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Movement of new direction from conjugated polymer to semiconductor composite polymer nanofiber

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Abstract: In the past few years, there was a tremendous growth in conjugated polymer nanofibers via design of novel conjugated polymers with inorganic materials. Synthetic routes to these conjugated polymers involve new, mild polymerization techniques, which enable the formation of well-defined polymer architectures. This review provides interest in the development of novel (semi) conducting polymers, which combine both organic and inorganic blocks in one framework. Due to their ability to act as chemosensors or to detect various chemical species in environmental and biological systems, fluorescent conjugated polymers have gained great interest. Nanofibers of metal oxides and sulfides are particularly interesting in both their way of applications and fundamental research. These conjugated nanofibers operated for many applications in organic electronics, optoelectronics, and sensors. Synthesis of electrospun fibers by electrospinning technique discussed in this review is a simple method that forms conjugated polymer nanofibers. This review provides the basics of the technique and its recent advances in the formation of highly conducting and high-mobility polymer fibers towards their adoption in electronic application.

Keywords: cadmium sulfide; conjugated polymer; fluorescent enhancement; nanofibers; quenching; sensing.

1 Introduction

Polymer is a large molecule composed of repeating structural monomer units, which are covalently bonded to each other. The monomers must contain functional groups or at least double bonds, which help to afford the covalent linkage between the repeating units and form the polymer chains. Because of being easily molded and their low-density properties, polymers are shown to have various attractive applications in the field of electronics, such as light emitting diodes (LED) (Burroughes et al. 1990), photoluminescence (Nibedita 2007), plastic laser (Tessler et al. 1996), and light-emitting electrochemical cells (Pei et al. 1996). Most of the polymers are easy to synthesize, and they are relatively inexpensive. Based on the chemical structure and arrangement of polymers, various physical structures such as liquid, rubber, amorphous glass, crystalline rubber or glass, and liquid crystalline thermosets are observed for suitable applications. Conjugated polymers are important as sensing materials for heavy metal ions through fluorescence quenching via stern Volmer behavior (Peng et al. 2015). The application of fluorescent-conjugated polymers as versatile sensory materials has been proven particularly attractive for environmental applications during the past decades because of high analyte sensitivity and ease of measurement. Fluorescent chemosensors based conjugated polymers have been developed, which can be used to detect metal ions and biological species. The quenching sites are typically generated through the integration of coordination sites, such as bipyridyl (bpy), terpyridyl (tpy), and quinoline groups (Thomas et al. 2007). When the polymer moved to polymer nanofibers, wide variety of applications available ranges from biomaterials, textiles, to tissue culture. These kinds of functional nanofibers recently emerged, which contain conjugated polymer and inorganic hybrid nanostructure. It has been proven that nano dimension of conjugated polymer possesses blue shifted absorption band due to bending and kinking of polymer backbone. Moreover, the red shifting of absorption occurs due to relatively relaxed and ordered conformations. The properties of nanofibers depend not only on composition but also on their structure, phase, shape, and size distribution. The nanosized materials with well-defined shapes are important for the success of bottom-up approaches towards future nanodevices. Nanodevices have potential applications in nanoelectronic devices, nano optical devices, and chemical sensors (Osterloh et al. 2003).

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To the best of our knowledge, there is no review article on conjugated polymer with metal sulfide nanofibers where photophysical interactions have been discussed. Based on the emerging field of conjugated polymer nanofiber, in this present review, we describe the conjugated polymer and its photophysical interaction with semiconducting metal sulfide nanofibers. Development of π-conjugated polymers remains a frontier area of research to design optoelectronic, photovoltaic, and light emitting devices based on energy and charge transfer process. We highlight the history, structure, properties (mainly band gap), various types, and mechanism of conjugated polymer. Different types of phenylene vinylene based donor-acceptor and its applications are discussed. We also discussed the photophysical (absorption, photoluminescence, band gap, and energy transfer) properties of conjugated polymer for interpreting electronic studies. This is directed towards polymer nanofiber and describes about preparatory technique using electrospinning with varying size and property. Such understanding will enable us to construct polymer nanofiber for suitable applications such as nanoelectronic, biomedical, and sensing applications.

2 Conjugated polymer

A conjugated polymer contains alternating single and double C-C bonds, and its highly conductive nature emerges (Skotheim and Reynold 2007). The possession of good optical and electronic properties makes conjugated polymers excellent alternatives for inorganic materials. These polymers have low density, ease of fabrication, stability, and good flexibility. Conjugated polymers have gained more importance due to their theoretically interesting properties and technologically promising future. Pi bonds are formed by the P_z orbitals in carbon atoms, which are perpendicular to the molecular plane and overlap with adjacent P_z orbitals. The delocalization of the π-electrons in the conjugated polymer is the major source of the semiconducting properties over the entire polymer moiety (Kushida et al. 2016).

As determined from quantum mechanics, electronic delocalization for the polymer structure is generated from two energy bands such as highest range of electron energies called valence band and lowest range of vacant electron termed as conduction band. In the presence of sufficient energy, an electron can jump from the valence band (lower energy) to the conduction band (higher energy), which creates electron in the conducting band and a hole in the valence band. The band gap of the conjugated polymer lies in the range of 1.5–3.0 eV for an electron transition. The conjugated polymers are becoming more interesting owing to their inherent electrical and optical properties in the field of chemosensors and photovoltaic devices (Keshtov et al. 2016) and display technology of organic light-emitting diode (OLED) (Mitschke and Bauerle 2000).

2.1 History of conjugated polymer

In 1862, polyaniline (MacDiarmid et al. 1987) was first discovered by H. Letheby, who called it aniline black. This is obtained by the oxidation process of aniline under warm condition (Huang et al. 1986). Aniline black can be used for dyeing and printing. Poly(sulfurnitride) (SN)x has high conductivity with good electrical properties, which is useful for inorganic explosive. In the presence of Ziegler-Natta catalysts, the polymerization of acetylene to polyacetylene chain is carried out successfully (Natta et al. 1958). Chiang et al. doped the resultant polyacetylene with strong acceptors (I_2 or AsF_5) and increased the conductivity significantly. A Japanese chemist, Shirakawa, explained a new way to regulate the ratio of cis-trans isomers. A highly crosslinked and extremely irregular product of acetylene can be polymerized in the presence of copper containing catalysts known as cuprene.

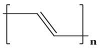
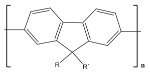
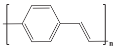
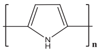
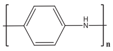
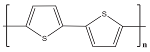
2.2 Structure of conjugated polymer

The structure and conductivity of few conjugated polymers are shown in Table 1. As can be seen in Table 1, alternated conjugated double or triple segments are providing p-orbital to overlap continuously, which is highly needed to make intrinsic conducting polymers. Conjugated polymers are leading to replace the metal in the way of charge carriers and orbital system. This is used to create free movement of electrons to make electronically more conductive.

2.3 Properties of conjugated polymer

The essential properties of conjugated polymers originate from their unique electronic structure. In the simple band structure scenario, the overlapped π orbitals form a valence band, whereas π* orbitals form a conduction band (Figure 1). The band gap, E_g, between these two bands is greater than 1 eV, which acts as an insulator. Chemical process of oxidation (i.e. removal of electrons from

Table 1: Structure of conjugated polymers with their physical properties.

Polymers (conductivity discovered)	Structure	Band gap (eV)	Conductivity (S/m)	Uses	References
Trans-polyacetylene (1977)	 1	1.5	10^5	Organic conductor	Shirakawa et al. 1977
Polyfluorene (1993)	 2	3.2	10^4	Insulator	Fukuda et al. 1993
Poly(*p*-phenylene-vinylene) (1979)	 3	2.5	10^{-3}	LEDs	Wnek et al. 1979
Polypyrrole (1979)	 4	3.1	10^2	Photoluminescence	Kanazawa et al. 1979
Polyaniline (1980)	 5	3.2	6.28×10^{-9}	Electronic devices	Diaz and Logan 1980
Polythiophene (1983)	 6	2.0	$10–10^3$	Solar cells	Waltman et al. 1983

the valence band) or reduction of a conjugated polymer (i.e. addition of electrons to the conduction band) has a great impact on the electronic structure and the conductive properties of the resulting conjugated polymer. Conjugated polymers are more flexible and susceptible to the structural distortion due to their polymeric nature and low dimensionality. The optoelectronic with mechanical properties of the conjugated polymers are particularly fascinating in the field of electronics industry. So, the polymers are used in various applications such as OLEDs, optical devices, photovoltaic devices, and chemosensor. Band gap is used to decide the application of the particular conjugated polymeric material. Larger band gap of poly(p-phenylene) is 3.0 eV, which absorbs more UV-light and dissipates the visible and infrared light in the solar radiation. Low band gap of polythiophene and polythiazole may be fitted for photovoltaic application. Advantages of organic conjugated polymers over metals include outstanding mechanical properties, flexibility, processability, and the wide array of accessible synthetic structures that allow one to tune the absorption, emission, conductivity, and other functionalities to improve their properties (Facchetti 2011).

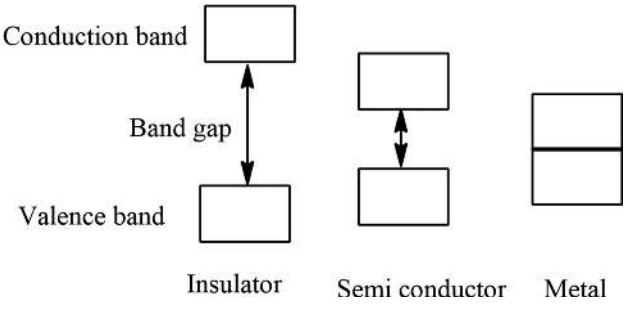


Figure 1: Electronic properties of solid state materials.

To increase the conductivity of conjugated polymers, the valence band has to be partially filled to the Fermi level, i.e. the band gap should adjust to zero. Minimizing the bond length of conjugated polymers resulted to reduce the band gap of the conjugated polymer. If the distance between carbons in the polymer backbone is identical and all the electrons can be delocalized along the backbone, the polymer would be metallic with no band gap. Reduction of the bond-length alternation can overcome the gap opening induced by "Peierls effect" and thus increase the conductivity of conjugated polymer. The first narrow band gap of semi-conducting polymer is invented as poly(isothia naphthene) (PITN).

