Advancements in the Synthetics and Applications of π -Conducting Poly (arylene vinylene) Materials: Mini review

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Advancements in the Synthetics and Applications of π -Conducting Poly(arylene vinylene) Materials: Mini review

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Abstract: *Lately, organic semiconductor materials have become essential in creating a more pleasant atmosphere for humanity. Thus, it is important to develop unfamiliar, high-performing conjugated materials. A summary of the most recent developments in the synthesis of poly-arylenevinylenes (PAVs), such as poly-phenylenevinylenes (PPVs). Furthermore, there are three main categories for the synthetic methodologies: P-Quinodimethane Intermediates Polymerization by an anionic and free radical mechanism in protic and non-protic solvents, Olefin Metathesis Polymerizations via living ROMP and Acyclic-Diene Metathesis (ADMET), and C-C Coupling Polymerizations by using three different techniques such as Mizoroki-Heck coupling, Suzuki coupling and Stille coupling. Ultimately, this overview offers a few different potential applications for PPVs, exemplified by the electroluminescence properties of PPVs which utilized in light-emitting diodes and organic solar cells.*

Keywords: Poly(arylene vinylene)s; Quinodimethane Intermediates; Metathesis; C-C Coupling; potential applications.

1. INTRODUCTION

Over the past decade. Multiple research teams have focused a significant amount of emphasis on the framework and implementation of novel π-conjugated organic semiconductors (OSCs) because of their promising semiconducting electronic components applicable to diverse opto-electronic uses and Functions in electrochemical systems [1-3], Examples include polymer light-emitting diodes (PLEDs)[4,5], organic-field-effect-transistors (OFETs) [4,6]and organic solar-cells (OSCs)[4,7]. Studying conjugated polymers (CPs) has been improving since the mid-1970s when doped polyacetylene was shown to be capable of excellent conductivity[8,9]. Scientists promptly shifted to alternating conjugated backbones although polyacetylene shows great potential because of the material's poor processability and low stability in ambient conditions, Fig. **1**, shown the heterocyclic such as thiophene, pyrrole, and furan, along with aromatic rings like benzene, were utilized as fundamental components in place of polyenes that exhibit a degenerative ground state[10,11].

Furthermore, employing units that alternately give (donor: **D**) and withdraw (acceptor: **A**) electrons along the polymer chain is one of the best strategies for lowering the optical and electrochemical band gaps of conjugated polymers[12,13], So, by increasing the degree of electron delocalization, which is achieved by raising the structure's coplanarity, the band gap is reduced[12,14]. In certain cases, intramolecular charge transfer (ICT) occurs during the excited state.

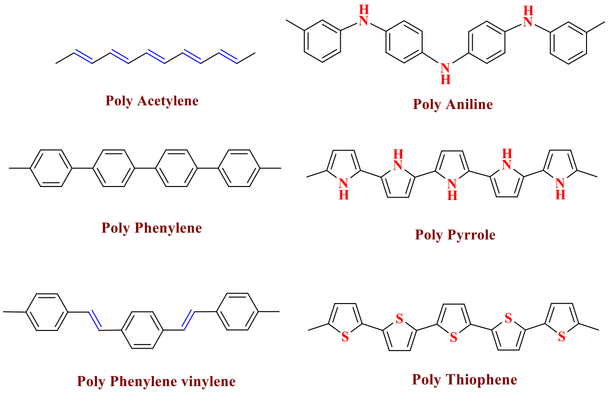


Fig.1.Example of some conjugated polymers.

However, in this specific scenario, the excited electron becomes distributed across regions with a deficiency of electrons[12,15]. Donor materials made of polymer derived from poly-thiophenesvinylenes (PTPVs)[4,10], poly-carbazolevinylenes (PCZVs), and poly-phenylenevinylenes (PPVs) derivatives are often used[4,12]. To achieve high power conversion efficiency (PCE) in device production above 5%, an **A**, which includes 1-(3-methyloxy carbonyl)propyl-1-phenyl-[6,6]-C_{61} (PCBM), a modification of a C_{60} derivative, pairs with such polymers[16].

