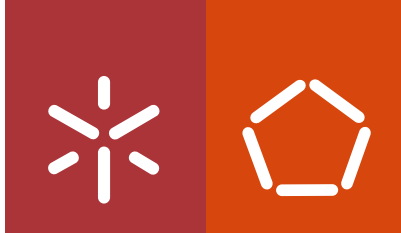


Universidade do Minho
Escola de Engenharia

Ana Luísa Delgado Lima

**Novel photo/conductive organic fibers
for flexible optoelectronics**



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Novel photo/conductive organic fibers for flexible optoelectronics

Tese de Doutoramento em Ciência e Engenharia de Polímeros
e Compósitos

Trabalho realizado sob a orientação da

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do

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e da

Professora Doutora Isabel Mercês Ferreira

setembro de 2016

STATEMENT OF INTEGRITY

I hereby declare having conducted my thesis with integrity. I confirm that I have not used plagiarism or any form of falsification of results in the process of the thesis elaboration. I further declare that I have fully acknowledged the Code of Ethical Conduct of the University of Minho.

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ABSTRACT

The continuous technological evolution that is moving toward the manufacture of smaller and more efficient devices allied with the growing environmental awareness concerning plastic materials has challenging researchers to develop new materials that could fulfill both premises. Optic/electronic materials are in constant evolution and are an example of a demanding field of research that could be found in most of now-a-day applications, from LEDs in cars and in housing light, batteries and anti-statics, among others. Between the several strategies to obtain materials with optic/electronic properties and taking into account all the environmental concerns. The development of composites or nanocomposites combining biodegradable polymers and environmental friendly processing techniques is an alternative. The final optical and/or electronic properties are provided by the introduction of functional materials, such as carbon nanotubes and porphyrins.

Therefore, in this work composites of carbon nanotubes (CNT) and cellulose acetate (CA), which is a biodegradable polymer, were developed in order to achieve the desired electrical conductivity through melt mixing processing, since CNTs are known as excellent fillers with amazing conductive properties. Also, porphyrins, which are conjugated macromolecules recognized not only by its optical but also by the possibility of having electrical properties were incorporated with the polymer and nanofibers were obtained through electrospinning. The results revealed that CNTs nanocomposites achieved the desired electric conductivity when 0.5 wt% of non-functionalized CNTs were melt mixing with CA. Metallation of porphyrins with a transition metal (iridium) affected severely of the final properties of the nanofibers, which exhibited distinct characteristics. CA fibers with the porphyrin showed fluorescence and high intensity emission, but they did not exhibit electrical properties. Whereas, the nanofibers prepared with the metallated porphyrin showed a lower emissivity but revealed the establishment of conductive paths.

Overall, the results of this research work demonstrated that it is possible to obtain CA based novel materials with optic and/or electronic properties by the incorporation of nanotubes or porphyrins.

RESUMO

Atualmente a tecnologia evoluiu para a produção de dispositivos com dimensões reduzidas mas também mais eficientes. Esta necessidade quando aliada às motivações ambientais sobre a crescente utilização de plásticos, tem desafiado investigadores a desenvolver materiais inovadores que cumpram ambas as premissas. Os materiais óptico/electrónicos utilizados em dispositivos, são um exemplo de uma área de pesquisa muito exigente. Estes podem ser encontrados na maioria das aplicações utilizadas no nosso dia-a-dia como em LEDs nos automóveis e na iluminação das nossas habitações, baterias e também como anti-estáticos, entre outros. Considerando as várias estratégias possíveis para obter materiais com propriedades óptico/electrónicas e tendo em conta todas as preocupações ambientais, o desenvolvimento de materiais compósitos ou nanocompósitos com polímeros biodegradáveis usando técnicas de processamento amigas do ambiente surge com uma alternativa. As propriedades ópticas e/ou electrónicas finais são proporcionados pela introdução de materiais funcionais, tais como nanotubos de carbono e porfirinas.

De acordo com este desafio, neste trabalho compósitos de acetato de celulose (CA), polímero biodegradável, e nanotubos de carbono (CNT), foram desenvolvidos através do processamento no fundido de forma a obter materiais que exibam algum nível de condutividade eléctrica, uma vez que os nanotubos de carbono são caracterizados como excelentes reforços com propriedades condutoras surpreendentes. As porfirinas, que são macromoléculas conjugadas conhecidas não só pelas suas propriedades ópticas mas também pela possibilidade de exibirem propriedades eléctricas, foram incorporadas no polímero obtendo-se nanofibras utilizando a técnica de electrospinning. Os resultados mostraram que os nanocompósitos com os nanotubos de carbono apresentaram a condutividade eléctrica desejada, quando 0,5 % em peso de nanotubos de carbono não funcionalizados foram incorporados no CA. Verificou-se também que a introdução de um metal de transição (irídio) nas porfirinas afectou as propriedades finais das nanofibras, obtendo-se fibras com características distintas. As fibras de CA com as porfirinas apresentaram fluorescência e uma alta intensidade de emissão, mas não exibiu propriedades eléctricas. Enquanto que as nanofibras preparadas com a porfirimina metalizada mostrou uma emissividade inferior, mas revelou alguma condutividade eléctrica.

No geral, os resultados desta investigação revelaram que é possível obter materiais inovadores com propriedades óptico/electrónicas baseados na incorporação de nanotubos ou porfirinas num polímero biodegradável.

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I

THESIS OUTLINE

This thesis is organized into eight main chapters built with published, submitted and “to be submitted” scientific papers. The present **Chapter I** describes the thesis content to provide the reader a clear overview about the structural organization and the issues discussed in each section of this thesis.

The general aspects related with novel materials with optic/electronic properties are revised in **Chapter II**. It is also given emphasis to the importance of using environmentally friendly polymers, as cellulose acetate. A brief review concerning the selected compounds used in the experimental work, carbon nanotubes and porphyrins, to achieve the desired optic/electronic properties and the processing techniques are made.

Chapter III describes the influence of melt mixing small amounts of as-received and pyrrolidine functionalized carbon nanotubes on the thermal stability of cellulose acetate matrix prepared with two different equipments. Concerning the study of the morphological dispersion of the as-received and functionalized carbon nanotubes on the polymer matrix, **Chapter IV** gives a detailed discussion in combination with the rheological, and the successful achievement of electrical properties.

Chapter V presents the synthesis of a new metallated porphyrin, based in a pentafluorophenyl-substituted porphyrin coordinated with an iridium metal transition. Both porphyrin and metal are known from literature from its extraordinary photophysical and photochemical properties and therefore are promising candidates for a wide range of applications from electrochromic devices, catalysts, sensors and even solar cells. **Chapter VI** describes cellulose acetate-based membranes prepared by electrospinning technique without and with iridium p-tolyl meso-substituted porphyrin. The main properties of the electrospun solutions and respective membranes are discussed in this chapter, including luminescence and electrical properties.

Chapter VII addresses to the synthesis of porphyrin arrays. In this chapter, the iridium p-tolyl meso-substituted porphyrin is employed has a base to constructed structures axially bonded to the center metal with multidentate ligands. This kind of approach allows the preparation of multiporphyrin assemblies that might be involved in energy charge transport.

Finally, **Chapter VIII** gathers the overall conclusions of the developed work considering its initial objectives, together with ideas for a future work.



LITERATURE REVIEW

Scope

The present chapter aims to provide to the reader fundamental information that will make easier the understanding of the research developed in the present work. For that, a literature review, including the most important concepts and definitions concerning the main themes are featured in the next pages. Thus, this chapter starts explaining the importance of developing materials with optic/electronic properties and the main approaches usually employed. Next, it is given emphasis to the polymer matrix properties as well to the functional compounds used to attain the desired properties. At last, the processing techniques used in this work will be described.

1. Materials with Optic/Electronic Properties

As the research moves towards the production of smaller and more efficient devices, become essential to develop new materials. In the last decade one of the most promising technologies fields are optic/electronic devices¹. These are here described as devices that exhibit optical and/or electronic properties, which already represents two large groups of materials with amazing properties, that are introduced in a wide range of now-a-day applications, such as light emitting diodes (LED) in cars and in housing lightning^{1,2}, non-linear optics (NLO)², photodetectors², lasing², electrochromism², battery², anti-static², EMI-shield², conducting fiber and films². In fact, there are several strategies to obtain materials with optic/electronic properties. Intrinsically conducting polymers are a specific group of polymers that show highly delocalized π -electron systems with alternate single-double bonds in the polymer backbone that can lead to these kind of properties in polymer materials (Figure 1)^{2,5}. The first conductive polymer that was discovered was polyacetylene (Figure 1) in 1977 by Heeger, MacDiarmid and Shriakawa, which was made conductive by doping bromine and iodine vapors during the reaction⁶. In most of cases the doping process, i.e., the introduction of electron acceptors/donor by partial oxidation(p-doping) or reduction(n-doping) was necessary to tune to a conductive polymer, which became to charged state⁶. This discovery triggered an extensive research on the chemical and physical aspects of conjugated polymers as polythiophenes, polypyrrole and polyaniline among others, in neutral (undoped) and charged (doped) states.

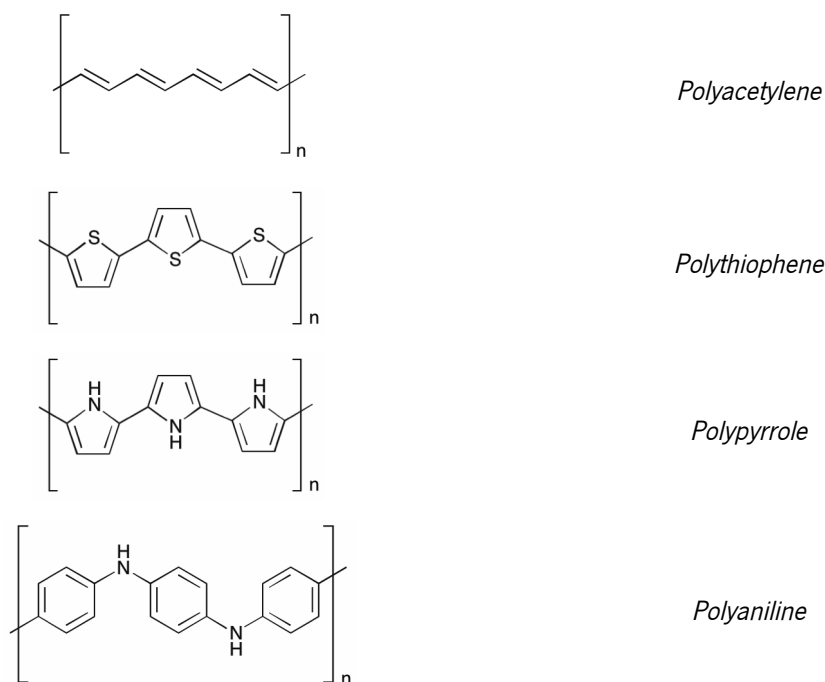


Figure 1 – Examples of conjugated polymers in neutral states.

As expected, these polymers have mainly applications as organic conductors in the fabrication of conductive layers, fibers, antistatic coatings, photovoltaic devices, displays and transparent electrodes, but also in chemical and electrochemical sensors as “electronic noses”, biomedical imaging and sensing, and as a corrosion inhibitor^{3,4}. Although, conjugated polymers are attractive for a number of applications, its use can be obstructed due to their poor processability and environmental stability and also due to the high prices^{2,4}. The presence of a conjugated structure through the polymer backbone and strong interchain interactions are the main responsible for the chain rigidity and high cristallinity that turns these polymers in their vast majority insoluble and infusible². To overcome some of these disadvantages a lot of research has been carried out in order to obtained materials with similar properties.

Polymer nanocomposites are known as reinforced polymer matrices with nanometric fillers (Figure 2)⁷. The combination of polymer and filler should result in a synergetic effect of the properties of both compounds, where the filler significantly improves or adjust the properties of the materials in which it is incorporated⁸. These materials are also considered as the 21st century materials due to its high performance an their unusual property combination and design possibilities⁹. Therefore, it is not surprising that developed nanocomposites are used in optic/electronic applications. Nano-oxide particles of silica, alumina, and zirconia showed up as promising fillers to transparent polymer reinforcement⁸. This quasi-spherical nanoparticles prevents the diffusion phenomena of light, having as

main market the production of special optical components as lenses, optical fibers, etc.^{8, 10}. The incorporation of nano-oxide as titanium dioxide (TiO_2) in polymeric matrices has already shown to add conductive and dielectric properties to the nanocomposite and zinc oxide (ZnO) can potentially be used as additive for anticorrosion coatings (Figure 2)^{8, 11}. Also, nano-oxides associated with a conductive matrix were the first materials to be applied in smart windows, conductive paints and rechargeable batteries⁸. Metallic nanoparticles are another important class of fillers of spherical shape, that when incorporated with a conductive matrix potentiates the electrical conductivity of the nanocomposite⁸. These types of nanocomposites showed to have a wide-range of applications from photovoltaic cells, anticorrosion coatings, supercapacitors, sensors to catalysts⁸. They can also exhibit magnetic properties (ex: iron nanofiller) associated with a conductive (polypyrrole) or an insulating (polystyrene) matrix, being applied as electromagnetic shield for electronic components⁸. Environmentally friendly nanocomposites of metallic particles with bacterial cellulose (BC) (Figure 2) were also developed with notable properties ranging glucose biosensors to conductive and semi-conductive nanocomposites¹².

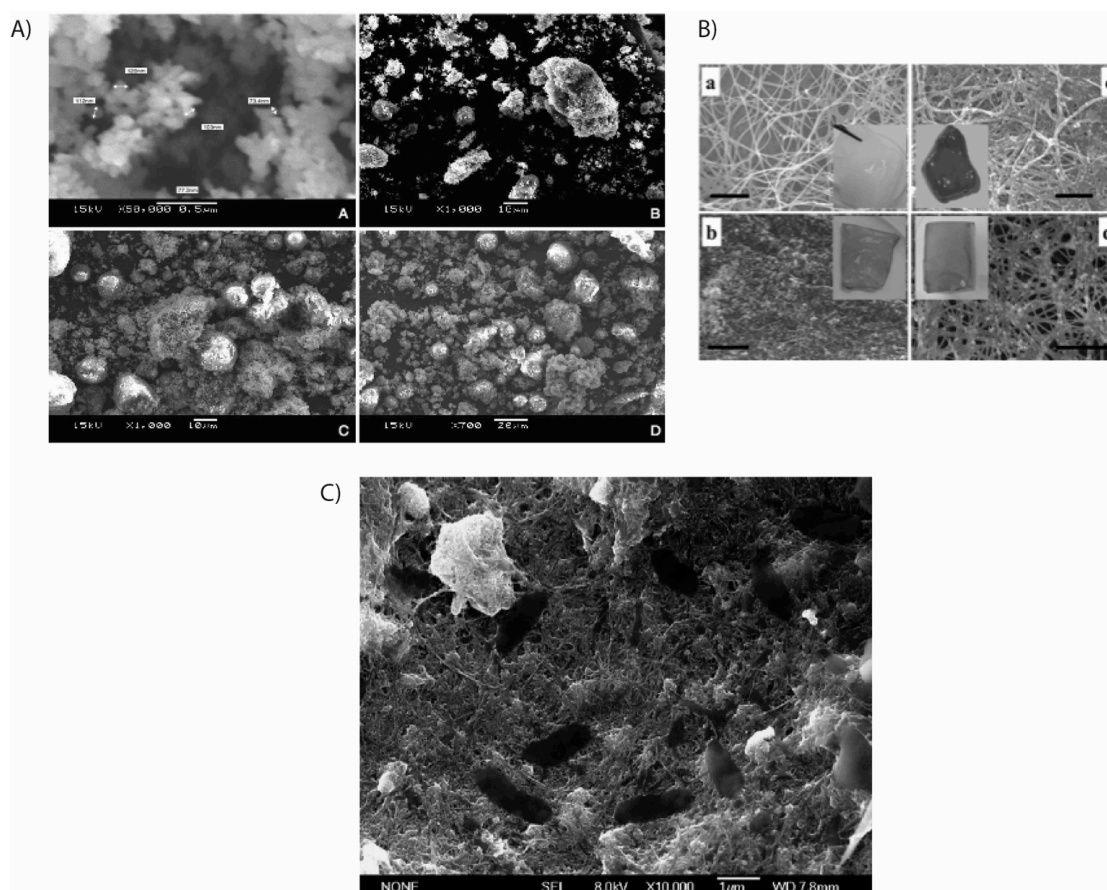


Figure 2 – Examples of various nanocomposites; A) SEM images of A-ZnO nanoparticles and ZnO nanocomposites with B-5 wt%; C-10 wt%; D-15 wt% of fly ash¹¹; B) SEM image of Bacterial Cellulose (BC)+metallic particles where a – BC; b – BC/Ag; c- BC/Au; d- BC/Cu (bar=1.5 μm)¹²; C) SEM image of Cellulose/Single-wall carbon nanotubes nanocomposites¹³.

Noble metals as gold (Au), silver (Ag) and platinum (Pt) can also be used as fillers to develop nanocomposites for optic/electronic, such as, optical filters⁸, high refractive index wave guide materials^{14, 15}, organic batteries¹⁴, microelectronics¹⁴ and non-linear optical materials^{8, 14}, which are often associated with polymers, such as polypyrrole, polyaniline, poly(terephthalate of ethylene), poly(acrylonitrile), among others (Table 1)^{8, 14}.

Table 1 – Nanocomposites of polymer/noble-metals and further applications (adapted from *Marquis et al.*⁸ and *Folarin et al.*¹⁴).

Polymer Matrix	Noble-metal	Application
Polyaniline	Gold	Sensor
	Copper	
Natural rubber		Latex gloves
Polytetraphthalate of ethylene	Silver	Bandpass filter
Polytetrafluoroethylene		Optical filler/sensor
Bisphenol A		Capacitor
Polypyrrole		Fuel cell
PANI-PSS	Platinum	
Polysulfone		Sensor
Poly(vinyl chloride)	Copper	Biotechnology
Polydimethylsiloxane	Gold	SERS*
Polymethylmethacrilate		Sensor
PEDOT:PSS	Silver/Gold	Electrochromic device
		Optical filters, Non-linear
poly(acrylonitrile)	Gold/Silver/Platinum	opticals, Sensors, Absorbers in different frequency bands

*Surface-Enhanced Raman Scattering

The unique structure of carbon nanotubes (CNTs) was identified in the early 1990s and since then it has attracted attention of researches all over the world¹⁶. CNTs are considered graphene sheets cylindrically curled with a high-length ratio, which gives them incredible electronic, mechanical and thermal properties¹⁶. Considering the outstanding properties of conjugated polymers (CP) and carbon nanotubes, the combination of both in a nanocomposite was inevitable. It was found that the coupling of CP/CNTs revealed synergistic effects with envisioned potential applications as supercapacitors^{17, 18}, sensors⁵, organic light emitting diodes (OLEDs)^{5, 8, 19}, solar cells⁵, high performance electrodes in rechargeable batteries⁸, electromagnetic shielding^{5, 20} and advanced electronic devices⁵. The properties revealed by the combinations of these compounds might be either a result of the functionalization of the CNTs by the CP, or the CPs are being doped with the CNTs⁵. It is also noteworthy that the electrical

properties of any nanocomposite it is dependent on the synthesis methods, which influences the interactions between the filler and the matrix⁸.

Despite the success of CP/CNTs nanocomposites, insulating polymeric matrices, such as cellulose and derivatives²¹⁻²³, polycarbonate²⁴, poly(methyl methacrylate)^{24,26}, poly(styrene)²⁶, and others, have also showed interesting optic/electronic properties at a lower cost when CNTs were incorporated (Figure 2). This issue is properly developed in a further chapter. Other carbon allotropes, such as carbon nanofibers^{20, 27}, fullerene²⁸⁻³⁰ and graphene^{20, 31-33} have also used as filler to enhance the electrical properties of nanocomposites.

Curiosity: Among the titanium dioxide particles, Rutile is commonly used in polymers as a white pigment. However, it is Anatase the TiO_2 spherical nanoparticle with diameters among 20 nm that is used to attained optoelectronic properties⁸.

2. Biodegradable Polymers

The evolution made over the years coupled with the exponential increasing advances on technology is translated in a constant search for materials improvement. As we have become more demanding, the rapid development of materials with tailored properties became essential, specifically in the case of conventional polymeric materials. These are petroleum-derived polymers applied in almost all industrial fields and consequently in all life sectors, as very durable products with tailor-made properties³⁴. Though, when these long-lasting polymers are used in products with a short life-span, such as in packaging, catering, surgery and hygiene³⁵, together with the intensive use, raised environmental problems related to waste management. Several strategies have been proposed to solve this problem, as creation of landfills, plastic incineration and recycling³⁴⁻³⁷. Unfortunately, these were not optimal alternatives due to the decreasing availability of landfills, toxic incineration emissions and the problem that not all the polymers can be recycled, as well as the energy consumption^{35, 38}. Therefore, the well-known waste disposal problems of polymers allied to the increasing price of oil and the increasingly demanding environmental standards stimulated the interest on biodegradable polymers, which were first introduced in 1980s³⁶⁻⁴¹.

The biodegradability is a material property that does not only depend on its origin but also on the chemical structure and the degradation environment of the material. This property is not exclusively associated with materials from renewable sources as starch, chitosan or cellulose, which are formed

during the growth cycle of organisms, but also with petroleum-derived polymers, as poly(glycolic acid), poly(lactic acid), poly(ϵ -caprolactone), poly(butylene succinate), among others (Figure 3)^{35, 39, 42, 43}. The biodegradation process according to Albertsson and Karlsson⁴⁴ occurs from the action of enzymes and/or the chemistry deterioration promoted by living organisms as bacteria and fungi or its secretion products^{39, 45}. The end-products of this process according the ASTM standard D-5488-94d and the European Standard EN 13432:2000, are carbon dioxide, new biomass and water or methane (depending if the process is aerobic or anaerobic)^{35, 43}. Nevertheless, it is worth to refer that the biodegradability definition is not worldwide accepted as equal, mostly due to the variability of environments and the reference points employed (degradation rate, composting, etc.)^{35, 38}. As a result, many different definitions have been officially adopted depending on the background of the defining organization and their particular interests^{34, 35, 38}.

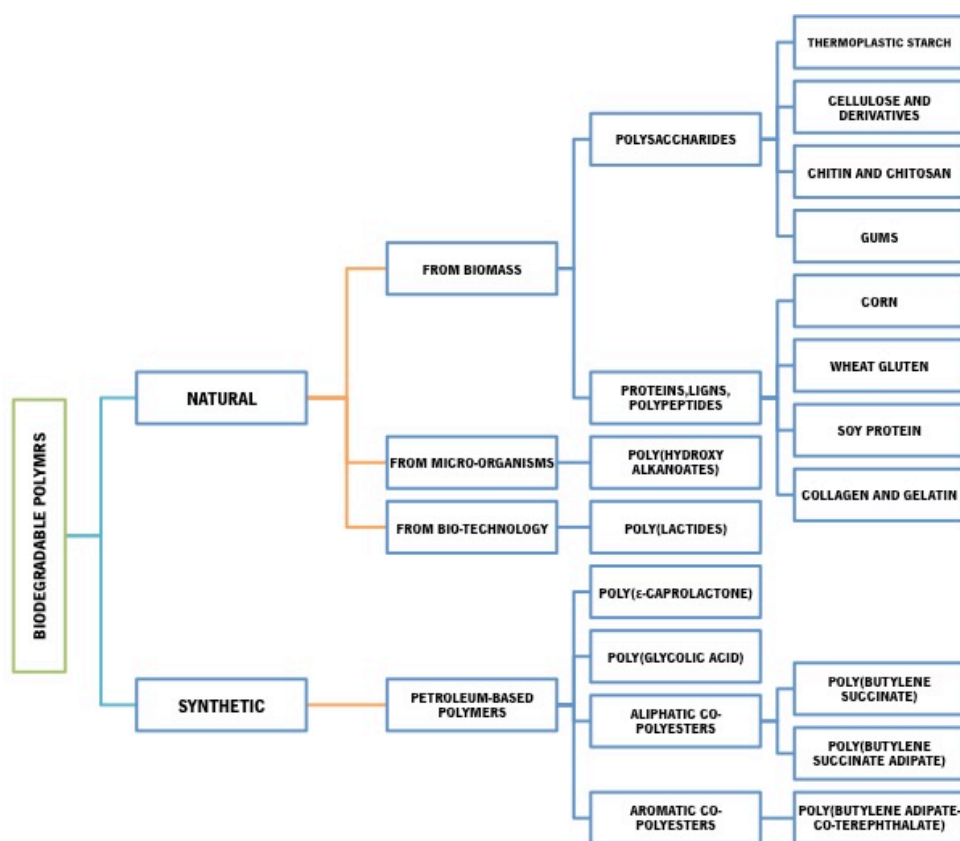


Figure 3 – Biodegradable polymers diagram.

Among the biodegradable polymers from renewable sources or the so called natural polymers, starch and cellulose can be produced at low cost and in large scale³⁹. Cellulose as the most abundant biomacromolecule is the main constituent of plants^{36, 41, 46-50}. It is mostly obtained from wood and cotton,

and the pulp is already being extracted from agricultural by-products as bagasse, stalks and crop straws⁵¹. Besides the plant origin, cellulose can also be produced from non-plant resources, such as bacteria (*Acetobacter xylinum*) and by sea creatures – tunicate cellulose (*Microcosmus fulcatus*)^{51, 52}. Cellulose is a polysaccharide composed of chains of D-glucose molecules also called anhydroglucose units (AGU), linked to 1,4-β-D-glucosidic bonds (Figure 4)^{37, 41, 48}. It is described as a complex three-dimensional polymer provided with hydroxyl functions placed at C-2, C-3 (secondary hydroxyl group) and C-6 (primary hydroxyl group), responsible for the intra and intermolecular hydrogen bonds and also for the hydrogen bond linkage to water molecules^{36, 41, 47, 48, 53, 54}.

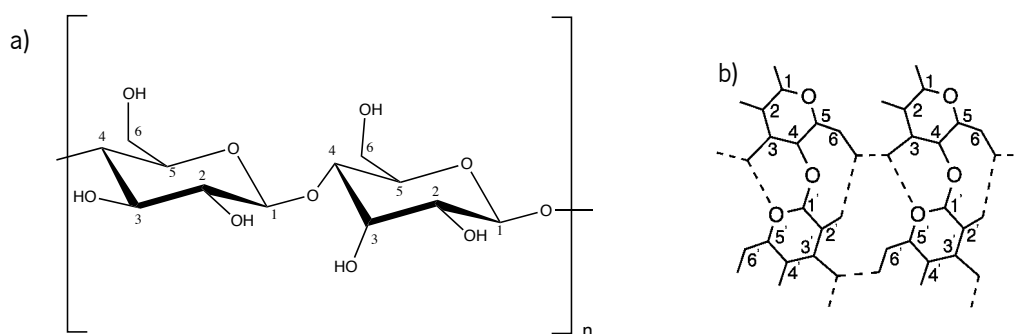


Figure 4 – a) Cellulose structure and b) Example of intra and intermolecular hydrogen bonding.

Cellulose is also known as a highly crystalline polymer with a fibrillary structure that displays both crystalline and amorphous domains (these last are more available to react in a chemical modification process)^{37, 41, 47, 52, 53, 55}. These cellulose characteristics and the high molecular weight of the polymer are directly related with the infusibility, and insolubility in almost all solvents, except aggressive hydrogen bond-breaking solvents such as N-methylmorpholine-N-oxide, which difficult the material processing^{41, 48, 56, 57}. Consequently, it is usual to convert cellulose into its derivatives to make it more processable and to reach some tailor properties^{37, 41, 48, 57, 58}.

Curiosity: Not all the polymers from renewable sources are biodegradable. Polythioesters are a group of polymers produced by bacteria, but also persistent to microbial degradation⁵⁹.

2.1 Cellulose Acetate

Cellulose acetate (CA) is one of the most important cellulose derivatives, which can be handled quite easily when compared to cellulose or to most of the other natural polymers^{49, 58, 60, 61}. It is used in a worldwide range of industrial applications from membranes, fibers, films, plastics, and filters to components in adhesives and also pharmaceutical products (Figure 5)^{41, 48, 49, 62-64}.

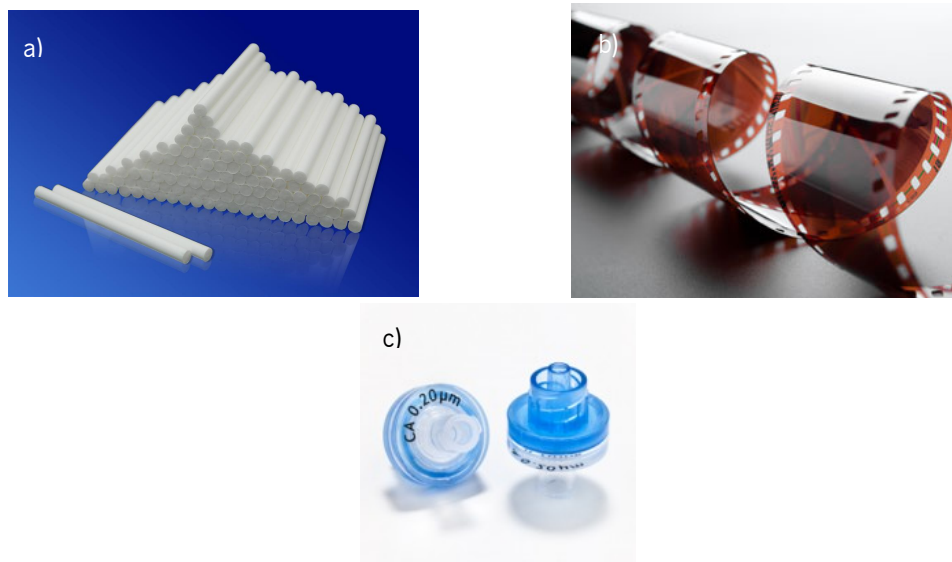


Figure 5 – Examples of cellulose acetate applications a) Filter rods of cigarette; b) photographic film; c) syringe filters.

Cellulose acetate was first prepared by France's B. Naudin and Paul Schützenberger in 1865 by heating cotton and acetic anhydride at 140 °C in a closed vessel⁶⁵⁻⁷². However, it was not until 1894 that the first industrial process was patented by Charles Frederik Cross and Edward John Bevan in the UK and CA was prepared using sulfuric acid or zinc chloride as catalyst at atmospheric pressure^{67, 68}. This material was essentially cellulose triacetate, which was not soluble in common solvents at the time, and only in 1903 an acetone-soluble CA was prepared by George Miles by partially hydrolyzing it^{64, 65, 67, 69, 70, 72, 73}. In the same year Arthur D. Little patented CA for its applications as a textile fiber and the Swiss brothers, Henri and Camille Dreyfus at Basel using Mile's acetone process produced photographic films in 1910 and acetate lacquers used to coat aviation cloth and on airplane wings at the outbreak of World War I (1914-1918) substituting the highly flammable nitrocellulose^{64, 67, 72-74}. With the end of war, the acetate fibers demand dropped but in 1919 the British Celanese company promoted the first acetate yarn and the generic term of "artificial silk" was adopted in 1924^{67, 72}.

The degree of substitution (DS) of CA, which corresponds to the average number of acetate groups in each anhydroglucose unit originally provided with three hydroxyl groups from cellulose, can vary between zero and three, where zero corresponds to natural cellulose and three to the completely substituted cellulose (cellulose triacetate)^{49, 75, 76}. As an example, in a CA with DS of 1.5, 50 % of the hydroxyl groups are acetylated and the other 50% are free⁷⁷. The substitution occurs preferentially on the C-6 and C-2 carbon positions of cellulose (Figure 6), and the introduction of the acetate groups increases its solubilization, changes the polarity and the aggregation behavior, but it also facilitates the reaction with others chemical species^{49, 75, 78, 79}. Since the introduction of a new group as acetate breaks the hydrogen bonds and introduces new interactions between substituents^{49, 75, 78, 79}. CA can also be produced in a range of different DS, the most common is 2.5⁸⁰.

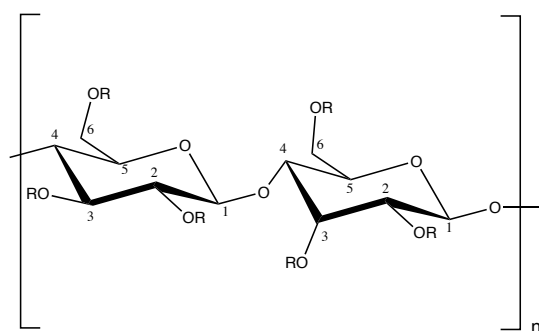


Figure 6 – Cellulose acetate structure; R = H or COCH₃(according to acetylation degree).

Despite it is accepted that cellulose is a biodegradable polymer, the cellulose acetate biodegradability was at first a controversial subject^{76, 80}. Some authors stated that CA with a high degree of substitution was biodegradable, while others disagree and others still consider that CA was only biodegradable after chemical modification^{41, 76, 80-83}. However, currently CA is recognized as a biodegradable polymer within the scientific community⁸⁰. Once it was found that a deacetylation initial step promoted by chemical hydrolysis or by acetyl esterase enzymes, a common microorganism, played a key role on CA biodegradation⁸⁰. Several studies have confirmed that CA is indeed biodegraded under aerobic or anaerobic conditions, and that the DS increase has also influence and is associated with a biodegradation rate decrease^{80, 84}. Once the CA structure deviates from the original readily biodegradable structure of cellulose. Even though the biodegradation rate is decreased, the biodegradation is not inhibited^{41, 76, 80, 81, 83}. CA polymer can also be photo-chemically degraded by UV radiation shorter than 280 nm (far UV light region). Although, far-UV radiation is not present in normal sunlight (max. 300 nm) and therefore CA is poorer photodegraded even having in consideration the

presence of impurities that could absorb in this region^{80, 85}. The presence of other substance that absorbs light, such as photosensitizers (triphenylsulphonium trifluoromethanesulfonate and diphenyliodonium trifluoromethylsulfonate) and some pigments as titanium dioxide (photocatalytic oxidation) generates radicals that react with CA structure promoting the degradation by near UV-light^{80, 84-87}.

Curiosity: Although compostable polymers are not the main issue of this work, it is of interest to refer that these are a subgroup of biodegradable polymers and are biologically decomposed under composting conditions. Therefore, compostable polymers are always biodegradable, while the reverse is not true.

3. Functional Compounds

Functional compounds are here defined as the components, which will meet the desired properties to create novel materials combined with the cellulose acetate. A brief overview of each component is essential to understand its selection in order to achieve new materials that may exhibit optic/electronic properties.

3.1 Carbon Nanotubes

The interest in carbon nanotubes by the observation of tubular forms of carbon with nanometric dimension were first brought to the scientific community attention in 1991, when they were first introduced by Sumio Iijima⁸⁸⁻⁹⁰. However, it was just in 1993 together with Berthume⁸⁸ and USA co-workers that the first carbon nanotubes were synthesized. Since their discovery, nanotubes have stimulated the development of studies in various fields, such as, physics, chemistry and material science and a phenomenal number of publications. These are carbon allotropes such as diamond, graphite, graphene and fullerene (Figure 7)⁹¹⁻⁹³.

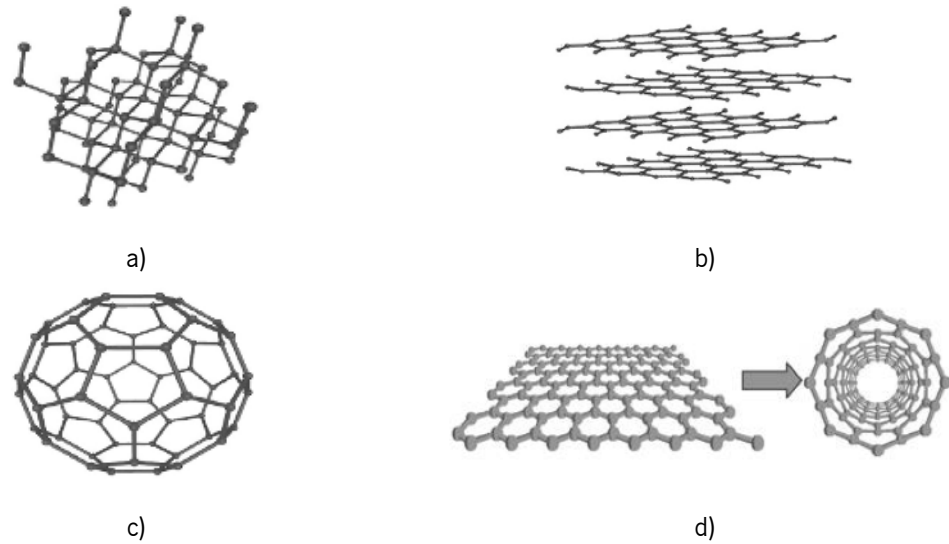


Figure 7– Carbon allotropes a) Diamond; b) Graphite (graphene is a single plate of graphite); c) Fullerene d) Carbon nanotubes^{88, 92}.

The tubular structure of CNTs with diameters in the nanometer scale (1 - 100 nm) and lengths that can reach millimeters is brought by the rolling up of graphene sheets (Figure 7)⁹⁴. These can be divided in two main categories: single-wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT), depending on the production process and the number of rolled-up planes^{32, 89-91, 94, 95}. While the first is constituted with only one rolled-up graphite plane, the second has several parallel and concentric graphite planes rolled-up with Van Der Waals interactions between layers (Figure 8)^{32, 89-91, 94, 95}.