The conjugated poly(phenylene vinylene)s (PPVs) are composed of alternating paraphenylene and alkene units with interesting properties such as solid-state packing, linear structure, and strong fluorescence. The flexible alkyl or alkoxy substitutions in PPVs side chains increase the solubility and crystallinity of the polymers. The molecular packing of the PPV backbone in the solid state is influenced by the side chains, which affect the electronic structure of the conjugated systems. The optical and electronic properties of the conjugated polymers can be tuned by the side chain structure.

2.4 Band gap

The electronic band has been formed because of the continuous interaction between atomic orbitals (Figure 2). Throughout the complete series of atoms, the electrons are delocalized in each orbital. The range of delocalization and the bandwidth are determined by using the strength of interaction between the overlapping orbitals. The band gap structure of the conjugated polymers is observed from the interaction between the pi-orbitals of the repeating units. Both polyphenylene vinylene and polythiophenes have relatively large optical band gaps and are not able to utilize the near-IR photons, which limit the performance of the corresponding devices. Basic one-dimensional (1D) quantum mechanics shows that larger pi-conjugation will lead to smaller energy band gap. Novel strategies must be developed to have a better control over the band gap and energy levels. Two major structural designs are developed for lower band gap of the conjugated polymer: (i) stabilizing the quinoid resonance structure and (ii) utilizing donor-acceptor interactions (Cheng et al. 2009).

As compared to aromatic form, the quinoid form has a smaller band gap but is energetically less stable because quinoid structure requires destruction of the aromaticity and a loss in the stabilization energy. It is demonstrated that the quinoid form can be stabilized by fusing another aromatic ring to the polymer backbone. The band gap of the conjugated polymer can also be modulated by the donor-acceptor (D-A) approach. The idea is to use alternating electron donating (D) and electron withdrawing (A) units to modulate the band gap of the polymer, also known as “D-A” conjugated polymer.

2.5 Conjugated polymers

Conjugated polymers are classified based on its structure, nature, and conductivity. In this section, few conjugated polymers based on polyacetylene, polyaniline, polypyrrole, poly(carbazole), poly(quinoline), poly(quinoxaline), poly(pyrazine), and poly(*p*-phenylene-vinylene) are discussed. Table 2 represents the essential conjugated polymers, which are used for various applications.

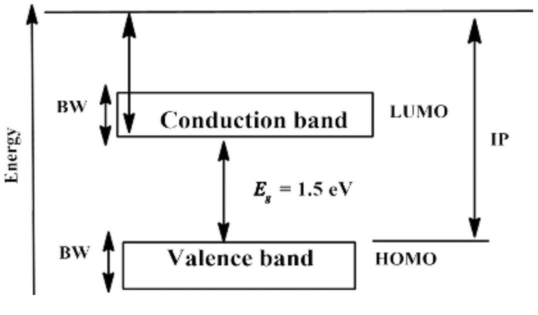
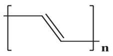
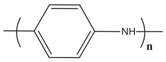
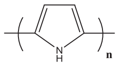
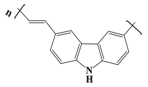
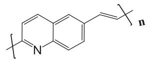
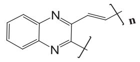
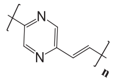
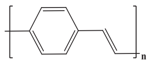


Figure 2: Detailed band structure showing the energy band gap and associated parameters.

Table 2: Various representatives of conjugated polymers.

Chemical name	Structure
Trans-polyacetylene	 7
Polyaniline	 8
Polypyrrole	 9
Poly(carbazole)	 10
Poly(quinoline)	 11
Poly(quinoxaline)	 12
Poly(pyrazine)	 13
Poly(*p*-phenylene-vinylene)	 14

2.5.1 Polyacetylene

Polyacetylene is obtained by polymerization of acetylene into a black insoluble powder using zeiglar Natta catalyst with high molecular weight. In 1970, Shirakawa et al. used titanium as catalyst instead of zeiglar Natta catalyst to synthesize polyacetylene as homogenous layer. In the process of doping, polymers can become highly conductive by the insertion or injection of electrons. Partial oxidation (p-doping) with electron acceptors (e.g. I_2, AsF_5) in the polymer chain or partial reduction (n-doping) with electron donors (e.g. Na, K) requires the charge carriers. Polaron, bipolaron, and soliton are few examples of charged defects in the polymer chain, which could be available as the charge carrier.

Table 3: Cis and trans form of polyacetylene.

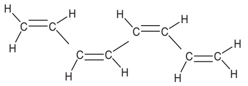
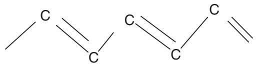
Polyacetylene	Structure	Conductivity σ (273 K) ($\Omega^{-1}cm^{-1}$)
Cis-polyacetylene	 **15**	1.7×10^{-9}
Trans-polyacetylene	 **16**	4.4×10^{-5}

Table 3 represents the *cis* and *trans* forms of polyacetylene (**15, 16**). Around 85% of the positive charge is delocalized over 15 C-H units to give a positive soliton in the I_2-doped *trans*-polyacetylene. During doping process, insulator or semiconductor type of polymer has conductivity in the range of 10^{-10} to 10^{-5} Scm^{-1}, which is near to metallic conducting segment (1–10^4 Scm^{-1}). Iodine-doped polyacetylene (>10^{-5} Scm^{-1}) has higher conductivity, compared with undoped polyacetylene (MacDiarmid et al. 1984).

2.5.2 Polycarbazole

Because it possesses prominent photoconductive properties, polycarbazole is used as host material, with a combination of active layers in OLEDs and with TiO_2 in dye-sensitized solar cells (DSSCs). In the polycarbazole structure, reactive secondary amine presents at the 9-position and can be modified using a number of side chains. Grignard reaction is used to synthesize poly(3,6-carbazole) using palladium or nickel in several pathways. The solubility and processability of the polymeric materials depend on the nature and length of the side chains on the nitrogen in polycarbazole. Due to good hole transporting properties, polymers with 3,6-carbazole exhibited several interesting performance in the field of LEDs (Yin and Feng 2015). Poly(3,6-carbazole) has been invented as the first device for blue light emission due to its short conjugation length. Table 4 shows the optoelectronic values of few poly(carbazole) derivatives (**17–19**).

2.5.3 Polyquinoline

Polyquinoline is known as an intrinsic n-type semiconducting polymer, which showed outstanding mechanically and optically clear film-forming property (Agrawal and Jenekhe 1996). It is an attractive candidate for electron transporting material due to the high electron affinity of the quinoline moiety. Incorporation of vinylene linkages in the polymer backbone results in the increasing band gap between quinoline rings. Few polyquinolines were revealed as significant materials for the production of photo light-emitting diodes (PLEDs) and electroluminescence (EL) (Jeqou and Jenekhe 2001). With the literature background, quinoline functionalized polymers (**20–22**) with their HOMO/LUMO and band gap values are shown in Table 5.

Table 4: Polycarbazole related conjugated polymer.

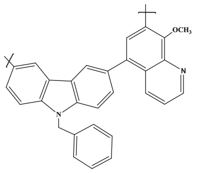
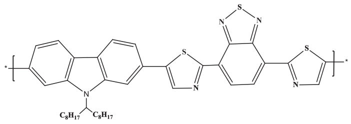
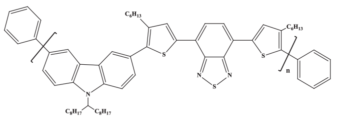
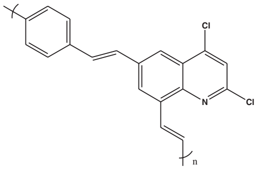
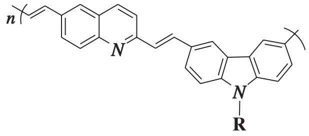
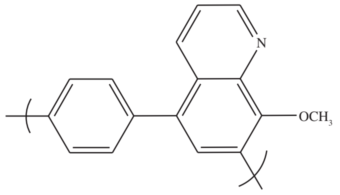
S. no	Chemical structure	HOMO/LUMO	Band gap	References
1	 **17**	5.14/−1.06	4.08	Tang et al. 2003
2	 **18**	−5.54/−3.56	1.98	Lee et al. 2011
3	 **19**	−5.45/−3.56	1.89	Kim et al. 2011

Table 5: Polyquinoline related conjugated polymer.

S. no	Chemical structure	HOMO/LUMO (eV)	Band gap (eV)	References
1	 **20**	−6.64/−4.09	2.55	Karpagam and Guhanathan 2014
2	 **21**	−6.36/−3.75	2.61	Upadhyay and Karpagam 2016
3	 **22**	−5.29/−1.47	3.82	Deng et al. 2017

2.5.4 Polyquinoxaline

Polyquinoxaline is an effective electron acceptor and able to constitute intramolecular charge transfer (ICT) with donor molecules. Due to high electron affinity and electron withdrawing nitrogen atoms present in polyquinoxalines, they were found to be useful as n-type building block (Huang et al. 2006). Polyquinoxaline has been effectively used for the electron-transport component for OLEDs (Wang et al. 2009). Poly(5.8-quinoxaline) has relatively high electron affinity (Ered) = –2.00 V versus Ag/Ag+), and the backbone of the polymer is easily decorated with flexible side chains to afford soluble analogues. Several quinoxalines containing donor-acceptor alternating copolymers have been explored in efforts to prepare low band gap and electroluminescent materials. Quinoxaline-substituted donor-acceptor (D-A) polymers have been developed, and they are a promising material in photovoltaic application and were successfully incorporated in small molecules and polymers as the electron transport component in OLEDs. Few common examples of quinoxaline containing conjugated polymers are listed in Table 6.

