



## Intrinsic Conducting Polymers: New age material for photovoltaic devices

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**Abstract :** Intrinsic Conducting Polymers (ICP) or simply conducting polymers have rejuvenated the scientists and engineers alike with possibility of ICPs in designing photovoltaic devices, to an extent that polymeric photovoltaics present the tantalizing possibility of producing coatings that function as sunlight-harvesting paints that can be directly applied on roofs or even as an integral part of fabrics to produce electricity. In this article, the principles behind generating the photovoltaic effect in conjugated polymers, present scenario, and the exciting possibilities envisioned in the field is discussed and reviewed.

**Index Terms - Intrinsic Conducting Polymers (ICP), Photovoltaics, Poly(p-phenylenevinylene), Polyaniline, Polythiophenes**

### I. INTRODUCTION

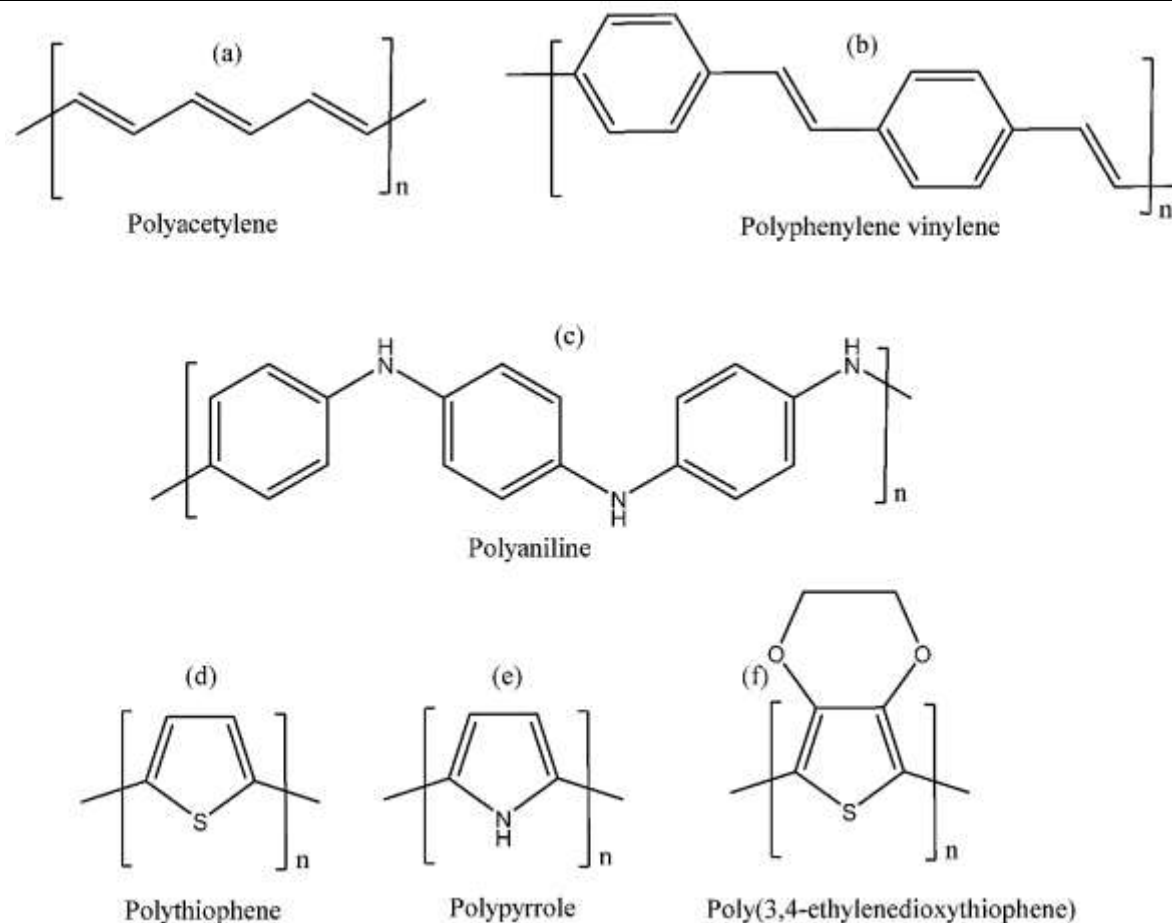
Energy starved humans are ever looking for new sources and materials for energy generation and storage. Last century witnessed the development of semiconductor based photovoltaic solar cells as an alternate source of energy, but with limitations in efficiency and portability. With onset of 21<sup>st</sup> century the discovery and development in Intrinsic Conducting Polymers (ICP) or simply conducting polymers have rejuvenated the scientists and engineers alike with possibility of ICPs in designing photovoltaic devices, to an extent that polymeric photovoltaics present the tantalizing possibility of producing coatings that function as sunlight-harvesting paints that can be directly applied on roofs or even as an integral part of fabrics to produce electricity. MacDiarmid, Shirakawa, and Heeger [1] brought the unique properties of conjugated polymers to the fore in 1977 when they discovered that chemical doping of these materials resulted in increases in electronic conductivity over several orders of magnitude. Ever since electronically conducting materials based on conjugated polymers or intrinsic conducting polymers have been applied in diverse usage such as sensors, biomaterials, light-emitting diodes, polymer actuators, and corrosion protection agents. In this article, the principles behind generating the photovoltaic effect in conjugated polymers, present scenario, and the exciting possibilities envisioned in the field is discussed and reviewed.

