Conjugated polymers: Synthesis and applications in optoelectronics

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RESUMEN

En los últimos 50 años el desarrollo de polímeros conjugados para aplicaciones en energía y optoelectrónica ha generado un gran interés debido a su uso como conductores, en celdas solares o en dispositivos electrónicos. El continuo avance de esta tecnología precisa de nuevos polímeros con propiedades adecuadas para cada uso. Se presenta una revisión del estado del arte de la tecnología de polímeros conjugados y las diferentes estrategias para la obtención de polímeros útiles para cada área.

Palabras clave: polímeros conjugados, polímeros conductores, celdas solares, sensores poliméricos.

SUMMARY

In the last 50 years the development of conjugated polymers for applications in optoelectronics and energy has attracted great interest because of its use as conductive polymers, in solar cells or electronic devices. The continuous progress of such technology needs new polymers with suitable properties for each use. A review of the state of the art of polymer technology and the efforts for obtaining the most suitable polymers for each area is presented.

Key words: conjugated polymer, conducting polymer, solar cells, polymeric sensors.

RESUM

En els últims 50 anys el desenvolupament de polímers conjugats per aplicacions en energia i optoelectrònica ha atret gran interès degut al seu ús com a conductors, en cel·les solars o en dispositius electrònics. El continu avanç d'aquesta tecnologia necessita de nous polímers amb propietats adequades per a cada ús. Es presenta una revisió de l'estat de l'art de la tecnologia de polímers conjugats i les diferents estratègies d'obtenció de polímers adients a cada àrea.

Mots clau: polímers conjugats, polímers conductors, cel·les solars, sensors polimèrics.

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1. INTRODUCTION

In 1963, Weiss *et al*. reported the synthesis of polypyrrole, prepared by pyrolysis of tetraiodopyrrole under an inert atmosphere in the presence of iodine. Polypyrrole was obtained as a black, amorphous insoluble solid in organic solvents [1]. At the time of the discovery, very little was understood about the properties of polypyrrole. It was not until 1977, when MacDiarmid, Shirakawa and Heeger reported the conducting properties of doped polyacetylene, that polypyrrole and other conducting polymers attracted the attention of the scientific community (Figure 1) [2].
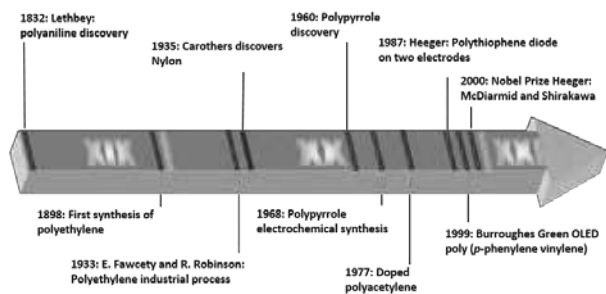

Figure 1: *Milestones in polymer chemistry and conjugated polymers.*

Although polyacetylene is one of the most extensively studied conducting polymers, it presents several practical limitations such as its high instability in presence of air. Consequently the development of new kinds of conducting polymers has received much attention. An special case is the family of polyheterocycles constituted of polymers such as the aforementioned polypyrrole (PPy) or polythiophene (PT), polyaniline (PANI) or poly(3,4-ethylenedioxythiophene) (PEDOT) to name some examples. In general, these materials display good thermal stability, high conductivities and can be easily prepared (Figure 2) [3, 4].
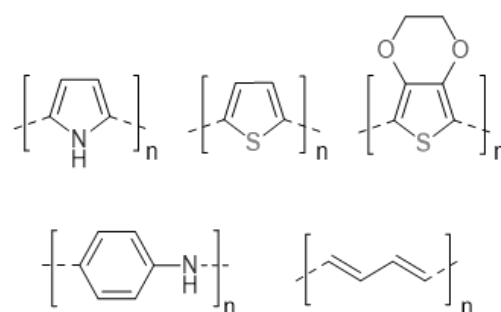

Figure 2: *Structure of some conjugated polymers.*

2. SYNTHESIS OF CONJUGATED POLYMERS

Conjugated polymers can be synthesized in two different ways, either chemically or electrochemically [5]. The election of the methodology is important since the properties of the materials depend greatly on the type of polymerization. In turn, the chemical method can be broken into two types of polymerization: by organometallic coupling or by treatment with a proper oxidant.

2.1. ORGANOMETALLIC COUPLING
The most common chemical reactions used to prepare conjugated polymers are the Suzuki and the Stille couplings, using both a catalyst, typically a palladium complex. These two versatile reactions use as starting materials a halogenated derivative and a boronic acid derivative or a stannylated derivative respectively (Figure 3) [6, 7].

2.2. CHEMICAL OXIDATIVE POLYMERIZATION
Polymerization by chemical oxidation is based on the treatment of the proper monomer with an oxidant [7] such as $FeCl_3$ or $(NH_4)_2S_2O_8$ (Figure 4).

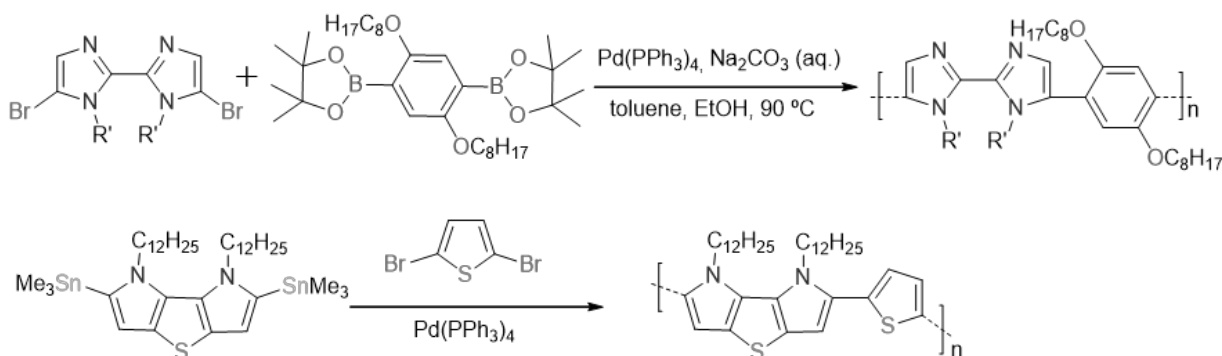**Figure 3:** *Polyaromatic polymers synthetised by cross-coupling reactions [6].*
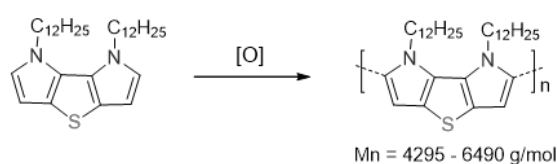

$$Mn = 4295 - 6490 \text{ g/mol}$$

Figure 4: *Preparation of a conjugated polymer by chemical oxidation [7].*

The oxidizing agent, usually $FeCl_3$, generates a radical cation which initiates the polymerization process (Figure 5). As with other synthetic methods, the choice of the suitable solvent, the temperature and amount of the oxidizing agent are key factors which determine the backbone length and the quality of the final polymer [8].
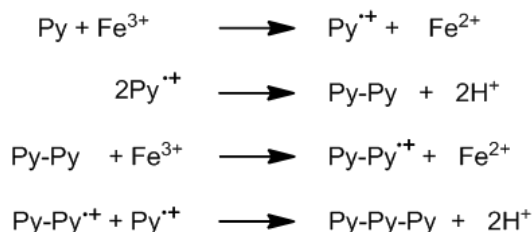
$$Py + Fe^{3+} \longrightarrow Py^{\bullet+} + Fe^{2+}$$

$$2Py^{\bullet+} \longrightarrow Py\text{-}Py + 2H^+$$

$$Py\text{-}Py + Fe^{3+} \longrightarrow Py\text{-}Py^{\bullet+} + Fe^{2+}$$

$$Py\text{-}Py^{\bullet+} + Py^{\bullet+} \longrightarrow Py\text{-}Py\text{-}Py + 2H^+$$