2.5.5 Polypyrazine

Polypyrazine acts as an electron acceptor and plays an important role to induce luminescence properties with pyrazine-based electron-deficient unit (Ying et al. 2014). Functional pyrazines have been mainly developed due to their broad optical absorption, bright photoluminescence, and bipolar characteristics. There is a growing interest in the design and synthesis of pyrazine enriched with functional chromophores to enhance optical and charge transporting properties. For example, pyrazine derivatives such as thienopyrazine and pyridopyrazine are mostly applied as electron-deficient monomers for low band gap polymers, which exhibited promising performance in polymer solar cells (PSCs) (Qin et al. 2012). Moreover, small organic molecules contain pyrazine moiety, such as pyrazino[2,3-g]quinoxaline and thiadiazolo[3,4-g]-quinoxaline, and have developed as efficient fluorophores for LEDs. By the proper combination of the donor-acceptor units, light-harvesting ability, charge carrier mobility, and condensation structures can be easily tuned. Therefore, it is very necessary to explore a novel pyrazine-based acceptor unit and investigate their structure-property relationship. Pyrazine-based conjugated polymer is represented in Table 7. Pyrazines containing carbazole hybrids are interesting due to their excellent emission and thermal properties.

2.5.6 Poly(p-phenylene vinylene)

PPV is one of the most important classes among various conjugated system, which is first introduced in LED. In this study, phenylene vinylene analogue was used as

Table 6: Polyquinoxaline related conjugated polymer.

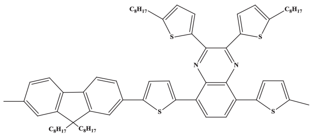
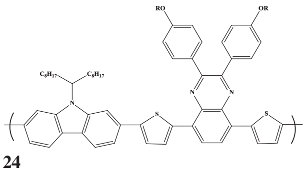
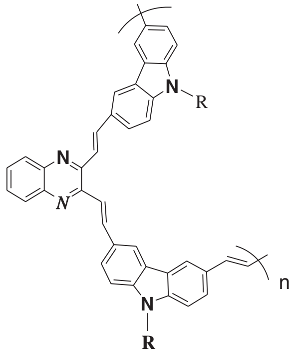
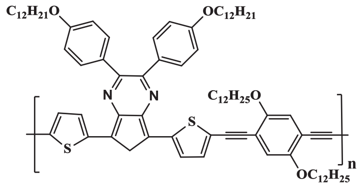
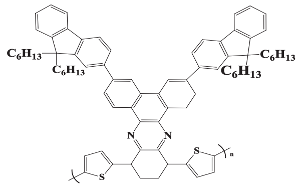
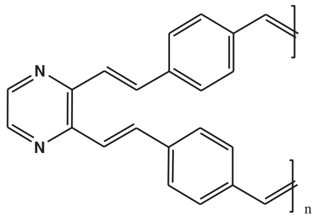
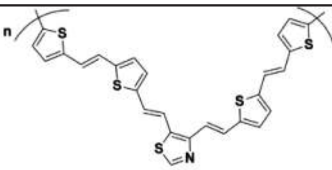
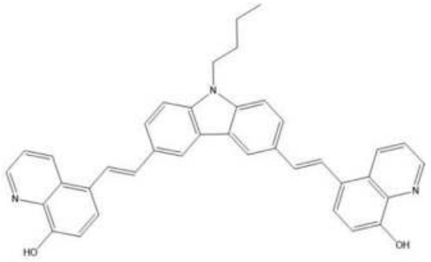
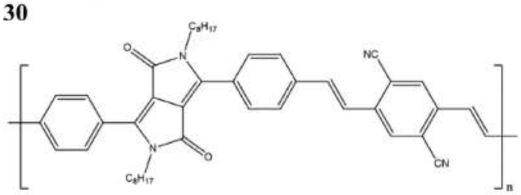
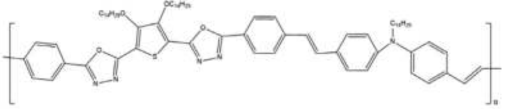
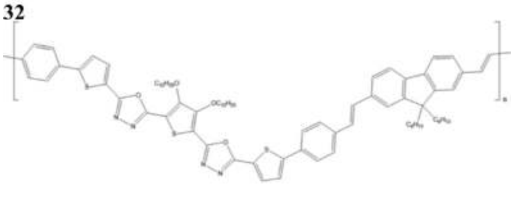
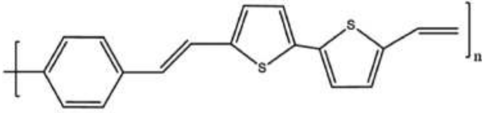
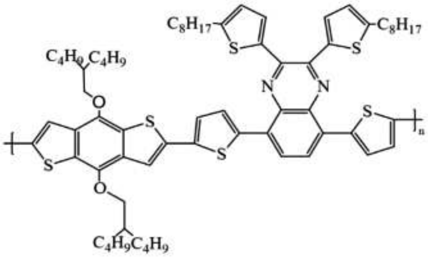
S. no	Chemical structure	HOMO/LUMO	Band gap	References
1	 23	4.34/2.46	1.88	Zhang et al. 2011
2	 24	5.34/3.33	2.01	Lee et al. 2011
3	 25	−5.57/−3.24	2.33	Upadhyay and Karpagam 2017

Table 7: Polypyrazine related conjugated polymer.

S. no	Chemical structure	HOMO/LUMO	Band gap	References
1	 PPE-DTTP 26	−4.64/−3.31	1.33	Qin et al. 2012
2	 27	−5.93/2.28	1.49	Wang et al. 2013
3	 28	Not calculated	2.53 (optical band gap)	Karpagam and Guhanathan 2012

transparent thin films for electroluminescent devices (Zhang and Zhu 2010). Chemical and electronic structure of such compounds can be easily modified in order to tune their optoelectronic properties. Wessling et al. developed the first route for PPV with rigid-rod microcrystalline structure. By using the Wessling method, the soluble derivatives of PPV such as poly(2-methoxy-5-(2′-ethyl-hexy1oxy)-*p*-phenylene vinylene) have been synthesized. PPVs are mechanically strong, highly crystalline, and environmentally stable due to low solubility towards atmospheric oxidation. PPVs are having limited application in the field of organic devices. Such class of materials with good stability, processability, and electrical and optical properties has been more on focus after the discovery of electroluminescence in PPV. Poly(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene) (MEH-PPV) acts as a promising laser dye due to its high fluorescence efficiency in solution (Gupta et al. 2015). Various poly(phenylene vinylene) structures are shown in Table 8. Poly(thiophene) and its derivatives **(29)** are synthesized through multistep reactions using Wittig reaction. Under the irradiation of UV light, all the polymers emitted bluish-green fluorescence with optical band gap (E_g) value of 1.55 eV. The ionization potential (HOMO) and electron affinity (LUMO) of energy levels are determined as −5.45 eV and −3.9 eV, respectively, (Mahesh and Karpagam 2016). A novel conjugated ligand 3,6-bis(8-hydroxyquinoline-5-propenyl)-N-butyl-carbazole **(30)** is synthesized using Wittig reaction (He et al. 2009). The number average molecular weight (M_n) of the carbazole-based conjugated polymer is 3800 Da from GPC analysis. Both the polymeric complexes emitted blue luminescence at 473 and 513 nm in DMSO solution and blue/green luminescence at 522 and 531 nm in solid state, respectively. The thermal stability of the polymer has shown the initial decomposition temperature at above 250°C. This literature proved that this kind of polymers is suitable for OLEDs application.

Table 8: Few examples of poly(p-phenylene vinylene) (PPV) conjugated polymer.

S. no	Polymer
1	 **29**
2	 **30**
3	 **31**
4	 **32**
5	 **33**
6	 **34**
7	 **35**

Using well-known Wittig condensation reaction, two novel diketopyrrolopyrrole (DPP) and p-phenylene vinylene alternating copolymers, poly(1,4-(2,5-dicyno)-phenylenevinylene-alt-2,5-dioctyl-3,6-bis(4-vinylenephenyl) pyrrole (3,4-c) pyrrole-1,4-dione) **(31)** and poly(1,4-(2,5-diethoxy)-phenylenevinylene-alt-2,5-dioctyl-3,6-bis(4-vinylenephenyl) pyrrole (3,4-c) pyrrole-1,4-dione), are synthesized (Qiao et al. 2010). They showed good solubility in organic solvents, possessed moderate molecular weight, and had well-defined structures and polydispersities. The optical band gap is 2.05, and the HOMO and LUMO are observed as −5.82 and −3.33 eV, respectively. These data indicate their potential use as red emissive materials in polymer light-emitting diodes (PLEDs). Vishnumurthy et al. (2011) synthesized diphenyl amine moiety carrying donor-acceptor **(32)** through Wittig polymerization reaction (Vishnumurthy et al. 2011). They showed good solvatochromic behavior in various organic solvents and good thermal stability. These new polymers showed good nonlinear optical (NLO) properties due to greater extent of delocalization in the molecules and were considered to be important materials in electronic applications such as photonic LEDs. By using Wittig reaction, a novel fluorine-oxadiazole based donor-acceptor (D-A) conjugated polymer **(33)** is synthesized with optical energy band gap of the polymer 2.42 eV (Murali et al. 2012). The HOMO and LUMO energy levels of the polymers are −5.45 eV and 3.58 eV, respectively, and thermal stability is achieved up to 320°C. The properties revealed that the polymer will be a good material in the area of OLEDs. Sanchez et al. (2015) reported various poly(thiophene) derivatives impended with PPV **(34)**, and this is spaced with different numbers of thio phenyl units (Sanchez et al. 2015). These studies revealed that the PPV-based polymers are useful for the organic photocells. Kim et al. (2016) have reported a novel quinoxaline containing electron acceptor building blocks with thieno[3,2-b]thiophene side chain **(35)** with reduced band gaps of 1.79 and 1.74 eV (Kim et al. 2016). In chloroform solution, the absorption bands are observed in the range of 350–700 nm, with HOMO and LUMO values of −5.34 and −3.55 eV, respectively. After introducing thieno[3,2-b]thiophene into the PPV, molecular modification resulted in the conjugated side chains, which would be a promising strategy for increasing crystallinity with red-shifted absorption. The photovoltaic performance of OPV devices is achieved by increasing the hole mobility of the donor polymers.

