



# Conjugated Organic Polymers for Optoelectronic Devices

# 18

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**Abstract**

Organic Light-Emitting Devices (OLEDs) have received much attention in the past two decades. The possibility of cost effective production of large area devices is the main attraction for doing research in this area. There has been a considerable progress in the development of materials and the device engineering for improving the efficiency of OLEDs. These significant developments have resulted in their commercialization. In this chapter we describe OLEDs. We discuss their working principles and the measurements that are normally made in these devices. We also discuss the different types of conjugated polymers which are used for specific purposes in these devices.

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**Keywords**

Electroluminescence · Conjugated polymers · OLEDs · PLEDs

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## 1 Organic Molecules in Optoelectronic Devices

Optoelectronic devices have been the focus of investigation in physics and chemistry for more than 50 years. The electroluminescence (EL) was first observed by Bernanose in 1950s, where he applied a high-voltage alternating current (ac) field to the crystalline thin films of acridine orange and quinacrine [1, 2]. Pope and his co-workers demonstrated the direct current (dc) driven EL using a single crystal of anthracene [3]. In the initial stages of development organic EL devices, the driving voltage was as high as 100 V in order to obtain significant light output [4–6]. A significant decrease in the operating voltage (~30 V) was observed with thermally evaporated film of anthracene [7]. Optoelectronic properties were studied mainly in the academic institutions due to low efficiency of these devices. The breakthrough in EL efficiency was first observed by C. W. Tang and Vanslyke at Eastman Kodak Research Laboratories (USA) by making a bilayer device [8]. This demonstration highlighted the potential of using organic thin films for a new generation of optoelectronic devices.

The motivation for doing research in organic-based optoelectronic devices comes from the possible cost-effective production of large area devices. Also the physical and chemical properties of organic molecules can be tailored according to the requirement of application by modifying the molecular structure. For example, color of emission of organic molecules can be adjusted by increasing or decreasing the pi electron conjugation. The synthesis of a large number of new organic molecules with the desired colors was reported, which emit different colors with good quantum yield. They are promising materials for multicolor displays and flexible devices.

Organic thin films have found to be useful in a number of applications, which are now getting commercialized [9, 10]. Organic light-emitting device (OLED) is the most successful application. Significant progresses have also been made in the thin film transistors and the organic solar cells. Organic light-emitting transistors and

**Table 1** History of major developments in OLEDs

S. No.	Discoveries and developments	Year	References
1.	Blue light emission from LED on Li complex	1953	A.B. Bermose, M. Comte, P. Vouaux, Blue emission from LED based on lithium complex, <i>J. Chem. Phys.</i> <b>50</b> (1953) 64–69 (in French)
2.	EL reported in anthracene crystals	1963	M. Pope, H. Knllmann, P. Magnante, Electroluminescence in organic crystals, <i>J. Chem. Phys.</i> <b>38</b> (1963) 2042–2043
3.	EL reported in tetracene	1976	J. Kalinowski, J. God lewski, R. Singnerski, Electroluminescence in tetracene crystals, <i>Mol. Cryst. Liq. Cryst.</i> <b>33</b> (1976) 247–259
4.	EL reported in PVK polymer	1983	R.H Partridge, Electroluminescence from polyvinylcarbazole films, <i>Polymer.</i> <b>24</b> (1983) 733–762
5.	Double layered OLED	1987	Tang, Van Slyke, U.S. Patent (1979) 4,164,431. U.S. Patent (1982) 4,356,429. Van Slyke, Organic electroluminescent diodes. <b>51</b> (1987) 913–915
6.	Single layered PLED	1990	R.H. Friends, J.H. Burroughes, D. Bardleywo, U.S. Patent 90/13148(1990)
7.	Double layered PLED	1993	N.C. Greenham, R.H. Friend, in <i>Solid state physics</i> (Academic, New York/London 1995), pp. 2–150
8.	Flexible OLED technology	2007	M. Hack, R. Hewitt, K. Urbanik, A. Chwang, J.J. Brown, Full colour top emission AMOLED displays on flexible metal foil, in <i>Proceedings of IMID/IDMC'06, Gigest conference</i> (Daegu, 2006), pp. 305–307

photodetectors have also attracted attention [11, 12]. We may also see organic materials in many more applications such as lasers, super capacitors, and memories in future [13].

This brief overview of organic electronics is not a comprehensive review of the entire field. Rather, it is intended to justify the current enthusiasm in exploring organic materials for various applications. In the latter sections of this chapter, we will describe concepts which will be useful to understand conjugated organic polymers for various applications. We will review the development of new conjugated polymers for OLEDs. A glance of discoveries in OLEDs are given in Table 1.

## 2 Benefits of OLEDs

The energy policies of present encourage maximum energy saving technologies. OLEDs are very competent in the light of these policies. OLEDs possess many advantages compared to both LCDs and LEDs, some of these are listed below [14]

- OLEDs are highly economical.
- OLEDs offer flexibility of processing.

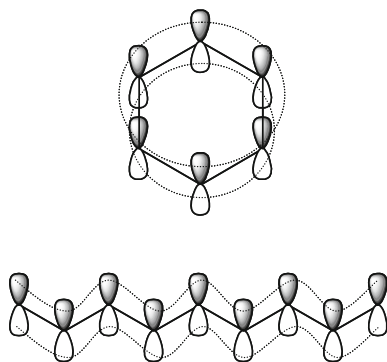
- OLEDs provide a greater range of colors and brightness.
- OLEDs also offer color tuning.
- OLEDs possess high energy saving potential.
- OLEDs are Mercury-free.
- OLEDs possess high luminous efficiency.

### 3 Electronic Structure of Conjugated Organic Molecules and Luminescence

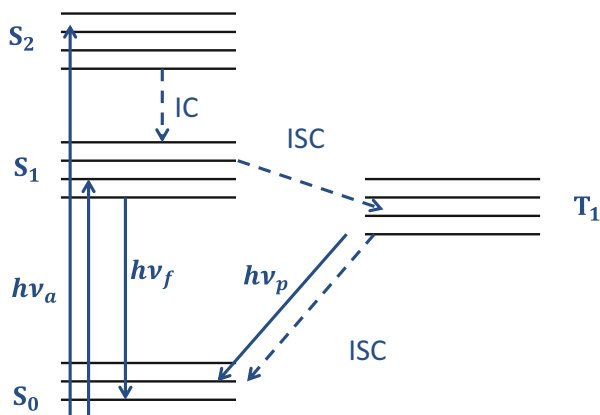
The conjugated organic molecules are used in organic electronics. These organic molecules have  $\pi$ -bonds in an alternate fashion. The overlap of atomic pz orbital leads to the formation of  $\pi$ -bond. The  $\pi$ -electrons in conjugated organic molecules are delocalized throughout the molecular backbone. Figure 1 shows a schematic of  $\pi$ -conjugated molecules.

A  $\pi$ -bond is formed after the  $\sigma$ -bond. The electrons in the  $\pi$ -molecular orbitals have higher energy than the electrons in  $\sigma$ -orbitals. Therefore the highest occupied molecular orbital (HOMO) is a  $\pi$ -molecular orbital in conjugated molecules. The ground state of molecules is a singlet as the number of  $\pi$ -electrons in the HOMO is even. It is these  $\pi$ -electrons in HOMO which participate in electronic transitions. The various photophysical processes, absorption, and emission of light in a conjugated organic molecule can be explained with the help of Jablonski diagram (Fig. 2). The HOMO of the molecule has two electrons with paired spin in the ground state and this state is shown as  $S_0$ . When an electron is promoted from HOMO to the lowest unoccupied molecular orbital (LUMO), it becomes the excited state of the molecule. In the excited state, the electron in the LUMO can have its spin paired or unpaired with the spin of the electron in the HOMO. Thus the excited state of the molecule can be singlet ( $S_1$ ) or triplet ( $T_1$ ). The radiative electronic transitions from  $S_1$  to  $S_0$  and  $T_1$  to  $S_0$  are known as fluorescence and phosphorescence, respectively. The non-radiative transition between the states of same spin multiplicity like  $S_1$  to  $S_0$  is known as internal conversion (IC). Intersystem crossing (ISC) is a non-radiative transition between the states of different multiplicity. Figure 2 also shows the typical time scale for these

**Fig. 1**  $\pi$ -conjugated molecules; formation of  $\pi$ -bond occurs due to the overlap of atomic pz orbitals



**Fig. 2** Jablonski diagram of energy levels in  $\pi$ -conjugated organic molecule



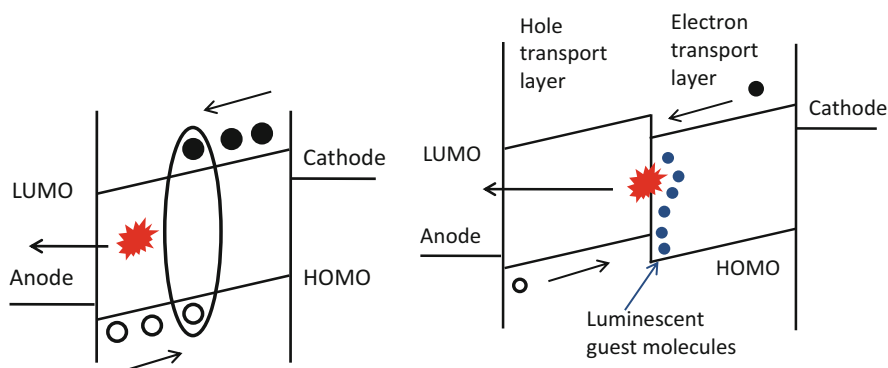
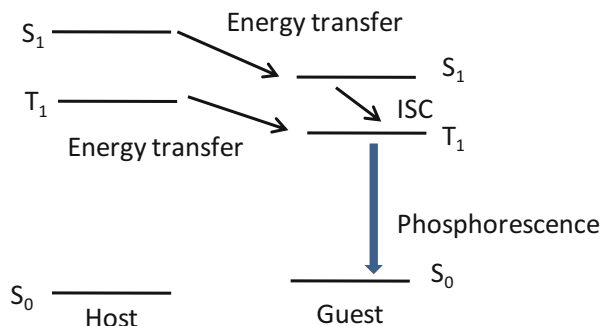
processes. The intensity of molecular fluorescence or phosphorescence is a consequence of interplay between different processes. The band gap in organic molecules depends upon the extent of  $\pi$ -electrons delocalization. The band gap may vary between 1 and 4 eV. Thus, depending upon the band gap the organic molecules may absorb and emit photons anywhere from near-infrared to near-UV region.

For emission to occur, the molecule needs to be in electronically excited state. One way of getting the excited state of a molecule is by absorption of light. The excited state can also be formed by a simple electron transfer reaction between anion and cation radical pair. This principle is used to obtain the chemiluminescence [15] and electrochemiluminescence [16] in solutions. The physical movement of cation and anion radicals in a solvent medium is important to form the excited state of molecules. Light emitting electrochemical cells using gels and polymers [17] are gaining attention but cells using liquids are less attractive for practical applications. A solid state analogue of this process is OLED. In OLEDs, the electrons and holes are pumped in to the LUMO and HOMO levels, respectively, to form the excited state. These electrons and holes then recombine to give electroluminescence.

## 4 Energy Transfer in Guest-Host Systems

Energy transfer from host donors to guest acceptors via Forster/Dexter mechanism is utilized to tune the color of emission and improve efficiency in OLEDs. Forster energy transfer is a long-range mechanism (up to  $\sim 10$  nm) due to dipole-dipole coupling between donor and acceptor [18]. Dexter energy transfer is a short-range mechanism (typically  $\sim 1$  nm) and it involves intermolecular electron exchange process [18]. Energy transfer from singlet to singlet can either be Forster or Dexter or involve both mechanisms. The triplet-triplet energy transfer is always through Dexter mechanism only. Figure 3 shows the schematic of light emission processes and energy transfer in guest-host systems of phosphorescent emitting layer in OLEDs.