### Intrinsic Conducting Polymers

Intrinsic Conducting Polymers or conjugated polymers have a framework of alternating single and double carbon-carbon (sometimes carbon-nitrogen) bonds (Figure 1). Single bonds are referred to as  $\sigma$ -bonds, and double bonds contain a  $\sigma$ -bond and a  $\pi$ -bond. All conjugated polymers have a  $\sigma$ -bond backbone of overlapping  $sp^2$  hybrid orbitals. The remaining out-of-plane  $p_z$  orbitals on the carbon (or nitrogen) atoms overlap with neighboring  $p_z$  orbitals to give  $\pi$ -bonds.

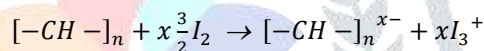
Although the chemical structures of these materials are represented by alternating single and double bonds, in reality, the electrons that constitute the  $\pi$ -bonds are delocalized over the entire molecule. For this reason, polyaniline (PAn) and poly(*N*-vinylcarbazole) (PVCZ) are considered to be conjugated polymers, with the nitrogen  $p_z$  orbital assisting the delocalization of the  $\pi$ -electrons. In some conjugated polymers such as polyacetylene (PA) and PAn, delocalization results in a single (degenerate) ground state, whereas in other polymers the alternating single and double bonds lead to electronic structures of varying energy levels.

The behavior of conjugated polymers is dramatically altered with chemical doping. As above described, the transition of  $\pi$ -conjugated polymer from insulator to metal is carried out by a “doping” process. However, the “doping” item used in conducting polymers differ significantly from traditional inorganic semiconductor [2]. Difference in “doping” item between inorganic semiconductors and conducting polymers are as follows: Intrinsic of doping item in conducting polymers is an oxidation (p- type doping) or reduction (n-type doping) process, rather than atom replacement in inorganic semiconductors. Using polyacetylene as a sample, for instance, the reaction of p- and n- doping is written as:

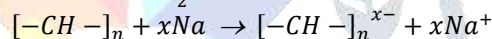


**Figure 1: Commonly used conjugated polymers in production of photovoltaic devices**

Oxidation with halogen (p- doping)



Reductive with alkali metal (n-doping):



It is the p-doped polymers that have wide applications in the electrochromic devices, rechargeable batteries, capacitors, membranes, charge dissipation, and electromagnetic shielding. Synthesizing and characterizing n-doped materials are comparatively less frequently explored.