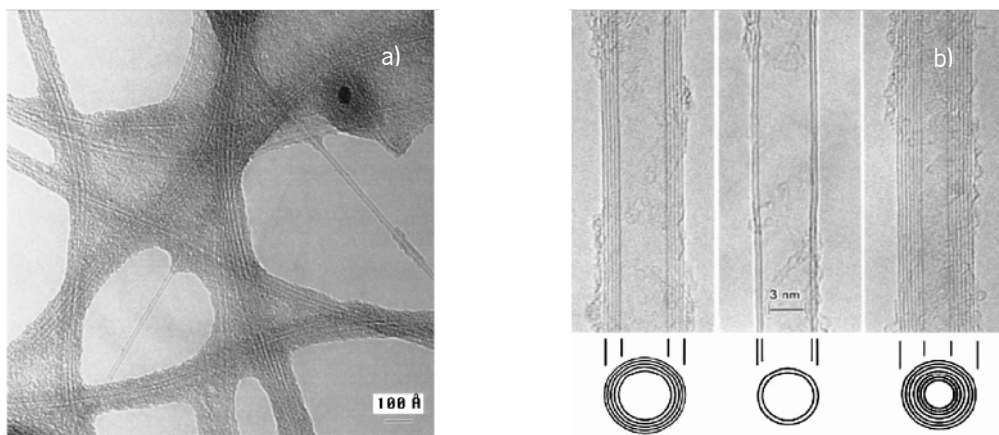


Figure 8 - TEM images of carbon nanotubes a) SWCNT; b) MWCNT with 5, 2 and 7 layers (from left to right)⁹⁴.

Depending of the rolling angle of the graphene sheet along an (m, n) lattice vector, CNTs acquire different chiralities, armchair ($\theta=0^\circ$, $(n=m)$), zig-zag ($\theta=30^\circ$, $(0, n)$) or chiral ($30^\circ < \theta < 90^\circ$, $(n \neq m)$) (Figure

9)^{90, 91, 95}. Along with the nanotube chirality, the (m,n) indices determine the diameter of the nanotube⁹⁰. These will directly affect the nanotube optical, mechanical and electronic properties (Figure 9)^{90, 91, 94}. Armchair nanotubes type and only one-third of the zig-zag nanotubes are considered metallic, while the rest are semiconducting^{90, 93}.

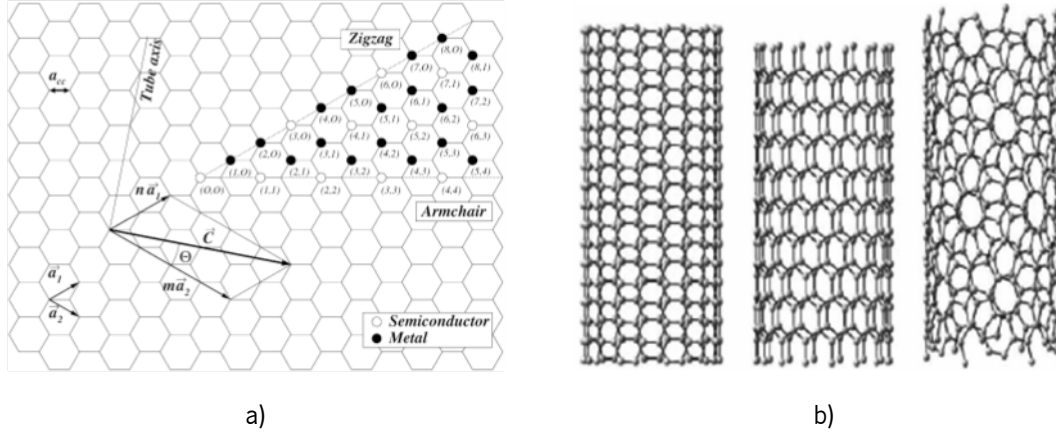


Figure 9 – Chiral forms of CNTs a) Graphene sheet diagram; b) CNTs structure with different chirality, armchair, zig-zag, and chiral (from left to right)^{90, 95}.

Carbon nanotubes have high flexibility, low mass density and excellent mechanical properties due to the high aspect ratio that can be greater than 1000 and by the strong sp^2 carbon-carbon bonds^{24, 94}. It has a very high Young modulus (1.2 TPa) and tensile strength (50 - 200 GPa)^{94, 96}. They also show good physical properties, electrical conductivity and thermal stability, according to Table 2^{24, 32, 89, 94, 97}.

Table 2 - Physical properties of CNTs and others materials^{32, 94}.

Properties	Graphite	Diamond	Fullerene	SWCNT	MWCNT
Density (g/cm³)	1.9 - 2.3	3.5	1.7	0.8	1.8
Electrical conductivity (S/cm)	4000 ^p , 3.3 ^c	10 ⁻² - 10 ⁻¹⁵	10 ⁻⁵	10 ² - 10 ⁶	10 ³ - 10 ⁵
Thermal conductivity (W/(mK))	298 ^p , 2.2 ^c	900 - 2320	0.4	6000	2000
Coefficient of thermal expansion (K⁻¹)	-1 x 10 ^{-6 p} 2.9 x 10 ^{-5 c}	[1 - 3] x 10 ⁻⁶	6.2 x 10 ⁻⁵	Negligible	Negligible
Thermal stability in air (°C)	450 - 650	< 600	±600	> 600	>600

p – in plane; c – c-axis

Therefore, CNTs gather very appealing properties that make them attractive for a wide range of applications in many scientific and technologic fields, as gas and biologic sensors, tips for atomic force microscope (AFM), photovoltaic cells devices, superconductors, electrochemical actuators and nanowires among others^{88, 94, 98, 99}. They can also be used as reinforcement agent when combined with other materials, like polymers^{24, 88, 89}. However, CNTs normally exist as a mixture with various chiralities, diameters and lengths²⁴. They are also provided with some defects and impurities²⁴. In addition, due to CNTs small size they are usually curled and twisted, and tend to easily form aggregates displaying only a small fraction of its potential when combined with polymers²⁴. Therefore, one of the main difficulties is to achieve a good dispersion in a polymeric matrix⁸⁹.

Although CNTs surface are characterized by a considerable chemical inertness, the surface functionalization aiming to improve their interaction with polymers by physical or chemical modification to attach specific molecules or functional groups has been performed^{24, 89, 100, 101}. CNTs can be modified through non-covalent interactions that concern physical adsorption and/or wrapping of polymers or other molecules and by covalent bonding, which involves the formation of strong chemical bonds with CNTs^{24, 89, 90}. The non-covalent functionalization comprises mainly the use of surfactants, such as sodium dodecylsulfate (SDS) and sodium dodecylbenzene sulfonate (NaDBBS) in order to decrease CNT aggregation in water, biomacromolecules, such as the immobilization of proteins and DNA, adsorption of aromatic molecules as pyrenes and porphyrins, and polymer wrapping (Figure 10)^{89, 90, 102}. This process led to CNT improvement dispersion in both aqueous media and organic solvents, due to polymer/CNT π -stacking interactions, electrostatic interactions or decoration of CNTs with micelles, which unfortunately might be weaker than covalent bonding avoiding an efficient transfer of the load when employed as filler in a nanocomposite^{89, 101}. Concerning the covalent approach, it is desirable to generate CNT derivatives with specific sidewall groups to improve their compatibility with solvents and polymers¹⁰¹. This is typically achieved with oxidative treatments using strong inorganic acids or oxidizing agents, that generates a high amount of waste and possibly damaging the CNT structure¹⁰¹. The functionalization by the oxidation with oxygen, air, concentrated sulfuric or nitric acid, aqueous hydrogen peroxide and acid mixtures, results in the attachment of carboxylic acid (-COOH) and hydroxyl (-OH) groups (Figure 10)⁸⁹. Among them, and despite the inevitably structural defects (especially if ultrasonication process is used) and the CNT shortening caused by oxidation, the functionalization with -COOH groups is more convenient than others due to the large variety of reactions that can be conducted by this group, i.e., this group can be used as precursor for further chemical reactions, such

as silanation, esterification, thiolation and polymer grafting^{89, 90}. Moreover, CNTs have been covalently functionalized with other groups, such as, thiocarboxylic and dithiocarboxylic esters, carbenes, nitrenes, electrophiles, peroxy radicals, and even fluorination, chlorination, bromination, hydrogenation and azomethine ylides dipolar cycloaddition were found as successful reactions^{89, 90, 102, 103}. Regarding the covalent functionalization with polymers, two main methodologies can be employed: “grafting from” and “grafting to”. The first methodology involves growing polymers from CNT surfaces via *in situ* polymerization of monomers initiated by chemical species present in sidewall and CNT edges²⁴. The main advantage of this approach is the possibility of efficiently grafting high molecular weight polymers, which growth is not limited by steric hindrance giving nanocomposites with high grafting density²⁴. Even so, a strict control of the initiator and substrate amount is required, as well an accurate control of the polymerization reaction conditions²⁴. Following this approach several reactions were already employed, such as atom transfer radical polymerization (ATRP), reversible addition-fragment chain transfer (RAFT), ring opening polymerization (ROP), free radical, anionic/cationic, reductive/oxidative polymerization, condensation reaction among others (Figure 10)^{24, 89}.

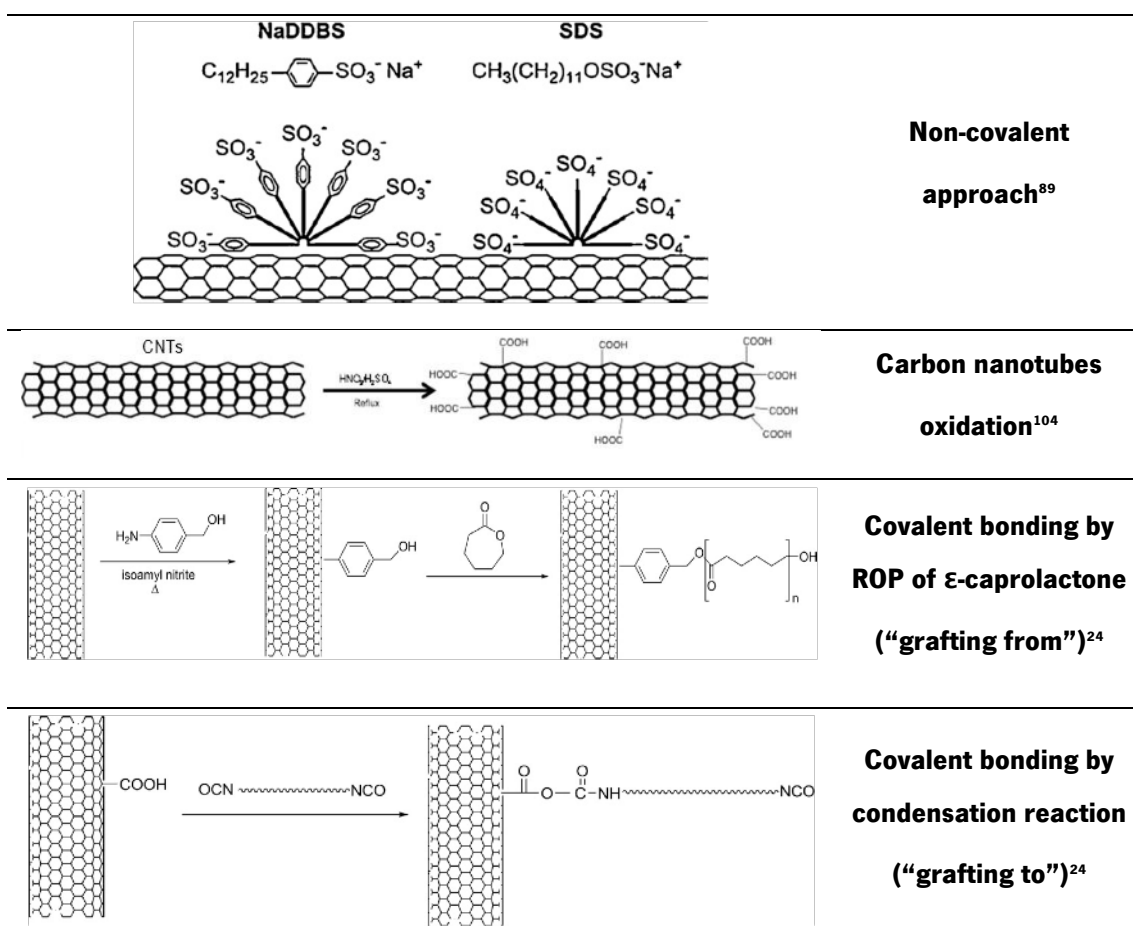


Figure 10 – Carbon nanotubes functionalization.

The second methodology “grafting to” involves the reaction among ready-made or commercially available polymers of controlled molecular weight with reactive species present in the CNTs^{24, 89}. The fact of using commercial polymers is already an advantage considering the “grafting from” method. However, a low grafting density is usually achieved due to sterically hindrance of additional macromolecules caused by the initial polymer chains binding²⁴. This method involves several reactions and different linkages among the CNTs and various polymers, such as the formation of ester or amide linkages between oxidized CNTs and polymers, the grafting initiated by a radical mechanism, nucleophilic addition, coupling reactions, cycloaddition, condensation and sonochemical reactions (covalent bonding of CNT/polymer by ultrasonication) (Figure 10)^{24, 89}.

Curiosity: Electron-beam (EB) irradiation can be used as an efficient method to modify CTNs with –COOH terminated groups, which turn to be useful sites to further modifications¹⁰¹. Also, it was observed that depending on the EB dose employed the pristine graphitic structure of the CNTs were deformed or destruct¹⁰¹.

3.2 Porphyrins

During the 20th century to the present, many occurring porphyrins and synthetic derivatives have been synthesized¹⁰⁵. The main structure of porphyrins is based on porphin, which consist of four pyrrole units linked at their β -positions by methin groups (=CH-) (Figure 11)¹⁰⁶⁻¹¹⁰. Also, the electronic spectra of porphyrins are commonly interpreted as $\pi - \pi^*$ transitions, with a characteristic sharp, intensive absorption band called Soret or B band between 400-500 nm with molar absorptivities of the order of 10^5 and less intensive bands denominated Q bands between 500-700 nm¹¹⁰⁻¹¹⁶. The theoretical interpretation of porphyrin electronic spectra is commonly provided by the four-orbital Gouterman's model developed in 1960s¹¹¹⁻¹¹⁴. This model tries to conjugate the free-electron model of a cyclic polyene and the Hückel's orbital molecular model¹¹⁷. Beyond that, Gouterman consider the resonance character of the intern ring of 18 π -electrons delocalized, since according to Hückels rule of aromaticity ($4n+2$, where $n=4$), where only 18 π -electrons of the porphyrin 22 π -electrons are delocalized^{106, 107, 117, 118}. Figure 11 shows numbered porphin and also the tautomerism resulted from an intermolecular double-proton transfer first suggested by Becker, Bradley and Watson¹¹⁹, and the path of the 18 π -

electron cyclic polyene ring^{120, 121}. The Greek letters are used to distinguish the types of carbon position in the porphin macrocycle^{105, 119}. The positions 2,3,7,8,12,13,17,18 are referred as β -positions, the 1,4,6,9,11,14,16,19 as α -positions and the 5,10,15,20 as meso-positions^{59, 120}.

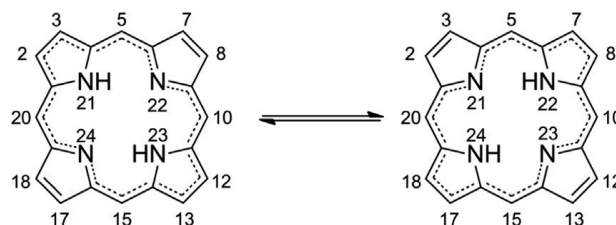


Figure 11 – Example of a numbered porphin according the IUPAC nomenclature¹²⁰.

A porphyrin is essentially a porphin with peripheral substituents. According to these substituents and to porphyrin nature, porphyrins can be grouped in three main categories (with examples)¹²²:

- 1) Porphyrins prepared from natural heme (which is a specific porphyrin with an iron molecule incorporated and part of hemoglobin): protoporphyrin IX, hematoporphyrin IX, meso-porphyrin IX, deuteroporphyrin IX (Figure 12)¹²³;
- 2) Alkyl substituted porphyrins: etioporphyrin (EtioP), octaethylporphyrin (OEP) (Figure 12);
- 3) Meso-tetraphenyl and derivatives: meso(tetraphenyl)porphyrin (TPP), meso(tetratolyl)porphyrin (TTP), meso(pentafluorophenyl)porphyrin (TPFPP), meso(tetra 4-pyridyl)porphyrin (Figure 12).

There are also water soluble porphyrins, such as, tetraphenylporphyrin sulfonate (TPPS), tetrakis-(aminophenyl)porphyrin (TAPP), tetrakis-(4-carboxyphenyl)porphyrin (TCPP) and tetrakis-(4-methylpyridyl)porphyrin (TMPyP)¹²². The same porphin numeration is applied to porphyrins.

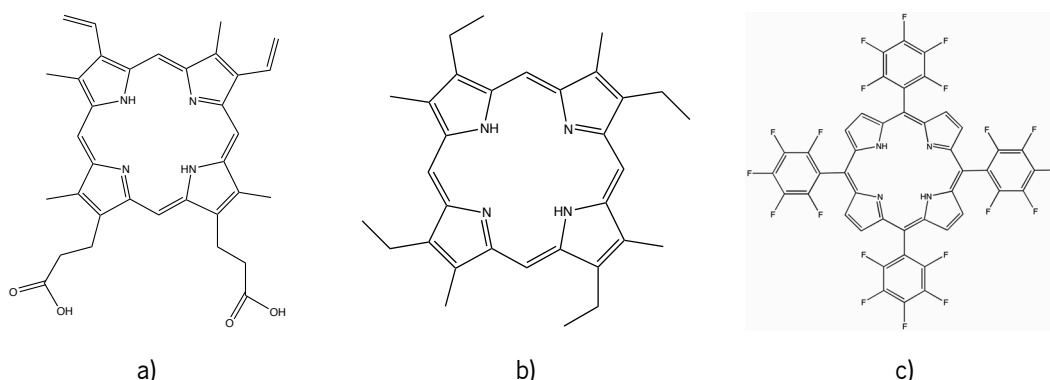


Figure 12 – a) Protoporphyrin IX b) Etioporphyrin c) Pentafluorophenyl porphyrin.

In this work, porphyrins with meso-substituents (i.e., at the 5,10,15,20 positions) will be described in more detail. The synthesis of this type of porphyrins was first proposed by Rothmund^{106, 124-126} and it is

based on the reaction between pyrrole and aldehyde under acidic and anaerobic conditions at high temperatures (140-200°C) (Figure 13). However, due to reaction low yields it has been repeatedly modified and improved, in particular by authors as Adler and Longo in the 60s, and Lindsey in 80s^{106, 126}.

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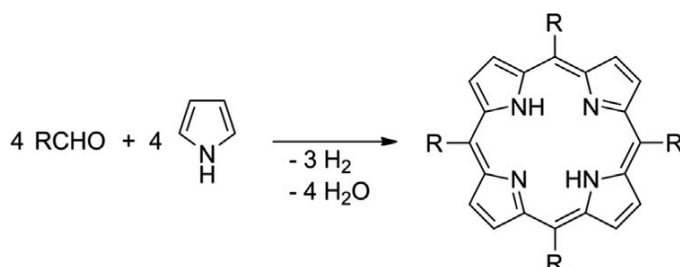


Figure 13 – Synthesis of meso-porphyrins by Rothmund¹⁰⁶.

Porphyrins are not only interesting macromolecules because of the wide variety of possible peripheral substituents that can be attached and the structural changes made in the macrocycle itself, but also by the capability to form complexes with most of the elements in the periodic system^{106, 110}. This allows a great variety of properties, such as reactivity, electronic, magnetic properties and even biological functionalities can be found¹⁰⁶. These particular porphyrins are known as metalloporphyrins and are usually synthesized by metallation of the free-base porphyrin with metal ions in solution (Figure 14).

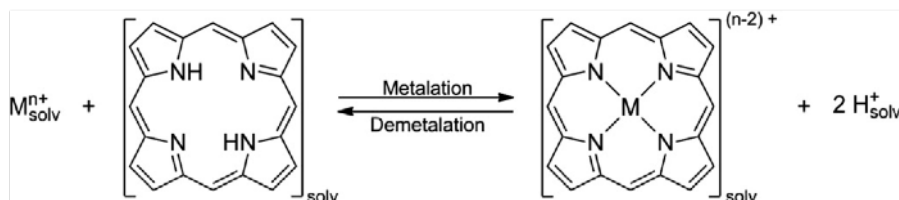


Figure 14 – Example of the metallation and demetallation of a porphyrin in solution¹⁰⁶.

The process of metal atom incorporation in the porphyrin are known to occur through different stages: the deprotonation of the porphyrin to produce the dianion P^{2-} and the dissociation of the metal atom from the metal precursor, followed by the coordination of the four nitrogen atoms to the metal. However and based on spectroscopic data, it was first proposed by Fleischer and Wang¹³⁰ the formation of a “sitting atop complex” intermediated (STA complex), where both metal ion and pyrrole hydrogen atom are bind to the porphyrin center^{106, 110, 130, 131}. From this data, it is actually believed that the metallation mechanism includes the partial desolvation of the metal ion, the SAT formation and deprotonation¹⁰⁶.

¹³². However, and even with some experimental evidence of the existence of the SAT complex provided by NMR, EXAFS (extended X-Ray adsorption fine structure), UV-Vis and FTIR, a final proof of its existence remains elusive and it is still in debate^{106, 133}. Porphyrins act as dibasic acids (has two hydrogen ions to donate to a base), and the respective metal complex usually exists in II oxidation state. When the metal ion coordinated has a charger greater than two, it leads to the addition of further steps, such as, charge neutralization that occurs with axial ligands^{106, 134}. Metallation is also preferred to occur in concentrated solutions, since diluted solutions tend to slow the metallation process and longer reaction times that can lead to the decomposition of the starting material or product¹³⁴. It may also occur in the absence of strong acids, which can retard the metallation process ¹³⁴. The facility of the coordination of a metal ion in a porphyrin it is known to depend mainly of the available space between the porphyrin core and the ionic radius of the metal ion^{106, 110}.

Metalloporphyrins are therefore macromolecules of great interest having numerous applications due to its properties, from light-gathering processes, metal-catalyzed reductions, chemical biosensors, photovoltaic cells (Figure 15), spectrometric reagents, photoinduced energy transfer processes (Figure 15), to the use as a coating material for quartz microbalance-based chemical sensor^{110, 115, 135-137}. Due to its potentiometric response to anions, several metalloporphyrins can also be employed as electroactive components in membrane of ion selective electrodes¹¹⁰.

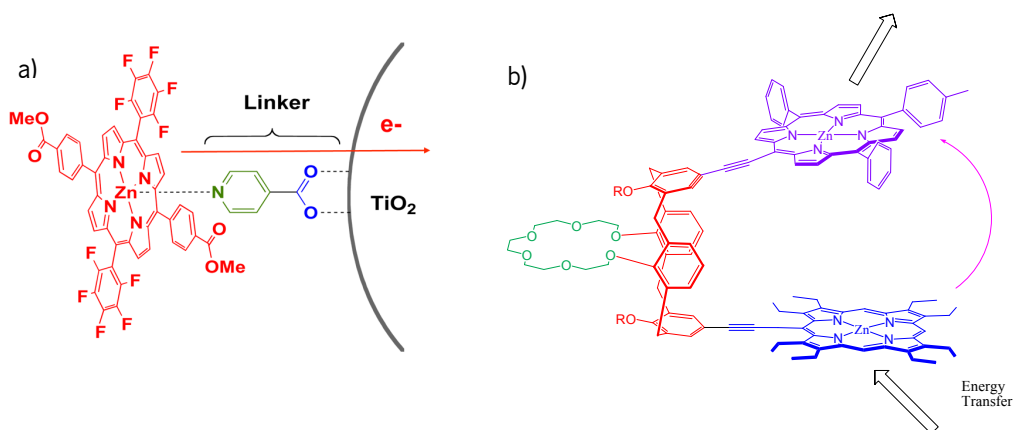


Figure 15 – a) Zinc-porphyrins attach to a linker showed to be relevant for the optimization of dye sensitized solar cells¹³⁶; b) photoinduced energy transfer observed in the tweezer molecular system containing porphyrins, calixerene and crown ether¹³⁷.

Curiosity: Besides heme, other porphyrins are also an important part of living systems, as chlorine (magnesium reduced porphyrin) in chlorophyll, which is active in the photosynthesis apparatus, the enzyme cytochrome P450 and cobalt complexes in vitamin B12, which are involved in biological

phenomena^{106-110, 115, 138, 139}. Also, porphyrins that already exist in nature are usually β -substituted and its main function is to bind a metal ion which act as a center for a significant biochemical event^{109, 138}.

3.2.1 Porphyrin Arrays

The assembly of porphyrins and metalloporphyrin arrays has attracted considerable interest, since the relative ease of synthesis, stability and properties diversity provides an advantageous class of building blocks for the construction of multicomponent systems¹⁴⁰. Furthermore multiporphyrins have been considered materials for several applications, molecular sensing, transport of energy charge, catalyze, molecular electronics and new photonic materials, molecular wires and molecular switches, nonlinear optics, electrochromic, molecular elements of information storage and even for photodynamic therapy tumors inspiring the continuous synthesis of porphyrin assemblies¹⁴⁰⁻¹⁴². Porphyrin arrays are also promising candidates for selective molecular recognition, which results from the specific geometry of cavities by porphyrin planes¹⁴⁰. Another field largely studied is the porphyrin core modification, which can be achieved by replacing the pyrrolic nitrogen atoms with other heteroatoms, by rearranging the methane bridges (porphycene), or by introducing one or more additional pyrrole moieties resulting in expanded porphyrins, or even by the inversion of one of the pyrrole rings resulting in inverted or confused porphyrins (Figure 16)^{140, 143}.

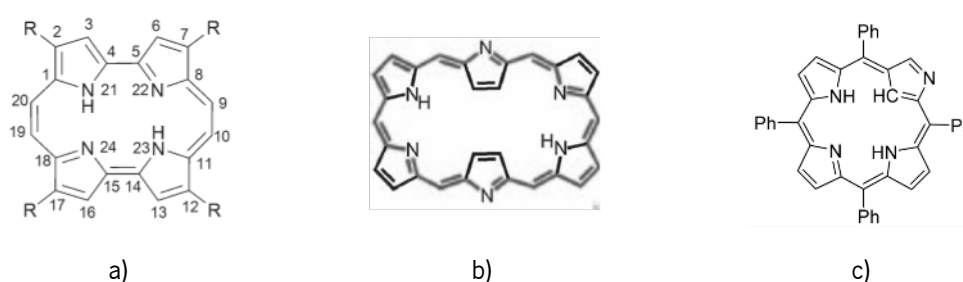


Figure 16 - Examples of a) Porphycene¹⁴³; b) Expanded Pophyrin¹⁴⁴ and c) Confused porphyrin¹⁴⁵.

The porphyrin assemblies by direct linking through the meso-meso carbons without any spacer has been reported, as also the covalent binding using bridging element among the meso-meso, meso- β or β - β carbons of two porphyrins (Figure 17)^{140, 141}. Other alternative is the face-to-face porphyrins, which are held in parallel conformation due to its rigid or multiple linking that allows the coordination of the

metal ion to act in concert in catalytic processes, such as in the reduction of dioxygen and dinitrogen (Figure 17)^{140, 141, 146, 147}. Porphyrins can also be held together by other interactions than coordination bonds, such as electrostatic interactions and hydrogen bonding among substituents located on the porphyrin periphery^{140, 148, 149}.

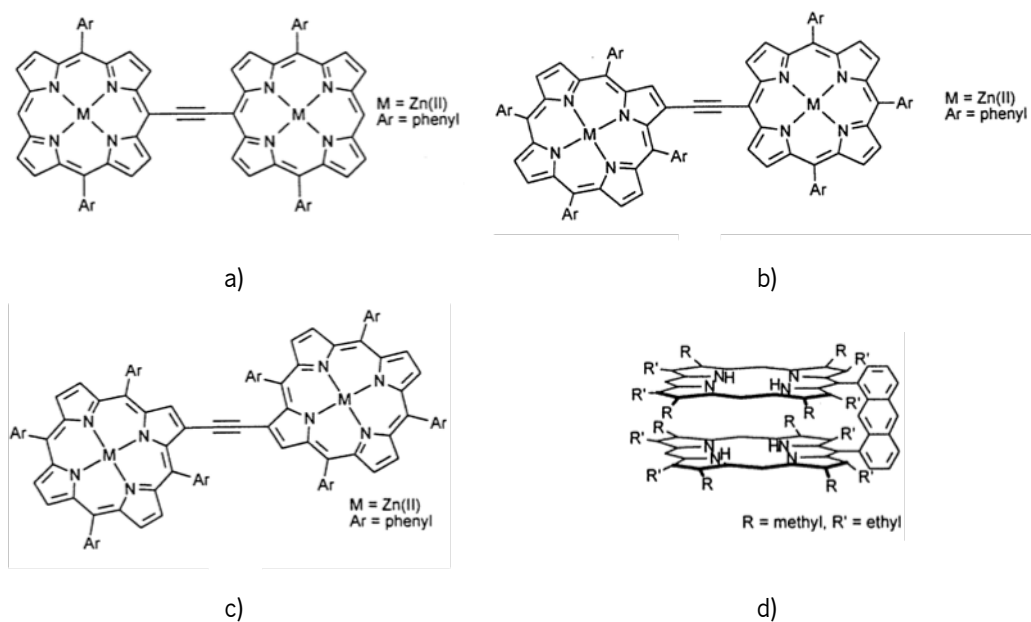


Figure 17 – Porphyrin assemblies by direct linking, a) meso-meso; b) β –meso; c) β - β and d) Face-to-face¹⁴⁰.

Therefore, a methodology based on coordination chemistry can be found, where multiporphyrins arrays can be grouped, as presented in Figure 18.

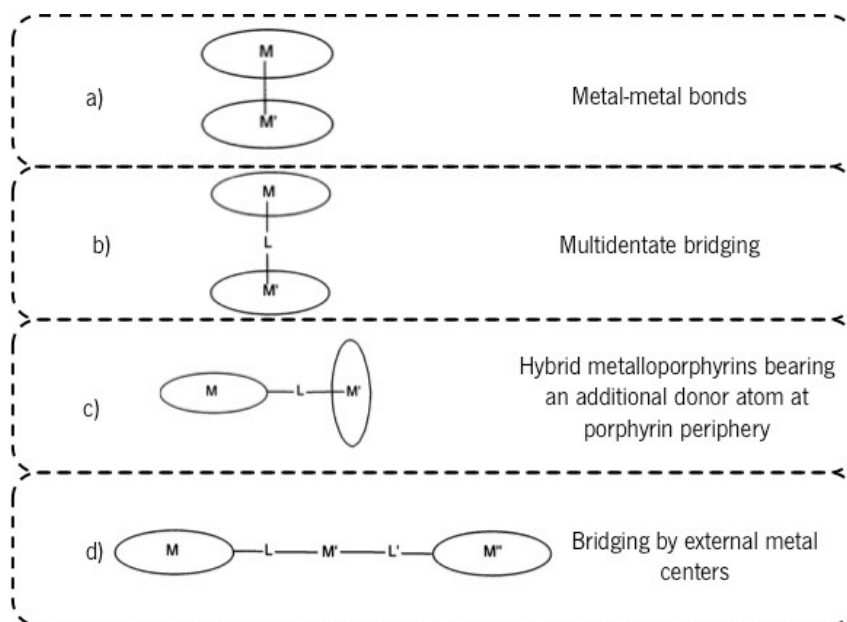


Figure 18 – Methodology based on coordination chemistry for multiporphyrins (adapted from¹⁴⁰).

The group constituted by hybrid metalloporphyrins with additional donor atoms at porphyrin periphery (c) and the bridging with external metal centers (d) has been the most studied (Figure 18)^{140, 141, 149, 150}. However, this work will focus in porphyrin arrays with multidentate bridging (b), which is considered a very rich class of metallomultiporphyrin systems and where the coordination bonds metal-ligand are thermodynamically as strong as covalent bonds but kinetically more labile¹⁵¹. These features allow an easier synthesis and modification of novel molecules with new functionalities, as well as the repeatedly assembled/disassembled under control conditions promoted by the presence of coordination sites¹⁵¹. Therefore, metalloporphyrin arrays have draw major attention considering the possibility of building long and rigid porphyrin structures suitable for the next generation of electronic devices¹⁵². The applications prospective of these new materials are huge due to their optical and electronic properties, such as, light harvesting¹⁵³⁻¹⁵⁵, molecular tweezers^{140, 152, 153}, sensors¹⁵³, dye-sensitized solar cells¹⁵³, nonlinear optics^{147, 152}, conductive and luminescence materials^{147, 152} and biomedical imaging¹⁴⁷.

Among various multidentate ligands, aliphatic and aromatic amines have been the most employed and have already proven its successful incorporation as bridging ligands^{152, 156, 157}. Although the substitution of aliphatic by aromatic amines, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), and pyrazine (pyz) adds an intermolecular stabilization and therefore are frequently used to attained porphyrin arrays (Figure

19)¹⁵⁶. Thus, several researchers have successfully assembled metalloporphyrin arrays with different lengths according to reaction conditions and metalloporphyrin/ligand ratio using DABCO and pyz as bridging ligand and metalloporphyrins with various center metals, such as ruthenium (Ru)¹⁵⁷⁻¹⁶⁰, zinc (Zn)^{153, 161, 162}, iron (Fe)¹⁵⁹, osmium (Os)¹⁵⁹, magnesium (Mg)¹⁵² and rhodium (Rh)^{157, 163}. The substitution of DABCO and other small ligands with longer multidentate bridging molecules, such as the widely used 4,4'-bipyridine (bpy) showed to promote the construction of larger porphyrin arrays by axial coordination¹⁶⁰. These conjugated structures were successfully prepared with metalloporphyrins with transition metals such as, Zn^{146, 153, 156, 164-166}, Rh^{157, 163, 167, 168}, Fe¹⁵⁹, Ru^{157, 159}, Os¹⁵⁹, cobalt (Co)^{147, 156} and Mg¹⁵². Others nitrogen ligands already studied included hydrazine^{169, 170}, 4,4'-bipyrimidine^{157, 163}, 3,3'-azopyridine¹⁶⁷, s-tetrazine¹⁷¹, diaza-pyrene¹⁷⁰, 5,5'-dicyano-2,2'-bipyridine¹⁵⁷ and bis(pyridyl)urea¹⁷² (Figure 19).

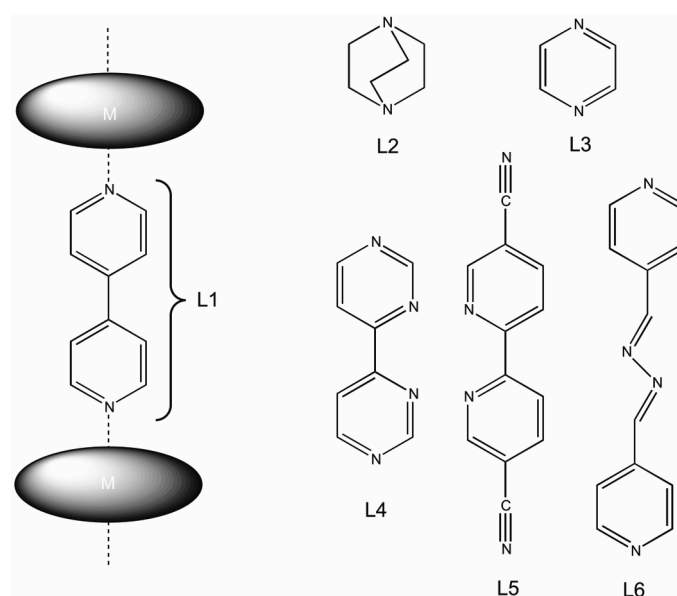


Figure 19 – Metalloporphyrin arrays with different axially bounded ligands. L1=bpy; L2=DABCO; L3=pyz; L4=4,4'-bipyrimidine; L5=5,5'-dicyano-2,2'-bipyridine; L6=1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene.

Curiosity: Shelnutt et al^{142, 173} have constructed porphyrin nanotubes with lengths in the order of microns and diameters ranging 50-70 nm, by the combination of electrostatic and hydrophobic interactions of porphyrins containing ionic substituents in aqueous solutions, respectively porphyrin a) and b) of Figure 20.

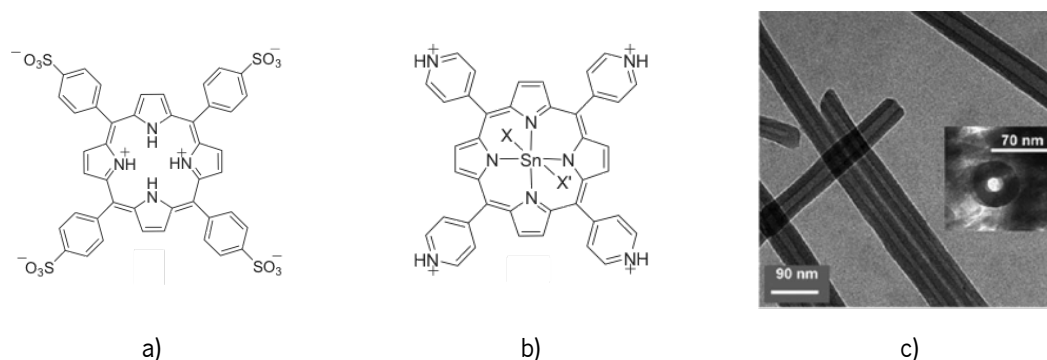


Figure 20 – a) free-base porphyrin; b) Sn^{IV} -porphyrin and c) TEM image of porphyrin nanotubes¹⁴².