**Fig. 3** Schematic of energy transfer and light-emission processes in host-guest systems in phosphorescent OLEDs



**Fig. 4** (a) Schematic diagram of a single layer OLED, and (b) bilayer OLED. Hole transporting layer is a diamine and electron transporting layer is Alq3

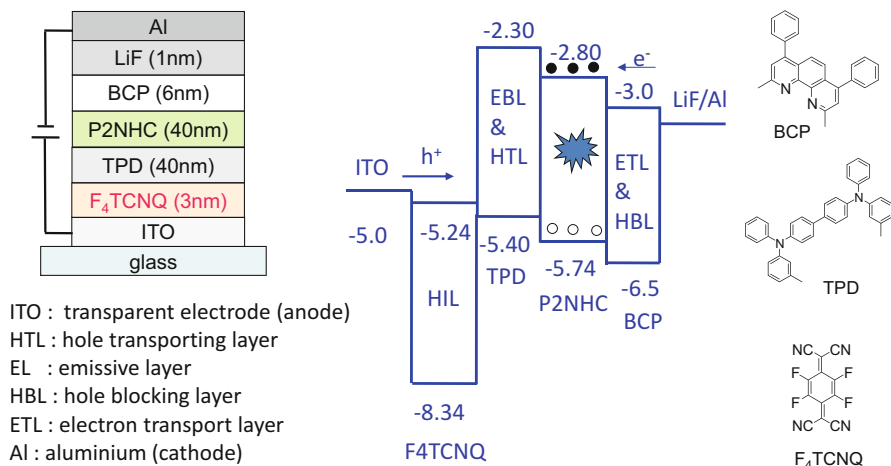
## 5 Working of an OLED

The electrical energy is converted into light energy in an OLED. Figure 4a shows the schematic energy level diagram of the single layer OLED. Cathode and anode injects electrons and holes into the LUMO and HOMO of organic thin film, respectively. These injected electrons and holes move towards each other under the influence of applied electric field and when they meet on to the same organic molecule, that is, hole in the HOMO and electron in LUMO, it becomes the excited state of organic molecule. The excited state may diffuse to other molecules if it is long lived (e.g., triplet), and its properties are conserved during the diffusion. In other words, the excitation of organic molecule behaves like a quasi-particle and this is termed as an exciton. The exciton binding energy in organic molecules is of the order of 0.5–1.0 eV [19]. The electron and hole in the excited molecule may recombine radiatively by emitting a photon. The emission so obtained is called electroluminescence (EL). The energy of the emitted photon depends on the band gap energy of the excited organic molecule.

The recombination of injected electrons and holes gives high electroluminescence efficiency in OLED. In case the injected carriers do not meet each other than the EL efficiency of OLED is less or even zero. In organic molecules, the mobility values of electron and hole are very different. As a result, one of the injected carriers (e.g., hole) moves faster than the other carrier (e.g., electron) and reaches the opposite electrode without recombination. This is normally the case in single-layer device. An efficient strategy to prevent the leakage of injected carriers was first demonstrated by Tang and Vanslyke in 1987 [8]. They fabricated a bilayer device with hole transport layer (HTL) and electron transport layer (ETL). Figure 4b shows the schematic energy level diagram of a bilayer device. In this device, diamine functions as HTL and tris(8-hydroxyquinolino) Al(III) (Alq<sub>3</sub>) as a ETL. The injected carriers move towards the diamine/Alq<sub>3</sub> interface and are not able to cross over the interface because of high energy barrier. They pile up at the interface and form the molecular excitons which emit light. The interface may also be doped with other low band gap guest molecules for harvesting the excitons [20]. The other advantage of this bilayer structure is that excitons are formed away from the conductive contacts which are known to quench the excitons. This particular demonstration has highlighted the importance of using multilayer architectures in order to improve the EL efficiency of the OLEDs. Nowadays, functionally distinct organic layers such as hole inducing (HIL), hole transporting (HTL), hole blocking (HBL), electron transporting (ETL), electron blocking (EBL), emissive layers, etc. are used in OLEDs to improve the overall EL efficiency [21]. Table 2 shows the different components of a multilayer OLED. Figure 5 shows the schematic of a multilayer OLED. It also shows the

**Table 2** The different components of a multilayer OLED, their function and representative examples

S. No	Component	Functions/properties	Materials
1.	Substrate	Provides support for PLED	Glass/plastic foil
2.	Anode	A transparent anode with good electrical conductivity, high work function suitable for hole injection in HOMO of organic layer	Indium tin oxide
3.	Hole Transport Layer (HTL)	Smooth surface over ITO, supports efficient hole injection by reducing energy barriers in case of red-green emitting polymers	PEDOT:PSS, PVK, cross-linked conjugated polymers
4.	Emissive Layer (EML)	Light emitting polymers	PPV, MEH-PPV, CN-PPV, Derivatives of Polythiophene, Polyfluorenes, poly (1,4-phenylenes) etc.
5.	Electron Transport Layer (ETL)	Provides balanced injection of charge carriers	1,3,4 Oxadiazole
6.	Cathode	Facilitates electron injection in polymeric materials	Li, Ba, Ca, Al etc



**Fig. 5** The schematic of an high efficiency multilayer structure OLED, its corresponding schematic energy level diagram, and the molecular structure of the molecules used

schematic energy level diagram and the molecular structure of the organic molecules performing different functions.

The multilayer OLED is complete in all functional aspects. It has 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>TCNQ)/N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) at the anode which efficiently injects and transports holes and 4,7-diphenyl-1,10-phenanthroline (BCP)/LiF/Al as a composite cathode which injects and transports electrons to the P2NHC (emissive layer). TPD and BCP layers also separate the emissive layer from the anode and cathode, respectively, as a result of which the electroluminescence of 3,6-dipyrenyl-N-hexylcarbazole (P2NHC) does not get quenched due to electrodes. TPD and BCP layers also confine the injected electrons and holes in the P2NHC layer. The device exhibit high electroluminescence efficiency at low turn-on field due to efficient hole and electron injection accompanied by exciton formation and radiative recombination.

In the later sections we discuss functionally distinct organic layers which are used in the high efficiency OLED.

## 6 Materials for OLEDs

### 6.1 Anode Materials

The function of anode is to inject holes into the HOMO level of organic molecules and therefore high work function materials are desirable for efficient injection of holes into the HOMO level. Indium Tin Oxide (ITO) coated on glass is the most popular anode material because it has the following advantages: (a) transparent in



the visible region, (b) can make “contact” with the organic molecules, and (c) high work function for efficient hole injection. The work function of ITO is typically 4.5 eV, which can be increased up to 5.1 eV by UV ozone treatment [9]. The other materials which can be used for the anode, besides ITO, are Poly (3,4-ethylene dioxy-2,4-thiophen)-polystyrene sulfonate (PEDOT:PSS) [22], noble metals like gold and platinum [23]. PEDOT:PSS is a conducting polymer and its thin films are transparent to the visible spectrum. Thin films (<1 nm) of gold and platinum are also transparent to the visible spectrum. The work function of gold and platinum are 5.1 eV and 5.6 eV, respectively [9].

## 6.2 Hole Injection Materials (HIM)

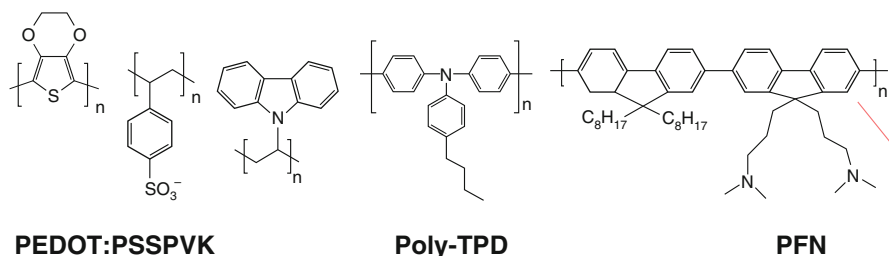
An efficient OLED requires a multilayer device architecture, therefore the interfacial structure at the organic-metal and organic-organic interfaces play an important role in devices. A thin film (~1–2 nm) of HIL acts as an interface connection layer between the anode and the HTL. It improves the film forming property and facilitates efficient hole injection from anode to the HTL [24]. As a result, the operational voltage decreases and less amount of heat is generated inside the device. The frequently used HILs are PEDOT:PSS, copper phthalocyanine (CuPc), or various inorganic buffer layers like TiO<sub>2</sub> [25]. CuPc layer on ITO has proved to be an effective HIL [23]. PSS-rich PEDOT:PSS was also used as HIL [23]. The exact mechanism of “modification” by PEDOT:PSS is still unclear but the most accepted one is the creation of interfacial dipoles on surface of PEDOT:PSS that helps the injection of holes to the HTL [26]. The surface of bare ITO is undesirably rough and spikes on bare ITO normally shunt the device. Coating of ITO with PEDOT:PSS layer helps to avoid these problems. However, the commercially available PEDOT:PSS solutions have unpredictable short shelf-life (nearly 6 month). An electron acceptor molecule (F<sub>4</sub>TCNQ) is also used as HIL on ITO anode [23]. More recently, inorganic compounds like ZnO have also been used as thin buffer layer between ITO and HTL [27].

## 6.3 Hole Transport Layer (HTL)

The use of HTL with thickness (40–100 nm) on top of ITO with or without HIL serves the following functions: (a) gives an interface with the emissive layer (b) provides energy barrier for electron and confines them to the emissive layer, and (c) transport holes to the emissive layer for the exciton formation.

The general requirements for organic molecules to be used in as HTL are: (a) high hole mobility, (b) their HOMO level in the thin film should be close to the work function of the anode in order to facilitate easier hole injection, (c) high glass transition temperature, (d) high stability of its cation radical, and (e) large optical band gap in order to avoid the absorption of visible light as emitted by the emissive layer.

The frequently used small molecules in HTL are N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), N,N'-diphenyl-N,N'-bis



**Fig. 6** Molecular structure of polymers used at the interfaces in OLEDs

(1-naphthylphenyl)-1,1'-biphenyl-4,4'-diamine (NPD), and copper phthalocyanine (CuPc). The polymers used as HTL are PEDOT:PSS, poly-N-vinylcarbazole (PVK), poly(4-butyl-phenyl-diphenyl-amine) (poly-TPD), etc. [23, 28] (Fig. 6). The mobility values for holes in small molecules TPD and NPD are  $2 \times 10^{-3}$  and  $3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively [9]. The mobility values for holes in polymers PVK and poly-TPD are  $2.5 \times 10^{-6}$  and  $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. These molecules have low electron affinity (2–2.5 eV), and hence they also function as electron blocking layer.

#### 6.4 Electron Transport Layer (ETL)

The use of ETL with thickness (~6–10 nm) between the emissive layer and cathode facilitates electron injection during the device operation. The ETL also helps to confine holes within the emissive layer due to its large work function. The general requirements for organic molecules to be used as an electron transporting layer are: (a) the energy of LUMO level is close to the work function of cathode for easier electron injection, (b) high mobility values for electrons for efficient transport into the emissive layer, (c) high glass transition temperature, (d) high stability of anion radical, and (e) large optical band.

The frequently used small molecules in ETL are tris(8-hydroxyquinolino) Al (III) (Alq<sub>3</sub>), 4,7-diphenyl-1,10-phenanthroline (BCP), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (Bphen), 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI), and Oxidazole derivatives [9]. The mobility value of electron in Alq<sub>3</sub> is  $1.4 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$  [9] and hole is  $2 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [9]. The value electron mobility of BCP and Bphen is in the order of  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [29].

#### 6.5 Cathode Interfacial Materials (CIM)

The electron injection from the cathode can be improved by decreasing the work function of cathode. The use of a thin layer (~1 nm) of a CIM in contact with the cathode decreases the work function of the cathode (e.g., Al) and facilitates electron injection. The popular materials used in CIF are LiF, CsF, and Li<sub>2</sub>O [23]. The barrier to electron injection has been shown to decrease by 0.4 eV in the case of Alq<sub>3</sub>/LiF/Al

than Alq<sub>3</sub>/Al [30]. The mechanism of lowering in work function using CIM is debated. It was speculated that free Li atoms are formed at the Alq<sub>3</sub>/LiF/Al interface, which in turn forms Alq<sub>3</sub> anion [31]. However, the use of CIM along with Al (4.2 eV) is equivalent to using low work function cathodes like Ca (2.87 eV) and Mg (3.66 eV) [9]. Water/alcohol soluble conjugated polymers poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) have also been used as a cathode interfacial layer in organic devices [32].

## 6.6 Cathode Materials

The function of cathode is to supply electrons into the LUMO. The requirements for cathode materials are as follows: (a) low work function to facilitate efficient electron injection into the LUMO, (b) wetting properties to ensure good contact with adjacent organic layers, (c) stable to ensure long lifetime of device, and (d) transparent when used in “top-emitting” OLEDs.

The most popular cathode material is Al (4.2 eV). The other materials which are commonly used for cathode are LiF/Al (3.6–3.8 eV), Ca/Al, Mg/Ag (2.9 eV), and Ba/Al (2.6 eV) [21, 23]. Very low work function materials such as Cs, Ca, etc. need to be capped with another stable metal film such as Al, Ag to avoid oxidation.

## 6.7 Light-Emitting Materials

The material that gets the most value in OLED is the one used in emissive layer. The organic molecules to be used in the emissive layer must have high photoluminescence quantum yield in the thin solid film. The other requirements of a light emitting materials are as follows: (a) compatible HOMO and LUMO for efficient carrier injection from electrodes or adjacent organic layers, (b) good film forming property, (c) large stokes shift, (d) high glass transition temperature, (e) good solubility in suitable solvents is essential for polymers as they can only be deposited via spin coating, and (f) efficient energy transfer from the host, if used as a guest (dopant).

