

UNIVERSIDADE DE LISBOA INSTITUTO SUPERIOR TÉCNICO

Advanced dendrimers for capture and storage of sustainable energy

Rita Figueiredo Pires

Supervisor: Doctor Vasco Daniel Bigas Bonifácio

Co-Supervisor: Doctor Teresa Maria Alves Casimiro

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Abstract

The global energy demand for new sustainable power generation solutions, fostered by a climate change triggered energetic revolution, is leading to the development of novel materials. In this work, devices with a photodiode-like behaviour were fully developed using a new class of donor-acceptor dendrimers. These novel materials were designed, synthesized and combined with ruthenium sensitizer dyes, allowing the fabrication of low-cost devices assembled in a single layer of a biocompatible matrix. Exploring different electrodes, low dark current devices with a counter-electrode dependent response have been successfully assembled at room temperature. The best photodiode system was achieved using a hybrid material, combining a poly(imidazolone amine) (PIMAM_{G1}OMe) dendrimer with a commercial dye sensitizer [Ru(dcbpy)₂(NCS)₂], and a stainless steel counter electrode. This device achieved a specific detectivity of 8.8×10^8 Jones (at -0.4 V) and a low dark current density of 10 nAcm⁻².

The development of new energy storage systems is also a huge concern, especially due to exponential growth of novel, energy demanding applications. Next-generation portable and flexible electronics are pushing researchers to develop flexible, lightweight and environmentally friendly energy storage devices. Supercapacitors (SCs) have attracted increasing interest mainly for their outstanding properties, such as fast charge/discharge capacity, small size, highly reliability and wide range of operation temperatures. SCs are components that lay in the forefront of new energy storage promising devices, including flexible and wearable electronics. Microbial fuel cells (MFCs) are envisaged as novel renewable power sources. Exoelectrogenic bacteria in MFCs are capable to oxidize organic matter to produce energy. Yet, the low current production is MFCs is still a drawback. However, when MFCs are externally or intrinsically coupled to a SC, the energy accumulated is then released in a high current and can be used, for example, to charge small wearable devices. In this work new aromatic polythiourea polymers were designed, synthesized and investigated as potential capacitive materials. In preliminary studies, PPMTU, a model linear aromatic polythiourea was coated on screen printed electrodes to evaluate its performance as MFCs supercapacitors. Using two different exoelectrogenic bacteria, Geobacter sulfurreducens and Shewanella oneidensis, the capacitive performance of PPMTU was investigated. Despite not fully optimized, the results so far point show that polythiourea-based MFCs, using G. sulfurreducens as a biolelectricity source, are promising sustainable energy systems.

Keywords: Hybrid photodiodes; Donor-acceptor dendrimers; Supercapacitors; Aromatic polythioureas; Microbial fuel cells.

Resumo

A procura global de novas soluções sustentáveis de energia, motivada por uma revolução energética desencadeada por alterações climáticas, tem conduzido ao desenvolvimento de materiais inovadores capazes de satisfazer novos desafios. Neste trabalho foram fabricados dispositivos com um comportamento semelhante a fotodíodos, e desenvolvidos usando uma nova classe de dendrímeros do tipo doador-aceitador. Os novos materiais foram projetados, sintetizados e combinados com corantes de ruténio, permitindo a fabricação de dispositivos de baixo custo, incorporados em camada única e usando uma matriz biocompatível. Obtiveram-se com sucesso dispositivos a operar a uma baixa corrente no escuro e com uma resposta dependente do contra-elétrodo. O melhor sistema obtido usa um dendrímero de poli(imidazolona amina) (PIMAM_{G1}OMe), um corante de ruténio comercial [Ru(dcbpy)₂(NCS)₂], e um contra-elétrodo de aço inoxidável. Este dispositivo alcançou uma detetividade específica de 8,8×10⁸ Jones (a -0,4 V) e uma baixa densidade de corrente escura de 10 nAcm⁻².

O desenvolvimento de novos sistemas de armazenamento de energia é também é uma das grandes preocupações da sociedade global, principalmente devido ao crescimento exponencial de novas aplicações que obrigam a um elevado consumo energético. A próxima geração de dipositivos eletrónicos portáteis e flexíveis está a pressionar o desenvolvimento de dispositivos de armazenamento de energia flexíveis, leves e ecológicos. Os supercondensadores (SCs) são materiais altamente atrativos, principalmente devido às suas excelentes propriedades para uso em dispositivos optoelectrónicos, tais como a rápida capacidade de carga e descarga, as reduzidas dimensões, a elevada fiabilidade e a ampla gama de temperaturas de trabalho. Os SCs estão na vanguarda do desenvolvimento de dispositivos para o armazenamento de energia, incluindo os dispositivos eletrónicos flexíveis e incorporados em vestuário. As células de combustível microbiano (MFCs) são já consideradas como novas fontes de energia renovável. No entanto, a eficiência de produção de energia é muito baixa, constituindo uma desvantagem destes sistemas. Contudo, quando as MFCs são acopladas a um SC, a energia acumulada é libertada numa corrente mais alta e pode ser usada para carregar pequenos dispositivos. Neste trabalho foram projetados, sintetizados e investigados, novos polímeros de politioureias aromáticas, como potenciais materiais capacitivos. Em estudos preliminares, a PPMTU, uma politioureia aromática linear foi usada como um polímero modelo para revestir elétrodos impressos, e foi avaliado o seu desempenho como SCs em MFCs. Utilizando duas bactérias produtoras de eletricidade diferentes, a G. sulfurreducens e a S. oneidensis, estudou-se o desempenho capacitivo da PPMTU. Apesar de preliminares, os resultados obtidos mostram que MFCs acoplados a politioureias, usando G. sulfurreducens como fonte de bioeletricidade, são sistemas de energia sustentável muito promissores.

Palavras-chave:Fotodíodoshíbridos;Dendrímerosdoadores-aceitadores;Supercondensadores;Politioureias aromáticas;Células de combustível microbianas.

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Thinking that a PhD thesis is just the work developed by only one person is not true. I was being selfish if I say that this work is all mine, because this journey would never be possible without the help of important people that gave me orientation, that encouraged me when the work was not going well, supported all my decisions, and was always there when I needed the most. They are a crucial are part of all this process, therefore acknowledging them it is so important.

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Abbreviations

- ACF Activated carbon fibres
- ACN Acetonitrile
- ArPTU Aromatic polythiourea
- BHJ Bulk heterojunctions
- bs Broad signal
- BSA N, O-bis(trimethylsilyl)acetamide
- CMOS Complementary metal-oxide-semiconductor
- CNT Carbon nanotubes
- COF Covalent organic framework
- CP Conductive polymers
- CV Cyclic voltammetry
- D* Specific detectivity
- D-HPD Dendrimer hybrid photodiode
- DMF N,N-dimethylformamide
- DSSC Dye sensitized solar cells
- EAFc Ethanolamine ferrocene
- EDLCs Electrochemical double layer capacitors
- EQE External quantum efficiency
- ESSs Energy storage systems
- FTO Fluorine-doped tin oxide
- GW Gigawatts
- HOMO Highest occupied molecular orbital
- HPD Hybrid photodiodes
- IEA International Energy Agency
- ITO Indium tin oxide
- LB Lysogeny broth medium
- LPTU Linear polythiourea
- LUMO Lowest unoccupied molecular orbital
- MDA 4,4'-Diaminodiphenylmethane
- MFC Microbial fuel cell
- MOF Metal organic framework
- MSC Microbial supercapacitor

- MWCNT Multi-walled carbon nanotubes
- N-719 Di-tetrabutylammonium *cis*-bis(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)
- ruthenium (II)
- OD Optical density
- OPD Organic photodiode
- PAni Polyaniline
- PEDOT Poly(3,4-ethylenedioxythiphene)
- PIMAM Poly(imidazolone amine)
- PIMAMO Poly(imidazolone amine) oxide
- ppm Parts per million
- PPMTU Poly(p-phenylmethanethiourea)
- PPy Polypyrrole
- PPTU Poly(p-phenylenethiourea)
- PURAM Poly(urea amidoamidine)
- PURAP Poly(urea aminophenyl)
- PURAPO Poly(urea aminophenyl) oxide
- PVDT-TrFE Poly(vinylidene-trifluorideethylene)
- REN21 Renewable energy policy network for the 21st Century
- SBM Shewanella basal medium
- scCO₂ Supercritical carbon dioxide
- SCs Supercapacitors
- Solar PV Solar photovoltaics
- ss Stainless steel
- SWCNT Single-walled carbon nanotubes
- TAPA Tris(4-aminophenyl)amine
- Tetrakis N,N,N' N'-Tetrakis(4-aminophenyl)-1,4-phenylediamine
- TMO Transition metal oxides
- TPA Triphenylamine
- TREN Tris(2-aminoethyl)amine
- UHP Urea-hydrogen peroxide adduct
- VRE Variable renewable energy sources

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Outline

This thesis is composed of five main chapters. Chapter I is an overview about the central theme of this thesis: energy conversion and storage. Here, are presented some statistics related with the production and consumption of energy at worldwide level. Also, it is explained the need to develop new materials for conversion of new renewable energy sources and the development of new energy storage devices.

Chapter II is focused in the development of new materials for solar energy conversion. Although the project was initially designed for the development of an organic solar cell, the materials synthesised did not work as solar cells but as photodiodes (the working principle is the same, however their response is different). This chapter is the combination of two articles already published and presents a brief review about photodiodes, their properties, working principles and recent applications, followed by the description of the work developed to produce these photodiodes.

Chapter III is devoted to energy storage, through the development of new conductive polymers to work as electrode materials for supercapacitors. Here, a brief overview about supercapacitors production is presented, identifying the different types of supercapacitors, their working principles and the influence of their components in the supercapacitor performance. Following this description, the synthesis of three different conductive polymers were described.

Chapter IV describes the application of the synthesized materials for their use in bioelectricity. Here, the materials developed in Chapter III are being applied in the study of microbial fuel cells to evaluate their performance as electrodes for microbial fuel cells.

Chapter V presents the concluding remarks of this PhD project, as well as the prospects for future work.

All chapters use a single reference style, citations being given by sequential numbers and listed in the end of each chapter. Finally, an Appendix section is also presented at the end of this document with supporting information for Chapters II, III and IV (Appendix I, II and III respectively).

Chapter I

Energy

In this chapter a brief overview of the state of the art of energy resources consumption, as well as their predictions, is made for the next few years. The data collected for the elaboration of this chapter is mostly based on the 2019 Insight Fostering Effective Energy Transition report of the world economic forum, the global status report of renewables 2018 from the Renewable energy policy network for the 21st Century (REN21) and the world energy outlook 2018 of the International Energy Agency (IEA).

The Energy System

Energy is the motor of life. Being essential to human society and economic activity, energy provides access to affordable modern energy services and is a prerequisite to eliminate poverty and reduce inequalities. Available in different forms (*e.g.* potential, kinetic, electrical, chemical, nuclear, thermal), energy is present in many daily activities. The first law of thermodynamics is related with the conservation of the energy and states that the total energy of an isolated system is constant. Energy can be transformed but can be neither created nor destroyed.

The current energy production is channelled for three major needs: heating, transportation and power. As shown in Figure I.1, fossil fuels are the current major resource to produce energy. The imminent threats related to the possibility of fossil fuels extinction, the increasing oil prices (above 72 Euro/barrel in 2018) and their growing environmental impact (*e.g.* CO₂ emissions and air pollution), the tendency observed in the past few decades, has been the reduction of their usage and an increasing energy production by using renewable energies and nuclear power.¹



Figure I.1. Renewable energy in the total final energy consumption (by sector) in 2015.1

In the past decades it was observed a 5.4% average growth rate of modern renewable energies^{*}, indicating a gradual change in the energy system. With the actual polices the scenario is not favourable, and if the fossil fuels consumption is maintained the situation will be incomputable in the next decades. In that sense, the International Energy Agency (IEA) created a set of policies, defined as new policies and sustainable policies scenarios.² The Paris Agreement, sealed in 2015, is contributing to this change to low carbon sources in energy

^{*} Hydropower, solar, wind, geothermal and modern biofuel production (including modern forms of waste-tobiomass conversion) are renewable technologies that are often termed "modern renewable energies".

production, and its main goal is to reduce the greenhouse-gas emissions. A long-term goal is to keep the global average temperature 2 °C above pre-industrial levels (and limit this increase to 1.5 °C), trying to reduce substantially the risks and effects of climate change.³

Although a demand for changes in the energy system is necessary and a shift to renewable energies is inevitable, this cannot be realized without a technologic revolution, reducing production costs and improving the efficiency of renewable energies.⁴ The main expected challenges will be related with the migration of some industries (*e.g.* petrochemistry), from fossil fuels to low-carbon resources. However, according to the International Renewable Energy Agency (IRENA), with the implementations of REmap policies (based on a low-carbon technologic pathways) the prediction to year 2050, is that around 70% of the global energy supply mix should be low-carbon (including renewables, nuclear, carbon capture and storage) as shown in Figure I.2. Fossil fuels will continue to be used as a resource, however with a reduced role in energy production.⁵



Figure I.2: Prediction of renewable energy usage by sector and technology in 2050 using REmap policies. CSP: concentrating solar power, PV: photovoltaics.⁵

The Electricity Sector

The electricity sector is experiencing a change in the energy system and endures a dramatic transformation. Electricity power accounts for 19% of total final consumption today compared to just over 15% in 2000. Since 2000, the global electricity demand is growing *ca.* 3% *per* year, around two-thirds faster than the total final consumption, reaching a value of 22 200 Terawatt-hour (TWh). Developing economies account for around 85% of this increase while in

advanced economies a modest growth is expected. Being the heart of modern life, electricity is fundamental for the industrial and services sectors and digital economy. With the current awareness of fossil fuels exhaustion, the access to cleaner, universally available and affordable electricity is in the core of strategies for economic development and greenhouse-gas emissions reduction. Not only the new and sustainable policies scenarios have been slowly implemented, but also a huge investment in this sector has been made. In 2050, renewables will dominate the power generation sector, becoming a key pillar of a cost-effective energy system. Hydropower will remain the largest low-carbon source for electricity. However, solar photovoltaic (PV) costs are predicted to fall almost 40% until 2040 and this convergence of cheaper renewable energy technologies with the improvement of the installed capacity will promote competitiveness between solar PV and wind power. The investment, especially from countries such as China, India or United states, will increase and the power market will become more flexible, creating conditions to a smooth shift from fossil fuels to renewables.^{2,5}

In 2017, the energy capacity additions achieved 310 gigawatts (GW), being wind and solar PV generation responsible for nearly half of them. Countries such as China are experiencing the major growth in this sector with the addition in 2017 of 53 GW of energy capacity and being responsible for 60% of both global PV demand and cell manufacturing. Yet, globally the renewable energy market is experiencing a capacity reduction. Except for geothermal, all the other renewable energies have declined.²

The solar and wind power have been dominating the renewable energy market, mainly due to the need of new sustainable polices implementation and their continuous reduction of production costs, making them very attractive alternatives. However, the implementation of renewable energies experiences different levels around the world and, depending of the phase of integration of variable renewable energy sources (VRE) into the electricity systems, countries face different challenges. If the VRE is embryonic, like in case of Indonesia, Korea, Russia and South Asia, the number of solar and wind power plants still do not have significant impact in the system level, which make their challenge implement minor changes to operating patterns. Japan, Brazil, Turkey, India, Mexico, Canada, France, China, United Sates and Australia are with a VRE share between 5-10%. Although still far away from a good renewable system implemented with new power flow patterns, these countries are improving and have been investing to improve their systems flexibility and efficiency.²

The VRE share starts to be determinant when the VRE share is higher than 10%. Here the electricity supply starts to have a significant level of uncertainty and variety. The major challenges start at this point. Countries in this phase, namely Germany, Italy, Kyushu (a subsystem of Japan) and the United Kingdom, are becoming concerned about the power supply robustness, the system flexibility and the supply-demand balance. In the case of Denmark, Portugal, Spain, Ireland and South Australia, the system experiences have periods where VRE makes up almost all generation of electricity. Here, the main challenge is to provide advanced technical options to ensure system stability, with a necessary change in operational and regulatory approaches. In that way it will be possible to achieve higher phases where the VRE output frequently exceeds the power demand (days to weeks) being possible to provide supply in some periods entirely by VRE. After solving the problem of seasonal energy storage, the VRE supply achieves the last phase being able to supply the energy system on seasonal or interannual timescales leading to a more sustainable and greener energy system.²

As the VRE level increases, more technical, market, regulatory aspects and institutional frameworks electricity systems need to be taken into consideration. This should ensure the provision of sufficient flexibility to maintain a continued security of supply. This requires measures to enhance the system flexibility, ranging from integrated planning and system operation to new tools for control centre operation, and to the establishment of new service products that are able to support the system with timescales of sub-seconds to days (Figure I.3). Many systems with high rates of VRE, such as Denmark, Italy and Portugal, have managed to achieve very low or zero levels of VRE curtailment. This was possible by ensuring adequate systems flexibility that has traditionally come from thermal generation and hydropower capacity, together with a combination of pumped storage hydropower, interconnections and demand-side response from large industrial and commercial consumers, which today, between them, provide around 375 GW of flexibility worldwide.²



Figure I.3: Growing needs and range options for flexibility.²

Energy Storage

With the worldwide remarkable growth of renewable energies, the installed storage capacity is a huge concern since they can rarely provide immediate response to the demand. As these sources do not deliver a regular supply easily adjustable to the consumption needs, over the past decades the electrical energy storage systems (ESSs) have been suffering an extraordinary (r)evolution.

The balance between the supply and demand through the short- to long-term storage periods is fundamental, and several ESSs have already being developed. These systems play an important role in the integration of intermittent renewable sources (*e.g.* wind, solar), as they smooth the output and enhance renewable energy versatility in micro-generation systems. This allows them to supply and distribute steady electrical power. The diversity of ESSs is tremendous. With different operation modes, life cycles, and materials used, ESSs can be classified in different categories. Figure I.4 shows the different types of ESSs based on their primary source of energy, (further discussed in chapter III).^{6,7}



Figure I.4: Different ESSs categories according to their primary source of energy.7

Pumped storage hydropower (pumped hydro) is currently responsible for the majority of energy storage, although it is only able to storage 2% of the global power generation (153 GW). Despite pumped hydro is still expanding its storage capacity (*e.g.* in China is expected to increase almost 70%), the growth of decentralized production, due to the expansion of renewable energies, means greater network load stability problems and requires energy storage, generally as a potential solution. Lithium ion and lead batteries are dominating the battery installed capacity (Figure I.5), but they are only responsible for 4GW of the global energy storage capacity since their short-term storage capacity cannot withstand high cycling rates, or store large amounts of energy in a small volume. This has led to the development of other (long-term) type of batteries, such as flow or sodium-sulfur batteries.^{2,8,9}

Chapter I: Energy



Figure I.5: Worldwide battery storage energy system installed capacity in 2016.9

The emergence of energy storage is a crucial element in renewable sources energy management, since it will allow energy to be released into the grid when it is more valuable (peak hours). Although batteries are gradually becoming suitable ESSs, powering different applications and turning storage more efficient, convenient and reliable, some limitations have been targeted. These include their lifetime, the amount and the wide range of raw materials needed (including metals and non-metals), and importantly, the environmental impact associated to their manufacturing, use, transportation, disposal and recycling. These issues are under discussion and are the main motivation for the continuous investment in less hazardous, "environmentally-friendly" materials to produce new batteries able to feed a demanding energy sector.

The Low-Carbon Emission Transition

As mentioned above, the Paris Agreement established that after 2020 the greenhouse gases emissions, mainly CO₂ emissions, should be drastically reduced to diminish the global warming effects.