Figure 5: *Chemical oxidative polymerization mechanism of pyrrole [8].*

2.3. ELECTROCHEMICAL OXIDATIVE POLYMERIZATION

The first example of electrochemical polymerisation of a CP was described in 1968 when a film of polypyrrole was obtained on a platinum electrode by exposing a solution of pyrrole in sulfuric acid to an oxidation potential [9]. Nowadays, the electrochemical polymerization is performed on a three electrode cell. In such device a reference electrode measures and controls the potential of the working electrode whereas the counter electrode passes all the current required to balance the observed current on the working electrode (Figure 6) [10]. The working electrode acts as a substrate for the electro-deposition of the polymer. It is necessary that at the time that the polymer is deposited, by an oxidative process, oxidation of the electrode does not occur. Therefore, inert electrodes of Pt, Au, SnO_2, ITO (Indium Tin Oxide) and stainless steel substrates must be used. The counter electrode is made of glassy carbon or a metal foil, typically Pt or Au. The reference electrode is usually a saturated calomel electrode (SCE) or Ag / AgCl system (useful for aqueous and non-aqueous solvents).
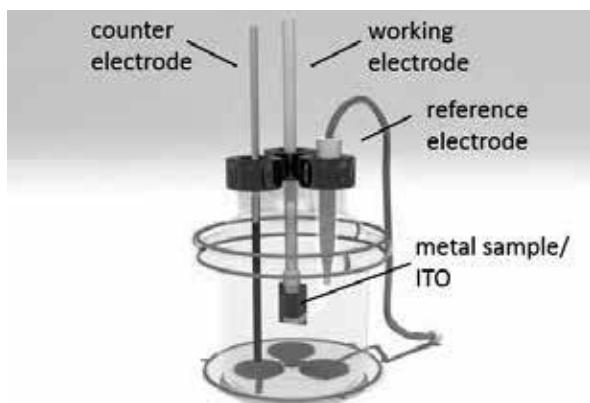

Figure 6: *Three-electrode electrochemical cell.*

During the electrochemical polymerization a current is passed through a solution of the monomer and the deposition of the polymer occurs (in the anode). In order to perform a proper deposition of the polymer, the following five variables must be taken into account:

- Deposition time and temperature
- Solvent type (aqueous or organic solvent) and purity
- Electrolyte type
- Electrode system
- Deposition load

All these parameters determine the morphology of the polymer film and its mechanical and electrical properties which dictate the final properties of the material and its usefulness (Table 1).

Table 1: *Advantages and disadvantages of chemical and electrochemical polymerization.*

Polymerization Method	Advantages	Disadvantages
Chemical	- Large scale production - Post-polymerization covalent modification - Various options to modify the CPs	- Cannot produce thin films - Complex synthesis of monomers
Electro-chemical	- Preparation of very thin films (20 nm) - Monomers easy to be synthesized - Molecule occlusion inside the CPs - Polymer is doped simultaneously during its formation	- Difficult removal of the polymer from the electrode once synthesized - Difficult covalent modification of CPs

In principle, the chemical approach can be considered a general methodology, whereas electrochemical synthesis is restricted to systems with monomers amenable to be oxidized in the presence of a potential that forms free radical reactive species (Figure 7). Some of the best known conductive polymers such as PEDOT can be obtained in both ways, but many CPs with modified monomers can be only synthetized by chemical polymerization [11].
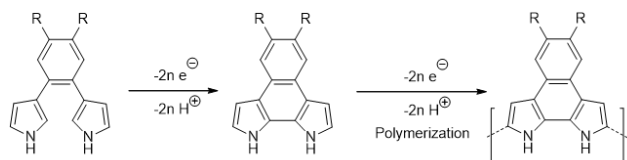

Figure 7: *Electrochemical polymerization of a bipyrrole [11].*

3. CONDUCTIVITY IN CONJUGATED POLYMERS

Conductivity is a measure of electrical conduction. Thus, it measures the ability of a material to pass the current. Typically materials having a conductivity less than 10^{-8} S / cm are considered insulating materials while materials with values of conductivity in the range of 10^{-8} to 10^3 S / cm are considered semiconductors (Figure 8).
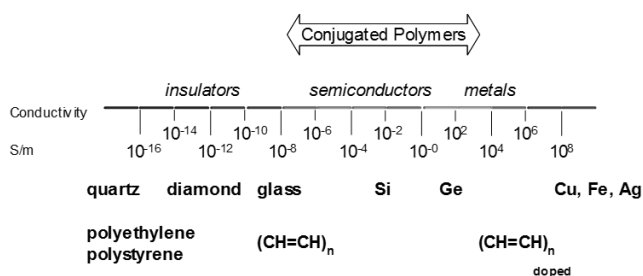

Figure 8: *Conductivity of conjugated polymers.*

Conjugated polymers exhibit alterations in their unsaturated backbone, which give the polymer the semiconducting properties. Several studies have shown that the planar form of the conjugate system maximizes the overlap between different π orbital, which is critical for conductivity. Such a system is described as an electronic function delocalized throughout the chain. Delocalization allows mobility of the charge along the polymer chain and between adjacent chains, but it is limited by disorder and coulombimetric interactions between electrons. One way to increase the mobility of the charges is the use of a polymer containing intercalated acceptors (A) and donors (D) monomers along its backbone (...-A-D-A-D-A-...), thus charges travels faster and more efficiently by the polymer chain. An alternative method is the doping of the polymer [12]. This process is analogous to the doping of inorganic semiconductors and implies a reductive (n-doping) or oxidant (p-doping) treatment of the polymer. The conductivity of such polymers could be increased up to 12 orders of magnitude (10^2 S / cm) depending on the type of polymer and doping (Table 2) [13].

Table 2: *Conductivity of common conjugated polymers.*

Conductive polymer	Maximum conductivity (S / cm)	Doped
Polyacetylene (PA)	200-1000	n, p
Polyparaphenylene (PPP)	500	n, p
Polyparavinylene (PPV)	1-1000	p
Polypyrrole (PP)	40-200	p
Polythiophene (PT)	10-100	p
Polyaniline (PANI)	5	n, p

The doping process introduces charge carriers as polarons (an electron or a hole, plus a distortion of the charge's surroundings) or bipolarons within the polymer (Figure 9). The movement of these charge carriers through the conjugated polymer chain generates an electrical current [14].
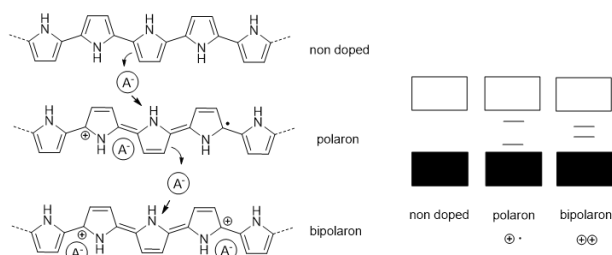

Figure 9: *Polymer doping: polarons and bipolarons. Effect on the conduction and valence bands* [14].

The process of doping decreases the gap between the valence and the conducting bands. Thus, small band gaps provide with higher conductivities. On the other hand, doping adds a counterion to the polymer which, in turn, can be used to enhance the solubility of the conducting material and hence its processability (Figure 10).
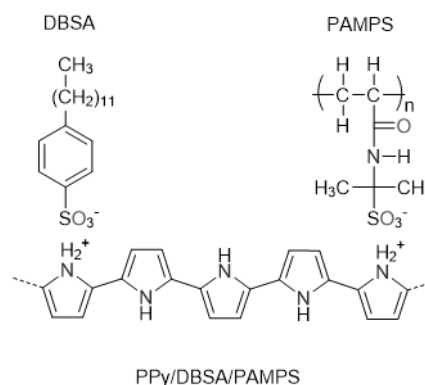

Figure 10: *PPy doped by addition of two different species, DBSA (dodecyl benzene sulfonic acid) and PAMPS (poly(2-acrylamido-2-methyl-1-propane sulfonic acid).*

4. ELECTRONIC CHARACTERIZATION OF CONDUCTIVE POLYMERS

In order to assess the electrical properties of conducting polymers two main techniques have been adopted: the so called four point probe technique (4PPT) to measure conductivity and voltamperometry to gain insight in the redox behavior of the material. In this context it is also worth mentioning the electrochemical impedance spectroscopy (EIS) which allows very sensitive analysis of the dielectric properties of the polymers.