The emitting layer may also be doped with another highly luminescent guest molecule. Energy transfer from the host (primary exciton) to guest (secondary exciton) makes possible to change the color of emission. This strategy is widely used in harvesting triplets excitons in phosphorescent OLEDs [23].

The color of emission of an OLED is decided by the band gap of the polymer used in the emissive layer. If a blue-emitting polymer is used in the emissive layer then electroluminescence spectrum of the device will also be blue. To make a display like television, we require white light emission. For an organic molecule, it is difficult to emit such a broad spectra. The way white light easily generated is by mixing blue, green, and red emitters in suitable ratio in the active layer. The synthesis of white light-emitting polymers is little difficult but has been done. In the later section, we review the polymers synthesized and used in fabricating blue, green, red, and white light-emitting OLEDs.

## 7 Performance Parameters of OLEDs

The performance of an OLED is measured in terms of various parameters. They are current efficiency (cd/A), brightness (cd/m<sup>2</sup>), power efficiency (W/W), lifetime, and internal and external quantum efficiency. The internal quantum efficiency ( $\eta_{\text{int}}$ ) is the number of photons generated in the device per injected carrier, and it can have a maximum value of 100%. External quantum efficiency ( $\eta_{\text{ext}}$ ) is the number of photons emitted out of the device per injected carrier in the forward or viewing direction. The light out-coupling efficiency ( $\xi$ ) of device is limited by absorption losses and guiding of electroluminescence within the device and its substrate. For a refractive index of the emissive medium  $n$ ,  $\xi$  for a flat interface is given by:  $\xi \approx 1/(2n^2)$  [9].

Internal quantum efficiency is determined by various factors. Charge balance factor ( $\gamma$ ) accounts for the ratio of electrons and holes injected (ideally 1) into the device and the probability of their recombination (ideally 1). Spin statistics predicts the formation of triplet and singlet state in the ratio of 3:1 from the uncorrelated electron and hole recombination. The emission from these states depends upon the quantum yields of fluorescence ( $\phi_F$ ) and phosphorescence ( $\phi_P$ ). In ground state, most organic molecules have a total spin of  $S = 0$ , and during the course of electronic transition, the spin remains conserved. The fluorescence quantum yields close to 1 have been reported for many organic molecules [23]. The electronic transitions involving a change in spin multiplicity are spin forbidden. Therefore the phosphorescence from the  $S = 1$  (triplet) state to the singlet state is generally inefficient and almost all energy is lost to the non-radiative processes. Transition from the triplet state is partially allowed in certain heavy metal complexes, such as Iridium (Ir), due to mixing of metal orbitals. Heavy metal complexes of iridium and platinum have high phosphorescent quantum yield and they are used to harvest the triplet excitons formed in the emitting layer [10].

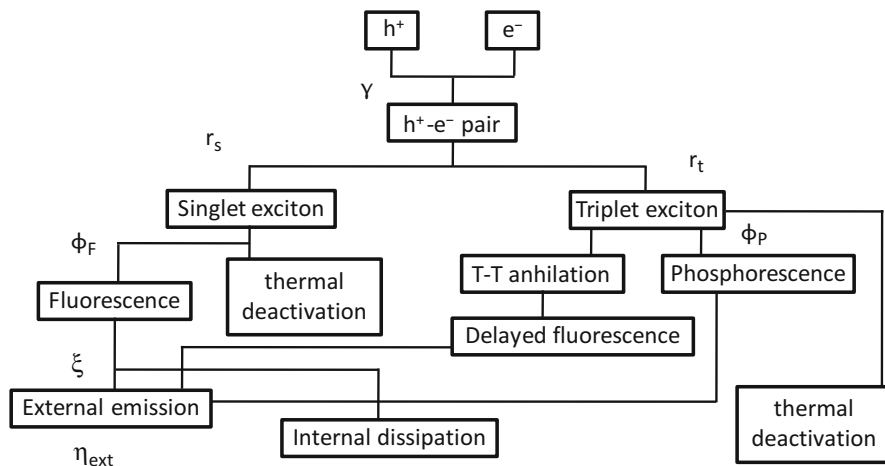
Taking into all the above factors, external quantum efficiency ( $\eta_{\text{ext}}$ ) can be written as

$$\eta_{\text{ext}} = \xi \gamma (r_s \phi_F + r_t \phi_P) \dots \quad (1)$$

where  $r_s$  and  $r_t$  are singlet and triplet state formation efficiencies. Figure 7 shows the various processes that follow electron-hole recombination in OLEDs. Internal quantum efficiency of nearly 100% and external quantum efficiency of  $19.0 \pm 0.5\%$  have been demonstrated using a heavy metal (Ir) complex [33].

## 8 Conjugated Polymers in LED

The EL in conjugated organic polymers based on poly(N-vinyl carbazole) (PVK) and doped with luminescent dyes was first reported by Partridge [34]. Friend and co-workers described an EL device based on conjugated poly(p-phenylenevinylene)



**Fig. 7** Schematic of the external quantum efficiency

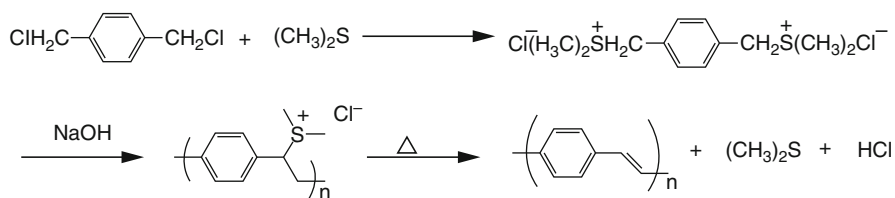
(PPV) [1]. The EL efficiency and low turn-on voltage of this device projected conjugated polymers as promising candidates for commercial application. Since then a number of polymers with different emission color have been synthesized and tested. In the following sections we first describe the popular chemical reactions adopted to synthesize conjugated polymers and then we review the development of most promising polymers for blue, green, red, and white light emission.

## 9 Chemical Synthesis of Optoelectronic Polymers

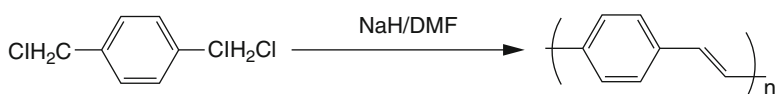
There are many polymerization techniques to prepare light emitting polymers. The synthesis of different light emitting polymers as reported in literature exploited mainly four important C–C bond forming techniques. These include soluble precursor polymer route, dehydrohalogenation reactions, transition metal-catalyzed coupling polymerizations, and condensation polymerizations. In this section, we present representative examples of all the above mentioned reactions.

### 9.1 Soluble Precursor Route

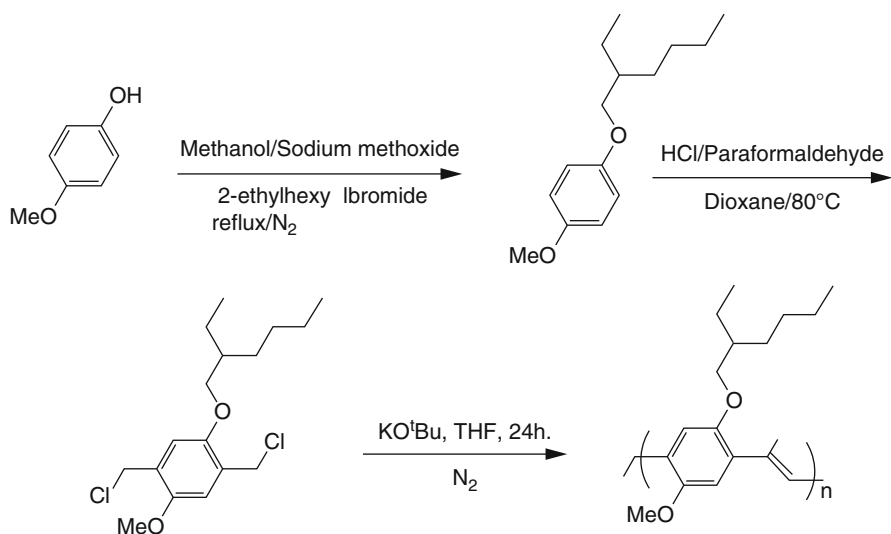
This is the most extensively used strategy for the synthesis of PPV and its derivatives. The polymer produced by this method possess very high molecular weight, and their films are highly oriented by stretching during conversion of the precursor polymer to its conjugated form (Scheme 1) [35]. The conversion temperature can be reduced to 100 °C by using bromide derivatives instead of chlorides, thus enabling the fabrication of flexible devices [36].



**Scheme 1** The Wessling-Zimmerman precursor route to PPV



**Scheme 2** Synthesis of PPV using dehydrohalogenation reaction



**Scheme 3** Glitch polymerization of MEH-PPV

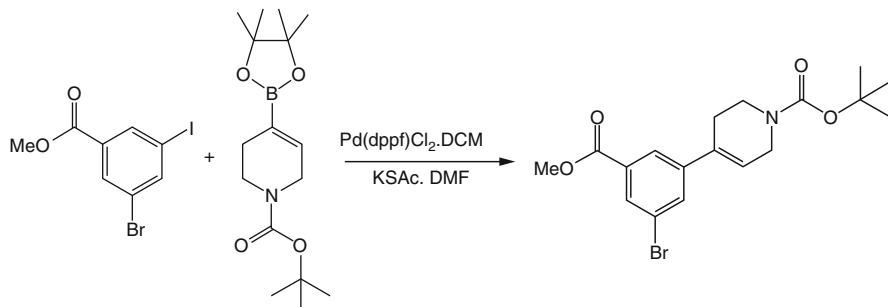
## 9.2 Dehydrohalogenation Reactions

These reactions are employed to synthesize different PPV derivatives. Unsubstituted PPV is synthesized by the dehydrohalogenation of dichloroethylene in the presence of sodium hydride and DMF solvent [37] (Scheme 2).

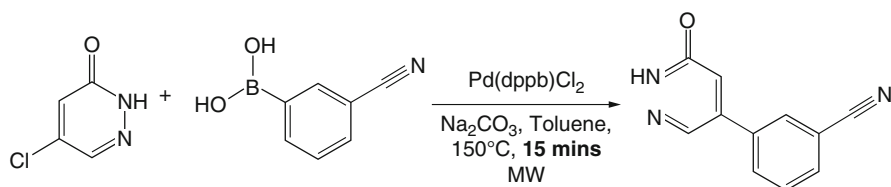
Glitch polymerization is most widely used for the synthesis of PPV derivatives. Mainly alkyl or alkoxy substituted PPV derivatives are synthesized using this method [38, 39] (Scheme 3).



X = Br, I, Cl, sulfonyl



**Scheme 4** Representative examples of Suzuki-Miyura Coupling reaction



**Scheme 5** Representative example of microwave assisted Suzuki-Miyura Coupling reaction

## 9.3 Transition Metal-Catalyzed Coupling Polymerizations

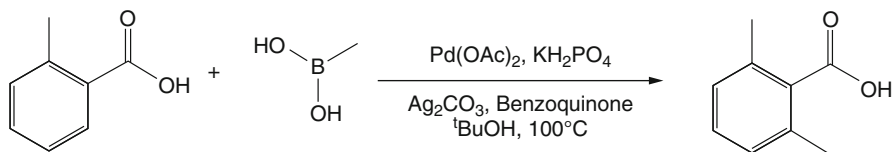
### 9.3.1 The Suzuki-Miyaura Coupling

The Suzuki coupling reactions are mainly for the cross-coupling reaction of organoborons with organohalides. The organoboron are present in the form of a boronic acid or ester. These reactions offer very high tolerance toward various functional groups and by-products containing boron can easily be removed. These reactions are most commonly used to form aryl-aryl bonds and are very effective for the synthesis of highly substituted conjugated aromatic products. Suzuki coupling has found extensive use for the preparation of alternating copolymers [40, 41] (Scheme 4).

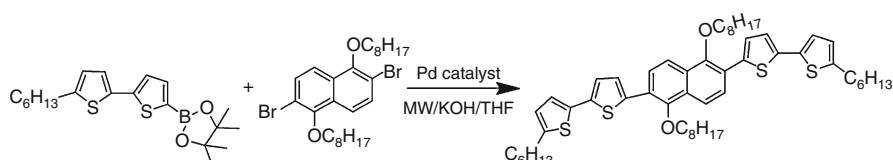
In presence of microwaves, Suzuki reactions get accelerated (Scheme 5).

This reaction can also be used to obtain aromatic alkylations. C-H insertion negates the necessity to begin with an aryl halide, improving the atom efficiency of the process (Scheme 6).