## II. PHOTOVOLTAIC EFFECT IN INTRINSIC CONDUCTIVE POLYMERS

### *Photovoltaic semiconductors.*

For inorganic semiconductors, the mechanism of charge generation from incident photons is well established. Because these materials are typically crystalline solids, their electronic structure can be described in terms of energy bands. For an idealized semiconductor, the electronic structure consists of a conduction band and a valence band separated by an energy gap, the size of which depends upon the material. In the case of silicon, for example, the band gap is 1.12 eV, whereas for gallium arsenide, it is 1.4 eV. Although there are different types of band gaps (direct and indirect), for simplicity, we are restricting our discussion to materials with direct band gaps (optical transitions between free electrons and holes are allowed).

The band gaps of most semiconducting materials are typically between 0.1 eV and 2.2 eV, and as such are comparable to the energies of photons whose frequencies lie within (or just outside) the visible spectrum. It is energetically feasible, therefore, that an incident visible-light photon has sufficient energy to excite an electron from the valence band into the conduction band of the material. As a consequence of this single event, two charge carriers are produced - an electron in the conduction band and a hole in the valence band. Although the hole that is produced is simply an empty electronic state, which can be occupied by other electrons in the valence band, it behaves as though it is an independent carrier of positive charge.

### *Photovoltaic polymers.*

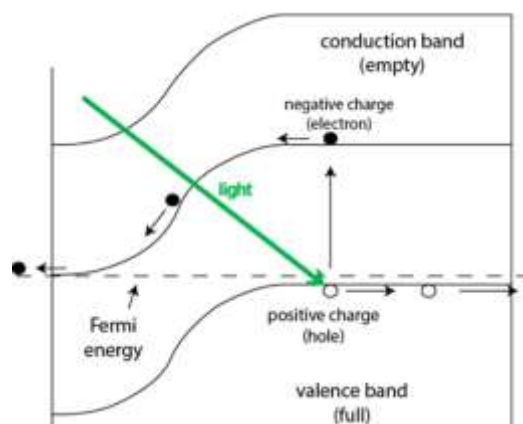
Conducting polymers also act as semiconductors, and their electronic properties appear to be analogous to those of inorganic semiconductors. It is important to note that ICPs lack the crystallinity required for the occurrence of energy bands as in the solid state. ICPs are almost amorphous, thus it is important to understand the mechanism of charge transport.

The characteristics of the  $\pi$ -bonds are the source of the semiconducting properties of these polymers. First, the  $\pi$ -bonds are delocalized over the entire molecule; and then, the quantum mechanical overlap of  $p_z$  orbitals actually produces two orbitals, a bonding  $\pi$  orbital and an antibonding  $\pi^*$  orbital. The lower energy  $\pi$ -orbital produces the valence band, and the higher energy  $\pi^*$ -orbital forms the conduction band. The difference in energy between the two levels produces the band gap that determines the optical properties of the material. Most semiconducting polymers appear to have a band gap that lies in the range 1.5 – 3.0 eV, which makes them ideally suited as optoelectronic devices working in the optical light range.

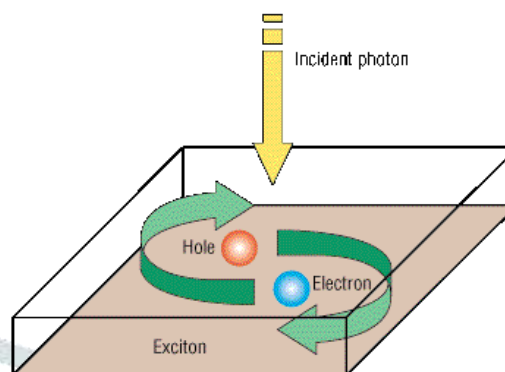
### Putting induced charges to work

The charge conduction mechanism appears to be more complex for conducting polymers than for inorganic semiconductors. Although the action of an incident photon on a conducting polymer excites an electron from the valence band into the conduction band, the resulting electron and hole are bound, and their motion through the material is coupled. These coupled moieties are known as excitons and are responsible for many of the electronic properties found in the most common and efficient polymer based electronic devices.

In conventional semiconductors, the excited electron and the resulting hole migrate freely to opposite electrodes, where they can do useful work in an electrical device (Figure 2). In a conducting polymer, however, the electron and hole that are generated by the incident photon are bound into an exciton (Figure 3).