4. Processing Techniques

Along the years, melt mixing has become a processing technique broadly employed in the preparation of polymer nanocomposites^{89, 174, 175}. This technique permits the development of new functional polymers by direct mixing the molten polymer with the respective filler usually under shear stress (Figure 21)^{89, 174}. The simplicity of this process along with the approximation to compounding and fabrication facilities commonly used in commercial practice turns melt mixing one of the most promising methods to nanocomposites preparation¹⁷⁶. Furthermore, it is considered an economical and flexible technique where the use of solvents is not required, making it an environmentally benign process^{89, 174, 176}.

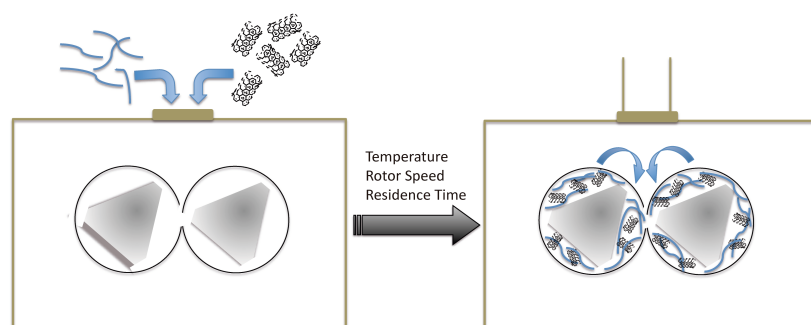


Figure 21 – Example of a melt mixing scheme.

Concerning literature it can be found an extensive application of melt mixing to prepare nanocomposites with silicates, where intercalation and clays exfoliation was already successfully achieved as well the improvement properties of carbon nanotubes nanocomposites^{89, 174, 177}. Though, the main scientific technical challenge of this process is the achievement of an efficient dispersion of the filler on the polymer matrix, which may be resolved by adjusting the processing conditions or even by

modification of the polymer or/and the filler⁸⁹. The nanocomposites prepared by adding CNTs will be discussed in more detail in Chapters III and IV.

The other processing technique also employed in this work to prepared materials with optic/electronic properties is electrospinning, which was first studied by Cooley¹⁷⁸ and Morton¹⁷⁸ in 1902, Zeleny¹⁷⁹ in 1914 and patented by Formhals^{48, 180} in 1934. However, it was only in 1994 that the electrospinning concept was created and started to gain much attention as an alternative and efficient technique to produce nanofibers from the sub-micron to nanometer diameter range by applying an electric field by means of a DC source to draw a polymer (solution or melt)^{48, 178, 180-184}. The basic requirements are a syringe with a needle to carry the polymer solution, a high voltage power supply to provide the electric force for drawing the jet and a collector or target to collect the fibers (Figure 22)^{48, 178, 180, 182, 183, 185}. It is a simpler, easier, versatile and flexible technique able to replace other nanofiber production methods such as phase separation, template synthesis, self-assembly and drawing among others^{48, 178, 180, 184, 186}. Concerning the main experimental parameters that were found to affect the morphology of the electrospun fibers, the processing (voltage, flow rate, tip-to-collector distance), solution (viscosity, polymer Mw, concentration, surface tension) and the ambient (temperature and relative humidity) parameters showed to be the main factors¹⁸³. Table 3 shows the general effects on fiber morphology promoted by varying the electrospinning parameters.

Table 3 – Morphology effects in electrospun nanofibers¹⁸³

<i>Processing parameters</i>	<i>Effect</i>
Voltage	Decrease in fiber diameter with increase in voltage
Flow rate	Decrease in fiber diameter with decrease in flow rate, generation of beads with too high flow rate
Tip-to-Collector distance	Generation of beads with too small and too large distance, minimum distance required for uniform fibers
<i>Solution parameters</i>	<i>Effect</i>
Viscosity	Low causes bead generation; high increases fiber diameter, beads disappear
Concentration	Increase in fiber diameter with increase of concentration
Molecular Weight	Reduction in the number of beads and droplets with increase of molecular weight
Surface Tension	No conclusive link with fiber morphology, high surface tension results in instability of jets
Conductivity	Decrease in fiber diameter with increase in conductivity
<i>Ambient parameters</i>	<i>Effect</i>
Temperature	Increase in temperature results in decrease in fiber diameter
Relative humidity	High humidity results in circular pores on the fiber

Electrospinning confers unique properties to nanofibers, mainly based on the fibers large surface area, lower structural defects and enhanced mechanical properties¹⁸³. Its versatility permits to electrospun fibers made of different materials from polymer to even ceramics allowing the application of these nanofibers in several fields, from biomedical to clothing, filtration, sensors and energy^{178, 183, 185}. Among the vast number of available polymers, cellulose acetate has been a material of choice for research in multiple industries from textiles to biomedical¹⁸². The abundance and the “green” properties such as biodegradability and the good solubility in a wide range of solvents among with the wide array of applications have turned this polymer a focal point¹⁸². Therefore, an intensive research amongst the CA electrospinning including the processing parameters study, the solvents selection and the huge number of possible applications for electrospun CA (Figure 22) can be easily found in literature¹⁸².

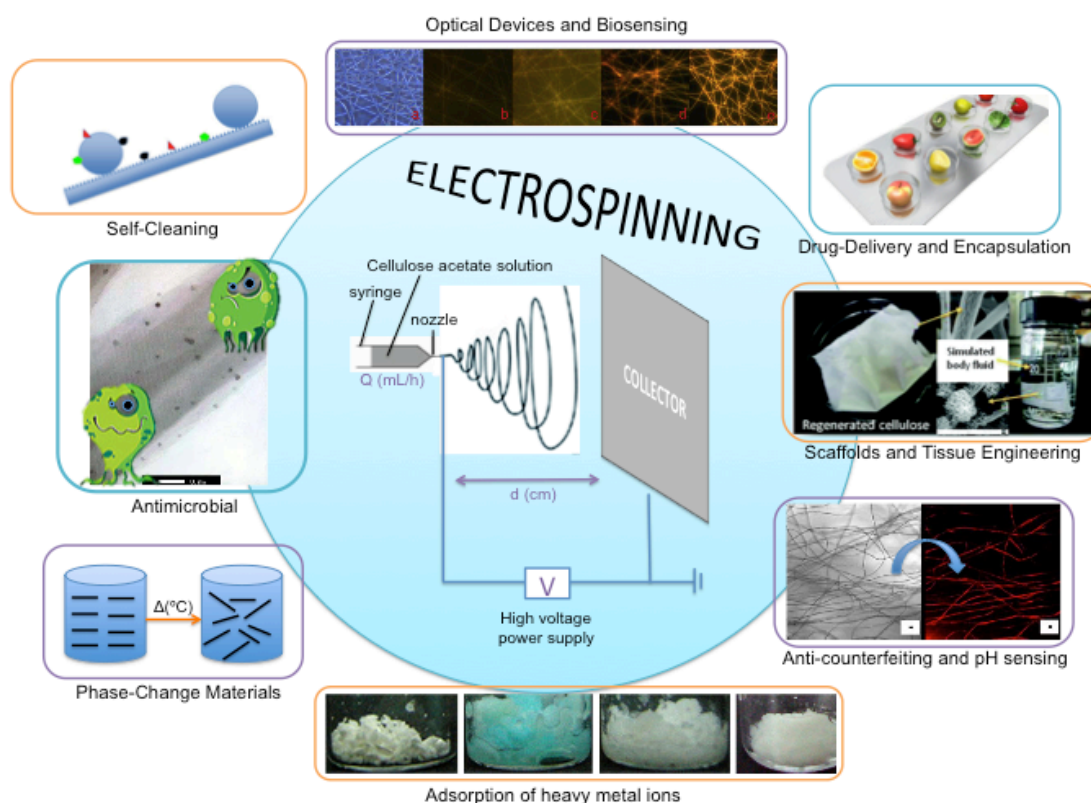


Figure 22 – Electrospun CA applications: adsorption of heavy metal ions¹⁸⁷, phase-change materials¹⁸⁸, antimicrobial mats^{189, 190}, self-cleaning¹⁹¹, optical devices and biosensing^{192, 193}, drug-delivery and encapsulation¹⁹³⁻¹⁹⁶, scaffolds and tissue engineering^{193, 197}, anti-counterfeiting and pH sensing¹⁹⁸.

The selection of solvents showed to be of major importance since it has direct influence on the fibers morphology¹⁹⁹. The webs density, the fibers diameter, presence of beads and the fiber shape (helical, ribbon-like) can be controlled by varying the solvent or the ratio between a system of solvents¹⁹⁹. Therefore, cellulose acetate has already been electrospun from single solvent systems to tertiary solvent system. Although, it was possible to electrospun CA from individual solvents as acetone (Ac), chloroform, methanol (MeOH), formic acid, N,N-dimethylformamide (DMF), acetic acid, and dichloromethane (DCM) it showed not to be the ideal option^{182, 199-206}. Thus the addition of a co-solvent is preferentially used to optimize the electrospinning process^{199, 200}. In this case, the combination of solvents with different properties, such as a high boiling point solvent (dimethylacetamide, water) and a relatively low boiling point solvent (acetone, DCM) permits an easier electrospinning process²⁰⁰. Binary solvent systems, such as acetone/dimethylacetamide, methylethylketone/dimethylsulphoxide, dichloromethane/ethanol, chloroform/methanol, acetic acid/water and acetic acid/acetone, among

others were therefore preferentially used to electrospun CA¹⁹⁹⁻²⁰⁵. Some researchers have also employed a tertiary system made of acetone, dimethylformamide and trifluoroethylene²⁰¹.

Curiosity: CA can also be blended with other polymers that cannot be electrospun individually, such as poly(ethylene oxide), poly(ethylene glycol) that acts as a phase-change material and poly(urethane), which showed to reinforce the fibers tensile strength²⁰⁷⁻²⁰⁹. Also, the electrospinning of CA with silk fibroin showed heavy metal adsorption capabilities, which can be employed in wastewater, while the blending with egg albumen enable the formation of edible films^{195, 210}.

5. Main Objective

The literature review summarized the intensive research and the development of new and tailored properties materials caused by the demanding current market and the constant evolution of technologies. This work aims to contribute to this research field and add novel knowledge. Therefore, the main objective it is to develop cellulose acetate based materials with optical and/or electronic properties. To achieve this objective two main functional compounds were chosen, carbon nanotubes and porphyrins. These when incorporated in the polymer matrix are expected to accomplish the referred desired properties. Since CNTs are known as excellent fillers with amazing conductive properties, and porphyrins are conjugated macromolecules known by its optical but also by the possibility of manifest electrical properties. In addition and owing to the rising environmental awareness the processing techniques employed in this work are absent of solvents, such as melt mixing, or use a diminutive volume to prepare nanofibers such as electrospinning.

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THE INFLUENCE OF MELT MIXING ON THE STABILITY OF CELLULOSE ACETATE AND ITS CARBON NANOTUBE COMPOSITES

Cellulose derivatives, such as cellulose acetate (CA), are commonly used due to their ease of processing. These polymers present interesting mechanical properties and biodegradability, but low thermal stability under melt processing conditions. Composites of carbon nanotubes (CNTs) and cellulose derivatives are expected to present enhanced properties, depending on the effect of nanotubes on polymer structure and thermal properties. This work aims to investigate the influence of melt mixing on the stability of CA and its CNT composites. Composites with 0 wt%, 0.1 wt% and 0.5 wt% CNTs, as-received and functionalized with pyrrolidine groups, were prepared using a batch mixer and an extruder. Chain scission of CA occurred during processing, but the effect was considerably reduced in the presence of CNTs. The incorporation of small amounts of CNTs (with or without functionalization) decreased polymer degradation by thermomechanical effects induced during polymer processing.

Delgado-Lima A., Paiva M.C., Machado A.V., The influence of melt mixing on the stability of cellulose acetate and its carbon nanotube composites, J. Polym Eng, 2016, DOI:10.1515/polyeng-2015-0388

1. Introduction

Carbon nanotubes have been extensively used as a reinforcement along the last years, mainly due to their high performance and excellent electrical properties^{1, 2}. The integration of these nanometric particles with high area to volume ratio, in polymer matrix, has the potential to enhance the composite properties at small CNT loads³. Several polymers have been investigated as matrix for carbon nanotube composites⁴. Natural polymers are particularly interesting as they do not pose environmental problems at the end of their lifetime⁴. Among all biopolymers, cellulose is the most abundant natural polymer on earth, presenting excellent mechanical properties due to its highly crystalline structure. This characteristic turns out to be a major drawback for polymer processing, as it renders the polymer infusible and insoluble in common solvents and thus difficult to shape⁵⁻⁷. To overcome this problem, cellulose acetate is a commonly used derivative that is processable, biodegradable and a non-toxic polymer^{5, 6, 8}. It can be employed as a matrix to develop materials with tailored properties by adding carbon nanotubes or others compounds. Due to industry demand for cost effective production, the bio-nanocomposites should be produced by industry-ready technologies such those based on melt mixing⁹. Nowadays most CA or cellulose/CNTs novel composites are produced using solution-based techniques¹⁰⁻¹⁷. Switching to melt mixing processing would bring the advantage of a low environmental impact due to the solvent-free nanocomposite preparation^{9, 18}. Since cellulose-based polymers are prone to thermal degradation, it is important to investigate the effect carbon nanotubes addition on polymer structure and molecular weight during processing using conventional melt mixing techniques^{19, 20}. Also, CNTs are frequently covalently functionalized to improve the polymer/CNT interface in the composite. The functional groups bonded to the CNT may react with the polymer, inducing reactions that would not take place otherwise. In this work the CNTs surface was functionalized by the 1,3-dipolar cycloaddition of azomethine ylides using a one-pot solvent free experimental procedure reported elsewhere²¹. The functionalized nanotubes, CNTNH, were characterized by thermo-gravimetric analysis showing a weight loss of approximately 15 % at 800 °C, similar to the results obtained in previous studies²¹. According to those studies, the functional groups bonded to the CNTs under these conditions are mainly pyrrolidine (Figure 1). Also and in comparison with the work of others authors as Li M. et al ²², who bonded carboxylic acid groups, this kind of functionalization is both less aggressive for the CNTs and for the environment, since it does not use combinations of strong oxidizing acids (Figure 1). Thus, nanocomposites of CA/CNT were prepared by melt mixing using 0.1 and 0.5% wt. CNTs, both in a

batch mixer and a mini twin-screw extruder. The produced materials were characterized in terms of the CA molecular weight distribution and thermal properties.

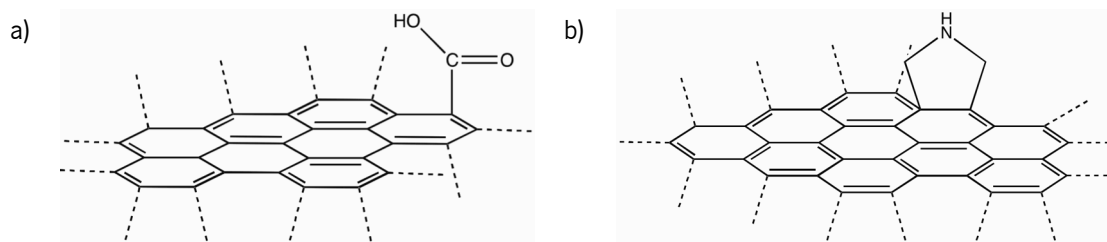


Figure 1 – a) Carbon nanotube functionalization with acidic groups; b) less aggressive functionalization with pyrrolidine groups.

2. Materials and Methods

2.1 Materials

The CNTs were multiwall from Nanocyl (Nanocyl SA, Belgium), NC 7000, produced via a catalytic carbon vapor deposition process with an average diameter and length of 9.5 nm and 1.5 μm , respectively. All of the chemicals were purchased from Sigma-Aldrich (Sigma-Aldrich Química, S.L., Sintra, Portugal), including benzyloxy- carbonylglycine (Z-Gly-OH 99%), paraformaldehyde (reagent grade), diethyl ether, ethanol and n-hexane, and were used without further purification. The CA with an acetylation degree of 39.8 wt% was also acquired from Sigma-Aldrich.

2.2 Preparation of the Nanocomposites

The functionalization of the CNT surface was accomplished *via* 1,3-dipolar cycloaddition reaction of the azomethine ylide formed by reaction of Z-Gly-OH with paraformaldehyde, according to procedure reported elsewhere²¹. Cellulose-based nanocomposites were prepared by melt compounding using two equipments: an intensive batch mixer (Haake Rheomix 600 OS, $v=60\text{ cm}^3$) and a MicroLab co-rotating twin-screw extruder Rondol (L/D=20/1, nominal screw diameter=10 mm, die=2 mm). Nanocomposites

with 0.1 and 0.5 wt.% of functionalized and non-functionalized carbon nanotubes were prepared in the batch mixer at 230 °C with a rotor speed of 100 rpm during 8 minutes. In the extruder, the samples were produced under constant processing conditions, at a screw speed of 100 rpm and a temperature profile along the extruder barrel between 130 and 250 °C using a throughput of 1.4 g/min. In both cases cellulose acetate and carbon nanotubes were previously dried in an oven at 80 °C overnight and pre-mixed before processing.

2.3 Characterization Methods

The molecular weight of cellulose acetate and respective nanocomposites was determined by Gel Permeation Chromatography (GPC) using a GPC Waters Alliance 2695. The samples were dissolved in tetrahydrofuran - THF (1.5 mg/mL), the homogeneous solution was filtered through a syringe filter (hydrophobic polytetrafluoroethylene) with a pore size of 0.45 µm before injection. The measurements were performed at a flow rate of 1 mL/min and 80 µL for each solution were injected in a system containing three PLgel MIXED-B columns (7.5 x 300 mm, particle size 10 µm) at 25°C and a refractive index-detector at respectively 35°C.

Differential scanning calorimetry (DSC) measurements (Table 1) were performed on a Perkin Elmer Diamond equipment under flowing argon atmosphere between 30 and 270 °C at a heating rate of 10 °C/min. The melting temperature was determined as the peak onset temperature and the cristallinity degree was calculated using Table 1, where ΔH was determined for each sample, Φ corresponds to the mass fraction of the CNTs for the nanocomposites, and the value of ΔH_f^0 of cellulose acetate was 58.8 J/mol²³.

$$\chi_c (\%) = \frac{\Delta H_f (Sample)}{(1 - \phi)\Delta H_f^0 (CA)} \times 100 \quad \text{Equation 1}$$

Thermogravimetric analysis (TGA) measurements were performed on a TGA Q500 from TA Instruments under a nitrogen constant flow. CNTs functionalization was confirmed by a temperature sweep between 100 and 800 °C at 10 °C/min, starting with an isothermal plateau at 100 °C during 2 min. The analysis of the nanocomposites was performed by a temperature sweep between 30 and 600 °C at a heating rate of 10 °C/min to evaluate the thermal stability of the material.

3. Results and Discussion

3.1 Gel Permeation Chromatography

Gel permeation chromatography chromatograms of the polymer matrix before and after processing are presented in Figure 2. Before processing, CA presents a lower retention time, which is associated with higher molecular weight. After processing in a batch mixer, HK, and twin-screw extruder, ME, the chromatograms curves shifted to higher retention times, indicating a molecular weight decrease. This may be enhanced by hydrolysis of the glycosidic bonds, due to residual moisture, accelerated by temperature and catalyzed by acetic acid product of deacetylation²⁴⁻²⁶. Also, the CA processed in the ME systematically showed higher molecular weight compared to the CA processed in the HK. In spite of the higher shear forces developed in the ME, the longer residence time in the HK (8 min in HK vs. 4 min in ME) seems to have a strong effect on polymer chain scission. These samples also show broader peaks when compared to CA before processing, which can be associated to a higher polydispersity. In order to understand the effect of the processing method on CA molecular weight, the percent variation of the retention time (RT(%)) at the curve maximum, (RT_{max}), was measured for each material, relative to as received CA (RT_{CA}) using Equation 2.

$$RT(\%) = \frac{RT_x - RT_{\text{CA}}}{RT_{\text{CA}}} \times 100 \quad \text{Equation 2}$$

RT(%) is proportional to the polymer average molecular weight, the greater RT corresponding to the lower polymer average molecular weight (Figure 2). Therefore, it is evident that the presence of CNTs, either pristine or functionalized, decreased the polymer degradation, and this effect is independent of their concentration, at least from 0.1 to 0.5 wt.% of CNTs. The presence of the CNTs in this case could act as a physical barrier for the acetic acid produced during the deacetylation of CA, delaying the chain-scission of the nanocomposite, since the produced acetic acid promote the rupture of the glycosidic bonds. All the nanocomposites processed in the HK showed greater CA degradation compared to the extruded ones.

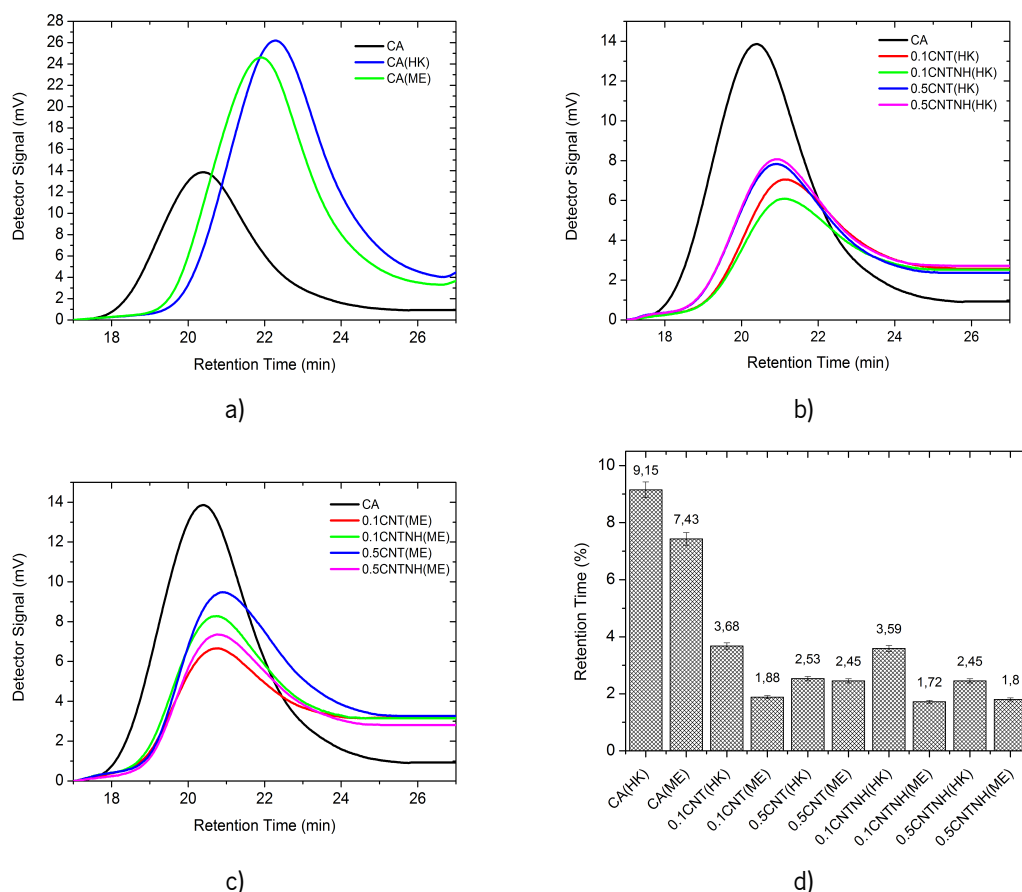


Figure 2 – a) Gel permeation chromatography chromatograms of cellulose acetate before and after processing; b) and c) GPC chromatograms of cellulose acetate from the composites prepared in the batch mixer, HK and mini-extruder, ME, respectively, compared with pure CA processed by the same process; d) % variation of retention time of CA and nanocomposites.

3.2 Thermal Stability of Nanocomposites

The thermograms of CA before processing (CA), after processing in a batch mixer (CA(HK)) and in the mini-extruder, (CA(ME)) (Figure 3) present an onset of thermal degradation, under nitrogen at 323, of 342 and 349 °C, respectively. Moreover, the polymer is completely degraded at approximately 360, 385 and 392 °C, respectively.

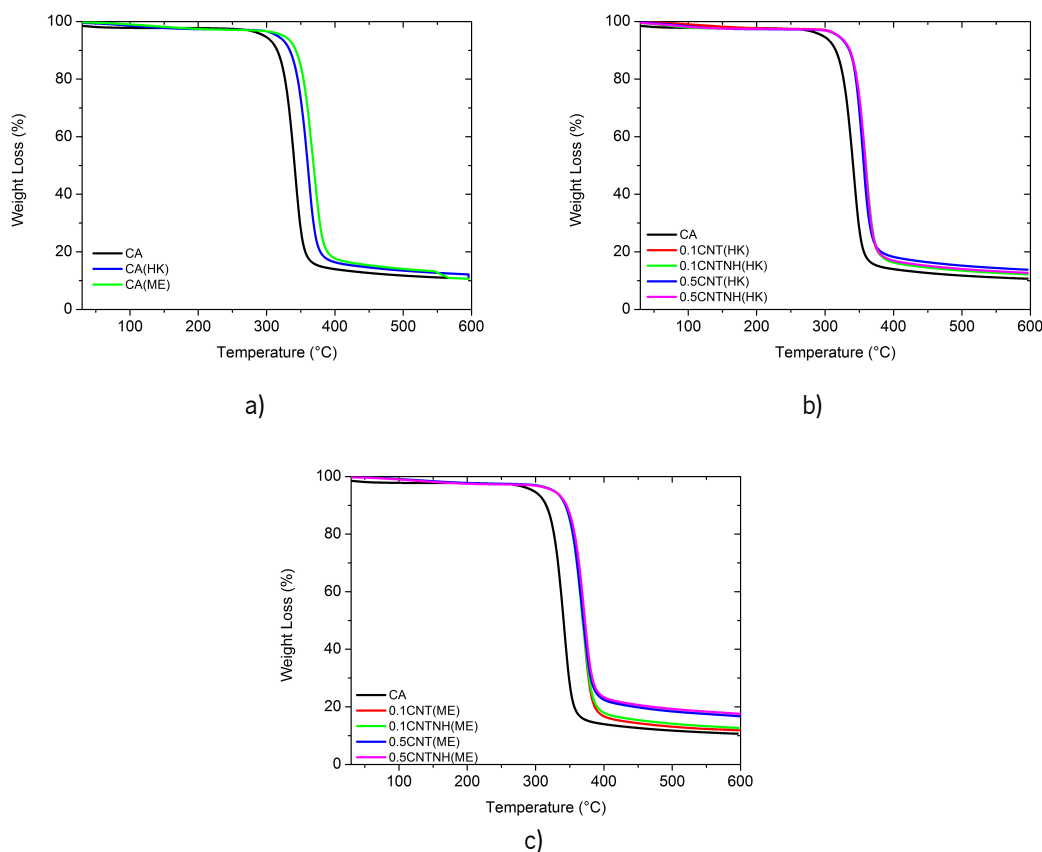


Figure 3 - Thermal stability of a) pure cellulose acetate and processed CA; b) pure CA with carbon nanotube CNT and functionalized nanotubes CNTNH processed in the Haake mixer; and c) in the mini-extruder.

According to Zavastin et al.²⁷ the weight loss of CA corresponds to the pyrolysis of the polymer backbone followed by deacetylation. Pure CA exhibits lower thermal stability before processing compared to CA after processing, in spite of its higher molecular weight. Li. M. et al.²² observed that the incorporation of CNTs functionalized with carboxylic groups on the cellulose acetate polymer improved the thermal stability of the nanocomposite. In the present study, a similar trend is noticed for nanocomposites prepared using CNTs or functionalized CNTNH (Figure 3). Although, CA/CNTs nanocomposites showed a lower molecular weight comparing to the as-received CA polymer, this result indicates that the incorporation of CNTs could lead to the stabilization of the CA polymer matrix, resulting in the improvement of the thermal stability of CA/CNTs nanocomposites. In this case, the CNTs may be increasing the thermal conductivity, homogenizing the composite temperature and reducing thermal gradients generated across the insulating material, thus reducing thermal degradation, and enhancing its thermal stability. The CNT may also provide a physical barrier against the diffusion of the volatile products generated during thermal decomposition, such as, acetic acid for the CA polymer matrix, which may catalyze polymer degradation. This physical barrier effect was already observed on poly(terephthalate of ethylene)/CNT and on poly(ethylene 2,6-naphthalate)/CNT

nanocomposites^{28, 29}. The samples prepared in the ME show higher thermal stability, probably due to the higher molecular weight of these materials compared to those prepared in the HK (Figure 3). Table 1 presents the DSC results obtained for the glass transition, onset melting temperature and the cristallinity degree of pure cellulose acetate and nanocomposites. The onset melting temperature and the degree of cristallinity of cellulose acetate show a similar trend, as the results obtained by TGA (Figure 3). Cellulose acetate nanocomposites prepared in the ME exhibits higher melting temperature (T_m) than the materials prepared in the HK, which can be associated to the larger degradation during samples preparation in the latter. The crystallization degree (χ_c) calculated is also in agreement with the previous analyses showing a measurable cristallinity, although incipient, for the samples processed in the HK and the ME. The crystalline domains could originate on the organization of the shorter macromolecular chains formed due to chain-scission during processing. Furthermore, the presence of the functionalization in the CNTs did not affect significantly the glass transition and melting temperature, as well as the cristallinity degree.

Table 1 – Thermal properties of cellulose acetate and nanocomposites.

Samples			T _g (±1°C)	T _m (±1°C)	χ_c (%)
CA			208.0	-	-
CA(HK)			190.6	206.2	3.9
CA(ME)			188.7	215.3	2.9
CA+0.1%	CNT	HK	187.2	208.0	3.8
		ME	190.9	216.6	3.6
	CNTNH	HK	190.8	209.4	4.3
		ME	189.5	216.0	4.3
CA+0.5%	CNT	HK	190.7	209.2	6.3
		ME	189.1	217.0	5.6
	CNTNH	HK	190.7	213.1	6.3
		ME	193.1	217.7	5.5

CA, Cellulose acetate; CNT, carbon nanotube; CNTNH, functionalized nanotubes; HK, batch mixer; ME, mini-extruder; T_g, glass transition temperature; T_m, melting temperature; χ_c , crystallization degree.

4. Conclusions

The effect of CNTs and functionalized CNTs with pyrrolidine groups on the polymer structure and thermal properties of cellulose nanocomposites during its preparation by melt mixing was successfully investigated. The incorporation of small amounts of CNT (with or without functionalization) enhanced the composite stability by delaying the polymer degradation by thermo-mechanical effects induced during polymer processing. Despite polymer degradation, the processed CA and respective nanocomposites presented higher thermal stability compared to the as-received CA. The functionalized CNTs could withstand the processing conditions, since the composites thermal properties were similar to those of the composites with non-functionalized CNT. The samples prepared in the mini-extruder experienced less degradation during processing, emphasizing the relevance of the processing conditions on the final composite properties.

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IV

CELLULOSE ACETATE/CARBON NANOTUBE COMPOSITES BY MELT MIXING

Cellulose acetate is produced from a natural polymer and presents excellent properties, finding applications in a variety of areas. Unlike cellulose, this polymer is melt processable and may be molded into parts, as well as, formed into fibers or films. In this context, the production of conductive cellulose acetate composites that may be processed into conductive fibers, or integrated into parts to provide specific functionalities, is an area of increasing interest. The present work aims to prepare electrically conductive composites based on cellulose acetate and carbon nanotubes by melt mixing. The nanocomposites were produced with as-received and chemically functionalized nanotubes, using a batch intensive mixer and a twin-screw extruder. The morphology of carbon nanotube dispersion, the rheological behavior and the electrical conductivity of the final composites were evaluated. The rheological percolation was achieved for the composites with 0.5 weight % of CNT, for both as-received and functionalized, produced by extrusion, while the electrical percolation was observed only for the composites with pure CNT.

Delgado-Lima A., Paiva M.C., Machado A.V., Cellulose acetate/carbon nanotube composites by melt mixing, Journal of Polymer Research (submitted).

1. Introduction

Along the years the extensive production of conventional/non-biodegradable polymers has brought environmental issues related with plastic waste management, which could be potentially solved by its replacement with biodegradable polymers¹⁻³. Due to the increasing demand of environmental friendly materials, biodegradable polymers and green processing techniques have attracted the attention and their applications opened into a wider range of sectors besides medical, tissue engineering, agriculture and biotechnology, as electronics, automobile and construction^{2, 4-6}. Cellulose is an example of a biodegradable polymer which is also an abundant polysaccharide easily modified to yield a derivative such as cellulose acetate^{7, 8}. Cellulose acetate is a melt processable polymer with excellent mechanical properties and an attractive aspect, and may be processed by current industrial polymer melt processing techniques^{9, 10}. Besides the controversial subject about CA biodegradability by some authors, it is currently recognized as a biodegradable polymer within the scientific community¹¹⁻¹³. Like the other polymers, it may reach tailored properties through composite preparation, using specific reinforcements to convey the target properties¹⁴⁻¹⁶. Carbon nanotubes (CNT) are a class of carbon-based nanoparticles with high electrical conductivity and excellent mechanical properties, frequently used to prepare electrically conductive polymer nanocomposites¹⁶⁻²².

The achievement of electrical conductivity on polymer/CNT nanocomposites at low incorporation ratios requires the establishment of a conductive pathway throughout the matrix forming a percolating network, which depends on the CNT dispersion state²². The incorporation of small amounts of CNT minimizes the negative effect of CNT agglomerates upon the composite rheological and mechanical properties, and also reduces the negative economical impact²². The main objective is to achieve good dispersion of the CNT in the polymer matrix during nanocomposite preparation and to establish strong interfacial bonding, simultaneously developing a percolating network and enhancing the composite mechanical properties^{16, 23, 24}. However, when incorporated in a polymer matrix the CNT have a strong tendency to agglomerate due to their physical entanglement and to Van der Waals interactions among them, hindering their efficient wetting with the melted polymer and decreasing the effective stress transfer from the polymer to the CNT, thus limiting the improvement in composite properties^{16, 23, 25}. The enhancement of the polymer/CNT interactions has been achieved through CNT surface modification using a range of chemical and physical approaches, frequently based on treatment with strong oxidizing

acids, causing the CNT breakage and reducing their aspect ratio, consequently leading to a loss of CNT and composite properties²⁴.

Several polymers have been used to prepare CNT nanocomposites, but there are few examples in the literature concerning cellulose acetate (CA), particularly through melt compounding. Li et al.²⁶ prepared CA/CNT nanocomposites by melt compounding with as-received CNT and with CNT functionalized with carboxylic groups (COOH). They demonstrated the establishment of a specific interaction between the acid group and the CA ester groups, that lead to improved interfacial adhesion, as well to a higher thermal stability and dynamic mechanical properties, when compared to the nanocomposites prepared with as-received CNT²⁶. Despite the enhancement of the thermal and mechanical properties, the CNT acid functionalization showed a negative effect on the electrical properties of the nanocomposite. The electrical volume resistivity of the functionalized CNTs was higher and could be attributed to the deterioration of the graphene structure during the aggressive functionalization²⁶. Despite this example, most literature of CA/CNT nanocomposites concern solvent-based composite preparation techniques, which are usually less environmental friendly. Gang Ke^{27, 28} covalently modified CNT with CA using 2,4,6-trichloro-1,3,5-triazine as an intermediate to prepare a potential material to be used in applications that need specific sorption and insulation, as cigarette filters. Luo et al.²⁹, Ahmad et al.³⁰ and Badawi et al.³¹ have also incorporated CNT into cellulose acetate, in the form of membranes. The first combined the electrospinning and layer-by-layer techniques to achieve a material for tissue engineering applications, while Ahmad et al.³⁰ and Badawi et al.³¹ prepared membranes for CO₂/N₂ gas separation and water filtration, respectively, by phase inversion with functionalized CNT.

Therefore, the main goal of the present study is to investigate the effect of incorporating as received CNT and pyrrolidine-functionalized CNT (CNTNH) in the preparation of cellulose acetate nanocomposites, as well as, the effect caused by the preparation of the nanocomposites using different melt processing techniques – a batch process (Haake intensive mixer) and a continuous process (twin-screw extrusion).

2. Materials and Methods

2.1 Materials

Multi-Wall Carbon Nanotubes NC 7000 were obtained from Nanocyl SA, Belgium. According to the supplier, these CNT were produced via catalytic carbon vapor deposition (CCVD) achieving typical average diameters and lengths of 9.5 nm and 1.5 μm , respectively. Cellulose acetate with an acetylation degree of 39.8 wt.% ($M_n \approx 50\,000\text{ g/mol}$) was employed as polymeric matrix and supplied by Sigma-Aldrich.