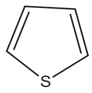
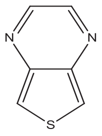
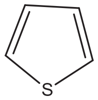
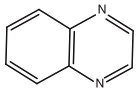
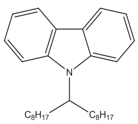
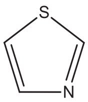
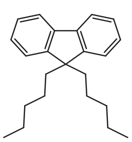
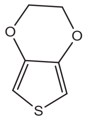
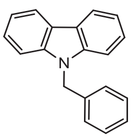
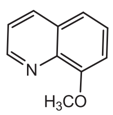
3 Donor-acceptor conjugated polymer

Donor-acceptor conjugated polymer may be categorized into three groups, which includes the conjugated backbone, substituents, and side chain (Zhang and Wang 2012). The conjugation backbone of the polymers is quite important for conjugated polymer with respect to their physical properties related to photovoltaic performance in organic devices. The desired optoelectronic properties of the conjugated polymer are based on the chemical structural approach of donor and acceptor monomers. They can easily form interchain interactions that favor the charge transport and influence the electronic structure of conjugated polymers.

By choosing suitable donor and acceptor moieties, the band gap and energy levels of conjugated polymer can be controlled. If the (HOMO) donor and the (LUMO) acceptor moiety are very near, band gap of the conjugated polymer can be reduced. The valence and conduction bands during the process of polymerization and the HOMO and LUMO energy levels of the repeating unit disperse. As compared to the acceptor moiety, the π-conjugated bridges are mostly combined with the donor moiety because of their more electron-releasing character. The most important thing in the conjugated polymer is to find out the combination of either more or less as the donor moiety and more as the π-conjugated bridge.

There are several electron-rich compounds such as carbazole, thiophene, and pyrrole used as an electron-donating moieties with various substitution patterns, which gives the various chemical transformation. Choosing the electron acceptor groups is also important to achieve conjugated donor-acceptor polymers. Some promising acceptor units such as quinoline, quinoxaline, thiazole, and pyrazine can be used to achieve the efficient synthesis in conjugation. To modulate their energy levels to the optimal positions, it is important to choose electron-deficient units as the acceptor moiety to construct donor-acceptor conjugated polymers. By employing electrochemical or chemical polymerization, a number of conjugated polymers have

Table 9: Donor-acceptor related conjugated polymer.

Donor	Acceptor	E_g^{opt}	E_g^{el}	T_d	References
 36	 41	1.60	1.63	138	Keshtov et al. 2013
 37	 42	–	–	323	Zhanyuan et al. 2013
 38	 43	1.85	1.89	315	Jang et al. 2011
 39	 44	1.88	1.92	–	Ammar et al. 2015
 40	 45	4.13	4.13	295	Ninghua and Feng 2015

been synthesized. Few examples of donor and acceptor are established in Table 9 with their optical, electrochemical band gap and thermal stability.

3.1 Synthesis of PPV type of conjugated polymer

The synthetic process of conjugated polymers has been greatly developed during the past few years. C-C single bond formed between two unsaturated carbons using chemical or electrochemical synthetic process for the production of aryl-aryl coupling (Sotzing et al. 2004). Cross-coupling reactions using transition metal gives a powerful tool for Csp^2-Csp^2 and Csp-Csp^2 bond formation for the synthesis of conducting polymers. Wittig reaction is often used for the synthesis of conjugated polymer, which may extend the conjugated length through the process of consecutive transformations. On the basis of recent literature, the various reactions for the preparation of conjugated polymer are explained.

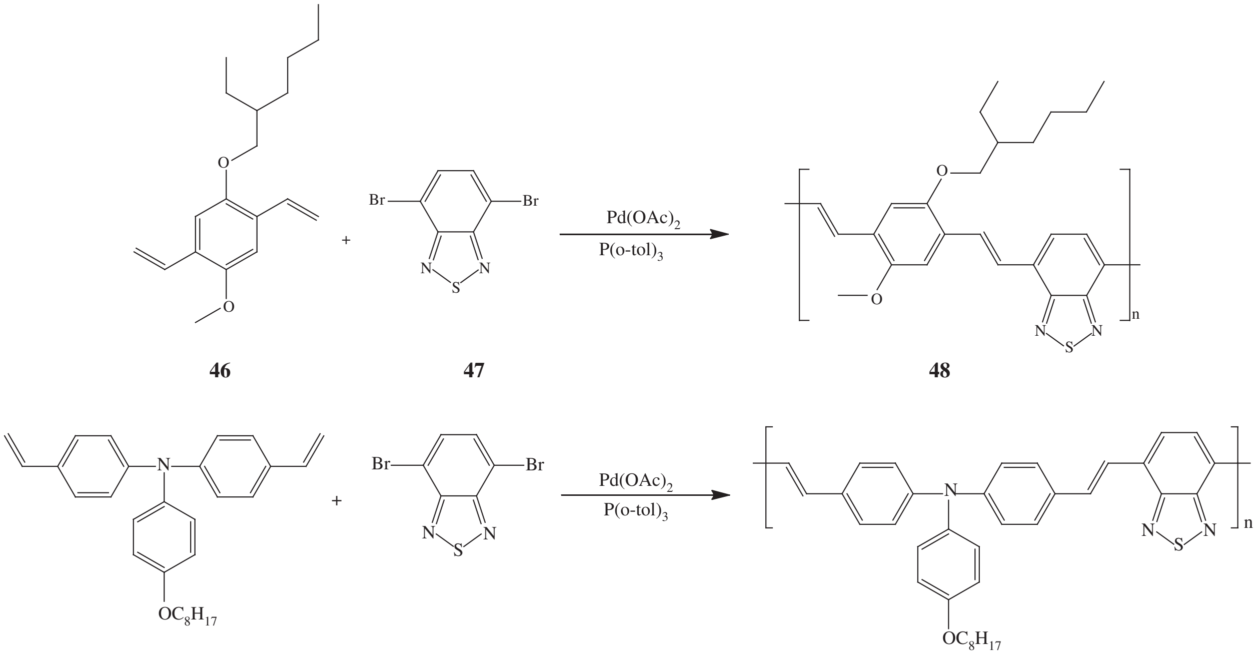
3.1.1 Heck reaction

Electron-rich aryl amine/dialkoxyphenylene and electron-deficient 2,1,3-benzothiadiazole type of polymers can be synthesized by Heck reaction in the presence of palladium acetate as catalyst. This reaction has tendency to form *trans* coupling in the presence of palladium halide group and form stable phosphine-free catalyst in this reaction. Synthetic scheme of triphenylamine- and benzothiadiazole-based polymer is represented in Scheme 1. Fabrication of the bulk heterojunction device is developed to study the photovoltaic properties of the copolymers.

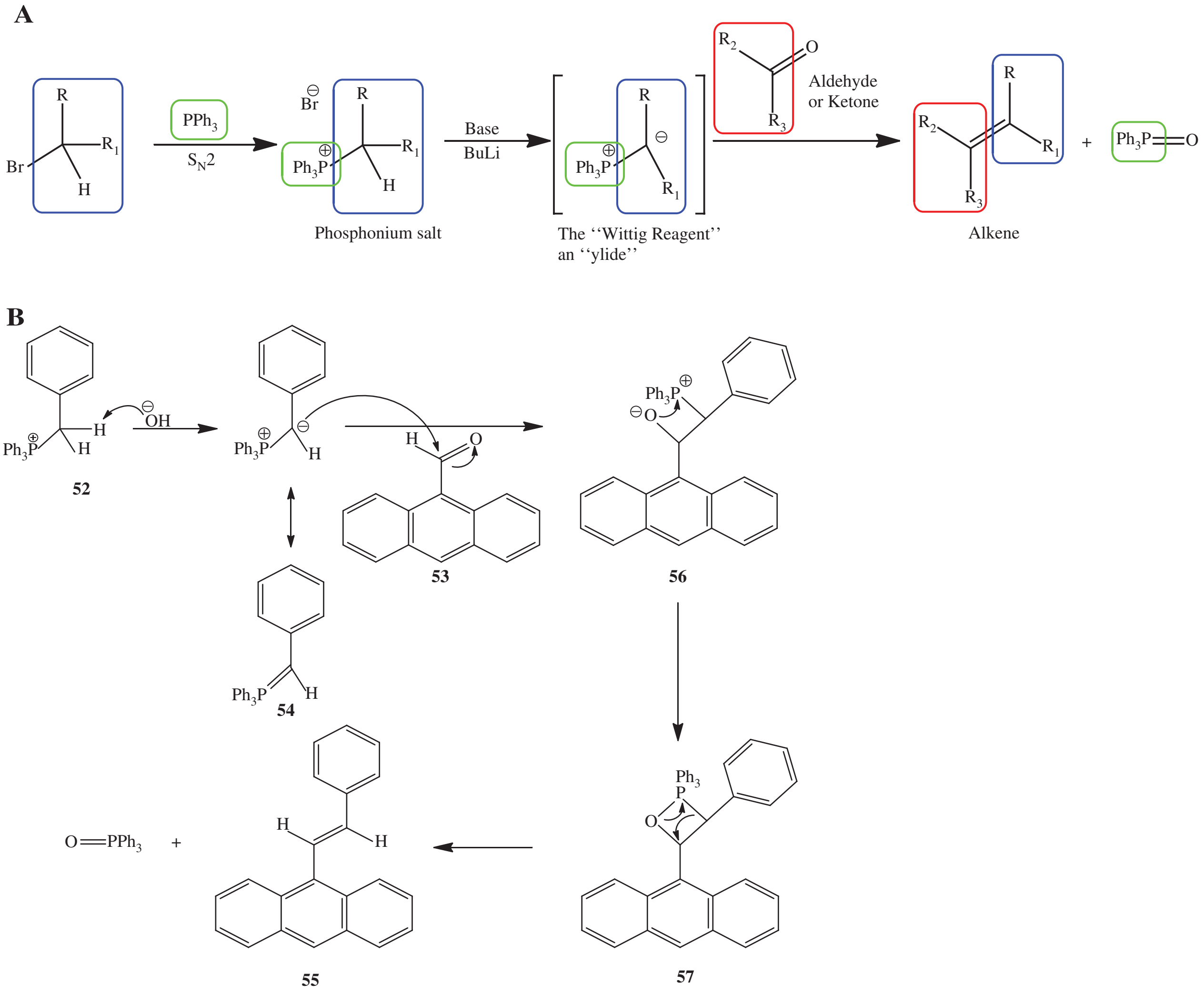
3.1.2 Wittig polycondensation

A chemical reaction of an aldehyde or ketone (deprotonated with a strong base) with a triphenyl phosphonium ylide (neutral compound) gives alkene, which is known as Wittig polycondensation reactions. Scheme 2 represents the mechanistic pathways of Wittig reaction. The carbon-carbon bond formation in stereochemistry corresponds directly with the Z/E stereochemistry of the alkene products. Wittig polycondensation reaction can be used to synthesize the donor-acceptor conjugated polymers and useful for the synthesis of leukotriene methyl ester (Lakshmi and Ravikant 2013).