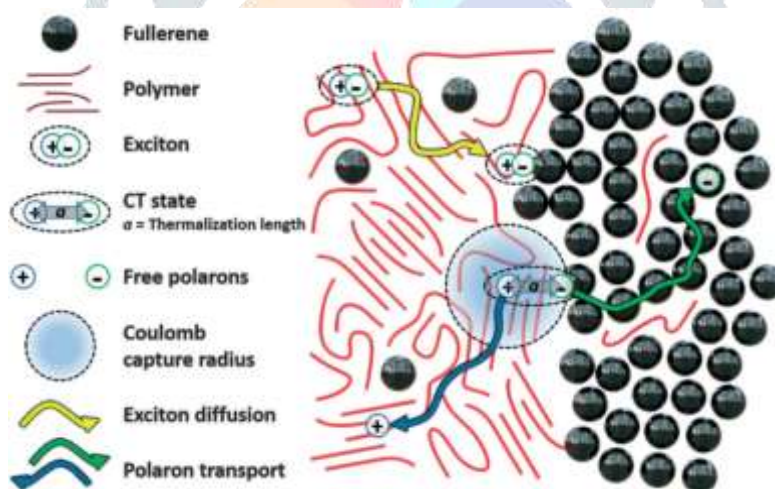


**Figure 2: Photovoltaic charge generation in a conventional semiconductor junction**



**Figure 3: Photo induced Excitons in the conjugate polymer interface**

How then, can we obtain any useful work from a conducting polymer if the electron and hole are not separated? It turns out that the bound exciton can be split at interfaces (Figure 4). The simplest interface is created at the junction between the electrode and the conducting polymer. Under open circuit conditions, holes are collected at the high work function electrode (indium tin oxide, ITO), and electrons are collected at the low work function electrode (aluminum). Indeed, the  $V_{oc}$  generated by these devices depends upon the work function difference between the two electrodes.



**Figure 4: Schematic of exciton dislocation, diffusion and charge separation processes in a polymer heterojunction active interface**

Unfortunately, the exciton-splitting process that occurs at a conducting polymer-electrode interface is not very efficient and is one of the causes of the low quality of early polymer photovoltaics. Another cause of the very low efficiencies of early devices is the effect of impurities, such as oxygen, which act as traps to the migrating excitons. Attempts to improve the efficiency of the exciton-splitting process led to the development of new conducting-polymer species that contained electron donating and electron-accepting species. By creating interfaces among conducting polymer molecules of differing electron affinities, it is possible to enhance the probability of electron transfer between molecules. This process (photoexcited charge transfer) causes the bound charges to separate, and the junction formed at the donor-acceptor interface is analogous to a semiconductor heterojunction.

These heterojunctions work very well at separating excitons that arrive at the junction. Unfortunately, the lifetime of excitons is short, and only excitons that are formed within  $\sim 10$  nm of the junction will ever reach it. This short exciton range clearly limits the efficiency of these photovoltaic devices. In an attempt to develop a more efficient photovoltaic structure, interpenetrating networks of electron-accepting and electron-donating polymers have been produced [3]. With these materials, the number of heterojunctions within the polymer blend is greatly increased, and thus the probability that an exciton will encounter a junction and be separated.

Research into polymeric photovoltaics is at a very early stage, but the results are encouraging. The best materials produced so far, using a polythiophene molecule as a hole-acceptor (to enhance the absorption of sunlight), have an energy conversion efficiency of 7% when irradiated with green light and about 2% in sunlight. Although these materials are currently much less efficient than their



silicon counterparts, they do produce much higher open-circuit voltages. By using calcium anodes (which need to be capped to prevent oxidation in the atmosphere) and an ITO cathode, open-circuit voltages greater than 2 Volts have been reported [4].

Silicon-based solar devices, on the other hand, have open-circuit voltages that are less than 1 Volt. The higher open-circuit voltages produced by the polymer-based devices mean that, compared with silicon cells, fewer polymer-based cells need to be cascaded together to obtain the same net output voltage. This may have significant advantages in certain low-power applications.