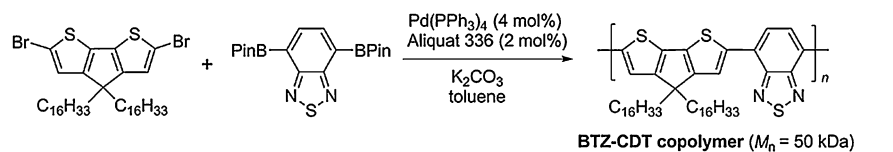
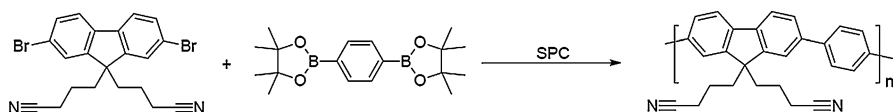
Nehls et al. synthesized thiophene-naphthalene oligomer via microwave-assisted Suzuki coupling of the appropriate bromo and boronic acid derivative [42] (Scheme 7).



**Scheme 6** Representative example of Suzuki-Miyura Coupling reaction



**Scheme 7** Synthesis of thiophene-naphthalene oligomer via microwave assisted Suzuki-Miyura Coupling reaction



**Scheme 8** Synthesis of benzothiadiazole-cyclopentadithiophene (BTZ-CDT) copolymers via Suzuki polycondensation

### 9.3.2 Suzuki Polycondensation

Suzuki polycondensation reaction was discovered in 1987. Since then, it has been utilized for the synthesis of polyarylenes as a powerful tool. A typical procedure for Suzuki polycondensation [43, 44] (Scheme 8).

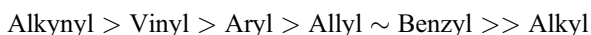
Advantages of Suzuki Reactions:

- Mild reaction conditions.
- Availability of common boronic acids.
- Inorganic by-products are easily removed from reaction mixture.
- Stereoselective.
- Less toxic than other competitive methods (i.e., Boronic acids are environmentally safer and less toxic than organostannanes.).
- Reaction will take place in the presence of other functional groups.
- Protecting groups are not always necessary.
- Relatively cheap reagents, easy to prepare, and GREEN.



### 9.3.3 The Stille Coupling

This is a very versatile reaction and an excellent alternative to the Suzuki reaction. In this reaction, organostannanes are used instead of organoboron. The tin atom bears four functional groups; therefore, it is very important to have very good understanding of the rates of transmetallation reaction of each group. Relative rate of transmetallation:



The main attraction and advantage of the Stille coupling reaction is the use of organostannanes which are easily prepared, purified, and stored. An important benefit of these reactions is their tolerance (better than Suzuki Coupling) to many functional groups and can also be carried out in neutral conditions. Compounds like aromatic ketones, biaryl derivatives, and styrenes can be synthesized using this reaction [45, 46] (Scheme 9).

Carsten et al. polymerized thiophene containing monomers with stannyl groups via microwave-assisted Stille coupling reaction [47]. Stille reactions are very versatile and are widely used to synthesize functional/multifunctional light emitting polymers.

### 9.3.4 Heck Coupling

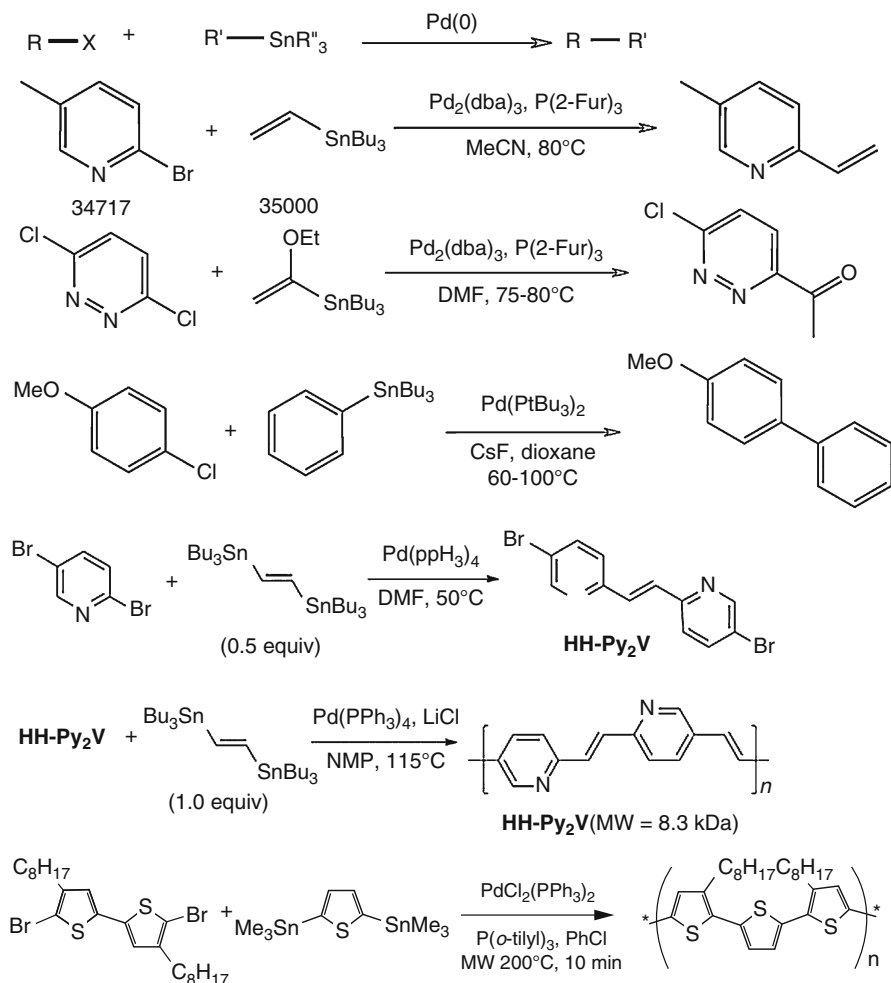
The Heck reaction is a cross-coupling reaction of an organohalide with an alkene to make a substituted alkene using palladium as a catalyst and a base. Heck coupling reaction can be described as a palladium-catalyzed C–C formation between aryl/vinyl halides and activated alkenes in presence of a base. The reaction starts with the oxidative addition of aryl halide to the palladium atom, which is followed by coordination and migratory insertion of the olefin to the palladium. Bond rotation then places the two groups *trans* to each other to relieve the steric strain and subsequent  $\beta$ -hydride elimination results in a *trans* final product. Base-mediated reductive elimination regenerates the palladium(0) catalyst. The Heck reaction is of great importance, as it allows substitution reactions on planar  $sp^2$ -hybridized carbon atoms. Another advantage of this reaction is its excellent *trans* selectivity [48, 49].

Heck method is not suitable for the preparation of PPV homopolymers, but this method is more useful for the preparation of PPV-related block copolymers (Scheme 10). Heck reaction yields the same regular copolymer regiochemistry and double-bond configuration with a much higher yield, better purity, and also high luminescence efficiency.

### 9.3.5 Yamamoto Coupling

In Yamamoto coupling, C–C bonds of aryl halogenides are formed by mediation from a transition metal as catalyst, like bis(cyclooctadiene)nickel(0),  $\text{Ni}(\text{cod})_2$ . In Yamamoto coupling, only a single halogen functionalized monomer is required, offering diversity in monomers and simple reaction procedure.

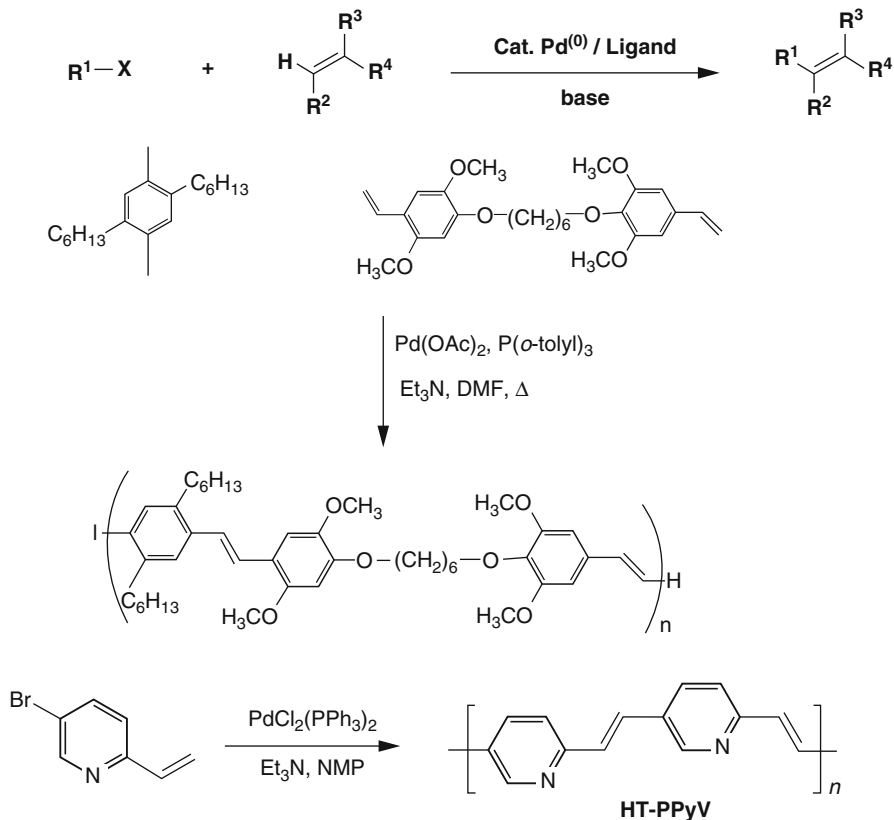
Yamamoto polymerization of a dihaloaromatic compound (AA-type monomer) gives a polymer. The main advantage of Yamamoto polymerization is that AA-type



**Scheme 9** Representative examples of Stille coupling reaction

monomers are straightforward to work with. For example, poly(9,9-bis(2-ethylhexyl)fluorene) was prepared by Yamamoto-type polycondensation of a 2,7-dibromofluorene with bis(COD)nickel and bipyridine [50, 51]. However, this method usually requires stoichiometric amounts of catalyst. Investigations on Ni-catalyzed reductive polymerization of 2,7-dibromofluorenes with excess zinc dust as a reductant led to the synthesis of highly conjugated and processable PFs (Scheme 11).

Lee and Hsu synthesized green-emitting polymers using Yamamoto coupling reaction by end capping N-aryl-1,8-naphthalimide and 1,8-naphthoilenearylimidazole derivatives into polyfluorene [52].



**Scheme 10** Representative examples of Palladium catalyzed Heck coupling reaction

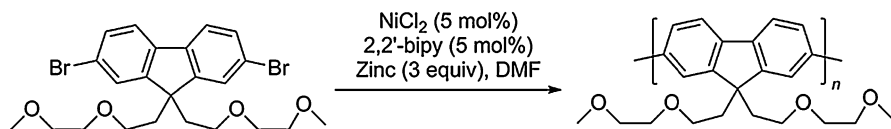
## 9.4 Condensation Polymerizations

### 9.4.1 Wittig Reaction

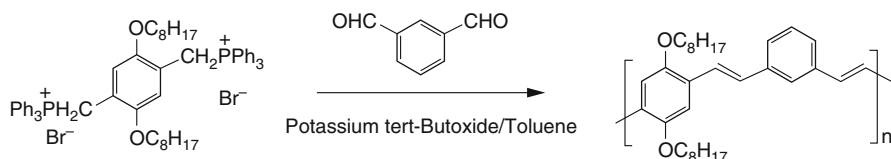
Wittig reaction is one of the most versatile methods for the synthesis of alkenes in which electrophilic carbonyl compounds such as aldehyde and ketone are attacked by a phosphorus ylide. Phosphonium ylides are readily formed by the addition of a suitable base to the corresponding phosphonium salt. Wittig polycondensation route was used for the preparation of well-defined alternating copolymers. Here we present one of the example related to PPV, Blau et al. synthesized poly(*m*phenylenevinylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) by Wittig reaction [53] (Scheme 12).