Furthermore, there are many reasons why poly-thienyl vinylenes (PTVs) is gaining popularity. For instance, it is a stiff and CP with excellent temperature stability. The donor moiety of the thiophene rings enhances the stability of A-doped derivatives by lowering the chemical potential-ionized complexes., preventing reduction by water vapor, when doped, PTHV exhibits greater capacitances than poly (*p*-phenylene vinylene)[17]. These building blocks exhibit strong electrical and thermal stability, as well as outstanding electro-optical properties.

Over and over, in polymer electronics, PPVs occupy a distinct historical position as they were the first polymer employed in the creation of a PLED. In 1990, PPV demonstrated yellowish-green electro-luminescence’s (EL) in a basic aluminum/PPVs/indium tin oxide (ITO) diode[18]. Also, Fig. **2**, the PCZVs that The PCZVs that were established on carbazole units attached at the 3,6-positions have been the subject of much research due to the simplicity of production of the polymers and starting moiety[19].

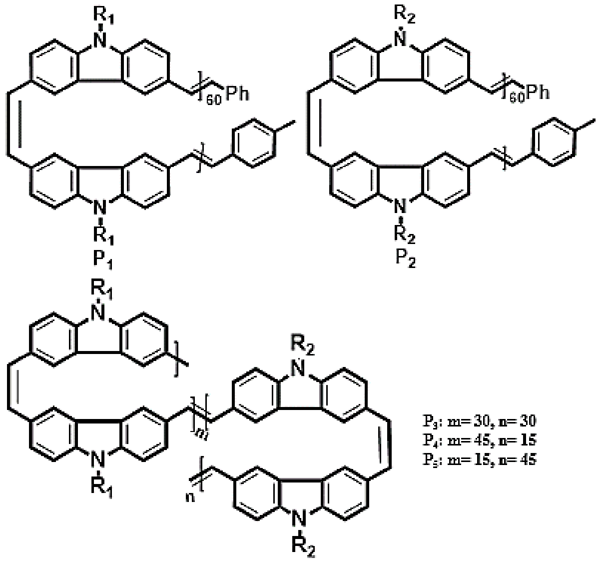


Fig.2. The homopolymers P_1 and P_2 and block copolymers P_3-P_5 by ROMP. (**R₁** = $-C_8H_{17}$, **R₂** = $-(CH_2CH_2O)_3CH_3$)[20].

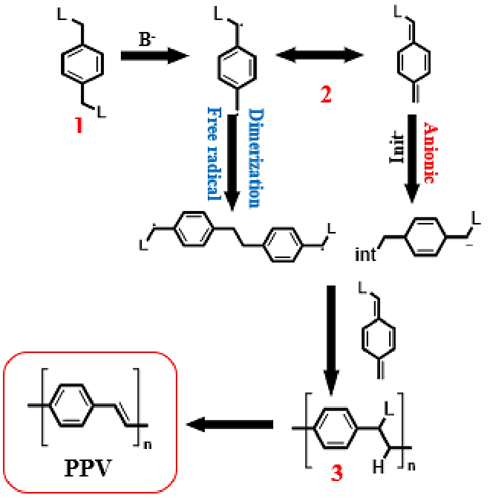
This review focusing on various synthetic route of PPVs and their electroluminescence characteristics, possible uses for these materials include organic solar cells and PLEDs, demonstrating their adaptability to a variety of optoelectronic devices. The goal of ongoing development is to broaden the application range of OSC technology.

2. SYNTHETIC ROUTES OF POLY (ARYLENE VINYLENE)S

Like many other CPs and non-CPs[20,21], PPV can be efficiently synthesized using a variety of various methods. The polymerization process can have a significant impact on the characteristics of the polymeric material, especially its electrical properties, even though we frequently believe that polymers made by various methods have the same chemical structure.