### III. DEVICE CONFIGURATION

Schottky devices have been made from conjugated polymers by several researchers [5]. These polymers include polyacetylene (PA), polythiophene (PTh), poly(2-vinylpyridine) (P2VP), PVCZ, poly(p-phenylenevinylene) (PPV), polypyrrole (Ppy), and polyaniline (Pan). In general, ITO-coated glass is coated with the polymer, which in turn is coated with aluminum (Figure 5a) or another low work function metal such as magnesium or calcium.

Heterojunction and p-n-junction devices can be configured in a similar fashion to Schottky devices, except that the polymer layer now consists of bilayers of a p-type polymer and a n-type polymer [6]. In addition, p-n junctions can be formed between n-type silicon and p-type conjugated polymers [7].

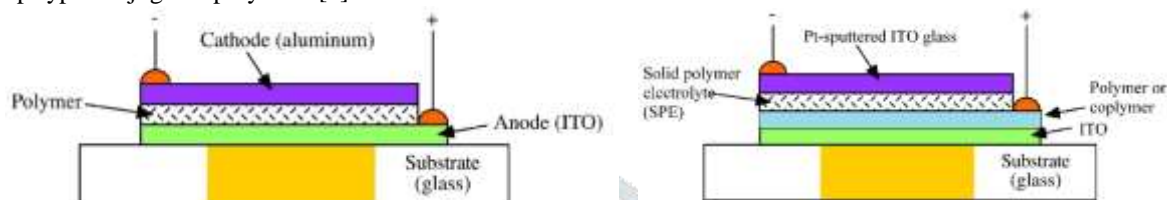


Figure 5 (a) Schematic Schottky photovoltaic device

(b) Figure 5b. Schematic photoelectrochemical device

Photoelectrochemical cells have been made from PPy [8] and poly-(3-methylthiophene) (P3MTh) [9]. The used configuration is illustrated in (Figure 5b). In this case, the polymer is coated onto the ITO-coated glass, and solid polymer electrolyte (SPE) is sandwiched between this polymer-coated electrode and a platinumized ITO-coated glass counter-electrode. A liquid electrolyte can be used instead of the SPE.

The level of oxidation in the inherently conducting polymer has a dramatic effect on the photovoltaic efficiency. Highly oxidized materials are the most conducting, but they are less photo-efficient (fewer excitons generated per photon absorbed). Fully reduced materials are highly resistive but the most photo efficient.

### IV PREVELENT ICPs FOR PHOTOVOLTAIC APPLICATION

Three classes of conjugated polymers have attracted attention for use in photovoltaic devices in recent years:

**1. Poly(p-phenylenevinylene)s PPV.** So far, most success has been achieved by using photovoltaic devices containing PPVs. As early as 1994, Marks and co-workers described the fabrication of PPV-containing photodiodes with a structure similar to Figure 5. The PPV layer was obtained by spin coating the sulfonium salt precursor and then heating the polymer to 250 °C in vacuo. These devices were capable of generating open-circuit voltages of ~1.2 V when aluminum and magnesium electrodes were used or ~1.7 V when calcium electrodes were used. Quantum efficiencies of ~1% were obtained at low-light intensity (0.1 mW/cm<sup>2</sup>).

As the overall efficiency of photovoltaic devices containing conjugated polymers is determined by the ability to generate excitons from incoming radiation, and then to separate these excitons at appropriate interfaces before they recombine. Given that typical exciton capture zones are limited to 10 nm or less, more efficient structures are needed. This stringent requirement led several workers to the idea that interpenetrating networks of donor (electron donating-hole accepting) and acceptor (electron accepting-hole donating) polymers should give better results.

One approach involves the use of functionalized PPVs [3]. The addition of cyano groups to a dialkoxy derivative of PPV forms the CN-PPV (Figure 6b), making it a better electron acceptor. Underivatized PPV is a good hole-transporting material. Using blends of MEH-PPV (Figure 6a), a soluble PPV derivative, as a hole transporter and CN-PPV as an electron transporter results in quantum efficiencies of up to 6%.