In 2018, the global energy-related CO₂ emissions grew 1.7%, reaching a historic high of 33.1 Gt of CO₂ (Figure I.6).¹⁰ This was the highest growth rate since 2013, and was driven by higher energy consumption resulting from a robust global economy, as well as from weather conditions in some parts of the world, due to increased energy demand for heating and cooling. Contrary to Europe, that observed a reduction of 1.3% in 2018, relative to 2017, China was responsible for 9.5 Gt of CO₂ emissions (with a 2.5% growth rate since 2017). However, the major growth rate was observed in the United States and India (3.1 and 4.8%, respectively).



Figure I.6: Energy related CO₂ emissions from fuel combustion by regions in 2018.

According to REmap polices, the transition from fossil fuels to low-carbon sources, that has been progressively made and that is still expected, became the major source of the global supply mix and is extremely important. Countries like China, for example, are aware of these new polices and the urgent need to reduce CO₂ emissions. Being one of the major contributors, China is investing in the implementation of new polices that contemplate the use of low-carbon sources in detriment of fossil fuels.¹¹⁻¹³

Investment in Energy

The energy sector is experiencing a period of transition. With the aging of conventional power plant fleets in many regions, the expansion of the VRE, the urgent need for flexible, reliable and affordable ESSs and the Paris Agreement directives, the perspectives in the investments on the energy sector changed significantly. Although fossil fuels still absorb most of the investments, the funds attributed for renewable sources and energy storage development have been increasing in the past decades. In 2015, 1.6 billion of Euros were invested worldwide, where half of that was invested directly in oil, gas and coal supplies. Still, the total investment in low-carbon energy, energy efficiency and electricity networks grew up 6% in 2015, and the total energy investment increased from 39% in 2014 to 45% in 2015.⁵

In 2018, China remained the largest market for energy investment, with an increase of the low-carbon electricity supply and networks, despite the total investment witnessed a decline in the past three years. The United States, the second country with more investment in energy, has been the responsible for the majority of energy supply investment growth in this decade, both in oil and gas, supported by more spending on shale and in the power sector. Compared to 2015, the investment in renewable power and gas remained relatively stable, but at high levels. From the top 10 energy market investing countries, the Middle East, India, and the Southeast Asia are

in the spotlight, mainly due to the VRE phase that these countries are experiencing, especially with the installation of new renewable sources and the development of the power sector.¹⁴

Following the new polices scenario defined by IEA, which holds up a mirror of current policy makers ambitions around the world, it is estimated that between 2018 and 2025 the annual investment in the energy sector could be around 2 billion of Euros, reaching 54 billion of Euros until 2040. In Figure I.7 it is possible to observe the cumulative investment by sector under the New Policies Scenario between 2018-2040. Although fossil fuels still have an important weight, the investment in the end-user sector will be almost 30% of the global energy investment. Also, the continuous investment in renewable sources combined with the reduction in their manufacturing costs, increase even more the investment made in this sector. ^{2,14,15}



Figure I.7: Cumulative investment needs by sector under the New Policies Scenario between 2018 and 2040. Other includes battery storage and carbon capture, utilization and storage.²

Final Remarks

Despite all efforts that have been made, the energy sector is still far from sustainability. It is crucial to advance the energy sector, focusing in new technologies, higher efficiency and storage capacity, in parallel with the implementation of new low carbon sources polices. Table I.1 overviews current strategies and future challenges in the energy sector.

	NOT ON TRACK	MORE EFFORT NEEDED	ON TRACK
POWER	Ocean Geothermal CCUS in power Coal-fired power Concentrating solar power	Onshore wind Offshore wind Hydropower Bioenergy Nuclear power Nuclear gas-fired power	Solar PV
ENERGY INTEGRATION	Renewable heat	Smart girds Demand response Hydrogen Digitalization Energy storage	
TRANSPORT	Transport biofuels Aviation	Fuel economy of cars and vans Trucks and buses International shipping Rail	
BUILDINGS	Heating Building envelopes	Cooling Appliances and equipment	Lighting Data centres and networks
INDUSTRY	CCUS and industry transformation	Chemicals Iron and steel Cement Pulp and paper Aluminium	

Table I.1: International Energy Agency radar of energy technology areas.*

*CCUS= carbon capture, utilization and storage.

According to New Policies Scenario, the global electricity generation will increase 60% (15 000 TWh) between 2017 and 2040. Although fossil fuels continue to be the major source for electricity generation, they will represent less than 50% and low-carbon technologies will account of half of the world's electricity generation. Although the future of renewables remains heavily dependent on policies frameworks and technological advances, they are expected to rise 40%, switching with coal (expected to decrease to 25% in 2040) in power mix. Natural gas will remain steady at over 20% as well as nuclear plants that will remain around 10% of global power mix, with China dominating its production. The power sector will be the major and the most important change for the energy sector due to the huge investments already made.²

Electrification brings benefits and according to new policies of IEA, a much stronger push for electric mobility, electric heating and electricity access could lead to a 90% rise in power demand till 2040. The shares of electricity in final consumption move up towards one-third, since almost half the car fleet goes electric and electricity makes rapid inroads into the residential and industry sectors. However, some significant parts of the energy system, such as long-distance road freight, shipping and aviation, are not "electric-ready" using the currently available technologies.²

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Chapter II

Photodiodes

Chapter II will overview the properties and recent applications of photodiodes and presents a novel strategy for the development of photodiode-like jelly dye-sensitized donor-acceptor dendrimers for energy and/or sensing biological applications.

Publications:

- R.F. Pires, A. Charas, J. Morgado, T. Casimiro and V.D.B. Bonifácio, "Photodiode-like behavior of jelly dye-sensitized donor-acceptor dendrimers" *J. Appl. Polym. Sci.* **2019**, 137, 48635.
- R.F. Pires and V.D.B. Bonifácio, "Photodiodes: Principles and recent applications", *J. Mat. NanoSci.*, **2019**, 6, 38-46.
- R.F. Pires and V.D.B. Bonifacio, "Polyureas", *Kirk-Othmer Encyclopedia of Chemical Technology*, **2017**, 1-12.

Poster Presentations:

- R.F. Pires, A. Charas, J. Morgado, T. Casimiro, V.D.B. Bonifácio, "Light, Ruthenium, Dendrimers... Action!", XXVI Encontro Nacional SPQ, Porto, Portugal, July 24-26th, 2019.
- R.F. Pires, A. Charas, J. Morgado, T. Casimiro, V.D.B. Bonifácio, "Donor acceptor dendrimers photodiodes", 11IDS, Madeira Island, Portugal, July 14-18th, 2019.
- R.F. Pires, J. Morgado, T. Casimiro, V.D.B. Bonifácio, "Dendrimer-based jelly photovoltaics", IN Workshop, Lisbon, Portugal, July 7th, 2016.

Photodiodes

Photodiodes can be described as semiconductor devices that are able to convert light into electric current. Also called photodetectors, photosensors or light detectors, they are very sensitive to light, allowing a fast conversion into electricity, being used in several applications such as biomedicine or image sensing.

The chase for a small size, low cost, long lifetime, low temperature responsive, high light response and sensitivity, low noise and high gain photodiode led to the development of new semiconductors (organic, inorganic or hybrid) to improve these qualities and also to try to avoid some critical issues like dark current and detectivity.¹

Photodiodes may be classified in several ways, depending on the type of construction (*pn*, PIN junction or avalanche), spectral response window width (broadband or panchromatic and narrowband, wavelength selective) or by the type of employed semiconductors (organic, inorganic or hybrid).²

Working Principles

All photodiodes operate in the same way. The structure of a photodiode can be a *p-n* junction or a PIN junction. A *p-n* junction is the combination of a *p*-type semiconductor (where holes are the majority charge carriers and free electrons are the minority) and a *n*-type semiconductor (free electrons are the majority charge and holes are the minority charge carries). The region where both *p*- and *n*-type semiconductors are joined is called the *p-n* junction. The natural tendency is the migration of electrons to holes to reach an equilibrium. However, in the *p-n* junction interface there is a depletion region that slows down electron transfer. In case of a PIN junction, there is an intrinsic semiconductor between the *p*- and *n*-semiconductors.³

Usually, the working principle of photodiodes is similar to solar cells. Both *p-n* junctions or PIN semiconductors can be used, but they operate under reverse bias conditions, this means that the *p*-side is connected to the anode and the *n*-side is connected to the cathode. As can be seen in Figure II.1, when a photon strikes the diode, an electron hole pair is created (photoelectric effect). If the absorption occurs in a diffusion length of the depletion region or inside the depletion region, these carriers are swept away from the junction through the built-in field of the depletion region. The electrons move towards the cathode and the holes move toward the anode, producing a photocurrent.⁴



Figure II.1: Working principle of a *p-n* junction photodiode.

Photodiodes can operate in photovoltaic or photoconductive mode. In the case of a photovoltaic mode, photodiodes work at zero bias and the dark current is minimal, thus are suitable for ultralow-light-level applications. Furthermore, the photovoltaic mode offers a simple operational configuration for low-frequency applications. When operating in photoconductive mode, the photodiode is reverse biased. This operation mode is important in case of organic photodiodes since it improves their response speed and linearity in a similar way as that of inorganic silicon semiconductors photodiodes. However, the enhancement of dark current is a drawback.⁵

Different types of photodiodes have been developed to improve specific needs. Besides common p-n and PIN junction types, previously described, avalanche photodiodes and Schottky barrier diodes are also an option.

Avalanche photodiodes are in its essence PIN junctions designed to operate with high reverse bias, approaching the reverse breakdown voltage. This phenomenon is reached when a high electric field is applied and carriers gain kinetic energy, thus generating additional electron-hole pairs through impact ionization. At a certain point the generated photocurrent will increase suddenly, giving origin to an avalanche breakdown point.^{6,7}

Mostly build using inorganic materials, these photodiodes are characterized by a detection efficiency, a gain at low bias voltage and a responsivity usually higher as compared to other photodiodes, making them useful, for example, as refield valves, protecting the systems from excess voltages, and also in some clinical and biomedical applications (*e.g.* pressure control devices). However, avalanche photodiodes require a very meticulous production, which increases manufacturing costs.⁸⁻¹⁰

Schottky barrier photodiodes are other particular type of photodiodes. Based on a metalsemiconductor (M-S) junction, these photodiodes have high quantum efficiency, speed response, low dark current, high UV-Visible contrast, which are notable advantages of these type of photodiodes. Compared with avalanche photodiodes, they have similar high response speed but are much easier to fabricate.¹¹⁻¹⁵

Photodiodes Characterization

To evaluate the photodiodes performance key parameters must be taken in account, both at an electrical and optical level.^{2,5,16,17} An overview of these parameters is given below.

Shunt Resistance (R_{SH})

Defined as the slope of the current-voltage curve at the origin. Experimentally it can be obtained by applying a voltage of ± 10 mV, measuring the current and calculating the resistance.

Series Resistance (Rs)

Used to determine the linearity of the photodiode in the photovoltaic mode, series resistance is a result of the resistance of the contacts and the undepleted material (*e.g.* silicon) and can be calculated using equation II.1:

$$R_S = \frac{(W_S - W_d)\rho}{A} + R_C \tag{II.1}$$

where W_S is the thickness of the substrate, W_d is the width of the depleted region, A is the diffused area of the junction, ρ is the resistivity of the substrate and R_c is the contact resistance.

Junction Capacitance (C_J)

Directly proportional to the diffused area and inversely proportional to the width of the depletion region, junction capacitance is obtained using equation II.2:

$$C_J = \frac{\epsilon_{Si}\epsilon_o A}{\sqrt{2\mu\rho(V_A + V_{bi})}} \tag{II.2}$$

Where ϵ_0 is the permittivity of free space (8.854x10⁻¹⁴ Fcm⁻¹ for silicon photodiodes), ϵ_{Si} is the substrate dielectric constant (11.9 in this case), μ (1400 cm²Vs⁻¹) is the mobility of the electrons at 300 K, ρ is the resistivity of the silicon, V_{bi} is the built-in voltage of the substrate and V_A is the applied bias.

Responsivity (R)

Responsivity is defined as the ratio between the photocurrent generation and the incident power, that can be calculated using equation II.3:

$$R(\lambda) = \frac{I(\lambda)_{ph}}{P(\lambda)_{in}}$$
(II.3)

where $I(\lambda)_{ph}$ is the photocurrent (in amperes) and $P(\lambda)_{in}$ is the incident optical power (in watts).

External Quantum Efficiency (EQE)

Defined as the electron number detected per incident photon, EQE is expressed through equation II.4:

$$EQE(\lambda) = \frac{R(\lambda)hc}{q\lambda} = \frac{1.24R(\lambda)}{\lambda}$$
(II.4)

where h is the Planck's constant, c is the speed of the light and q is the elementary charge. The operation (hc)/q can be approximated to 1.24 if the λ units are expressed in μ m.

Noise equivalent power (NEP)

NEP (λ) (expressed in WHz^{1/2}) gives the minimum detectable power per square root of bandwidth. It can be calculated using equation II.5:

$$NEP(\lambda) = \frac{\sqrt{\overline{l_n^2}}}{\sqrt{\Delta f_R(\lambda)}} \tag{II.5}$$

where the noise current spectral density is given by I_n and Δf is the electrical bandwidth of the noise measurement. The total noise current is the sum of all noise sources, including the shot noise from dark current and the low-frequency flicker noise (1/f). Also, the root-mean-square (rms) value for shot noise current (I_{sh}) is given by $I_{sh} = \sqrt{2q\Delta f I_d}$, where Id is the dark current. When the dark current shot noise is dominant, NEP(λ) can be determined using equation II.6:

$$NEP(\lambda) = \frac{\sqrt{2qI_d}}{R(\lambda)}$$
(II.6)

Specific Detectivity (D*)

Specific detectivity (expressed in cmHz^{1/2}W⁻¹) is one of the most important physical parameters, being the figure of merit to describe the ability to detect weak light. It can be calculated using equation II.7:

$$D^*(\lambda) = \frac{\sqrt{A}}{NEP(\lambda)} = \frac{R(\lambda)}{\sqrt{2qJ_d}}$$
(II.7)

where A is the device area and J_d is the dark current density. The second deduction can be used assuming that shot noise is the main component of the overall photodiode noise.

Linear dynamic range (LDR)

Defined as the range of incident optical powers within which the photocurrent versus power is a linear function. It is expressed in decibels and is calculated using equation II.8:

$$LDR(\lambda) = 20\log \frac{P(\lambda)_{max}}{P(\lambda)_{min}} = 20\log \frac{I(\lambda)_{max}}{I(\lambda)_{min}}$$
(II.8)

where $P(\lambda)_{max}$ is the maximum impinging power above which the response of the device deviates from linearity and $P(\lambda)_{min}$ is the minimum detectable optical power (or noise equivalent power, NEP). This expression can be approximated and uses the maximum and the minimum of the photocurrent limit, $I(\lambda)_{max}$ and $I(\lambda)_{min}$, respectively.

On/off ratio

This ratio can be calculated as the $I(\lambda)_{ph}$ to I_d ratio at fixed incident optical power and bias voltage conditions, which reflects the photosensitivity of a photodiode.

3dB bandwidth (f_{3dB})

Relative to the modulation frequency of input light when $R(\lambda)$ is approximately 0.707 (1/ $\sqrt{2}$) times higher than the obtained under illumination.

Frequency response (т)

Defined as the frequency response, τ is the time needed for the signal to rise or fall from 10% to 90% (or vice versa) of the final value respectively. This parameter can be estimated using equation II.9:

$$\tau = \frac{1}{2\pi f_{3dB}} \tag{II.9}$$

From all these parameters, EQE and D* are major performance indicators. Figure II.2 shows collected data^{5,18} for both inorganic, organic and hybrid photodiodes using different architectures, in the period from 1996 to 2018. As it can be seen, very good external quantum efficiencies and specific detectivities have been already achieved, especially in the visible region.

The non-uniformity (variations of responsivity at the photodiode active surface area) and non-linearity (variation of the ratio of the change in photocurrent to the same change in light power) are also parameters that should be taken in consideration, as well as the temperature influence in several parameters, such as the responsivity, in the breakdown voltage and also in the dark current.

Parameters such as responsivity, specific detectivity, external quantum efficiency or low dark current can have a huge variety between different devices. Ideal photodiodes should have the best performance at all levels, but the integration of all the required features has not yet been achieved. Usually the photodiodes developed have one or two excellent performance parameters, but the others are much lower compared to others. For that reason, several devices and materials have been investigated and combined to achieve the best performance.



Figure II.2: External Quantum Efficiency (EQE, blue dots) and Specific Detectivity (D*, black dots) of photodiodes reported in the period 1996-2018.

Inorganic Photodiodes

Currently, most of the commercially available photodiodes are composed by crystalline inorganic semiconductors. Although silicon was the first to be used, several inorganic semiconductors have also been widely used, such as GaP, Ga₂O₃, GaAs, AlSb, GaN, InGaAs (III-V semiconductors) or even ZnO, HgCdTe, Ge and CdS, since their high charge carrier mobility, small exciton binding energy, high stability were attractive properties for their extensive study.^{2,5,7,19-21}

The semiconductors purity and temperature growth are also very important factors that can have a tremendous impact in performance. For example, Arikata *et al.* described the growth of InAs/GaSb superlattice structures in GaSb substrates to be used as IR detectors through a method of metalorganic vapour-phase epitaxy, observing that the growth temperature influenced the results directly and that the highest performance of these devices was only obtained at 20 K (31% EQE at 3.5 µm).¹⁹ Also, El-Amir *et al.* studied the temperature dependence of high purity *n*-

type Mg₂Ge single crystals fabricated by thermal annealing, revealing a clear rectifying behaviour and an obvious photoresponse characteristic between 0.8 and 1.7 μ m, with a maximum zerobiased photoresponse of 7 mAW⁻¹ at 1.2 μ m.²⁰

Also, some heterostructure photodiodes such as Sb/WSe₂, Ge-on-Si, Cu doped SnS₂ nanoflakes, Bi₂Te₃-Si, GaSb and GaSb/AlSb superlattice buffer layers grown on Ga or Si have been explored, since combination of different semiconductors improved the performance.²²⁻²⁴ Liu *et al.* combined the unique optoelectronic properties of a topological insulator-based photodetector on Si with the complementary metal-oxide-semiconductor (CMOS) technology using for that a Si-based single crystal bismuth telluride (Bi₂Te₃) photoconductive detector able to achieve a responsivity of 3.64×10⁻³ AW⁻¹ at 1064 nm and 3.32×10⁻² AW⁻¹ at 1550 nm, showing a good potential for applications in future Si photonics.²⁴

Recently, tailorable optical properties (energy band gap and optical constants), large absorption coefficient in the UV–Vis range, long carrier diffusion lengths high charge-carrier mobilities, and low exciton binding energies at room temperature, raised a huge interest in the development of new 0D, 1D, 2D and 3D type halide perovskites.²⁵ Colloidal inorganic quantum dots (*e.g.* PbS or Ge) are also on the spot since offer some improvement in solution processability, size tuneable spectral sensitivity and higher compatibility with flexible substrates.^{26,27}

Tang *et al.* developed a stable, low cost and CMOS compatible Schottky junction photodiode using an Au-PbS colloidal quantum dot-indium tin oxide vertical junction. Under 1550 nm illumination, the authors achieved not only an EQE of approximately 400%, but also a responsivity of 5.15 AW⁻¹, a D* of 1.96×10¹⁰ Jones and a response time of 110 µs, fulfilling a satisfactory number of parameters at the same time that can be used in on-chip integrated optoelectronic circuits or infrared focal plane arrays.²⁶

Although we have now different available options to work under UV, visible or NIR wavelengths and also some of them work in a broadband spectrum, inorganic photodiodes still present major drawbacks. These include expensive and demanding manufacture, mechanical inflexibility, low operating temperatures and high driving voltages, thus narrowing their applications mainly to photodetection.²⁷

Organic Photodiodes

Due to their unique properties, organic semiconductors, based photodiodes brought a revolution in optoelectronics. An organic semiconductor can be defined as an organic material with semiconducting properties, conferred by π and π^* orbital delocalization. There is a huge multiplicity of organic semiconducting materials, covering a large spectrum of optical and spectral properties, that have been fully investigated as working organic photodiodes. These include both small molecules, such as pigments, and conjugated polymers with linear or dendritic architectures. Fullerenes (C₆₀, C₇₀, PC₆₀BM, PC₇₁BM) and polymers such as P3HT, F8T2,
PEDOT, PSS, PTB7-Th, PPDT2FBT, DPP-DTT, PCPDTBT, PCDTBT, MEH-PPV and P(NDI2OD-T2), are some examples of organic semiconductors that have been widely studied alone or in different cross combinations.²⁸⁻³³

Organic semiconductors provide high charge carriers photogeneration yields, tuneable optical gaps from UV to NIR, and production of films over large areas (that can be amorphous) using simple and low cost processes (*e.g.* spin-coating, aerosol-jet printing, spray-coating, inject printing or screen printing).^{28,29,34} Similar to photovoltaic cells, such properties open the possibility of their use in broad applications, beyond photodetection, such as biomedical imaging and sensing, communications, control circuits or machine vision.^{35,36}

In organic semiconductors weak van der Walls forces are involved. The electrical properties are not due to electrons and energy bands, like in inorganic semiconductors, but arise from differences in energy levels, the lowest unoccupied molecular original (LUMO) and the highest occupied molecular orbital (HOMO). In Figure II.3, an energy-band diagram shows a typical heterojunction organic photodiode and the way it operates.