2.2 Sample Preparation

2.2.1 Nanocomposites

The CNT were covalently functionalized with pyrrolidine groups under mild reaction conditions as described elsewhere ³². The reaction conditions used for the functionalization were 250 °C during 3 hours. This procedure was used to test the effect of functionalization on the dispersion and compatibilization of the CNT in the CA matrix.

The nanocomposites were prepared by melt compounding using two approaches: i) an intensive batch mixer Haake Rheomix 600 OS, $v=60\text{ cm}^3$ (HK) and ii) a MicroLab co-rotating twin-screw extruder Rondol C3045 (ME) with $L/D=20/1$, nominal screw diameter=10 mm, die=2 mm, and feeding rate of 1.37 g/min. The screw profile is composed of two main zones, the drag, which also comprises the feed zone with conveying elements and the mixing zone with kneading elements staggered at 60° and 90° (Figure 1). The conveying elements are known to control the speed of transport and distributive mixing, while the kneading elements induce chaotic mixing from different hydrodynamic stress levels promoting variable scales of distributive/dispersive mixing ³³. Cellulose-based nanocomposites with 0.1 and 0.5 wt.% of as-received and functionalized CNTs were prepared in both equipments. For the batch process a temperature of 230 °C and 100 rpm was applied for 8 minutes. Similar samples were produced in the mini-extruder at a screw speed of 100 rpm and using the temperature profile presented in Figure 1.

In both cases, CA and CNT were previously dried in an oven, weighted and mixed in powder form before processing.

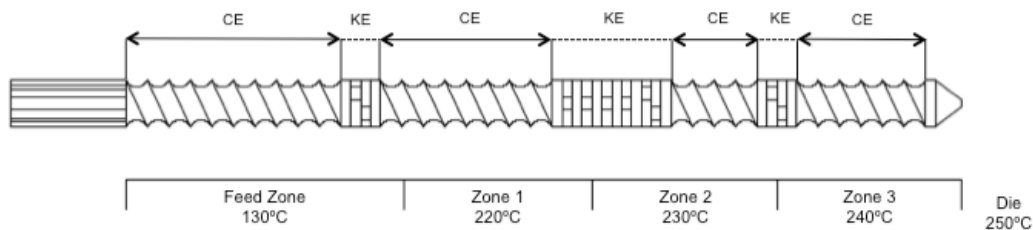


Figure 1 - Screw configuration and temperature profile; CE – Conveying Elements; KE – Kneading Elements.

2.2.2 Preparation of samples by compression molding

The characterization of the electrical and rheological properties of the composites prepared by both techniques was performed on compression molded plates and disks, produced on a Moore Hydraulic Heated Press. For the rheological measurements, the composites prepared in both equipments were molded into disks with 25 mm diameter and 1 mm thickness. For the electrical measurements, rectangular plates with 85x75x1 (length x width x thickness, mm³) were prepared for the batch mixer composites. The electrical resistivity of the composites prepared on the mini-extruder was measured directly on the extruded filaments. The compression molding of plates and disks was performed at 250 °C applying a maximum pressure of 25 bar and cooling under pressure until the press temperature dropped to 60°C.

2.3 Characterization Methods

The dispersion of the CNT agglomerates formed during processing was analyzed by optical microscopy using a BH2 Olympus transmission microscope. Thin sections of 3 μm thickness were cut from the extruded filaments perpendicularly to the filament axis direction using an ultra-microtome Leica EM UC6 equipped with a glass knife with an angle of 45°. Samples were also cut along the filament axis direction and the analysis results showed a comparable agglomerate morphology to the perpendicular direction, indicating that no considerable orientation effects were induced during extrusion³⁴. The microscope images were collected with a Leica DFC280 camera coupled to the microscope, using a 20x objective and 3.3x eyepiece. The quantitative particle analysis was performed by means of a digital

image processing software Leica Application Suite 4.4 and a minimum area of $8.80 \times 10^4 \mu\text{m}^2$ from at least 4 different cut sections were analyzed for each sample and composition. The data collected from the image processing was used to plot the statistical distribution of CNT agglomerates, provided by the representation of the cumulative agglomerate area ratio distribution, F , against the agglomerate area, A . F is calculated as the variation of the agglomerate area ratio, obtained by ranking the areas of the n agglomerates measured in increasing order of magnitude, and calculating each area ratio, F_j , from the smaller to the larger agglomerate, as described in Equation 1^{34, 35}. The numerator $\sum_{i=1}^j A_i$ represents the sum of the agglomerate areas from the smaller to the j^{th} agglomerate, and the denominator is the total agglomerate area, $A = \sum_{i=1}^n A_i$ where n represents the total number of agglomerates.

$$F_j = \frac{\sum_{i=1}^j A_i}{A} \times 100 \quad \text{Equation 1}$$

Cryo-fractured nanocomposites sputtered with a gold/platinum mixture were observed by scanning electron microscopy (SEM) on a NanoSEM FEI Nova 200, at an acceleration voltage of 5.00 kV in secondary electron image mode. The rheological measurements were performed using a rotational rheometer (AR-G2, TA Instruments), with 25 mm diameter parallel plates with a gap of 1 mm, in a frequency range from 1×10^{-2} to 1×10^2 Hz, at 240 °C. A constant strain of 5% was used after determination of the linear viscoelastic region by an amplitude sweep. The disks were dried for at least 4h at 80 °C before each measurement. The nanocomposites volume resistivity was measured using a two-probe method by applying a voltage between -10 and 10 mV on opposite sides of the sample and measuring the resultant current through it, using a Keithley 6487 picoammeter/voltage source at room temperature. Previously to the assays, the ends of the filaments from the ME processing (area approximately 0.02 cm^2 and lengths between 1.2 – 1.7 cm) were coated with a silver conductive lacquer, where the probes contacted the sample. The electrical contacts on the sample plates prepared in the batch mixer were obtained through gold coating by thermal evaporation. The resistivity was calculated based on Ohm's law and taking into account the geometrical factors. The electrical resistivity of the filaments was calculated using the equation:

$$R = \frac{\rho \cdot L}{s} \quad \text{Equation 2}$$

Where R is the filament resistance that can be calculated from the I-V curve slope, ρ the resistivity of the material, L the length of the filament and s the cross section area.

The electrical resistivity of the plates was also calculated from Equation 2, where s is the electrode area (constant = 5 mm), and L corresponds to the average thickness of the sample.

3. Results and Discussion

Figure 2 shows representative optical microscopy images of the samples with 0.5 wt.% of as-received and functionalized CNT both prepared in the batch mixer and in the mini-extruder. The analysis of the optical microscopy images allowed the quantification of the non-dispersed CNT fraction, which is relevant as it correlates with the dispersion level achieved³³. The most striking difference is observed between the as-received and functionalized CNT, rather than between the samples processed with different techniques. All the composites prepared with as-received CNT showed a smaller number of agglomerates compared to the composites with CNTNH.

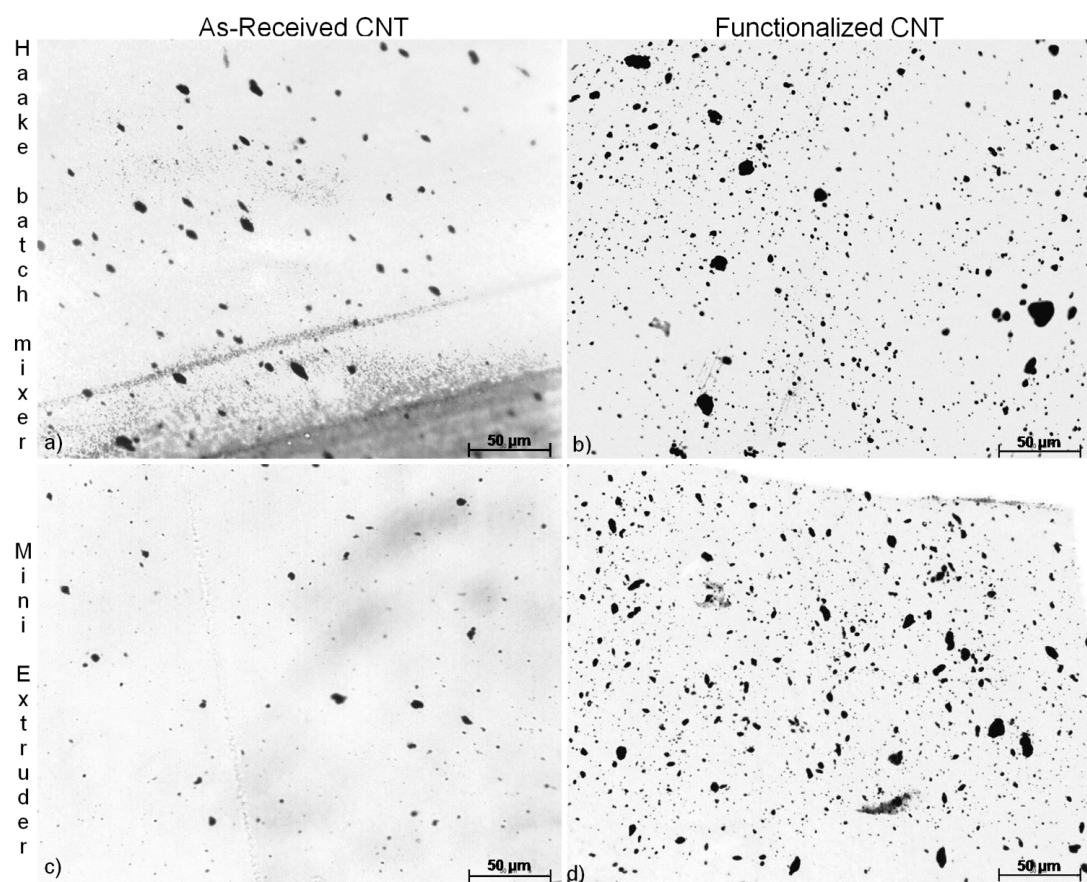


Figure 2 - Optical microscopy images of the samples prepared in the batch mixer a) 0.5CNT(HK); b) 0.5CNTNH(HK) and in the mini-extruder c) 0.5CNT(ME); d) 0.5CNTNH(ME).

The statistical analysis of the CNT agglomerate areas confirms that a much larger number of agglomerates is found in the composites with CNTNH, and that it is almost the double for the composites prepared in the HK, relative to those prepared in the ME (Table 1). The agglomerate area ratio, A_R , defined as the sum of all the agglomerate areas measured divided by the total composite area

analyzed, provides a good indicator of the overall dispersion achieved. Smaller A_R values indicate that less CNT agglomerates remain in the composite, and thus a higher fraction of CNT was effectively dispersed. The A_R results presented in Table 1 show that the CNT dispersion in CA was 3-4 times more efficient compared to the dispersion of CNTNH. The processing in the ME was more effective for CNT dispersion compared to the processing in the HK. Table 1 presents F , the cumulative agglomerate area ratio distribution as a function of the agglomerate area, for all the nanocomposites.

Table 1 – Optical microscopy analysis.

Samples	Agglomerate Area Ratio, A_R (%)	Number of agglomerates/per unit area (mm^2)	Maximum agglomerate area (μm^2)	$A\chi_{70\%}$ (μm^2)^{a)}
0.5CNT(ME)	1.38	931	90.7	28.2
0.5CNTNH(ME)	6.73	4449	260.3	27.6
0.5CNT(HK)	2.08	1741	386.0	69.5
0.5CNTNH(HK)	6.01	8792	775.2	26.9

^{a)} Maximum area of the agglomerates contained in 70% of the total agglomerate area

Keeping in mind that the as-received CNT were more effectively dispersed than the CNTNH by both processing methods, but attending to their agglomerates size distribution Figure 3 shows that the nanocomposites processed in the ME and the CNTNH composite processed on the HK have a larger population of small agglomerates, with 70% of the total population presenting agglomerate areas smaller than $28 \mu\text{m}^2$. It is observed that processing with the HK always leaves a considerable fraction of remaining large agglomerates, for pure and functionalized CNT composites. Thus, the shear rate applied to the polymer melt along the ME screw length, combined with the intensive mixing in the kneading blocks, results in a more efficient rupture of the large CNT agglomerates into smaller ones.

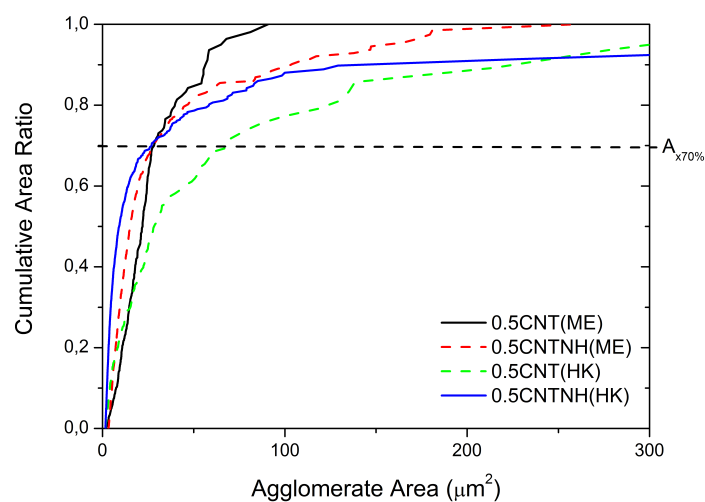


Figure 3 - Cumulative agglomerate area ratio distribution.

While optical microscopy provides images of the nanocomposites, CNT agglomerate phase, SEM images of their cryo-fractured surfaces show the dispersed CNT, i.e., the CNT fraction that is individually dispersed across the CA matrix. Figure 4 depicts typical SEM micrographs showing the presence of individually dispersed CNT across the composites. The micrographs evidence a higher concentration of dispersed CNT, either as-received or functionalized, on the composites processed by ME, compared to HK.

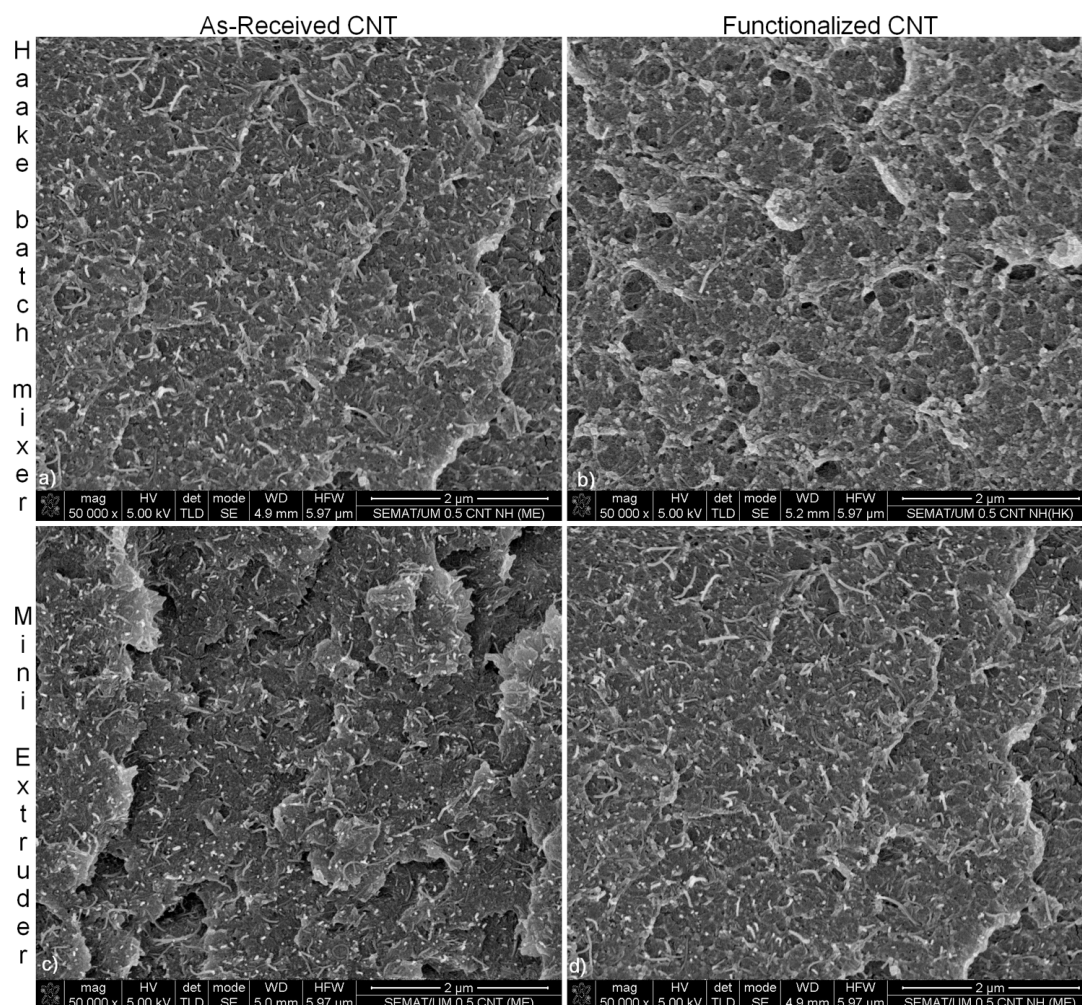


Figure 4 - Representative SEM micrographs of the nanocomposites processed in the batch mixer a) 0.5CNT(HK); b) 0.5CNTNH(HK) and in the mini-extruder c) 0.5CNT(ME); d) 0.5CNTNH(ME).

The pyrrolidine groups on the CNTNH surface are expected to have good affinity to the CA matrix through hydrogen bonding, as represented in Figure 5. These enhanced interactions are expected to result in a stronger CA/CNTNH interface, thus improving the composite mechanical properties. However, the CNTNH surface functionalization does not necessarily facilitate the nanotube dispersion in the polymer melt. In fact, the agglomerates of functionalized CNTNH may be more stable and difficult to break into smaller agglomerates, compared to those of pristine CNT. If this is the case, higher stress levels will be required to break the stable agglomerates into consecutively smaller ones, otherwise a lower overall dispersion will be observed, as well as the survival of large agglomerates. However, the higher affinity between CNTNH and the CA matrix may enhance the CNT dispersion through erosion from the agglomerates surface into the bulk polymer melt, thus leading to a considerable individual CNTNH dispersion into the CA matrix.

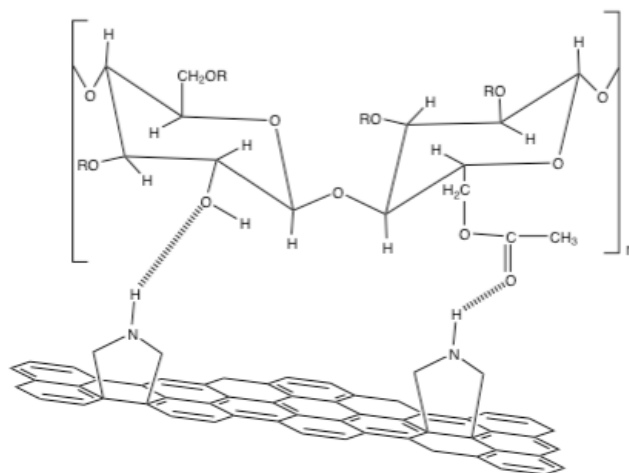


Figure 5 - CA/CNTNH interaction through hydrogen bonding ($R = \text{COCH}_3$ or $R = \text{H}$ according to acetylation degree).

As shown by optical and electron microscopies, the processing method and CNT treatment has a strong influence on the CNT dispersion in CA. It is well known that the nanoparticle dispersion state will affect the rheological behavior of the nanocomposites^{36, 37}. In the present work the CA and nanocomposites dynamic rheological properties were assessed by measuring the complex viscosity (η^*), the storage (G') and loss (G'') modulus as a function of frequency (ω), and calculating $\tan(\delta)$, the ratio G''/G' , as represented in Figure 6.

It is well documented that for polymer nanocomposites the values of G' and G'' increase with CNT concentration, evidencing the contribution of CNT/polymer interactions to the melt elastic behavior^{20, 37}. The η^* of the CNT composites is higher than that of the polymer, the latter presenting a Newtonian plateau at low frequencies. This plateau disappears for composites containing a well dispersed CNT network able of imposing the elastic behavior across the frequency range. In the present work the deviation from the Newtonian plateau behavior was observed for the composites with 0.5 wt.% of CNT and CNTNH prepared by ME (Figure 6 a and b). A clear decrease in the slope of G' vs. ω was observed only for these composites (Figure 6 c and d). This effect was reported by Du et al.³⁶ concluding that good CNT dispersion and long polymer chains induce higher restraints to the polymer mobility leading to a lower slope of G' vs. ω in the low frequency range, and higher G' values at low frequencies. This also indicates a better load transfer between the nanotube network and the polymer^{38, 39}.

The variation of $\tan(\delta)$ with frequency provides relevant information about the damping characteristics of the composites relative to the pure polymer. The lower values of $\tan(\delta)$ measured for the nanocomposites indicate higher elastic behavior of the polymer melt (higher G') interpreted as

hindrance of polymer relaxation in the presence of the CNT network³⁷. Figure 6 e and f show that CA undergoes a transition from elastic to viscous behavior at a frequency near 10 Hz, at which $\tan(\delta) = 1$, and thus $G'' > G'$ for higher frequencies. A shift of this transition to lower frequencies was observed for all composites. Those prepared in the HK shifting in ω by one order of magnitude, while those prepared in the ME shifting by nearly two orders of magnitude. Below this frequency value (at $\tan(\delta) = 1$) the dissipative behavior of the melt increases with decreasing ω for CA and composites, except for the 0.5 wt% CNT and CNTNH prepared by ME, that nearly stabilizes around a $\tan(\delta) \approx 1$ (Figure 6 e and f).

In brief, the rheological data indicate a clear influence of the CNT presence in the CA melt behavior. However only the ME composites with 0.5 wt% CNT and CNTNH presented the rheological response characteristic of the establishment of a CA/CNT percolated network.

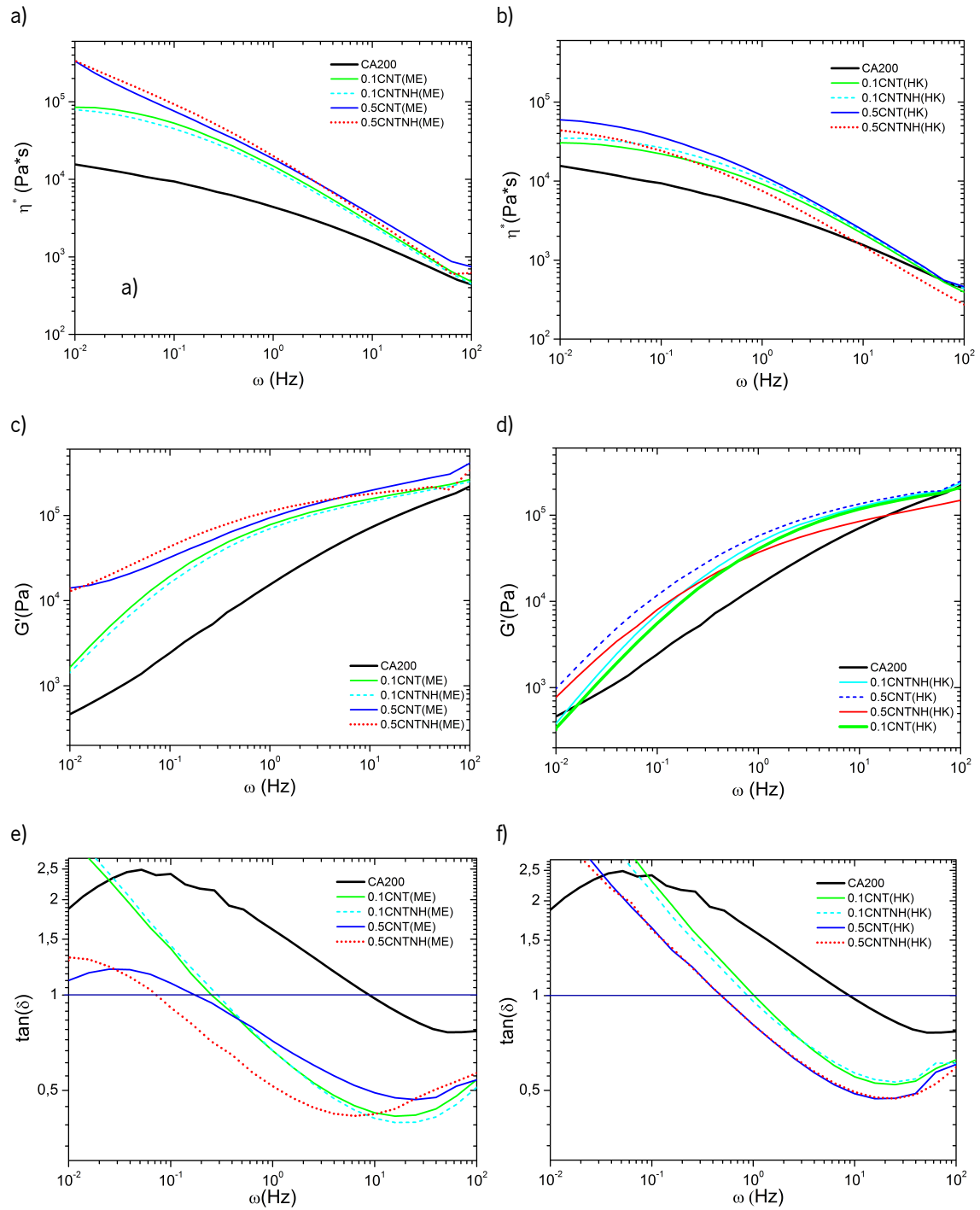


Figure 6 - Complex viscosity (a and b), Storage modulus (c and d) and $\tan(\delta)$ (e and f) of CA and nanocomposites prepared by melt mixing (left) and in the Haake mixer (right).

The electrical resistivity of the nanocomposites was measured to evaluate if the electrical percolation was reached. The rheological and electrical percolation are closely related, although the rheological percolation is reported to be attained at lower CNT content^{136, 38}. The electrical resistivity results obtained for CA and its composites are presented in Figure 7.

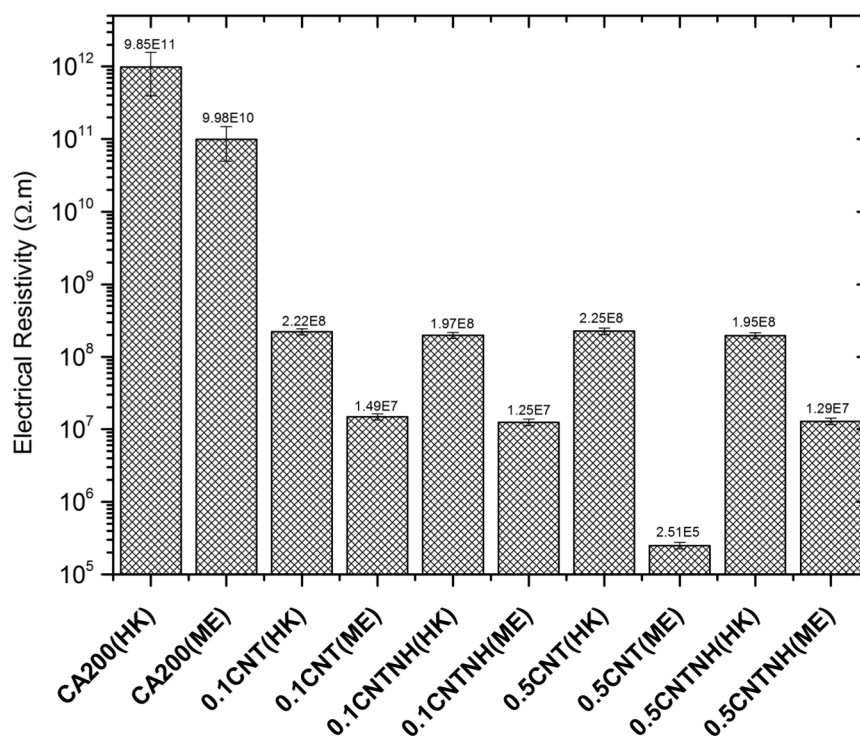


Figure 7 - Electrical resistivity results.

Higher electrical resistivity was obtained for composites with similar CNT content produced in HK relative to ME. This result correlates with the poorer CNT dispersion observed for HK composites by optical microscopy. The insulating character of the CA polymer matrix was confirmed by the high resistivity obtained, near the limit of the measuring equipment.

The composites prepared with 0.1 wt.% CNT show a significant reduction of electrical resistivity by three orders of magnitude relative to the polymer. The composite prepared in the ME containing 0.5 wt% of as-received CNT presented the lower resistivity, already in the semi-conducting range, thus reaching both rheological and electrical percolation threshold. These results are in line with the efficient CNT dispersion observed by optical and electron microscopies. However, the composite with 0.5 wt.% CNTNH (ME) did not reach the electrical percolation threshold, probably due to the poorer CNT dispersion observed by optical microscopy.

4. Conclusions

The present study demonstrates the relevance of the processing method and chemical functionalization on the dispersion of the nanoparticles in the polymer melt, and consequently on the melt and solid state properties.

The morphological analysis showed that smaller CNT agglomerates were formed and better dispersion was achieved when the melt mixing was performed by twin-screw extrusion. The functionalization of the CNT did not facilitate the dispersion of their agglomerates in the polymer. However, the rheological percolation was observed for the composites with 0.5 wt.% CNT either pure or functionalized, prepared by extrusion. The poorer dispersion of the functionalized CNT limited the composite electrical conductivity. However, a large reduction of the electrical resistivity was found at a low CNT concentration, 0.5 wt.% CNT, presenting an electrical conductivity of 2.5×10^5 S/m.

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V

NOVEL IRIDIUM-PENTAFLUOROPHENYL PORPHYRIN COMPLEX BEARING LARGELY π -EXTENDED LIGAND

The novel iridium-pentafluorophenyl porphyrin complex (TPFPPIrCl(CO)) was successfully synthesized by chemical reaction with the iridium (I) metal precursor [Ir(COD)Cl]₂. The complex was identified with the axial Cl and CO ligands by UV-Visible, ¹H, ¹³C NMR spectroscopy as well the ¹H/¹³C correlated techniques and by mass spectrometry.

Delgado-Lima A., Mauricio A.F., Machado A.V., Novel Iridium-Pentafluorophenyl Porphyrin Complex Bearing Largely π -Extended Ligand. Material Letters (submitted).

1. Introduction

Porphyrins are an important class of compounds involved in biological phenomena, such as, the enzyme cytochrome P450, heme and protoporphyrin (iron porphyrins) from hemoglobin and myoglobin, respectively, and chlorine (magnesium reduced porphyrin) in chlorophyll¹⁻¹⁰. They also found attractive applications in mimicking enzymes, as reaction catalyst and photosensitizers, in photodynamic therapy, molecular electronic devices and solar energy conversion^{1, 3-5, 11}. Porphyrins derive from porphin and consist of substituted aromatic macrocycle rings of four pyrrole rings substituted at β and/or meso positions linked by a methine bridge^{1, 2, 5, 11}. They are of great interest mostly due to the capability of forming complexes with most of the elements in the periodic system, by the loss of the two inner NH protons and further metal coordination, showing distinctive properties from the porphyrin initial precursor^{6, 12, 13}. In the case of a favored octahedral geometry by the metal ion, the porphyrin coordination sphere is normally completed with ligands¹¹. It is also of great importance to mention that the facility of the coordination of a metal ion with a porphyrin depends mainly on the available space between the porphyrin core (approximately radius = 75-90 pm), and the ionic radius of the metal ion, therefore, does not exist a single metal insertion procedure that can be applied to all metals and porphyrins^{5, 6, 11, 12}. While for 3d metals, the ionic radius matches the available space of the porphyrin core, resulting in a planar geometry with the porphyrin¹². For larger ions coordination, 4d and 5d, the metal ion is usually positioned outside the porphyrin plane⁵. Iridium, a 5d⁹ transition metal, has attractive properties, such as, high melting point, chemical stability, superior oxidation resistance and high electrical resistivity. Which makes iridium complexes promising materials for a wide range of applications, such as, heavy-metal-ion sensors, catalysis and switching layers in electrochromic devices¹³⁻²¹. Though, iridium has been successfully employed in the preparation of cyclometalated compounds²²⁻²⁶ with remarkable photophysical and photochemical properties, with applications in important fields, such as organic emitting diodes (OLEDs), dyes sensitizing solar cells, sensors, biology and photocatalysis, only a few examples can be found in the literature about its incorporation in porphyrins^{13, 14, 27-31}. Therefore, the synthesis of iridium porphyrins complex would be of great scientific and technological importance. The pentafluorophenyl substituted porphyrin (TPFPP) (Figure 1), which is oxidatively more robust and has better solubility in common organic solvents than its phenyl analogue, is a promising porphyrin¹⁴.

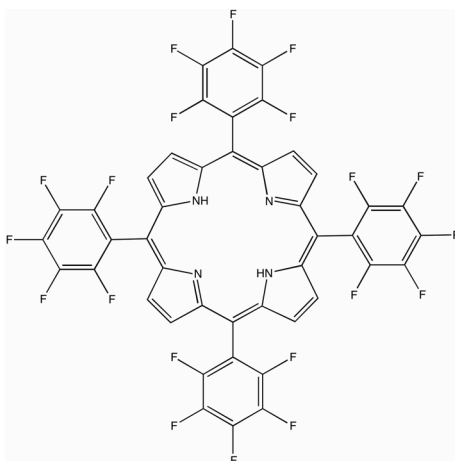


Figure 1 – Pentafluorophenyl substituted porphyrin (TPFPP).

The substitution of hydrogen terminated species by fluorine atoms are known to turn possible the electronic transport properties to switch from a p- to a n- type, making this porphyrin of particular relevance and a capable candidate for thin film based electronic devices³². Gas-sensor is also a suitable application, since TPFPP coordinated with Zn atoms demonstrated a significant enhancement in gas-response of ammonia-sensing¹⁵. Moreover, the TPFPP is an appropriate platform to several substitutions, once the pentafluorophenyl group of the porphyrin is not a chemically inert group, suffering aromatic nucleophilic substitutions with a range of nucleophiles (RO⁻, RNH₂, RS⁻)^{14, 16-23}. For example, Samaroo *et al.*¹⁶ showed the efficacy of using TPFPP as a core platform to obtain porphyrins bearing functionalities that are important to photodynamic therapeutics (PDT), as sugars, cationic groups, and moieties that impart amphipathic solubility properties. These can be used for noble purposes as cancer treatment or as a potential antibacterial or antiviral compound¹⁶.

2. Materials and Methods

2.1 Materials and Characterization

The porphyrin 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPFPP) (98%purity) was purchased from Sigma-Aldrich. Reagents and solvents, namely chloro(1,5-cyclooctadiene)iridium (II) dimer ([Ir(COD)Cl]₂) (97% purity) was purchased from Sigma-Aldrich, xylene, dichloromethane and n-hexane were purchased from Acros Organics and used without further purification. Thin layer chromatography

was performed in Merck pre-coated silica gel 60 F-254 plates and silica gel 60 M (0.04 – 0.063 mm) from Macherey-Nagel was used for column chromatography. ^1H and ^{13}C NMR spectrum were performed in a Bruker Avance III, 400 MHz in CDCl_3 . All the compounds were characterized by ^1H and ^{13}C NMR spectroscopy including $^1\text{H}/^{13}\text{C}$ correlation techniques, which were recorded on a Bruker Avance III, 400MHz in deuterated CHCl_3 . The spectra were internally referenced to the residual proton tetramethylsilane (TMS, $\delta=0.00$ ppm) and the chemical shifts (δ) are reported as part per million (ppm). Absorption spectra were measured at a Shimadzu UV-2401PC UV-Vis spectrophotometer in CH_2Cl_2 in a range between 300 and 700 nm, and mass spectrometry (ESI) was performed on an APEXQe FT-ICR MS (Bruker Daltonics, Billerica, MA), equipped with a 7T actively shielded magnet. Ions were generated using a Combi MALDI-electrospray ionization (ESI) source. Ionization was achieved by electrospray, using a voltage of 4500 V applied to the needle, and a counter voltage of 300 V applied to the capillary. Samples were prepared by adding a spray solution of 70:29.9:0.1 (v/v/v) CH_3OH /water/formic acid or 70:29.9:0.1 (v/v/v) CH_3CN /water/formic acid to a solution of the sample at a v/v ratio of 1 to 5 % to give the best signal-to-noise ratio. Data acquisition was performed using the ApexControl software version 3.0.0, and data processing was performed using the DataAnalysis software, version 4.0 both from Bruker Daltonics.

2.2 Synthesis of TPFPP Metalloporphyrin

The TPFPP $\text{IrCl}(\text{CO})$ metalloporphyrin was synthesized adding the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (261.9 mg, 0.39 mmol) to a solution of free-base porphyrin (246.9 mg, 0.26 mmol) in xylene ($[\text{C}] = 6.5\text{E-}3$ M) (Figure 2). The resulting mixture was refluxed for 4 days and allowed to cool to room temperature followed by solvent evaporation to dryness. The resulted residue was purified by column chromatography on silica gel with n-hexane/dichloromethane and it was isolated in 5% yield. Found in ^1H NMR (400MHz, CDCl_3 , 25°C) δ ppm: 9.02 (s, 8H, $\beta\text{H-pyrrole}$). And ^{13}C NMR (400MHz, CDCl_3 , 25°C) δ ppm: 105.98 ($\text{C}_{5,10,15,20}$), 128.98 ($\text{C}_{2,3,7,8,12,13,17,18}$), 141.52 ($\text{C}_{1,4,6,9,11,14,16,19}$), 119.84 (Cp) UV-Vis (CH_2Cl_2) λ abs nm: 413.5, 526.0, 557.5. ESI-MS: $\text{C}_{45}\text{H}_8\text{ClF}_{20}\text{IrN}_4\text{NaO}$ $m/z = 1250.96$.