2.1 *P*-Quinodimethane Intermediates Polymerization

The different techniques of polymerization of cycophandienes based on PPV and PCZV contain interesting intermediates. Now let's explore it, **(a)** Reaction mechanism: *P*-quinodimethane is the active propagating monomer in all precursor methods. It is produced *insitu* by mixing a base with an appropriate precursor monomer solution. Regarding *p*-xylene, it is modified by suitable leaving-group (LG) at the α and α' positions to produce premonomer **1**, as for the basic medium, the driving force for the elimination process was the 1,6 position to afford the *α*-substituted quinodimethane **2**, After being polymerized to form the α-substituted poly-xylylene intermediate **3**, it can afterwards be eliminated to produce PPV, examined in-depth via Junkers et al[3,22]. **(b)** Variations: The propagation step was determined by an anionic or free radical mechanism and preferred based on the solvent environments[23-25]. Scheme **1**, 1st in protic solvents inhibit the anionic route, which causes radical polymerization. Additionally, 2nd aprotic-polar solvents and strong basic medium facilitate the development of anionic chains. As well as initially identified as an incidental reaction that generates small molecules during radical polymerization[12,26].



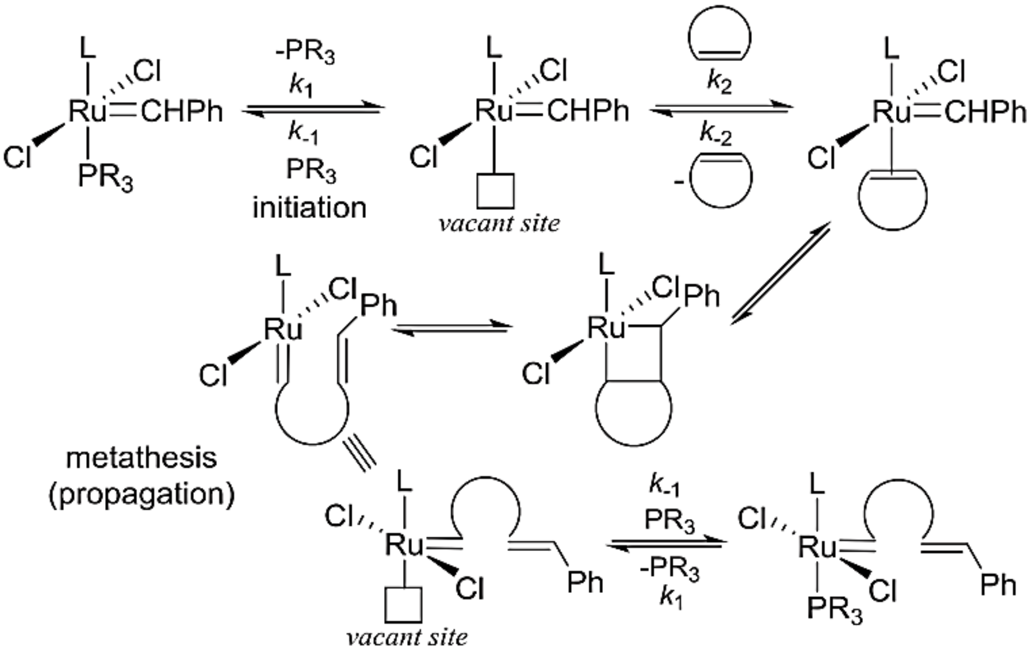
Scheme. 1. Polymerization of PPV by radical and anionic pathway[27].

2.2 Polymerization of Olefin via Metathesis

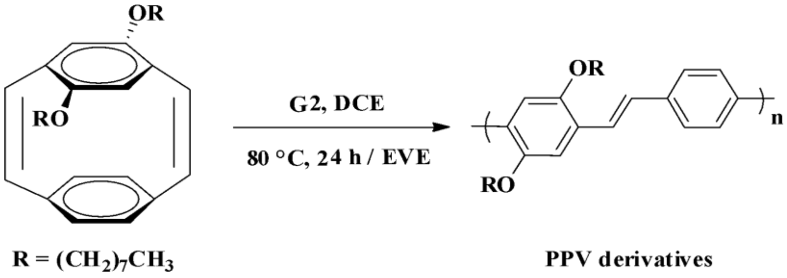
A variety of numerous organic molecules being synthesized (bases, fine chemicals, medicines, etc.) as well as polymeric and advanced components has been acknowledged to benefit from olefin metathesis, and it is commonly recognized that metallic-carbene (alkylidene) complexes are essential to this catalysis[27].