Figure II.3: Schematic representation of a heterojunction organic photodiode with the representation of the energy band diagram. When both LUMO and HOMO of the donor lie at energies sufficiently higher than those of the acceptor, it will be energetically favourable for an exciton to reach the interface to dissociate, leaving a negative polaron on the acceptor and a positive polaron on the donor. For efficient photocurrent generation the charge separation (2) should be readily followed by a geminate recombination (4) after a photon absorption event (1), and where the transfer to contacts (3) should compete with interfacial recombination (5).²⁹

The first and simplest organic photodiode was made by a layer of the organic material sandwiched between an anode, typically indium tin oxide (ITO), and a cathode (usually low work function metals such as AI, Ca, or Mg). However, due to the lack of direct separation of the exciton

into free charges, caused by the week screening of the Coulomb interactions of the electron-hole pair, the quantum yield of these homojunctions was very low.

In this sense, planar bilayer heterojunctions (Figure II.3) and bulk heterojunctions (BHJ) architectures (Figure II.4) came up as a solution for more efficient devices. With an interface between electron donor and acceptor species, electrostatic forces are produced due to differences in electron affinity and ionization potential.





Today, the mainstream approach is focused on the development of optical systems that offer a narrow band spectral selectivity and multi-color detection, which became a key parameter for the development of new photodiodes. The strategy relies in the modification of either the composition or the thickness of the photoactive layer using narrowband materials for the active layer to tune its optical absorption exclusively to the region of interest where both the donor and acceptor materials absorb only in the desired wavelength range. Deckman *et al.* developed a fully-printed OPD array capable of RGB light separation printed on a PEN substrate by blade-coating PEDOT:PSS, a polyethylenimine cathode interlayer and the photo-active layer, and screen-printing on top a patterned PEDOT:PSS anode, achieving an average EQE of ~37% at -4V bias over the whole visible spectrum, a dark current of 0.5 nAcm⁻² and five orders of magnitude of LDR. This broadband OPD is an example of a photodiode that can simplify the fabrication of a spectral-selective photosensor and full-color imagers.³¹

Chuang *et al.* also reported an example of a highly sensitive OPD that had an extended spectral response, from the UV to NIR (~1200 nm). Incorporating two NIR dopants into the OPD, the device exhibit simultaneously a broad spectral response (with R= 23 AW⁻¹ under a lower reverse bias, -3.5V), and a good quantum efficiency (EQE ~5500%).³⁵

Currently, the range of available semiconductors is very high, and OPDs production processes are far appealing due to their simplicity. For example, Strobel *et al.* described the first inkjet and aerosol-jet printed OPD. Exploring the high-performance of non-fullerene acceptor IDTBR combined with P3HT, this digitally printed device exhibits a broadband spectral response with responsivities up to 300 mAW⁻¹ that can compete directly with current available technologies based on Si.³²

If the electrostatic forces are higher in the acceptor than in the donor, then the interfacial electric field drives charge separation, promoting photogenerated excitons break up, thus improving device efficiency. Yet, organic photodiodes are still a challenge, with some flaws that need to be overcome. These include photocurrent sensitivity to temperature, low charge carrier mobility, thickness dependence, limited light absorption across the solar spectrum and the need of a strong driving force to break up photogenerated excitons.

Hybrid Photodiodes

Although both inorganic and organic photodiodes have shown some disadvantages and drawbacks, precluding higher expansion to the market, when combined they overcome most of these issues. This is why one of the reasons why organic-inorganic hybrid photodiodes (HPDs) have drawn tremendous attention in the past few years.

With unique physical properties such as low temperature solution processability, high photosensitivity or mechanical flexibility, combined with the freedom of rational designing of numerous combinations between organic polymeric and inorganic semiconductors, HPDs revolutionized the world of photodiodes with new applications in astronomy, nuclear physics or spectroscopy.^{37,38}

The *p*-*n* junctions of HPDs usually takes advantage of the intrinsic properties of *n*- type of silicon and several III-V and II-VI semiconductors, such as ZnO, ZnSe CdSe nanocrystals, or GaN, that have an higher electron mobility, with the *p*-type nature of organic semiconductors, usually polymeric materials such as PEDOT:PSS, P3HT or graphene, with higher hole mobility, photosensitivity and optical properties than inorganic semiconductors.^{37,39-42} Also, inorganic-organic hybrid halide perovskites, combined with different conductive polymers (*e.g.* PDPP3T PCBM, or PEDOT) and inorganic semiconductors (*e.g.* Si, Ga) have aroused much interest, due to their long carrier diffusion length, low excitation binding and bandgap tunability, still air deterioration is an unsolved problem.⁴³⁻⁴⁶

HPD devices are now more stable, with longer lifetimes, and in some cases working at lower dark currents. However, the strategy to incorporate hybrid materials implies a deeper investigation in the impact of these materials in the device performance. For example, Pickett *et al.* have shown the influence of two diketopyrrolopyrrole (DPP)-based donor-acceptor copolymers with different backbone conformations incorporated in an inverted non-fullerene photodiode architecture. Using ZnO nano-patterned films as the electron transport layer, photoresponsivity is highly affected. This behaviour could be explained with an enhanced transport of carriers, due to the planar backbone conformation of the PBDT-TTDPP copolymer.³⁹

One of the biggest challenges of HPDs development is related to low dark current operation. A huge number of combinations between the inorganic and organic is possible, and device fabrication may differ quite significantly. BHJs have been widely used to fabricate HPDs photoactive layers. Due to the large *p-n* interfacial area, BHJs are able to produce ideal photogenerated charge separation. However, high reverse saturation current related with the charge injection may turn a disadvantage. Nevertheless, there is always the possibility to form a lower electron barrier into cathode/*n*-semiconductor interface and a lower hole injection barrier between the anode/*p*-semiconductor interface, making the option of using planar heterojunctions also beneficial in some cases. In this sense, HPDs are typically built in a mixed planar heterojunction/BHJ organic semiconductor architecture. Also the production of inverted HPDs, where the polarity of charge collection is inverted (following the positive results obtained for some organic photodiodes),³¹ has gained considerable attention, once the device stability may be increased along with easier production. Figure II.5 shows one example of an inverted HPD architecture.^{18,37,39}



Figure II.5: Schematic representation of an inverted HPD architecture.

Inverted architectures using nanocrystals are also an interesting approach. Ha *et al.* developed a planar heterojunction composed by PBDTT-FTTE and CdSe nanocrystals having a low dark current and a high detectivity, which is an attractive alternative to produce digital image sensors.³⁷ Dou *et al.* also demonstrated that inverting a halide perovskite HPD device highly improve its performance.

Operating at room temperature, the photodetectors exhibit a large detectivity (10¹⁴ Jones), a linear dynamic range (over 100 dB) and a fast photoresponse with a 3-dB bandwidth up to 3 MHz.⁴⁷

Recent Advances in Photodiodes Design

In the last decades, we witnessed a huge evolution in photodiodes fabrication, with a special focus on the use of improved materials and architectures. These achievements allowed the development of new types of photodiodes for specific applications. Table II.1 lists a selection of recent progress that has been made in the field.

Material	Туре	Year	D* (Jones)	Responsivity (AW ⁻¹)	EQE (%)	Application	Ref.
Au-PbS CQD	Inorganic (Schottky)	2018	1.96×10 ¹⁰	5.15	400	Optoelectronic circuits and IR focal plane arrays	26
n-Mg₂Si single crystal	Inorganic (Schottky)	2019	-	0.014ª	-	Short wavelength IR light	48
Cu(acac)₂/n-Si	HPD	2018	4.6×10 ⁹	0.009	5.53- 8.34	UV photodetector	49
Si/Bi₂Te₃-graphene ^b	HPD	2019	2×10 ⁹	8.9	17.4	Light sensing	50
FAPbBr₃ QDs/graphene	HPD	2018	-	1.154×10 ⁵	3.42×10 ⁷	Low intensity image sensor	51
PEIE/PCDTBT:PC70BM/MoOx	OPD	2019	10 ³	-	-	Color discrimination	52
Perovskite/Black phosphorus /MoS ₂	HPD	2019	1.3×10 ³	11	80	Sensor	53
PEDOT:PSS/Merocyanine(Pyrl)/C ₆₀ °	OPD	2019	-	0.71	18	Ultranarrowband organic photodiodes	54
Lisicon PV-D4650:PCBM ^d	OPD	2019	2.19×10 ¹³	0.44	82	Image sensors	55
MoO₃/BHJ/LiF:AI Red Green Blue Panchromatic	OPD	2019	1.55×10 ¹² 1.89×10 ¹² 1.8×10 ¹² 10.1×10 ¹²	- - -	18 19.6 24.6 65.1	Image sensors	56
GR/GQDs ^e	DUV PD	2019	1.1×10 ¹³	0.11	-	DUV optoelectronic devices	57
(PEA) ₂ (MA) ₅₉ Pb ₆₀ l ₁₈₁ /Spiro-OMeTAD	HPD	2019	2.2×10 ¹²	0.53	-	Photodiodes applications	58
Si type	Inorganic	2019	-	0.274	~45	X-ray	59
MoO _x /DBP/DBP:C ₆₀ /C ₆₀ /BCP	OPD	2019	-	-	~37	Optoelectronic pulse meter sensor	60

Table II. 1: Recent examples of photodiodes developed for imaging and X-ray applications.§

[§] Measurements performed at particular wavelengths are specified. ^a1.4 μm. ^b635 nm. ^c481 nm. ^d660 nm. ^e256 nm.

Enhanced photodiodes (faster, more responsive, with high detectivity and low dark current), have been developed using materials such as nanocrystals,^{12,41} quantum dots,⁶¹ halide perovskites,^{46,51} ZnSSe/p-GaAs,⁶² and polymer blends (*e.g.* PCBM and MEHPPV).⁶³ Image sensing (*e.g.* CMOS active pixel sensors)^{16,31,64,65} is one of the most important applications of photodiodes, but other type of image sensors for cell imaging,⁶⁶ to be used under cryogenic conditions^{67,68} or in space⁶⁹ are also emergent challenges.

Photodiodes play an important role in medicine. Simple X-ray detection⁷⁰⁻⁷² and pulse oximetry are key examples of applications. Pulse oximetry is of major importance in routine clinics since is an efficient and non-invasive way to measure blood oxygen saturation. In this case, the use of flexible materials is a huge advantage, allowing wearable devices (*e.g.* ring-shaped)⁷³ that

can be used in fingers, feet, forehead, chest or wrists.^{74,76} In cardiovascular related diseases they are used in monitorization (usually silicon-based avalanche photodiodes),^{77,78} in blood volume measurements (photoplethysmograms), in early detection of some cardiovascular problems,⁷⁹ or in Positron Emission Tomography–Magnetic Resonance Imaging (PET-MRI).⁸⁰ Other bioapplications such as artificial retinal implants,³³ smart for monitoring vital signs,⁸¹ or bio-HPD that contain DNA have been also explored.⁸²

Another interesting application is the detection of analytes by fluorescence and chemiluminescence using microfluidic systems.^{83,84} Here, the development of organic and hybrid photodiodes was crucial, since the devices use small molecules such as copper phthalocyanine and fluorene or polymers such as PCDTBT, PH3T or PC₆₀BM to fabricate fluorescence detectors for biomarkers and molecular probes, and chemiluminescent sensors.^{34,85,86} These microfluidic biosensors allowed the detection of pathogens such as *E. coli* or *Campylobacter jejuni.*⁸⁷

Jelly Dendrimer Hybrid Photodiodes

As previously mentioned, the combination of the unique properties of inorganic and organic semiconductors inspired the development of new materials and new HPD devices in the past few years. However, critical issues such as low dark current and detectivity are still to overcome, thus fostering the search for novel solutions.

Ruthenium dye sensitizers

Wildly studied and used in photovoltaic devices, namely dye sensitized solar cells (DSSC), ruthenium complexes present unique photoelectrochemical properties (*e.g.* high stability in the oxidized state). Modifications of the ruthenium ligands allow different absorption properties, associated to a metal to ligand charge transfer process, that influences the DSSC performance. Ru(II) polypyridyl complexes were the first generation of DSSC sensitizers that reached good efficiencies. For example, the ruthenium complex *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'- dicarboxylato)ruthenium(II), commonly known as N-719 dye (Figure II.6), is one of the most studied sensitizers.^{88,89} Based on this type of sensitizer, several systems were later developed using substituted bipyridine ligands. These modifications confer an amphiphilic character to the complex, thus improving their binding to the surface. Also, the decrease in the charge, increase the dye loading and, importantly, enhances the device stability at high temperatures.⁹⁰



Figure II.6: Chemical structure of the N-719 Ru(II) dye.

Other thiocyanate-free, and more robust, ruthenium complexes have been also studied. Yet, the transition from thiocyanate donors to other ligands has not been fully successful.⁸⁸ Porphyrins have also been also heavily studied, since they have two intense optical absorptions that are tuneable depending of the functionalization of the macrocycle. A high performance is achieved taking advantage of their impressive absorption coefficients and playing with donor and acceptor decoration.^{89,91}

Despite the high performances achieved in DSSC, the presence of a transition metal in ruthenium- and porphyrin-based dyes are associated to certain problems caused by the presence of metals since they are often toxic, more expensive and with limited availability. Therefore, researchers have been much focused in the development of new metal-free organic dyes.⁹²

Metal-free dye sensitizers

The design of metal-free organic dyes is a challenge. Their high flexible design, low toxicity, high molar extinction coefficient, highly tunable energy levels, low price and environmental impact, and relatively easy synthesis attracted an increasing attention in past few years.^{93,94}

These organic dyes are based on a D- π -A push-pull structure, where electron donor (D) and electron acceptor (A) groups are linked through a π -conjugated bridge. Different organic dyes have been developed using diverse building blocks, such as phenothiazine, squaraine, imidazole, benzimidazole diketopyrrolopyrrole, perylene, pyrazine, dihydropyrrolo[3,4-c]pyrrole-1,4-dione, terthiophene, hydantoin, ullazine, coumarin, indole or triphenylamine (TPA). To build metal-free organic dyes different modifications from the donor site unit, the combination with different acceptor units to rearrange in a D- π -A sequence have been made in order to achieve the best performance. Among these building units, the TPA donor (Figure II.7) gained a special interest mainly due to its electron transport properties and easy availability. Reasons why TPA has been widely explored as a core unit, together with different linkers and acceptors, or in new architectures (*e.g.* dendrimers), improving the performance and the stability of the sensitizer.^{93,95}



Figure II.7: Chemical structure of triphenylamine, an electron donor unit.

Dendrimers as Photoactive Species

The introduction of D- π -A conjugated polymers in photodiodes design is very attractive, in the sense that in-chain donor-acceptor interactions may promote a bandgap reduction.^{96,97} Dendrimers, in particular, usually present a high responsivity and specific detectivity in a broadband spectrum, thus emerging as highly promising materials in this field.⁹⁸

Classified as highly branched and monodisperse macromolecules, dendrimers are synthetic polymers with a well-defined 3D architecture (Figure II.8). Since 1978, when Fritz Vogtle reported from the first time their divergent synthesis, the development of dendrimer polymers turned unstoppable. The available synthetic routes explore almost unlimited variations, in an interplay between the core and the monomer composition, that may follow a divergent or a convergent synthetic route. Due to their outstanding properties, dendrimers have been extensively studied in many different applications such as drug delivery, imaging, cancer therapeutics, purification processes, catalysis, and also in optoelectronic and photonic applications.^{98,99}



Figure II.8: Schematic representation of a dendrimer structure. The lines represent generations, polymer layers sequentially added (starting from the core) during the dendrimer growth process.

Regarding optoelectronic properties, dendrimers allow the precise location of active moieties and enable highly efficient electron transfer processes (between donor and acceptor

species), being crucial and highly advantageous since it is known that high efficiencies are reached when the photoactive species are close enough to enable an excited state charge transfer.^{100,101} For example, Rajavelu *et al.* used TPA, an excellent electron donor, as a core and connected it with an electron acceptor through a π -bridge. The resulting dendrimer was found to be a material with enhanced chemical, thermal and photo stability.¹⁰² Several combinations and modifications can be done to improve the performance of donor-acceptor dendrimers. Moreover, the reproducibility, the polydispersity and the difference between batches, usually a drawback in linear or hyperbranched polymer, may be diminished using dendrimers. Although problems involving their purification, due to use of hazardous solvents in high quantities, and low yields have been an obstacle for their exploitation. In 2012, Restani *et al.* developed a methodology to synthesize polyurea (PURE-type) dendrimers using a greener technology, a supercritical fluid-assisted high yielding polymerization using carbon dioxide as a solvent and as a reagent (C1-feed stock), thus avoiding the use of organic solvents and complex purification steps.¹⁰³

Supercritical CO₂ in Green Synthesis

Mostly known as a greenhouse gas, CO₂ can be also used as green, alternative solvent and extensively explored in supercritical-assisted technologies. A supercritical fluid is a highly compressive gas that above its critical temperature (T_c) and pressure (p_c) has no longer a vaporliquid equilibrium, but it continues to have gas-like diffusivity and viscosity properties and liquidlike density properties. Under a supercritical state the fluids increase their mass transport capacity and diffusion coefficient if compared to normal gas and liquid phases conditions.^{104,105} Different substances, others than CO₂ (e.g. water, methanol, ethanol, propane, acetone) can be used as supercritical fluids. Yet, as shown in Figure II.9, CO₂ has a relatively accessible critical point (7.38 MPa and 304.1 K), being non-toxic, non-flammable, environmentally acceptable, relatively cheap, available (industry sub-product), chemically inert under many conditions, readilv thermodynamically stable and with particular solvating properties. Therefore, supercritical CO₂ (scCO₂) became one of the most desirable compounds to work under supercritical conditions. Nowadays, scCO₂ is used in several processes, such as synthesis (hydrogenations, oxidations, polymerizations), extraction (being the most popular process for coffee decaffeination) or drug encapsulation. Moreover, in some cases, CO₂ can be used also explored as a reagent and be incorporated in chemical structures.^{103,106,107}



Temperature, T (K)

Figure II.9: Carbon dioxide phase diagram.

Device Architecture

Inspired by nature, biomimetic solar cells or "artificial leaves" have been presented as novel organic photovoltaic devices. Using biocomplexes as photosensitizers (*e.g.* chlorophyll), the architecture of artificial leaves enables electron transfer between photoelectrodes and biocompatible components (*e.g.* agarose gels or lipid membranes).¹⁰⁸ The idea to create a device built under room temperature conditions using a simple architecture, reducing cost and the manufacturing steps, is a very appealing challenge.¹⁰⁹

In this work, following a biomimetic strategy and exploring the exceptional properties conferred by a dendritic polymer architecture, a new jelly dendrimer hybrid photodiode-like device (D-HPD) based on an active single layer was developed (Figure II.10). The new D-HPDs comprise poly(imidazolone amine) (PIMAM) dendrimers having donor (TPA derivative) and electron acceptor (imidazolone) units.^{102,110} These were synthesized in two steps, by a green approach using scCO₂, and ruthenium dyes (N-719 and ferrocene-derived N-719) were tested in combination with donor-acceptor dendrimers.



