrane-pre.

Post-functionalization with ZnTTQPc was performed by submerging 0,07 g of nanofiber membrane produced by the multi nozzle setup in 50 mL of a ZnTTQPc/THF solution for 12 h. After the adsorption, the membranes are rinsed in a clear THF solution so that all unbound phthalocyanines are removed. Then the membranes are rinsed in demineralized water to remove all remaining solvent and left to dry at room temperature. This membrane is further denoted as membrane-post.

During both functionalization methods an almost equal ZnTTQPc concentration was used as starting point. For both solutions (ZnTTQPc in formic acid/acetic acid and ZnTTQPc in THF) a final ZnTTQPc concentration of about $4 \times 10^{-6} \text{ mol L}^{-1}$ was obtained (similar to Erdogmus and Nyokong³⁸). In fact, ZnTTQPc was added to the solution until the normalized absorbance reached a value of 1 at the wave length that corresponds with the Q-band (see Figure 4 below). As such, similar amounts of ZnTTQPc were used initially during both functionalization methods. Also both functionalization methods were performed at room temperature.

Singlet Oxygen Production

Singlet oxygen may be determined by two main methods, using chemical quenchers or using luminescence at 1270 nm. The method applied in this work makes use of singlet oxygen scavengers or quenchers. The 1,3-diphenylisobenzofuran (DPBF) is known to be an exclusive and widely used quencher in organic solvents.³⁹ The reaction of singlet oxygen with DPBF yields endoperoxide as shown in Figure 3.

Irradiations for singlet oxygen studies were performed using a General Electric Quartz lamp (300 W), 600 nm glass (Schott) and water filters, to filter off ultraviolet and far infrared radiations respectively. An interference filter, 670 nm with a band of 40 nm, was placed in the light path just before the cell

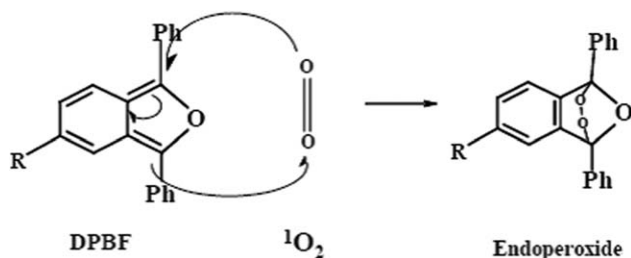


Figure 3. Reaction of DPBF with singlet oxygen.

containing the sample. The cell contained a volume of 3 mL of DBPF solution and a nanofiber membrane with a weight of 4.5×10^{-3} g and a width of 1 cm and a length of 3 cm (3×10^{-4} m²).

DBPF was used to compare the release of singlet oxygen in the THF at room temperature. Membranes -pre and -post were suspended in THF for these studies. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentrations of DPBF was lowered to 3×10^{-5} mol L⁻¹. DPBF degradation was monitored in the UV-vis spectrophotometer at 413 nm.

RESULTS AND DISCUSSION

Electrospinning and Characterization of Nonfunctionalized Nanofiber Membranes

Table I summarizes the solution properties that play an important role in the electrospinning process such as viscosity, conductivity and surface tension. Further it includes the properties of the nanofiber membrane that are important for water filtration purposes. Additional measurements have demonstrated that similar values are obtained for these properties when using with functionalized membranes (data not shown). The average nanofiber diameter is determined at 168 ± 19 nm. BET-analysis calculates the specific surface area to be $12 \text{ m}^2 \text{ g}^{-1}$. For both the nonfunctionalized and functionalized nanofibers. This is much higher than literatures values on conventional textiles.¹⁰

The membranes are used without any further reinforcement. The clean water permeability and the pathogen removal efficiency for *E. coli* of the nonfunctionalized polyamide nanofiber membrane was determined to be $23,000 \text{ L h}^{-1} \text{ bar}^{-1} \text{ m}^{-2}$ and $3.2 \text{ Log}_{10} \text{ CFU}/100 \text{ mL}$, respectively. Decostere et al.¹ had previously reported a CWP value of $6000 \text{ L h}^{-1} \text{ bar}^{-1} \text{ m}^{-2}$ and a $2 \text{ Log}_{10} \text{ CFU}/100 \text{ mL}$ removal for polyamide nanofiber membranes, produced on a multinozzle system. The improvement in filtration properties is based on the optimization of the materials production method and the use of a thinner membrane. This resulted in a more uniform membrane with a higher CWP value and a better pathogen removal efficiency. Even with these improvements the membrane remains vulnerable to fouling which can affect the filtration properties and eventually lead to clogging of the membrane. An additional improvement is necessary to decrease the potential of fouling.