2.2.1 Polymerization via Ring-Opening-Metathesis (ROMP)

Ring strain becomes key to ROMP[25,28], as shown in scheme **2**. The living ROMP, an improvement on olefin metathesis, is an effective technique for creating polymers with controllable forms, sizes, and activities. Grubbs-2nd generation of ruthenium complex-catalyst are extensively employed in this method for the manufacture



Scheme. 2. General ROMP mechanism based on active ruthenium-carbene catalysts[28].



Scheme. 3. The Grubbs 2nd Generation Catalysts to afford the PPV[29].

of co-polymers through random or block and the final modification of derivatives of PPV[8,20,30], scheme **3**.

2.2.2 Acyclic Diene Metathesis (ADMET) Polycondensation

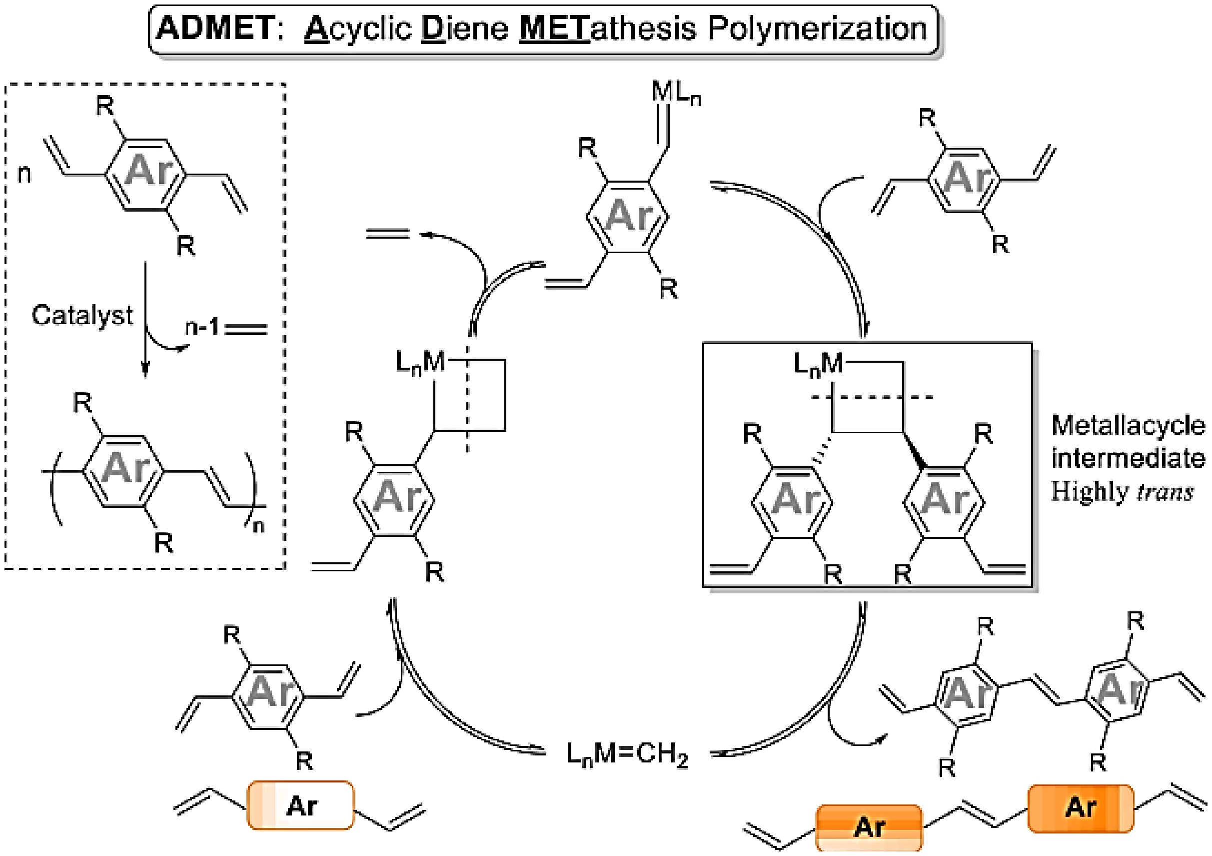
Scheme **4** shows the fundamental reaction mechanism of ADMET polymerization of divinyl aromatics (divinylbenzene, etc.), which is a condensation polymerization that progresses accompanied by formation of ethylene [31]. Due to the steric bulk of the metallacycle intermediate, there is an equilibrium in this catalysis, and the olefinic double bonds in the resulting polymers/oligomers extremely exhibit trans. Even if the first methods for ADMET polymerization (of substituted divinylbenzenes) produced combinations of oligomers [31,32].