Figure II.10: Schematic representation of a jelly dendrimer hybrid photodiode-like device.

Experimental Section

Materials

Carbon dioxide was obtained from Air Liquide with purity higher than 99.998%. All chemicals and solvents were used as received without further purification. Tris(4aminophenyl)amine (TAPA, 97%), tris(2-aminoethyl)amine (TREN, 97%), N.Obis(trimethylsilyl)acetamide (BSA, 95%), DMF anhydrous (99.8%) and platinum foil, 0.025 mm thick (25x25 mm), 99.9% (metal basis), were purchased from Alpha Aesar. Benzoin (>98%) was purchased from TCI and 4,4'-dimethoxybenzoin from MP, di-tetrabutylammonium cisbis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (Ru(dcbpy)₂(NCS)₂, 95%), urea, NaBH₄ (98%), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl], ≥98%), gelatin and agarose gel were purchased from Sigma-Aldrich. H₂O₂ (35% v/v) was purchased from Labchem. AISI 304 stainless steel foil, 0.914 mm thick (annealed), was purchased from Goodfellow.

Methods

UV-Vis spectra were obtained in a UV-1700 PharmaSpec Spectrometer from Shimadzu over the spectral range of 200 to 900 nm with a scan rate of 100 nm•min⁻¹ at 25 °C in 1.0 cm quartz cuvettes. The fluorescence spectra were recorded at 25 °C on a PerkinElmer LS 45 Luminescence Spectrometer with a slit with of 5 nm at a scan rate of 240 nm•min⁻¹. The fluorescence spectra of the donor-acceptor dendrimers and dye sensitizer solutions were measured in DMSO (excitation at $\lambda_{abs,max}$, absorbance < 0.1). The NMR spectra were recorded on a Bruker ARX 400 MHz equipment. ¹H and ¹³C NMR chemical shifts are reported as ppm

(parts per million). Due to low solubility it was not possible to obtain the ¹³C NMR spectra of all dendrimers. Dried samples were analysed by FTIR in a Spectrum BX from PerkinElmer with a spectrum acquisition of 16 scans, in the range 4000 to 600 cm⁻¹. The current-voltage (*I–V*) curves of D-HPDs were measured under exposure to AM1.5G solar simulator at 65 mWcm⁻² (Oriel instruments 92250A-1000). The HOMO and LUMO energy levels of **3**, **9** and **10** were estimated by cyclic voltammetry (CV) using a three-electrode scheme. The measurements were performed at 50 mVs⁻¹ in an electrolyte solution of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile (HPLC grade). The working electrode was a platinum disc, the reference electrode was a saturated calomel electrode (SCE), and the counter electrode was a platinum wire. The solutions were degassed by purging N₂ prior to the measurements. HOMO and LUMO levels were estimated as corresponding to the onset potentials for oxidation and reduction, respectively, after reference in the measured potentials to the vacuum level (Fc/Fc⁺ redox couple as external reference).

Synthesis of PURAM_{G1} (1)

The synthesis of poly(urea amidoamidine) (PURAM) dendrimers followed our reported protocol.¹⁰³ Typically, the synthesis was performed in a 33 mL stainless steel high-pressure cell that was loaded with 0.5 g of TAPA (1.7 mmol), 1.7 mL of BSA (6.9 mmol) and 1 mL of anhydrous DMF (co-solvent, to allow full solubilization) under stirring conditions. The reactor was then closed with two aligned sapphire windows, connected to the CO₂ line charged with gas to approximately 0.1 MPa and placed in a thermostated water bath at 40 °C to assure control and avoid gas leakage from the reactor. After that, the pressure was finally adjusted to 18.5 MPa by addition of further CO₂ to solubilize the substrates. The reaction was allowed to proceed under a supercritical conditions for 20 h before washing during 1 h and depressurization. In the second step of the reaction, the cell was opened to add more TAPA (1.5 g, 5.25 mmol) and BSA (2.9 mL, 12.0 mmol). The mixture was kept at 120 °C for 17 h under stirring. Acetone was then added to the cell and the crude product was removed and separated by filtration under vacuum as a dark purple solid (2.0 g) with 93.6% yield. The low solubility of the PURAMG1 dendrimer in most organic solvents (including DMSO) precluded a full characterization. FTIR (KBr) υ (cm⁻¹): 3379 (Ar-NH₂), 1697 (C=O, urea), 1635, 1625, 1594 (N-H, urea), 1504 (Ar-H), 1315 (Ar-H), 1271. The ¹H NMR spectrum shows a broad signal at 6.82 ppm.

Synthesis of PIMAM_{G1} derivatives (2) and (3)

Poly(imidazolone amine) (PIMAM) dendrimers **2** and **3** were synthesized using two different benzoins, 2-hydroxy-1,2-diphenylethanone (benzoin) and 4,4'-dimethoxybenzoin, respectively. The synthesis followed a modified protocol.¹¹¹ In a 50 mL round bottom flask, benzoin (0.4 g, 1.8 mmol) or 4,4'-dimethoxybenzoin (0.5 g, 1.8 mmol) were added to PURAMG₁ (0.5, 0.4 mmol) and the mixture was heated using an oil bath (170 °C) under argon atmosphere

and stirred for 17 hours. The mixture was then washed with acetone and a black solid was collected by filtration under vacuum. PIMAM_{G1} (**2**): Yield: 60.0% (0.4 g). FTIR (KBr) υ (cm⁻¹): 3446 (Ar-NH₂), 1636 (C=O, imidazolone), 1507 (Ar-H), 1309 (Ar-H), 1273 (Ar-H), 832, 618. ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.93 (t, *J*= 6.7 Hz, 12H), 7.84–7.77 (m, 6H) 7.71–7.56 (m, 24H), 7.55–7.30 (m, 36H). PIMAM_{G1}OMe (**3**): Yield: 40.0% (0.3 g). FTIR (KBr) υ (cm⁻¹): 3421 (Ar-NH₂), 1619 (C=O, imidazolone), 1508 (Ar-H), 1312 (Ar-H), 1260 (Ar-H), 1175 (C-O-C). ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.88 (d, 4H, *J*= 8.0 Hz), 6.99 (d, 4H, *J*= 8.0 Hz overlapped with the peak at 6.89 ppm), 6.89 (bs, 24 H) and 3.81 (s, 6H).

Oxidation of PIMAM_{G1}OMe (4)

Following a modified protocol,¹¹² in a 50 mL round bottom flask, 100 equivalents (0.8 g, 8.8 mmol) of the urea-hydrogen peroxide adduct (UHP, previously synthesized)¹¹³ were added in four portions (25 equivalents each time with intervals of 15 min, 1 h of total reaction time), to **3** (0.2 g, 0.08 mmol) at 85 °C (oil bath). Then, the mixture was washed with water and the solid was collected by filtration and dried under vacuum. PIMAMO_{G1}OMe (**4**) was obtained as a dark green solid (0.09 g) in 51.4% yield. FTIR (KBr) υ (cm⁻¹): 3379 (Ar-NH₂), 1697 (C=O), 1635, 1625, 1594, 1504 (Ar-H), 1315 (Ar-H), 1271. ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.63-6.91 (broad signal), 5.42 (broad signal) and 3.84 (broad signal).

Synthesis of PURAP_{G1} (5)

Poly(urea aminophenyl) (PURAP) dendrimer was obtained following the protocol described for **1**. In the first step, TREN (0.1 mL, 0.7 mmol) and BSA (0.7 mL, 2.7 mmol) were added to the high-pressure cell, followed by TAPA (0.6 g, 2.1 mmol) and more BSA (1.2 mL, 4.8 mmol) in the second step. The crude product was collected by addition of acetone and filtration under vacuum. The product was dried under vacuum, giving a purple oil (0.3 g) in 46.4% yield. FTIR (NaCl film) υ (cm⁻¹): 3390 (Ar-H), 1654 (C=O, urea), 1399 (CH₂). ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.43–7.05 (m, 12H), 7.04–6.32 (m, 24H), 3.44 (s, 12H). ¹³C NMR (101 MHz, DMSO-*d6*) δ : 171.5, 143.2, 138.6, 124.1, 114.8, 114.7, 22.5.

Synthesis of PURAP_{G1}OMe (6)

Using the protocol described for 3, 4,4'-dimethoxybenzoin (0.2 g, 1.1 mmol) was added to PURAP_{G1} (0.2 g, 0.2 mmol). The mixture was washed with diethyl ether and a black solid was obtained (0.2 g) in 60.2% yield. FTIR (KBr) υ (cm⁻¹): 3408 (Ar-NH₂), 1656 (C=O, imidazolone ring), 1597, 1507 (Ar-H), 1310 (Ar-H), 1256 (Ar-H), 1161 (C-O-C). ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.68 (m, 24H), 7.08–6.82 (m, 36H), 4.05–3.63 (m, 30H). The spectrum shows a small contamination with 4,4'-dimethoxybenzil (4,4'-dimethoxibenzoin oxidation byproduct) at 7.83 (d, 4H, *J*= 8.0 Hz), 7.12 (d, 4H, *J*= 8.0 Hz) and 3.81 (s, 6H).

Oxidation of PURAP_{G1}OMe (7)

Following the protocol described for **4**, a total of 1.0 g of UHP (0.01 mmol) were added to **6** (0.2 g, 0.0001 mmol). The mixture was then washed with water, the solid was filtered and dried under vacuum. PURAPO_{G1}OMe (**7**) was obtained as a dark green solid (0.1 g) in 48.3% yield. FTIR (KBr) υ (cm⁻¹): 3385 (Ar-NH₂), 2837, 1661 (C=O), 1600, 1506 (Ar-H), 1309 (Ar-H), 1253, 1174. ¹H NMR (400 MHz, DMSO-*d6*) δ : 7.95-7.70 (broad signal), 7.13-6.82 (broad signal), 3.83 (s, 6H).

Reductive Amination of Ferrocenecarboxaldehyde (9)

on a reported protocol,¹¹⁴ in a 50 mL Based round-bottom flask, ferrocenecarboxaldehyde (8) (0.5 g, 2.3 mmol) was added to a stirred solution of 40% aqueous ethanolamine (7.2 mL in 18 mL of water) at 0 °C. The solution was allowed to warm to room temperature and stirred for 2 days. The reaction mixture was washed with water and the orange solid dried under vacuum. Next, the solid was reduced using NaBH4. In a 50 mL round-bottom flask, the orange solid was added to a suspension of NaBH4 (0.2 g, 6.5 mmol) in 30 mL of ethanol. The solution turned immediately yellow-orange and was allowed to stir for 2 h at room temperature under nitrogen atmosphere. The volatiles were removed under vacuum and the product extracted with diethyl ether. The combined organic phases were washed with water and dried over anhydrous MgSO4. The solvent was evaporated, and 9 was obtained as a yellow-orange solid (0.3 g) in 46.6% yield. FTIR (KBr) v (cm⁻¹): 3423 (OH/NH), 3082, 2900, 2832, 1429, 1062. ¹H NMR (400 MHz, CDCl₃) δ: 4.19-4.15 (m, 4H), 4.13 (s, 5H), 3.64 (bs, 2H), 3.55 (s, 2H), 2.78 (bs, 2H). ¹³C NMR (101 MHz, CDCl₃) δ: 85.7, 68.8, 68.7, 68.6, 68.5, 68.3, 68.0, 60.5, 50.5, 48.4.

Synthesis of Ru(dcbpy)₂(NCS)(EAFc) (11)

Following a modified procedure,¹¹⁵ in a 50 mL round-bottom flask, commercial Ru(dcbpy)₂(NCS)₂ (**10**) (0.09 g, 0.08 mmol) was added to a stirred solution of **9** (0.1 g, 0.4 mmol) in NaOH aqueous solution (0.02 g, 0.4 mmol, 2.8 mL) and poured into an oil bath at 50 °C for 2 hours. The mixture was then cooled to room temperature and 15 mL of water was added. The pH was adjusted to 1, and the precipitated solid was collected by filtration under vacuum. Ruthenium dye **11** was obtained as a purple solid (0.0424 g) with 38.1% yield. FTIR (KBr) υ (cm⁻¹): 3416 (NH), 3074 (Ar-H), 2101 (C=S), 1705 (Ar-H), 1609 (Ar-H), 1258 (C-CH₂), 1230 (C-CH₂). ¹H NMR (400 MHz, DMSO-*d*6) δ : 9.40 (d, 2H, *J*= 4 Hz), 9.14 (bs 4H), 8.97 (bs, 2H), 8.33 (d, 2H, *J*= 4Hz),7.70 (bs 2H), 7.57 (bs, 2H), 4.21-4.08 (m, 10 H) 3.63 (bs, 2H), 3.15 (bs, 4H), 2.91 (bs, 1H), 1.55 (bs, 4H), 1.29 (d, *J*= 4 Hz, 4H), 0.91 (t, *J*= 8 Hz, 6H). ¹³C NMR (101 MHz, DMSO-*d*6) δ (ppm): 165.73, 165.16, 158.55, 157.12, 139.79, 134.35, 125.39, 74.09, 69.52, 67.85, 64.41, 23.06, 19.18.

D-HPD device fabrication

To prepare the D-HPD device matrix, 0.03 g of agarose were solubilized in 0.8 mL of water at 60 °C in a glass cuvette ($3.8 \times 3.4 \times 0.4$ cm), and DMSO solutions (0.2 mL) of dendrimers **3**, **4**, **6** or **7** and/or dye sensitizers **10** or **11** were added (5 mM for both components). After being solubilized, the mixture was cooled down to room temperature and full jellification was observed after 1 hour. To build the D-HPD device, the jelly was cut (1.5×1.5 cm, 2.25 cm² total area), placed in contact with tape-masked ITO (indium tin oxide) (100 nm thick)-coated glass substrates (photoanode) and covered with the counter electrode (platin or stainless steel). (The glass/ITO substrates were previously cleaned under ultrasounds with distilled water and a non-ionic detergent followed by distilled water, acetone, and isopropyl alcohol and then dried under a N₂ flow. The thicknesses of the gels were measured with a profilometer (DEKTAK 6M). Current-voltage (*I-V*) measurements were performed between -1.0 and 1.5 V in the dark, under illumination, under illumination after 15 minutes of continuous exposure and under dark after 15 minutes of lamp switch off.

Results and Discussion

To prepare the target donor-acceptor dendrimers, precursors **1** (PURAM_{G1}) and **5** (PURAP_{G1}) were first synthesized using our green supercritical-assisted polymerization protocol,¹⁰³ using CO₂ as solvent and as a reagent (C1 feedstock) (Scheme II.1). The incorporation of CO₂ in the PURAM dendrimer backbone as urea linkages allows further functionalization (*e.g.* reaction with selected benzoins) leading to PIMAM dendrimers.

Precursor **1** was found to be insoluble in common organic solvents and water. The reason for this could be explained by π - π interactions between the arylamine moieties (TAPA), which promote aggregation, thus precluding the full characterization of PURAM dendrimers. However, this solubility issue was overcome by changing the dendrimer core from TAPA to an aliphatic amine (TREN). Using this strategy, a more soluble precursor **5** was obtained. In the next step, **1** and **5** were reacted with benzoin derivatives to obtain the corresponding donor-acceptor PIMAM dendrimers. Solubility enhancement was more pronounced when 4,4'-dimethoxybenzoin was used, in comparison with benzoin, probably due to the presence of bulkier methoxy groups. For this reason, dendrimers **3** and **6** were selected for further studies.

To test the dendrimers stability and evaluate their performance under an oxygen-rich atmosphere, dendrimers **4** and **7** were synthesised by oxidation of **3** and **6**, respectively. The oxidation was successfully achieved using a urea-hydrogen peroxide (UHP) adduct under solventless conditions. The oxidation confirmed a high stability under oxidative conditions and, for our surprise, also improved its solubility.

[Ru(bpy)₃]²⁺ is one of the most studied systems in dye-sensitized photovoltaic cells, not only for is chemical stability, but also for the long-lived excited state at room temperature and good luminescent properties.¹¹⁶ To compare the effect of Ru(II) dye sensitizers in the performance of our D-HPD devices we synthesized a new heterobimetallic dye complex, having rutheniumferrocene (Ru-Fc) conjugated units. Ru(dcbpy)₂(NCS)(EAFc) (**11**), was prepared from commercial Ru(dcbpy)₂(NCS)₂ (**10**) and an ethanolamine ferrocene derivative, EAFc (**9**). The reductive amination of ferrocenecarboxaldehyde (**8**) was performed using ethanolamine, thus avoiding Fc dimerization (Scheme II.2).¹¹⁷



Scheme II.1: Synthesis of donor-acceptor PIMAM and PIMAMO dendrimers.



Scheme II.2: Synthesis of heterobimetallic Ru-Fc complex dye 11.

The UV-Vis absorption and the emission of photoactive dendrimers in DMSO solution and dye sensitizers are summarized in Table II.2.

 Table II.2: Absorption, emission and energy band-gap for donor-acceptor dendrimers and dye sensitizers in DMSO.

Material	λ _{max} (nm)	λ _{em} (nm)	E _g (eV)
PIMAM _{G1} OMe (3)	292	402	3.69 ^b
PIMAMO _{G1} OMe (4)	430	528	-
PURAM _{G1} OMe (6)	425	485	-
PURAMO _{G1} OMe (7)	420	518	-
Ru(dcbpy) ₂ (NCS) ₂ (10)	515	n.d.	2.33
Ru(dcbpy)₂(NCS)(EAFc) (11)	541ª	n.d.	1.77 ^b

^aA band with similar intensity is observed at 402 nm. ^bThe energy band-gap was calculated from the on-set of absorption, at lower energies, using the equation $E_g = \frac{1240}{\lambda} (eV)$.¹¹⁸

A good overlap between the absorption and the emission spectra was observed (see Figure A I.1 in Appendix I). Despite the low values of the fluorescence intensity of the oxidized dendrimers **4** and **7** is higher than the corresponding precursors **3** and **6**. This fluorescence turnon could be also interesting for the development of organic peroxide sensing devices, such as triacetone triperoxide (TATP),¹¹⁹ or for cell signalling.¹²⁰ The large emission red-shift observed upon oxidation, most pronounced in **4** (63 nm, 52 nm in the absorption) than in **7** (33 nm), has been reported for conjugated polymers.¹²¹ Both systems present a large Stokes shift (98 nm), which may be attributed to the polar nature of the oxidized dendrimers. Preliminary CV studies were performed for dendrimer **3** and dye complex **11**. This allowed us to estimate the HOMO and LUMO energy levels of **3**, corresponding to the onset potentials for oxidation and reduction, respectively, upon referring to the vacuum level (Figure II.11A).



Figure II.11: Cyclic voltammograms showing the redox potentials of dendrimer 3 (A) and Ru-Fc dye complex11 (B). The arrows in B show the oxidation peaks.

