

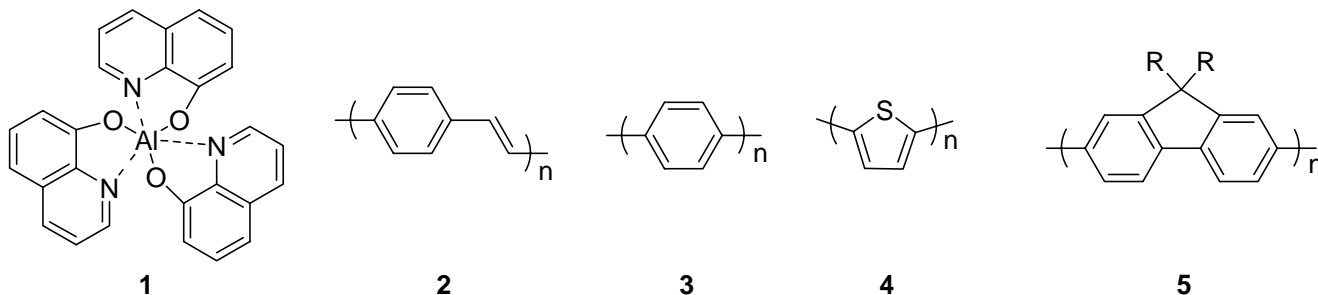
# ELECTROLUMINESCENCE OF CONJUGATED AROMATIC POLYMERS IN ORGANIC LIGHT EMITTING DIODES

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## INTRODUCTION

Organic electroluminescent materials have been the subject of intense research for use in light emitting diodes (LEDs). When compared with liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) require lower energy input, have a wider viewing angle with improved color contrast, and can be made much thinner.<sup>1</sup> The electroluminescence (EL) of organic compounds was first demonstrated in 1953 by Bernanose<sup>2</sup> but was not significantly developed until 1987 when Tang and Van Slyke<sup>3</sup> constructed a device employing aluminum tris(8-hydroxyquinoline) **1** as the luminescent material. The first example of a polymer-based OLED was published by Friend et al.<sup>4</sup> in 1990 in which poly(*p*-phenylene-vinylene) (PPV) **2** was used as the emissive layer. Since this discovery, many conjugated polymers have been developed for use in LEDs including poly(1,4-phenylene) (PPP) **3**, poly(thiophene) **4**, and polyfluorene **5**.

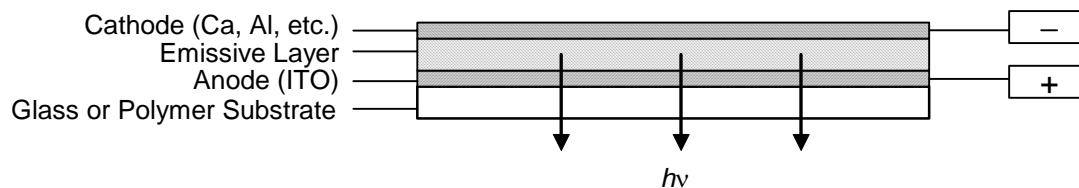


Polyfluorene-based materials can emit color across the entire visible range<sup>5</sup>, possess high thermal stability, and can be easily functionalized at the methylene bridge for fine tuning of emissive properties. These characteristics make polyfluorene homo- and co-polymers attractive components for luminescent materials in OLEDs. This report will review the use of conjugated polymers as electroluminescent materials in OLEDs with a focus on the synthesis and emissive properties of polyfluorene homo- and co-polymer derivatives. The mechanism of EL in organic compounds and device configuration will also be discussed.

## ELECTROLUMINESCENCE OF ORGANIC MATERIALS

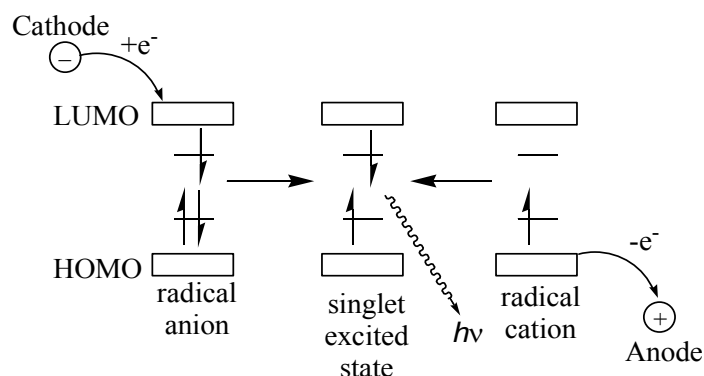
In a simple LED, a thin film of luminescent material is sandwiched between two electrodes as shown in Figure 1. The cathode typically consists of a thin film of metal such as calcium or aluminum

which can be evaporated onto the emissive layer. The anode most commonly used is a semi-transparent indium-tin oxide (ITO)-coated glass or polymer substrate. If a polymer substrate is used, the possibility of creating an ultra-thin, flexible display becomes apparent.