Out of the various syntheses of PPVs by various C-C coupling reactions such as Wittig, Heck, Gilch, etc., Wittig reaction is the simplest and easiest method in bulk because carbonyl carbon (ketone or aldehyde) may



Scheme 1: Synthetic scheme of triphenylamine and benzothiadiazole based conjugated polymer using Heck reaction route.

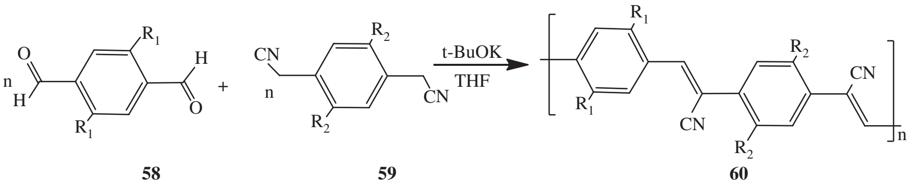


Scheme 2: Wittig reaction mechanism (A) and detailed mechanism (B).

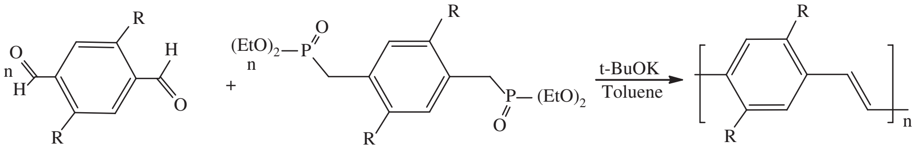
be reacted with an ylide in the presence of base in polar aprotic solvent to form a C=C bond (Andrew et al. 2009).

3.1.3 Knoevenagel condensation

The Knoevenagel reaction played an important role for the synthesis of new conducting materials and involved the reaction of carbonyl group (aldehyde or ketone), which involved the methylene type of Z-CH_2-Z′; group Z indicates the electron withdrawing groups such as COR, COOR, SOR, CN, etc. The synthetic scheme for cyano derivative of PPV is depicted in Scheme 3. The final reaction has been catalyzed using inorganic bases such as ammonia, ammonium salts, $CuCl_2$, and $ZnCl_2$, respectively. This is one of the most vital methods for the synthesis of C-C bond formation. The C-C type of compounds is useful in cosmetics, perfumes, and pharmaceuticals.



Scheme 3: Synthetic procedure for PPV by Knoevenagel polycondensation.



61 62 63

Scheme 4: Horner-Wadsworth-Emmons polycondensation for PPV synthesis.

3.1.4 Horner-Wadsworth condensation

Horner-Wadsworth-Emmons reaction is the most significant reactions in the conjugated PPV synthesis. In this type of condensation reaction, the desired compounds are produced as *trans*-selectivity or, in the case of olefins with tri-substituted C=C double bonds, result in E-selectivity (Scheme 4). The main importance of this reaction is α,β-unsaturated ketones that are *trans* or *E*-configured. Several procedures are available for the formation of carbon-carbon double bonds such as water or HX elimination reaction, pyrolytic method, etc. The polycondensation of PPV synthesis is shown in Scheme 4.

4 Application of conjugated polymer

Due to their fundamental behavior in the process of doping, conjugated polymers are found to be attractive. These types of polymers provide a route for plastic electronic devices in their neutral state. Compared to other materials, these polymers have excellent mechanical properties, flexibility, processability, and wide array of accessible synthetic structures that can alter the photophysical properties with applications in the field of electronic materials in conjugated polymer.

4.1 Light-emitting diode

Applying electric field to a luminescent material gives a non-thermal generation of light in electroluminescence (EL). There are few inorganic semiconductor materials such as GaAsP, GaAs, SiC, etc. that have been well known (Nelson 2002). In 1980, fluorescent organic dyes containing devices are used for commercial application. By using expensive techniques of sublimation or vapor deposition, inorganic semiconducting and organic dye materials were deposited as thin films, which were not good for fabrication of large size devices. The discovery of electroluminescence in conjugated polymers has been a great innovation for the development of light emitting devices. The most important property of conjugated polymer is the tunability of their emissive colors, which can be changed by their structural modification. In addition, the conjugated polymer film is sandwiched between electrodes in single layer LED and semi-transparent material such as indium tin oxide (ITO) used as anode, but metals such as Al, Ca, or Mg are used as cathodes in oppositely charged carriers (electrons and holes). When electrons and holes combine to form singlet and triplet in excited states, this is known as excitons. The process of fluorescence and phosphorescence is relaxed by the singlet state and triplet state.

4.2 Photovoltaic devices

The conjugated polymers are used mostly to construct photovoltaic devices (Bae et al. 2013). These devices are used to convert the radiative energy such as solar energy into electricity. The photons are absorbed to form excitons with the help of electrodes, the carriers are collected, and these carriers are driven into an external circuit. The device efficiency is increased by adjusting donor-acceptor heterojunction and to make more efficient electron acceptor layer. Further development has been achieved by replacing bilayer heterostructure with bulk- heterojunction. In this bulk-heterojunction device, composite films of conjugated polymers and molecular electron acceptors are used to increase the interface between the donors and acceptors.

4.3 Sensors based on conjugated polymers

Sensor material is highly needed in the industry for quantity control of different processes to measure parameters such as temperature, pressure, vacuum, flow, etc. Chemical sensors are required for the detection of hazardous gases during industrial processes. For the detection of toxic gases, chemical sensors based on metal-oxides have been used. However, the metal-oxide sensors suffer from a major drawback in spite of being selective. Sensors based on metal oxides generally operate at very high temperature, which is not desired for detecting hazardous chemicals evolving from industrial processes. The active layer of sensors has been replaced by conducting polymers viz., polypyrrole (PPy), polyaniline (PANI) (Narang et al. 2015), polythiophenes (PTs), and their derivatives and has been a huge interest in the scientific community. As compared to the commercially available metal oxide sensors, conducting polymer based sensors contain better characteristics such as short response times and high sensitivities at room temperature. Sensor based on conjugated polymer with good mechanical properties can be altered by electrochemical process (Melavanki et al. 2008).

Chemosensors have attracted tremendous interest in the field of scientific research because they can be easily fabricated at room temperature. Chemosensor is used to detect several types of chemicals either in gaseous or liquid form at room temperatures. Several synthetic techniques have been developed for the fabrication of chemosensor such as spin-coating, dip coating, drop-coating, solution casting, and Langmuir-Blodgett techniques. Chemosensors exhibited fast response time and very high sensitivity with poor selectivity. The selectivity of chemical sensors can be improved by ion selective membrane as a layer over the conducting polymer sensors. The ion selective membrane allows only a specific analyte to interact with the conducting polymer and produce detectable change in its physio-chemical properties.

4.4 Biosensors

A device that comprises of a biological sensing element or with transducer is known as biosensor. Temperature, pH, and ionic strength can affect the biomolecules because they are very weak and generally have short lifetime in solution. This led to the development of the concept of immobilization of these biomolecules in a suitable matrix; however, decreased enzyme activity is due to the immobilization of biomolecules against environmental conditions. Metabolites such as glucose, urea, cholesterol, etc. in blood are very important in clinical diagnostics for biosensors based on conducting polymers viz., polypyrrole (PPy), polyaniline (PANI), and polythiophene (PTh). Biosensors used by the conjugated polymer are amperometric, potentiometric, conductometric, optical, calorimetric, and piezoelectric. Conducting polymers offer many important features that make them potential candidates as electrodes for miniaturized biosensors.

4.5 Field effect transistors

Conjugated polymers showed technologically relevant properties such as absorption and emission of light or electrical (Chiang et al. 1977), photoconductivity (Moemer and Silence 1994), and field effect transistor (Zaumseil and Sirringhaus 2007). Conjugated polymers typically offer the advantage that they are light weight and flexible materials, which can be processed from solution by spin coating (Arias et al. 2004) and also serve as a large band gap host in polymer LEDs. Alternatively, conjugated polymer derivatives have been successfully applied in organic field effect transistor (Drolet et al. 2005). This makes them produce low-cost, large-area employments and opens up a new field of applications such as packaging matrix displays (Sandberg 2008). Semiconducting polymers exhibit a field-effect mobility (for holes) of the order 10^{-5} cm^2/Vs, which is about five orders of magnitude lower than the mobility required for the potential application in plastic thin film transistor (1 cm^2/Vs).

4.6 Laser devices

The ultimate enhancement of emission is amplified to stimulate emission for laser devices. Lasing from conjugated polymers is first observed by Moses in 1992 from a solution of MEH-PPV (Moses 1992). The first observation of lasing from conjugated polymer in the solid state was from a blend of MEH-PPV and titania nanoparticles with polystyrene in 1997 (Hide et al. 1996). There has been considerable interest in attempting to develop optically and electrically pumped polymer lasers. To date, only optically pumped lasing has been observed for conjugated polymers, but it is hoped to eventually obtain electrically pumped polymer laser diodes. Materials from which lasing has been observed are substituted poly(para-phenylene) (Diaz-Garcia et al. 1997), polyfluorenes (Yoshida et al. 2005), poly(diphenylacetylene)s, (Frolov et al. 1998), and polythiophenes (Granlund et al. 1998).