### 9.4.2 Horner-Emmons Condensation

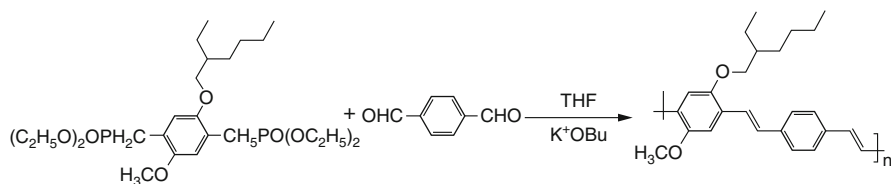
Horner-Emmons condensation is a practical modification of Wittig reaction that is used for the synthesis of PPV related alternating copolymer [54]. Wittig polymers have high molecular weight and it contain certain amount of *cis*-vinylene double bonds. Horner-Emmons condensation has some advantages over Wittig reaction



**Scheme 11** Nickel catalyzed Yamamoto coupling



**Scheme 12** Synthesis of PPV derivative by Wittig reaction

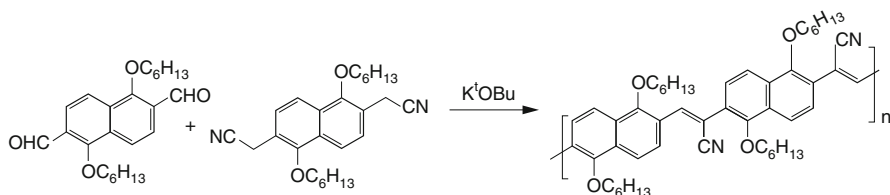


**Scheme 13** Synthesis of Poly(MEHPV-alt-PV) by Horner-Emmons condensation

such as, newly formed double bonds are purely *trans* in nature, it shows good regioselectivity, high degree of conversion, and finally good yield [55]. Kim et al. prepared poly (MEHPV-alt-PV) by using Horner-Emmons condensation is displayed in Scheme 13. The reaction consist of substituted phosphonate ester reacted with terephthalaldehyde under the presence of potassium *tert*-butoxide to produce alternating copolymer [55].

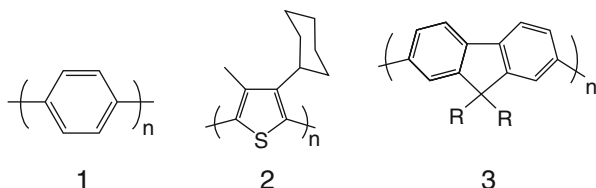
### 9.4.3 Knoevenagel Coupling Route

Emissive polymers containing vinylene linkages are also prepared by using Knoevenagel coupling reaction, in which carbon-carbon double bonds are formed between respective monomers. Knoevenagel condensation based on the reaction between aldehyde groups with active methylene species requires strong electron withdrawing substituent groups (CN, for example) [55]. Employing Knoevenagel condensation numerous PPV-related homo and copolymers with CN containing vinylene units have been synthesized. Hanack et al. prepared cyano substituted poly(2,6-naphthylenevinylene) (CN-2,6-PNV) by using Knoevenagel condensation reaction between two monomers, namely, 1,5-bis(hexyloxy)-2,6-naphthalenediacetonitrile and 1,5-bis(hexyloxy)-2,6-naphthalenedicarbaldehyde in the presence of a strong base is shown in Scheme 14.



**Scheme 14** Synthesis of poly(2,6-naphthylenevinylene) by Knoevenagel condensation

**Fig. 8** Molecular structures of different families of blue-emitting polymers

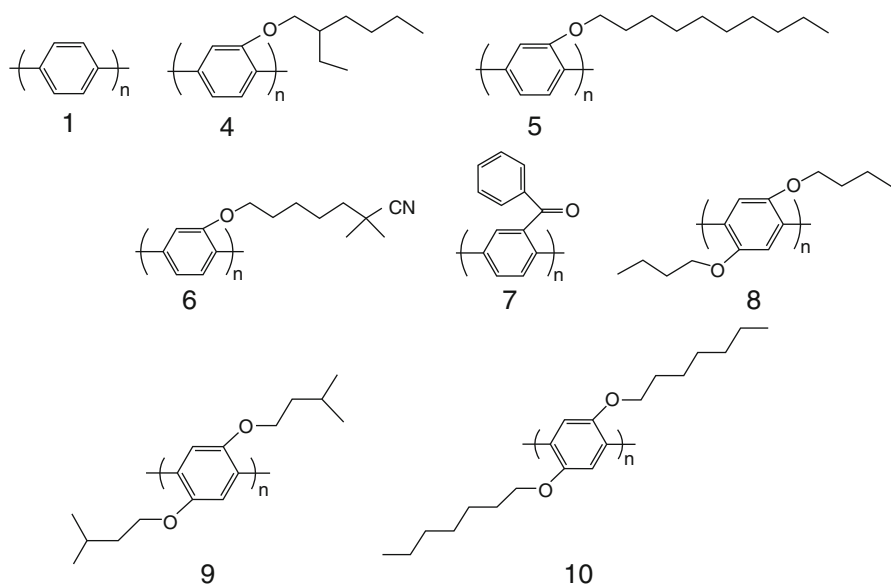


## 10 Blue, Green, Red, and White Light-Emitting Polymers

### 10.1 Blue-Emitting Polymers

The fluorophores that are responsible for blue light emission typically contain phenyl, or fluorene, or heterocycles such as thiophene, etc. in their chemical structure. Figure 8 shows the molecular structures of different families of blue-emitting polymers. These fluorophores may be present in the main chain of polymer or as its side chain. The presence of side chain play an important role and its function is to increase interaction, decrease planarity for color shift in the emission spectrum, and to enhance solubility of polymers [56].

Poly(p-phenylenes) (PPPs) is an important class of blue-emitting polymers. Figure 9 shows the molecular structures of different PPPs derivatives. PPPs can make neat thin films which emit at ~460 nm. Electrochemically polymerized Poly(p-phenylene) (PPP) was also observed to exhibit light-emitting properties [56, 57]. It was found that the reaction condition for polymerization affect the light-emitting properties. The polymers obtained electro-reductively with charges of 50 and 100 mC/cm<sup>2</sup> show EL maxima in the region between 450 and 550 nm while that with a charge of 1 mC/cm<sup>2</sup> falls at about 600 nm [58, 59]. PPPs have poor solubility and low quantum efficiency (QE) which made them less attractive for blue OLED. The issue of poor solubility was addressed by attaching the alkyl chains in the polymer backbone. Many PPPs derivatives were synthesized. Monoalkoxy substituted PPPs, poly[2-(6'-cyano-6'-methylheptyloxy)-1,4-phenylene] (CN-PPP) (6), poly(2-decyloxy-1,4-phenylene) (DO-PPP) (5), and poly[2-(2'-ethylhexyloxy)-1,4-phenylene] (EHO-PPP) (4) are soluble in organic solvents [60, 61]. The three polymers show nearly identical PL spectra, with PL and EL maxima at 420 nm. A PL quantum yield for the polymers in a 1% solution is 85% and the yields in films



**Fig. 9** Molecular structures of PPV polymers

ranges from 35% to 46%. The best external QE for LEDs with a structure of ITO/PVK/PPPs/Ca are 3.0, 2.0, and 1.4% for **4**, **5**, and **6**, respectively, where PVK is poly(N-vinylcarbazole).

Poly(2-benzoyl-1,4-phenylene) (PBP) (**7**) is soluble in common organic solvents and thermally stable up to 400 °C [62]. The polymer film having thickness of 15 nm, when photo excited at 390 nm exhibit PL maximum at 433 nm, slightly less than that of PPPs but higher than that of alkoxy substituted PPPs. Quantum yield of PBP in chloroform was measured to be 15%. A LED having a structure of ITO/PVK-PBP (3:1) blend/PBD-PMMA (3:1) blend/Ca/Al exhibits an EL maximum at 446 nm with an EQE of 0.17%, where PBD and PMMA are 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole and poly(methyl methacrylate), respectively.

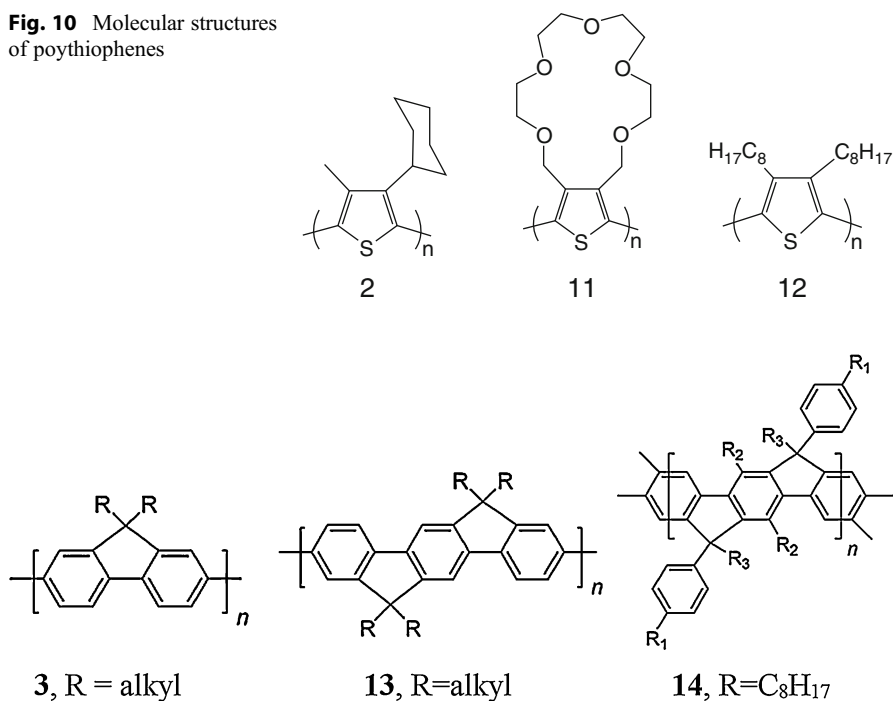
Photophysical properties of dialkoxy substituted PPVs (**8**, **9**, and **10**) have also been studied [62]. The absorption spectra are reported to be similar and unaffected by the length of the alkyl chain or isomeric structures. The peak absorption wavelength is at about 336 nm. Degree of polymerization, length of alkoxy substituent, and preparation methods affects the absorption maxima of the resultant molecules. The intensity of absorption changes with the length of the alkoxy groups. Poly(2,5-dibutyloxy-1,4-phenylene) (**8**) in methylene chloride shows an extinction coefficient  $6.4 \times 10^6 \text{ cm}^2/\text{mol}$  whereas poly[2,5-bis(3'-methylbutyloxy-1,4-phenylene)] (**9**) shows an extinction coefficient  $3.8 \times 10^6 \text{ cm}^2/\text{mol}$ . The PL maxima of **8**, **9**, and **10** in chloroform appear at 410 nm. Poly(2,5-diheptyloxy-1,4-phenylene) (**10**) when synthesized by oxidative coupling using anhydrous  $\text{FeCl}_3$  as a catalyst has a band gap of 3.5 eV and a PL maximum for a film at 400 nm with a strong secondary peak

at 500 nm [63]. The result suggests that during the preparation of the polymer some defects would have been produced which leads to the secondary emission.

Thiophene-based polymers can also give blue emission. The band gap of polythiophenes can be controlled by steric hindrance via bulky side chain substituents on the thiophene unit [64]. Poly(3-cyclohexyl-4-methylthiophene) (PCHMT) (**2**) (Fig. 8) possesses large band gap. The PL maximum of **2** in chloroform was observed at 460 nm. The bilayer device of **2** with PBD as an electron transporting layer sandwiched between ITO and Ca gives an EQE of 0.6% and an EL maximum at 460 nm. It is also reported that single-layer device of polythiophene with crown ether unit attached to positions 3 and 4 (**11**) gives an EL maximum at 470 nm [65]. Poly(dioctylthiophene) (**12**) in toluene shows a PL maximum at 470 nm [66]. A LED with a structure of ITO/**12**/In also shows EL maximum at 470 nm. The stereo interactions between the alkyl chains is likely responsible for short chain length and blue color in polythiophenes. However, the QE values of all LEDs prepared with this material are not promising (Fig. 10).