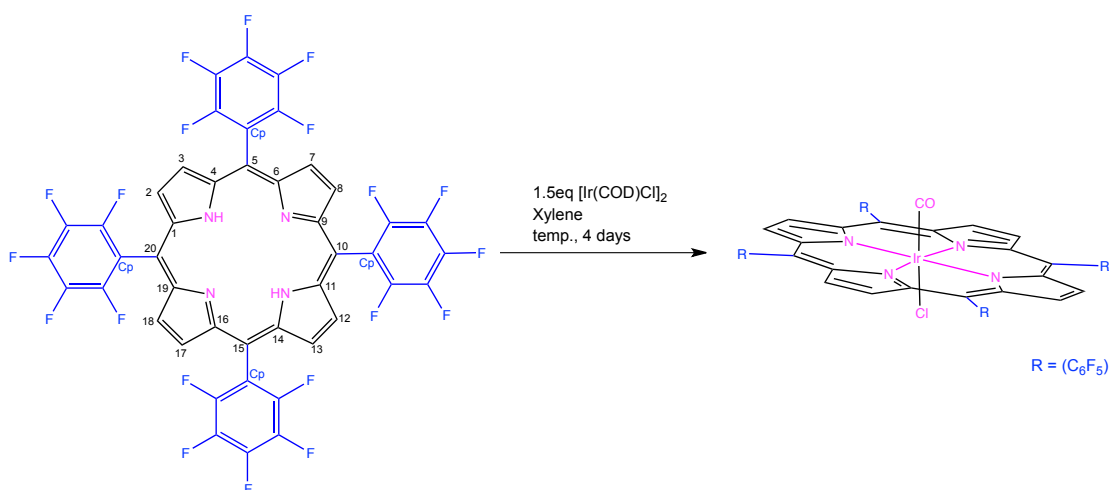


Figure 2 – Scheme reaction of TPFPP metallation with iridium.

3. Results and Discussion

As mentioned, TPFPP is of huge interest and is used on the research of new materials to be employed in a wide range of applications including (not only oxygen) sensing²⁴⁻²⁹, catalysts³⁰⁻³⁵, imaging agents³⁶, microbial photodynamic activation³⁷ and even as biodiesel fluorescent markers³⁸. Therefore, combining the attractive properties of TPFPP with the iridium metal, by the synthesis of a porphyrin complex became a great challenge. The first attempts were performed in IrCl_4 without reaction success. Similarly to the iridium coordination in other porphyrins procedure, the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (COD = cyclooctadiene) was used as the metal precursor³⁹⁻⁴³. Since iridium is a six-coordinated atom, CO and Cl axial ligands neutralize the molecule and complete the coordination sphere (Figure 2). The first experiments were performed in smoother solvents, as acetone and pyridine, but no reaction evolution was detected. Clearly, the solvent selection was of major relevance and higher boiling temperatures were preferable⁵. Also, the coordination ability of the solvent by the presence of lone pairs or electron-rich donor atoms might affect the reaction, avoiding the coordination of the metal in the porphyrin. Therefore, the iridium porphyrin (TPFPPIrCl(CO)) was obtained after a 4 days reaction, in reflux using a high boiling point and non-coordinating solvent, xylene. Despite the success of this reaction, the yield of 5% demonstrates that it is difficult to incorporate a large metal atom in sterically hindered porphyrins. The iridium porphyrin complex was isolated from a column chromatography using a binary system of solvents of n-hexane/dichloromethane, and its presence was confirmed by UV-Vis spectroscopy, ^1H and ^{13}C NMR spectroscopy including $^1\text{H}/^{13}\text{C}$ correlation techniques and electrospray ionization mass spectrometry (ESI-MS) (see supplementary information). Figure 3 presents the UV-Vis spectra of

porphyrin TPFPP and metallated TPFPPIrCl(CO) and an enlargement in the region of 450-650 nm. The spectrum of porphyrins shows two $\pi\text{-}\pi^*$ electronic transitions. An intense B- or Soret band between 350-500 nm with molar absorptivities (ϵ) of $10^5 \text{ M}^{-1}\text{cm}^{-1}$, and four lower intense ($\epsilon \approx 10^4\text{-}10^1 \text{ M}^{-1}\text{cm}^{-1}$) Q-bands between 500-750 nm as a result of the presence of protons on two diagonally situated pyrrole nitrogen^{5, 38, 44}. The coordination of iridium with the porphyrin core induces significant changes in the UV-Vis spectrum. Specifically, the main difference consists in the 2 Q- bands of the metalloporphyrin with displaced wavelengths, which also reveals the existence of axial ligands by the difference between the more intense Q(0,0) band at 526.0 nm and the less intense Q(1,0) band at 557.5 nm⁵. The formation of dimers and higher aggregates was not observed, since red or blue shifts and broadening of the Soret band were not detected⁴⁵⁻⁴⁷.

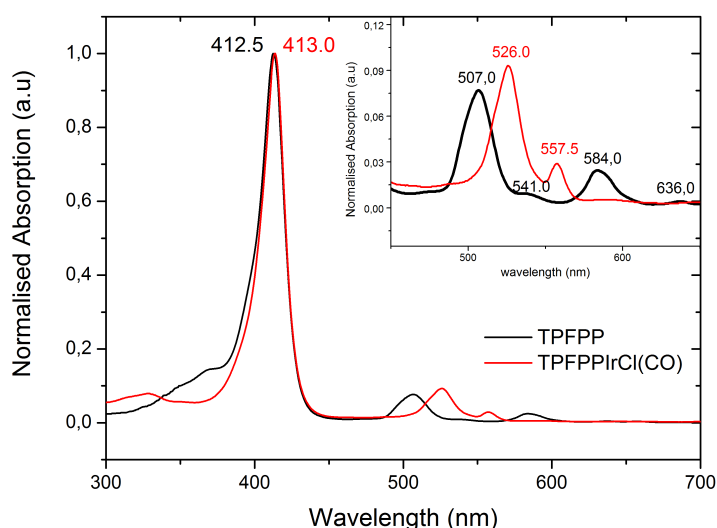


Figure 3 - UV-Vis spectra of free-porphyrin TPFPP and metallated TPFPPIrCl(CO). The inset is a magnified view of the UV range of the Q-bands (450-650 nm).

The NMR spectrum of the commercial TPFPP is in agreement with literature⁴⁸, where the pyrrole protons are observed at negative chemical deviations of $\delta(\text{ppm})$ -2.87 (s, 2H, NH) due to the shielding effect promoted by the association of ring currents with the π -system of the aromatic macrocycle⁴⁹. The deshielding of the peripheral protons that are presented at 8.96 ppm respectively (d, 8H, β H-pyrrole) is also a consequence of the previous effect⁴⁹. The peaks at approximately $\delta(\text{ppm})$ 7.27 and 1.55 are assigned to the residual peak of deuterated solvent and water, respectively. The coordination of iridium in the center of the TPFPP ring was confirmed by ^1H NMR due to the absence of the NH protons at approximately -3 ppm, which were successfully substituted by the metal atom (Figure 4). The proton signals at the β positions did not undergo a significant chemical deviation $\delta(\text{ppm})$ 9.02, which is also in

concordance with literature^{48, 50}. As expected, only the carbons at the β -positions have direct proton correlation (see supplementary information). A very concentrated solution was necessary to identify the C-F bonds of TPFPP at δ (ppm) 135-150, which were probably covered by the background noise on the metallated porphyrin spectrum. The iridium porphyrin complex identification was confirmed by ESI-MS in the presence of Na⁺ with a correspondent mass of 1250.96 g/mol, in agreement with the theoretical mass of 1251.14 g/mol.

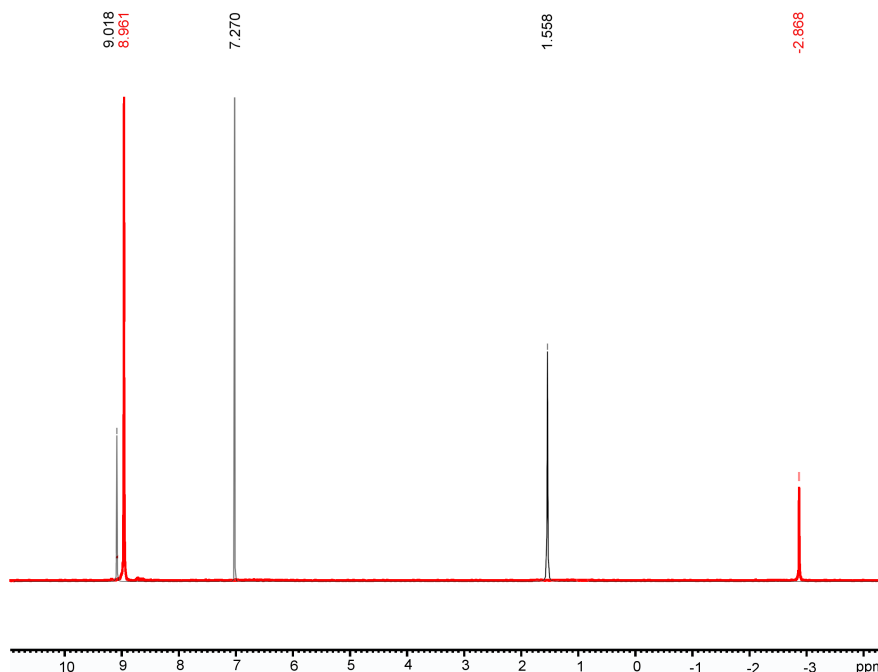


Figure 4 - ¹H NMR spectra of TPFPPIrCl(CO) metalloporphyrin (black line) and of the free-porphyrin TPFPP (red line).

4. Conclusions

A novel iridium-pentafluorophenyl porphyrin complex (TPFPPIrCl(CO)) was successfully synthesized. The iridium center metal was stabilized with Cl and CO ligands, which completed the coordination sphere. The reaction was enhanced at higher boiling temperatures, in the absence of solvents or other compounds with lone pairs of electrons or electron-rich donors that avoid the metallation reaction. As future work, the reaction conditions and compound separation will be optimized to increase the reaction yield and to exploit the capacities of this new compound in several applications.

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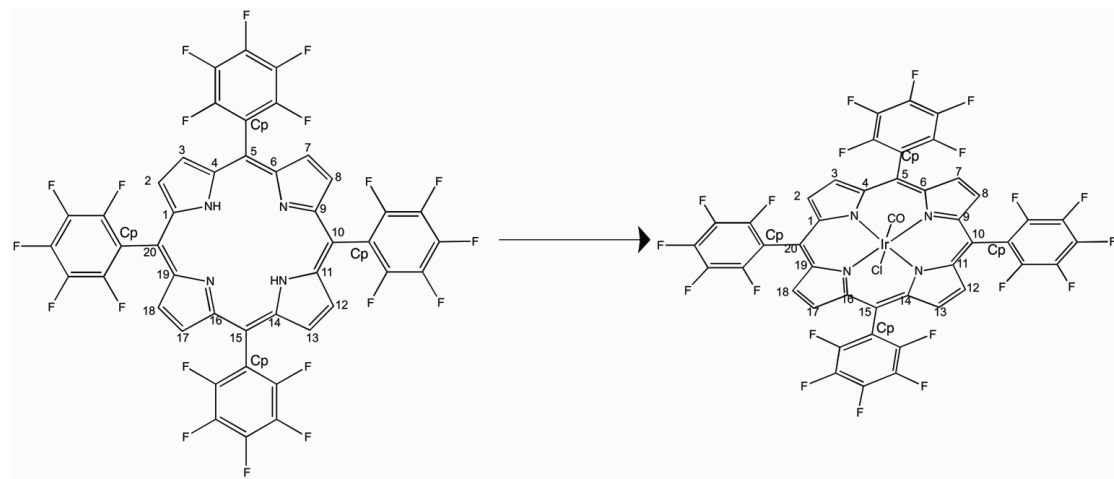
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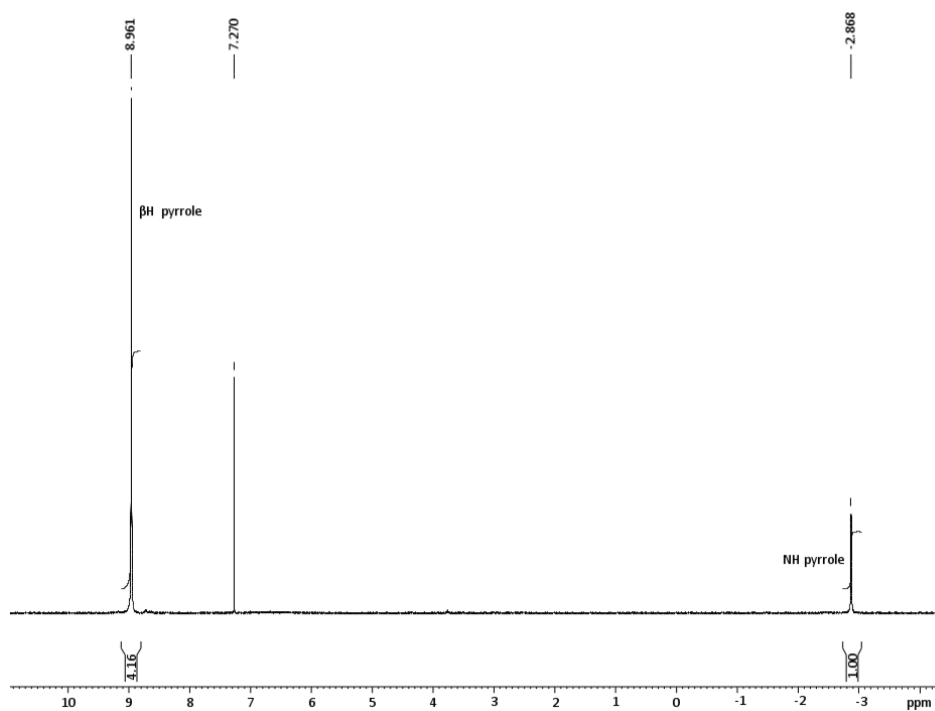
Supporting Information

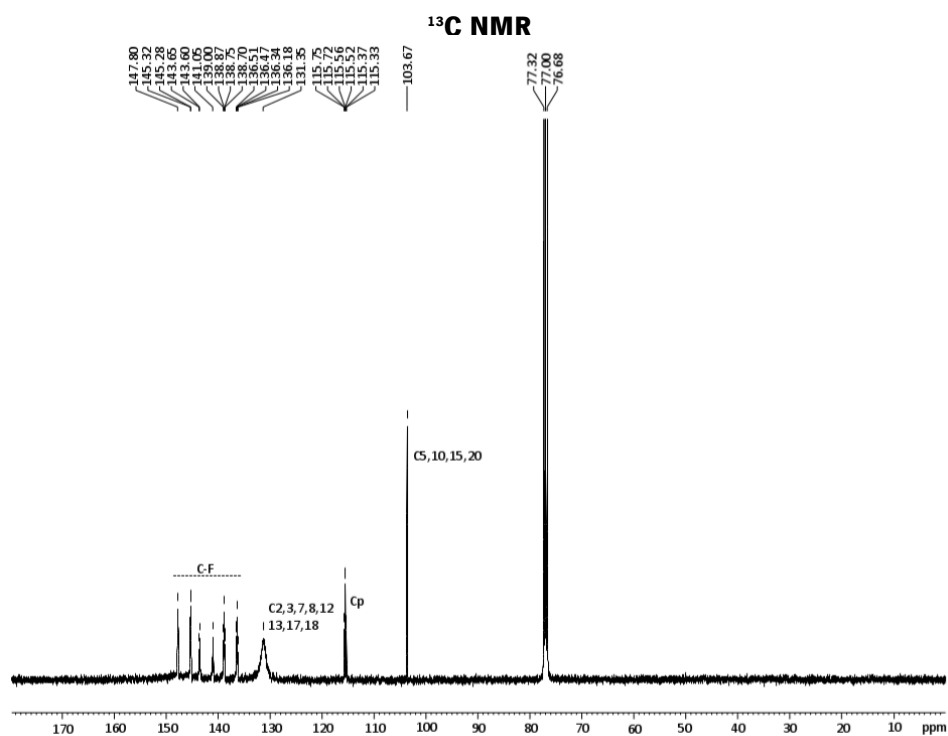
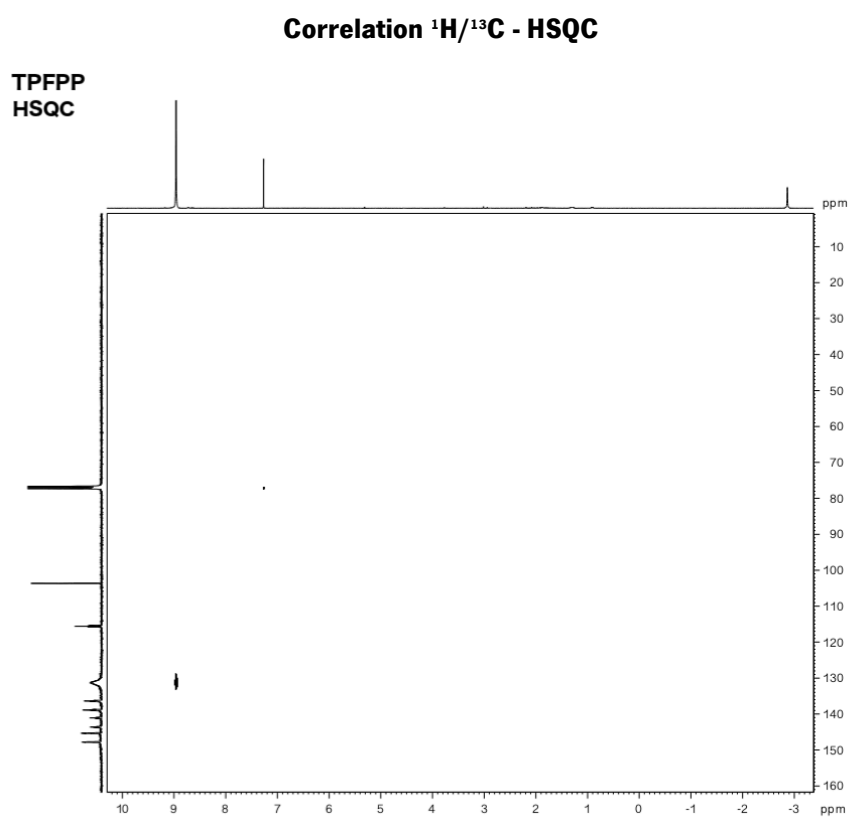
I. Scheme of the metallation of the TPFPP



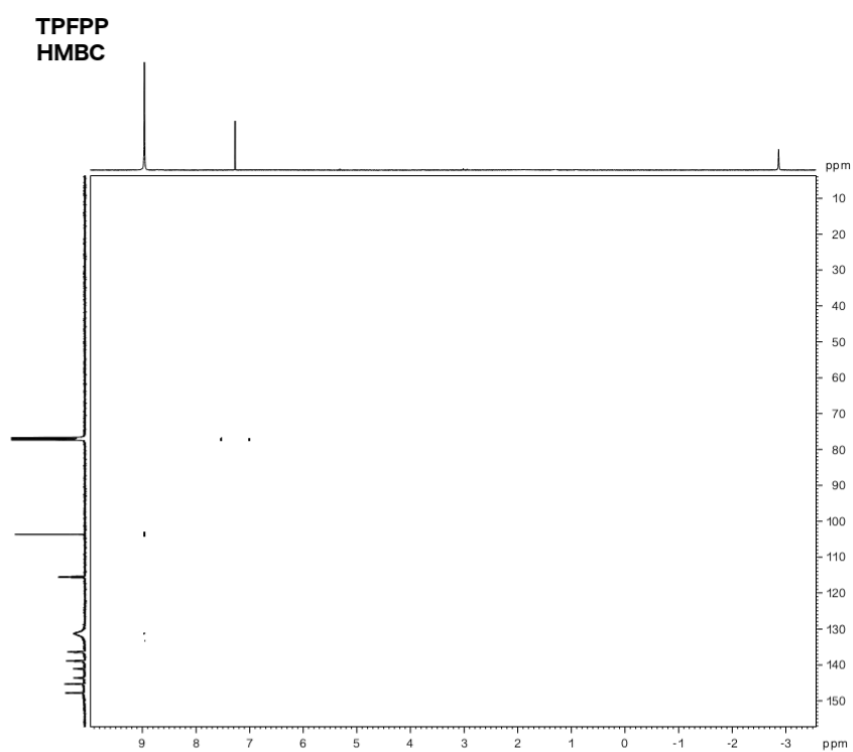
II. NMR spectra of the free-porphyrin TPFPP in CDCl₃

¹H NMR



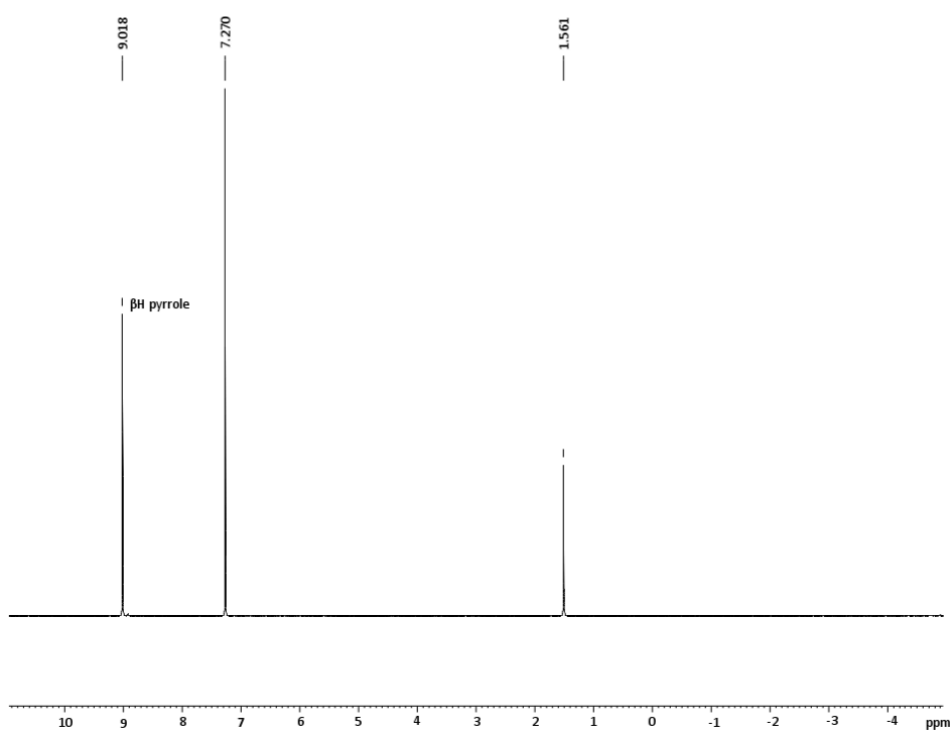


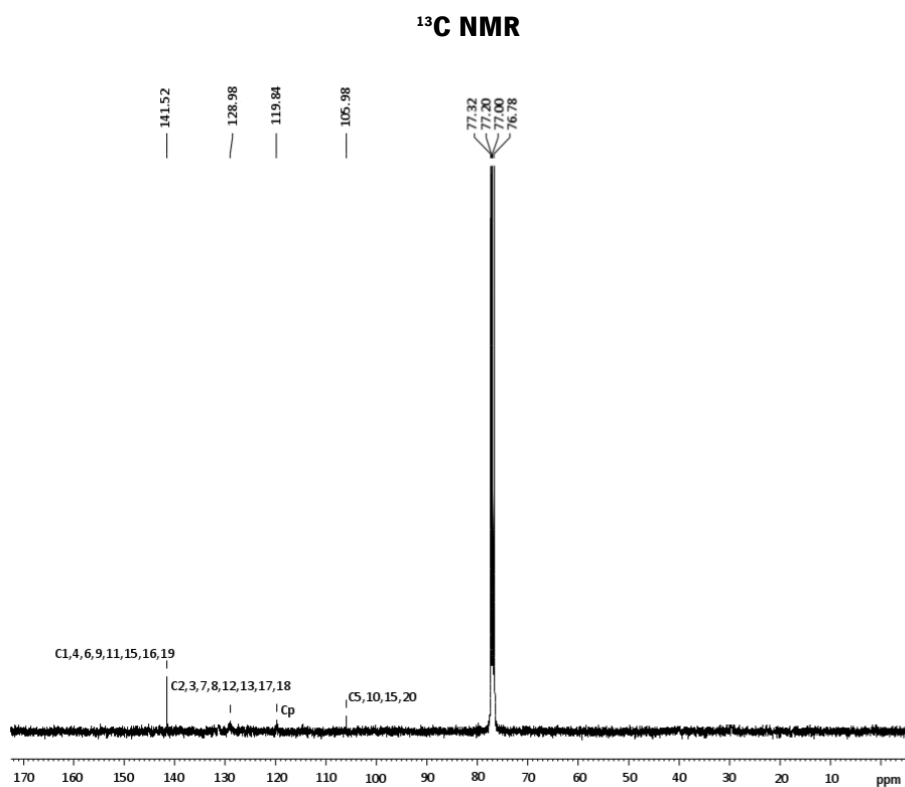
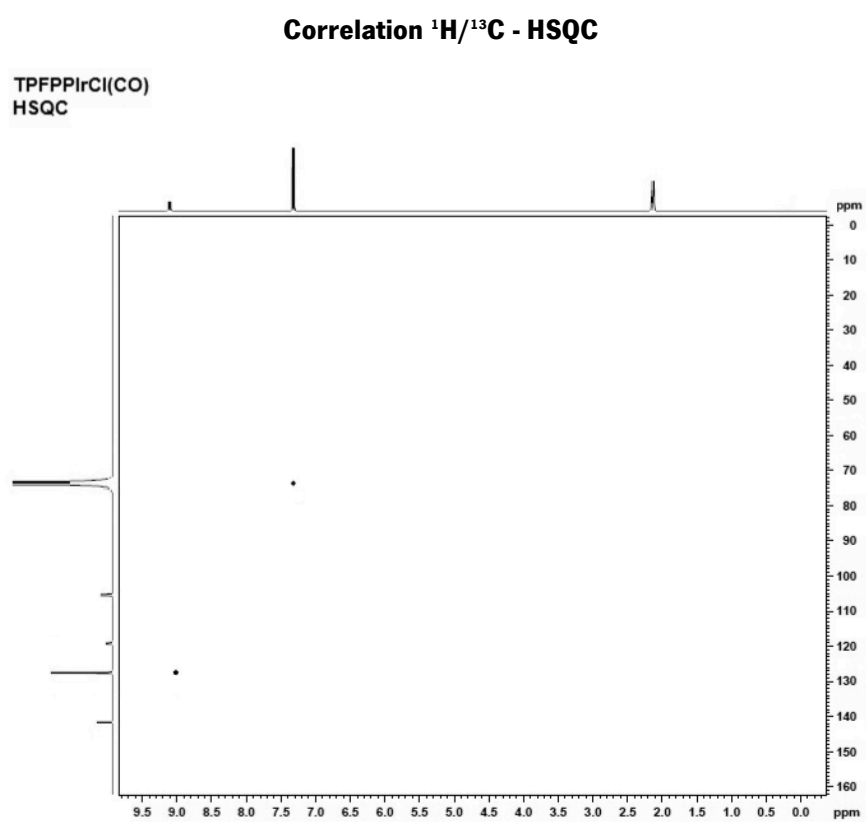
Correlation $^1\text{H}/^{13}\text{C}$ - HMBC



III. NMR spectra of the metalloporphyrin – TPFPPIrCl(CO) in CDCl_3

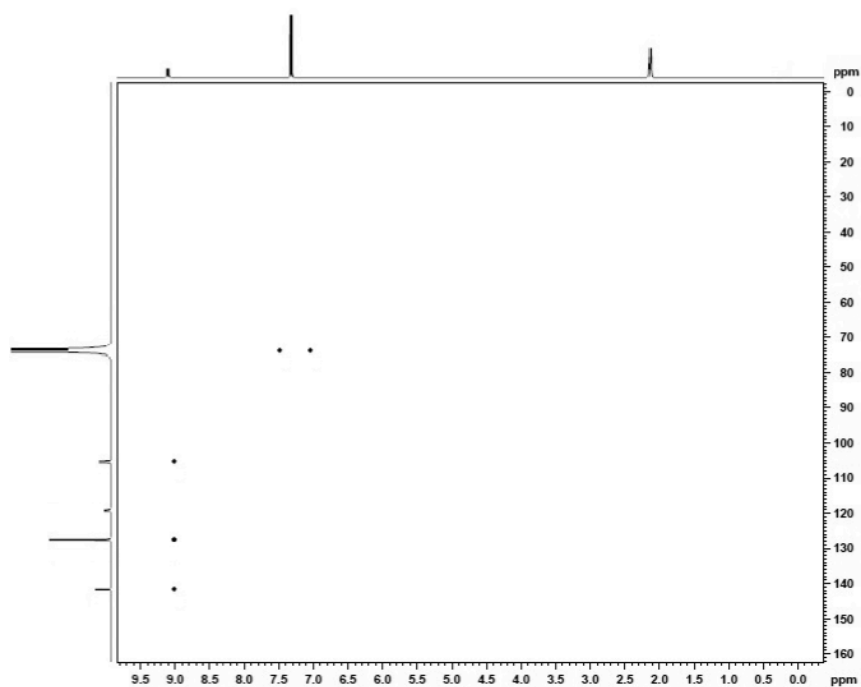
^1H NMR



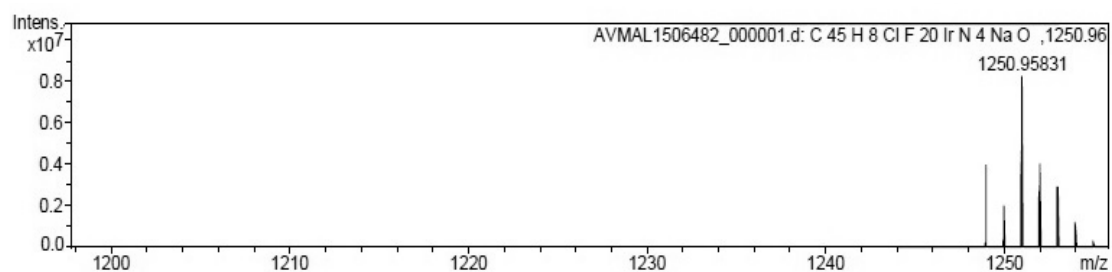


Correlation $^1\text{H}/^{13}\text{C}$ - HMBC

TPFPPIrCl(CO)
HMBC



IV. Mass Spectra of TFPPIrCl(CO)Na



VI

FLUORESCENT AND CONDUCTIVE CELLULOSE ACETATE-BASED MEMBRANES WITH PORPHYRINS

The unique properties of electrospun nanofibers combined with functional compounds allow the preparation of novelty materials that can be employed in a wide range of applications. Among a vast number of polymers, Cellulose Acetate (CA) it is considered easy to electrospun and it was employed as the polymeric matrix, where free and iridium-porphyrins were incorporated. Two different solvent systems were employed according to the porphyrin used, and the best dispersion level on both the electrospun solution and the membranes, was achieved with the iridium porphyrin. The nanofibers with this porphyrin also exhibited electrical properties, while the fluorescence was quenched by the presence of specific axial ligands.

Delgado-Lima, A., Borges, J.P., Ferreira, I.M., Machado, A.V., Fluorescent and Conductive Cellulose Acetate-Based Membranes with Porphyrins, Nano Today (submitted).

1. Introduction

Nanofibers prepared by electrospinning with functional compounds, such as metals, semiconductors, ceramics, among others, display specific structural features (phase morphologies and surface topologies) and unique properties that make these materials very interesting from their optical, electronic, photonic, catalytic and magnetic properties. Therefore they gather some of the desired requirements for diverse applications, such as fuel and solar cells, electronic sensors, energy harvesting and storage systems and others^{1, 2}. Among several candidate compounds, porphyrins and its metallic derivatives are known as important conjugated organic macrocycles with amazing and variable properties and were the chosen compounds to attain the target nanofibers optic/electronic properties³⁻¹⁰. The growing interest in these macrocycles combined with the unique features of the electrospinning technique, such as the nanofiber high specific surface and high aspect ratio, with the possibility of making materials with optic/electronic properties, has generated an increasing interest among researchers in the last decade. For example, nanofibers with fluorescence sensing properties able the rapid detection of 2,4,6-trinitrotoluene trinitro- toluene (TNT)¹¹, hydrogen chloride (HCl) gas¹², and towards nitroaromatic explosives¹³, were prepared from polymer/porphyrin conjugation. PCL-Porphyrin and PCL-Metalloporphyrin(Zn) electrospun nanofibers were prepared as a fluorescent chemosensor for detection of histamine⁸ and poly(N-vinylpyridine)/porphyrin derivatives^{14, 15}. Electrospun platinum(II) and palladium(II) metalloporphyrins were also employed as optical chemical sensors with a remarkably enhanced dynamic response when compared to compact films^{16, 17}. Also copolymers of poly(acrylonitrile) with iron-porphyrin or a diamino-substituted porphyrin were successfully electrospun into nanofibers^{18, 19}. The first porphyrin act as a photosensitizer and in conjugation with TiO₂ particles showed photocatalytic activities in the photodegradation of methyl red¹⁹, while the second showed a great potential to applications in chemical sensors, molecular wires, and photoresponsive materials¹⁸. Nanofibers composed of polystyrene with encapsulated or bounded porphyrins showed also excellent photophysical properties with a strong antibacterial effect^{20, 21}. The electrospun of cellulose acetate (CA) has already been extensively studied and several research papers have been published²²⁻³⁰. Although there are some works on the electrospinning of polymers with porphyrins, none of them uses the cellulose acetate combined with 5,10,15,20-tetrakis(p-tolyl)porphyrin (TTP) or its derivative replaced with iridium TTPIr, which will be investigated in this work aiming to obtain materials with optic/electronic properties. Therefore, in this work prior to the preparation of the nanofibers the

Hildebrand and Flory-Huggins parameters were predicted and the viscosity and surface tension of the respective solutions were studied. CA and CA containing porphyrins were electrospun and the obtained membranes formed of nanofibers were characterized in terms of morphology, topography, fluorescence, chemistry, thermal stability and electrical conductivity.

2. Materials and Methods

2.1 Materials

The cellulose acetate with an acetylation degree of 39.8 wt% and the porphyrin 5,10,15,20-tetrakis(p-tolyl)porphyrin (TTP) (purity 98%) were acquired from Sigma-Aldrich and their structural formula is represented in Figure 1. The respective metallated porphyrin (TTPIr) was synthesized according to the literature³¹ (Figure 1 c). The free-base TTP (150 mg, 0.22 mmol) and the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (225.3 mg, 0.33 mmol) were added in xylene and refluxed for 4 days. The solution was purified through column chromatography and the metalloporphyrin was isolated with 70.7% yield, respectively. The solvents employed in this work were acetone (Ac), dichloromethane (DCM), ethanol (Et) and dimethylacetamide (DMAc), purchased from Sigma-Aldrich and used without further purification.

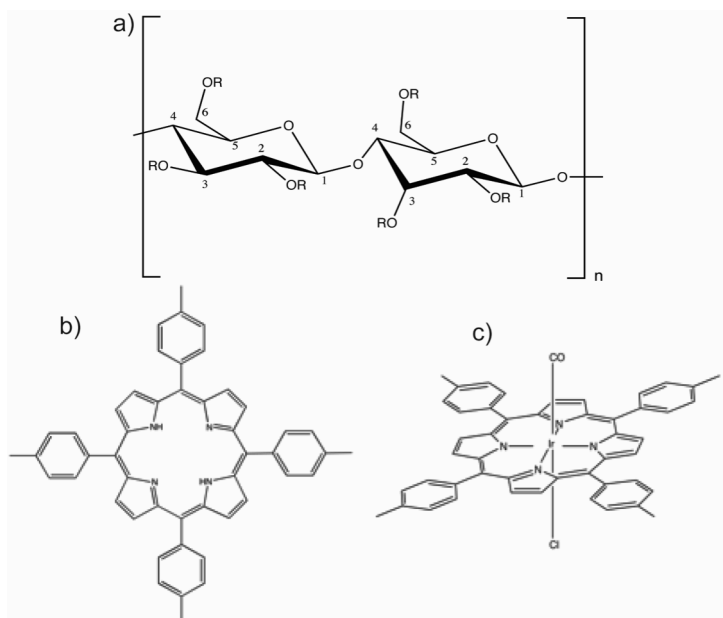


Figure 1 – a) Cellulose acetate $\text{R}=\text{H}$ or $\text{R}=\text{COCH}_3$ (according to acetylation degree); b) porphyrin TTP and c) metallated porphyrin TTPIr.

2.2 Preparation of the CA Solutions

The CA solutions for electrospinning were always prepared using mixed-solvent systems at room temperature with fixed concentrations of 10 and 12 wt% of CA. Considering the solutions prepared from CA and porphyrins, both the TTP and the TTPIr were fixed at 5 wt% relatively to CA. The systems of solvents employed to prepare the solutions were designated as A and B, where A corresponds to the mixed-solvents DCM/Et in a ratio of 80/20 (w/w) and B to the solvent system constituted by DCM/Et/DMAc, where the DMAc solvent was fixed at 10 wt% relatively to the remaining solvents (DCM and Et). The spinning solutions were obtained after at least 10h stirring.