The measured potentials were referenced to the zero vacuum-level using the $Fc^{0/+}$ redox couple as an external reference.¹²² As we measured $E_{1/2}(Fc^{0/+})= 0.42$ eV and the energy level of $Fc^{0/+}$ is 4.80 eV below the vacuum-level, we calculated the HOMO and the LUMO energy using Equations II.10 and II.11:

HOMO (
$$eV$$
)= - ($E_{onset,ox}$ + 4.38) eV (II.10)

LUMO (
$$eV$$
)= - ($E_{onset,red}$ + 4.38) eV (II.11)

Therefore, for dendrimer **3**, the HOMO and the LUMO values are -5.49 and -3.12 eV, respectively. Complex **11** shows three separated anodic couples in the 0-1.0 V window (*vs.* SCE electrode) (Figure II.11B), whose half-wave potentials were $E_{1/2}$ [1]= 0.417, $E_{1/2}$ [2]= 0.568 and $E_{1/2}$ [3]= 0.884 eV (*vs.* saturated calomel electrode). We attribute the first peak to the Fc^{0/+} process, as a similar value was determined for the half-wave potential of Fc/Fc⁺ in free ferrocene (used as external reference). The second peak is probably assigned to the Ru^{II/III} process, as described in related Ru(II) complexes.¹²³ The HOMO energy of complex **11**, determined from the

onset of the first oxidation wave ($E_{onset,ox}$ = 0.33 eV) using Equation II.10, was estimated as -4.71 eV. The LUMO energy of **11** was estimated by adding the optical band gap (Table II.2) (2.06 eV) to the HOMO energy, as -2.65 eV. The HOMO and LUMO values of **10** shown in Figure II.14 were obtained from literature.¹²⁴

Next, *I-V* measurements were performed to evaluate the performance of the new materials as potential HPDs components. To overcome solubility issues, classical non-vacuum depositions were avoided (*e.g.* spin coating, drop cast)¹²⁵ and replaced by homogeneous jelly layers. Thus, several matrixes were investigated. Ionic liquids have already been used as a matrix in dye sensitized cells, mainly due to their solvating properties, non-flammability, non-volatility and high conductivity.^{126,127} Considering the low solubility of the dendrimers in common organic solvents and/or water, the first matrix tested was an ion jelly, a mixture of an ionic liquid and gelatin.¹²⁸ Interestingly, the chosen ionic liquid, [Bmim][CI], allowed the full solubilization of the dendrimers in the range of the working concentrations (10 mM). Also, the easy deposition of the gel into the electrode and the possibility of preparing a dendrimer stock solution were very attractive. However, *I-V* measurements showed that ion jelly leads to short-circuiting devices and this matrix had to be discarded (see Figure A I.2 in Appendix I).

Alternatively, we found that agarose is a biocompatible, simple and mechanically flexible matrix that has been previously used in the preparation of hydrogel-based photovoltaic cells.⁹ Therefore, we investigated different percentages of agarose, with the addition of co-solvents, and dendrimers in several concentrations in order to establish a suitable matrix that could enable the production of working D-HPDs. The best formulation was found to be an agarose concentration of 3% (w/w) in a 20% DMSO aqueous solution, which showed a positive response when the *I-V* measurements were performed (see Figure A I.3 in Appendix I). Using this matrix, donor-acceptor dendrimers and/or dye sensitizers (5 mM), films with 400 µm thickness were produced after jellification in glass cuvettes. By this way, simple D-HPDs were fabricated using a single jelly layer assembled between an anode (ITO glass) and a counter electrode (platin or stainless steel) (Figure II.12).

The device components (dendrimers and dyes) were tested both separately and mixed, using different dark/illumination experimental conditions and counter electrodes. Current density-voltage (*J-V*) curves were measured in the dark, under illumination, under illumination after 15 min. of continuous exposure and under dark after 15 min. of lamp switch off (see Figure A I.4 in Appendix I). Also, all measurements were performed under solar light illumination, to evaluate a broadband response of this simple architecture. It was observed that dendrimers **6** and the corresponding oxidized derivative **7** do not respond to applied current (data not shown). Contrary, dendrimer **3** and its oxidized derivative **4** showed a (different) response under dark and under illumination (see Figure A I.5 in Appendix I). Hence, their performances were evaluated in the presence of both **10** and **11** dye sensitizers. The obtained *J-V* curves are shown in Figure II.13.



Figure II.12: Fabrication of donor-acceptor dendrimer hybrid photodiode-like devices (D-HPDs). Glass cuvettes with gels containing donor-acceptor dendrimers **3** (A) and **4** (B), and mixtures of **3** with Ru dye **10** (C) and Ru-Fc **11** (D). The gel layers were cut using a cake cutter mold (E). Assembled D-HPD device (tape-masked ITO photoanode + photoactive gel + counter electrode) shown under simulated solar illumination (F).



Figure II.13: Comparison of *J-V* curves of D-HPD devices: **3** mixed with dyes **10** or **11** using platin or stainless steel counter electrodes (A), and **4** mixed with dye **11** using platin or stainless steel counter electrodes (B). Representation using a semi-logarithmic scale.

The performance of the D-HPD devices was found to be counter electrode dependent. Devices using only 3 and a platin counter electrode operate in positive bias in dark current and in reverse bias under illumination. With a stainless steel electrode, the device works in reverse bias both in dark and illumination conditions. The addition of 10 to dendrimer 3 leads to positive bias operation under illumination, which reverses to negative bias after 15 min. of illumination (Figure II.13A). Despite 10 does not significantly affect the current densities under illumination, with a stainless steel counter electrode we observe a reduction of dark current density (10 nA•cm⁻²), thus enabling a better performance. Oxidized dendrimer 4 showed a similar performance using platin or stainless steel counter electrodes, working both in reverse bias (Figure II.13B). In both systems, the addition of **11** leads to operation modes at higher current densities. Noticeably, the introduction of a dye sensitizer, either **10** or **11**, leads to an improvement of the D-HPD device. Comparing the graphs in Figure II. 13A (platin vs. stainless steel), the performance of the system is quite similar, independently of the used counter electrode, when the systems are under illumination. We also observed that, in general, this type of devices shows reversible operation modes since similar initial and final current density and voltage values (dark recovery) are obtained.

The movement of the voltage between dark and illumination measurements is not affected by the counter electrode used, like in the case of other counter electrodes found in literature.¹²⁹ Here, the major contributions for these changes could be due to the charge injection and extraction between electrodes and the organic semiconductors with the introduction of dye sensitizers in the device.¹³⁰

The photocurrent responses observed for the D-HPD devices may be rationalized by a mechanism similar to the one observed in previous studies on gel photovoltaic devices,³⁷ and is presented in Figure II.14.



Figure II.14: Energy band alignments of ITO anode, sensitizer dyes **10** and **11**, dendrimer **3**, platin and stainless steel cathodes. The LUMO energy for **3** was determined by two ways, by cyclic voltammetry (-3.12 eV) and by adding Eg to the HOMO energy (-1.8 eV). The mechanism of photocurrent generation (A-C) is represented only for the [**3+10**] D-HPD device. Platin= Pt, stainless steel= ss.

Both **10** and **11** sensitizer dyes, after absorbing light, are able to inject the generated photocurrent at the ITO surface (Figure II.14A). Dendrimer 3 probably regenerates **10** or **11** oxidized species (Figure II.14B). Also, **10** and **11**, with lower LUMOs will assist electron injection from dendrimer **3** at the ITO surface (Figure II.14C). Thus, the lower LUMO value of **10** may account for the better performance of this device. Also, the increased performance of devices using a stainless steel electrode can be explained by the higher energy gap between this electrode and dendrimer **3**.

The specific detectivity (D*) of D-HPDs was calculated using equation II.12:47

$$D^* = \frac{J_{ph}/L_{light}}{(2qJ_d)^{1/2}}$$
(II.12)

where J_{ph} is the photocurrent, L_{light} is the incident light intensity, J_d is the dark current and q is the elementary charge (1.602×10⁻¹⁹ C). Table II.3 show the calculated D* values for the tested D-HPDs.

Table II.3: Specific detectivity of D-HPDs devices.

Device ^a	Dark current	D*	
	Voltage (V)	(Jones ^b)	
[3]Pt	0.05	3.4×10 ⁷	
[3]ss	-0.45	8.2×10 ⁷	
[3+10] _{Pt}	-0.45	3.3×10 ⁸	
[3+10] _{ss}	-0.40	8.8×10 ⁸	
[3+11] _{Pt}	-0.20	6.9×10 ⁸	
[3+11] _{ss}	-0.20	6.9×10 ⁸	
[4] _{Pt}	-0.50	3.6×10 ⁷	
[4] _{ss}	-0.60	4.3×10 ⁷	
[4+11] _{Pt}	-0.20	1.0×10 ⁸	
[4+11] _{ss}	-0.15	1.4×10 ⁸	

^aPlatin= Pt, stainless steel= ss. ^bJones= cmHz^{1/2}W⁻¹.

As can be seen in Table II.3, the device using dendrimer **3** mixed with the dye sensitizer **10**, working with a stainless steel electrode, [**3**+**10**]_{ss}, not only allowed a large reduction of dark current density but also led to a specific detectivity enhancement.

Conclusions

In summary, we have synthesized donor-acceptor dendrimers, that mixed with a sensitizer dye, in one single layer and using an agarose matrix, enabling the fabrication of photodiode-like behavior devices (D-HPDs). The best working system was found to be a combination of a PIMAM_{G1}OMe dendrimer mixed with the commercial dye sensitizer Ru(dcbpy)₂(NCS)₂ and a stainless steel counter electrode. Despite the actual D-HPDs devices have a light-to-dark current low ratio, for practical applications, they offer an equilibrium between a good low dark current (usually an issue in this type of devices) and photodetectivity. Moreover, the better performance achieved by the use of stainless steel electrodes, compared to platin, is a plus, thus enabling lower cost devices. Further optimization of the materials, and translation to a flexible support, are undergoing.

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Chapter III

Supercapacitors

This chapter is divided in two main sections: an overview of the properties and recent applications of supercapacitor materials, and the synthesis of new potential electrodes based on linear aromatic polythioureas (LPTU) and LPTU functionalized polyurea dendrimer (PURE_{G4}-LPTU₆).

Supercapacitors

As mentioned in Chapter I, a transition from fossil fuels to renewables is urgently needed. This process brings some concerns regarding energy storage, pushing forward the development of new solutions to increase capacity and answer market needs.

Among lithium-ion batteries, other solutions have been explored such as capacitors, fuel cells and supercapacitors (SCs) with different power and energy densities (Figure III.1). Described also as ultracapacitors or electrochemical capacitors, SCs use high surface area electrode materials and thin electrolytic dielectrics to achieve larger capacitances. Based on nonfaradaic/faradaic charging/discharging systems, SCs are known for their high power density (often > 10 kW/kg), long life cycle (> 100 000 cycles), fast dynamic charging rates (within seconds), wide range of temperature stability, no memory effect and the good stability; majors advantages that fomented a growing interest in this ESS and that may can complement or even replace batteries.¹⁻³



Figure III.1: Ragone plot of different electrochemical energy conversion systems.⁴

Working Principles

SCs are more similar to batteries than traditional capacitors, since these only have two conducting electrodes separated by an insulating dielectric material. Structurally, they are constituted by two electrodes submerged in an electrolyte and separated by an insulator, an ion permeable material soaked with electrolytes that allows ionic transfer between the electrodes. SCs operate at lower voltage than batteries, to minimize electrolyte decomposition, and for that reason it is necessary to find a balance between the maximum operating voltage and the best

performance. Several factors contribute to the performance of SCs, such as the chosen electrode materials (symmetric or asymmetric), the electrolytes and the cell structures. The charge storage mechanism may also influence their properties and storage capacity. Depending on the charge storage mechanism, SCs can be classified in three categories: electrochemical double-layer capacitors (EDLCs), hybrid capacitors or pseudocapacitors.^{2,4,5}

EDLCs use electrostatic ion adsorption/desorption at the electrode-electrolyte interface to storage energy, generally using highly porous carbon materials to potentiate their capacitance (Figure III.2A). On the other hand, the pseudocapacitors charge storage mechanism relies in a reversible faradaic redox reaction between the electroactive materials and electrolyte ions, using conducting polymers or metal oxides (Figure III.2B). In the case of hybrid capacitors, they use both EDLC and pseudocapacitor mechanisms, mixing the electrochemical double layer ion adsorption/desorption and reversible faradaic reactions (Figure III.2C).⁵⁻⁷



Figure III.2: Schematic representation of the working mechanisms of electrochemical double layer capacitors (A); pseudocapacitors (B); and hybrid capacitors (C).⁵

Performance Evaluation

At an electrochemical level, the techniques usually applied in SCs characterization are cyclic voltammetry (CV), galvanostatic charge discharge tests (CD) and electrochemical impedance spectroscopy (EIS). To evaluate the SCs performance, key parameters must be considered. An overview of the most important parameters is given below.^{2,6,8-10}

Capacitance (C)

Capacitance, usually given in Farad units (F), can be defined as the ratio between stored (positive) charge and applied voltage, and is highly dependent on the characteristics of the
electrode material. In case of EDLCs, capacitance is measured through the charge that each parallel plate can store *per* unit of potential difference applied to its terminals and can be calculated using equation III.1,

$$C = \frac{\epsilon A}{d} \tag{III.1}$$

where ϵ is the permittivity of the dielectric material that separates the plates (expressed in F/m), *A* is the plates surface area (in m²) and *d* is the distance between them (in this case the thickness of the dielectric layer). In the case of pseudocapacitors, the pseudocapacitance can be calculated through the derivative of charge acceptance (Δq) and changing potential (ΔV), as demonstrated in equation III.2,

$$C = \frac{d(\Delta q)}{d(\Delta V)} \tag{III.2}$$

Energy density (E) and power density (P_{max})

When a SC is charged, a cell voltage (V) will be built up across the electrodes and the energy (E) and power density (P_{max}) that can be calculated through the equations III.3 and III.4 respectively,

$$E = \frac{1}{2}CV^2 \tag{III.3}$$

$$P_{max} = \frac{V^2}{4R} \tag{III.4}$$

where C is the capacitance (in Farads), V the nominal voltage (in volts) and R the equivalent series resistance (in ohms).

Equivalent series resistance (R)

Generally used to determine the power density (P_{max}), R is the sum of the various types of resistance, including the mass transfer resistance of ions, the intrinsic resistance of the electrode material and the electrolyte, and the contact resistance between the current collector and the electrode.

Cycle-life

Used to evaluate SCc stability, the cycle-life is one of the most important parameters to measure the overall performance. Usually some cycle-life evaluation tests involve the electrode undergoing charge and discharge cycling in a certain electrolyte, and their initial and final capacitances are compared. The cycle-life depends on many factors, such as the cell type, the charging/discharging rate, the electrode material, the electrolyte, the operating voltage and the temperature.

Self-discharge rate

The self-discharge rate is related with the potential losses of a charged electrode during a period of storage time where the current leakage leads to a decrease of the cell voltage.

Thermal stability

The thermal stability is an important parameter since most of SCs work in a temperature range from 30 to 70 °C (higher in some cases). The temperature can affect all the properties above mentioned, such as energy and power densities, self-discharge rate, cycle-life, thus reducing SCs performance. It is also very important to evaluate the electrolyte stability under the working temperature.

Electrolyte

The electrolyte, being responsible for the ionic conductivity, and electrodes charge compensation, has a direct influence over the SCs performance. Electrolytes can strongly influence key parameters such as the cell voltage, the cycle stability, the operating temperature, and energy and power density, since these parameters are highly dependent of their stability and specific characteristics. Electrolytes may be classified in three major classes: liquid, solid-state (or quasi-solid-state) and redox-active electrolytes. Figure III.3 show some examples of SC working electrolytes.^{6,11}

Liquid electrolytes can be aqueous or non-aqueous. Aqueous electrolytes (acid, alkaline or neutral) have drawn much attention, since they are abundant, low cost, highly conductive, environmentally benign and allow higher capacitances due to smaller distances between solvated ions. However, the major drawback of aqueous electrolytes is their limited voltage window range (*ca.* 1.2 V). Higher values lead to cell destruction due to water electrolysis.¹²

In the other hand, non-aqueous electrolytes can be divided in three types: organic, ionic liquids or mixtures of them. Organic electrolytes, such as propylene carbonate (PC), or some salts such as TEABF₄, SBP-BF₄, LiPF₆ or LiClO₄, have as main advantages a wide electrochemical stable potential window (ESPW), usually between 2.5 and 2.8 V, a high energy and power density (comparing with aqueous electrolytes) and the tendency to be less corrosive, a reasons why are widely used in commercial SCs.



Figure III.3: Classification of electrolytes for supercapacitors devices.⁶

However, the non-aqueous electrolyte toxicity, flammability, higher cost (due to complex processing and purification) and their lower conductivity, and reduced specific capacitance are some drawbacks that need to be overcome.¹³ lonic liquids, when compared to organic electrolytes, are less toxic, have a higher operating voltage (to 6 V), and are thermally stable (with low vapour pressure). Since ionic liquids have a large asymmetric organic cation and an inorganic or organic anion, it is possible to tailor different compositions and formulations to achieve the best performance. Yet, ionic liquids are costly and typically have a low conductivity, due to their high viscosity and low ion mobility. This leads to the formulation of non-aqueous electrolytes that are mixtures of both organic electrolytes and ionic liquids, taking advantage of their best properties.^{8,14,15}

The development of solid-state (or quasi solid-state) electrolytes brought flexibility to SCs. There are two main types of solid electrolytes: dry polymers (*e.g.* LiCl in PEO) and gel polymers, (*e.g.* aqueous H₂SO₄, KOH or H₃PO₄ in PVA). Relatively to liquid electrolytes, solid-state electrolytes have a higher operation temperature range, are more stable, are non-toxic, easier to manipulate and do not have leakage associated problems, thus reducing manufacturing costs. Gel polymer electrolytes are the most used solid-state electrodes (specially in pseudocapacitors). The polymeric frameworks are plasticizers that hosts organic/aqueous solvents and have high ionic conductivity at room temperature and good mechanical strength, if compared with dry polymer electrolytes. Yet, their stability and capacitance are lower than dry polymer electrolytes,

due to their inherent low pore penetration and limited temperature range. Inorganic electrolytes (e.g. Li₂S-P₂S₂ glass-ceramic electrolyte) have been also investigated, although they are not so commonly used.^{6,16-19}

Redox-active electrolytes are a recent trend in SCs electrolytes. This class of electrolytes incorporate different redox mediators which are electrochemically active to achieve the best SCs performance, particularly capacitance. The faradaic reactions can contribute to an extra capacitance, achieved not only from the electrode, but also from electrolyte redox reactions. Redox-active electrolytes can be also divided in aqueous (*e.g.* KI), non-aqueous (organic, such as (Et₄N₂)B₁₂F₁₁H/PC, or a combination between two different ionic liquids) or solid electrolytes, like the case of a gel polymer formed by PVA/KI and water. These strategies allowed some capacitance and energy density improvement. The use of redox-active electrolytes is also associated to an increase of self-discharge due to migration of some species between the electrodes.^{6,8,19-21}

The interaction between the electrolyte and inactive components (namely collectors, binders and separators) and with active electrode materials is crucial. Depending on the type and nature of the electrolytes these interactions can have a profound influence in SCs performance and reliability.

Electrode Active Materials

SCs can be divided in different types depending on the mechanism of action, as mentioned before, using different electrode active materials. These materials are summarized in Figure III.4.^{9,22-24}



Figure III.4: Classification of supercapacitors, regarding their mechanism of action.