Even higher quantum efficiencies (up to 29%) with overall power conversion of ~2% (using a simulated solar spectrum) were obtained [4] using a modified organic solvent soluble polythiophene (Figure 7a) as the hole acceptor and a cyano derivative of PPV

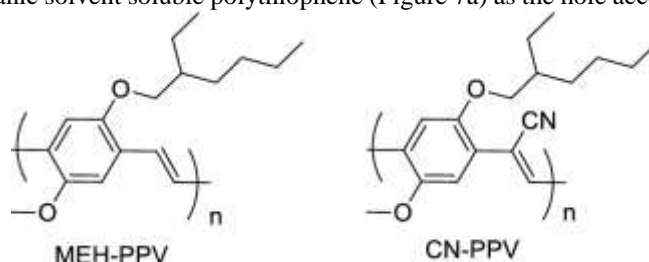
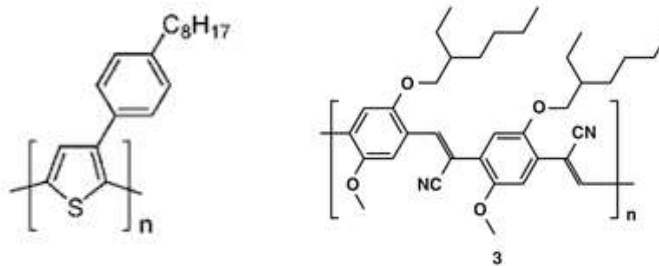


Fig. 6 Functionalized PPVs. (a) MEH-PPV (b) CN-PPV



7a. Polythiophene

7b. MEH-CN-PPV

**Figure 7. Structure of (a) POPT p-type and (b) MEH-CN-PPV n-type, polymer**

(MEH-CN-PPV) (Figure 7b) as electron acceptor. Perylene is another electron acceptor that increases the quantum efficiency to 6% [10]. An alternative approach uses  $C_{60}$  as the electron acceptor [11], giving a quantum efficiency of ~29% and an energy conversion efficiency of 2.9%.

**2. Polyanilines.** These are perhaps the most versatile of the ICPs with respect to processing options. Schottky barrier devices containing polyanilines have also been produced [12]. They can be made using either chemical or electrochemical oxidation accordingly. The electrochemical method can be used to produce thin films directly on conductive substrates such as ITO. The chemical method can be used to produce a material with the de-doped emeraldine base (EB) form soluble in solvents such as 1-methyl-2-pyrrolidinone (NMP) and some doped forms. The materials are doped with appropriate surfactants such as dodecyl benzenesulfonic acid (DBSA), camphor sulfonic acid (CSA), or p-toluenesulfonic acid (pTS), all of which are soluble in common organic solvents.

The dopant has a marked effect. Interestingly, acid doping increased the engineering conversion efficiency from 0.04% (undoped) to 0.57% poly-acrylic acid-(doped) to 0.88% (pTS-doped).

Polyaniline has been widely used in photoelectrochemical cells [13-15]. Early researchers [13] investigated the photoelectrochemical reduction of chloral ( $CCl_3CHO$ ) to trichloro ethanol ( $CCl_3CH_2OH$ ). Scientists used PAn electrodes to induce the photoelectrochemical reduction of peroxodisulfate [14]. Photocurrents generated at polyaniline are potential and electrolyte-dependent [15, 16].

**3. Polythiophenes.** The photoelectrochemical properties of PThs have also been of interest for some time [7, 17-19]. Their ability to electrodeposit regular structures with minimal impurities makes it possible to attain high photocurrents [17]. The photocurrents that can be attained using PTh based electrodes have been enhanced by using conjugated linkers to introduce electron acceptors to the PTh chain [18].

The electron-accepting NO<sub>2</sub> group facilitates charge separation upon irradiation, resulting in sustained photocurrent. More recently, a photoelectrochemical cell that uses a solid polymer electrolyte based on poly(ethylene oxide) (PEO) was described. Quantum efficiencies of up to 0.6% could be achieved [9].