2.3 Preparation of Membranes

The membranes were prepared using an electrospinning apparatus, where the previously prepared solutions were placed in a plastic syringe of 1 mL (inner diameter = 4.50 mm) with a tip caliber of 25 G (inner diameter = 0.61 mm). This set was fixed horizontally on the syringe pump (KdScientific KD100) and all the air was manually removed from the solution in the syringe to guarantee the absence of air bubbles that can cause fiber defect. The tip of the syringe was connected to a high-voltage DC power supplier (Glassman High Voltage Inc.) that generated a positive DC voltage, while the grounded counter electrode was connected to a stationary aluminum foil collector. An auxiliary electrode with a ring shape (at the same potential as the syringe tip) was used to control the electrospun area and to ensure that no fibers were deposited outside the designed collector. The electrospinning conditions used to prepare the membranes are listed in Table 1, being the membranes of CA and CA with porphyrins electrospun under the same conditions. The electrospinning process was carried out in a closed acrylic box at a temperature of approximately 22°C and relative humidity of 45%. After processing all the membranes were dried at 80°C for about 12 hours.

Table 1 – Electrospinning conditions.

Solutions	Solvent System [wt%]	Electrospinning Conditions			
		Q(mL/h)	d(cm)	ΔV (kV)	t(min)
CA10(A)	DCM/Et [80/20]	0.5	15	16	10
CA12(A)					
CA10+TTP(A)					
CA12+TTP(A)					
CA10(B)	DCM/Et/DMAc [72/18/10]	0.1	15	20	60
CA12(B)					
CA10+TTPIr(B)					
CA12+TTPIr(B)					

Q=flow rate; d=tip-to-collector distance; ΔV =applied voltage; t=time.

2.4 Characterization of the Solutions and Membranes

The viscosity was measured under steady state shear flow in a shear rate range from 0.01 to 1000 s⁻¹ using a stress-controlled rheometer Bohlin Gemini HR nano, with a cone-plate geometry (20 mm diameter and 2°) at room temperature. A solvent trap was used during measurements in order to avoid solvent evaporation.

The surface tension of the electrospinning solutions was studied using a KSV NIMA Langmuir and Langmuir-Blodgett Troughs (KSV NIMA L & LB Troughs) at room temperature (approximately 20°C). The surface tension of 1.8 mL aliquots (x3) was obtained by the difference of the surface tension between the aliquot and the reference value of water 72.75 mN/m³².

The membranes were analyzed by FTIR spectroscopy with a FTIR4100-Jasco in the range of 4000-500 cm⁻¹ with an attenuated total reflectance accessory (ATR) using a resolution of 8 cm⁻¹ with 64 repetitions scans average per sample. For comparison the TTP and TTPIr powder were compressed into KBr pellets and analyzed in the transmittance mode using the same parameters. All the samples, including the membranes, were previously dried. Raman and emission spectroscopy were carried out on a LabRAM HR Evolution Raman spectrometer (Horiba Scientific, France) coupled with a Horiba Scientific's LabSpec 6 spectroscopy suite that provides a complete instrument control and data processing. The Raman spectra were acquired with a 532 nm laser excitation wavelength (0.1% laser

intensity), with an acquisition time and accumulation of 30 s in a range between 500 – 1800 cm^{-1} , while the emission spectra were collected with the same laser wavelength with 0.01% intensity and an acquisition time and accumulation of 5 s in a range between 300 – 800 nm.

The morphology and the measurement of the fibers diameter (50 fibers/sample) were analyzed by scanning electron microscopy (SEM) on a NanoSEM FEI Nova 200, at an acceleration voltage of 5.00 – 10.00 kV in second electron image mode coupled to an energy dispersive X-ray (EDAX- Pegasus X4M) spectrometer. Previously to the SEM analysis the samples were sputter coated with a gold/platinum mixture, leaving an uncoated area to perform the EDX analyses. An Olympus BX51 microscope with X-Cite series 120Q fluorescence excitation of ultraviolet, blue and green light was used to observe the membranes at different irradiation light.

Atomic force microscopy was performed in a Keysight 9500 Scanning Probe Microscope, the images were kindly provided by Keysight Linz Company. The system was equipped with the standard 90 μm scanner and the samples were analyzed with the continuous force volume (CFV) mode $k=2$ N/m, mod.frequency=600 Hz, amplitude=300 nm, 0.5 Hz scan speed; (including Current imaging on sample E using CFV mode), and the Kelvin Probe Force Microscopy (KFM) mode $k=2$ N/m, $f=65$ kHz. Additionally, a 2D matrix of fast force sweeps was applied (300-1000 sweeps per second), which allowed the mechanical data measurement (topography). Current data at conventional imaging speeds using the KFM mode were acquired.

Static contact angles were also measured on the sample surface through the sessile drop method using an OCA20 contact angle instrument (DataPhysics Instruments GmbH, Filderstadt, Germany). Samples were cut in a rectangular specimen with 0.5 x 1 cm. Water microdrops (volume $\approx$ 5 μl , Milli-Q water) were generated with an electronic micrometric syringe and deposited on the substrate surface according to the so-called pick-up procedure. The contact angle was determined after 5 s of the moment of the drop deposition and settling. Image acquisition, analysis and contact angle determination was performed using the SCA20 v.4.3.12 software (Dataphysics Instruments GmbH, Filderstadt, Germany). A total of five drops of each probe liquid was dispensed and each drop was placed in a different region of the sample. The results correspond to the average and are presented with the respective standard deviations.

The thermal stability of both porphyrins, CA and respective membranes were studied using a TGA Q500 from TA Instruments within a temperature range of 60 – 800 $^{\circ}\text{C}$ under N_2 atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$

3. Results and Discussion

3.1 Properties of the Solutions

According to literature the solvent system Ac/DMAc is one of the most employed to prepare electrospinning solutions of CA^{25, 26, 33, 34}. While this solvent was good for CA, when the porphyrins were incorporated in the polymer a suspension of large particles was obtained (independently of the addition order of the components) and the membranes presented sizable defects (large projections of material). To overcome this issue, and in order to choose a different solvent system suitable for both porphyrins and polymer, the Hildebrand (δ) and Flory-Huggins (χ) parameters were previously estimated. The δ of the system of solvents was calculated considering the overall contribution of each solvent according to equation Equation 1³⁵:

$$\delta = \sum_i \phi_i \delta_i \quad \text{Equation 1}$$

Where ϕ_i corresponds to the volume fraction of the solvent and δ_i is the Hildebrand parameter. δ derives from the cohesive energy density of the solvent and it is fundamentally a liquid property value that indicates the relative solvency behavior of a specific solvent³⁴⁻³⁶. Therefore, solvents with similar Hildebrand values are miscible, once they have an identical cohesive energy that allows mixing^{35, 36}. The Flory-Huggins parameter (χ), which only considers the solvent interaction, complements this analysis by indicating which solvent is thermodynamically more stable for a specific polymer^{35, 37, 38}. Thus, lower χ values suggest that the solvent is favorable to dissolve the polymer. Even though, these calculations only take into account the solvents and the polymer, since no data is available for these porphyrins, the results provide a good approach to predict an appropriate system of solvents. The Ac/DMAc solvent system was then substituted by two different systems, DCM/Et, with a δ of 21.4 MPa^{1/2} and DCM/Et/DMAc with a δ of 21.5 MPa^{1/2} (Table 2). These showed to be suitable solvents to dissolve CA, since it is known that this polymer is ideally soluble in solvents or system of solvents with Hildebrand parameters between 19.43 and 25.57 MPa^{1/2}^{34, 37}. Since the χ values of CA and of solvents DCM and EtOH were not found in literature, it was possible to predict a relationship based on similar molecules, such as chloroform (CHCl₃) and methanol (CH₃OH), respectively (Table 2). Thereby the interaction CA – solvents can be organized according the following order: $\chi(\text{DMAc}) \approx \chi(\text{DCM}) \ll \chi(\text{EtOH})$, showing that

the DMAc and DCM solvents are thermodynamically more stable for CA and ethanol acts as a non-solvent.

Table 2 – Hildebrand and Flory-Huggins parameter of CA(DS=2.5).

Solvent ^{*2}	δ (MPa ^{1/2}) ^{*1}	Flory-Huggins parameter (χ)
Dichloromethane ^{*2}	20.2 ^{*2}	– ^{*4}
Ethanol ^{*2}	26.2 ^{*2}	– ^{*4}
Dimethylacetamide ^{*2}	22.5 ^{*2}	0.28
Chloroform ^{*3}	18.8 ^{*3}	0.34
Methanol ^{*3}	29.3 ^{*3}	1.87
DCM/Et	21.4	– ^{*4}
DCM/Et/DMAc	21.5	– ^{*4}

^{*1} SI units; ^{*2} From Hansen³⁹ and Barton³⁵; ^{*3} From Ghorani³⁴; ^{*4} No data available.

The solution prepared using DCM/Et solvent system with CA and TTP showed a fine purple suspension and fluorescence when excited with a 365 nm wavelength (Figure 2). This solution was used successfully to obtain electrospun membranes. However, the same solvent system with the metallated porphyrin (TTPIr) was unsuccessful. Therefore, to the previous solvent system was added DMAc, a less volatile solvent with a higher boiling point^{26, 37} and also a higher dielectric constant (Tb=166.0°C, ϵ =37.8) comparing to the DCM (Tb=39.8°C, ϵ =8.9) and Et (Tb=78.4°C, ϵ =24.55) solvents²⁶. The obtained solutions with the TTPIr porphyrin were red colored and homogeneous, although the fluorescence was quenched, due to the incorporation of the metal into the porphyrin (Figure 2).

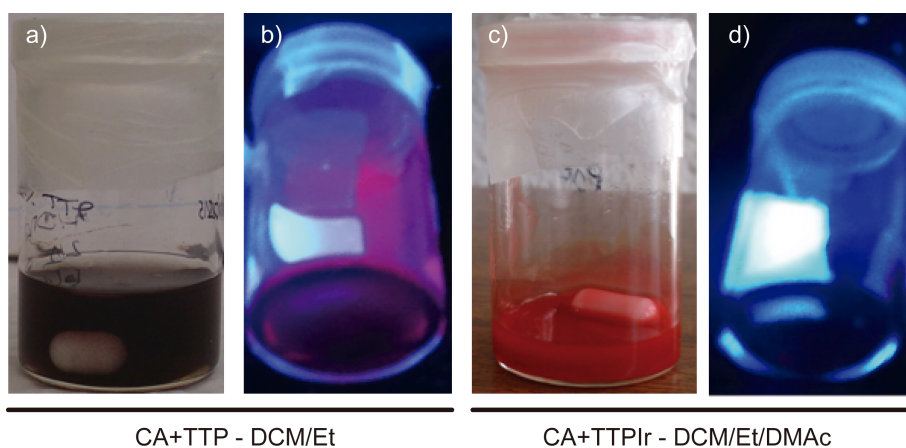


Figure 2 – Spinning solutions at daylight (a and c) and under UV radiation (b and d).

The rheological behavior and the surface tension of the electrospinning solutions were investigated to study the influence of the porphyrins incorporation in the CA and to help to define the electrospinning parameters

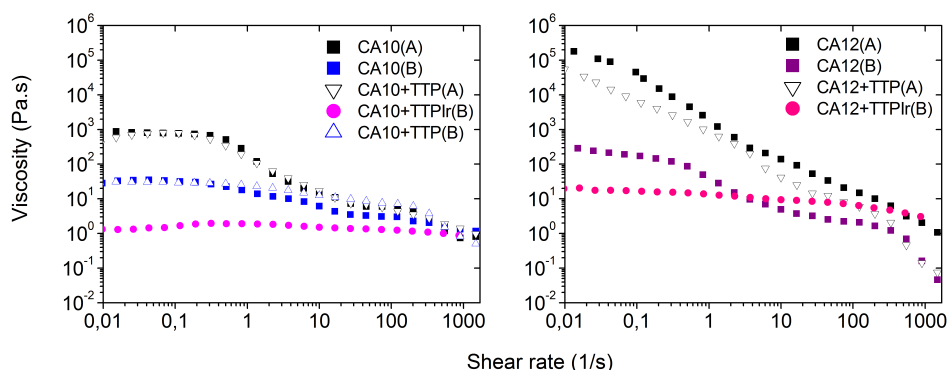


Figure 3 – Flow curves of the electrospinning solutions.

As demonstrated in Figure 3 the system of solvents employed show a strong influence in the presented flow curves. The different rheological behavior between the two systems of solvents can be due to its capacity to dissolve CA as a consequence of the solvents ratio used. The solvent system A, which showed a higher viscosity, is composed by 80 wt% of a CA solvent, dichloromethane and 20 wt% of a non-solvent, ethanol, while, the solvent system B, which presented a lower viscosity, is composed by a higher ratio of the CA solvent (both DCM and DMAc) 90 wt% respectively, and only 10 wt% of the non-solvent ethanol. Therefore, solvent system B has higher capacity to dissolve CA, which results in lower viscosity. This effect is even more pronounced when the CA concentration increases from 10 to 12 wt%. Although, and as it is known the effect of increasing viscosity with increasing polymer concentration²⁶, the solvent system A shows a more pronounced viscosity increase compared to solvent system B, which again arises from its lower capacity to dissolve CA. The incorporation of the metallated porphyrin, TTPIr, into the system promoted a viscosity decrease, explained by an easier chain alignment when the shear stress is applied. This could result from the higher capacity of TTPIr to disperse in this system enabling the formation of a homogeneous solution. In this system, it was also observed an approximation of a Newtonian fluid rheological behavior, where the viscosity is almost independent of the shear rate. These effects can be mainly attributed to the addition of the metallated porphyrin, once the same solution prepared with the non-metallated porphyrin did not show this tendency and the same viscosity was kept for CA solution for lower shear rates. Furthermore, the introduction of the non-metallated porphyrin in the system did not show a significant variance on the viscosity compared with CA.

The surface tension of the solutions is quite important for the fibers projection during electrospinning process and it is more likely a function of the solvent system than the polymer concentration³³. Figure 4 shows the surface tension of the prepared solutions, being the measurements taken at 15 s and 30 s, after the deposition of the solution on the equipment. The introduction of DMAc on the solvent system A, DCM/Et did not promoted a significant variation on the surface tension of the solutions, probably due to the small amount of DMAc added.

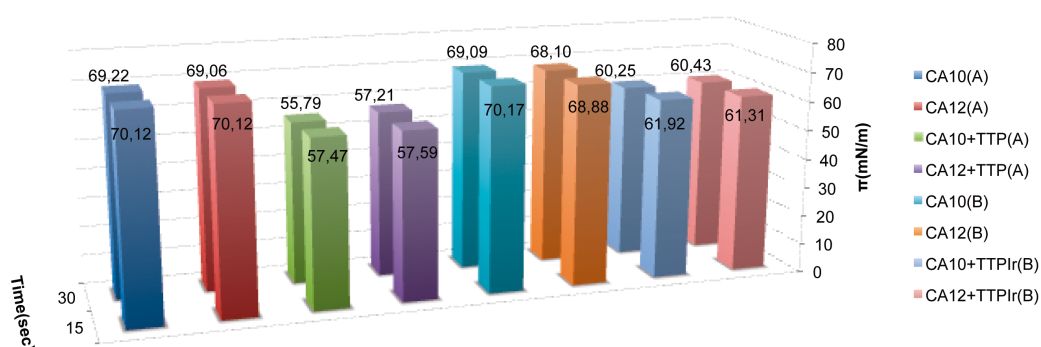


Figure 4 – Surface Tension (π) of the spinning solutions.

The incorporation of both porphyrins in the system lead to a slight decrease of surface tension, which is more pronounced for the non-metallated porphyrin (TTP), i.e., the latter turns out to be easier to electrospun, since the applied electric field necessary to overcome the surface tension and to obtain nanofibers is lower. In practice this slightly difference was reflected in a potential adjustment needed to electrospun the solutions prepared with the TTP from 16 kV to 20 kV with TTPIr. This is also reflected in the flow rate from 0.1 to 0.5 mL/h, respectively and consequently to a higher mass throughput that resulted in a reduction of the electrospinning time from 60 to 10 min (Table 1).

3.2 Properties of the Electrospun Membranes

The infrared absorption spectra of TTP, TTPIr porphyrins and the cellulose acetate membrane are presented in Figure 5.

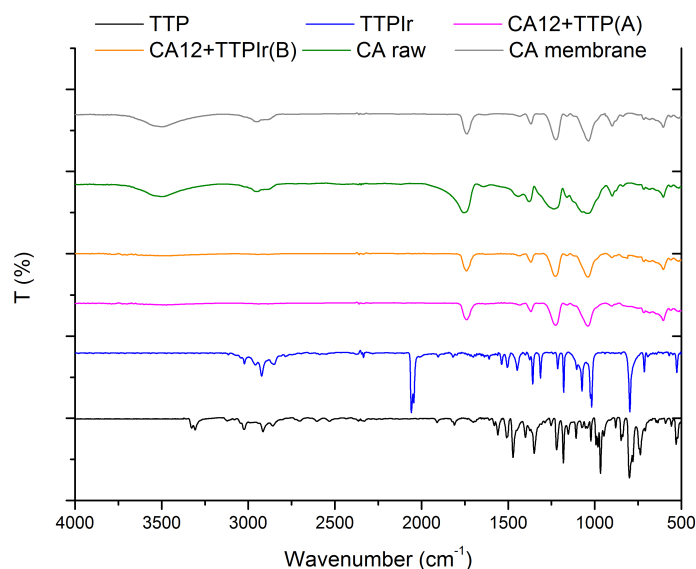


Figure 5 – FTIR spectra of CA raw and membrane, electrospun membranes of CA with the respective porphyrins (TTP and TTPIr), TTP and the respective metalloporphyrin TTPIr.

FTIR spectrum of the cellulose acetate membrane with 12wt%-(A) is similar to the spectrum of CA raw material. Moreover, membranes prepared with the system of solvents A and B are identical revealing that the electrospinning did not promote any chemical changes in the polymer. Thus, in Figure 5 it is possible to identify the main characteristic bands of cellulose acetate, which are supported by various studies^{29, 40-45}. A broad band at 3471 cm^{-1} that corresponds to the hydroxyl group (OH) stretching, a sharp and strong intensity band at 1741 cm^{-1} that corresponds to the symmetrical stretching and a weak band at 1621 cm^{-1} assigned to the asymmetrical stretching of the ester groups (carbonyl, $\text{C}=\text{O}$) are identified. The weak intensity bands at 2870 and 2933 cm^{-1} are assigned to the C-H stretching vibrations of the CH_2 and CH_3 groups, while the 1370 cm^{-1} band to the C-H bending. The C-O stretching was observed as a strong intensity band at 1216 cm^{-1} , as well the C-O symmetric stretching of the primary alcohol at 1025 cm^{-1} . The C-O-C asymmetrical stretching is assigned as a weak band at 1136 cm^{-1} and the band at 895 cm^{-1} is assigned to the β -glucosidic linkages between sugar units that form the polymeric chain of cellulose acetate. From Figure 5 it is clearly observed the successful metallation

of the TTPIr by the absence of the N-H stretching band between 3300-3293 cm^{-1} and of a sharp peak at 740 cm^{-1} associated with N-H out-of-plane deformations (these peaks are only present in the free-base TTP porphyrin)⁴⁶. Also, only on the metallated porphyrin is observed a sharp band at 2044 cm^{-1} that could correspond to one of the axial ligands (-CO, carbon monoxide). The bands at 3025 - 3000 cm^{-1} and 2910 - 2800 cm^{-1} are associated to the C-H stretching of the phenyl groups and the later to the C-H stretching of the methyl groups (aliphatic hydrogens), and the peak at 1179 cm^{-1} is associated with the stretching of the C-H of the pyrrole⁴⁶.

Regarding the spectra of the membranes with the porphyrins (Figure 5), the main bands of cellulose acetate previously discussed are easily identified, while the porphyrins correspondent bands are not detected due to a lower incorporation of porphyrins compared to the CA. In order to complement the information collected by FTIR spectra, Raman spectroscopy was performed in the same compounds with a laser of 532 nm wavelength, which permitted a clear identification of the incorporated porphyrins on the CA membranes (Figure 6). It is also noteworthy that Raman spectra were performed mostly in the fingerprint zone, where it is clearly observed that the incorporation of the iridium atom and the axial ligands had a strong influence in the bonds vibrations of the porphyrin molecule.

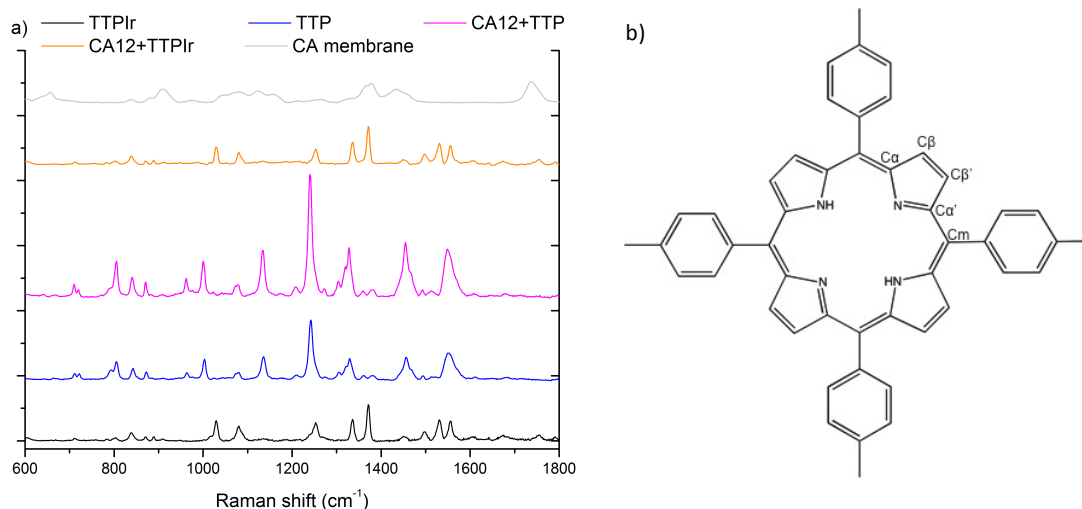


Figure 6 – a) Raman spectra of CA membrane, electrospun membranes of CA with the respective porphyrins (TTP and TTPIr), TTP and the respective metalloporphyrin TTPIr. b) Structure of TTP.

Concerning the polymer, the main bands are identified on the electrospun CA membrane (Figure 6)⁴⁷⁻⁵⁰. The 1733 cm^{-1} band is ascribed to the carbonyl (C=O) stretching vibrations in the acetyl groups, while the vibrations of the CH_3 groups within the acetyl groups are identified as a shoulder at 1363 cm^{-1} and

at 1449 cm^{-1} . The band at 1377 cm^{-1} has correspondence to the various deformations of the cellulose backbone $\delta(\text{CH}_2)$, $\delta(\text{HCC})$, $\delta(\text{HCO})$ and $\delta(\text{COH})$. Between 1300 - 1000 cm^{-1} region it is observed the signals of the asymmetric vibrations of CC and CO bonds of the cellulose backbone (1164 cm^{-1}) and the symmetric ring vibrations (1097 cm^{-1} and 1121 cm^{-1}) and ring stretching (1041 cm^{-1} and 908 cm^{-1}) of COC groups. At lower Raman shifts it is observed the vibrations of the bonds within CH_3CO acetyl groups, particularly the deformation vibrations $\delta(\text{COO})$ at 655 cm^{-1} and 601 cm^{-1} .

Regarding the porphyrin, the bands between 1400 and 1660 cm^{-1} are usually assigned to the stretching frequencies of $\text{C}_\beta - \text{C}_\beta'$ and $\text{C}_\alpha - \text{C}_m$ bonds and the region between 1300 - 1450 cm^{-1} is usually attributed to the stretching motions of the bonds $\text{C}_\alpha - \text{C}_\beta$ and $\text{C}_\alpha - \text{N}$ (Figure 6)^{51, 52}. Therefore, from both porphyrins spectra the bands at 1552 cm^{-1} (TTP) and 1557 cm^{-1} (TTPIr) can be attributed to the $\text{C}_\beta - \text{C}_\beta'$ bond stretching, symmetric stretching of $\text{C}_\alpha - \text{C}_m - \text{C}_\alpha'$ bonds and the bending formation of $\text{C}_\alpha - \text{N}(\text{H}) - \text{C}_\alpha' / \text{C}_\alpha - \text{N} - \text{C}_\alpha'$ bonds (only for TTP) including rocking of the hydrogen atoms on the C_β atoms⁵³. It is possible to observe some differences between the porphyrins in this region, since the nitrogen (N) atom and consequently the bond vibrations are changed due to the presence of the iridium atom. The bands that are identified in both porphyrins at 1080 cm^{-1} could be assigned to the rocking of the hydrogens in the carbon atoms (C_β) in the macrocycle and the band at 1136 cm^{-1} only observed for TTP could be assigned to the rocking of the hydrogen atoms on nitrogen atoms, it can also be assigned to the symmetric stretching of the $\text{C}_m - \text{C}_\alpha - \text{C}_\beta$ bonds⁵³. Moreover, it is of great importance to mention the absence of the band at 963 cm^{-1} in TTPIr, which could be assigned to the NH-NH bonds, and as expected, it is only identified at the non-metallated porphyrin - TTP⁵³. The bands at 900 - 1400 cm^{-1} are assigned to the stretching vibrations of $\text{C}_\alpha\text{C}_\beta / \text{C}_\alpha\text{N}$ ⁵².

The Raman spectra of electrospun membranes of cellulose acetate with porphyrins are also showed in Figure 6 - a), where due to the stronger signals of the porphyrins when compared to CA, it is only possible to identify the peaks correspondent to the porphyrins although the nanofibers were prepared with the CA polymer. Therefore, the CA signal in the wavelength range must have a very low intensity. Moreover, the presence of the porphyrins in the membrane was confirmed and no chemical reaction had occurred with the polymer, since new bands are not identified. Also, the porphyrins main characteristic bands are identified in the membrane with TTP and TTPIr (Figure 6).

The steady-state fluorescence emission at a 532 nm wavelength excitation and the fluorescence imaging of the electrospun membranes are observed in Figure 7.

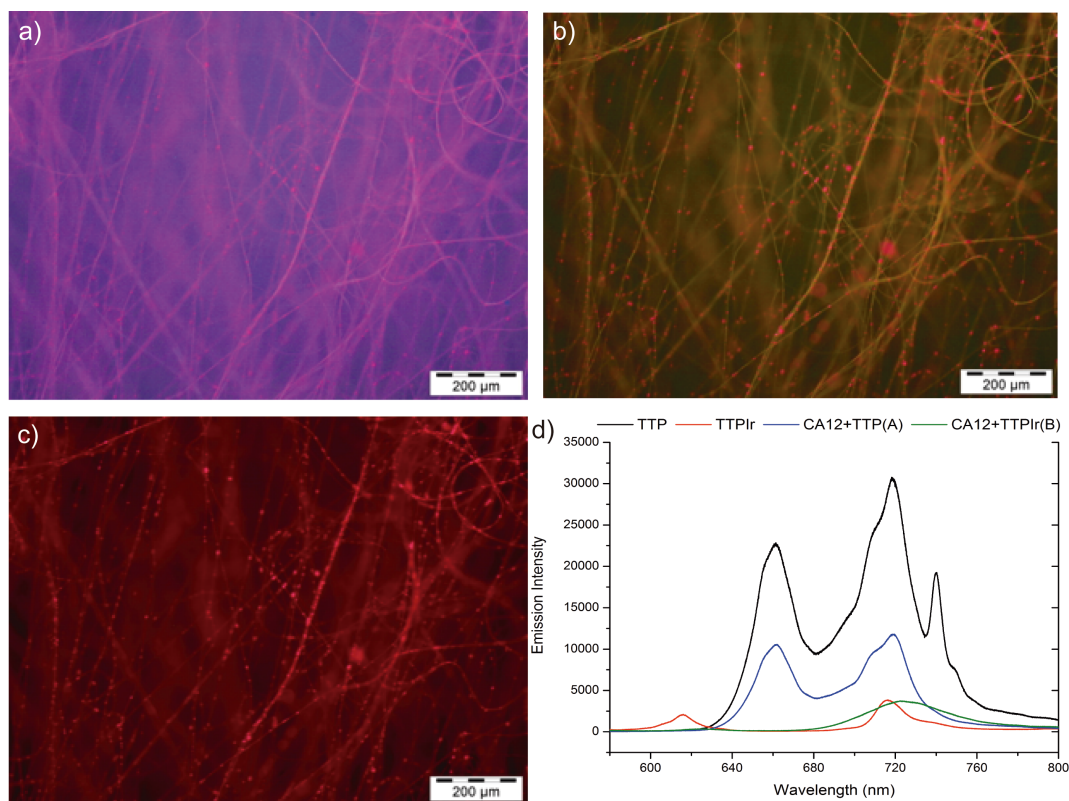


Figure 7 – Fluorescence imaging of the electrospun membranes prepared with 12wt%CA and TTP with the respective wavelengths a) UV 360-370 nm; b) Blue 460-490 nm; c) Green 510-550 nm and d) Emission spectra of TTP, TTPIr and CA electrospun membranes with porphyrins excited with 532 nm wavelength.

Typically the TTP porphyrin is fluorescent as previously mentioned in Figure 2 for the solutions of electrospinning. Therefore the electrospun membranes were also observed by fluorescence microscopy, and under blue light the membranes show a red-yellowish coloration that changes to red when excited with green light (Figure 7). The emission spectra of membranes shown in Figure 7 –d) confirm this result, since the TTP alone or when incorporated with CA and excited at 532 nm wavelength show two main emission peaks located at approximately 660 nm and 720 nm, although a slightly lowering on the peak intensity for CA+TTP is observed, which is related to lower quantity of material analyzed as already observed in the microscope images where it is clear that the porphyrins form small spots into the fibers. A significance lowering on the emission intensity of the TTPIr and the CA+TTPIr membrane is observed, which explains why when observing the fluorescence of both membrane or TTPIr alone at microscope no emission is seen. The explanation can be due to the incorporation of the iridium metal and the axial ligands Cl and CO that formed a stable complex without charge, which quenched the fluorescence of the metalloporphyrin. This effect was also observed in other porphyrins with transition

metals such as copper, cobalt and nickel, and can be mainly attributed to the heavy metal effect that relies in the enhancement of strong intramolecular spin-orbit interactions by the metal ion⁵⁴⁻⁵⁹. Sherman et al.⁶⁰ observed the reduction on fluorescence lifetime promoted by the interaction between a porphyrin and $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ particles. The author assigned the quenching to one or the combination of the possible effects, quenching by energy transfer, electron transfer or by the enhancement of the intersystem crossing⁶⁰. Koren et al.^{61, 62} also showed that the fluorescence of the Ir(III)-octaethylporphyrin could be changed by binding different axial molecules.

The thermal stability of both porphyrins, polymer and the electrospun membranes were studied by thermogravimetric analysis (Figure 8).

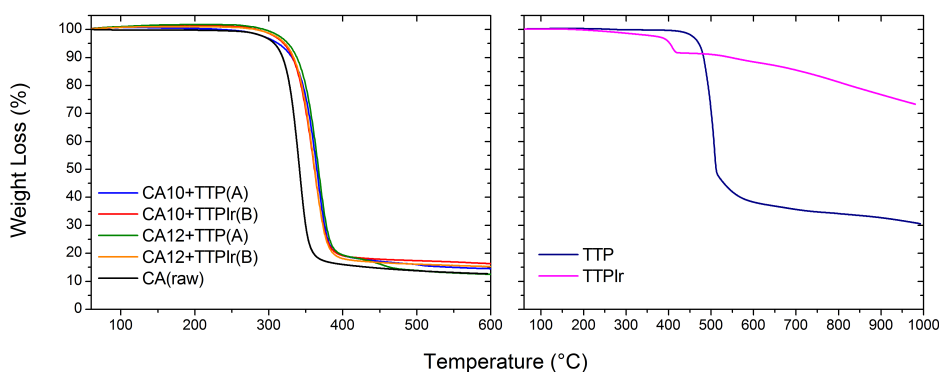


Figure 8 – TGA onset temperature of the porphyrins, raw CA and electrospun membranes.

As expected the TTP porphyrin showed a high thermal stability of 484 °C. Similarly to others metalloporphyrins, such as, the metal-tetraphenylporphyrin, TTPIr shows two onset temperatures⁶³. The first at a lower temperature (381 °C), which corresponds to the tolyl group or hydrogen atoms release and the second at approximately 523 °C due to the degradation of the porphyrin skeleton. The incorporation of both porphyrins into the CA matrix showed an enhancement of the thermal stability of the polymer. This result is expected since the thermal stability of the porphyrins is much higher than the polymer. However, the amount of incorporated porphyrin is not enough to make a significant difference between CA membranes incorporated with TTP and TTPIr.

Figure 9 shows the SEM microstructures of the unload and loaded CA electrospun membranes with porphyrins from solutions with a polymer concentration of 12 wt% in DCM/Et(A) and DCM/Et/DMAc(B) solvent system. Since the morphology of the membranes prepared with either the CA concentration of 10 or 12 wt% are identical, only the results with 12 wt.% are presented. Therefore, these micrographs are representative of each sample, where a general overview of the nanofibers is given with a

magnification of 1000x (scale 100 μm) and a more detailed picture is observed with a 10000x (scale 10 μm) magnification.

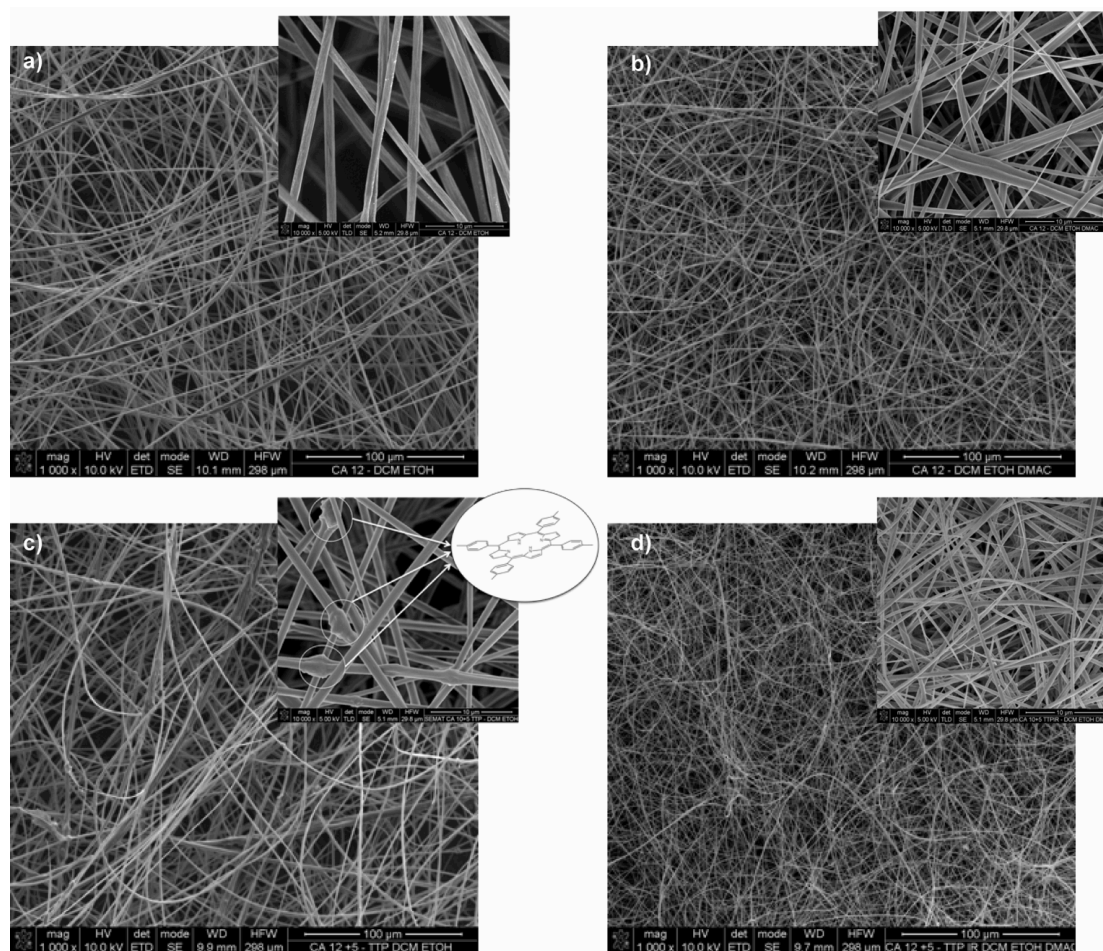


Figure 9 – SEM images of electrospun membranes. a) CA in DCM/Et(A); b) CA in DCM/Et/DMAc(B); c) CA+TTP in DCM/Et(A); CA+TTPIr in DCM/Et/DMAc(B).