To enhance capacitance, the EDLC electrode materials are usually made of highly porous carbon materials. The requirements for a good electrode material, especially for carbon-based, are a unique combination of chemical and physical properties that may deliver materials with high conductivity, surface area and temperature stability. Moreover, a control of the pores structure, and an easy manufacturing process, along with low cost raw materials, are very attractive and promoted the development of different electrode materials during the past years. Nowadays, these materials are divided in three classes: activated carbons, carbon nanotubes and carbon aerogels, and graphene nanosheets. Conversely, pseudocapacitors have a mechanism of action that relies in a reversible faradaic redox reaction between the electroactive materials and the electrolyte ions. In this case, the most studied materials are transition metal oxides (TMO) and conducting polymers (CP). Hybrid capacitors electrode materials combine the best properties of two different electrodes: a supercapacitor and a battery electrode. There are numerous options to create a hybrid system, thus being possible to assemble different materials with unique capacitive properties. So, these materials are usually classified in hybrid composites, asymmetric hybrid electrodes and battery-type electrodes.^{5,8,25}

Activated Carbon

Currently, most of the commercial SCs electrode materials result from physical (thermal) and/or chemical activation (*e.g.* by phosphoric acid, potassium hydroxide, zinc chloride or sodium hydroxide) of carbon-rich organic precursors such as coconut shell, wood, coal or nutshell. Albeit their low cost, large surface area and easy scalability to industrial production, these materials present a broad and unoptimized pore structure, resulting in a 30-60% inaccessible surface area by the electrolyte and consequently do not contribute to the desired capacitance.^{8,26} To overcome this issue, and increase the surface area, activated carbon fibres (ACF) are being developed as a promising solution. Using electrospinning, fibbers are spun and then subjected to a heat treatment (under controlled atmosphere) resulting in ACFs with *ca.*10 µm of diameter. This strategy increase the surface area, that combined with a controlled pore size distribution, good mechanical properties (light weight and high tensile strength) and high electrical conductivity, make ACFs very suitable to be used as SCs electrode materials. Nevertheless, the complex production and long-term stability are still major drawbacks.²⁷⁻²⁹

Carbon Nanotubes

Carbon nanotubes (CNT) may be cylinders of one (single-walled carbon nanotubes – SWCNT) or more (multi-walled carbon nanotubes – MWCNT) layers of graphene. These nanostructures are highly conductive and can achieve lengths from <100 nm to several centimetres, and diameters typically between 0.8 and 2 nm in case of SWCNT and 5 to 20 nm for MWCNT. CNTs are generally synthesized by catalytic decomposition of selected hydrocarbons

or by growth on conductive substrates, being possible to obtain materials with a very efficient electronic contact avoiding binding materials. Yet, their low specific capacitance, as a result of its hydrophobic nature, is a disadvantage.^{30,31}

Graphene

Graphene paper or graphene nanosheets are promising SCs electrode materials, mainly due to the ability of producing aerogels. Graphene may be obtained through different processes, such as graphene oxide reduction, and chemical or electrochemical exfoliation of graphite Graphene-like carbon nanosheets (produced by metal-assisted catalytic carbonization of organic materials or biomasses), have interesting particular properties, namely flexibility, good electrical conductivity, large surface area and a plentiful number of surface functional groups, making them highly promising electrode materials. However, the high production cost and the irreversible sheet restacking (forming graphite), that leads to reduced surface area and capacitance, are the main obstacles for delayed commercialization.^{22,30,32}

Carbon aerogels

Carbon aerogels can be defined as highly porous carbonaceous materials with a regular pore structure and a monolithic internal structure. Owner of high electrical conductivity, mechanical stability and mesoporosity, carbon aerogels are good electrodes candidates since due to these properties they present a good capacitance retention, and an easy ion transportation at high current densities.^{2,33}

Transition Metal Oxides

Transition metal oxides are very suitable as pseudocapacitive electrode materials since they offer a variety of oxidation states, and can undergo coupled, fast and reversible redox reactions at overlapping potentials with a pseudocapacitive behaviour that can be translated in an almost rectangular CV. It is important that these materials contain numerous active sites where the surface redox reactions may occur at high rates, resulting in electrode materials with higher energy density. Furthermore, it is important to choose materials with low resistivity, to ensure high power densities, and mechanical, chemical and thermodynamic stability to ensure cyclability.²²

In particular, ruthenium oxide (RuO₂) is a very attractive TMO active electrode material. Existing in both crystal and amorphous hydrous phases, RuO₂ has a high specific capacitance, a long cycling life, a good thermal stability, a high rate capability and participates in highly reversible redox reactions in a wide potential range. Yet, is extremely costly due to its scarcity, the main reason for its low availability. To overcome this problem, RuO₂ nanoparticles are combined with other active materials (*e.g.* manganese oxide, MnO₂) and non-active materials, such as nanoporous gold.^{34,35} MnO₂ is cheaper and has similar capacitance to RuO₂, however its conductivity and chemical stability (in acidic conditions) is very low, reasons why SCs exclusively made of MnO₂ are very rare, being usually combined with carbon-based materials or TMOs.³⁶

Vanadium-based materials with different oxidation states (*e.g.* vanadium oxide, nitride, sulphide, mixed metal vanadates, vanadyl phosphates) have been investigated as SCs electrodes. However, their low electrical conductivity, poor cycling stability, low specific capacitance and low energy are major drawbacks. To overcome these issues, vanadium-based materials are integrated in micro/nano-structures to form hybrid composites.^{37,38}

Transition metal sulphides (TMS) have been also studied as electrode materials, incorporating compounds like cobalt sulphide, molybdenum sulphide, nickel sulphide or nickel-cobalt sulphide. Typically presenting an easy pathway for electron transport, TMS have higher capacitances and conductivities than their oxide and counterparts. However, they present some cycling stability problems, a reason why they are usually hybridized with graphene.^{8,22}

Conducting polymers

Conducting polymers (CP), with energy densities significantly higher than carbon-based materials (normally 2-5 times), allows an easy and direct electrodeposition in the current collector and make possible the control of their structure and film thickness. Flexibility was a key factor for the huge development of these materials. Yet, there are some problems that arise from the polymers repeated shrinkage and swelling, upon charge-discharges events, that promote degradation and compromise cyclability and power energy. The solution found was the combination of CP with carbon-based materials and/or metal oxides instead of using CP as single electrode materials. Moreover, several CP have been investigated in order to develop better electrode materials, and polypyrrole (PPy), poly(3,4-ethylenedioxythiphene) (PEDOT), polyaniline (PAni) are currently the most used.^{3,27}

Polypyrrole

PPy is a very attractive good pseudocapacitive material, mainly due to its mechanical flexibility, high capacitance, tuneable electrical conductivity, low cost, and easy production (*e.g.* through pyrrole oxidation or electrochemical polymerization). Also, with the possibility of direct growth on the current collector (in the case of electrochemical polymerization), and structure and film thickness tuning, leading to high conductivity. Yet, as the majority of CPs, a major drawback is its cyclability, the reason why is typically combined with graphene nanosheets or doped with anions (*e.g.* β -naphthalene sulfonate anions).³⁹

Poly(3,4-ethylenedioxythiphene)

PEDOT, in its oxidized form, is very similar to PPy in terms of capacitance, mechanical flexibility and good electrical conductivity. Since cyclability is a problem, PEDOT its frequently combined with CNT or graphene composites.^{8,18}

Polyaniline

PAni is a flexible polymer that may exist in different oxidation states. It can be grown directly onto current collecting substrates and has been reported to have a low self-discharge. This CP is highly versatile, allowing many modifications. Yet, in the case of doping with a strong inorganic acidic media the performance was found to decrease. Hence, when the doping is done using a weak organic acidic media the morphological features are superior, although the conductivity is still reduced. It is also much dependent on the types of electrolytes, being necessary to choose the most appropriated in each case (*e.g.* after doping an acidic electrolyte leads to better performance). Typically, this CP is combined with other materials to improve its performance, as the case of reduced graphene oxide.³⁹⁻⁴¹

Hybrid composites

As mentioned before, different electrode materials, such as TMO, CNT, graphene, and CPs are usually combined to obtain materials with enhance performance. For example, hybrid composite electrodes incorporate carbon derivatives into CPs or TMOs, mixing the typical behaviour of EDCL and pseudocapacitors. Wu *et al.* exploited a CNT-PAni composite electrode to develop a vertical-aligned-structure and obtained a high electrochemical performance with high energy density, cycling stability and large specific capacity, when compared to the performance of isolated components.^{39,42-44}

Asymmetric hybrid electrodes

Combining Faradaic and non-Faradaic processes, asymmetric hybrids electrodes combine an EDLC and a pseudocapacitor electrode. Due to the difficulty to find CP negative electrodes, normally asymmetric hybrids are the combination of an activated carbon negative electrode with a positive CP electrode. It is known that CP electrodes have higher capacitances and lower resistances than activated carbon electrodes. Yet, they also have lower maximum voltages and less cycling stability. With the combination of both electrodes, an asymmetric hybrid is able to achieve higher energy and power densities than comparable EDLCs, and better cycling stability than pseudocapacitors.^{45,46}

Battery-type electrodes

Battery-type electrodes also combine two different electrodes. However, in this case it is the combination of a SC electrode with a battery electrode, merging the charging capability of SCs with the power with cycle life properties of batteries. SCs electrode materials can be activated porous carbons, graphene, CPs and intercalated lithium compounds. Materials that experience Faradaic redox during charging and discharging process are usually selected. Some studies have been made using lead dioxide, nickel hydroxide and Li₄Ti₅O₁₂ as the electrode and activated carbon as the counter electrode. Although battery-type hybrids have not been so extensively studied (like other SCs), promising results, especially using Li based systems have been already achieved, but there is still the need to evaluate its full potential.^{9,47,48}

Other electrode materials

Metal Organic Frameworks

Metal organic frameworks (MOFs) are emerging new electrode materials. These porous coordinated polymers are constituted by a metal cation centre linked by organic ligands that can be organized in 1D, 2D or 3D architecture. MOFs are characterized by having large surface areas, low density and high porosity. Also, they can be synthesized through simple methods, allowing the possibility to control their structure and pore functionality just by varying the metal ions (or metal clusters) and organic linkers. Despite these interesting properties, due to their low conductivity, their performance yield is still low and for that reason are used as composites with carbon.^{4,49-51}

Covalent Organic Frameworks

Covalent organic frameworks (COF) are the combination of organic building blocks linked through strong covalent bonds creating porous crystalline polymers with 2D or 3D architectures. Like MOFs, COFs are very attractive electrode materials since they have a high surface area, and a tuneable pore size and structure design. Also, if combined with redox active species they may display a pseudocapacitive behaviour. However, the lower electrical conductivity and stability retract practical applications.^{4,51-53}

MXenes

MXenes are a family of 2D compounds with a $M_{n+1}X_n$ formula, where M is a transition metal and X is a carbide and/or carbamide, with *n*=1, 2 or 3 (*e.g.* Nb₂C, Ta₄C₃ or Ti₃C₂). Presenting high conductivity, good mechanical properties and being hydrophilic they aroused much interest for energy storage purposes. Yet, MXenes suffers from re-staking, which decreases their surface

area and consequently their capacitance. To overcome this problem MXenes may be used in composites with CNTs and CPs, which improve their flexibility and capacitance.^{4,8,51}

Polyureas

Already studied for different industrial applications, polyureas are very attractive for their elasticity and strength properties.⁵⁴ Specifically, polyureas have been already demonstrated to have sizable pyroelectric, piezoelectric and nonlinear optical properties demonstrating a good potential as capacitive dielectrics and potential high energy density.⁵⁵ Moreover, when deposited in CNTs, the resulting composites show improved mechanical properties and performance.^{56,57} In particular, aromatic polythioureas (ArPTU) have been reported as versatile materials having high electric field operation, high energy density and high-field loss minimization, also producing films high breakdown strength and charge-discharge efficiency. In these materials the molecular weights are a critical parameter since high molecular weight ArPTUs are amorphous, and this morphology may reduce conductivity and solubility.⁵⁷⁻⁵⁹

Recent Applications

Although an ideal SC device has not been found, recently new types of electrolytes and electrodes have been developed trying to improve SCs performances and applicability. ⁶⁰ SCs were firstly used in electric, hybrid electric and fuel cell vehicles. However, flexibility was the key factor that boosted the development of new SCs multifunctional applications, especially in the fabrications of wearable devices, following the market needs of having products able to storage/release huge amounts of energy in very short times.⁶⁰

Photo-supercapacitors

One of the firsts demands that stimulated the growth of photovoltaics (PVs) was energy storage. A photo-supercapacitor is a system where a solar PV cell and a SC are integrated in a single device, showing potential to be integrated in flexible power devices and to be used in some aerospace applications.⁶¹ Based on third generation solar cells, photo-supercapacitors are usually composed by a solar cell (*e.g.* dye-sensitized, quantum-dots-sensitized, organic or perovskite) combined with a SC.⁶²⁻⁶⁴ For example, Scalia *et al.* integrated a dye-sensitized solar cell (DSSC) with a carbon based poly(vinylidene difluoride) (PVDF) EDLC and obtained a photo electrical conversion and storage device with a total efficiency of 3.72% and high frequency discharge capability.⁶⁵ On other hand, Suprayogi *et al.* used a DSSC integrated with a BaTiO₃-PVDF symmetric SC to study the effect of the annealing temperature of ZnO compact layer and TiO₂ mesoporous in photo-supercapacitor performance.⁶⁶

Piezoelectric supercapacitors

The development of new implantable/wearable healthcare devices, like sphygmomanometers or spirometers (incorporated in wristbands), normally used to monitor physical activity and other analytical applications (*e.g.* diet tracking, rehabilitation or mental stress detection) stimulated the investigation of new flexible and fast energy storage systems.⁶⁷⁻⁶⁹

Gilshteyn *et al.* described the combination of mechanical flexibility with optical transparency in the fabrication of energy storage devices integrating a piezoelectric PVDF-trifluoroethylene (PVDF-TrFE) copolymer film into a flexible supercapacitor system (SWCNT film/PET electrodes and PVA/H₂SO₄ electrolytes) to harvest and store the energy. This device achieved a specific capacitance of 50 Fg⁻¹.⁷⁰ Ahmed *et al.* in other hand, used PVDF-TrFE-based electrospun nanofibers decorated with PEDOT-CNT/rGO composites to produce piezo-electric pressure sensors.⁷¹ Using a polarized PVDF, Wang *et al.* developed a tactile sensor able to simultaneously detect temperature and force field in the solid supercapacitor.⁷²

Electrochromic supercapacitors

Electrochromic SCs may be obtained using materials that are able to change their colour during electrochemical reduction/oxidation processes. TMOs and CPs deposition over transparent current collectors (*e.g.* ITO or FTO) led to electrochromic SCs.⁷³ Yang *et al.* used tungsten (IV) oxide (WO₃) films on FTO glass to develop a multifunctional glass window combining energy storage (with a specific capacitance of 639.8 Fg⁻¹) the electrochromism in a single device.⁷⁴ Yun *et al.* also developed an electrochromic SC using WO₃ and a Li-doped ion gel containing hydroquinone, thus achieving a high area capacitance (~13.6 mF/cm²) and a high coloration efficiency (~61.9 cm²/C), a device that demonstrates a tremendous potential in smart electroche materials have been developed, such as PAni/graphene-CuS,⁷⁶ NiO nanoparticles,⁷⁷ V₂O₅ double-gyroids⁷⁸ or W₁₈O₄₉/PAni composites.⁷⁹ Despite the development of new electrochromic electrodes, the brittleness and the high cost of ITO and FTO make them unsuitable for flexible electronics applications, being also a concern the development of

Self-healing supercapacitors

With long life cycling, it is inevitable that SCs suffer from mechanical problems (*e.g.* deformations). To avoid device failure, self-healing SCs have been already developed in order to restore the configuration and electrical properties of the device, achieved with the introduction of self-healing materials. Interestingly, by an autonomous way or through some external stimuli (pH,

heat or light) SCs devices may be restored.^{11,80} For example, Huang *et al.* developed a self-healing yarn based SC using magnetic electrodes around a self-healing polymer shell, were a strong magnetic attraction allows device restoration.⁸¹ Additionally, it is important to choose the right electrolyte, since electrolyte is one of the key factors in self-healing SCs performance to create a self-healable and highly stretchable SC. Huang *et al.* also reported the development of an electrolyte comprising polyacrylic acid dual crosslinked by hydrogen bonding and vinyl hybrid silica nanoparticles, demonstrating over 100% of self-healing after 20 breaking healing cycles with excellent stretchability.⁸²

Self-healing SCs have a huge potential to be used in portable and wearable electronic devices (*e.g.* smart clothes) but the fabrication of good multifunctional SCs is still a challenge. Chen *et al.* developed one of the best multifunctional SCs, a material with impressive properties such as an area capacitance of 885 mFcm⁻², an energy density of 123 µWhcm⁻², a superhigh stretching strain of 800%, rapid optical healing capability, and significant real-time healability during the charge–discharge process.⁸³

Thermally chargeable supercapacitors

Thermally chargeable supercapacitors store low-grade thermal energy (input energy that is not used and is released to the surroundings in form of waste) to be further used in powered devices such as wearable electronics and sensors.⁸⁴⁻⁸⁶ For instance, Kim *et al.* developed a novel method to storage this energy developing a thermally chargeable solid-state supercapacitor using graphene coated PAni and a CNT electrode sandwich with a polystryrene sulphonic acid film. Using a small temperature difference (5K), this thermally chargeable SC produces 38 mV with a large areal capacitance of 1200 Fm^{-2.87}

Shape-memory supercapacitors

Since energy storage devices produce irreversible deformations in wearable electronics, bendable smart phones and biomedical devices, the development of shape-memory materials (namely alloys and polymers) to recover their original dimensions after severe deformations has been a priority.⁸⁸⁻⁹⁰ Shape-memory SCs have been also used in smart energy storage textiles.⁹¹

Microbial supercapacitors[†]

Bacteria such as *Shewanella spp.*, *Geobacter spp.* or *Proteobacteria spp.* species have the ability to produce electricity. Microbial supercapacitors (MSCs) convert biomass directly to electricity or fuel, acting as biological pseudocapacitors, and electron harvesting from these microorganisms may be explored as a novel strategy for renewable energy generation and storage.⁹²⁻⁹⁵

Some capacitive bioanodes have been already developed. Deeke and co-workers created an integrated system coating the capacitive layer (a mixture of activated carbon powder and a PVDF solution) directly into the current collector.⁹⁵ Hen *et al.* grown *Geobacter spp.* on a single-layer graphene film and 3D graphene-scaffolds electrodes.⁹⁶ Despite these promising studies, to achieve good performances many parameters need optimization, such as the potential anode and the development of new materials that promote a good biofilm adhesion.

In summary, several factors critically influence the performance of SCs. Different electrolytes, electrode materials and their combinations can be crucial to a good performance. Flexibility brought freedom to broader SCs applications. Yet, the search for a perfect system is ongoing, and the development new materials is the foreseen as the key for success. In this work, novel CP electrode materials, based on polythioureas, were designed, synthesised and further investigated as potential candidates for microbial SCs electrodes.

Experimental Section

Materials

All chemicals and solvents were used as received without further purification. *p*-Phenylenediamine, epichlorohydrin, lithium bromide (LiBr), carbon disulphide (CS₂) and 4,4' diaminodiphenylmethane (MDA, \geq 97.0%) were purchased from Sigma-Aldrich. Tris(4-aminophenyl)amine (TAPA, 97%), tris(2-aminoethyl)amine (TREN, 97%), were purchased from Alpha Aesar. *N*,*N*,*N*',*N*'-Tetrakis(4-aminophenyl)-1,4-phenylediamine (tetrakis) was purchased from Carbonsynth Limited. Polyurea dendrimer generation 4 (PURE_{G4}) was synthesized using our reported protocol.⁹⁷

Methods

NMR spectra were recorded on a Bruker ARX 400 MHz equipment. ¹H and ¹³C NMR chemical shifts are reported as ppm (parts per million). Dried samples were analysed by FTIR in

[†] This topic will be discussed in detail in Chapter IV.

a Spectrum BX from PerkinElmer with a spectrum acquisition of 16 scans, in the range 4000 to 600 cm^{-1} .

Synthesis of aromatic polythioureas

The synthesis of aromatic polythioureas followed a modified protocol.⁹⁸ Typically, CS₂ was added dropwise to a stirring solution of the aromatic amine (1 mol) in 10 mL of ethanol (or DMF in case of branched amines). The reaction was kept at 60 °C under stirring for 4 h. After cooling to room temperature, the solution was filtered under vacuum and the solid was washed with ethanol, methanol and hexane obtaining a solid that was further characterized by FTIR and NMR. Table III.1 list the amine monomers studied in the synthesis of polythioureas, as well as the products obtained.

Table III.1: Amine monomers and respective polymers obtained following the general protocol for the synthesis of aromatic polythioureas.



^aSolubility issues precluded full characterization and structural elucidation.