4.1. FOUR POINT PROBE TECHNIQUE

In order to characterize the conductivity of polymers, the resistivity (X), which is the inverse of conductivity, is determined. Conductivity is expressed in Ω^{-1} units, also known as Siemens (S), per distance unit, usually meters or centimeters (S/m, S/cm). The resistivity is calculated from the resistance of the material (R) which can be obtained in different ways, for instance, the technique of the four points probe. This technique was originally developed by Wenner in 1916 for measuring Earth resistivity. Valdes in 1954 adopted the 4PPT for measuring the resistivity of semiconductors [15]. The 4PPT is currently widely used in the semiconductor industry for monitoring the production of conductive materials [16] The 4PPT is based on applying a constant current (I) through two electrodes placed on the surface of the material, then the change of potential (V) is measured with the aid of another pair of electrodes. The resistivity of the material can be calculated by the following equation: $\rho = RCF (V_{measured} / I_{measured})$, where RCF is the correction factor of the resistivity depending on the size of the structure, thickness, size of electrodes and electrode position (Figure 11) [17, 18].
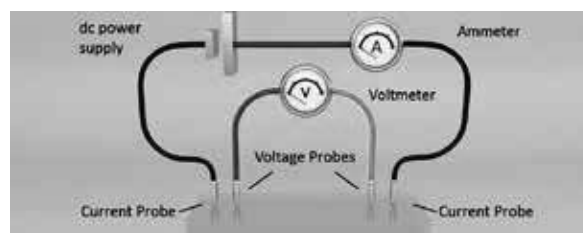

Figure 11: *Scheme of 4PPT.*

There are other techniques for measuring the conductivity, perhaps the simplest is based on the direct measurement of the resistance generated by the polymer by applying a known potential. In this case, where there is not geometric information of system the conductivity value is given in Siemens square units.

4.2. CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) is used to characterize the redox properties of the material and also allows inferring whether it is conductive or not. The apparatus is similar to that used in a three electrode setup for electropolymerization, the only difference is the replacement of the power supply by a potentiostat. The technique provides with the values of the potentials of reduction / oxidation and information about the reversibility of the redox process [19]. The measurement consists in applying a cyclic potential sweep between two voltage values at a constant rate. The typical aspect of a CV for a reversible reaction is shown in (Figure 12).
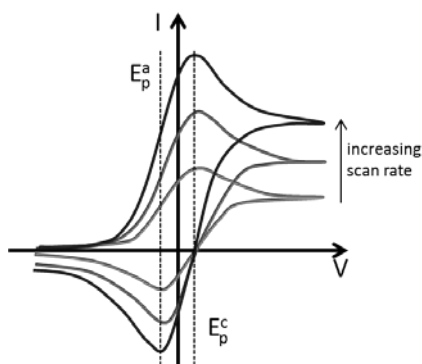
Figure 12: *Voltammogram for a reversible reaction.*

On the other hand, in a quasi-reversible reaction, where the electronic transfer is not reversible, I-V curves are shifted toward more reductive potentials. This phenomenon can be ascribed to the fact that the equilibrium at the surface is not quickly established. In these cases the peak separation is not constant but varies depending on the rate constant (Figure 13).
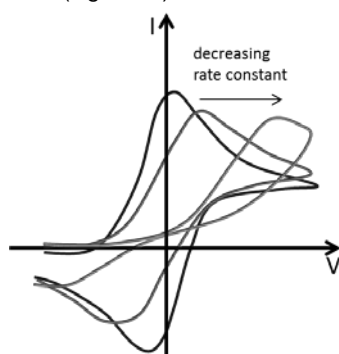
Figure 13: *Voltammogram for a quasi-reversible reaction.*

5. APPLICATIONS IN OPTOELECTRONICS

Conducting polymers possess optical and electrical properties similar to metals and inorganic semiconductors, and additionally display attractive properties associated with conventional polymers, such as easy processability and tunability. This unique combination of properties has given to conductive polymers a wide range of applications such as electrochromic devices, OLED's, batteries and supercapacitors, and photovoltaic cells.

5.1. ELECTROCHROMIC DISPLAY AND SOLID-STATE ELECTROCHROMIC CELL

Conductive polymers can be used in manufacturing electrochromic devices (Figure 14). A common example of electrochromic device is used to alter the opacity of crystals.
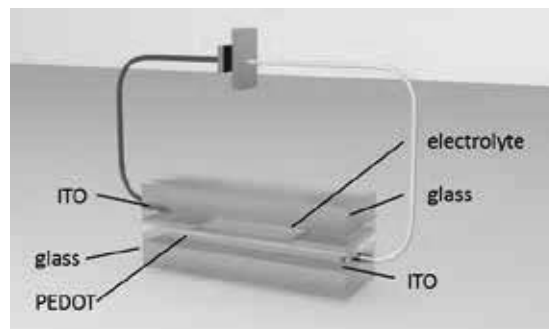
Figure 14: *Scheme of an electrochromic device.*

Materials that exhibit a reversible color change over a reversible charge and discharge process are called electrochromic materials. Electrochromic devices are typically constructed by combining an electrode covered with a thin layer of an electrochromic compound, an electrolyte, a transparent polymer and a complementary electrochromic material as a counter electrode. An example of such device contains amorphous Li_yVO_x, poly(oxyethylene) as electrolyte and the conductive polymer PEDOT. The device changes the color from blue / purple opaque to transparent blue sky with only a voltage of +1.5 V. The time required to change from one color to another at room temperature is just 4 seconds, and the polymer stability in repeating the cycle of oxidation / reduction is durable [20].

5.2. OLEDs: ELECTROLUMINESCENT DEVICES

The phenomenon of electroluminescence was first discovered by Destriau *et al*. in 1936 by sandwiching ZnS and phosphor powder between two electrodes [21]. In the early 60s General Electric introduced in the market the first red light-emitting diodes (LEDs) based on the inorganic semiconductor GaAsP [22]. In the following years of the decade, electroluminescence of organic materials was observed in anthracene crystals. In the mid-80s van Sylke and Tang at the same time as Saito and Tsutsui rekindled the field of organic LEDs using fluorescent salts of organic products. The big breakthrough in the field was achieved by Friend who reported, in 1990, the first OLED made of an organic polymer [23]. The polymer, PPV (Poly(*p*-phenylenevinylene), is insoluble and difficult to process, however, Friend found a method to process it by thermal conversion of a precursor polymer. With this technology in hand, it was possible to build displays of various sizes by printing techniques. The first organic LED of PPV emitted green-yellow light and had a quantum efficiency of only 0.05%. Several years later, in 1996, Philips developed a dialkoxy substituted PPV derivative which displays a value of quantum efficiency of 2.1% [24]. In comparison with conventional semiconductors, CPs are endowed with a large number of advantages such as their mechanical and optical properties. For instance, only the family of polythiophenes emits

light in a broad range of wavelengths from blue to the infrared (Table 3).