Characterization of the Functionalization Agent

The synthesis and characterization of (4)-tetra[2-thioquinoline]phthalocyaninato zinc(II) (ZnTTQPc) has been previously described in Erdogmus and Nyokong.³⁸ It was determined that

Table I. Properties of the Nanofiber Membrane and Its Solution

Property	Value	Unit
Electrospinning solution		
Viscosity	470	Pa s
Conductivity	0.639	mS cm ⁻²
Surface tension	0.0361	N m ⁻¹
Polyamide nanofiber membrane		
Average fiber diameter	167.9	nm
Grammage	15	G m ⁻²
Specific surface area	12.22	m ² g ⁻¹
Clean water permeability	23000	l h ⁻¹ bar ⁻¹ m ⁻²
Pathogen removal efficiency (<i>E.coli</i>)	3.2	Log ₁₀ CFU/100 mL

ZnTTQPc has a high singlet oxygen quantum yield, which gives indication of the potential of this complex as photosensitizer in applications where singlet oxygen is required. This phthalocyanine is less suited for cancer treatment (PDT) because its lack of solubility in water. However as a functionalization agent for water filtration membranes, this could be an advantage. It has a very low affinity for water and therefore it is likely to remain in the membrane after functionalization and not leach out.

The solubility of ZnTTQPc in different solvents is investigated by measuring the UV-Vis spectra of the different solutions (Figure 4). The phthalocyanine can be used as a functionalizing agent when it has a good solubility in different solvents. The ZnTTQPc is characterized by an intense Q band in the visible region and B band in the UV region. The THF and chloroform solutions show a clear Q band at 684 and 690 nm, respectively. In some solvents, the ZnTTQPc may aggregate which can be detected by a widened Q band, in this case the Q band is narrow which indicates that ZnTTQPc does not aggregate in these solvents. In line with this, ZnTTQPc has a good solubility in a formic acid and acetic acid mixture. As such, ZnTTQPc is soluble in the 50/50v% formic acid/acetic acid solvent mixture that is used in the electrospinning solution. The split in the Q band of the acid solution is a direct result of the acidity. This split could be the result of demetalation or protonation of the ZnTTQPc. Because of the acidity of the solvent mixture, the

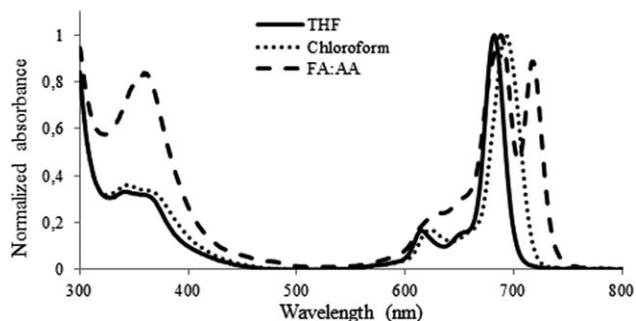


Figure 4. UV spectra of ZnTTQPc dissolved in THF, Formic acid:Acetic acid (FA:AA) and chloroform.

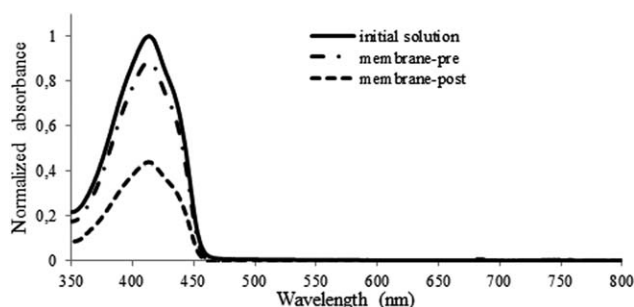


Figure 5. UV spectra of DPBF/THF solutions. Initial DPBF/THF solution and after 30 min of irradiation membrane-pre and membrane-post in THF.

ZnTTQPc will have partially protonated but will still be capable of producing singlet oxygen. The ZnTTQPc can thus be used to compare the two functionalization methods.