5 Quenching of conjugated polymer

Decrease in fluorescence intensity of a substance is known as quenching and results in a variety of molecular interactions. A few important processes include energy transfer, molecular rearrangement, excited state-reactions, ground state complex formation, and dynamic quenching. Fluorescence quencher such as aniline, bromobenzene, carbon tetrachloride, ethyltri thiocarbonate, halide ions, and metal ions has been studied with different pathways (Peng et al. 2015). This is comparable to the quenching of pyrene and perylene by dimethyl terephthalate (DMTP) and N,N-dimethylaniline (DMA). Figure 3

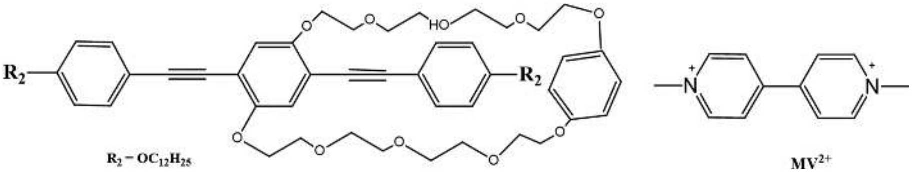


Figure 3: Structure of poly(phenylene ethylene) (PPE) and N,N′-dimethyl-4,4′-bipyridium (MV^{2+}).

depicts the structure of organic soluble poly(phenylene ethylene) (PPE) functionalized with cyclophane receptor, which forms complex with N,N′-dimethyl-4,4′-bipyridium (MV^{2+}), and results in fluorescence quenching.

5.1 Types of quenching

5.1.1 Collisional quenching

Dynamic or collisional quenching involves the formation of a complex, which occurs when the fluorophore in its excited state and the quencher diffuses its energy transfer. The process of radiative or non-radiative deactivation converts the fluorophore and the quencher to their respective ground state. A new band in the absorption spectra has been observed in the form of spectral shift, which was explained using Stern-Volmer equation:

$$F_0 / F = \tau_0 / \tau = 1 + k_q \tau_0 (Q) = 1 + K_D (Q), \tag{1}$$

where,

F_0 = fluorescence intensities in the absence of quencher,

τ_0 = fluorescence lifetimes in the absence of quencher,

F = fluorescence intensities in the presence of quencher,

τ = fluorescence lifetimes in the presence of quencher,

K_q = bimolecular quenching constant fluorophore,

Q = quencher concentration,

K_D = Stern-Volmer constant (K_{SV}), and

$$K_D = k_q. \tag{2}$$

If slope is equal to K_D, a plot of F_0/F versus Q is expected to be linear.

5.1.2 Static quenching

This type of quenching involves the formation of fluorophore (non-fluorescent complex) with the quencher in the ground state. In the presence of light, quenching process can be directly returned to the ground state level without emission of a photon.

$$F + Q \rightleftharpoons F - Q. \tag{3}$$

For the complex formation, the association constant is given by

$$K_s = \frac{(F - Q)}{F \times Q}, \tag{4}$$

where,

F and Q = concentration of the complex,

F = concentration of uncomplexed fluorophores,

Q = quencher concentration and

F_0 = total concentration of fluorophores.

$$(F_0) = (F) + (F - Q) \tag{5}$$

$$K_s = \frac{(F_0) - (F)}{(F)\,(Q)}. \tag{6}$$

Replacing the fluorescence intensities with fluorophore concentration yields a Stern-Volmer equation.

$$F_0 / F = 1 + K_{sv}\ (Q). \tag{7}$$

In the above equation, quenching constant K_{sv} is now the association constant. The uncomplexed fluorophores are observed in static quenching, and this may be due the complexed fluorophores (non-fluorescent). This uncomplexed fraction is not affected by the quencher, and hence, the lifetime is τ_0. Static and dynamic quenching is found to be $\tau_0/\tau = 1$, $\tau_0/\tau = F_0/F$ (Pina et al. 2013).

5.2 Mechanism of quenching

5.2.1 Intersystem crossing

In intersystem crossing, the quenching process by halogens depends on the fluorophore structure. Intersystem crossing mechanism is explained in Figure 4. The quenching process in conjugated polymer may occur due to charge transfer, intersystem crossing, and electron exchange. The excited singlet state is shifted to cause the excited triplet with a heavy atom. Carbazole-based thiophene-, quinolone-, and quinoxaline-based conjugated polymer are excited in triplet state with heavy atom.

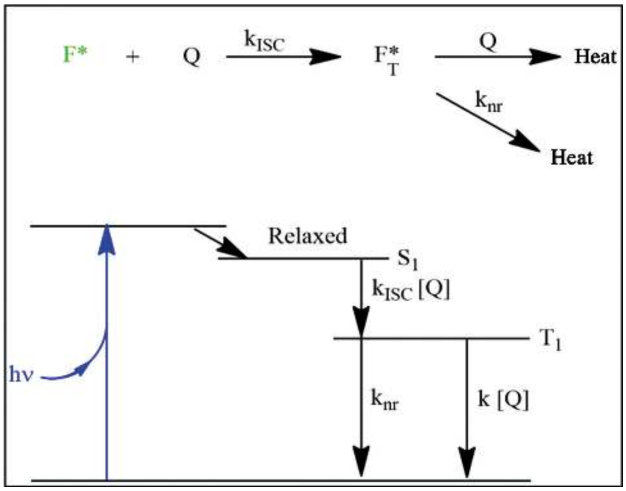


Figure 4: Intersystem crossing mechanism.

5.2.2 Electron exchange

The electronic energy transfer mechanism with fluorescence quenching behavior showed a huge application in photochemical synthesis. Using electronically excited donor molecule allows photophysical and photochemical changes in the acceptor molecule. Electronic energy transfer (EET) mechanisms mostly occur in two ways: through Dexter (double-bond electron exchange) and Forster (dipole-dipole coupling) energy transfer. Dexter energy transfer dominates the organic fluorophore systems by the process of nonradiative decay and the fluorophore returns to the ground state (Figure 5). The main point for Dexter energy transfer is that it requires close interaction between the donor and acceptor of the conjugated polymer, which results in direct orbital overlap between carbazole-based donor and acceptor (Chen et al. 2012) (Figure 6).

5.2.3 Photo-induced electron transfer

Photo-induced electron transfer (PET) has been extensively investigated because of its interesting photo chemistry in its excited states. The main objective is to understand how to induce electron transfer from excited donor to acceptor, which is faster than the other process such as fluorescence, internal conversion (IC), and intersystem crossing (ISC). The formation of a charged species in a conjugated system can also be described using a donor-acceptor model using charge transfer assemblies. The donor-acceptor (D-A) is covalently bonded to make intra-molecular electron transfer easier but not for intermolecular electron transfer.

A photon of energy (hν) creates an excited donor state, which subsequently undergoes an electron transfer to an acceptor molecule to form the charge separated species. There are several other reports on photo-induced electron transfer in supramolecules such as porphyrin linked C_{60} and oligo thiophene linked fullerenes.

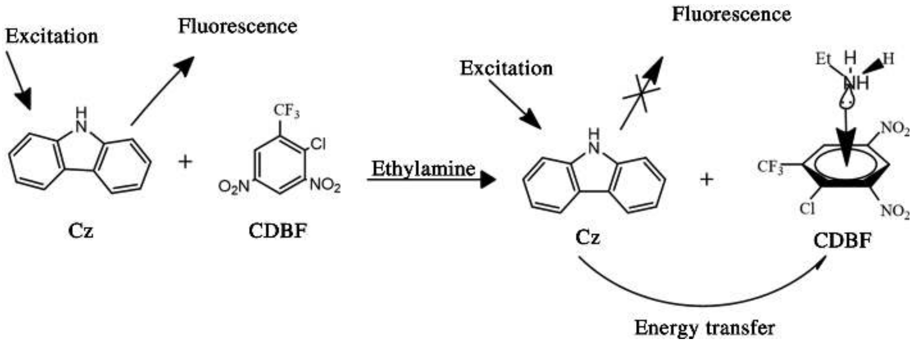


Figure 5: Electronic energy transfer mechanism.

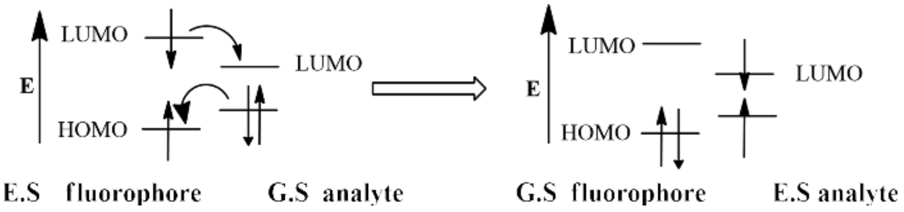


Figure 6: Double exchange transfer by nonradiative decay.

The most commonly used electron-rich compound is dimethylaniline (DMA), which has assumed as electron acceptors.

6 Metal ion sensing of conjugated polymer

Cations play an important role in a wide range of chemical reactions, and more attention has been focused on the development and detection of chemosensors for the biologically and chemically selective species. Chemosensors-based metal ion fluorescence is the first choice due to its simplicity and high detection limit, which appears to be particularly attractive.

Due to their high sensing properties, thermal stability, and good processability, they are also used as sensory materials. Fluorescent metal ion sensory materials such as pyridine, quinoline, benzimidazole, and terpyridine have been reported as conjugated polymers. This consisted of hetero-donor systems such as carbazole (Carbas et al. 2011), thiophene containing quinoxaline (Li et al. 2014), quinolone-based chemosensor (Tu et al. 2010).

6.1 Modes of fluorescent detection

In the absence of metal ion, fluorophore has little or no fluorescence, but in the presence of metal ion, it becomes fluorescent. Conformational restriction induced upon binding can result in the increase of fluorescence efficiency. Quenching in the presence of metal ion did not show fluorescence, but in the absence of metal ion, it exhibited high fluorescence, which involves the selection of a fluorophore. Figure 7 depicts about the shifting of emission behavior. The fluorophore can shift fluorescence through transition metal (fluorescence quencher) and leads to low fluorescence and enhanced emission (fluorescence enhancement) and to high fluorescence.