Table 3: *Electroluminescent materials used in OLEDs.*

Electroluminescent materials	
Emission Color	Luminescent material
Red	Cyano derivative of PPV, PTOPT (poly (3-(4-octyl phenyl 2,2'-bithiophene)))
Yellow	PCH (poly(3-cyclohexane thiophene))
Orange	MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene])
Green	PPV (poly(*p*-phenylene vinylene))
Blue	PEDOT (poly(3,4-ethylenedioxy thiophene)), PCHMT (poly(3-methyl-4-cyclohexane thiophene))

Polymer LEDs are particularly attractive for its use in screens due to the variety of colors that can be produced and their processability [25]. Each LED is fabricated by sandwiching a polymer layer between two electrodes (Figure 15). Electrons are injected from the cathode (made of aluminum, calcium, and indium) into the LUMO of the polymer. At the same time, holes are generated at the anode (usually ITO). Then an exciton, a neutral quasiparticle which consists of an electron bound to an electron hole, is formed. The exciton can migrate under the electric field and, finally, recombines radiatively to yield electroluminescence.
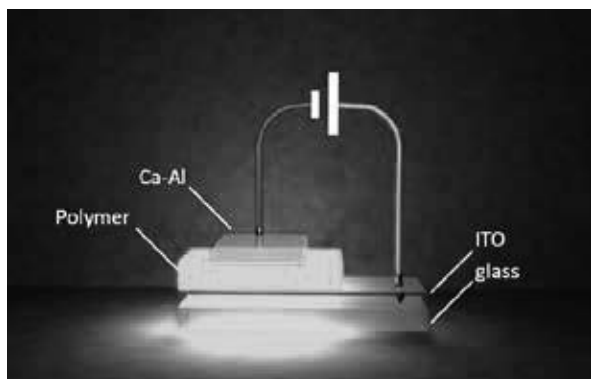

Figure 15: *Scheme of a OLEDs device.*

5.3. SOLID STATE RECHARGEABLE BATTERIES
Batteries are devices that store electrical energy in the form of chemical energy. Ideal batteries should allow an indefinite number charge cycles. For this purpose, it has been proposed the use of polyaniline as a cathode for the manufacture of rechargeable batteries [26]. An example of this technology has been disclosed by the group of Trivedi [25] who has prepared a dry cell type battery replacing MnO_2 with polyaniline (130-170 W·h / Kg) in a Leclanché battery (Figure 16). Such batteries should be advantageous due to its lower cost compared to Ni-Cd (40-60 W·h / Kg) and its low environmental impact.

5.4. SUPERCAPACITORS
A capacitor is a device that stores electrical energy when a magnetic field is applied across a dielectric material (Figure 17).
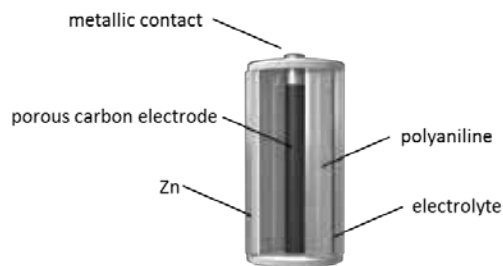

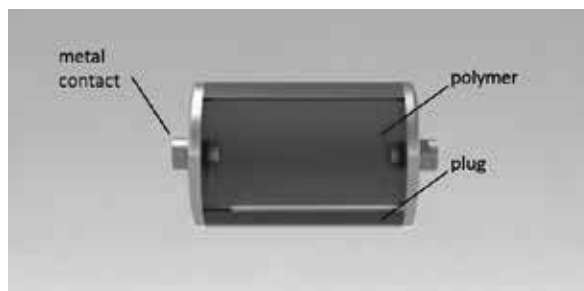**Figure 16:** *Solid state battery scheme using polyaniline [25].* supercapacitors

Figure 17: *Supercapacitor scheme.*

Electrochemical capacitors use a charged double layer formed at the electrode/electrolyte interface, therefore depends on the capacitance of the electrode area. In an ideal capacitor, the stored charge amount is proportional to the potential difference. A redox capacitor is based on the Faraday pseudo-capacitance of two dimension materials or nearly two dimensions. These capacitors are made of metal oxides or CP's, such as PEDOT because of its rapid kinetics and their high chemical stability [27]. Supercapacitors are intended to work in conjunction with batteries in electrical devices to provide peaks of power when needed. This combination helps to reduce the size of the batteries and increase their span life.

5.5. CONDUCTIVE INKs: FLEXIBLE ELECTRONICS
Another promising application of CPs is the production of inexpensive printed circuit boards. This new technology is predicated on the possibility to work with CP's in solution which avoids the more expensive deposition in vacuum. In order to be practical, the use of soluble CP's in electronics requires the development of techniques for accurate printing for all components of the board, which does not change the self-assembly of polymer molecules [28]. In this regard, inkjet printing (IJP) has emerged as a technique for producing LEDs and high-resolution displays. However, IJP has not yet been applied to organic transistors due to its low resolution of 20-50 nm, which is limited by the flight direction of the ink drops and its spread on the substrate. This definition is still not enough to obtain Thin-Film Transistors (TFTs) without electrical defects in the device.

One of the most used polymers for electronic inks is the mixture PEDOT: PSS. This blend is partly soluble in water and is marketed as a suspension in water which can be printed by inkjet methods (Figure 18).
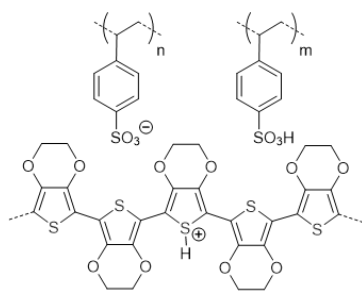
Figure 18: *PEDOT:PSS.*

5.6. PHOTOVOLTAIC CELLS

Crystalline silicon solar cells have dominated the photovoltaic market since the early 1950s. The conversion efficiency of such solar cells ranges from 8 to 29%. Nevertheless, the production of such devices is still expensive and complex. As an alternative, in recent years, it has been sought the development of solar cells based on inexpensive organic materials such as conductive polymers [29]. The foreseeable advantages of this new kind of devices are its low price, easy processability and intrinsic flexibility.

The working mechanism of solar cells is straightforward. Photons of light are absorbed by a semiconductor generating an exciton. Then, the electron is excited from the valence band into the conduction band. This mechanism is operational in silicon based cells; however, there are some important differences between inorganic and organic cells. Whereas in inorganic semiconductors its high dielectric constant allows an easy dissociation of the exciton (low binding energy), organic polymers are characterized by a lower dielectric constant and a higher exciton binding energy. To overcome this drawback, organic solar cells are made of two types of materials: an electron acceptor (A) and a donor (D) (Figure 19b, c). Therefore, the charges are generated by a photo-induced electron transfer between the two components (Figure 19a).
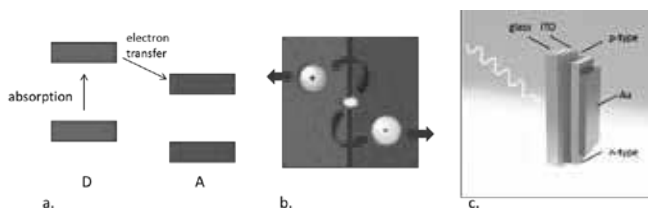

Figure 19: *Structure and basic processes in a solar cell.*

For an efficient performance of the cell, the spectrum of the photoactive layer must overlap the solar emission spectrum in order to capture the maximum of incident light. On the other hand charge separation is the key step. Thus, ideally, charges generated by photoinduced electron transfer in the donor (D, p-type semiconductor) must be transferred efficiently to the acceptor (A, n-type semiconductor) (Eq. 1).
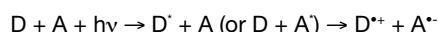
$$D + A + h\nu \rightarrow D^* + A \text{ (or } D + A^*) \rightarrow D^{\bullet+} + A^{\bullet-}$$
Equation 1.