ZnTTQPc Functionalized Membrane Production

The membrane further denoted as “membrane-pre” is produced using the pre-functionalization method by adding ZnTTQPc to the electrospinning solution before spinning. The duration of electrospinning is chosen so that the grammage is 15 g m^{-2} , as such the pre-functionalized and post-functionalized nanofiber membranes are easily comparable in terms of grammage. The measured average fiber diameter is $159 \pm 24 \text{ nm}$. Changing the composition of the electrospinning solution can influence the steady state behavior; however in this case, the small amount of phthalocyanines does not affect the steady state conditions. The resulting nanofiber membrane is very pale green. Through this method the ZnTTQPc can be distributed both in the center and more towards the surface of each individual nanofiber.^{2,13} The amount of ZnTTQPc can be calculated based on the electrospinning conditions. To obtain a 16 wt % solution, 4.32 g of polyamide 6 was dissolved in 20 mL of a 50/50 v/v% formic acid (density 1.22 g cm^{-3})/acetic acid (density 1.05 g m^{-3}) solution. This solution contained also $4 \times 10^{-6} \text{ mol L}^{-1}$ ZnTTQPc and resulted in 0.29 m^2 of nanofiber membrane. As such $2.8 \times 10^{-7} \text{ mol Zn m}^2$ or $1.85 \times 10^{-8} \text{ mol Zn g}^{-1}$ was incorporated.

The membrane further denoted as “membrane-post” was produced by dipcoating 0.07 g (or 0.005 m^2) of a non-functionalized membrane in 50 mL of a ZnTTQPc/THF solution for 12 h. Afterward, it was rinsed twice in clear THF to remove all unbound ZnTTQPc. The UV spectra of the washing solvent were analyzed and no ZnTTQPc could be detected in the solution. After the functionalization, the membranes were uniformly colored green. Because the membrane was fully immersed into the functionalizing solution, the ZnTTQPc are adsorbed onto the surfaces of each individual nanofiber and not only on the top surface of the membrane. The amount of ZnTTQPc for this post-functionalized membrane can be calculated based on these dipcoating conditions. The dipcoating solution contained $4 \times 10^{-6} \text{ mol L}^{-1}$ ZnTTQPc. It is estimated that after 12 h of dipcoating about 30% of this ZnTTQPc is actually attached to the membrane, which is similar to results obtained with for example methylene blue. This results in $1.3 \times 10^{-5} \text{ mol Zn m}^{-2}$ or $8.6 \times 10^{-7} \text{ mol Zn g}^{-1}$. As such about

46 times more ZnTTQPc can be incorporated with this post-functionalization technique.

Singlet Oxygen Production

DPBF is known to be an exclusive and mostly used quencher of singlet oxygen in organic solvents. The singlet oxygen productions of membrane-pre and membrane-post are compared by monitoring the degradation of singlet oxygen quencher DPBF in THF to determine which functionalization method is most appropriate for the enhancement of the filtration properties of the polyamide nanofiber membrane. To produce singlet oxygen, the ZnTTQPc needs to be excited by visible light. Figure 5 shows UV spectra of the initial DPBF/THF solution and of the solution after 30 min of irradiation of the functionalized nanofiber membranes. The dipcoated membrane-post has a much higher DPBF removal efficiency than the electrospun membrane-pre.

For all spectra, the absorbance of DPBF at 413 nm is determined and plotted in Figure 6 in function of time. The non-functionalized membrane removes DPBF at the same rate as membrane-pre. Because of the high specific surface area of the nanofiber membrane, it is capable of adsorbing not only the ZnTTQPc but the DPBF as well. Thus, it is likely that prefunctionalized membrane-pre does not effectively produce singlet oxygen, but that the removal of DPBF in solution is caused by adsorption rather than by reaction with singlet oxygen.

Postfunctionalized membrane-post is clearly capable of removing significantly more DPBF than membrane-pre and the non-functionalized membrane. After 30 min the concentration of DPBF has decreased with 55%. When taking into account that 10% is caused by adsorption (based on the results with the non-functionalized membrane), the removal by reaction with singlet oxygen reaches 45%. This difference in removal is attributed to the fact that much more ZnTTQPc can be incorporated with the post-functionalization technique. Further, the visible light has much better access to the ZnTTQPc on membrane-post, since they are distributed on the surface of the individual nanofibers and will therefore have better access to visible light, although the use of different solvents during the preparation of the membranes could also play a minor role.⁴⁰ In contrast with the biocides used in our previous studies, the pre-functionalization method is not suited for photosensitizers, since access to visible light is key in producing singlet oxygen, even if a longer reaction time (30 min compared to 80 min as

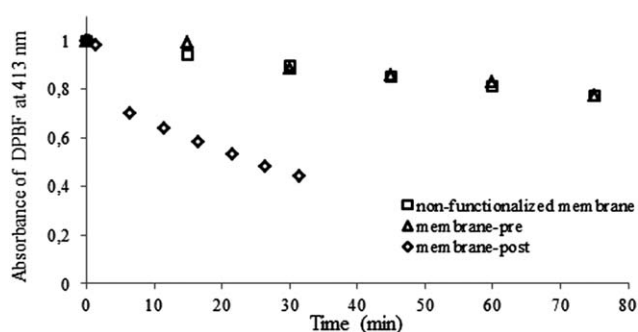


Figure 6. Absorbance of DPBF at 413 nm in function of time.