The fluorine-based polymers is other important family of blue-emitting polymers. Figure 11 show the molecular structures of typical fluorene derivatives such as polyfluorenes (PFs, **3**), 5,6-polyindeno-fluorenes (PIFs, **13**), 7,8 and ladder-type polyphenylenes (LPPPs, **14**). In solution, they emit blue to blue-green which gets

**Fig. 10** Molecular structures of polythiophenes

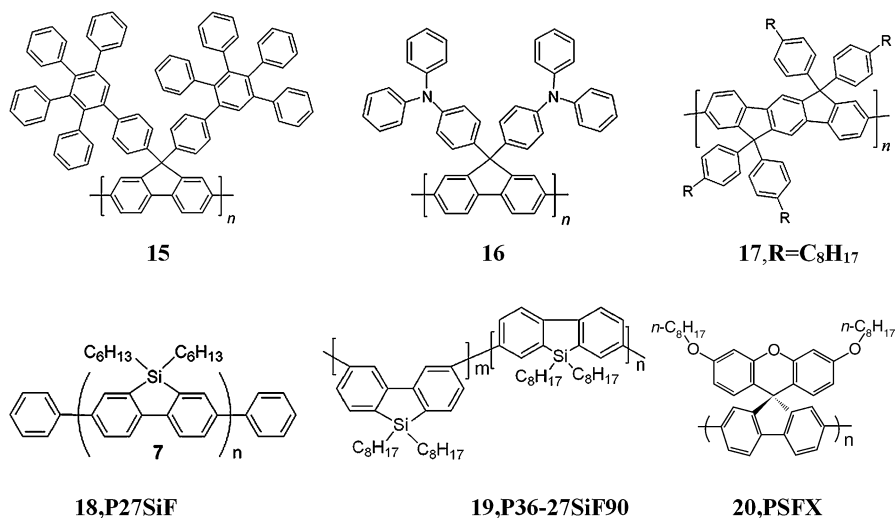


**Fig. 11** Typical fluorine based blue-emitting conjugated polymers

red-shifted with increasing rigidity of the polymer chain with emission maxima of 420 nm for **3**, 430 nm for **13**, and 450 nm for **14**. The first PLED for blue color emission was made in 1991 [67]. A layer of poly(9,9'-di-n-hexylfluorene)(PDHF) (**3**) was formed by spin-coating its solution in chloroform onto ITO glass and a layer of magnesium-indium alloy on the polymeric layer was vacuum-deposited. The EL spectrum of PDHF exhibited the emission maximum at 470 nm with a shoulder at 420 nm and a FWHM of  $\sim 200$  nm. In the solid state broad emission bands at longer wavelengths  $\sim 530$  nm also appears [68–71]. The cause of long-emission band for **3**, **13**, and **14** has been correlated to the emission from the ketonic defects which get incorporated in the polymer backbone as 9-fluorenone units [72–77].

Craig et al. purified the monomers used in the synthesis of polyfluorenes to ensure reduced levels of fluorenone defects in the corresponding polyfluorenes. The synthesized polymer demonstrated pure blue and more stable electroluminescence when exposed to high temperatures [78]. Green EL was suppressed by incorporating a novel buffer layer of tetrakis(4-(5-( $\alpha,\alpha,\alpha$ -trifluoromethylphenyl))-2-oxidiazolyl)phenyl)methane (CF3OXD) between emissive layer and the Ca/Ag or Ba/Ag cathode [73]. The problem of ketonic defects in fluorene-based polymer was also addressed by replacing the alkyl groups in the methine bridges with the aryl substituents (Fig. 12). The greater stability of blue emission in molecule **15**, **16**, and **17** arises due to high resistance to oxidation and a reduction in excimer diffusion to a ketone defect sites. Efficient, stable blue-emitting LEDs have been fabricated using the polymers **15**, **16**, and **17** [79, 80].

The other important strategy adopted to avoid long-wavelength emission in polyfluorenes was replacing the vulnerable C-9 carbon in polyfluorene by a heteroatom, such as silicon. Many new polymers were synthesized. The optical properties of polymer poly(9,9-dihexyl-2,7-dibenzosilole) (**18**) were similar to that of poly



**Fig. 12** Stable blue-emitting polyfluorenes



(9,9-dioctyl-2,7-fluorene) (PFO) [81]. Thin film of P27SiF show photoluminescence (PL) emission maxima at 425 nm and has two vibronic sidebands at 449 and 482 nm. The PL efficiencies of **18** and PFO were also similar ~60%. Of the two polymers, **18** was found to be more thermally stable and maintained its color purity even after annealing at 250 °C for 16 h whereas films of PFO degraded as indicated by the appearance of a broad green band centered at 535 nm. The electroluminescence emission spectrum measured on a single layer device in the configuration ITO/PEDOT/**18**/Ba/Al showed emission maxima at 431 and 451 nm and efficiency slightly superior to that of the corresponding device fabricated with a single layer of PFO. The copolymerization of 3,6-silafluorene unit into the 2,7-silafluorene gave P36-27SiF90(**19**) [82]. The copolymer did not show undesirable long wavelength emission and it was thermally stable. The device of the copolymer with a configuration of ITO/PEDOT:PSS/PVK/**19**/Ba/Al exhibited an external quantum efficiency of 1.95%, a luminous efficiency of 1.69 cd/A, and a maximum brightness of 6000 cd/m<sup>2</sup>. Homopolymers and copolymers of spirofluorene were also found to give stable blue emission [83]. Fluorene-9,9'-(2',7'-di-*n*-octyloxyxanthene)](PSFX) (**20**) have high quantum efficiency of close to 1 in solution and 0.92 in thin film. Its optical properties were found similar to PFO. An OLED fabricated using PSFX as the emitting layer ITO/PEDOT/**20**/TPBI/Mg:Ag/Ag exhibits an efficient, stable blue emission and a maximum external quantum efficiency of 1.74%. The EL spectrum remains unchanged even at high brightness (10<sup>3</sup>cd/m<sup>2</sup>). High PL quantum efficiencies of fluorene-based polymers and their good performance in devices make them promising candidates for OLEDs.

## 10.2 Green-Emitting Polymers

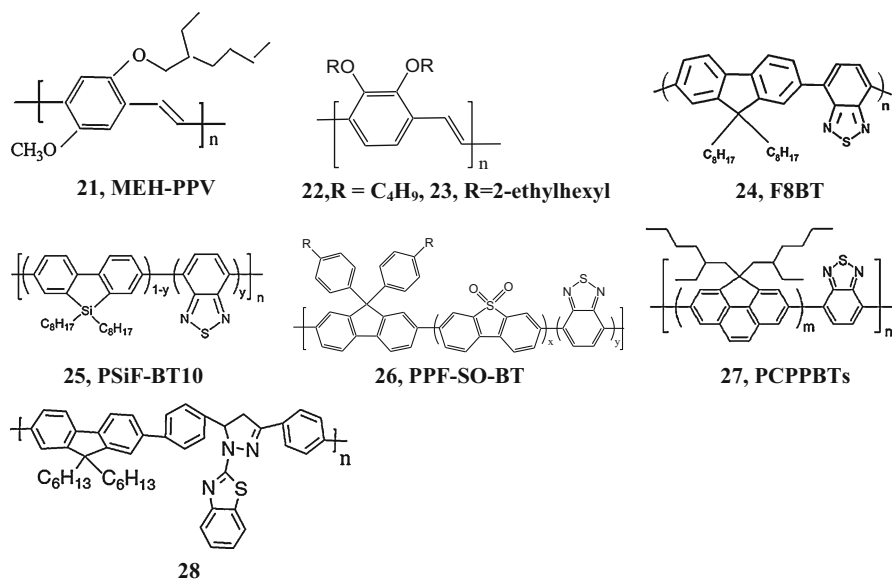
In the photoluminescence (PL) spectrum, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] MEH-PPV as a solid thin film emits yellowish-red light with  $\lambda_{\max}$  at 593 nm and shoulder peaks at 640 nm and 707 nm. Nguyen et al. have blue shifted this emission of MEH-PPV by blending MEH-PPV with poly[9-vinylcarbazole] (PVK) and TiO<sub>2</sub> nanoparticles [84]. The single layer devices based on the blended polymer films were fabricated in the configuration ITO/(PVK: MEH-PPV) + TiO<sub>2</sub>/Al have shown green electroluminescence. The optical properties of PPVs were also found to depend on the substitution pattern of the alkoxy groups in the polymer backbone. 2,3-dialkoxy substituted PPVs as synthesized by Holmes and co-workers have shown significant blue-shift in the emission maximum and they were also having high PL and EL efficiency in the solid state [85–87]. The di-butoxy-PPV shows green emission with  $\lambda_{\max}$  at 530 nm and a PL efficiency of 40%. Bigger alkyl groups increases the steric constraints as in (**23**) leads to a further blue-shift in the emission with  $\lambda_{\max}$  at 513 nm and a drop in PL efficiency to 28%. The PL efficiency of MEH-PPV was only in the range of 15%–20% [88–89].

Benzothiadiazole is an electron deficient monomer unit which was used in copolymerization with fluorene to red-shift the blue emission of polyfluorenes (PFs) to green region [90]. The polymer Poly(9,9-dioctylfluorene-alt-benzothiadiazole)

(F8BT, **24**) synthesized shows PL emission peaks at 545 nm and has a shoulder peak at 576 nm and a long wavelengths tail that extends up to 750 nm [91]. Single-layer device with the configuration ITO/ZnO/Cs<sub>2</sub>CO<sub>3</sub>/F8BT/MoO<sub>3</sub>/Au containing thick layer of F8BT as the emissive layer shows excellent current efficiency of more than 20 cd/A at a brightness of ~1000 cd/m<sup>2</sup> [92]. The peak external quantum efficiency (EQE) of the device was close to 7% (Fig. 13).

Yong Cao and coworkers synthesized green-emitting poly[2,7-silafluorene-co-benzothiadiazole]PSiF-BT10 (**25**) by incorporating 2,1,3-benzothiadiazole (BT) into the backbone of blue-emitting poly(2,7-silafluorene) (PSiF) [93]. The peak emission wavelength and PL quantum efficiency of PSiF-BT10 as a solid thin film were measured to be 530 nm and 0.52, respectively. This  $\lambda_{\text{max}}$  is very close to that of a similar fluorene derivative (PFO-BT10) for which  $\lambda_{\text{max}}$  is 533 nm. The PL quantum efficiency of PFO-BT10 was 0.68, a little higher than PSiF-BT10. The polymer LED with the configuration of ITO/PEDOT:PSS/PVK/PSiF-BT10/Ba/Al showed the maximum EQE of 3.81% and current efficiency of 10.6 cd/A.

Yu et al. (2013) synthesized green-emitting PPF-SO-BT (**26**) polymers containing 9,9-bis(4-(2-ethylhexyloxy) phenyl)fluorene (PPF), dibenzothiophene-*S,S*-dioxide (SO), and benzothiadiazole (BT) units with varying ratios [94]. Of these polymers, PPF-SO15-BT1 exhibited highest fluorescence quantum yield (~0.67) and good thermal stability. Light-emitting diodes (LEDs) using PPF-SO15-BT1 as the emissive layer in the device configuration ITO/PEDOT:PSS/PVK/PPF-SO15-BT1/CsF/Al have shown green electroluminescence. The maximum brightness and the maximum current efficiency measured in this device are 30,314 cd/m<sup>2</sup> and 17.6 cd/A, respectively.

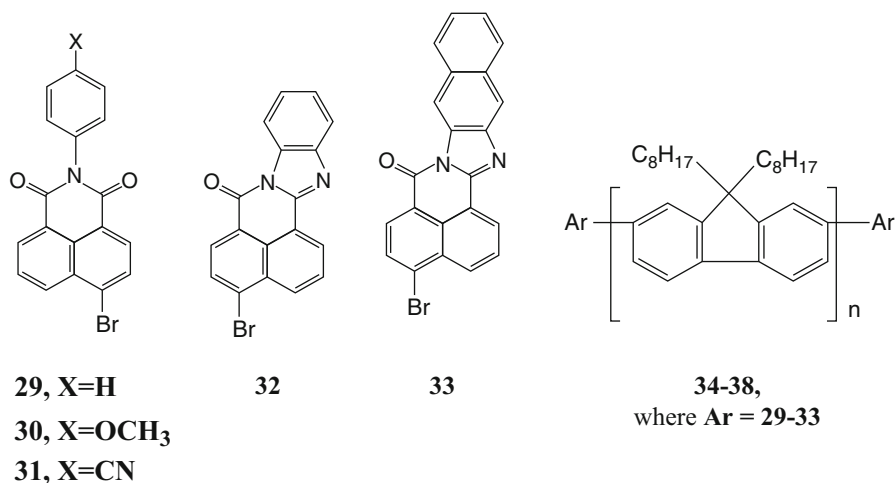


**Fig. 13** Molecular structures of different green-emitting polymers

The BT units were also copolymerized with cyclopenta[*def*]phenanthrene derivatives to give poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-poly(2,1,3-benzothiadiazole) (PCPPBTs, **27**) [95]. The introduction of BT unit resulted red-shifted emission. The color of emission was found to be varying with the amount of BTs. The PL spectra were having two emission peaks at around 410 and 530 nm in thin films. The polymer LEDs of combination (ITO/PEDOT/polymer/Ca:Al) of PCPPBTs exhibited emissions  $\lambda_{\text{max}}$  at 508–528 nm. Among all the devices fabricated, the best device was the one with PCPPBT10, which showed the highest luminous efficiency of 1.25 cd/A and the highest brightness of 1170 cd/m<sup>2</sup>. This study established that PL efficiency can be improved by randomly copolymerizing the BT into the PCPP.