It is essential that the charge separation would be thermodynamically and kinetically favorable. However, part of the energy of the absorbed photon is lost in competitive processes such as fluorescence or non-radiative decay. It is also important that the charge separation is stabilized,

so the photogenerated charges could migrate toward the electrodes and avoid their recombination (Figura 20).
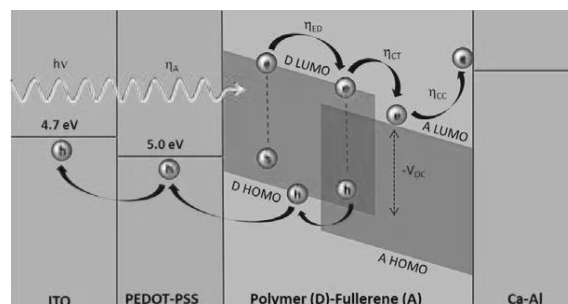

Figure 20: *Electronic transfer in solar cells (PEDOT-C_{60} cell).*

The first organic solar cell was reported by Tang [30, 31] *et al.* in 1979. The device was made of copper phthalocyanine as a donor and a perylene derivative as acceptor. The photoactive materials were placed between a transparent ITO electrode (Indium tin oxide) and a silver cathode. Total energy conversion was about 1% (Figure 21).
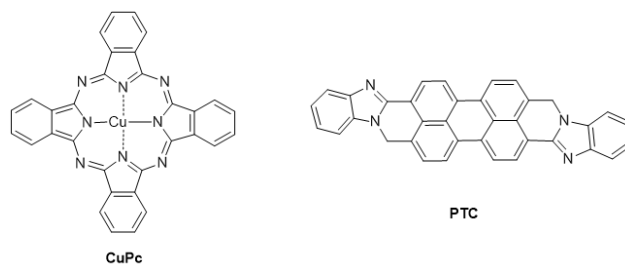

Figure 21: *Copper phtalocyanine (CuPc) and perylene derivative (PTC)* [30, 31].

Nowadays, by virtue to its strong electronegativity and high electron mobility, fullerene (C_{60}) and its derivatives (usually PCBM) have become the standard acceptors for organic solar cells (Figure 22) [32].
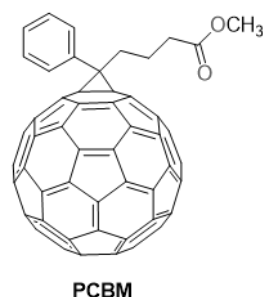

Figure 22: *Phenyl-C61-butyric acid methyl ester (PCBM)* [32].

One of the main limitations of the classic bilayer architecture of solar cells is the small interface area between the donor and acceptor. As a consequence, only a small fraction of the excitons can reach the interface due to their short lifetime. This problem was addressed with the introduction of the bulk heterojunction cells (BHJ cells). In this kind of device a blend of donor and acceptor is used to ensure maximum contact surface area (Figure 23).
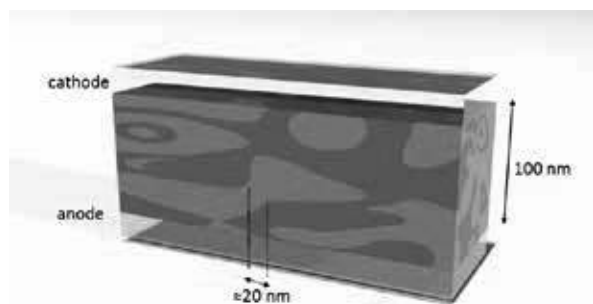
Figure 23: *Structure of a Bulk Heterojunction Cell.*

BHJ cells were first disclosed by Heeger and Friend in 1995 [33, 34]. Reported efficiencies for such devices are as high as 10%. Typical polymer donors for BHJ cells are polyfluorenes and polyphenylenes (i.e. [2-methoxy-5-(2'-ethylhexyloxy)-ρ-phenylene vinylene]) (MEH-PPV)) [35]. However, these cells still possess a limited load mobility and poor absorption of visible light. The use of soluble polythiophenes, especially poly(3-hexylthiophene) (P3HT) with a high mobility of charge and broader absorption of the visible spectrum than their predecessors, became a standard in organic solar cells the first decade of the 21th century (Figure 24).

Other suitable polymers used in the design of BHJ cell are based on alternating heterocycles, for instance, PCPDTBT (Figure 25) which contains subunits of benzodithiazole and bithiophene and extends the absorption of the polymer above 900 nm. Cells prepared with this polymer reach efficiencies up to 3.5% [36]. Another example of such kind of polymers is a copolymer which consisted of thieno[3,4-b]thiophene and benzodithiophene as alternating units. This copolymer reaches efficiencies of 7-8% (Figure 24) [37-39].
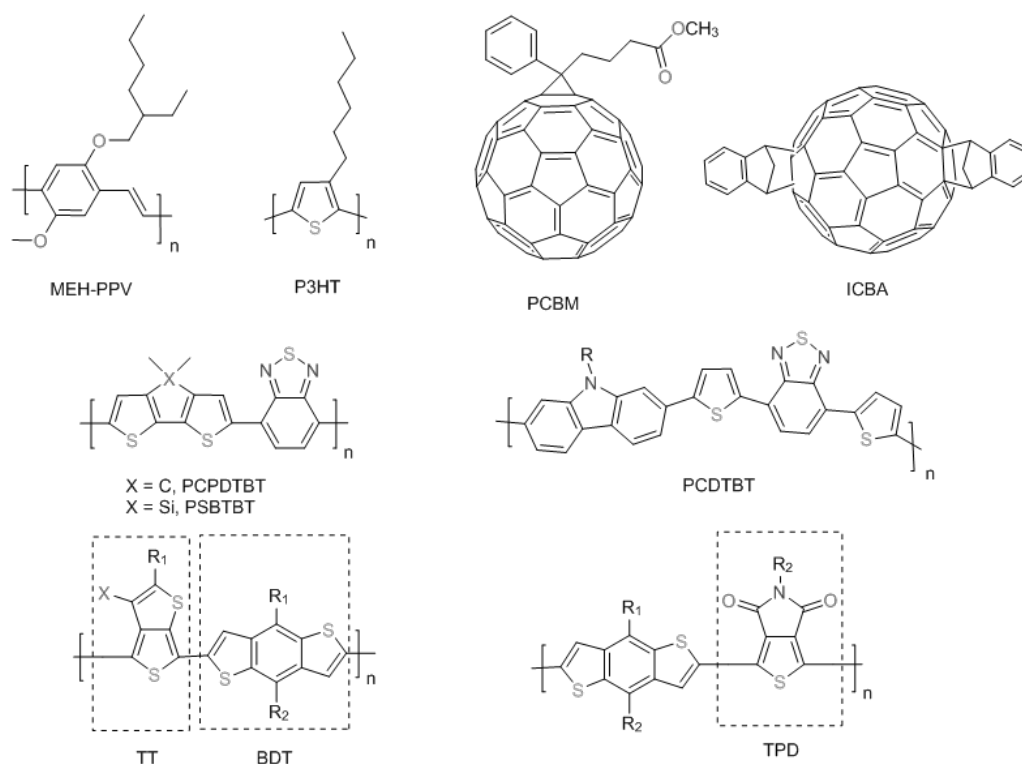
The success of a particular type of polymer depends to a great extent on the magnitude of the band gap between the HOMO and the LUMO. In order to modulate this parameter [40], five factors should be taken into account: aromaticity of the monomers, rigidity of the polymer backbone, interchain coupling, inductive and mesomeric effects and electronic nature of the rings (Figure 25).
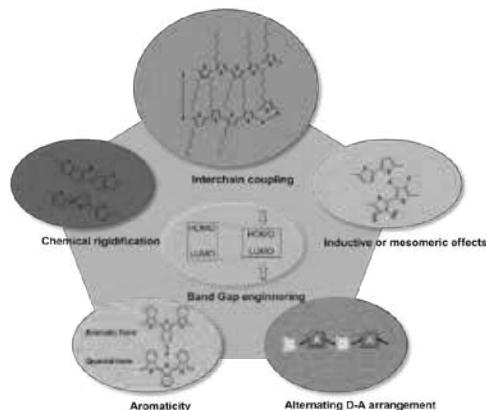

Figure 25: *Strategies to reduce the band gap.*

Thus, for polyaromatic polymers two possible resonance structures can be drawn, an aromatic form and a quinoid form. The latter is less stable since the aromaticity of the subunits is lost, and therefore the energy gap is smaller. The intercalation of double bonds into the benzene polymer, increasing the π delocalization through the chain, enhances the quinoid character of the polymeric backbone (Figure 26).
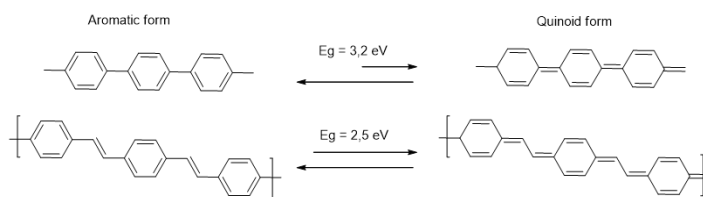

Figure 24: *Acceptors and donors used in BHJ cells* [33-39].