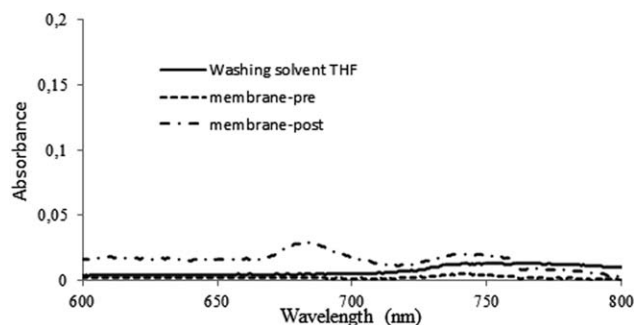


Figure 7. UV spectra of ZnTTQPc/THF solution to detect leaching. Membrane-pre and membrane-post after 30 min in THF (3 mL) and washing solvent THF (50 mL) of membrane-post.

applied). The post-functionalization method has thus the best potential in improving the antibacterial and antifouling properties of the polyamide nanofiber membrane using photosensitizers.

Based on Figure 6, the activity of the post-functionalized membrane-post can be calculated. After 30 min 45% of the initial DBPF ($3 \times 10^{-5} \text{ mol L}^{-1}$) was removed by reaction with singlet oxygen. As such the removal rate is $4.3 \times 10^{-7} \text{ mol DBPF L}^{-1} \text{ min}^{-1}$. The experiment was performed in 3 mL of reaction volume and a nanofiber membrane with a weight of $4.5 \times 10^{-3} \text{ g}$ containing $8.6 \times 10^{-7} \text{ mol Zn g}^{-1}$. As such this nanofiber membrane contained $3.86 \times 10^{-9} \text{ mol Zn}$, which results in a reaction rate of $0.33 \text{ mol DBPF mol}^{-1} \text{ Zn min}^{-1}$. This about 27% of the activity ($1.22 \text{ mol DBPF mol}^{-1} \text{ Zn min}^{-1}$) reported by Erdogmus and Nyokong.³⁸ However, by incorporating the ZnTTQPc on a membrane, the ZnTTQPc can easily be reused, which offers a benefit in the application for water filtration.

Leaching

The prevention of leaching is key when using functionalized nanofiber membranes for water filtration. The absence of leaching will ensure that the environment is not polluted with phthalocyanines that produce singlet oxygen which is toxic to all organisms. For the moment, at very small scale this would not be a problem, however at larger scale it could be problematic. Also the membranes will lose their properties in the long term, when they lose the functionalizing agent.

As ZnTTQPc is a non water-soluble phthalocyanine, leaching of the ZnTTQPc in water cannot be easily detected, since UV/Vis will not be able to detect dissolved phthalocyanines. Therefore the leaching from the post-functionalized membranes was investigated by evaluating the washing solvent after functionalization. Membrane-pre was washed with 50 mL of pure THF to remove all unbound ZnTTQPc. When analyzing the UV-vis spectra of this solution, no ZnTTQPc could be detected, thus if leaching occurred, the concentration is below detection limit (Figure 7). It can be concluded that even without the desired covalent bond, ZnTTQPc are suitable for use as a functionalizing agent for membranes.

During the determination of singlet oxygen production by ZnTTQPc, leaching was also monitored. During these experiments, a small peak at 684 nm is measured in the spectrum of

membrane-post after 30 min (Figure 7). No peak is measured in the spectrum of membrane-pre. The difference is to be expected since in membrane-post all ZnTTQPc is on the surface and could therefore leach out easier than in membrane-pre in which the complexes can also be present in the center of the nanofiber. The peak at 740 nm can be attributed to the use of a molecular sieve in the solvent (used for drying the THF).