Fluorene and benzothiazolopyrazoline units were copolymerized to give Poly(9,9-dihexylfluorene-*alt*-benzothiazolopyrazoline, **28**) [96]. This polymer possessed good thermal stability. As a solid thin film, the polymer emits green light ( $\lambda_{\text{max}}$  at 501 nm) with high (PL) quantum yield of 47%. Polymer light-emitting diode (PLED) fabricated with the configuration of ITO/PEDOT/PVK/polymer/Ba(4 nm)/Al(160 nm) emit green light with  $\lambda_{\text{max}}$  at 501 nm. The maximum brightness and the maximum EQE achieved were 1726 cd/m<sup>2</sup> and 1.59%, respectively.

Lee et al. synthesized a series of polyfluorenes (P1-P5) which were end-capped by *N*-aryl-1,8-naphthalimide and 1,8-naphthoilenarylimidazole derivatives in an attempt to red-shift the blue emission of (PFs) into the greenish region [96]. The color of emission was tuned by controlling the content of **29–33**. The electroluminescence (EL) spectra of polymers (**34–38**) exhibit greenish-blue, bluish-green, pure green, and yellowish-green emission with the corresponding peak emission ( $\lambda_{\text{max}}$ ) at 465 nm (for **35**), 490 nm (for **34** and **36**), 500 nm (for **37**), and 545 nm (for **38**). Of these polymers, **37** could give pure green emission in the device. The maximum brightness achieved for this polymer was ~6500 cd/m<sup>2</sup> with a current efficiency of 0.56 cd/A (Fig. 14).

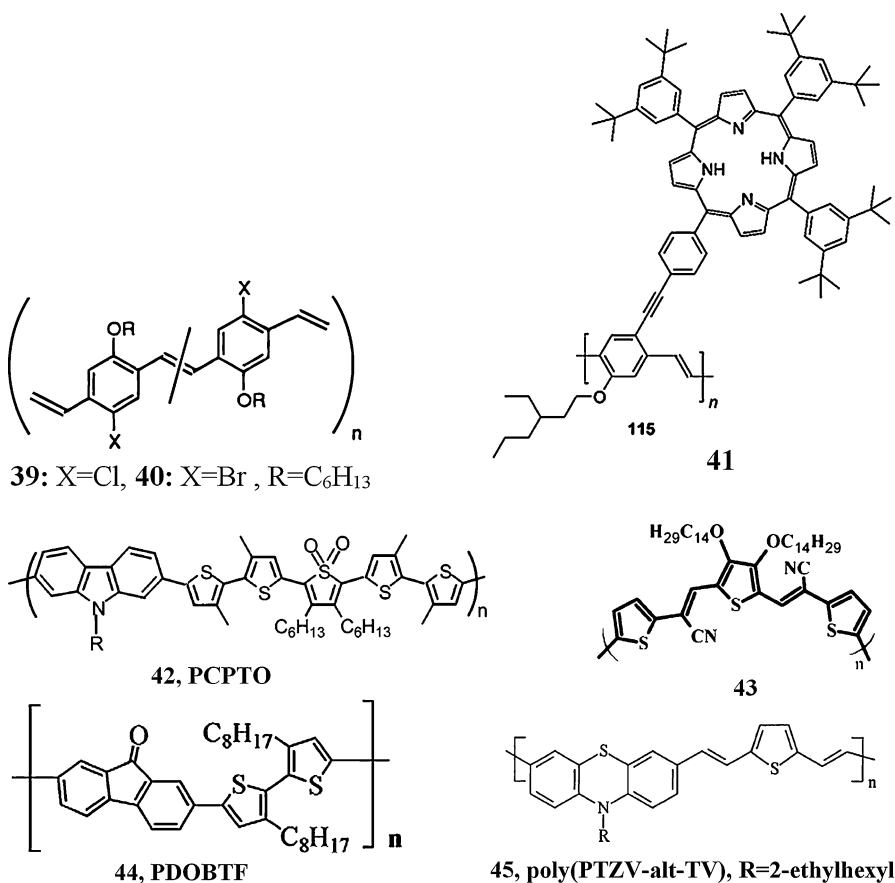


**Fig. 14** Molecular structures of green-emitting polymers

### 10.3 Red-Emitting Polymers

Gurge and co-workers studied the asymmetrically substituted, “push-pull” family of PPVs, i.e., poly(2[5-chloro-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene) and poly(2[5-bromo-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene), **39** and **40**, respectively (Fig. 15) [97]. These polymers gave strong EL emission in the ~620 nm (orange-red to red) spectral region even without fine-tuning of emission characteristics. Single-layer LED of configuration ITO/**39**/Ca exhibited an output brightness of ~20 cd/m<sup>2</sup> at 30 V pulsed input voltage using 1 mA of current [97].

Lo and Burn synthesized polymer (**41**) (Fig. 15) by incorporating a red-emitting porphyrin as a side chain to the PPV unit by a rigid phenylacetylene linker [98]. Red emission with  $\lambda_{\text{max}}$  at 604, 653 nm were observed in PL studies which suggest that the red emission originated from the porphyrin chromophore. But the EL device performance was rather poor.



**Fig. 15** Molecular structures of red-emitting polymers

Morin and Leclerc synthesized 2,7-carbazole-based light-emitting homopolymers and copolymers [99]. Wherein, poly(*N*-(2-ethylhexyl)-2,7-carbazole-*alt*-3,3',4''',3''''-tetramethyl-3'',4''-dihexyl-2,2':5',2'':5'', 2''':5''',2''''-quinquethiophene-1'', 1''-dioxide) (PCPTO) (**42**) (Fig. 15) emits red light with  $\lambda_{\text{max}}$  at 638 and 671 nm. The fluorescence quantum yield in chloroform solution was measured to be 25% for PCPTO.

Manjunatha and co-workers synthesized narrow band gaped donor-acceptor type polymer from cyanovinylenepoly{3,30-(3,4-ditetradecyloxythiophene-2,5-diyl) bis[2-(thiophen-2-yl)prop-2-enenitrile]} (**43**) (Fig. 15) [100]. The polymer exhibited red-fluorescence in solution as well as in solid state. The peak emission wavelength of polymer in solid thin film was measured to be 647 nm. The PL efficiency of the polymer was determined to be 43%.

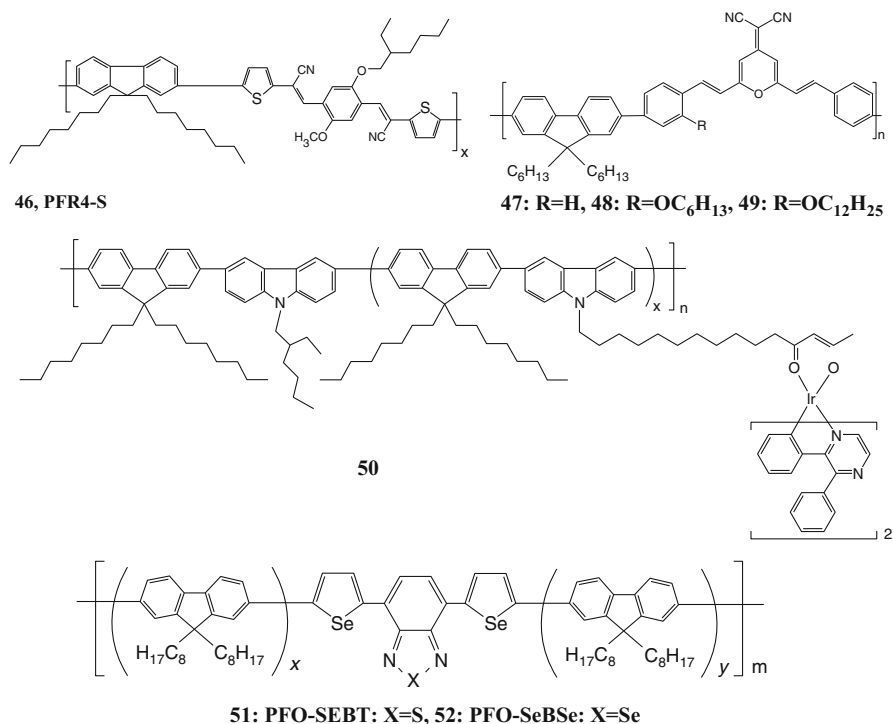
Fluorenone and dialkylbithiophene were copolymerized to give regioregular, alternate copolymer poly[(5,5'-(3,3'-di-*n*-octyl-2,2'-bithiophene))-*alt*-(2,7-fluoren-9-one)] (PDOBTF) (**44**) (Fig. 15) by different preparation methods [101]. The photoluminescence studies showed that PDOBTF emits red light with  $\lambda_{\text{max}}$  at 643 nm in the solid state.

Kim and co-workers synthesized an alternating copolymer poly(PTZV-*alt*-TV) (**45**) (Fig. 15) using Wittig polycondensation between 10-(2-ethylhexyl)-phenothiazine-3,7-dicarbaldehyde and thiophene bis(phosphonium) salt [102]. The PL emission of poly(PTZV-*alt*-TV) as a thin film was having  $\lambda_{\text{max}}$  at 584 nm. Electroluminescent device was fabricated in an ITO/PEDOT/poly(PTZV-*alt*-TV)/Ca/Al configuration which showed maximum brightness of 140 cd/m<sup>2</sup> and a luminous efficiency of  $1.3 \times 10^{-2}$  cd/A. However, at different voltages emission at 650 nm was also observed. The EL emission spectrum of the device showed a broad emission range (500–800 nm).

Cho and co-workers were able to tune the color of emission of polyfuorenes by copolymerization of fluorene with different comonomers. They were able to synthesize pure red-emitting poly{9,9-dioctylfluorene-2,7-diyl-*alt*-2,5-bis(2-thienyl-2-cyanovinyl)-1-(2'-ethylhexyloxy)-4-methoxybenzene-5'',5''-diyl} (PFR4-S) (**46**) by doing Suzuki coupling of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxabororan-2-yl)-9',9'-dioctylfluorene and 2,5-Bis{2-(4'-bromothieryl)-2-cyanovinyl}-2-(2'-ethylhexyloxy)-5-methoxybenzene [103]. The PL and EL emission peaks of PFR4-S as a solid thin film were at 674 nm. Single-layer LED devices fabricated from this polymer emitted pure red light. The CIE coordinate values  $x = 0.66$ ,  $y = 0.33$  of the device was almost identical to the standard red ( $x = 0.66$ ,  $y = 0.34$ ) as demanded by the National Television System Committee.

Peng and co-workers synthesized a series of red-light-emitting copolymers (**47–49**) using fluorene and 2-pyran-4-ylidenemalononitrile (PM) [104]. The PL emission of these polymers in thin films emit red color with  $\lambda_{\text{max}}$  around 641–662 nm and additional peaks in the range 704–712 nm. The absolute PL quantum yields of the polymer as solid thin films were measured to be about 4–7%. The PLEDs fabricated with the configuration of ITO/PEDOT/polymer/Ba/Al emit red light with EQE of 0.21–0.38%.

Ying and co-workers copolymerized 3,6-dibromo-*N*-alkylcarbazole having red-emitting Iridium complex in the alkyl chain with fluorene to give poly



**Fig. 16** Molecular structures of red-emitting copolymers of fluorene

(fluorene-alt-carbazole) (**50**, Fig. 16) based copolymers [105]. Iridium complex in the ratio of 1 mol% to that of host polymer was sufficient to completely quench the emission of host polymer. The polymer PFCzIrBpz-1 in the device configuration ITO/PEDOT:PSS/polymer+PBD/Ba/Al gave an orange-red emission. The phosphorescent polymer light-emitting diodes (PhPLEDs) showed a maximum luminous efficiency (LE) of 5.58 cd/A and a maximal luminance of 8625 cd/m<sup>2</sup>.

Yang and co-workers synthesized a series of copolymers, using alkyl-substituted fluorene and 4,7-diselenophen-2'-yl-2,1,3-benzothiadiazole (SeBT), or 4,7-diselenophen-2'-yl-2,1,3-benzoselenadiazole (SeBSe) as the comonomers (**51**, **52**, Fig. 16) [106]. The PL emission peaks as solid thin films were found to depend upon the content of comonomer. The PL and EL is dominated by narrow-band-gap species and peaked at 670–790 nm. The double layer devices made from these two types of copolymers in the configuration ITO/PVK/polymer/Ba/Al reached an EQE of 1.1% and 0.3%, respectively.