2.3 Polymerization via Pd-Catalyzed C-C Coupling

Significant developments in metal-catalyzed cross-couplings have transformed synthetic organic chemistry in recent decades[12,13]. The power of those processes to facilitate interactions among sp^2-C was simplified assembly of trend conducting molecules. Researchers can investigate novel characteristics by combining easily produced halo- and metallo-arenes. Olefinic moieties remain viable in these processes despite their more challenging production, creating additional opportunities the rigid material drying has been shown to alleviate the problem of chain termination, even though these polymerizations are often susceptible to proto-dehalogenation, de-borylation, and de-metallation[33].

The Pd-catalyzed C-C couplings, especially the ones that involve aromatic donors, there is apprehension regarding the interchange of aromatic moieties between the metallic atom with the associated tri-hydrogen phosphide PH_3 act as a ligand[12]. This side reaction resulted in the integration of PH_3 centers into the polymer backbone of poly-phenylenes. However, this phenomenon has not been extensively investigated in the PPV[34].

Another challenge stems from the propensity of catalysts made of soluble metals to aggregate and form nano-molecules[35]. These nanoparticles have a major impact on field-effect transistor mobility and light-emitting and photovoltaic device performance at concentrations below 1%. The necessary sensitivity can be achieved through impedance evaluations and X-ray fluorescence[35,36], even if conventional organic chemistry instruments like NMR spectroscopy and UV/Vis/IR spectrophotometry



Scheme. 4. Basic ADMET condensation polymerization mechanism[31].

are not sufficiently sensitive to detect such low impurity levels. Although the palladium nanoparticles cannot be eliminated by traditional precipitation techniques, but by agitating the resultant mixture with azo-thioformamide at room temperature, the metal is dissolved by complexation and makes selective polymer precipitation possible[37,38]. Alternatively, palladium-supported graphite (Pd/C) eliminated aryl exchange with phosphine ligands and successfully decreased contamination by a factor of 100–1000[39].

2.3.1. Mizoroki-Heck coupling polymerization in comparison with Suzuki coupling polymerization

PPV is the product of the coupling based on Heck reaction for CTCP. In contrast to previous cross-coupling processes, monomer preparation is simple since this approach does not need monomer metalation[40]. The Heck-coupling polymerization has been reexamined recently as an arylation-direct synthesis method that is both atom-efficient and ecologically benign[41]. Heck processes-coupling mechanism is different from that of Suzuki processes-coupling and other cross processes-coupling. Following eliminative reduction in Pd-catalyzed Suzuki CTCP, a Pd (0) complex, referred to as (**a**), with three vacant coordination sites is formed. After coordinating with the π-bond orbitals of the polymeric back bone, this complex migrates to the end carbon-halogen bond of the extended monomer-moiety[3,12,42]. In contrast to other cross-coupling processes, carbopalladation and β-hydrogen elimination result in the formation of a triple co-ordinated Pd (II) complex called (**b**) in The Heck-coupling polymerization. CTCP can go forward if reduction removal of hydrogen halides from **2** is achieved with coordination of the polymeric back bone. Intermolecular transfer of **1** will take place, nevertheless, if reductive elimination occurs following **2** diffusion into the reaction mixture as a result of **2** poor coordination ability, and the synthesis of PPV via step-growth polymerization using the polymerized Heck processes-coupling with $tBu_3PPd(Ar)Br$ as a unfamiliar possibility for CTCP Scheme **5** [43].