It can be concluded that the leaching of the functionalizing agent cannot be fully avoided, however when evaluating larger quantities (50 mL) of solvent, the concentration of the functionalizing agent is below detection limit. Furthermore, it should also be taken into account that the selected ZnTTQPc does not dissolve in water and therefore does not have the same affinity for water as it does for THF. When trying to add small amounts of ZnTTQPc in water, it precipitates. For this reason, even if it would leach out, the ZnTTQPc is less likely to produce singlet oxygen in the environment compared to water-soluble phthalocyanines.

CONCLUSIONS

Polyamide nanofiber membranes which have good characteristics for use in water filtration can be functionalized with zinc phthalocyanines. Two different methods have been used to integrate zinc phthalocyanines into the nanofiber membranes. The one step pre-functionalization method which had been proven to be successful for other functionalizing agents, such as nanosilver and organic biocides, is not suited for the functionalization with phthalocyanines since this study shows that no singlet oxygen can be produced. Only a post-functionalization method which ensures that the phthalocyanines are on the surface of the nanofibers where they have more access to visible light has potential in improving the antibacterial and antifouling properties of the membranes. This potential was demonstrated by singlet oxygen production measurement, but needs to be confirmed in future studies by actual filtration experiments.

Short term leaching tests (50 mL) could not detect any leaching of the ZnTTQPc used in this study which indicates that they are successfully incorporated onto the nanofiber membrane. This is due to large specific surface area of the membrane which allows the ZnTTQPc to be easily adsorbed. Thus, a covalent bond between the membrane and the ZnTTQPc is not necessary for a successful functionalization. Therefore a wide range of zinc phthalocyanines with very different structures have potential as functionalizing agents. It can be concluded that the PA nanofiber membranes functionalized with zinc phthalocyanines have potential as water filtration membranes. This should be further explored in future research, especially in areas where electricity is not available, but visible light is abundant. The functionalized filters should now be investigated in filtration mode as the high clean water permeability value which is a key property of the polyamide nanofiber membranes, allows to filter large amounts of water without the need for extra pressure.

ACKNOWLEDGMENTS

Financial support from The Agency for Innovation by Science and Technology of Flanders (IWT) and the Ghent University Special

Research Fund is gratefully acknowledged. The work was also funded by the Department of Science and Technology (DST) and the National Research Foundation (NRF) of South Africa through DST/NRF South African Research Chairs Initiative for Professors of Medicinal Chemistry and Nanotechnology. The project was partially funded by FP7-PEOPLE-2009-IRSES PROCOTEX.