7 Conjugated polymer nanofibers

According to the National Science Foundation (NSF) and fiber science-related literature, structures having at least one dimension of 100 nm or less are called nanofibers (Camposeo et al. 2013). Nanofibers have been at the forefront of much modern engineering and science research due to their novel, significantly improved biological, chemical, and physical properties. There are mainly four types of nanostructures: zero (0D) (e.g. nanoparticles), one (1D) (e.g. nanowires, nanotubes, and nanofibers), two (2D) (e.g. films and layers), and three (3D) dimensional structures (e.g. polycrystals). Among them, 1D nanostructures (Persano et al. 2013) have been in the focus of quite extensive studies worldwide, because they represent the smallest dimensional structures with high aspect ratios and degrees of flexibility. Hence, these 1D nanostructures can be exploited as elements in nanodevices with various applications, such as supercapacitors, chemicals, and biosensors and in optoelectronics and tissue engineering (Li et al. 2010, Xia et al. 2010, Agranovich et al. 2011, Hsieh et al. 2011, Fasano et al. 2013, Liu et al. 2013, Qu et al. 2013, Goryacheva et al. 2015). Traditionally, an advantage of polymeric materials is that they can be synthesized and processed on a large scale at relatively low cost. Nano application and nanotechnology development continue

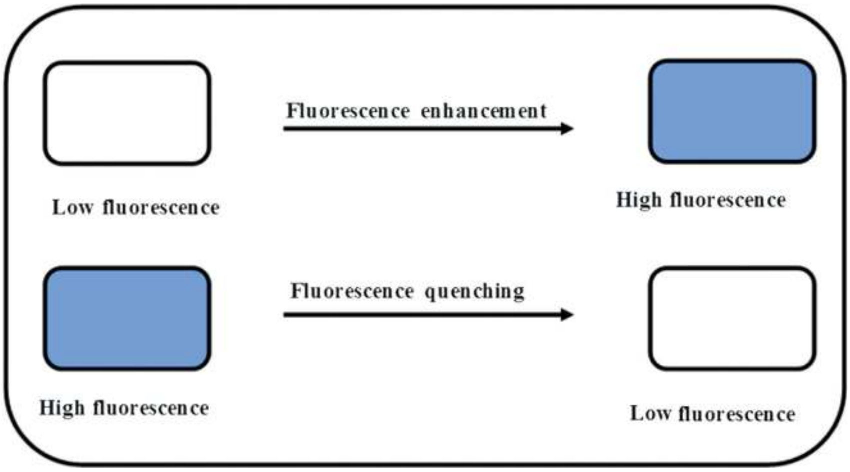


Figure 7: Shift in the emission.

to stir the scientists' and engineers' interest for exploring the best combination of materials and 1D nanostructure. A few examples of such combinations are carbon nanotubes, inorganic semiconductor nanowire/nano belts, metallic nanotubes/nanowires, and conjugated polymer nanofibers/nanotubes (Fasano et al. 2015). The conjugated polymer 1D nanostructures possess certain highly attractive characteristics, such as an easily controllable bandgap, high mechanical flexibility, and greater biocompatibility, compared to those of many inorganic materials. In addition, conductivity of conjugated polymers typically ranges from 10^{-10} to 10^{-5} Scm^{-1}. However, conductivity is usually enhanced via chemical or electrochemical redox reactions. But the conductivity of conjugated polymer can also increase by reducing its size and converting to 1D nanostructure. Up to now, a large number of approaches have already been demonstrated for preparing PANI 1D nanostructures, including chemical routes, such as hard physical template guided synthesis and soft chemical template synthesis (interfacial polymerization, template-free method, dilute polymerization, and reverse emulsion polymerization) and a variety of lithography techniques (Long et al. 2011). However, the drawbacks of these techniques are required post-synthesis process, relatively poor control of the size and morphology uniformity, poorly oriented nanostructure arrays, and high costs, which may limit their production on a large scale. Thus, physical approaches such as electrospinning are more advantageous compared to the abovementioned techniques, especially for the mass production of continuous nanofibers. Nanofibers are synthesized by the process of electrospinning, which has more applications such as vascular draft, tissue engineering, food packing, and actuators. This has been developed in a number of applications in the area of chemical and biological sensors, LEDs, rechargeable batteries, and electromagnetic shielding. The number of amazing characteristics can be obtained for fibers by decreasing diameter from micrometers to sub-microns or nanometers.

7.1 Theory and principle of electrospinning

Electrospinning is a fiber-spinning technology that is used to produce long, 3D, ultrafine fibers (Zeleny 1917). According to the report of Frenot and Chronakis, nanofibers produced by the electrospinning technique have diameters in the range of 100 nm to 1 µm and length up to kilometers (Frenot and Chronakis 2003). Electrospun nanofibers attract in diverse applications, such as biomedical engineering (Wang et al. 2002), tissue regeneration (Phani et al. 2014), smart textiles (Ko and Yang 2008), and membrane filtration technology (Jaroszczyk et al. 2009). The viability of this technology is evidenced by the easiness of the spinning procedure and the simplicity of handling electrospinning instrument (Khan 2012). The most amazing characteristics of electrospun nanofibers include high surface area-to-volume ratio of well-interconnected nanofiber webs, flexibility in surface functionalities, tunable surface properties, high permeability, and good mechanical performance (Huang et al. 2003). The principle of the electrospinning technique is first described by Zeleny, and his published work is devoted on the behavior of fluid droplets at the end of metal capillaries (Zeleny 1914). Later on, in 1934, Formals has established the commercialized system of electrospinning for the fabrication of textile yarns (Formals 1934). Further development of the electrospinning forms a polymer melt rather than a polymer solution using an air-blast to assist fiber formation, which is patented by Norton in 1936 (Norton 1936). The conceptual principle of electrospinning is based on the employment of the external electric field to induce polymer fluid transformation by the elongation and whipping of the jet. In 1969, Taylor introduced the concept of Taylor cone, which is associated with the deformation of a liquid surface into a characteristic shape induced by electric fields. The theoretical analysis of the disintegration of liquid drops under electric fields and the calculation of the electric force acting on fine jets of the critical voltage for inducing jet elongation (Taylor 1969) are studied. Recently, the electrospinning process has gained huge popularity, and the publication of works related to electrospinning increased over the years.

8 Technical aspects in electrospinning

The fiber formations during electrospinning of conjugated polymers are characterized by few preliminary analysis such as solubility and molecular weight analysis. From the technical point of view, the electrospinning equipment is inexpensive compared to robust and straightforward nanofiber production machines. The standard laboratory electrospinning unit generally consists of a metallic capillary needle, which is connected to a high-voltage power supply and a grounded collector. The droplet of the spinning solution is discharged from the capillary needle in a continuous flow, and the feed rate of the discharged droplet is adjusted using an infusion syringe pump. The electric field is applied at the tip of the capillary needle attached to the syringe, which is loaded with a spinning of polymer solution, to induce an electric charge on the surface of the hanging droplet. The hanging droplet of the spinning solution is applied at its surface tension and then develops mutual charge repulsion due to excess pressure. The contraction of the surface charges to the counter electrode is caused by a force directly opposite to the surface tension of the liquid droplet (Fang and Reneker 1997).

8.1 Effect of voltage

The applied voltage in electrospinning is an important role in fiber characterization. Polymer flow towards the collector and the polymer is controlled by adjusting the current. While increasing the voltage, spinning current is increased. This leads to incidence of beaded morphology and reduces the surface area. Increase or decrease of voltage can result to change of morphology and structure of fibers.

8.2 Effect of collector

The physical properties of electrospun fibers are affected by the nature of collectors (Kongkhlang et al. 2008). The most commonly used collector is rotating drum collector. With this collector (due to drum speed), the diameter of the fiber can be controlled. Rotating disk is used for creating uniaxial aligned fibers. Fibers are affected by speed and type of collector disc or drum. The speed of collector can be improved by the crystal orientation of fibers, which is due to polymer chain alignment in the direction of fiber axis.

8.3 Effect of polymer concentration and solution viscosity

The electrospinning process relies on the phenomena of the uniaxial stretching of a charged jet. The stretching of the charged jet is mainly affected by changing the concentration of the polymer solution. When the concentration of the polymeric solution is low, the applied electric field and surface tension cause the entangled polymer chains to break into fragments before reaching the collector. These fragments cause the formation of beads or beaded nanofibers. Increasing the concentration of the polymeric solution will lead to an increase in the viscosities, which then increase the chain entanglements overcome the surface tension and ultimately result in uniform beadles of electrospun nanofibers. The morphologies of the beads depict an interesting shape change from around droplet-like shape (with low viscosity solution) to a stretched droplet or ellipse to smooth fibers (with sufficient viscosity) as the solution viscosity changes. The effect of the concentration and viscosity is also reported by Doshi and Reneker (1995). The optimum viscosity of electrospun nanofiber is 800–4000 cp. An experiment with PAN (polyactylonitrile) solution showed that smooth electrospun nanofibers could be prepared when the viscosity of the solution is kept at 1.7–215 cp. The determination of critical value of the concentration/viscosity is also essential to obtain beadles nanofibers (Baumgarten 1971).

8.4 Effect of solution conductivity

Solution conductivity not only affects the Taylor cone formation but also helps in controlling the diameter of the nanofibers. Solution with lower conductivity and the surface of the droplet will not change to form a Taylor cone, as a result, no electrospinning will take place. Increasing the conductivity of the solution to a critical value will not only increase the charge on the surface of the droplet to form Taylor cone but also cause decrease in the fiber diameter. Increase in conductivity beyond a critical value will again hinder Taylor cone formation and electrospinning. An ideal dielectric polymer solution will not have enough charges in the solution to move onto the surface of the fluid; hence, the electrostatic force generated by the applied electric field will be insufficient to form a Taylor cone and initiate electrospinning process. The conductivity of a polymer solution could be controlled by the addition of an appropriate salt to the solution. The addition of salt affects the electrospinning process in two ways: (i) it increases the number of ions in the polymer solution, which results in the increase of surface density of the fluid and the electrostatic force generated by the applied electric field, and (ii) it increases the conductivity of the polymer solution, which results in the decrease in tangential electric field along the surface of the fluid.