Figure 26: *Addition of double bonds to stabilize the polyphenylene quinoid form*

Another strategy to reduce the band gap is the rigidifycation of the polymer to achieve a planar system. A planar backbone allows parallel *p* orbitals to interact what, in turn, enhances the conjugation and facilitates charge delocalization. Roncali [41, 42] *et al*. verified this phenomenon by limiting the rotation of a polythiophene by adding heteroatomic bridges between the thiophene rings (Figure 27).
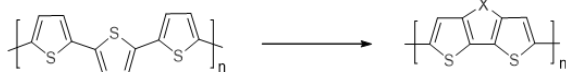

Figure 27: *Rigidifycation of polythiophene [41, 42].*

Substitution of the monomers with electron withdrawing and donating groups also tunes the energy gap. In general, electron donating groups increase the energy of the HOMO and withdrawing groups decrease the LUMO. For instance, the band gap of polythiophene is reduced from 2.0 to 1.5 eV with the incorporation of alkoxy groups (PEDOT) [43]. Even a more dramatic effect can be achieved with the installation of alternating amino and nitro groups [44] (Figure 28).
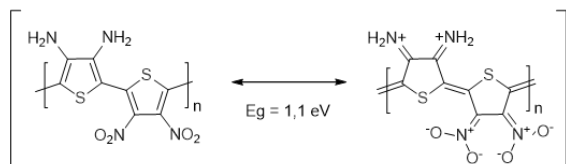

Figure 28: *Effect on the band gap of polythiophene by substitution with electron withdrawing and donating groups [43].*

Arguably, the most extended strategy to control the band gap is the copolymerization of donors and acceptors subunits (-ADADA-) [45] (Figure 29).

Figure 29: *Acceptor-donor copolymers [45].*

The electronic properties of acceptor-donor polymers can be explained in light of the perturbation theory. According to this theory, in acceptor-donor polymers the HOMO is more energetic than the donor's HOMO and the LUMO displays lower energy than the acceptor's LUMO. Hence, the band gap is reduced (Figure 30) [46].

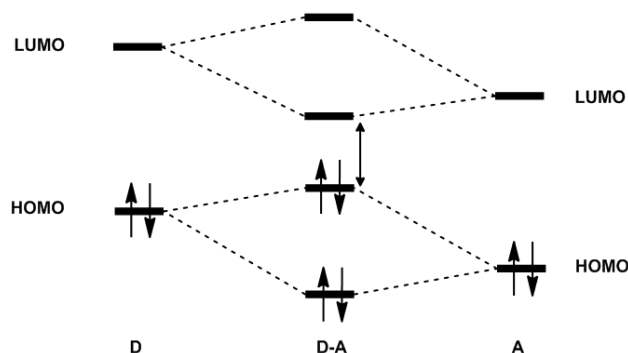

Figure 30: *Reduction of the HOMO - LUMO gap in acceptor-donor copolymers [46].*

Finally, another important factor which determines the band gap is the presence of intermolecular interactions induced by secondary forces in the solid state which allow the delocalization between chains [47]. Therefore a highly stereoregular coplanar structure with an extended conformation is a prerequisite for achieving a domain with crystalline order.

5.7. POLYMER SENSORS
The development of sensors for inorganic species and biomolecules from CPs has become a major focus of attention by many research groups in recent years, due to their versatility and high sensibility.

5.7.1. Conjugated polymers as biosensors
Conducting polymers are versatile materials suitable for biomedical applications given their biocompatibility. As such, CP have found many uses in medicine such as biosensors [48-51], tissue engineering [52-54], neural probes [55-57], drug-delivery [58, 59], and bio-actuators [60-62]. In particular, the first biosensor was created by integrating an enzyme to an electrode [63], from that discovery there have been many advances in the world of biosensors and currently metabolites, hormones, antibodies or neurotransmitters can be easily monitored for clinical purposes. The principle of a biosensor is simple. In short, the interaction of the sensor with the analyte generates a chemical signal which is transmitted to a transducer, in turn, it is converted it into an electric signal. Depending on how the signal is transmitted, different types of transducers have been used: amperometric, potentiometric, conductimetric, optical, among others. In the case of an amperometric transducer, the produced current is measured when a specific product is oxidized or reduced; the CP is responsible for the electron transfer process (Figure 31) [64].

Table 4: *Immobilization techniques of biomolecules on conducting polymers for biosensing devices.*

| Immobilization	Advantage	Limitations
Adsorption	- Simple	- Desorption with time - Limited control over the immobilization - Random orientation on the surface
Entrapment	- Simple - Elements close in space	- Potential loss of activity of the biomolecule - Need of high concentrations of biomolecules
Afinitty binding	- Control over the orientation of the molecule - High accessibility of the analytes	- Requires prior immobilization of one of the related molecules
Chemical conjugation	- Control on the immobilization - High accessibility of the analytes - Minimal loss of biomolecules	- Complex - The conditions are not always appropriate for biomolecules - Potential loss of activity of the biomolecules
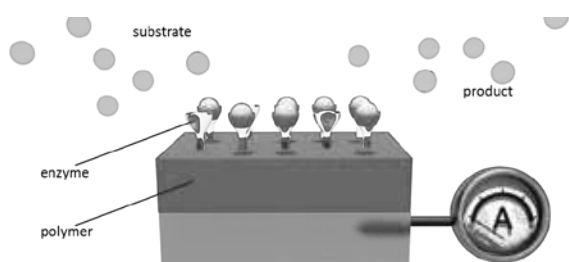
Figure 31: *Amperometric biosensor with electronic transfer [64].*

Usually redox mediators such as ferrocene, prussian blue, or their derivatives are used to improve the electronic transfer of the biochemical reaction. Thereby the selectivity and sensitivity of the biosensor is improved. These mediators can be trapped or incorporated as dopants, or chemically conjugated to the monomer. There are various methods to trap the biomolecule depending on the type of sensor being used (Table 4) [3].

Probably, the physical adsorption of the analyte is the simplest method. An example of this technology is a sensor for glucose which consisted in a glucose oxidase absorbed into a polypyrrole matrix. This sensor is able to work in the 2.5-30 mM range using dimethylferrocene as an electron transfer mediator [65].

The intrinsic fluorescence of some conjugated polymers has been capitalized to design new biosensors [66]. For instance, Whitten *et al.* reported in 1999 a sensor for avidine based on poly(2-methoxy-5-propoxy sulfonate phenylene vinylene) and a viologen derivative (Figure 32).
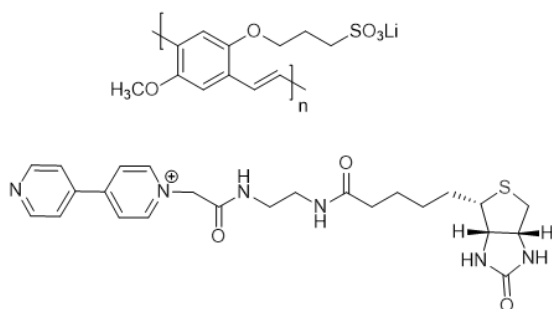

Figure 32: *Poly (2-methoxy-5-propoxy sulfonate phenylene vinylene) and viologen derivative [66].*

A viologen derivative conjugated with biotin quenches the fluorescence of the polymer. However, in the presence of avidine the quencher is removed from the polymer which, in turn, restores the fluorescence of the polymer (Figure 33) [67].
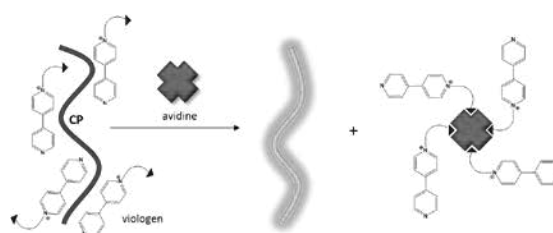