Semenikhin et al. have presented evidence that irradiation causes photoelectrochemical dedoping of poly(3-methylthiophene) or polybithiophene [19], and it is known (see later) that the level of doping influences the magnitude of the photovoltaic effect observed. There is at least one reference to the use of polythiophenes to create p-n-junction devices [20]; however, no data on efficiency are given.

## V. RFUTURE PROSPECTS OF ICPs BASED PHOTOVOLTAICS

There is room for improvement in various areas, perhaps best identified by returning to the steps involved in the generation of the photovoltaic effect:

1. exciton creation
2. exciton diffusion
3. electron transfer to charge transfer complex,
4. electron-hole separation in built-in field
5. carrier transport to electrodes
6. electron transfer at electrodes
7. and electric power.

Yoshino et al. have considered these steps and suggested that  $\eta$  (energy conversion efficiency) can then be expressed as a product of five terms [21].

$$\eta = \frac{N_{exc}}{N_{ph}} \frac{N^{e-h}_{ct}}{N_{exc}} \frac{N^{e-h}_{free}}{N^{e-h}_{ct}} \frac{eV_{oc}}{h\nu} FF = \alpha(\omega) \Phi_{ex} \phi_{e-h} \xi_{en} FF$$

where

- $N_{exc}$  = number of electron-hole pairs (excitons)
- $N_{ph}$  = number of photons
- $N^{e-h}_{ct}$  = number of interfacial composite charge transfer (ct) excitons
- $N^{e-h}_{free}$  = number of excitons that undergo charge separation
- $eV_{oc}$  = electrical energy
- $FF$  = fill factor
- $\alpha(\omega)$  = efficiency of photon collection

$\Phi_{ex}$  = the quantum efficiency of the excitonic dissociation  
 $\phi_{e-h}$  = quantum yield of free electrons in acceptor parts and holes in donor parts  
 $\xi_{en}$  = energetic factor  
 $eV_{oc}/h\nu$  (is the fraction of absorbed photon energy that can be converted to electrical energy)

Yoshino and co-workers discussed, the most room for improving polymeric photovoltaics lies in improving  $\xi_{en}$  and the fill factor. They suggest the use of selective p- and n-doped donor-acceptor networks in which absorption and primary charge separations occur in undoped parts, and charge collection is by p-i and i-n fields. (The intrachain junctions created by p-doping donor regions are p-i junctions. Likewise, i-n junctions are created by n-doping the acceptor regions.) Spectral sensitization by an excitonic antenna molecular component M, which has  $h\nu$  absorption close to the charge transfer gap, can improve the  $\xi_{en}$  factor. Thus, there is a need to have high light-collection efficiency, and to have order: at the molecular level if photogeneration and charge transport are to be efficient, and at the meso level if short distances between the site of irradiation and charge collection are to be realized (e.g., interpenetrating networks). These requirements pose some exciting challenges and present some fascinating opportunities

**High-light collection efficiency.** It is not surprising that there are few reports of attempts to improve the light-collection efficiency of conjugated polymers, given that the fundamental processes in polymer photovoltaic cells are still not well understood. In this regard, particular consideration needs to be given to the possibility that the most appropriate structure for exciton formation may not be the same as that for hole or electron transport. In addition, light absorption affects the polymer structure. For example, it has been reported that illumination of p-doped polythiophenes leads to its reduction or further undoping [19].

Two approaches to improving the high light-collection efficiency of polymeric photovoltaic devices could, therefore, be considered. A separate excitonic or dye layer can be used in the device. This approach effectively mimics that taken in liquid-junction photovoltaic cells [22], in which a light-harvesting dye is attached to a thin film of nanocrystalline  $\text{TiO}_2$ . The efficiency of these titania cells is fundamentally affected by how well the dye is bound to the semiconductor. This will also be important for dye-conjugated polymer devices.

Scientists have constructed a solid-state photocell with octaethylporphyrin, the light-harvesting or excitonic layer, sandwiched between a phenylene vinylene donor layer and fullerene acceptor layer [21]. Although the photo-current intensity is somewhat enhanced over the cell without porphyrin, a significant improvement is the wider spectrum obtained using conducting electroactive polymers (CEPs). There appear to be two different mechanisms of photo-induced illumination: from the donor side or from the acceptor side. This suggests that both donor-porphyrin and acceptor-porphyrin regions are contributing to charge generation.