SEM micrographs (Figure 9) and diameter analysis (Figure 10 and Table 3) of the fibers, indicate that increasing the CA concentration from 10 to 12 wt% resulted in solutions with higher viscosity and membranes with thicker nanofibers. This is a consequence of higher polymer chain entanglements and the overlapping between polymer chains in the solution, which is essential to maintain the continuity of the jet during the electrospinning process^{25, 33}. The introduction of DMAc into the solvent system promoted a strong reduction of the fiber diameter. The same effect was observed with the incorporation of the porphyrins however, it was more evident on the nanofibers with the metallated porphyrin (TTPIr). The observed reduction of the fibers diameter is related with the viscosity decrease of the spinning solutions previously shown (Figure 3). Therefore, in all cases, solutions with higher viscosity resulted in membranes with thicker nanofibers^{25, 26, 64-66}. Small agglomerates with diameters between 2-3 μm were observed only for the membranes prepared with the porphyrin TTP (Figure 9). These were not

considered beads but instead porphyrins agglomerates, which were already observed by fluorescence microscopy (Figure 7). This was an expected consequence of the CA+TTP solution suspension previously observed (Figure 2), where the strength of the relative forces between porphyrins showed to be higher than with the solvent leading to particle clumping⁶⁷. Also, hydrogen bonding between the nitrogen (N) atoms of the core and the hydrogens of the tolyl groups of near porphyrins can lead to porphyrin stacking and agglomeration. The introduction of the iridium and axial ligands into the porphyrin core seems to avoid the formation of this kind of bonding between porphyrins when incorporated in a CA solution, which was reflected in the absence of agglomerates and a uniform distribution of the metallated porphyrin (Figure 9).

Table 3 – Fiber mean diameter.

Membranes	Fiber diameter (μm)*	Membranes	Fiber Diameter (μm)*
CA10(A)	1.2 $\pm$ 0.3	CA12(A)	1.6 $\pm$ 0.2
CA10(B)	0.7 $\pm$ 0.2	CA12(B)	0.9 $\pm$ 0.3
CA10+TTP(A)	1.0 $\pm$ 0.2	CA12+TTP(A)	1.2 $\pm$ 0.1
CA10+TTPIr(B)	0.5 $\pm$ 0.1	CA12+TTPIr(B)	0.7 $\pm$ 0.2

*Mean fiber diameter.

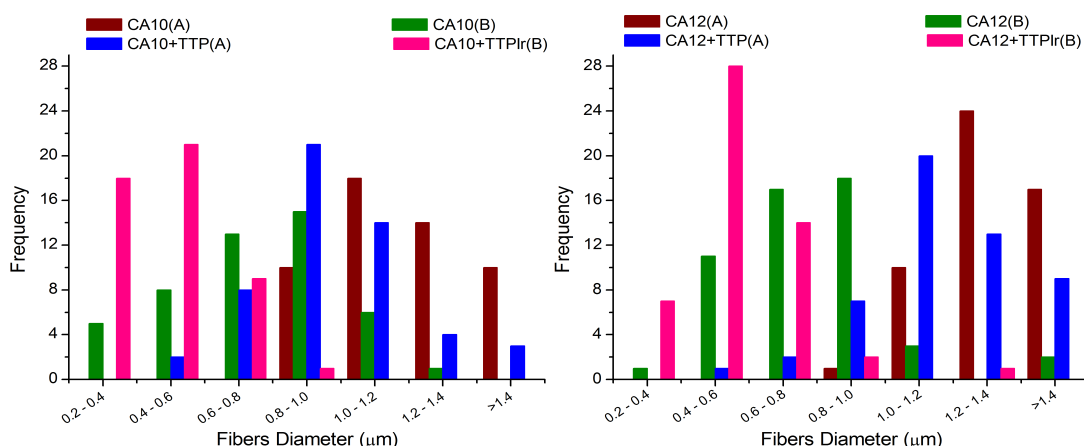


Figure 10 – Average fibers diameter and fibers distribution.

As it can be observed in Figure 10, fiber diameter of membranes prepared with the solvent system A, DCM/Et is independent of CA concentration, indicating a distribution skewed to the left (i.e., most of the data is concentrated on the right of the figure), which is associated with larger diameters. While the opposite scenario (distribution skewed to the right) is observed with the membranes prepared with B, DCM/Et/DMAc system, confirming the thinning effect induced by the presence of DMAc.

The conductive along the fibers of membranes with porphyrins were analyzed by atomic force microscopy (AFM) both in KFM and CFV mode, while the polymer matrix was only analyzed in CFV mode (Figure 11). The samples with 12 wt% of CA were chosen since no significant changes were observed in the membranes properties prepared with 10 and 12 wt% of CA.

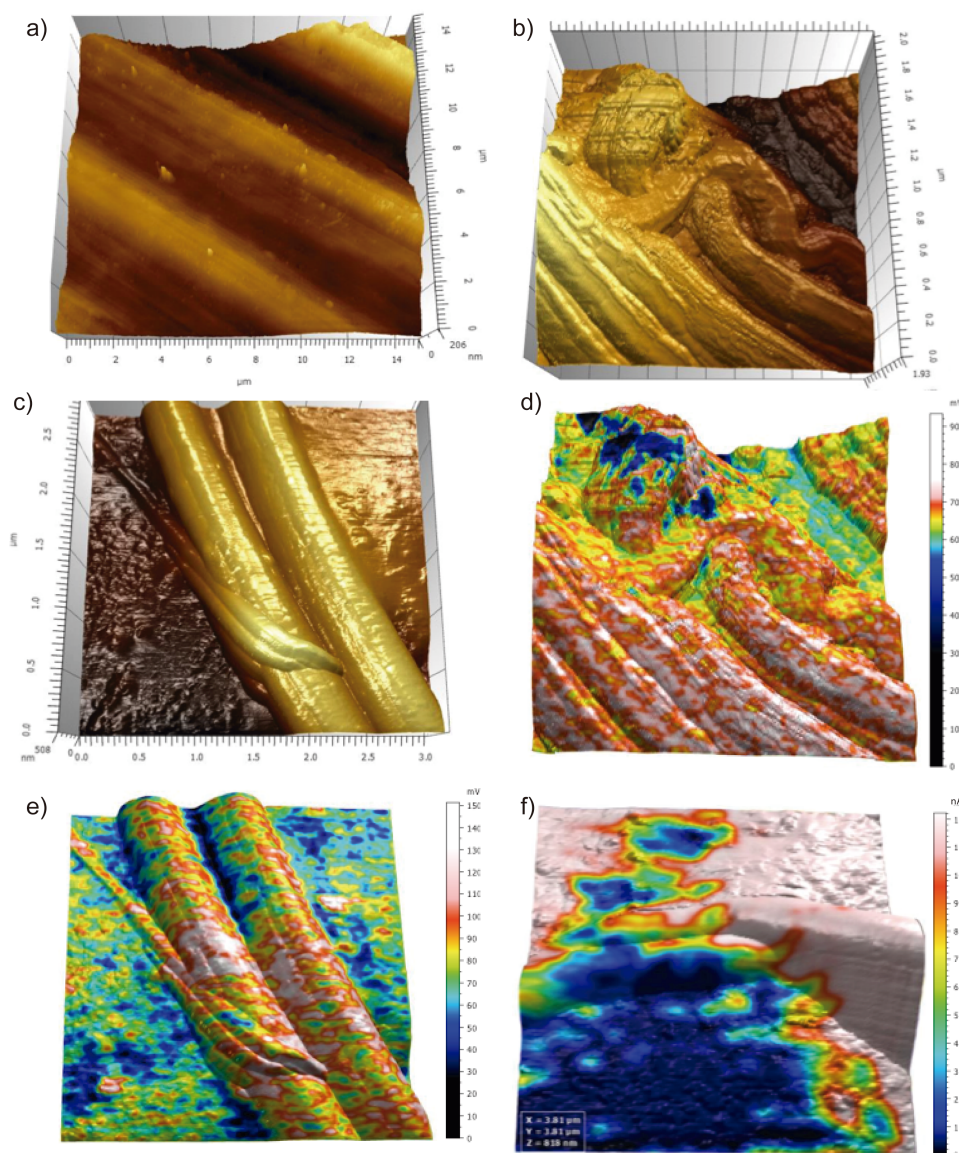


Figure 11 – AFM images of electrospun membranes, topography analysis: a) CA12wt% (15μm scan); b) CA12+TTP (2μm scan); c) CA12+TTPIr (2μm scan); surface potential: d) CA12+TTP (2μm scan) and e) CA12+TTPIr (3μm scan) and current image: f) CA12+TTPIr (4μm scan).

AFM images of CA electrospun nanofibers in CFV mode show linear fibers with bundles of strings with a thickness of few hundreds of nanometers to 2 micrometers (Figure 11 (a, b, and c)). Such difference could be a result of the difficulty in performing analysis with electrospun nanofibers, since flat surfaces are preferable. Concerning the KFM analysis, since no current could be established through the membrane with the TTP porphyrin, only images of the surface potential are showed, Figure 11 (d).

These revealed clear differences among fibers, where blue corresponds to a lower potential and blue/white up to 1V higher. Therefore, the darker domains observed on the top left could correspond to the TTP agglomerates observed by SEM and fluorescence microscopy (Figure 9 and Figure 7), while the remaining CA fiber show clearly a more homogeneous distribution of the surface potential. It seems that the presence of TTP agglomerates prevents/inhibits the establishment of a current circuit and therefore conductive properties. A change of few mV of potential through the fiber membranes was detected for the metallated porphyrin, probably due to the incorporation of the iridium on the porphyrin, which, as expected, promoted a more uniform distribution of the porphyrins on the CA fibers (Figure 11 (e)). It was also observed a slightly higher potential on the fibers comparing with surroundings. Additionally, this was the only sample where it was possible to acquired current image mapping, where highly conductive regions are showed as white/peak domains (approximately 12 nA maximum current) on the large fiber (Figure 11 (f)). Therefore, the establishment of these conductive domains can be a result of the higher dispersed metallated porphyrin, allowing the formation of networked structures with conductive properties. However, it is also observed smaller fibers situated in lower planes that exhibit mostly no conductivity (blue, dark areas). These could be zones of CA nanofibers without porphyrin. The heterogeneity of surface potential and conductive domains showed above can be related not only with the surface chemistry of the analyzed sample, but also with the surface roughness and the presence of voids on the sample, which have a major influence on AFM measurements and can have a strong effect on the results.

A low wettability of membranes can be advantageous for some practical applications, as so the change on the water contact angle (WCA) of the electrospun membranes of CA and CA loaded with porphyrins were also investigated, being the measurements taken at the initial 5 seconds after water drop and are shown in Figure 12 with representative photographs. As expected, CA nanofibers has a hydrophobic nature attributed mainly to the presence of the hydrophobic acetyl groups in the polymer structure and to the membrane nanofibers morphology^{68, 69}. From literature, cellulose triacetate, which has a higher acetyl content of 50% prepared by electrospinning showed a WCA of 141°, while deacetylated cellulose acetate could show lower WCA ranging 0.4°^{68, 70, 71}.

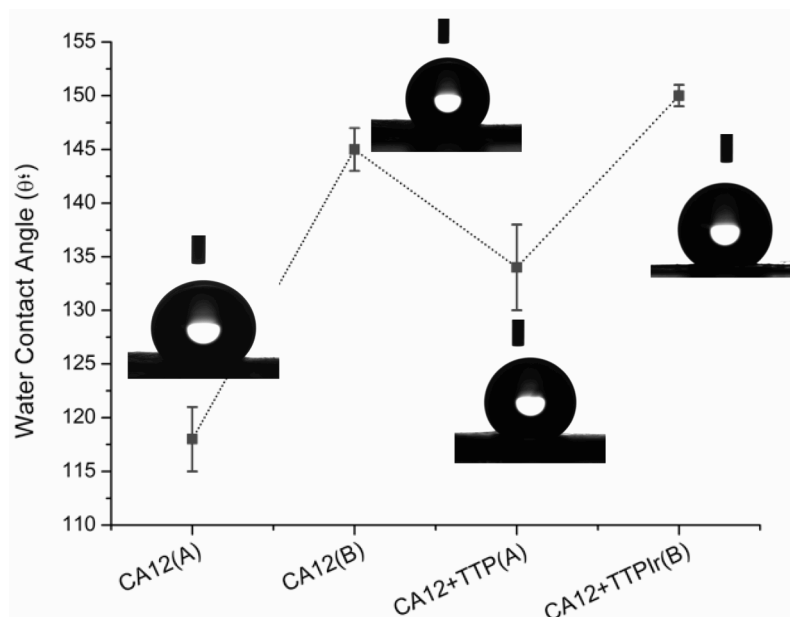


Figure 12 – Water Contact Angle of electrospun mats of CA and CA loaded with porphyrins and representative water droplet photographs.

CA mats obtained from the solutions with the solvent system B has a consistent higher WCA value (Figure 12), which is mainly related with thinner nanofibers observed by SEM (Figure 9)^{72, 73}. The reduction of the fiber diameter, which were already observed by Ma et al.^{72, 73} for PCL membranes, can develop hierarchical structures where the surface roughness are known to dramatically increases, as well as the fraction of contact area of the water droplet with the air trapped in the spaces between increasing the hydrophobicity of the respective membrane. Since, the WCA angle is inversely related to hydrophilic properties, it means that the higher contact angles presented lead to more hydrophobic membranes^{74, 75}. Electrospun membranes containing porphyrins depicted a slightly increase on hydrophobicity, which it was already expected since both porphyrins are water-insoluble and only a small amount was incorporated. However, according to Ma. M^{72, 73} it could be expected a wider WCA enhancement of the membranes with agglomerated TTP, similar to the membranes with micro-beaded fibers, such higher WCA was not observed. Instead, the thinner and uniform fibers obtained from the membranes with TTPIr showed higher WCA values, which are related with increasing of the surface roughness, once thinner nanofibers can trapped more air in between. Thus, it is noteworthy that WCA is not only affected by the polymer chemical structure but also by other parameters, such as porosity and roughness of the fibers web⁶⁸. From literature CA films prepared by different methods as phase inversion or solution casting have lower WCA compared to electrospun CA membranes. Since the electrospinning technique permits the trapping of more air (between fibers) under the falling water

droplet enhancing the WCA value^{74, 76, 77}. Also, depending of the solvent system employed and the electrospinning conditions, the fiber morphologies differ affecting the WCA results^{37, 72, 77, 78}

4. Conclusions

Cellulose acetate electrospun nanofibers were successfully prepared with the solvent systems DCM/Et(A) and DCM/Et/DMAc(B). The first system of solvents A, showed to be suitable for the preparation of CA nanofibers with the non-metallated porphyrin, TTP, but it needs small amount of DMAc to optimize the electrospinning process for metallated porphyrin, TTPIr. The solutions obtained from the system DCM/Et with the TTP showed to be purple with visible suspensions resulting in the formation of fibers with agglomerates, while the system DCM/Et/DMAc with the TTPIr showed a red homogeneous solution with an efficient porphyrin dispersion and smooth and thinner fibers. The diameter reduction was observed to be a consequence not only of the introduction of the DMAc solvent but also of the metallation of the TTP. The main absorption bands of the porphyrins and CA polymer were identified by FTIR and Raman spectroscopy and proved the incorporation of porphyrins into the CA membranes. Moreover, microscopy fluorescence has shown red luminescence of nanofibers with TTP under the excitation wavelength of blue and green light, although agglomerates of porphyrins when incorporated exhibited no electrical conductivity. Whereas, the nanofibers prepared with the TTPIr showed a lower emissivity but higher electrical conductivity as conductive paths can be established due to a more uniform distribution inside the membrane. The surface properties of the nanofibers were also improvement in hydrophobicity when the porphyrins were incorporated.

5. References

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VII

PREPARATION OF CA ELECTROSPUN NANOFIBERS WITH IRIDIUM-BIPYRIDINE COORDINATED PORPHYRINS

Porphyrins are very interesting compounds with an attractive potential to be used on molecular electronics. One of its advantages is the assembly of peripheral or axial ligands that may confer new properties to the porphyrin. Aromatic amines, such as bipyridine are of considerable interest and this was selected to coordinate the TTPIr metalloporphyrin in order to obtain axially bonded compounds. The ratio reaction was studied and the most promising compounds were sprayed on previous electrospun cellulose acetate nanofibers. Spectroscopic and cyclic voltammetry data including the calculus of the molecules energy band gap showed that the ideal metalloporphyrin/bipyridine ratio was 1/5. Also, the introduction of the bpy on the porphyrins showed to influence the fluorescence capacity of the molecule.

1. Introduction

The combination of different materials with the main objective of achieving a novel one, has been used by researchers around the world with success. Among various examples, the conjugation of conductive or even non-conductive polymers with carbon nanotubes (CNTs) achieving materials with interesting optic/electronic properties is widely used¹⁻⁴. Also, the incorporation of noble metals, such as gold, silver and platinum or nano-oxide particles of alumina, silica and others into polymers attaining materials that can be used as sensors or in optical fibers are other cases of success^{5, 6}. Concerning the several techniques that can be used to process these conjugated materials, the specific use of electrospinning technique has demonstrated its advantages due to the facility of fabrication as well as the ability to control composition, structural and functional properties^{7, 8}. This technique allows the preparation of materials composed of nanofibers with extremely small diameters (10 to 1000 nm) and a large surface-to-mass ratio⁷. The functionalities of these nanofibers can be adapted by changing the molecules located at the nanofibers surface⁷. Therefore, the preparation of materials with targeting fiber surface composition and morphologies can be employed in diverse fields, such as tissue engineering, drug delivery, medical implants, biosensors to military protective clothing, filtration and even supercapacitors, actuators and photovoltaic cells, among many others^{7, 9-11}. Among the vast number of polymers used to electrospun nanofibers, cellulose acetate¹²⁻¹⁶ was chosen has referred in chapter 6. In this particular case, it will act as a structural matrix for functional compounds, as porphyrins. Porphyrins in its turn are known due to its high conjugated macrocycle and the possibility of coordination of the nitrogen electron lone pairs with a vast number of metals, but also due to its versatile characteristics promoted by specific molecule design¹⁷⁻¹⁹. Since, the substitution of the peripheral substituents is possible and it has an impact on the final molecule properties¹⁷⁻¹⁹. These molecules showed a high and attractive potential to be employed as molecular electronics, which are molecules or collection of molecules, that can function as electronic components, which are much less toxic and could contribute to the continuing miniaturization of electronic components¹⁹. The assembly of these kinds of molecules by bridging the porphyrin additional metal center with conjugated molecules, such as bipyridine and other aromatic amines has attracted considerable interest as a new class of multicomponent systems¹⁹⁻³³. Furthermore, porphyrin arrays have been synthesized and are promise candidates to be used in several applications, such as on molecular sensing, transport of energy charge, catalyze, molecular electronics and new photonic materials, molecular wires and molecular switches, nonlinear optics, electrochromic, molecular elements of information storage and even for

photodynamic therapy tumors inspiring the continuous synthesis of porphyrin assemblies^{19, 20, 34-37}. Considering electronic applications in particular, it is known that the success of the assembly depends on the degree of the delocalization between the metal ion and the porphyrin and the relative energies and mixing of the orbitals¹⁹. Therefore, the metallation of the same porphyrin with different metals can achieve significantly different photophysical properties and redox chemistry¹⁹. Moreover, the relative orbital energies and consequently the electronic population of the central metal ion can also be affected by the coordination chemistry of ligand field effects¹⁹. As an example, the coordination of a non-luminescent Ni(II) porphyrin with pyridine raised the d_{z^2} orbital energy changing the photophysical properties¹⁹. In this work iridium(III) metalloporphyrin 5,10,15,20-tetrakis(p-tolyl)porphyrin (TTP) was coordinated with 4,4-bipyridine moieties in order to obtain axially bonded metalloporphyrin arrays. The reaction ratio between the metalloporphyrin and the bipyridine was studied. These arrays were sprayed on the surface of cellulose acetate electrospun membranes, which were previously activated by oxygen plasma treatment. The electrospun parameters were already defined on the previous chapter and the properties of the metalloporphyrin arrays and final sprayed membranes were studied by FTIR, Raman and emission spectroscopy. The formation of the arrays was also studied by cyclic voltammetry and UV-Vis spectroscopy and the success of the oxygen plasma treatment by the measure of the water contact angles. The adhesion of the array compounds to the CA membranes surface was observed with SEM images.

2. Materials and methods

2.1 Materials

The porphyrin 5,10,15,20-tetrakis(p-tolyl)porphyrin (TTP) (98% purity), the precursor chloro(1,5-cyclooctadiene)iridium I dimer ($[\text{Ir}(\text{COD})\text{Cl}]_2$) (97 % purity) and the cellulose acetate (CA) with an acetylation degree of 39.8 wt% were purchased from Sigma-Aldrich. The solvents, xylene, dichloromethane, n-hexane, chloroform, ethanol, toluene and dimethylacetamide were purchased from Acros Organics and used without further purification. The HCl 1 M solution was prepared from the dilution of HCl 37 % solution acquired from Sigma-Aldrich.

2.2 Synthesis of Porphyrin Arrays

Previously to the axial coordination of TTP it is necessary to introduce the metal transition into the core of the porphyrin (Figure 1). The metallation reaction of TTP with iridium is already described in literature³⁸. The free-base TTP (150 mg, 0.22 mmol) and the dimer $[\text{Ir}(\text{COD})\text{Cl}]_2$ (225.3 mg, 0.33 mmol) were added in xylene and refluxed for 4 days. The solution was purified through column chromatography and the metalloporphyrin was isolated with 70.7% yield, respectively. Found: δ_{H} ppm: 2.75 (s, 3H, $\text{CH}_3\text{-Ph}$), 7.60 – 7.62 (d, 8H, m-Ph), 8.12 – 8.22 (dt, 8H, o-Ph), 8.99 (s, 8H, $\beta\text{H-pyrrole}$). The porphyrin arrays were synthesized in toluene reflux by axial coordination of 4,4'-bipyridine (bpy) and the metallated porphyrin (TTPIr). The volume of toluene and the porphyrin molarity was maintained constant while the TTPIr/bpy ratio was altered. The stoichiometry and the reaction conditions employed in each reaction are elucidated in Table 1.

Table 1 – Stoichiometry and reaction conditions.

Compounds*	Stoichiometry				Solvent	T (°C)	Time (days)
	TTPIr (mmol)	Eq.	Bpy (mmol)	Eq.			
TTPIrL(0.1)	0.03	1	0.003	0.1	Toluene	110	4
TTPIrL(0.5)		1	0.015	0.5			
TTPIrL(1)		1	0.03	1			
TTPIrL(5)		1	0.15	5			
TTPIrL(10)		1	0.3	10			
TTPIrL(20)		1	0.6	20			

* Porphyrin concentration of 0.006 M in all the solution reactions.

Thin layer chromatography was performed in Merck pre-coated silica gel 60 F-254 plates and size-exclusion chromatography (Sephadex LH-20) was employed to purify the synthesized complexes in a time and labor effective way. Sephadex LH-20 was selected according its high chromatographic selectivity based mostly on the molecular mass of the analyte and on the differences in the hydrogen bonding between the dissolved components and the gel matrix composed of cross-linked hydroxypropylated dextran beads. The Sephadex LH-20 was washed, suspended and packed into the column (13 x 1 cm, length x width) with CHCl_3 +1 % EtOH at a continuous flow rate.

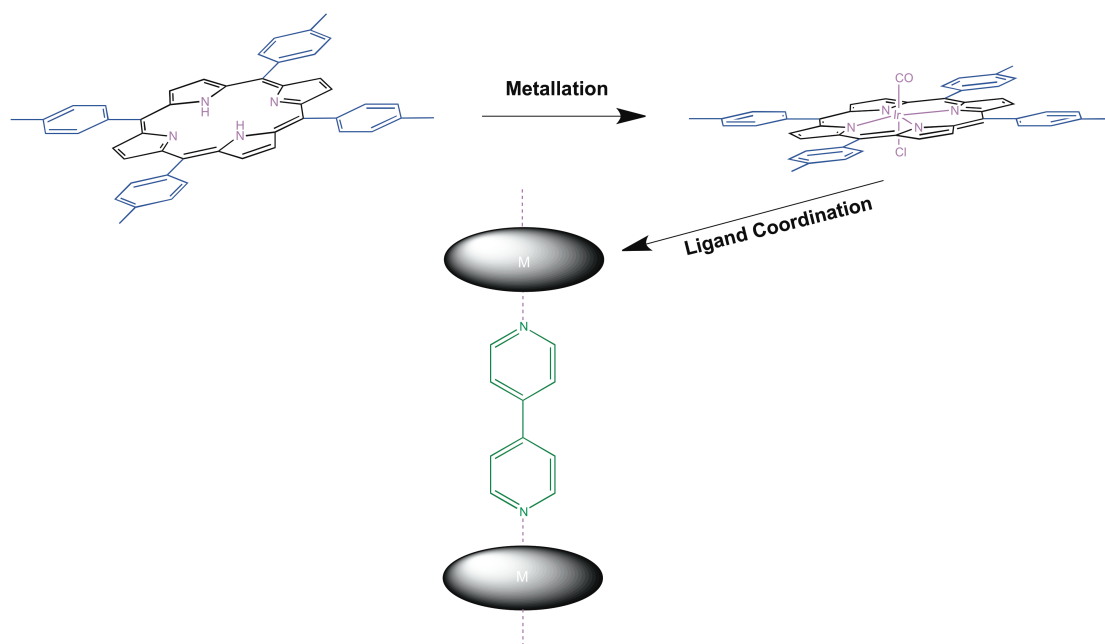


Figure 1 – Metallation and coordination reaction of TTPIr with 4,4'-bipyridine ligand.

2.3 Preparation of the Membranes

Cellulose acetate membranes were prepared by electrospinning of a 12 wt% CA solution in DCM/Et 80/20 (w/w). The method and the process parameters used to prepare the nanofibers are described on the previous chapter. In order to ensure the adhesion between the CA membrane and the porphyrin arrays, the CA nanofibers surface was negatively charged by oxygen plasma treatment. The nitrogen groups of the bpy attached as end groups of the porphyrin arrays were protonated in a solution with acidic character. The CA membranes were then carefully sprayed with 5 mL of this solution with the various synthesized porphyrin arrays and dried at 80 °C under vacuum.

2.4 Characterization Methods

Absorption spectra of the porphyrin arrays were measured at a Shimadzu UV-2401PC UV-Vis spectrophotometer in CHCl_3 in a range between 190 and 700 nm and transmission IR spectroscopy were performed in KBr compressed pellets while the membranes were directly analyzed using the attenuated total reflectance accessory (ATR) on a FTIR4100-Jasco in the range between 4000 to 500

cm⁻¹ and a resolution of 8 cm⁻¹ with 64 repetitious scans averaged per sample. Raman and emission spectroscopy were carried out on a LabRAM HR Evolution Raman spectrometer (Horiba Scientific, France) coupled with a Horiba Scientific's Labspec 6 spectroscopy suite that provides a complete instrument control and data processing. The raman spectra were acquired with a 532 nm laser excitation wavelength (0.1 % laser intensity), with an acquisition time and accumulation of 30 s in a range between 500 – 1800 cm⁻¹, while the emission spectra were collected with the same laser wavelength with 0.01 % intensity and an acquisition time and accumulation of 5 s in a range between 300 – 800 nm. Previously to cyclic voltammetry studies, the molar ionic conductivity (Λ) of all compounds was observed to ensure the neutral state before the pH adjustment and the change on the Λ after pH adjustment to an acidic character. This was determined from a Digital Conductivity Philips model PW 9527 at 25 °C in a thermostated water bath, dissolving approximately 9 mg/10mL of each sample in chloroform or in toluene and toluene with a pH=4. The resulting molar conductivity was determined using Equation 1³⁹, where k is the constant of the conductivity cell with a value of 0.89 and M the approximate molar concentration. To calculate the molar concentration the TTPIr, the monomer and the dimer, with a molar mass of 924.2 g/mol, 1173.2 g/mol and 2190.2 g/mol, respectively according to results was used.

$$\Lambda m(S.cm^2.mol^{-1}) = \frac{k \times (1 \times 10^6)(S/cm)}{M(mol/dm^3)} \quad \text{Equation 1}$$

Cyclic voltammetry (CV) was accomplished with a three-electrode arrangement, whereby the potential relative to a silver-wire reference electrode is scanned at a vitreous carbon disc-working electrode, while the resulting current flow through a platinum-wire auxiliary electrode is monitored in a quiescent solution. This study was performed at room temperature in chloroform (CHCl₃) solutions of the target compound ([C] = 9 mg/10mL) with 0.1 M of tetrabutylammonium bromide (TBAB) as supporting electrolyte. All the solutions were studied at different scan rates (20, 50, 100 and 300 mV/s) in the absence of oxygen and all the relevant data is presented with respect to ferrocenium/ferrocene (fc⁺/fc) as an internal reference ($E_{Fe} = 0$ mV) for ease comparison. Oxygen plasma treatment of CA membranes was performed in a Zepto instrument from Diener electronics in a chamber with a volume of 2.6d m³ and a generator of 40 kHz at a radio frequency power of 100 W during 120 s in oxygen atmosphere with a pressure maintained between 40 – 50 Pa. The membranes were sprayed immediately after the plasma treatment to maximize the effect of the treatment. The pH of the porphyrinic solutions was adjusted with HCl 1 M solution to a pH equal to 4 in a pH/ORPMeter HI 2211 Hanna instrument. The morphology of the sprayed membranes were analyzed by scanning electron microscopy (NanoSEM FEI Nova 200), in second electron image mode coupled to an energy dispersive X-ray (EDAX- Pegasus X4M)

spectrometer at an acceleration voltage of 3.00 – 10.00 kV. All the membranes were sputter coated with a gold/platinum mixture prior to SEM measurement. The fluorescence microscopy images were acquired in an Olympus BX51 microscope with X-Cite series 120Q fluorescence with an wavelength excitation on the ultraviolet, blue and green light range. The change in the hydrophobicity/hydrophilicity behavior of the CA membranes before and after oxygen plasma treatment was studied by measuring the water contact angle with OCA20 equipment (DataPhysics, Instruments GmbH, Filderstadt, Germany). A total of 5 microdroplets (Milli-Q water) with 5 μL volume were deposited on different places of the substrate surface according to the sessile drop method and the images were recorded. The image acquisition, analysis and contact angle determination was performed 5 s after the moment of the drop deposition using the SCA 20 software (Dataphysics Instruments GmbH, Filderstadt, Germany).

3. Results and Discussion

3.1 Preparation of Porphyrin Arrays

To synthesize the porphyrin arrays, solvents with lower boiling points, such as, dichloromethane, and cyclohexane were used in reflux and UV-Vis spectroscopy^{22, 25, 26, 30, 31} and TLC techniques were employed to observe changes on the compounds during reaction. However, only with toluene, as solvent of reaction, the TLC spot correspondent to the TTPIr and to the bpy started to disappear and new spots with a lower retention factor (R_f) were observed, indicating the TTPIr coordination.

No changes were observed on the absorption and FTIR spectra using 0.1 and 0.5 bpy molar equivalents, indicating that no reaction occurred using this stoichiometry (Figure 2). Moreover, it was possible to observe a less intense band at approximately 242 nm associated to the non-coordinated bpy band, confirming the non-coordination (Figure 2).

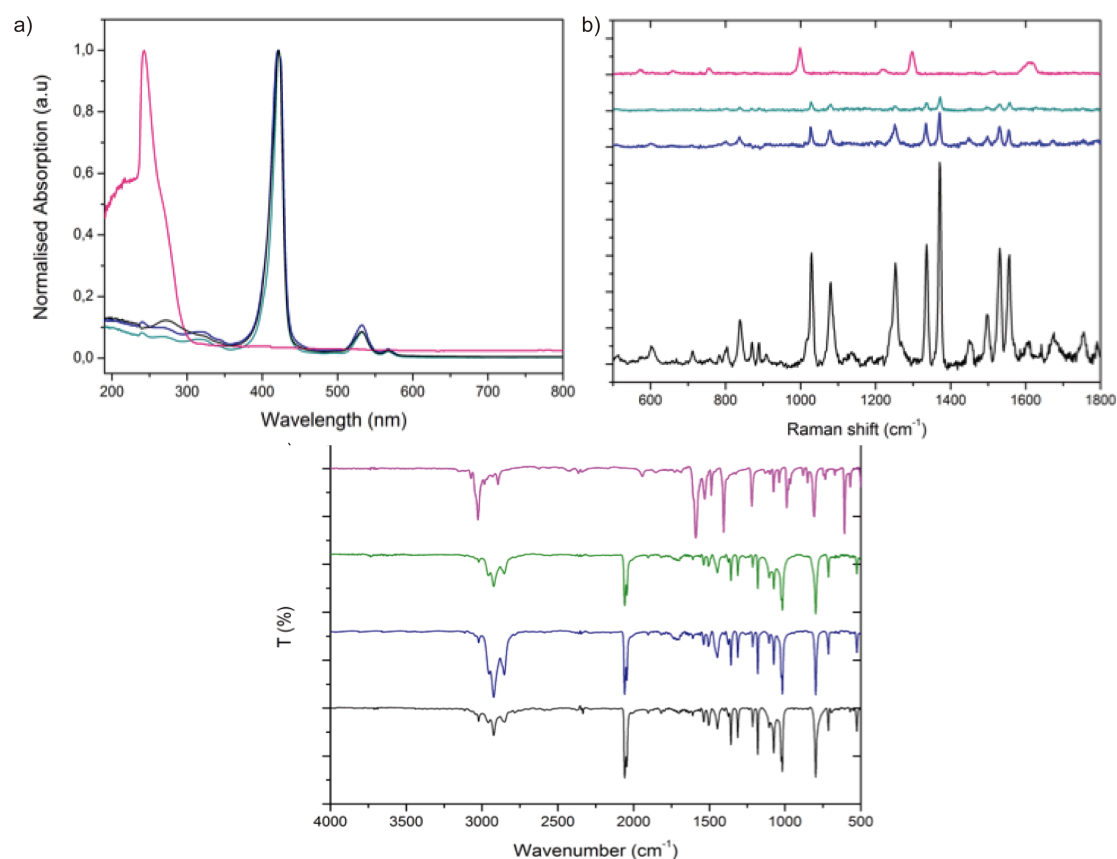


Figure 2 – a) UV-Visible and b) Raman spectra and c) FTIR spectra of bpy, metalloporphyrin TTPIr, TTPIrL(0.1) and TTPIrL(0.5) compounds (black – TTPIr; blue – TTPIrL(0.1); green – TTPIrL(0.5) and pink – BPY).

The respective FTIR and Raman spectra (Figure 2) also show the absence of a possible coordination between the bpy ligand and the TTPIr, since in the first technique it is possible to observe for both bpy equivalences (0.1 and 0.5) the presence of a strong band at approximately 2058 cm^{-1} correspondent to the $-\text{CO}$ axial ligand, which is initially present in the metalloporphyrin^{40, 41}. Raman spectra of TTPIrL(0.1) and TTPIrL(0.5) did not show any significant changes comparing to the TTPIr (Figure 2). The peaks between 1400 and 1660 cm^{-1} are usually assigned to the stretching frequencies of $\text{C}\beta - \text{C}\beta'$ and $\text{C}\alpha - \text{Cm}$ bonds and the region between 1300 – 1450 cm^{-1} is usually attributed to the stretching motions of the bonds $\text{C}\alpha - \text{C}\beta$ and $\text{C}\alpha - \text{N}$ ^{42, 43}. Also the bands identified at 1080 cm^{-1} could be assigned to the rocking of the hydrogens in the carbon atoms ($\text{C}\beta$)⁴³. Although, the UV-Vis, Raman and FTIR spectroscopy techniques did not show any evidence that the reaction occurred, from cyclic voltammetry technique it was possible to observe some changes that were related with a possible coordination of the TTPIr(0.5).

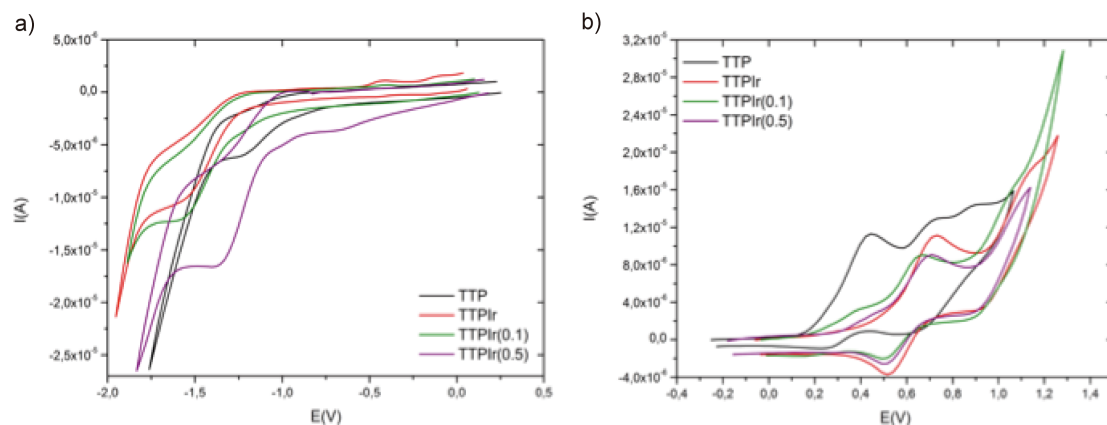


Figure 3 shows the cyclic voltammograms at 100 mV/s of TTP, TTPIr and respective compounds prepared from the reaction with 0.1 and 0.5 mol bpy. The redox reactions noticed from the TTP porphyrin are known to correspond to the porphyrin macrocycle itself similarly to others porphyrins⁴⁴. While the incorporation of a central metal, such as iridium, clearly induces some changes on the cyclic voltammograms and peak potential. This is promoted mainly by the strong interactions between the d electrons of the metal and electrons of the nitrogen atoms of the porphyrin ring, and also by the identity of the axial ligands⁴⁴.