Figure 33: *Avidin biosensor [67].*

5.7.2 Conjugated polymers for inorganic species sensing

Conjugated polymers can be used as sensors for anions and cations. The main feature of this family of sensors is the great enhancement of sensibility. On the other hand the fact that the receptor is the polymeric matrix itself can be advantageous in terms of applications. The detection and quantification of anions are important in many fields ranging from medicine to the preservation of the environment. For instance, sensors for fluoride are of great interest in the detection of nerve gases as well as for the manufacture of nuclear weapons [66]. In 2002 Miyata and Chujo reported the use of an organic boron polymer that is sensitive to the presence of fluoride in chloroform. The interaction of the polymer with fluoride changes the boron hybridization from sp^2 to sp^3, which quenches the polymer emission (Figure 34) [68].
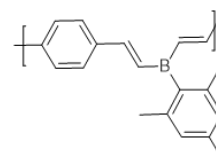

Figure 34: *Fluoride sensitive polymer, described by Miyata and Chujo [68].*

An alternative approach for fluoride sensing with polymeric sensors is predicated on the basicity of fluoride and its ability to form hydrogen bonds. Wang *et al*. in 2003 used this strategy to obtain a polymer derived from polyquinoleine, which could detect fluoride from dimethylsulfoxyde solutions. The presence of the anion produces a red shift of the fluorescence band [69]. The same group developed a series of copolymers containing fluorene and oxadiazole which showed a fluorescence amplification of more than 100 times upon addition of fluoride compared to the mon-

omeric sensor. This effect is ascribed to an increase in the number of binding sites along the polymer backbone. Such polymers display high selectivity for fluoride and are insensitive to other common anions such as Cl⁻, Br⁻, I⁻, BF_4^-, PF_6^- (Figure 35) [70].
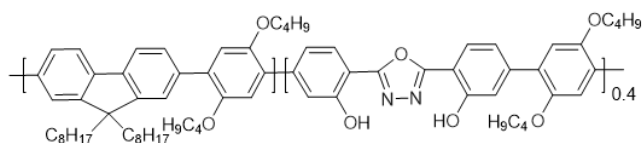

Figure 35: *Polymer described by Wang et al. with F⁻ selectivity (70).*

Cation selective sensors can be designed by the proper functionalization of conjugated polymers. In 2000, Swager and coworkers reported a potassium sensor which consisted of a poly(*p*-phenylene ethylene) containing peripheral crown ether. This system is based on the ability of 18-crown-6 ethers to form 2:1 complexes with the K⁺. Hence, the formation of the complex aggregates the polymer resulting in a redshift in the maximum absorption spectrum from 434 nm to 459 nm (Figure 36) [71].
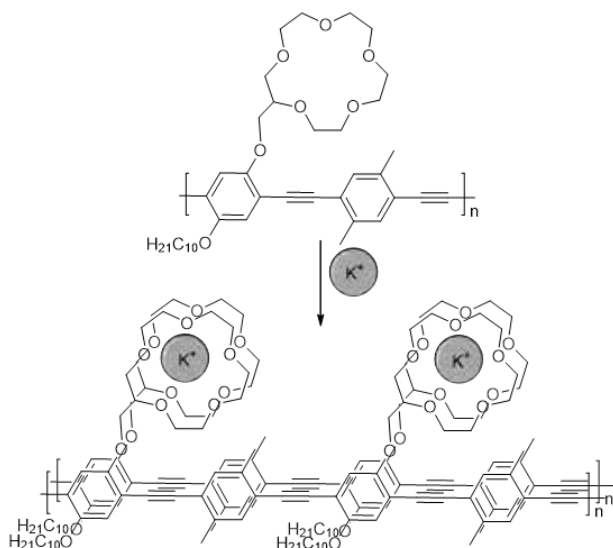

Figure 36: *Polymeric K⁺ sensor [71].*

Another important family of cation sensors developed is based on the incorporation of pyridine in the polymeric backbone. Pyridine containing polymers have been introduced as good sensors for cations, especially transition metal cations. In 2004, Wang *et al.* reported the design and preparation of a selective Pd^{2+} polymer (Figure 37) [66, 72].
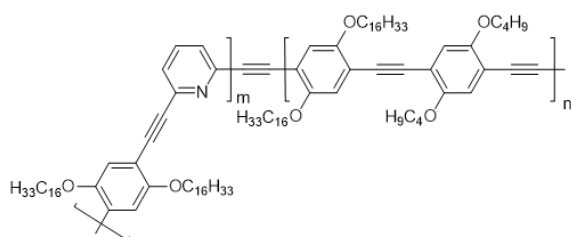

Figure 37: *Polymer described by Wang for detection of Pd^{2+} [66,72].*

6. CONCLUSIONS

The discovery of organic conductive materials by Heeger, Shirakawa and McDiarmid opened a new age in the field of Materials Science. In recognition to this achievement the three authors were awarded with the Nobel Prize in 2000. Since their pioneering work, research on conjugated polymers has become a major focus of attention due to their large number of applications, such as donor materials for solar cells, metal substitutive for conductive applications or as sensing devices in biosciences. Currently, an area of rapid growth is organic photovoltaics where conjugated polymers play a key role as electron donors. Although, a considerable effort has been devoted to this matter, still a number of problems remain to be addressed such as the morphology of the surface, the correct mixing of the donor and acceptor polymers and the efficient movement of the charge/hole formed during the light gathering. These factors have to be considered to obtain the maximum efficiency in solar cells. However, the future of the conjugated polymers is brighter than ever.

7. ACKNOWLEDGMENTS

8. REFERENCES

1. Street GB, *Polypyrrole: from powders to plastics.* In: Skotheim T.A., Ed. Handbook of conducting polymers, vol. I. New York: Marcel Dekker; 265-291, (1986).
2. Shirakawa H. Louis E.J., McDiarmid A.G., Chiang C.K., Heeger A.J.: *J. Chem. Soc*. Commun., 578-80, (1977).
3. Guimard N.K., Gomez N., Schmidt C.E.: *Prog. Polym. Sci*., **32**, 876-921, (2007).
4. Lee Y.H, Lee J.Y., Lee D.S.: *Synt. Met.*, **114**, 347-353, (2000).
5. Diaz A.F., Bargon J.,: Electrochemical synthesis of conducting polymers. In: Skotheim TA, editor. Handbook of conducting polymers, vol. I. New York: Marcel Dekker, 81–115, (1986).
6. Bao Y., Wang H., Li Q. Liu B., Li Q., Bai W. Jin B. and Bai R.: *Macromolecules*, **45**, 3394-3401, (2012).
7. Nguyen H.Q., Rainbolt E.A., Sista P., Stefan M.C.: *Macromol. Chem. Phys*., **213**, 425-430, (2012).
8. Cai T., Zhou Y., Wang E., Hellstrom S., Zhang F., Xu, S., Inganas O., Andersson M.R.: *Solar Energy Materials & Solar Cells,* **94**, 1275–1281, (2010).
9. Diaz A.F., Kanazawa K.K.: *J. Chem. Soc. Chem. Comm*., 635, (1979).
10. Allen A.J; Faulkner L.R. Electrochemical Methods, fundamental and applications; 2nd edition 2001, John Wiley and sons; New York
11. Nadeau J.M., Swager T.M.: *Tetrahedron*, **60**, 7141-7146, (2004).
12. Swager T.M., Samuel T.W.III, Guy J.D.: *Chem. Rev.*, **107**, 1339-1386, (2007).
13. Collier J.H., Camp J.P., Hudson T.W., Schmidt C.E.: *J. Biomed. Mater. Res.*, **50**, 574–584, (2000).