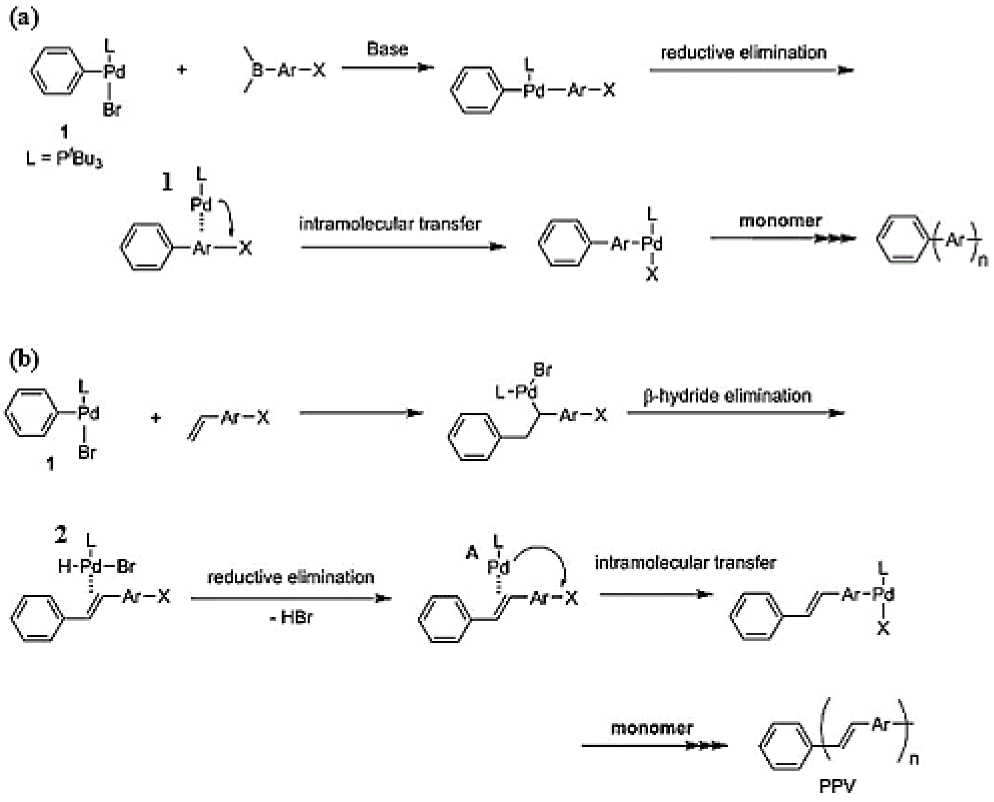
2.3.2. Stille coupling polymerization

Scheme **6** illustrates how PPV can be smoothly and modularly developed from 1,4-Diiodotetrafluorobenzene **4** and easily purchased 1,2-bis(tributylstannyl)ethylene **5** through the use of this polycondensation technique[3,43]. As well as the catalyst of $Pd(X)_4$ was prepared *in situ* via from $Pd_2(dba)_3$ and $AsPh_3$ to afford $Pd(AsPh_3)_4$[3,44]. The Stille polycondensation method yields PPV with a molecular weight that is typically less than 1000 kg/mol and is heavily influenced by the circumstances of the reaction.

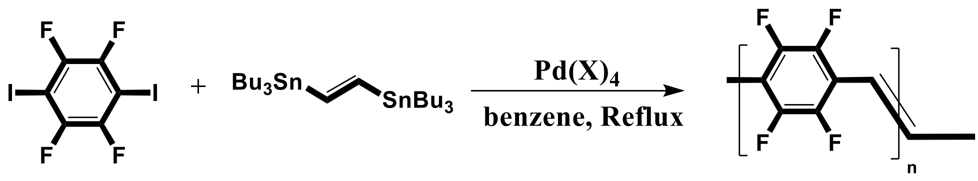
3. SOME APPLICATION OF PPVs

3.1. The use of PPVs in light-emitting diodes and their electroluminescence properties.

Polymer molecules are widely recognized for their ability to insulating[45]. On the other hand, adding conductive polymers (CPs), facilitated by the doping process, has revealed a range of additional characteristics. These newfound properties enable CPs to serve diverse purposes in today’s world[46]. Electroluminescence is among the notable features of CPs[47]. In 1989, a Cambridge research group achieved a significant milestone by developing a light-emitting diode (LED) using conducting polymers, this highlights the utilization of PPVs as a material for PLEDs[18,25].