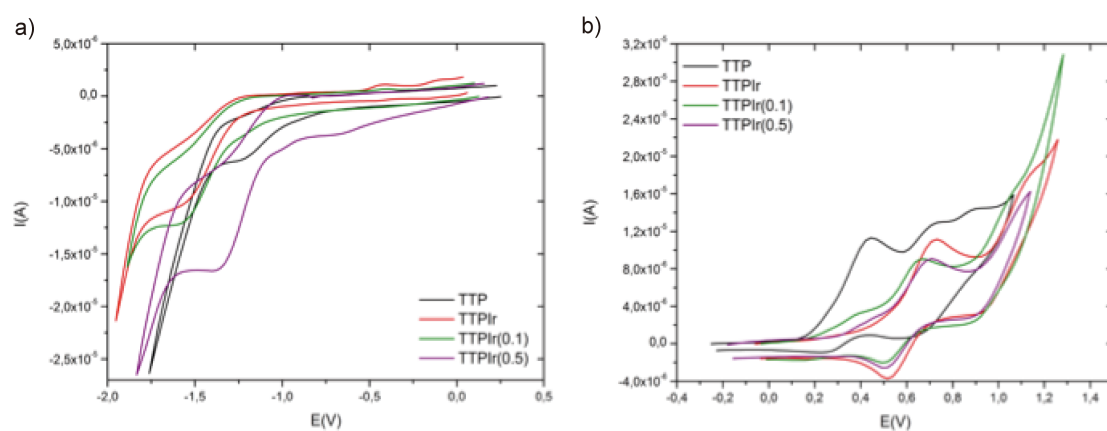


Figure 3 – TTP, TTPIr and TTPIr(0.1) and (0.5) cyclic voltammograms in chloroform with internal reference ferrocenium/ferrocene at a scan rate of 100 mV/s.

Although it is known that the full complex is always responsible for the compounds properties, it is possible to correlate the peaks with specific interactions. In this case, the introduction of the iridium with the Cl and CO axial ligands induced significant changes on the porphyrin cyclic voltammograms. A new quasi-reversible redox process on TTPIr with anodic compensation ($E_{p^{ox1}}=0.73$ V vs fc^+/fc) correspondent to a redox reaction on the iridium center can be observed, while the second reversible redox process ($E_{p^{ox2}}=1.11$ V vs fc^+/fc) is assigned to the porphyrin macrocyclic ring with a slightly

potential deviation from the porphyrin TTP. The latter is probably due to the overall contribution of the metal and the axial ligands. Concerning negative potentials (Figure 3(a)), while in the TTP porphyrin it was detected an irreversible process ($E_{p^{red1}} = -1.18 \text{ V vs } \text{Fc}^+/ \text{Fc}$), the conjugation with the iridium metal and ligands showed a quasi-reversible process ($E_{p^{red1}} = -1.26 \text{ V vs } \text{Fc}^+/ \text{Fc}$). Similar to TTPIr voltammograms, the TTPIr(0.1) shows the same processes, indicating the non-coordination of the metalloporphyrin with bpy. However, when the bpy molar amount is raised to 0.5, significant deviations were observed, such as the presence of the peak ($E_{p^{red1}} = -1.35 \text{ V vs } \text{Fc}^+/ \text{Fc}$) without anodic counterpart and the strong deviation of the redox processes. In this particular case and combining the results of FTIR, UV-Vis and CV, can be established that under this condition there is a presence of a mixture of compounds. Furthermore, these results also indicate that it is possible that some porphyrin molecules have been coordinated with bpy, but its amount it is too small to be identified by less sensitive techniques, such FTIR and UV-Vis. It is also relevant to mention that previously to CV characterization, the ionic conductivity revealed all neutral compounds. Therefore, the product of the reactions TTPIr(0.1) and TTPIr(0.5) were not used to prepared the CA-based membranes.

Applying the same methodology, the iridium metalloporphyrin was successfully axial coordinated with the bidentate ligand 4,4'-bipyridine, when the molar ratio TTPIr/BPY was equal or greater than one. Figure 4, based on UV-Vis spectra, depicts that the incorporation of the bpy ligand caused strong shifts of both Soret and Q-bands compared to the metalloporphyrin TTPIr.

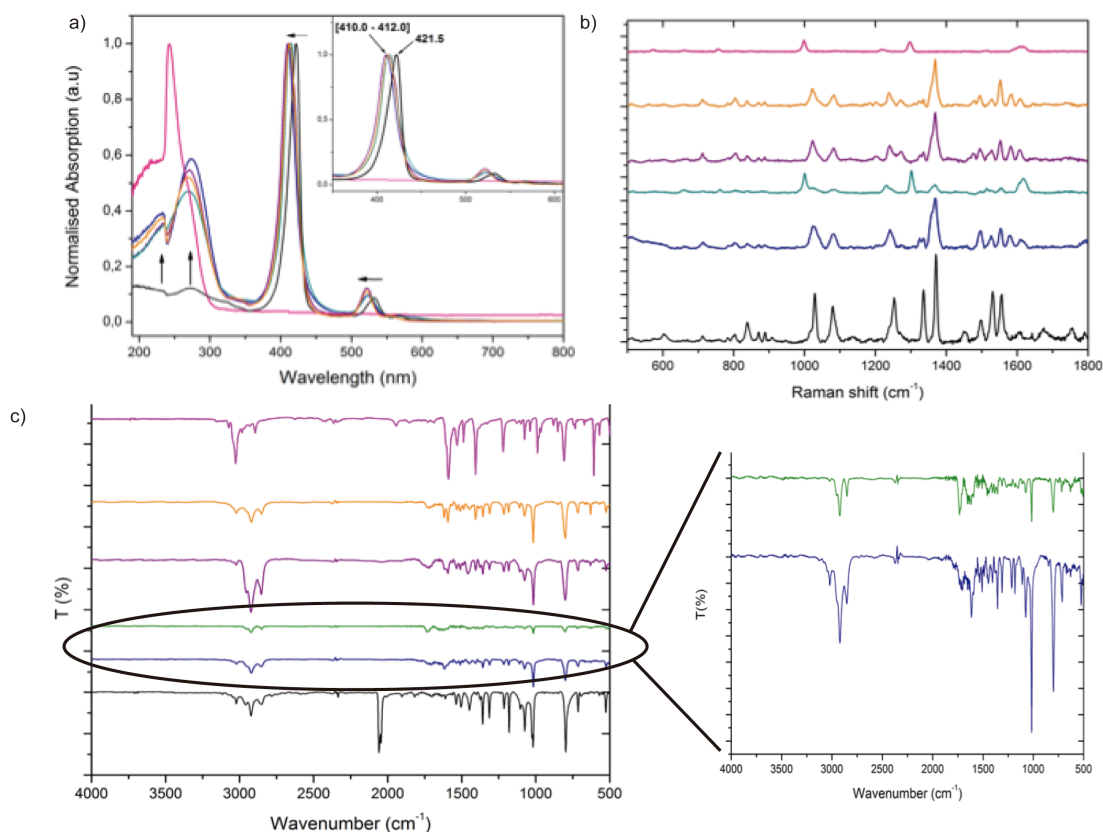


Figure 4 – a) UV-Vis and b) FTIR spectra of bpy, TTPIr, and TTPIrL complexes (black – TTPIr; blue – TTPIrL1; green – TTPIrL5; purple – TTPIrL10; orange – TTPIrL20; pink – BPY).

Although, it is not usual to observe UV-Vis spectra with such broad measurement range, in this particular case it permits to confirm the absence of the non-coordinated bpy ligand at 242 nm. An intensity increase of the bands between 200-300 nm can also be detected, which are already identified as less intense bands on the TTPIr and that are probably related with charge-transfer processes between the metal ion and the porphyrin^{45, 46}. These type of transitions are observed specially with transition metals with open d-shells and are generally weak⁴⁵. Accordingly to the UV-Vis spectra (Figure 4), the axial coordination of the TTPIr with the bpy ligand increases these kinds of processes, which is in line with the required properties for the development of optic/electronic materials.

Raman spectra (Figure 4) of the TTPIrL complexes showed the formation/deviation of bands due to the presence of the axially bonded bpy. Therefore, the band observed on the complexes at 1000 cm⁻¹ shows a deviation from the TTPIr promoted by the presence of the bonded bpy, while the bands between 1226 – 1241 cm⁻¹, indicate a deviation from the TTPIr at 1250 cm⁻¹. Also a new band is identified at approximately 1275 cm⁻¹ assigned to the axial bpy, the band at 1371 cm⁻¹ belongs to the TTPIr. FTIR spectra of the TTPIrL complexes, Figure 4(c), demonstrate the absence of the CO band at

approximately 2058 cm^{-1} for all the complexes that achieved successful axial coordination. The coordination of the conjugated bpy ligand showed to have some effect on the complexes vibrational spectra by a small shift for lower or higher energies with a wavenumber difference between 3 and 10 cm^{-1} of some bands compared to the TTPIr, but also with the formation of new bands assigned to the bpy ligand ring vibrations CN and CC stretching at 1592 cm^{-1} , 1487 cm^{-1} , 1407 cm^{-1} , respectively⁴⁷. The bands at approximately $1590 - 1445\text{ cm}^{-1}$, 1355 cm^{-1} and $1310 - 1178\text{ cm}^{-1}$ are identified in both TTPIr and TTPIrL complexes and are assigned to the C=C stretch in the phenyl and porphyrin, C=H bend in phenyl, C-H bend in phenyl and C-H and C-N stretch in porphyrin respectively⁴⁸. Also, the absence of the -NH corresponding band at approximately 3300 cm^{-1} confirms that no demetallation occurred and the stability of the iridium as a porphyrin metal center. Previous to cyclic voltammetry, the molar ionic conductivity of all compounds was measured confirming their neutral state (Table 3). The CV and the emission results (Figure 5) demonstrated that although some evolution on the CV voltammograms of TTPIrL1 could be notice, the emission curves and intensity stays very similar with the TTPIr. Thus, these results demonstrate that although all of the CO groups (FTIR spectra of Figure 4) of the TTPIr have been substituted with bpy, only monomers have been achieved and the molarity 1 to 1 was not enough to form longer arrays (Figure 5 - d)).

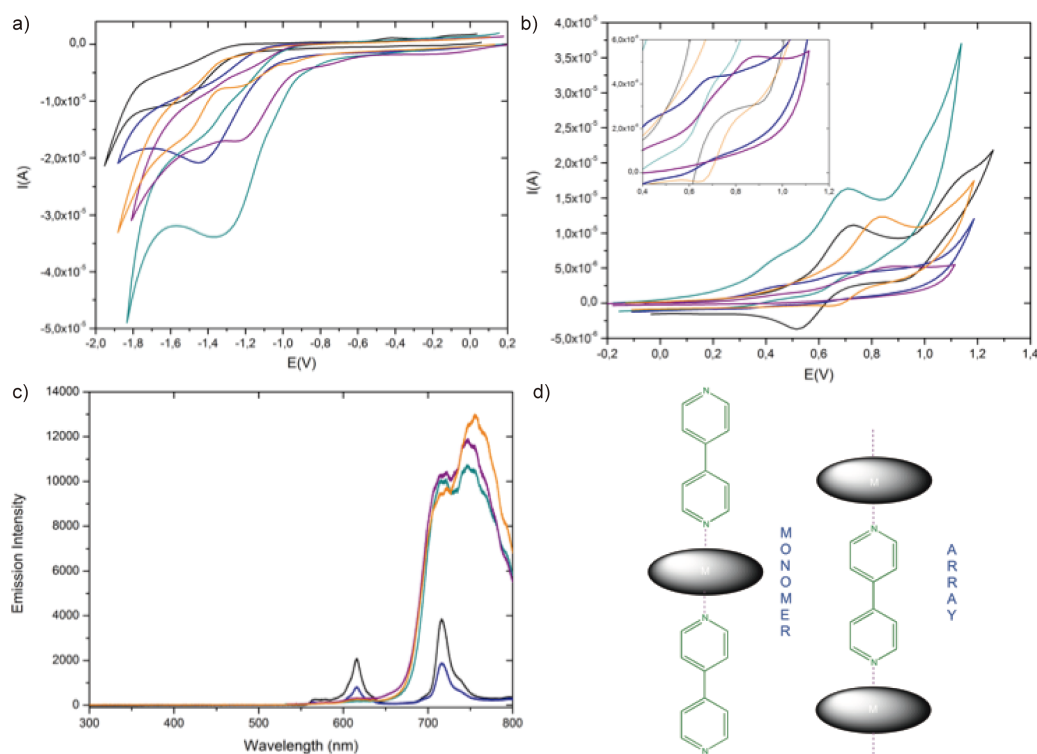


Figure 5 - a) and b) Cyclic voltammograms; c) emission spectra of TTPIr and TTPIrL complexes; d) monomer and arrays structure (black – TTPIr; blue – TTPIrL1; green – TTPIrL5; purple – TTPIrL10; orange – TTPIrL20).

The emission spectra in Figure 5 show a clear difference between the TTPIr, TTPIrL1 and the remaining complexes. The first have two emission peaks at approximately 615 nm and 716 nm, while the second have two more intense peaks at approximately 711 and 745 nm, confirming the change on the emissivity of the compounds due to the incorporation of the bpy axial ligand on the porphyrins. Similarly, to the analysis of the TTPIrL(0.5) it is also possible to identify a mixture of the non-coordinated TTPIr and the bpy coordinated TTPIr by the combination of different techniques.

TTPIrL cyclic voltammograms in Figure 5 evidence the change of the electronic state of the TTPIrL complexes comparing with TTPIr. At positive potentials the observed peaks have two different origins. The first between 0.4 and 0.7 V vs fc/fc is due to the oxidation of the iridium metal center and the second is attributed to the population and depopulation of the π and π^* levels of the porphyrin macrocycle due to its conjugation character⁴⁹. The presence of monomeric species and arrays with shorter and longer lengths, i.e., the presence of several species in the same compound, results in different levels of conjugation and therefore these peaks deviations. The same deviations are observed on the negative potentials, which are promoted by the presence of the coordinated bpy ligand, which is bonded to the porphyrin from the iridium metallic center. These processes (E_p between -1.4 and -1.2 V vs fc/fc) are not identified on TTP (not showed) and are more defined than on the TTPIr porphyrin. Also, the successful conjugation of the bpy with the porphyrin is expected to diminish the HOMO-LUMO gap (band gap), which can be estimated from the difference between the first oxidation and reduction potentials (Table 2)⁵⁰.

Table 2 – Electrochemical gap of the porphyrin and related complexes with bpy.

Compounds	Band gap (eV) ^a
TTPIr	2.30
TTPIrL1	1.87
TTPIrL5	1.75
TTPIrL10	1.90
TTPIrL20	1.80

$$^a E_{\text{HOMO}} = -(4.39 + E_{\text{ox}}) \text{ (eV)} \text{ and } E_{\text{LUMO}} = -(E_{\text{red}} + 4.39) \text{ (eV)}.$$

It is shown that the successful conjugation of the bpy reduces the gap energy of the respective complexes comparing to TTPIr by lowering the LUMO (making the reduction potential less negative) rather than raising the HOMO (reducing the first oxidation)⁵⁰. The best result was achieved with the TTPIrL5 complex with a band gap of 1.75 V. Since all the changes in voltammograms and spectra are the result promoted by the overall interactions of all the molecules that are present in the respective

compounds, the Sephadex purification was employed after each reaction. A mixture of monomers and arrays with different lengths were presented, and according to the ratio of these molecules and the presence of shorter or longer arrays different results were obtained. According to Table 3 the results of the molar ionic conductivity of the solutions prepared in chloroform and toluene are very similar confirming the neutral state of all compounds. However, when the pH solution was adjusted to 4 the Δm increased validating the protonation of all compounds, except the metallated porphyrin without bpy bonding.

Table 3 – Molar ionic conductivity of the solutions prepared to CV and further membranes spray.

Compounds	TTPIr	TTPIrL1	TTPIrL5	TTPIrL10	TTPIrL20
Δm (S cm ² mol ⁻¹)					
CHCl ₃ ^{*1}	0	2.5	25	18	40
Δm (S cm ² mol ⁻¹)					
toluene ^{*2}	0	1.7	19	14	30
Δm (S cm ² mol ⁻¹)					
acidic ^{*3}	0	130	113	100	200

^{*1} CHCl₃ solution; ^{*2} Toluene solution; ^{*3} Toluene solution with adjusted pH=4.

The results demonstrated that as the amount of bpy increases the compounds evolves, reaching the best values using a TTPIr/L ratio of 1/5. The explanation can be associated to the fact that to achieve the porphyrin arrays it is necessary one porphyrin molecule and two bipyridine molecules, i.e., TTPIr_(n)L_(n+1). Therefore, the 1/1 ratio is not suitable to form the long arrays and, at it best, in some molecules only a monomer state can be achieved. Whereas the 1/5 ratio showed the best results and may achieve longer arrays comparing to higher ratios (L=10 and 20). Since, in the latter, there are too many bpy molecules competing to the same porphyrin sites, resulting in shorter arrays.

3.2 CA-based Membrane with Porphyrin Arrays

Previous to the spray of the CA membrane with the acidic porphyrin array solutions, the CA surface was charged with the opposite charge of the porphyrin ligands (i.e. negative) in order to ensure the adhesion between membrane and arrays. For that, the membranes were exposed to plasma treatment in the presence of oxygen. The change on the surface charge of the CA membranes results on changing the

surface tension and consequently the water contact angle (WCA). Therefore, WCA measurements were employed on the CA membrane immediately after oxygen plasma treatment to confirm that the treatment was applied successfully^{51, 52}. The change of the water membrane behavior from hydrophobic ($\theta=118\pm3^\circ$) to hydrophilic (Figure 6) confirmed the conversion of the CA to a negatively charged surface^{52, 53}. This behavior was achieved since after treatment the water drop spread and no droplet could be statically recorded. Therefore, the frames videos (Figure 6 a-b-c-d) were recorded in order to show this effect.

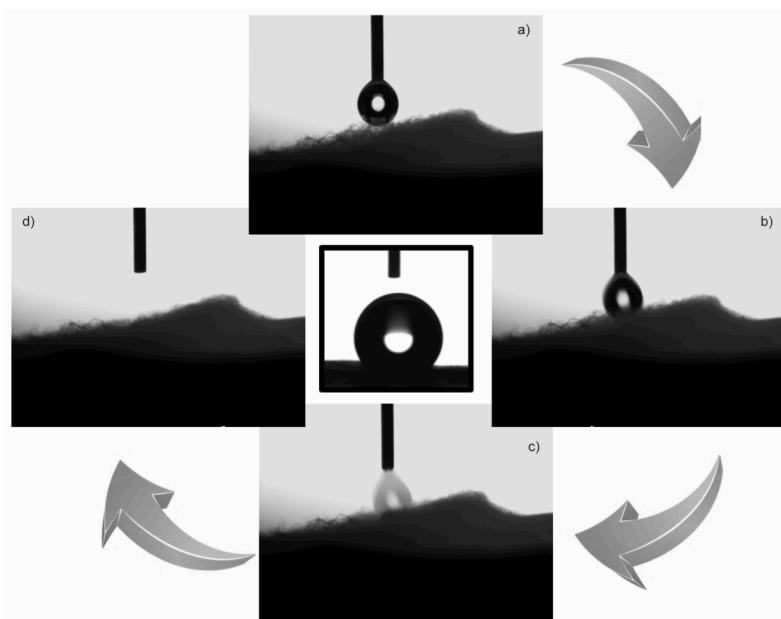


Figure 6 – Sessile drop water method of CA membranes before (center image) and after O₂ plasma treatment.

Posteriorly to oxygen plasma treatment, the CA membrane surfaces were sprayed with the respective compounds. Initially, porphyrin arrays were dissolved in dichloromethane, a volatile and an excellent solvent to dissolve these compounds. However, it is also a good CA solvent and the slight contact of the spray droplets with CA nanofibers was sufficient to destroy the fibers, as it can be observed in Figure 7 a) and b). Thus, DCM was substituted by toluene, which dissolves the porphyrin arrays but it is not a CA solvent. However, in this case, an oven at 80 °C was used to accelerate the evaporation rate of the solvent between depositions. As expected the porphyrin arrays adhered to the CA-membrane covering the nanofibers surface. Figure 7 b) to f) are representative SEM images, since similar morphologies were observed for all the coated membranes.

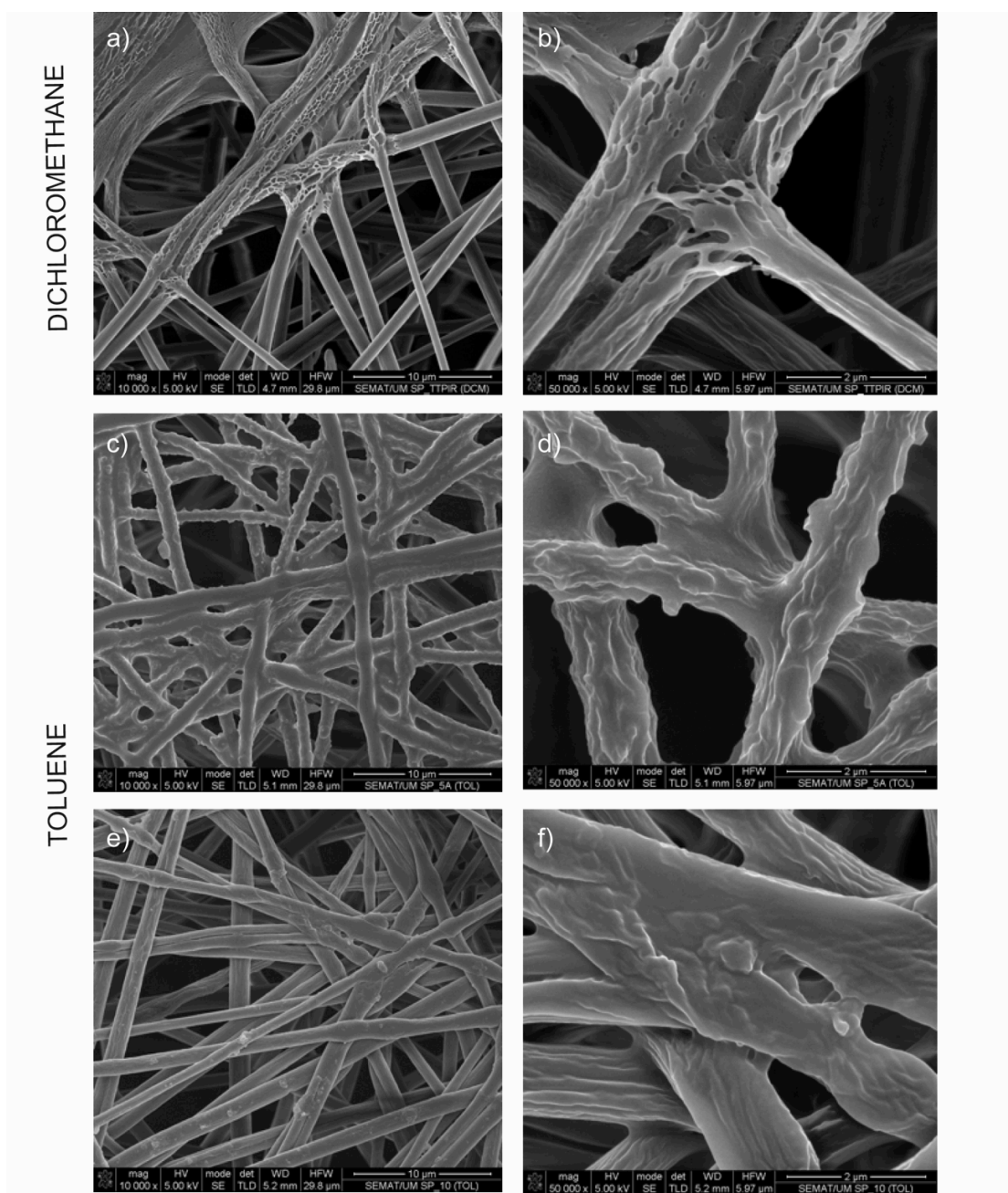


Figure 7 – Representative SEM images of sprayed CA-membranes; a) and b) CA/TTPiR₅ sprayed with DCM; c) and d) CA/TTPiR₅ sprayed with toluene; e) and f) CA/TTPiR₁₀ sprayed with toluene.

The adhesion between the CA membrane surfaces and the TTPIrL complexes were confirmed by the spectra techniques of FTIR, Raman and emission (Figure 8).

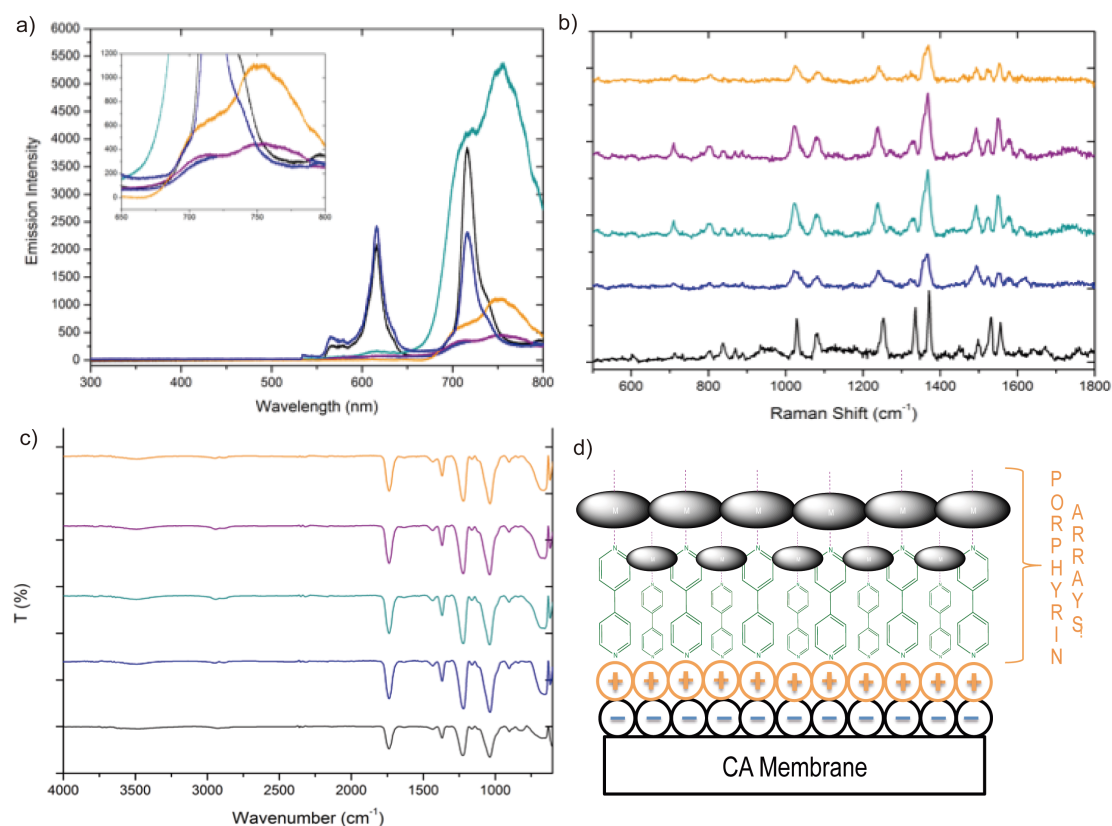


Figure 8 - a) Emission b) Raman and c) FTIR spectra of CA/TTPIr, and CA/TTPIrL complexes (black – CA/TTPIr; blue – CA/TTPIrL1; green – CA/TTPIrL5; purple – CA/TTPIrL10; orange – CA/TTPIrL20); d) adhesion scheme of CA-TTPIrL due to charge interaction.

Concerning the FTIR and Raman spectra, it was observed that these two analyses complement each other. While in the first, only the signals corresponding to CA bands were mainly identified⁵⁴⁻⁶⁰ probably due to the thinner layer of sprayed content, in the second only the porphyrin complexes signals, which were previously analyzed (Figure 4) are observed. In this case the sprayed membrane is excited with a specific wavelength in which the porphyrin complex signals are stronger disguising the polymer bands. It is noteworthy to refer, that the membranes used to perform both analyses were the same. Comparing the emission spectra of the TTPIrL compounds (Figure 5 - c) and the CA/TTPIrL sprayed membranes (Figure 8 - a), a lower emission intensity for the same bands (14000 to 6000) is noticed in the latter. This decrease is due to concentration onto the membrane when compared to the concentrate power form analyzed before. In the specific case of TTPIrL1, the spectrum is similar to TTPIr power form (bands at approximately 615 and 716 nm), while the others complexes show bands at approximately 711 and 745 nm, where the CA+TTPIrL5 distinguishes from the others due to a higher emission

intensity (Figure 8). The difference between the emission intensity of the CA/TPPIrL sprayed membranes validates the results previously obtained.

After analyzing the emission spectra of the sprayed membranes, fluorescence microscopy images were collected. When the CA membranes were sprayed with TPPIrL1, 5, 10 and 20 compounds, the fluorescence images are very similar. Therefore, representative images of the TPPIrL5 are displayed in Figure 9.

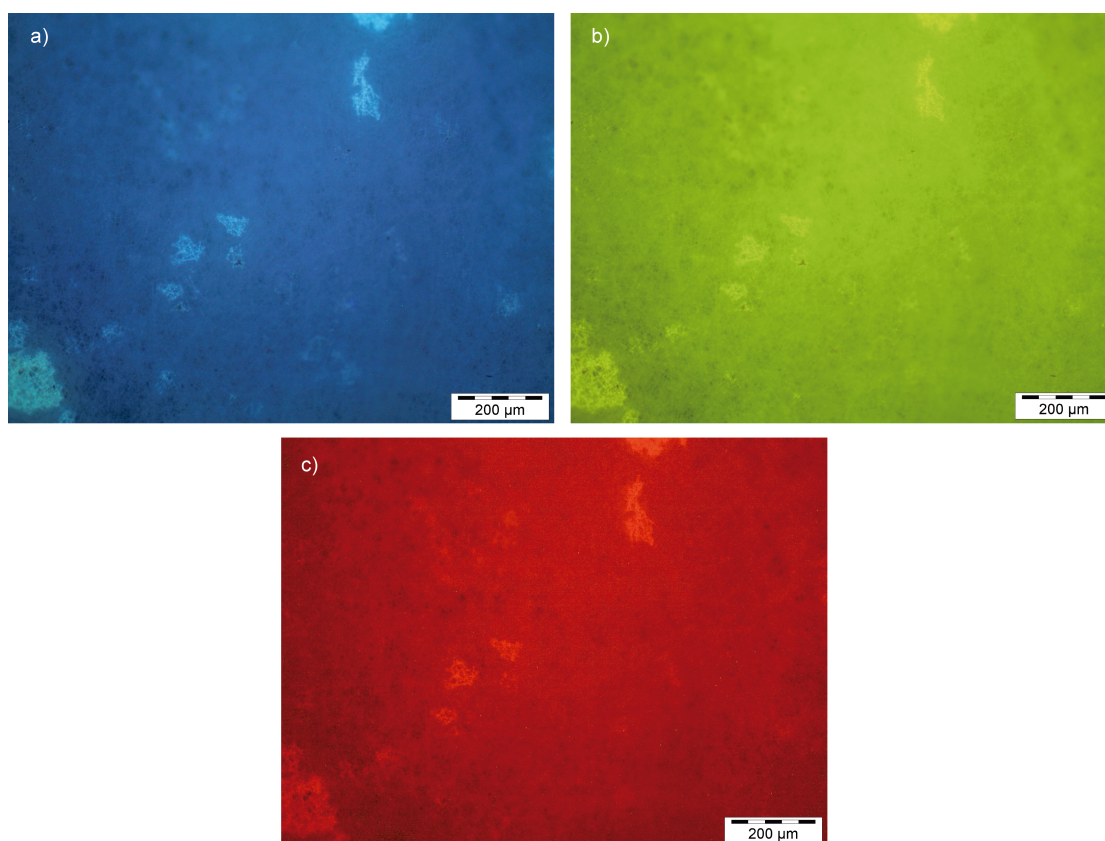


Figure 9 – Representative fluorescence imaging of the electrospun membranes prepared with 12wt%CA and TPPIrL.

As expected the substitution of the TPPIr axial ligands by the conjugated bpy molecule, turned possible to observe again the porphyrins through a fluorescence microscope capturing the images showed in Figure 9. These confirms again the successful incorporation of the bpy ligand axially bonded to the porphyrin, and as mentioned by Koren et al ^{61, 62} demonstrates that the fluorescence capacity of iridium porphyrins can be changed by the influence of different axial molecules, which were already mentioned in chapter VI. Therefore, it was perceived that the membranes exhibited fluorescence properties and emitted blue when excited with UV light, green when excited with blue light and red when excited with green light, as expected. The sprayed compounds presented to be distributed along the membranes, but also concentrated in some spots revealing some limitations of the handling sprayed technique.

These spots are observed as brighter spots, since an increase amount of TTPIrL is located in the same spot of the membrane.

4. Conclusion

In the present work porphyrinic arrays were successfully prepared by coordination of porphyrin iridium metal center with bipyridine ligands at ratios lesser than 1. Spectroscopic and cyclic voltammetry data including the calculus of the molecules energy band gap showed that the ideal metalloporphyrin/bipyridine ratio was 1/5. A solution of porphyrin arrays was applied on CA membranes surface, which were previously submitted to oxygen plasma treatment. The sprayed membranes exhibited fluorescence properties, which demonstrate that the fluorescence capacity of iridium porphyrins can be influenced by different axial molecules.

5. References

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VIII

CONCLUSIONS AND FUTURE WORK

1. Main Conclusions

This final chapter makes reference to the general conclusions accordingly to the fulfillment of the proposed objectives, which comprised the development of novel materials with optic/electronic properties. To achieve this objective and taking into account the growing environmental awareness, which teach us the necessity to respect, protect and preserve the natural world from its anthropogenic afflictions. There was an effort to seek for processing techniques more environmental friendly, which means, minimal or no use of solvents, as well polymers and other compounds with a minimum environmental impact (either by its toxicity or by the low amount employed). Therefore, cellulose acetate based materials with optic/electronic properties were developed.

Chapter III and **chapter IV** presented the melt mixing by two distinct techniques (mini-extruder and haake batch mixing) and the effect of the incorporation of carbon nanotubes in a cellulose acetate matrix. The presence of as-received or functionalized CNTs showed to enhance the composite stability caused by the processing thermo-mechanical effects on both techniques. However, the composites prepared in the ME experienced less degradation and achieved higher levels of dispersion. Concerning the CNTs, the functionalization did not facilitate the dispersion and although optical properties were not possible to achieve here, the addition of 0.5 wt% of as-received CNTs allowed the achievement of rheological percolation and presented electrical conductivity. **Chapter V** shows the synthesis of a new metalloporphyrin, which combines an iridium atom known by its amazing photochemical properties. Unfortunately, this compound was not incorporated in a polymer matrix due to its low yields.

Therefore, in the next chapters a different porphyrin was used to synthesized an iridium metalloporphyrin. This compound was incorporated into the cellulose acetate matrix to achieve the optic/electronic desired properties. **Chapter VI** presents the incorporation of this porphyrin with and without iridium into the cellulose acetate matrix and the processing through the electrospinning technique forming nanofibers. Even though iridium is a metal with fluorescence properties and are easily seen in a fluorescence microscope, these were quenched by the axial bonds on the porphyrin, but successfully electrical conductivity was achieved probably caused by the improved dispersibility achieved by the iridium porphyrins. Concerning the porphyrins without iridium, agglomerates were observed and contrary to the other porphyrin, conductivity was not achieved but fluorescence images could be captured. Also, the hydrophobicity of both membranes with porphyrins was increased.

Finally on **chapter VII** a different approach was used in order to try to improve the properties of the iridium porphyrins and cellulose acetate material. In this, the axial bonded groups of the iridium porphyrin were changed to conjugated molecules (4,4'-bipyridine) and several reaction ratios were studied. It was observed that only when the molar amount of bpy was equal or superior to 1 according

to the porphyrin, porphyrinic arrays were able to form and the best result was achieved with a 5 bpy molar amount. Cellulose acetate was electrospun and its surface was activated with oxygen plasma treatment turning its surface negatively charged. The final material was obtained by spraying positively charged porphyrins onto the cellulose acetate nanofibers surface. The sprayed nanofibers were able to be observed again with a fluorescence microscope, which were the successful result of changing the axial groups of the iridium porphyrins forming porphyrinic arrays.

2. Future Work

Considering all the work presented in this doctoral thesis and the results and conclusions accomplished, some suggestions of prospective work may include:

- The study of other compounds, that are not CNTs and porphyrins to achieved optic/electronic properties using similar processing techniques and cellulose acetate, which showed to be a great polymer matrix;
- The yield improvement of the iridium incorporation into the porphyrin identified on chapter V;
- The incorporation of other axially bond groups to the iridium porphyrin and the study of the effect on the fluorescence capacity when incorporated in a polymer matrix is also of major importance;
- The investigation of an improved sprayed technique to cover the nanofibers with functional compounds;
- And the study of the conductive properties of the final nanofibers prepared on chapter VII.