14. Bredas J.L., Electronic structure of highly conducting polymers.In: Skotheim TA, editor. Handbook of conducting polymers,vol. II. New York: Marcel Dekker; 1986. p. 859–913

15. Wenner F.: Bur. Stand. U.S. Bull. **12**, 469–478, (1915)

16. Schuetze A.P., Lewis W., Brown C. and Geerts W.J.: *Am. J. Phys*. **72**, 2, (2004)

17. Schroder D.K, *Semiconductor Material and Device Characterization* Wiley, New York, 1990.

18. Valdes L.B.: *Proceedings of the I.R.E.*, **42**, 420–427, (1954).

19. Allen A.J; Faulkner L.R.: Electrochemical Methods, fundamental and applications; 2nd edition 2001, John Wiley and sons; New York.

20. Gustaffson J.C., Liedberg B., Inganas O.: *Solid State Ionics*, **69**, 145, (1994).

21. Destriau G.: *J. Chim. Phys*., **33**, 587, (1936).

22. Mitschke U., Baèuerle P.: *J. Mater. Chem*., **10**, 1471-1507, (2000).

23. Burroughes J.H., Bradley D.D.C., Brown A. R., Marks R. N., Mackay K., Friend R. H., Burns P. L., Holmes A. B.: *Nature*, **347**, 539, (1990).

24. Salbeck J., Bunsenges B.: *Phys. Chem.,* **100**, 1666, (1996).

25. Gurunathan K., Murugan A.V., Marimuthu R., Mulik U.P. Amalnerkar D.P.: *Materials chemistry and physics,* **61**, 173-191, (1999).

26. Gustafsson, J.C., Inganas, O., Andersson, A.M.: *Synth. Met., 62*, 17, (1994).

27. Carlberg J.C., Inganas O.: *J. Electrochem. Soc.,* **144**, L61, (1997).

28. Sirringhaus H., Kawase T., Friend R. H., Shimoda T., Inbasekaran M., Wu W., Woo E. P.: Science, **290**, (2000).

29. Li G., Zhu R., Yang Y.: *Nature Photon., **6**, 153-161, (2012).

30. Tang, C. W. Multilayer organic photovoltaic elements. US patent 4,164,431, (1979).

31. Tang, C. W.: *Appl. Phys. Lett.,* **48,** 183–185, (1986).

32. Hummelen, J. C., Knight B.W., LePeq F., Wudl F., Yao Jie, Wilkins C.L.: *J. Org. Chem.,* **60**, 532–538, (1995).

33. Yu, G., Gao, J., Hummelen, J. C., Wudl, F., Heeger, A. J.: *Science,* **270,** 1789–1791, (1995).

34. Halls, J. J. Walsh JC.A., Greenham N.C., Marseglia E.A., Friend R.H., Moratti S.C., Holmes A.B.: *Nature,* **376**, 498–500, (1995).

35. Wudl, F., Srdanov, G.: Conducting polymer formed of poly(2-methoxy-5- (2'-ethylhexyloxy)-*p*-phenylene vinylene). US patent 5,189,136 (1993).

36. Park, S. H., Anshuman R., Beaupre S., Cho S., Coates N., Moon J.S., Moses D., Leclerc M., Lee K. Heeger A.J.: *Nature Photon. **3,*** 297–302, (2009).

37. Liang, Y. Y. Wu Y., Feng D., Tsai S.T., Son H.J., Li. G., Yu L.: *J. Am. Chem. Soc.,* **131**, 56–57, (2009).

38. Liang, Y. Y., Feng D. Wu Y., Tsai S.T., Li G.; Ray C., Yu L.: *J. Am. Chem. Soc.,* **131**, 7792–7799, (2009).

39. Chen, H. Y., Hou J.H., Zhang S., Liang Y., Yang G., Yang Y., Yu L., Wu Y., Li G.: *Nature Photon. **3,*** 649–653, (2009).

40. Roncali, J. *Macromol. Rapid Commun., **28,*** 1761, (2007).

41. Brisset H., Thobie-Gautier C., Gorgues A., Jubault M., Roncali J: *J. Chem. Soc., Chem. Commum.,* 1305, (1994).

42. Roncali J., Thobie-Gautier C. *Adv. Mater.*, **6**, 846, (1994).

43. Pei Q., Zuccarello G., Ahlskog, M., Inganas, O.: *Polymer, 35*, 1347, (1994).

44. Zhang Q. T., Tour J. M.: *J. Am. Chem. Soc., **120***, 5355, (1998).

45. Kitamura C., Tanaka S., Yamashita Y.: *Chem. Mater., **8***, 570, (1996).

46. Cheng Y.J., Yang S.H., Hsu C.S.: *Chem. Rev*., **109**, 5868–5923, (2009).

47. Van Mullekom H. A. M., Vekemans J. A. J. M., Meijer E. W.: *Chem. Commun.,* 2163, (1996).

48. Foulds N.C., Lowe C.R.: *J Chem Soc Faraday Trans*., **82**, 1259–1264, (1986).

49. Fu Y., Yuan R., Chai Y., Zhou L., Zhang Y.: *Anal. Lett*. **39**, 467–482, (2006).

50. Yamagishi F.G., Stanford Jr. T.B., VanAst C.I.: *Proc. Electrochem. Soc*., **18**, 213–223, (2001).

51. Kang S.K., Kim J.H., An J., Lee E.K., Cha J., Lim G.: *Polym J*., **36**, 937–942, (2004).

52. Collier J.H., Camp J.P., Hudson T.W., Schmidt C.E.: *J. Biomed. Mater. Res., **50***, 574–584, (2000).

53. Rivers T.J., Hudson T.W., Schmidt C.E.: *Adv. Funct. Mater*, **12**, 33–37, 2002

54. George P.M., Lyckman A.W., LaVan D.A., Hegde A., Leung Y., Rupali A.: *Biomaterials, **26***, 3511–3519, (2005).

55. Cui X., Hetke J.F., Wiler J.A., Anderson D.J., Martin D.C.: *Sensors Actuators A*, **93**, 8–18, (2001).

56. Cui X.Y., Martin D.C.: *Sensors Actuators B*, **89**, 92–102, (2003).

57. Xiao Y.H., Cui X.Y., Hancock J.M., Bouguettaya M., Reynolds J.R., Martin D.C.: *Sensors Actuators B, **99***, 437–443, (2004).

58. Abidian MR, Kim DH, Martin DC. *Adv. Mater., **18***, 405-409, (2006).

59. Li Y., Neoh K.G., Kang E.T.: *J Biomed. Mater. Res. A*, **73A**, 171–181, (2005).

60. Otero T.F., Sansinena J.M.: *Bioelectrochem. Bioenergy*, **42**, 117–122, (1997).

61. Tahhan M., Truong V.T., Spinks G.M., Wallace G.G.: *Smart Mater. Struct*. **12**, 626–632, (2003).

62. Spinks G.M., Xi B., Troung V.T., Wallace G.G.: *Synth. Met.*, **151**, 85–91, (2005).

63. Clarck L.C., Lyons C.: *Ann. NY Acad. Sci*., **102**, 29-45, (1962).

64. Gerard M., Chaubey A., Malhotra B.D.: *Biosensors Biolectron*., **17**, 345-359, (2002).

65. Tamiya E., Karube I., Hattori S., Sizuki M., Yokoyama K.: *Sensors Actuators*, **18**, 297-307, (1989).

66. Thomas III S.W., Joly G.D., Swager T.M.: *Chemical Reviews*, **107**, 1339-1386, (2007).

67. Chen L. McBranch D. W., Wang H.L., Helgeson R., Wudl F., Whitten D. G.: *Proc. Natl. Acad. Sci. U.S.A.,* **96**, 12287, (1999).

68. Miyata, M., Chujo, Y.: *Polym. J.,* **34**, 967, (2002).

69. Tong H., Wang L., Jing, X., Wang F.: *Macromolecules, **36***, 2584, (2003).

70. Zhou G., Cheng Y., Wang L., Jing X., Wang F.: *Macromolecules, **38***, 2148, (2005).

71. Kim J., McQuade D. T., McHugh S. K., Swager T. M.: *Angew. Chem., Int. Ed., **39***, 3868, (2000).

72. Huang H., Wang K., Tan W., An D., Yang X., Huang S., Zhai Q., Zhou L., Jin Y.: *Angew. Chem., Int. Ed.*, **43**, 5635, (2004).