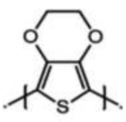
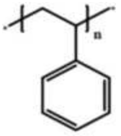
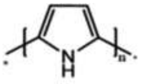
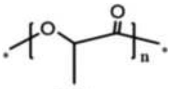
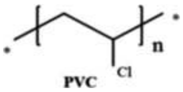
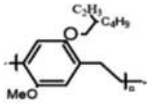
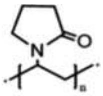
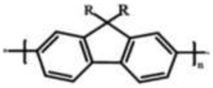
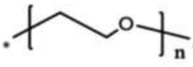
8.5 Effect of humidity and temperature

The environment factors such as relative humidity and temperature also affect the diameter and the morphology of the nanofibers (Huan et al. 2014). Humidity causes changes in the nanofibers diameter by controlling the solidification process of the charged jet. This phenomenon is mainly dependent on the chemical nature of the polymer. Humidity also plays an important in the creation of porous nanofibers when binary solvent system is used PMMA and a binary solvent system (dichloromethane (DCM):dimethylformamide (DMF) in 8:2 ratio to produce highly porous nanofibers). The more volatile solvent (DCM) starts to evaporate faster than less volatile solvent (DMF). This difference in rates of evaporation of the two solvents causes a cooling effects. This cooling effect results in the condensation of water vapor into water droplets. The water droplets settle on the fibers. As water is miscible with DMF, hence, the two mix well with each other on the inner and outer surfaces of the fibers. The complete evaporation of the solvents and the water droplets from the fibers result in the formation of the electrospun nanofibers.

9 Preparation of conjugated polymer nanofiber through electrospinning

According to literature survey, PPV is directly electrospun as pure materials to get defect-free fibers related to solubility and molecular weight (Chen et al. 2011). A feed solution is added to support the fiber formation for more spinnable compound. High molecular weight of the polymers is useful as supporting material (as shown in Table 10), such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) (Vohra et al. 2011), polystyrene (PS) (Luo et al. 2010), poly(vinylpyrrolidone) (PVP), poly(ε-caprolactone) (PCL), and PVA (polyvinyl alcohol). For the synthesis of different fibers, several electronic functionalities can be applied to fabricate the different devices and components, which mainly include the LEDs, photovoltaics, and field-effect transistors (FETs). In addition to this, a number of sensors, photonic components like optically pumped lasers, and waveguides have been developed (Devi et al. 2015). Figure 8 sketches about electrospinning setup, which is useful for the synthesis of nanofibers. This contains one vertical injection that fixes the polymer solution with the voltage.

Table 10: Chemical structure of electrospun conjugated polymers.

S. no	Conductor/semiconductor conjugated polymer	Insulating supporting polymers
1	 PEDOT	 PS
2	 PPy	 PLLA
3	 PANI	 PVC
4	 MEH-PPV	 PVP
5	 PF	 PEO

10 Role of metal sulfide in nanofibers

Cadmium sulfide (CdS) can be prepared by the reaction between hydrogen sulfide and cadmium vapor at 800°C. Cadmium salt acidified with hydrochloric acid by passing hydrogen sulfide gas into a solution leads to the formation of cadmium sulfide, and the final precipitate is dried to get greenockite as mineral. From aqueous solutions of cadmium salts, the sulfides can precipitate as sodium sulfide, which is continuously heating at 750°C, depending on the method of preparation and particle size. These forms can be prepared in colors ranging from lemon-yellow to orange and red. CdS, ZnS, CdSe, and ZnSe are used as buffer layers in Cu(In,Ga)(S,Se) (CIGS) photovoltaic devices. This application of metal sulfide nanofibers with its band gap is noted in Table 11. Due to their outstanding

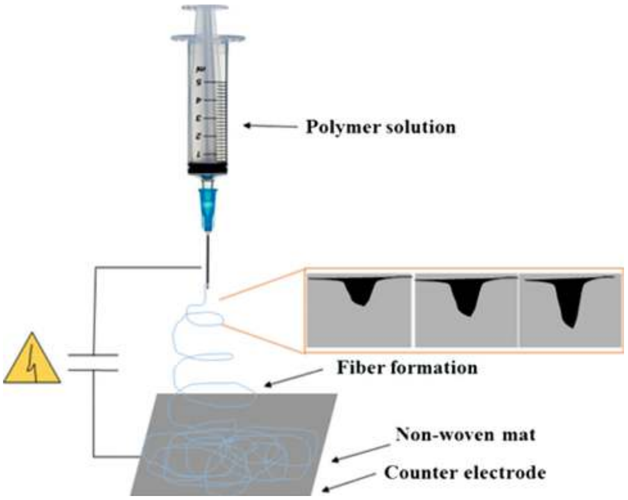


Figure 8: A typical sketch of electrospinning setup.

Table 11: Few examples of metal sulfide nanofibers.

Metal sulfide	Application	Band gap	References
CdS	LED	3.2	Wang et al. 2016
FeS	Sensors	3.0	Li et al. 2004
ZnS	Photo catalysis	3.5	Kong et al. 2011
SnS	Gas sensing	1.49	Tan et al. 2016
Ge_4S_{10}	Electrochemical sensing	3.1	Wang and Yuan 2010
MoS_2	Lubrication	1.2	Xue et al. 2004
CuS	Catalyst material	1.26	Sun et al. 2014
Ag_2S	Photonic material	1.0	Karami et al. 2013
PbS	Electronic material	0.41	Ghasemi et al. 2009

applications, such as large surface area, smaller pore size, and low weight, 1D nanoscale materials are used to make nanofibers, nanowires, nanorods, and nanotubes. The electrical and photovoltaic properties of composite nanofibers and cobalt-doped zinc oxide nanofibers/n-silicon diode were developed. Lithium batteries are effectively used in the carbon nanofiber/$LiFePO_4$ composites. The synthesized electrospun carbon/CdS coaxial composite nanofibers are developed to show the emission maxima and conductive properties of the nanofibers. Because of the electrochemical nature of the carbon nanofibers, they are used as electrodes for super capacitors, and they possess the physical properties that are useful for electronic and photonic applications.

10.1 Importance of cadmium sulfide

Investigation of the surface-modified cadmium sulfide with substituted poly(phenylene ethylene) is helpful to identify the impact of cross-links between the polymer and the nanofibers. Cadmium sulfide (CdS) is a kind of II–VI class of semiconducting luminescent materials with hexagonal wurtzite type structure, which has a melting point at 1600°C, and they have band gap energy of 2.42 eV. Thus, they have important role in the visible light detector among other semiconductors. CdS nanofibers can demonstrate quantum size effects at nanoscale, which has advantage in the field of opto-electronic properties. CdS has more number of applications in LEDs, photovoltaic devices, sensors, infrared window materials, fluorescent materials, and environment detection technology. In recent years, researchers have turned their interest towards the synthesis of nanometer-range dimension of CdS, which may lead to quantum dots lasers, single electron transistors, and several other biological applications. Because of their small size, CdS nanofibers have large surface energy, which makes it easy for them to aggregate

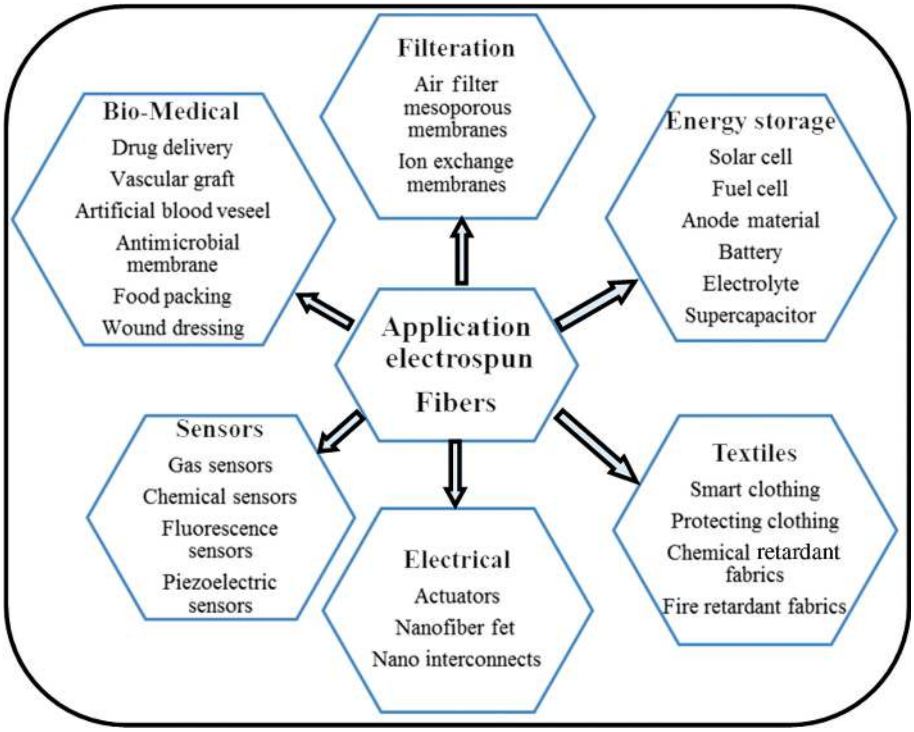


Figure 9: Application of electrospun fibers in different field modification of electrospinning.

to form large clusters and lose the fundamental feathers and functions of CdS nanofibers.

11 Application of nanofibers

Carbon glass and Kevlar fibers are used as reinforcements in composite developments for the application of traditional (micro-size) engineering fibers. The composite nanofibers can provide superior structural properties in the field of nanocomposites. Electrospun nanofibers have better mechanical properties compared to microfibers. Figure 9 depicts about the frontier application of nanofibers such as biomedical, filtration, energy storage, sensors, electrical, and textiles.

To create biocompatible thin films and implantable devices, the electrospinning method has been adopted. There are several parameters involved in electrospinning process such as concentration, applied electric field strength, deposition distance, and time, which affect morphology. A variety of shapes like branched fibers, flat ribbons, ribbons with other shapes, and fibers that were split longitudinally to form larger fibers were observed through the electrospinning process.

12 Conclusion

In this review, we have summarized the studies of some of the key conducting organic polymers, which have become important in recent years. The properties of conducting polymers are important to the development of an understanding of the basic electronic structure of the materials. A principal goal of the field of conducting polymers is to achieve a fundamental understanding of the relationship between chemical structure of the monomer units and electronic properties of the resulting conjugated polymer. The future of the field relies on creative synthesis of new systems and the attainment of completely aligned polymer chain in the solid state. The essential feature required for conducting polymer is conjugated systems with π-electron band structure. Such polymers can undergo charge transfer reactions electrochemically or with suitable electron donor or acceptor. Electrospinning of conjugated polymers represents a powerful technique to form functional micro- and nanofibers at low temperature, enabling both fundamental studies of the electronic properties of semiconducting polymers in confined dimensionalities with interesting applications in the field of opto-electronic and sensing.

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