Scheme. 5. Comparison polymerizations between (a) Suzuki process-coupling and (b) Heck process-coupling and have a suggested Pd-CTCP mechanism[43].



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Scheme. 6. Still coupling polymerizations through Pd catalyst[44].

PPV-based display units offer advantages over conventional technologies such as cathode ray tubes and liquid crystal displays. These advantages include superior mechanical features, adaptability for wide and curvy surfaces, and simplicity of processing. For example, PPV's extensible polymer chains allow for tensile strength that is comparable to aramid fibers[47,48].

Fig. **3**, illustrates the operating idea of an EL-technology. The single emissive layer of EL CPs between two electrodes allows holes and electrons from the connections between the electrodes to enter when an electrical field operates to it[49,50]. The interaction between these pairs of positively and negatively charged particles causes the emission of light particles (photons). Within the structure of PPV, a hole migrates more quickly than electrons. As a result, the recombination of holes and electrons happens in close proximity to the cathode.

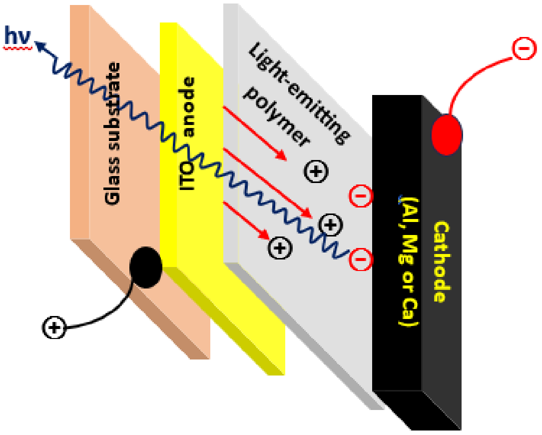

Fig. 3. An expanded design illustration of a typical single layer EL methodology[50].

3.2. Organic Solar cells

Organic solar cells made from polymers provide cost-effectiveness, ease of processing, and superior mechanical qualities compared to traditional solar cells.

Fig **4**, solar cells composed of [6,6′]-phenyl-C_{60}-butyricacid methylester (PCBM) and poly[2-methyloxy-5-(3,7-dimethyloctyloxy)]-*P*-phenylenevinylene (MDMO:PPV) has demonstrated excellent efficacy[51,52]. Poly(3-hexylthiophene-2,5-diyl) (P_3HT) and MEH-PPV are dopant-free hole-transporting materials (HTMs) used in hybrid solar cells, as well as methylammonium lead iodide perovskite and This yielded a power efficiency of 9.65%[53,54]. Additionally,

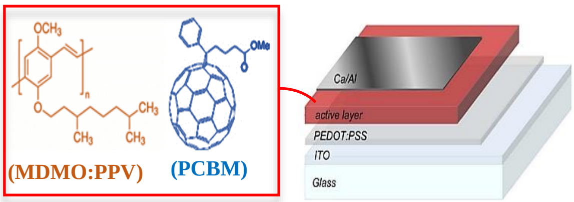

Fig. 4. Configuration of the investigated solar cells, which are organic (MDMO-PPV) cells[53].

OSCs were created using the co-polymer PPE-PPVs, which had electron poor moiety as non-fullerene and anthracene as the electron rich. However, when compared to the cell using the fullerene acceptor PCBM, these solar cells produced lower photovoltaic results[55].

4. CONCLUSION

To sum up, the creation of poly (arylene vinylene)s is an active area in the study of organic semiconductor materials, motivated by the need to develop cutting-edge materials for a wide range of technological uses. The development of synthetic methodologies such as C-C coupling polymerizations by using three different techniques such as Mizoroki-Heck coupling, Suzuki coupling and Stille coupling, olefin metathesis via living ROMP and Acyclic-Diene Metathesis (ADMET), and *p*-quinodimethane intermediates polymerization has made it possible to create novel polymeric architectures. with PPVs being a prominent example, these materials show intriguing qualities for use in optoelectronic devices. Organic solar cells can benefit from its exceptional electroluminescence, which also makes it a good fit for light-emitting diodes.

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