Poly(*p***-phenylenethiourea), PPTU (1):** FTIR (KBr) υ (cm⁻¹): 3351 (NH), 2968 (Ar-H), 1537 (C=S), 1278 (C=S), 830 (C=S stretching).¹H NMR (400 MHz, DMSO-*d*₆) δ: 9.30 (s, 4H, NH terminal ureas) 8.90 (s, 40H, NH ureas), 7.00 (d partially hidden, 4H, ArH terminal), 6.96 (d, *J*= 4.0 Hz, 80H, ArH), 6.54 (d partially hidden, 4H, ArH terminal), 6.51 (d, *J*= 8.0 Hz, 80H, ArH). ¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm): 180.26, 146.51, 127.92, 126.58, 126.43, 113.87 (see Appendix II, Figures AII.1, AII.2 and AII.3).

Poly(*p***-phenylmethylenethiourea), PPMTU (2):** FTIR (KBr) υ (cm⁻¹): 3213 (NH), 3029 (Ar-H), 3032 (Ar-CH), 1542 (C=S), 1259 (C=S), 818 (C=S stretching). ¹H NMR (400 MHz, DMSO-*d₆*) δ: 9.62 (m, 14H, NH), 7.36–7.31 (m, 28H, ArH), 7.18 (d, *J*= 8.0 Hz, 8H, ArH, terminal), 7.11 (d, *J*= 8.0 Hz, 20H, ArH), 6.87 (d, *J*= 8.0 Hz, 20H, ArH), 6.48 (d, *J*= 8.0 Hz, 21H), 4.87 (NH), 3.87 (s, 4H), 3.71 (s, 20H).¹³C NMR (101 MHz, DMSO-*d₆*) δ (ppm): 179.50, 138.64, 137.10, 129.19, 129.08, 128.61, 128.39, 128.25, 123.78, 113.80 (see Appendix II, Figures AII.4, AII.5 and AII.6).

Polymer 3: FTIR (KBr) υ (cm⁻¹): 3388 (NH), 1593 (Ar-H), 1501 (C=S), 1278 (C=S), 829 (C=S stretching) (see Appendix II, Figure AII.7).

Polymer 4: FTIR (KBr) υ (cm⁻¹): 3210 (NH), 2924 (Ar-H), 1498 (C=S), 1244 (C=S), 823 (C=S stretching) (see Appendix II, Figure All.8).

Synthesis of PURE_{G4}-PPTU (5)

Following a modified protocol,⁹⁹ 45 μ L (0.57 mmol) of epichlorohydrin were added dropwise to a stirring solution of PURE_{G4} (0.049 g, 6.2 ×10⁻³ mmol) in 1 mL of water. The mixture was stirred at room temperature



overnight. The water was removed under vacuum and a solution of 0.0026 g (5% mol) of LiBr in 1 mL of DMF was added, followed by the addition of 0.30 g (0.28 mmol) of PPTU solubilized in 3 mL of DMF. The mixture was kept under stirring at room temperature for 24 hours and then heated at 60 °C for 24 hours. After cooling to room temperature, the solution was washed several times with diethyl ether to remove DMF. The obtained solid was further washed with acetone and ethyl acetate and dried under vacuum. A dark brown solid (0.155 g) was obtained in 82.5% yield. FTIR (KBr) υ (cm⁻¹): 3270 (NH), 1626 (C=O), 1512 (C=S), 1256 (C=S), 831 (C=S stretching) .¹H NMR (300 MHz, DMSO-*d*₆) δ : 7.40-6.97 (m, 614H, ArH), 3.36 (m, 642H).¹³C NMR (101 MHz, DMSO-*d*₆) δ (ppm): 207.03, 180.44, 180.05, 162.79, 146.85, 146.68, 136.38, 128.31, 126.69, 126.51, 124.04, 114.57, 114.10, 114.05, 36.26, 34.66, 31.17 (see Appendix II, Figures AII.9, AII.10 and AII.11).

Results and discussion

The synthesis of linear aromatic polythioureas was successfully achieved. Following a modified protocol,⁹⁸ two polythioureas, PPTU (**1**) and PPMTU (**2**), both soluble in DMSO, were obtained and fully characterized.

By FTIR analysis, we were able to confirm the presence of the thiourea groups (*ca.* 1530 cm⁻¹). The typical distension of the C=S bond around 800 cm⁻¹ was also observed. Further characterization by NMR spectroscopy confirmed the synthesis of the desired polymers. The degree of polymerization (*n*), of PPTU and PPMTU was determined by the integration ratio of the signals of the protons from the polymer backbone and the protons from the terminal units.⁹⁸

The ¹H NMR of PPTU is reported in literature, by two independent groups, but no ¹³C NMR data is available. In one of the reports,⁹⁸ the NMR data is not correctly assigned in the experimental section (data shown probably refers to polyethylene thiourea, PETU, also synthesised by the authors in this work). However, in the text a multiplet in the region 6–8 ppm is assigned to the aromatic protons, and a singlet in the region 9–11 ppm is assigned to NH protons (400 MHz). In the other report,¹⁰⁰ the aromatic protons are assigned to a multiplet at 8.18 ppm and the NH protons assigned to a singlet at 10.65 ppm (250 MHz). Our ¹H NMR spectra (400 MHz), recorded in the same solvent, shows two doublets (6.96 and 6.51 ppm, 160H) that are partially superimposed with other two doublets (7.00 and 6.54 ppm, 8H) that are attributed to the polymer terminal units. From this data, the polymerization degree of PPTU was determined, and a value of *n*= 20 was found (*M*_w= 21000 gmol⁻¹, *n*~90, determined by GPC)⁹⁸. The ¹H NMR of *p*-phenylamine monomer in DMSO-*d*₆ show a singlet at 6.36 ppm (ArH, 4H) and a singlet at 4.16 ppm (NH, 4H). The ¹³C NMR spectrum of PPTU, shows the characteristic signal of a thiourea carbonyl (180.26 ppm).

The ¹H NMR of PPMTU is also reported in literature.¹⁰⁰ The aromatic protons are assigned to 7.91–7.98 ppm and the methylene protons to 4.08 ppm. The NH protons are displayed at 10.46 ppm. Our spectrum shows the aromatic protons in the region 7.33-6.47 ppm and the methylene protons at 3.71. The NH protons are displayed at 9.81 ppm. The chemical shift corresponding to the terminal units are also observed and were used to determine the polymerization degree. A value of n= 12 was found (M_W = 4000 gmol⁻¹, $n\sim$ 16; M_W = 8000-12000 gmol⁻¹,¹⁰¹ determined by GPC) ⁵⁸.

The control of molecular weight of ArPTUs is crucial for thin film fabrication. Usually, the deposition of these type of electrode materials is made by electrodeposition, drop cast or spin coating and it is important that polymers have a good solubility.⁷ Both PPTU ($M_w \sim 3000 \text{ gmol}^{-1}$) and PPMTU ($M_w \sim 2880 \text{ gmol}^{-1}$) estimated molecular weights are in range that allow the preparation of excellent thin films. Although slightly higher molecular weights lead to higher breakdown field strength and lower loss.¹⁰¹

Branched aromatic polythioureas, polymers **3** and **4**, were obtained as highly insoluble solids, which precluded characterization and further studies. The insolubility of this polymers may be attributed due to aggregation induced by strong π - π interactions. To overcome this problem

several synthetic strategies were investigated, varying both the monomers, monomers combinations (aromatic *vs.* aliphatic) and the polymerization methodology (*e.g.* ultrasound irradiation). Table III.2 lists the different studies that have been made to investigate the polymerization of branched aromatic polythioureas.

Table III.2: Reactions using aromatic and aliphatic amines using conventional heating and ultrasound irradiation.

Aliphatic amine	Aromatic amine	CS ₂	CS ₂ Method ^a		Products
(equiv.)	(equiv.)	(equiv.)		(h)	
TREN	<i>p</i> -Phenylenediamine	1.8	Heating	4 h	PPTU and
(1)	(1)				TREN salt
TREN	<i>p</i> -Phenylenediamine	3.6	Heating	4 h	TREN-p-
(1)	(2)				phenylene- TREN
TREN	<i>p</i> -Phenylenediamine	5.4	Heating	4 h	PPTU
(1)	(3)				
TREN	Tetrakis (1)	1.8	Heating	4 h	n.d. ^b
(1)					
Ethanolamine	<i>p</i> -Phenylenediamine	1.8	Heating	4 h	PPTU and
(1)	(1)				ethanolamine
					salt
TREN	<i>p</i> -Bromoaniline	3.3°	US	2 h	Bromoaniline
(1)	(1)				dimer
n.a.	TAPA	1°	US	2 h	n.d. ^b
	(2)				
TREN	<i>p</i> -Bromoaniline	3.3	US	2 h	n.d. ^b
(1)	(3)				
n.a.	<i>p</i> -lodoaniline	1	US	2 h	Product
	(2)				described in
					ref. 102

^aIn conventional heating the reactions were performed at 60 °C. US= ultrasound irradiation (260 MHz). ^bComplex mixture containing insoluble products. ^cIn this reaction, 3.3 equiv. of triethylamine were added. n.d.= not determinated TREN= tris(2-aminoethyl)amine, TAPA= tris(4-aminophenyl)amine, PPTU= poly(*p*-phenylenethiourea).

From the obtained results is possible to conclude that using conventional heating aromatic amines have the tendency to react between themselves than to react with aliphatic amines. In case of the ultrasound irradiation methodology, it is well known from literature^{102,103} that the reaction of aromatic amines with carbon disulphide is favourable and the corresponding dimers are easily obtained. Yet, in our case the reactions between aromatic and aliphatic amines were not successful.

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Aiming to develop novel polythiourea-based electrodes, PPTU was grafted in the surface of a polyurea dendrimer of generation four (PURE_{G4}), leading to a novel core shell electrode having a polyurea core (PURE_{G4}) and a polythiourea shell (PPTU), PURE_{G4}-PPTU (**5**). Therefore, this material would allow the exploitation of the effect of a 3D architecture in the dielectric properties of linear aromatic polythioureas and the potential of polyureas as electrode materials. PURE_{G4} has 48 primary amines in the surface. To construct the polythiourea shell, PURE_{G4} was reacted with epichlorohydrin (crosslinker), in the presence of PPTU, using lithium bromide as the catalyst.^{**99**} By ¹H NMR analysis, from the integration of the protons from the core and from the shell it was found an incorporation of 6 PPTU polymer units in the surface of PURE_{G4} (estimated $M_w \sim 32000 \text{ gmol}^{-1}$). As expected, the solubility of PURE_{G4}-PPTU₆ is lower than PPTU but is still soluble in DMSO (upon heating overnight), thus allowing thin film fabrication.

The synthesised materials were shown to be suitable to be deposited in current collectors (*e.g.* stainless steel) by drop cast. Figure III. 5 shows a picture of the homogeneous deposition of a PPMTU DMSO solution (50 μ L, 0.06 mg/ μ L) in a stainless steel electrode (15 mm x 15 mm), performed at 100 °C for 10 minutes.



Figure III.5: PPMTU drop cast thin film fabrication using a stainless steel electrode.

As mentioned before, the SC performance is dependent of many factors, namely the choice of the right electrolyte. Many different options are available (aqueous, non-aqueous, solid-state, quasi-solid-state and redox-active electrolytes) and several studies must be undertaken to find the most suitable for these particular electrodes. In preliminary studies, some tests were performed using aqueous solvents (acids and bases, however without success. A more detailed investigation is need in order to find a suitable electrolyte.

Conclusions and Future Perspectives

The synthesis of new materials with electrical energy storage potential to be used as organic supercapacitors, was performed with success. The design and synthesis of a novel coreshell material, having a polyurea dendrimer (core) and a linear aromatic linear polythiourea (shell), may lead to promising electrodes. This core-shell electrode combines polyurea and polythiourea groups, with a 3D architecture, could present interesting dielectric properties that need to be tested.

Future work will be focused in the determination of the electric energy storage capacity of the synthesised materials using suitable electrolytes. In parallel, these materials have already been investigated as potential electrodes for the development of microbial SC, a work that reported in Chapter IV.

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Chapter IV

Bioelectricity

This chapter focus on the evaluation of polythiourea-based polymers, described in Chapter III, as potential supercapacitors for microbial fuel cells.

The chapter is divided in two sections, composed of a brief overview on microbial fuel cells and microbial supercapacitors and the results and discussion of the experimental work undertaken in this field.

Microbial Fuel Cells

Electricity may be produced using different sources. Besides traditional power sources such as solar, wind or hydropower, electrochemical generation using fuel cells is also an attractive route. These fuel cells produce electricity through redox reactions using hydrogen or methanol. Microbial fuel cells (MFC) operate similarly to fuel cells. Yet, instead of using a metal catalyst at the anode, MFC uses microorganisms able to oxidize organic matter and transfer the produced electrons to the anode. These electrons then flow through a circuit to the cathode, where they are combined with protons and a chemical catholyte.¹

Working Principle

Since 1911, when Porter reported for the first time the use of microorganisms capable to generate energy, several microbial fuel systems have been developed. These systems become popular in 1960s, particularly when NASA started to explore the possibility of turning organic waste into electricity on space missions.²⁻⁵

The MFC working principle relies in the use of a specific bacteria species called exoelectrogens (*exo*= out of and *electrogen*= electrons producing bacteria), and their unique extracellular electrons transport.⁶ Figure IV.1 shows a general scheme of a MFC, composed essentially by an anode, a proton exchanger (optional membrane that allows charge transfer) and a cathode. At the anode surface occurs a bacterial biofilm growth were the oxidation reactions take place. The exoelectrogens at the anodic biofilm can transfer directly the electrons to the electrode, using cytochrome proteins or conductive pili, or indirectly using mediators. The oxygen is reduced to water at the cathode, due to the combination of the electrons from the circuit and the water protons.^{1,7}

Geobacter sulfurreducens and Shewanella oneidensis, among others (e.g. *Pseudomonas aeruginosa, Escherichia coli, Geobacter metallireducens*), are the most commonly studied electrochemically active bacteria. Although they have completely different metabolic abilities. *S. oneidensis* is a facultative anaerobic microorganism that is able to degrade (fully oxidize) a series of organic acids under aerobic conditions.⁸⁻¹² On the other hand, *G. sulfurreducens*, is an anaerobic bacteria that uses acetate, as well as lactate and fumarate, as carbon and electron source.^{12,13} In both cases, biofilm mediated electron transfer is made through a network of *c*-type cytochromes located in the periplasmic and extracellular space and in the outer membrane.¹⁴ *G. sulfurreducens* transfers the electrons directly using its conductive pili. Since they are good biofilm producers, that may achieve thicknesses up to 160 µm, the formation of nanowires through the biofilm is more convenient for electron transfer.¹⁵ Conversely, *S. oneidensis* produce poor biofilms, a reason why electron transfer is mainly accomplished through mediators (*e.g.* flavins).¹¹



Figure IV.1: Schematic representation of a microbial fuel cell and the mechanism involved in electron transfer at the anode electrode. Indirect transfer *via* mediators or fermentation products (A); Direct transfer *via* cytochrome proteins (represented in green) (B); Direct transfer *via* conductive pili (C). PEM= proton exchange membrane.⁷

Future Challenges of MFCs

Despite the continuous studies of MFCs during the past decades, there are still numerous challenges and problems that need to be overcome before a translation to the market. For example, problems regarding the integrity and performance of the anode electrolyte in a real, more complex, marine or lagoon environment (*e.g.* presence of sediments). Apart from these, there are still some unsolved or not fully understood questions related with the biofilm formation, the interaction of bacteria with the anode, inter-species cooperation, the electron transfer mechanisms, and the influence of environmental parameters.¹⁶⁻¹⁹ Also, at the cathode electrode level, the oxygen reduction is not effective (due to high over-potentials and low kinetics) being necessary to study the effect of new metal oxidants t (*e.g.* chromium, copper or cadmium).^{7,20}

Currently, the major challenge of operating MFCs is related with the low produced energy, which is several orders of magnitude lower than chemical fuel cells. This problem has led to the development of new hybrid systems where MFCs have been coupled with external off-the-shelf harvesting systems based mainly on supercapacitors, designated microbial supercapacitors (MSCs).

Microbial Supercapacitors

MSCs are hybrid systems were a SC is coupled to a MFC. In the first approaches, SCs and other harvesting systems, were coupled externally to a MFC system, where the low power produced was collected and then delivered in higher current pulses, thus allowing the charge of small electronic devices.²¹⁻²³ Another approach to explore the storage of the energy produced by MFCs is the use of the intrinsic capacitive properties of MFC electrodes. Following the development of new SC electrode materials (specially carbon-based) and the studies regarding the influence of the anode electrode in the MFC performance, integrated systems using MFC electrode materials as internal supercapacitors were investigated. Furthermore, some studies indicate that MFC biofilms can also storage electrons when the device is in operating in an open circuit for long periods of time, and that some cytochromes could possibly present a pseudocapacitive behaviour.^{9,24-28}

Despite the huge potential of MSCs, the current generation, which is a critical parameter, is still not very high. This fact is fostering new strategies, exploring different materials and experimental conditions. For example, Hen *et al.* grown *Geobacter spp.* on a graphene single-layer film and on 3D graphene scaffolds anodes and this MSC device achieved maximum current and power densities of 531.2 Am⁻² and 197.5 Wm⁻², respectively, high cycle stability, and specific capacitances of approximately 17.85 mFcm⁻².²⁹ In 2016, Santoro *et al.* were able to create a self-rechargeable MSC by the modification of both electrodes and demonstrated that an MFC integrated system is more efficient and cheap than an external coupled supercapacitor.³⁰

Although some progresses have been made, there are still numerous features to explore in the fabrication of MSCs. These include, electrode materials, different bacteria cultures (single or mixed), substrates and MSCs design. In this sense, MSCs can be tailored to develop sustainable systems that could be used in real situations, such as small electronic devices powering. Herein, we focused in the polymers synthesized on Chapter III and investigated them as possible electrode materials for the development of an integrated MSC device.

Materials and Methods

MFC and the hungate tubes preparation was performed under sterile conditions using a Bunsen burner flame. All the materials were previously sterilized. Samples were thermostatized using a digital dry bath from Labnet. The amperometric measurements were performed using screen-printed carbon electrodes (DRP-C110), a multi potentiostat model µStat 8000P and DropView 8400 software from Metrohm. Electrodes film deposition was made using a heating plate from IKA. The *Shewanella* Basal Medium (SBM), Lysogeny Broth (LB) with lactate and NBAF mediums were prepared according to the protocol described in Appendix III.

Bacteria Pre-incubation

Shewanella oneidensis MR1 wt (SOMR-1 wt, 1mL) was pre-incubated at 30 °C in a 50 mL Erlenmeyer with 30 mL of LB medium under aerobic conditions for 24 h. *Geobacter* sulfurreducens (2 mL) was incubated under anaerobic conditions at 35 °C in a sealed 50 mL flask with 30 mL of NBAF medium enriched with fumarate (53 mM) for 48 h.

MFC Configuration

The MFC apparatus is presented in Figure IV.2. A screen-printed carbon electrode (Figure IV.2A) was introduced inside a sealed flask, with (Figure IV.2B) or without (Figure IV.2C) polymer coating, and further filled with medium and bacteria culture. Next, the system was connected to a potentiostat and the amperometric measurements performed under controlled temperature.



Figure IV.2: Screen-printed electrode (A); microbial fuel cell apparatus before the addition of the bacteria culture without (B) and with (C) poly(*p*-phenylmetanethiourea), PPMTU, deposited on top of the working electrode.

Electrode Surface Coating

To analyse the capacitive properties and electrode performance of the synthesised aromatic polythioreas, described in Chapter III, the materials were deposited on the top of the screen-printed working electrode. Only the preliminary results obtained with PPMTU are presented.

Typically, 1 µL of a solution of PPMTU in DMSO was deposited on top of the working electrode at 50 °C, and the electrode was kept at this temperature for 15 minutes to remove

DMSO. A homogeneous layer of PPMTU was obtained (white disc in Figure IV.2C). To evaluate the influence of DMSO in the screen-printed electrode performance, a control experiment was made by deposition of 1 μ L of DMSO in the screen-printed electrode, following the above described procedure.