REFERENCES

1. Decostere, B.; Daels, N.; De Vrieze, S.; Dejans, P.; Van Camp, T.; Audenaert, W.; Hogie, J.; Westbroek, P.; De Clerck, K.; Van Hulle, S. W. H. *Desalination* **2009**, *249*, 942.
2. Daels, N.; De Vrieze, S.; Sampers, I.; Decostere, B.; Westbroek, P.; Dumoulin, A.; Dejans, P.; De Clerck, K.; Van Hulle, S. W. H. *Desalination* **2011**, *275*, 285.
3. Ma, Z.; Kotaki, M.; Ramakrishna, S. *J. Membr. Sci.* **2005**, *265*, 115.
4. Gopal, R.; Kaur, S.; Ma, Z.; Chan, C.; Ramakrishna, S.; Matsuura, T. *J. Membr. Sci.* **2006**, *281*, 581.
5. Homaeigohar, S. S.; Buhr, K.; Ebert, K. *J. Membr. Sci.* **2010**, *365*, 68.
6. Liang, D.; Hsiao, B. J.; Chu, B. *Adv. Drug Deliv. Rev.* **2007**, *59*, 1392.
7. De Vrieze, S.; Van Camp, T.; Nelvig, A.; Hagstrom, B.; Westbroek, P.; De Clerck, K. *J. Mater. Sci.* **2009**, *44*, 1357.
8. Botes, M.; Cloete, T. E. *Crit. Rev. Microbiol.* **2010**, *36*, 68.
9. Decostere, B.; Daels, N.; De Vrieze, S.; Dejans, P.; Van Camp, T.; Audenaert, W.; Westbroek, P.; De Clerck, K.; Boeckaert, C.; Van Hulle, S. W. H. *Water SA* **2010**, *36*, 151.
10. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223.
11. Yoon, K.; Kim, K.; Wang, X.; Fang, D.; Hsiao, B. S.; Chu, B. *Polymer* **2006**, *47*, 2434.
12. Basri, H.; Ismail, A. F.; Aziz, M.; Nagai, K.; Matsuura, T.; Abdullah, M. S.; Ng, B. C. *Desalination* **2010**, *261*, 264.
13. Barakat, N. A. M.; Abadir, M. F.; Sheikh, F. A.; Kanjwal, M. A.; Park, S. J.; Kim, H. Y. *Chem. Eng. J.* **2010**, *156*, 487.
14. Sheikh, F. A.; Kanjwal, M. A.; Saran, S.; Chung, W.-J.; Kim, H. *Appl. Surf. Sci.* **2011**, *257*, 3020.
15. Wei, Q. F.; Huang, F. L.; Hou, D. Y.; Wang, Y. Y. *Appl. Surf. Sci.* **2006**, *252*, 7874.
16. Li, A. L.; Mahendra, S.; Lyon, D. Y.; Brunet, L.; Liga, M. V.; Li, D.; Alvarez, P. J. *J. Water Res.* **2008**, *42*, 48.
17. Gregory, P. J. *Phorphyrins Phthalocyanines* **2000**, *4*, 432.
18. Nyokong, T. *Coordination Chem. Rev.* **2007**, *251*, 1707.
19. Guo, L.; Meng, F. S.; Gong, X. D.; Xiao, H. M.; Chen, K. C.; Tian, H. *Dyes Pigments* **2001**, *49*, 83.
20. DeRosa, M. C.; Crutchley, R. J. *Coordination Chem. Rev.* **2002**, *233*, 351.
21. Sheng, C.; Pogue, B. W.; Wang, E.; Hutchins, J. E.; Hoopes, P. J. *Photochem. Photobiol.* **2004**, *79*, 520.
22. Ochsner, M. J. *Photochem. Photobiol. B Biol.* **1997**, *39*, 1.
23. Maduray, K.; Karsten, A.; Odhav, B.; Nyokong, T. *J. Photochem. Photobiol. B Biol.* **2011**, *103*, 98.
24. Wainwright, M. J. *Antimicrobial Chemother.* **1998**, *42*, 13.
25. Calzavara-Pinton, P. G.; Venturini, M.; Sala, R. *J. Photochem. Photobiol. B Biol.* **2005**, *78*, 1.
26. Jori, G.; Brown, S. B. *Photochem. Photobiol. Sci.* **2004**, *3*, 403.
27. Minnock, A.; Vernon, D. I.; Schofield, J.; Griffiths, J.; Parish, J. H.; Brown, S. B. *J. Photochem. Photobiol. B Biol.* **1996**, *32*, 159.
28. Merchat, M.; Bertolini, B.; Giacomini, P.; Villanueva, A.; Jori, G. *J. Photochem. Photobiol. B Biol.* **1996**, *32*, 153.
29. Jančula, D.; Maršálek, B.; Novotná, Z.; Černý, J.; Karásková, M.; Rakušan, J. *Chemosphere* **2009**, *77*, 1520.
30. Šafařík, I. *Water Res.* **1995**, *29*, 101.
31. Ranjit, K. T.; Willner, I.; Bossmann, S.; Braun, A. *J. Phys. Chem. B* **1998**, *102*, 9397.
32. Jancula, D.; Drabkova, M.; Cerny, J.; Karaskova, M.; Korinkova, R.; Rakusan, J.; Marsalek, B. *Environ. Toxicol.* **2007**, *23*, 218.
33. Bonnett, R.; Krysteva, M. A.; Lalov, I. G.; Artarsky, S. V. *Water Res.* **2006**, *40*, 1269.
34. Mosinger, J.; Lang, K.; Kubát, P.; Sýkora, J.; Hof, M.; Plíštil, L.; Mosinger, B. *J. Fluoresc.* **2009**, *19*, 705.
35. Jesenska, S.; Plíštil, L.; Kubat, P.; Lang, K.; Brozova, L.; Popelka, S.; Szatmary, L.; Mosinger, J. *J. Biomed. Mater. Res. A* **2011**, *99*, 676.
36. Zügler, R.; Litwinski, C.; Torto, N.; Nyokong, T. N. *J. Chem.* **2011**, *35*, 1565.
37. De Vrieze, S.; De Schoenmaker, B.; Ceylan, O.; Depuydt, J.; Landuyt, L.; Rahier, H.; Van Assche, G.; De Clerck, K. *J. Polym. Sci.* **2011**, *119*, 2984.
38. Erdogmus, A.; Nyokong, T. *J. Mol. Struct.* **2010**, *977*, 26.
39. Young, R. H.; Brewer, D.; Keller, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 375.
40. Ogunsipe, A.; Maree, D.; Nyokong, T. *J. Mol. Struct.* **2003**, *650*, 131.