## 10.4 White Light-Emitting Polymers

Single polymer which can emit white light can be synthesized by incorporating two chromophores (blue and orange) or three chromophores (blue, green, and red) into a

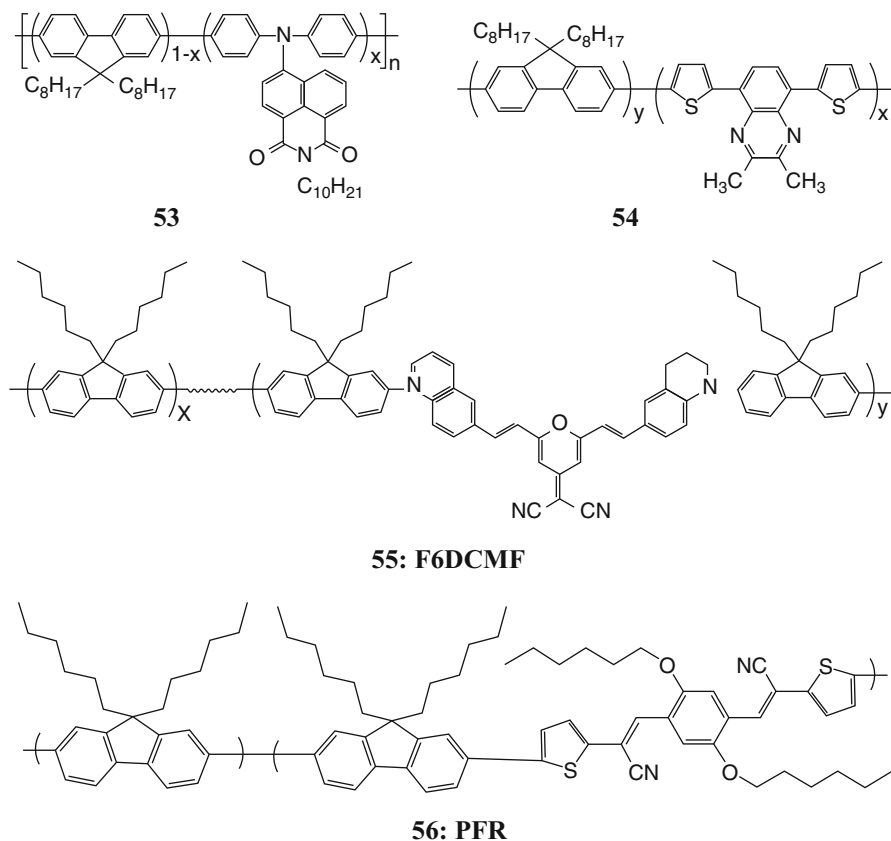
polymeric chain. It is very difficult to synthesize the latter; however, it offers better color quality while synthesis of the former type of white light-emitting polymer is easy. Tu and co-workers developed two component polymers for white light emission. They incorporated 1,8-naphthalimide (orange emissive) unit as dopant into polyfluorene (blue-emitting polymer) with varying dopant ratio [107]. A novel single-component polymer system (**53**) with 0.05 mol% of dopant showed white light emission. A white polymeric light-emitting diode (WPLED) fabricated with the configuration ITO/PEDOT:PSS/**53**/Ca/Al showed a current efficiency of 5.3 cd/A and a power efficiency of 2.8 lm/W at 6 V [107].

Sun and co-workers synthesized a series of copolymers by incorporating orange-emitting 2,3-dimethyl-5,8-dithien-2-ylquinoxaline (DDQ) unit in the backbone of PFO with varying mole ratio [108]. White emission could be obtained by carefully controlling the DDQ unit (~0.02 mol%) in the PFO backbone. The two distinguished emission peaks (blue and orange red) leading to white light emission were observed in the polymer PFO-DDQ002 (**54**) due to incomplete energy transfer from the PFO to DDQ. A WPLED fabricated with the configuration ITO/PEDOT/PVK/PFO-DDQ/**54**/Ba/Al showed high EQE and current efficiency of 2.64 and 4.1 cd/A, respectively. The CIE coordinates remained stable for different voltages.

Lee et al. synthesized a series of copolymers by incorporating 2-(2,6-bis-{2-[1-(9,9-dihexyl-9H-fluoren-2-yl)-1,2,3,4-tetrahydro-quinolin-6-yl]-vinyl}-pyran-4-ylidene)-malononitrile as the orange unit into a polyfluorene main chain as the blue host [109]. The polymer (F6DCM005) having 0.05 mol% of orange-emitting comonomer (DCMF) was found to emit white light with peak emission at 423/450 nm (blue) and at 580 nm (orange). The PLED fabricated in the configuration ITO/PEDOT:PSS/**55**/Ca/Al showed white light emission with CIE coordinates (0.33, 0.32). The maximum brightness and current efficiency achieved in the device were 1180 cd/m<sup>2</sup> and 0.60 cd/A, respectively [109].

Hsieh and co-workers synthesized copolymers (**56**, Fig. 17) by incorporating orange emitting chromophore 2,5-dihexyloxy-1,4-bis(2-thienyl-2-cyanovinyl) benzene in the mole ratio (0.1 and 0.025 mol%) into the polyfluorenes for getting white electroluminescence [110]. The PL peaks of copolymer films ~428 and 570 nm were due to fluorene unit and the orange chromophore unit respectively. The PLEDs of the copolymers PFR1 and PFR2 showed white light emission with CIE coordinates (0.36, 0.35) and (0.32, 0.30), respectively, which are close to white light emission (0.33, 0.33). The maximum EL brightness achieved with PFR1 and PFR2 were 5419 and 3011 cd/m<sup>2</sup>, respectively [110].

Lee and co-workers copolymerized 2-{2-(2-[4-{bis(4-bromophenyl)amino}phenyl]-vinyl)-6-tertbutylpyran-4-ylidene}malonitrile (TPDCM) (red emitter), {4-(2-[2,5-dibromo-4-{2-(4-phenylaminophenyl)vinyl}phenyl]-vinyl)phenyl}-diphenylamine (DTPA) (green emitter), and a 2,7-dibromo-9,9-dihexylfluorene (DHF)(blue emitter) in suitable ratios to get white light-emitting polymer [111]. White emission was observed in the polymer PG3R2 (**57**, Fig. 18) having the comonomers composition as 3 mol% of DTPA and 2 mol% of TPDCM. The WPLED device fabricated in the configuration ITO/PEDOT:PSS/polymer/Ca/Al showed white light emission with CIE coordinated of (0.33, 0.35). The peak luminance and current efficiency achieved were 820 cd/m<sup>2</sup> and 0.1 cd/A, respectively [111].



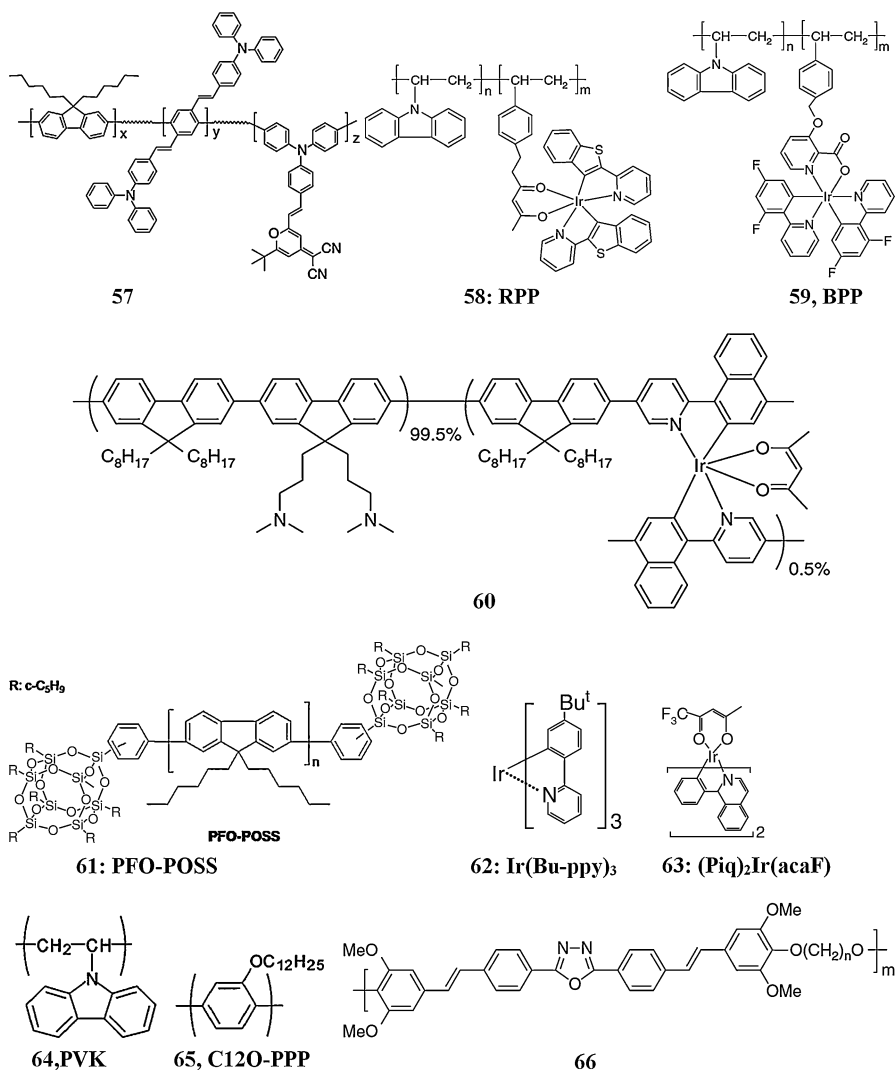
**Fig. 17** Molecular structures of white-emitting copolymers

Tokito and co-workers were able to get white light emission by blending red phosphorescent polymer (RPP) (**58**) and blue phosphorescent polymers (BPP) (**59**) [112]. The RPP and BPP when mixed with the ratio of 10:1 in a PLED having the configuration ITO/PEDOT:PSS/**58** + **59**/Ca/Al showed white EL with CIE coordinates of (0.34, 0.36). The EQE of white emission was measured as 4.5%.

Xiong et al. fabricated polymer white light-emitting diodes based on the blend of poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl]-end capped with polysilsesquioxane (PFO) and poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene-alt-2,7-(9,9-dioctylfluorene))-co-[2,7-(9,9-dioctylfluorene)-alt-5,5-bis(2-(4-methyl-1-naphthalene) pyridine-C2,N) iridium (III) acetylacetonate]] (PFN-NaIr05) (**60**) [113]. The PLED of the configuration ITO/PEDOT/PVK/PFO: PFN-NaIr05/Al with 5% PFN-NaIr in the blend showed white light emission having CIE coordinates of the (0.34, 0.35).

Xu et al. demonstrated white light emission by doping a blue-emitting oligomeric silsesquioxane-terminated poly(9,9-dioctylfluorene) (PFO-poss) (**61**) with green





**Fig. 18** Molecular structures of some other white-emitting copolymers

emitting *fac*-tris[2-(4'-*ter*-butyl)phenylpyridine]Iridium (III) [Ir(Bu-ppy)<sub>3</sub>] and red-emitting bis-(1-phenylisoquinolyl)Iridium(III)(1-trifluoro)acetylacetonate [(Piq)<sub>2</sub>Ir(acaF)] [114]. The electroluminescence spectrum was found changing with the concentration of the guests. The WPLED with the configuration ITO/PEDOT:PSS/PVK/PFO-poss+**62**+**63**/Ba/Al and with the doping concentrations of 0.14 wt% for **62** and **63**. The CIE coordinates of WPLED was around (0.33, 0.33). The maximum brightness achieved in the device was ~10,200 cd/m<sup>2</sup>.

White light emission has also been reported by utilizing excimer or exciplex formation. Chao and co-workers reported WPLED which utilized the exciplex formation between poly(N-vinyl carbazole) PVK (**64**) and poly(2-dodecyl-p-phenylene) (C12O-PPP) (**65**) [115]. A broad EL spectrum having emission from 400 to 700 nm was observed. The exciplex emission was arising from the recombination of the electron in the lowest unoccupied molecular orbital (LUMO) of C12O-PPP and the hole in the highest occupied molecular orbital (HOMO) of carbazole groups in PVK.

Lee and co-workers reported white light emission from a single-layered system based on oxadiazole and phenylenevinylene copolymer having ether linkage [116]. The emission spectrum of the above was found to be composed of red and blue-green components from different species, i.e., red component originated from the new excited dimer while blue-green component from an individual lumophore and excimer. The excited dimer generated in the above system was reported to be different from excimers/exciplex, typically observed in electro- and photoluminescence and could not be produced during these processes and could be seen only in the system under high electric field.

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## 11 Conclusion

Herein, the various components of making an efficient OLED are discussed. We first described the electronic transitions and energy transfer processes involved in conjugated polymers. The working of different types of device architectures, their efficiencies, and the measurement that are normally made in OLEDs are also presented. The various types of materials and their functional requirements as needed in the making of multilayer OLEDs are discussed. Several categories of blue, green, red, and white light-emitting polymers have been highlighted. Conjugated polymers have established their importance for optoelectronic device applications. They give high electroluminescence efficiency in OLEDs. The improved efficiencies of these devices are facilitating the commercialization of these devices.

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