The light-harvesting dye could be covalently attached to either the donor or acceptor material in the device. A wide variety of light-harvesting functionalities could be attached to the conjugated polymer. Thus, attaching conjugated substituents could enhance the light absorption of the polymer. For example, nitrostyryl side chains have been introduced into polythiophenes and shown to improve photoconductivity [23]. We have investigated photocurrent generation with similar styryl polythiophenes having photocurrent a range generation of donor and was acceptor observed groups for these Some polymers variation over in a the range of poised potentials, although this may have resulted from charge transport effects rather than enhanced exciton formation.

Alternatively, known dyes such as porphyrins and bi pyridyl metal complexes have been attached to conjugated polymer precursors [24, 25]. There are few reports at this time, however, of the preparation of the functionalized conjugated polymers and their use in photovoltaic devices.

**Order at the molecular level.** The synthetic approach used to produce the conducting polymer of interest determines the degree of order in the resulting material. A number of synthetic routes for polythiophenes have been shown to result in stereoregular polymers. The best known of these are the McCulloch and the Rieke methods using alkylated thiophenes [26].

The starting materials are also important. Using oligomers can have a dramatic effect on the polymerization potential required. In fact, it is necessary to use at least monosubstituted thiophenes if the overoxidation of the polymer is to be avoided during the polymerization process. It is known that polymers grown at more extreme potentials are more susceptible to introduction of defects, and that lowering the potential by starting even with bithiophene results in higher yield and greater regularity in the polymer structure [27].

Others have shown that the particular electrochemical method used for polymerization is also important. For example, using pulsed potential methods produces more crystalline polymer materials. Substituents attached to the thiophene monomer can lower the oxidation potential [28] and also, as is evidenced in the Reike and McCulloch methods [26], play an important role in inducing order. In addition to the alkylated monomers often used for this purpose, other researchers including Ochiai et al. [29] have attached chiral groups to the thiophene backbone.

The choice of dopant incorporated into the CEP during synthesis is another important aspect in inducing order [30]. This is most vividly illustrated with the polyanilines. Certain dopants, including CSA and DBSA, induce a structure that is more amenable to secondary doping, changing the polymer conformation from a tight coil to an expanded coil with a concomitant increase in conductivity. MacDiarmid and co-workers [31] introduced the concept of secondary doping and demonstrated the effect using m-cresol. More recently [32], we have shown that more "friendly" compounds such as thymol or carvacrol can generate the same effects.

Certain dopants have even been used to induce chirality in the polyaniline backbone. For example, using one enantiomer of camphor sulfonate is believed to induce helicity with a predominance of one enantiomer in polyaniline [33]. Chirality can also be induced in sulfonated water-soluble polyanilines using acid-base pair interactions [34].

Creating a highly efficient interpenetrating polymer network containing light harvesting molecules ensures efficient exciton generation, and the high interfacial nature of the polymer provides a means for separating and transporting the charge. The chemical and physical properties of all polymeric components therefore must be such that they are compatible (they do not phase-segregate) to enable formation of these efficient interpenetrating networks.



## VI. CONCLUSION

### *Promising prospects of ICP photovoltaics*

ICP polymers can exhibit electron-hole conduction similar to conventional semiconductors, an effect that is enhanced by chemical doping. Electrical currents are produced by separating the electron-hole pairs. This is done by forming interfaces between materials having different ionization potentials and electron affinities. Interfaces are created by superimposing layers of metals, inorganic oxides, and polymers, or by creating interpenetrating polymer networks. Although the best photovoltaic polymers produced so far are less efficient than their silicon counterparts, they produce much higher open-circuit voltages. Polymers are being developed that use dyes to increase light collection efficiency. Polymerization methods are being developed that increase the structural order, producing more efficient charge transport properties. Perhaps in near future, you can convert the outside of your house into one big solar collector using photovoltaic polymer paint.

## VII ACKNOWLEDGMENT

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