MFC Device Preparation

Under sterile conditions, 8 flasks were sealed with a septum and a capsule. Next, the electrode inserted, and the flask was degasified for 10 minutes using a N₂ line. After that, 8 mL of medium were added (10 mL in case of the flasks without bacteria culture). The electrodes were connected to the potentiostat, the flasks were placed in the dry bath and the acquisition of amperometric data started. After approximately 30 minutes, when the current measured was found to be stable (~0 μ A), 2 mL of bacteria culture were added to the flasks.

MFC Studies

The first experiment performed aimed to evaluate the influence of PPMTU in the bacteria culture. This experiment was divided in two steps: the study of the bacteria growth by optical density measurements (OD) and amperometric measurements.

To evaluate bacteria growth the following protocol was adopted. PPMTU (0.004 g) were added to 50 mL of LB medium and 50 mL of SBM medium³. Next, 1.5 mL of a fumarate solution (1.6 g/10 mL H₂O) were added to these solutions as well as to a 50 mL of LB medium and 50 mL of SBM medium (without PPMTU). Then, 10 mL of each solution were transferred to a hungate culture tube (4 tubes for each solution), and then degasified for 10 minutes using a N₂ line gas. Next, a pre-incubated *Shewanella oneidensis* MR1 wt solution (5 mL) was added to a solution previously prepared containing 5 mL of LB medium (with fumarate) and to 5 mL of SBM medium (with fumarate). Then 1 mL of *Shewanella oneidensis* MR1 wt diluted in LB medium was added to 3 hungates prepared with LB medium and 3 hungate tubes with LB medium and PPMTU. Also, 1 mL of *Shewanella oneidensis* MR1 wt diluted in SBM medium was added to 3 hungate tubes containing SBM medium and 3 hungates with SBM medium and PPMTU. The 12 hungate tubes were incubated at 30 °C and the optical densities (at 600 nm) were measured for 24 hours.

To perform the MFC amperometric measurements, the following protocol was adopted. PPMTU (0.004 g) were added to 50 mL of LB medium solution. Then, 9 mL of this solution and LB medium were added to 8 sealed flasks (4 of each solution). The screen-printed electrodes were introduced inside the flask and the solution were degasified for 10 minutes using a N₂ line.

³ The SBM medium stock solution (200 mL) was enriched with 1 mL of 1 g/10 mL casamid solution and 2 mL of mineral solution.

Next, 1 mL of pre-incubated *Shewanella oneidensis* MR1 wt was added to each flask. Then, the MFC solutions were incubated at 30 °C in a dry bath and the potentiostat was connected to the electrode to perform the amperometric measurements (E= -0.25 V, interval= 60 s) for 24 hours (assay 1).

Amperometric measurements were also performed using *Shewanella oneidensis* MR1 wt and *Geobacter sulfurreducens*. In these cases, PPMTU was deposited directly on top of the working electrode. Table IV.1 describes different experiments performed.

Table IV.1: Microbial fuel cells screening studies using *Shewanella oneidensis* MR1 (SOMR-1) wt and *Geobacter sulfurreducens* and poly(*p*-phenylmethylenethiourea (PPMTU).

Assay		Medium	PPMTU (mg/µL)	Nr. of electrodes	Amperometric conditions			
	Bacteria				E	Interval	Time	Temp.
					(V)	(s)	(n)	(°C)
1 SOMR-1 wt ^b	SOMR-1 wt ^b	LB	0	4	-0.25	60	24	30
			0.5	4				
2 G.	G sulfurreducens	NBAF	0	4 ^a	0.2	60	48	35
	O. Sulfurreduceris		0.5	4 ^a				
3	SOMR-1 wt [♭]	LB	0	4 ^a	0.2	60	48	30
			0.5	4 ^a				
4 SOMR-1 wt ^b		LB	0	2	0.2	60	48	30
	SOMP-1 wtb		0.25	2				
	SOMICT W		0.5	2				
			0.7	2				
5 5		LB	0 ^c	2	0.2	60	96	30
	SOMP 1 web		0.05	2				
	SOMIK-1 WI		0.5	2				
			0.7	2				
6 G	G. sulfurreducens	NBAF ^d	0 ^c	2	0.2	120	250	35
			0.025	2				
			0.05	2				
			0.07	2				
7 6	G. sulfurreducens	NBAF ^d	0°	3	0.2	120	250	35
			0.025	3				
			0.05	2				
8	G. sulfurreducens	NBAF ^d	0°	3	0.2	120	250	35
			0.025	3				
			0.05	2				

^aOne of the electrodes did not received the bacteria culture. ^bOnly 1 mL of pre-incubated bacteria culture was added. ^cOnly DMSO was deposited in the working electrode. ^dThe NBAF medium was enriched with 10 mM of fumarate.

Results and Discussion

PPMTU was chosen as model polymer, since in a previous report, its interesting capacity properties had already been demonstrated. ³¹ In order to understand the effect of PPMTU in the bacteria culture, namely to see if this material could be harmful (leading to death) or inhibit the bacteria growth, OD measurements (data not shown) were firstly undertaken. Through these measurements it was possible to observe that the bacteria growth in the presence of PPMTU is slightly higher than the normal bacteria growth. The amperometric results from this first experiment (assay 1) demonstrated that when the polymer is in solution the current production is not affected (Figure IV.3) and after an initial stabilization of the current, both MFC devices (with and without polymer in solution) produced practically the same current. From these data it was possible to conclude that bacterial growth is not affected by the presence of PPMTU and, surprisingly, seems to enhance bacteria growth.



Figure IV.3: Amperometric measurements of microbial fuel cells without (A) and with (B) PPMTU added to the culture medium of assay 1.

In the assays 2 and 3, half of the electrodes were coated with 0.5 mg of PPMTU on top of the working electrode. Using both *G, sulfurreducens* and *S. oneidensis* MR1 wt the results were not reproductible. In assay 2, neither uncoated or coated electrodes produced current (Figures IV.4A and IV.4D) with the exception of one MFC device using a coated electrode (Figure IV.4C), which presented a completely different result. It is possible to observe that the current production is ~0 μ A until approximately 12 hours and then a peak of 1.5 μ A is observed. Then the current is again ~0 μ A until 16 hours of experience. At this time a smaller current peak (~0.5 μ A) is observed and after 28 hours a high current peak (~4 μ A) is finally observed. However, this assay was not conclusive since the results were not coherent. It is unexpected that uncoated electrodes do not produce current (Figure IV.4A).

Then, the same protocol was performed but using *S. oneidensis* MR1 wt (assay 3). Figure IV.5A show the MFC devices after the assay. Here, it is possible to observe that specially devices 2, 6 and 7 there was a production of SOMR-1 wt. Yet, looking to the amperometric results of device 2 (Figure IV.5 B) there is no significant current production. This could be due to the fact of

Shewanella oneidensis is not a good biofilm producer, and consequently, the electron transfer to the anode was more difficult.



Figure IV.4: Amperometric measurements of MFC devices with uncoated (A) and coated electrodes using 0.5 mg of PPMTU in the absence (B) or presence (C and D) of *Geobacter sulfurreducens*.



Figure IV.5: Microbial fuel cell (MFC) devices using *Shewanella oneidensis* MR1 wt (SOMR-1) after assay 3 (A). MFC devices 1-4 used uncoated electrodes and devices 5-8 used coated electrodes with 0.5 mg of PPMTU (devices 1-5 did not received SOMR-1). Amperometric measurements using uncoated and coated electrodes (B) and (C).

Comparing Figures IV.5B and IV.5C, we can conclude that the current production is clearly affected when the electrode is coated with PPMTU (current reduction from ~0.5 to ~0.05 μ A). To study this effect PPMTU concentrations higher and lower than 0.5 mg/ μ L were used (assay 4). Despite the lower concentration, 0.25 mg/ μ L, did not shown any significant change during the experiment, for two MFC devices (0.5 and 0.7 mg/ μ L) a current increase was observed at the end of the experiment. This result helped to design assay 5, where these two concentrations were used, but for a longer period of time (96 h instead of 48 h).

A lower PPMTU coating concentration (0.05 mg/ μ L) was also tested, as well as uncoated electrodes treated with DMSO. Since these bacteria are able to reduce DMSO it was important to demonstrate that DMSO used in preparation of PPMTU coating do not interfere with the MFC performance.⁸ In the cases where MFC devices were coated with a very low PPMTU concentration (0.05 mg/ μ L), the polymer was practically absorbed by the working electrode (devices 3 and 4 in Figure IV.6A). Although the time of the experience was extended until 100 hours, the result of duplicates are only reproducible for devices 5 and 6 (0.5 mg/ μ L). It is also possible to observe that after approximately 70 hours most of the devices suffers some unjustified perturbation (Figures IV.6C-F).

The next experiments (assays 6-8) were performed using *G. sulfurreducens*. To promote the bacteria growth before the acquisition of amperometric data, 10 mM of fumarate were added to the NBAF medium. Similarly to acetate and lactate, oxidized at the anode and used as electron donors to promote bacterial growth, fumarate is an electron acceptor that will reduced at the cathode during anaerobic growth.^{32,33}

The amperometric data in Figures IV.7B and IV.7C shows some current peaks obtained during assay 6, where electrodes with lower polymer concentration were used (0.025 and 0.05 mg/ μ L). Electrodes coated with a higher concentration (0.07 mg/ μ L) do not produced current (Figure IV.7D). However, despite the promising results achieved in some assays, the amperometric data of duplicates are not reproducible, as well as the data obtained for uncoated electrodes treated with DMSO (Figures IV.7A-C).

The last two experiments (assays 7 and 8) were designed to overcome the reproducibility issues observed in assay 6. Unfortunately, bacterial growth did not occurred in both experiments, possible due to a problem with *Geobacter sulfurreducens* culture.


Figure IV.6: Microbial fuel cell device before the addition of *Shewanella oneidensis* MR1 wt (SOMR-1) (A) and at the end of the experiment (B). Amperometric results for uncoated electrodes treated with DMSO, devices 1 and 2, (C), and for PMDTU coated electrodes with 0.05 mg/µL, devices 3 and 4 (D), with 0.5 mg/µL, devices 5 and 6 (E) and 0.7 mg/µL, devices 7 and 8 (F).

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Figure IV.7: Amperometric results for MFC devices using *Geobacter sulfurreducens*. Uncoated electrodes treated with DMSO, devices 1 and 2 (A), and PMDTU coated electrodes with 0.025 mg/µL, devices 3 and 4 (B), with 0.05 mg/µL, devices 5 and 6 (C) and with 0.07 mg/µL, devices 7 and 8 (D).

Conclusions and Future Perspectives

The performance of microbial fuel cells may be influenced by different factors. In the investigation of novel microbial supercapacitors, it is crucial to evaluate the electrodes biocompatibility, to not compromise bacterial growth. PPMTU, a polythiourea with good capacitive performance was investigated as a potential microbial electrode for microbial fuel cells. Since PPMTU was found to have a positive effect in bacterial growth, different polymer concentrations and bacteria species were investigated. The best conditions obtained so far were achieved using a *Geobacter sulfurreducens* bacteria culture and required low PPMTU concentrations (0.025-0.05 mg/µL). Yet, this novel MCF device needs optimization before further studies.

In future work the MFC performance should be also studied using partially coated electrodes, to evaluate if current is being stored in PPMTU or is flowing directly to the electrode. Then, it will be very important to study the other polythioureas synthesized, described in Chapter III, and evaluate their performance as potential MSC devices.

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Final

Remarks

This thesis was focused on the design, synthesis and performance evaluation of novel devices for energy conversion and storage, a topic of high concern and priority, mainly due to climate changes imputed to extensive use of fossil fuels. Changes in the power sector framework are imperative and the use of sustainable solutions making use of renewable resources, such as solar or wind power, must be urgently undertaken and become a reality in a near future. Yet, device architecture and efficiency, still has major drawbacks and technological advances are a big challenge to researchers in the field. It is also urgent to reduce associated production costs, especially in solar PV devices, as well as the improvement of the materials used in this technology. Progress in sustainable energy conversion and storage will be only possible with solid investment in the development of new improved materials, enabling also the production of more flexible and portable electronics. Moreover, the decentralization of power sources and the boost of energy production, brought new problems related with the energy storage. The hydropower plants are not enough, and it is necessary to develop new, faster, flexible, high capacitive and portable devices. For this reason, this thesis was focused in the development of novel materials for energy related applications, based in dendrimer polymers, namely with potential to convert solar energy (photodiodes) and to store energy, being investigated the storage of bioelectricity produced by bacteria (microbial fuel cells).

The initial idea for the application of the materials described in Chapter II was its use on artificial leaves, mimetic solar cells. Yet, these materials worked only as photodiodes. Despite of having the same working principle as photovoltaic devices, in photodiodes the *J-V* output is different, as well as the potential applications. However, photodiodes are also very important in our society, especially for poor and undeveloped regions, being wildly used in medical applications or as sensors. Moreover, the device developed by us showed the best performance using a very cheap stainless-steel counter electrode. Also, the simple fabrication, using biocompatible materials, assembled at room temperature and in the presence of oxygen, is a great advantage in comparison with the ones previously reported. Several synthesised materials showed reduced solubility that preclude further studies. It would be interesting to introduce monomer modifications (*e.g.* alkyl groups) to increase solubility by preventing the formation of aggregates.

As previously mentioned, another goal of this thesis was the development of novel materials for energy storage. The chase for new flexible and high capacitive materials is huge, fostered by new technologic advances. As a proof of concept, we decided to investigate the ability of these materials to store the energy produced by microbial fuel cells (MFCs). The anaerobic or facultative anaerobic bacteria selected in our studied are present in some wastewater treatment facilities and are considered an industrial by-product. Since the major disadvantage of MFCs is the low current production, their use as coupled supercapacitive materials is highly attractive since will allow the storage and further current release in higher density. Small MFCs devices coupled with supercapacitors have already reported and are suitable to charge small wearable electronics. Space in another potential market, since MFCs may be used to fuel space missions, a strategy long pursued by NASA.

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Notwithstanding the promising results already achieved, our MFC devices need optimization, namely the performance studies using different electrode coating schemes. It is also important to increase reproducibility and test the effect of a dendrimer architecture on the devices performance, materials that were synthesised but not possible to investigated under the thesis timeframe.

Finally, it should be highlighted that the work developed in this thesis led to three peerreviewed international publications (a book chapter, a review paper and a research article), and several poster communications were presented in national and international scientific conferences. Also, a review about supercapacitors is under preparation, and a research article regarding the fabrication of novel microbial fuel cells coupled with supercapacitors is also expected after conclusion of undergoing optimization studies.

Appendix

Appendix I



UV-Vis and emission spectra

Figure AI.1: Spectra of D-HDP components in DMSO. Absorbance (a) and emission (c) of PIMAM_{G1}OMe dendrimer and absorbance (b) of Ru(dcbpy)₂(NCS)(EAFc) dye sensitizer.

Fabrication of D-HPD devices using ion-jelly as a matrix

Preparation of the ion-jelly matrix. Solutions of 10 mM of donor-acceptor dendrimers **3**, **4**, **6** and **7** and dye sensitizers **10** and **11** in [Bmim][Cl] were prepared at 60 °C until complete solubilization of the compounds. Then 250 mg of these solutions were mixed with 250 mg of gelatin and 50 μ L of H₂O and the solution was heated at 60 °C until complete dissolution. The solution was cooled to room temperature to promote jellification.

Preparation of the ion-jelly D-HPD device. In a hot plate (~ 60 °C), the ion-jelly matrix, previously warmed, is spread into a tape-masked ITO glass substrate. Then the ITO glass is cooled to room temperature and the counter electrode (platin or stainless steel) was attached. The measurements were performed between -1.0 and 1.5 V in the dark, under illumination, under illumination after 15 min. of continuous exposure and under dark after 15 min. of lamp switch off.

Appendix



Figure AI.2: *J-V* measurements of ion-jelly and donor-acceptor dendrimer PIMAM_{G1}OMe (**3**) using a platin counter electrode.

J-V measurements of agarose matrix



Figure AI.3: J-V measurements of agarose gel 3% (w/w) under illumination and dark conditions using a platin (A) or a stainless steel (B) counter electrode. Representation using a semi-logarithmic scale.

J-V measurements of D-HPD devices



Figure AI.4: Comparison of *J-V* curves of D-HPD devices after 15 min. of continuous illumination and 15 min. after lamp switch off: **3** mixed with dyes **10** or **11** using platin or stainless steel counter electrodes (A), and **4** mixed with dye **11** using platin or stainless steel counter electrodes (B). Representation using a semilogarithmic scale.

Appendix II

Characterization of PPTU



Figure All.1: FTIR spectrum of poly(*p*-phenylenethiourea) (PPTU) using a KBr disk.



Figure All.2: ¹H NMR spectrum of the *p*-phenylenediamine (top) and polymer poly(*p*-phenylenethiourea) (PPTU, bottom) in dmso-*d6*.



Figure All.3: ¹³C NMR spectrum of the poly(*p*-phenylenethiourea) (PPTU) in dmso-*d6*.

Characterization of PPMTU



Figure All.4: FTIR spectrum of poly(p-phenylmetanethiourea) (PPMTU) using a KBr disk.



Figure All.5: ¹H NMR spectrum of the 4,4'-diaminodiphenylmethane (top) and polymer poly(p-phenylmetanethiourea) (PPMTU, bottom) in dmso-*d6*.



Figure All.6: ¹³C NMR spectrum of the poly(p-phenylmetanethiourea) (PPMTU) in dmso-d6.

Characterization of polymer 3



Figure All.7: FTIR spectrum of polymer 3 (KBr disk).

Characterization of polymer 4



Figure All.8: FTIR spectrum of polymer 4 (KBr disk).

Characterization of PURE_{G4}-PPTU



Figure All.9: FTIR spectrum of PURE_{G4}-PPTU (KBr disk).



Figure All.10: ¹H NMR spectrum of the PURE_{G4}- PPTU in dmso-*d6*.



Figure All.11: ¹³C NMR spectrum of the PURE_{G4}- PPTU in dmso-*d6*.

Appendix III

Shewanella Basal Medium (SBM) with lactate

To prepare 1L of SBM medium, 0.225g of K₂HPO₄, 0.225g of KH₂PO₄, 0.46g of NH₄Cl, 0.117 g of MgSO₄ • 7H₂O and 0.225g of (NH₄)₂SO₄ are solubilized in deionized water. Then, 10 mL of 1M of HEPES pH=7.2 (buffer) was added. Next the pH was corrected to 7 using NaOH. Next, 3.53 mL of lactate was added to the solution and total volume (1L) was obtained with water. Finally, the solution was autoclaved.

Lysogeny Broth (LB) with lactate

To prepare 1L of LB medium, 5g of yeast extract, 10g of tryptone and 10g of NaCl were solubilized in deionized water. Then, 3.53 mL of lactate was added and the and total volume (1L) of the solution was completed with water. Finally, the solution was autoclaved.

NBAF medium with fumarate

To prepare 1L of NBAF medium, 0.42g of KH₂PO₄, 0.22g of K₂HPO₄, 0.24g of NH₄Cl, 0.38g of KCl, 0.36 of NaCl, 0.04g of CaCl₂, 0.1g of MgSO₄ • 7H₂O, 1.8g of NaHCO₃, 0.5g of NaCO₃, 2.04g of sodium acetate, 0.1g of yeast extract, 0.03g of Na₂SeO₃ was solubilized in 1L of deionized water. Then the pH was corrected to 7 with HCl. Next, sodium fumarate was added to the solution (the amount of sodium fumarate added depends of the final concentration that it is desired). Then the solution is transferred to small flasks that and the solution was degasified with a CO₂ + N₂ line gas for 15 minutes. Next the flasks were sealed with a septum and encapsulated to be further autoclaved under anaerobic conditions.