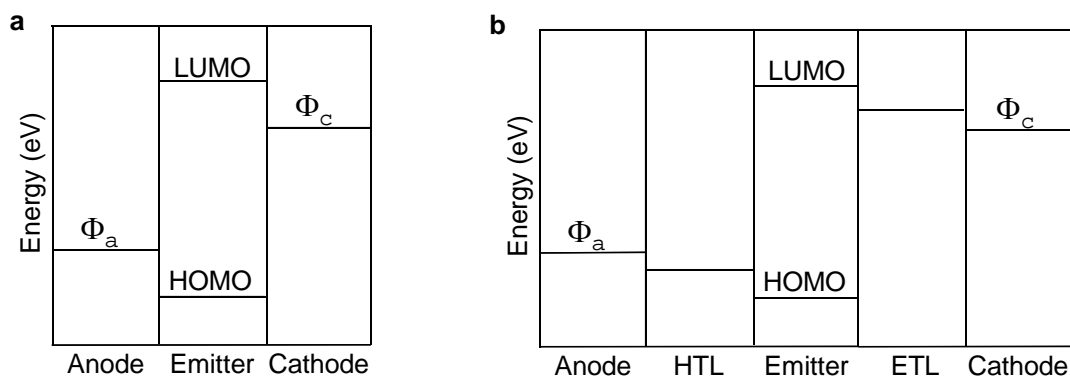
**Figure 1.** Schematic representation of single-layer OLED.

When an electrical current is applied across the device, electrons are injected into the lowest unoccupied molecular orbital (LUMO) at the cathode to form radical anions and holes are injected into the highest occupied molecular orbital (HOMO) at the anode to form radical cations.<sup>6</sup> These charge carriers migrate throughout the emissive layer under an electrical bias forming singlet and triplet excited states when oppositely charged species combine. The excited singlet state can relax radiatively and emit light (Figure 2).



**Figure 2.** The emission of light from the singlet excited state generated by charge combination.<sup>6</sup>

In the single layer device described in Fig. 1, the organic EL layer needs to be capable of maintaining high quantum efficiency as well as good hole and electron injection and mobility. Since most materials cannot meet this demand, multi-layer devices have been designed to improve charge injection and mobility. Critical factors in constructing efficient EL devices are the barriers to hole and electron injection. If there is a large mismatch in energy between the HOMO and the anode work function ( $\Phi_a$ ) or the LUMO and the cathode work function ( $\Phi_c$ ), charge injection will be poor.<sup>7a</sup> Incorporation of a layer with either good hole or electron affinity between the emissive layer and the electrode reduces the energy barrier to charge injection (Figure 3). Many such materials have been evaluated for use as hole and electron transporting layers.<sup>7</sup>



**Figure 3.** Energy-level diagram of (a) single layer OLED and (b) multilayer OLED with a hole transporting layer (HTL) and electron an transporting layer (ETL).

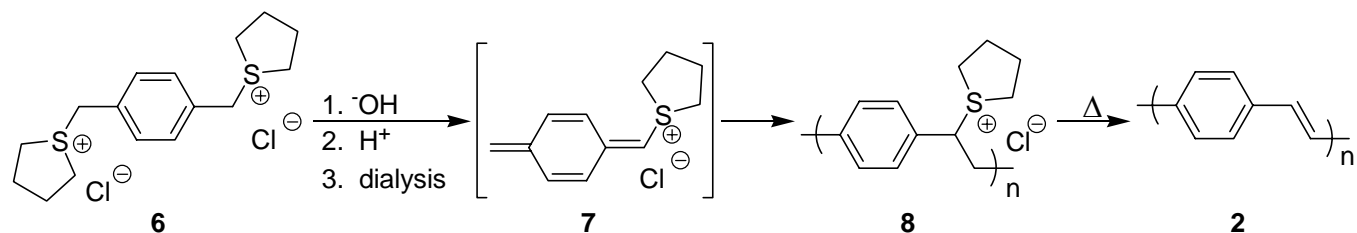
## POLYMER LIGHT EMMITING DIODES

### PPV based devices

Conjugated polymers are organic semiconductors in which the  $\pi$ -molecular orbitals are delocalized along the polymer backbone. Polymer-based OLEDs are attractive due to their excellent film forming properties and their ease of application over large surfaces through simple, economically viable coating techniques such as spin coating or ink-jet printing. Small molecule emissive materials are typically coated as thin films via vacuum-deposition which is difficult over large areas and is not as cost effective.

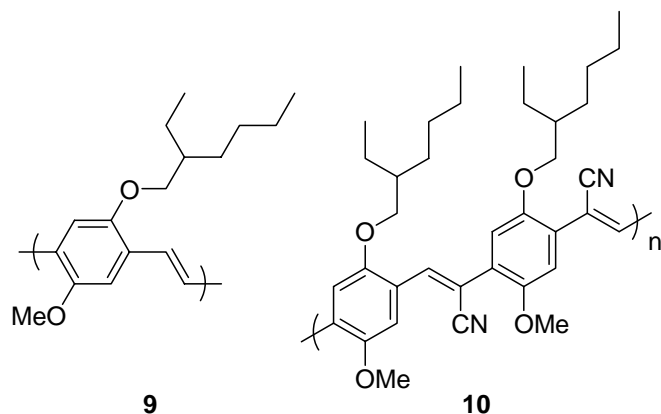
As previously stated, PPV was the first polymer that was shown to display electroluminescence. Since direct synthesis of PPV produces an insoluble material, an alternative route was developed to allow the spin-coating of a soluble precursor polymer from solution (Scheme 1).<sup>4</sup> Addition of slightly

**Scheme 1.** Soluble precursor route to PPV.



less than 1 equivalent of NaOH to bis-sulfonium salt **6** followed by acidification and purification by dialysis yields the polymeric species **8** via *p*-xylylene intermediate **7**. The precursor polymer **8** can be spin-coated from solution onto an ITO-coated substrate then converted to PPV upon heating. An alternate route to producing PPV films involves derivatizing the backbone with solubilizing groups. One such polymer that has received considerable attention is the alkoxy functionalized derivative **9**. This compound along with other PPV derivatives such as the cyano alkoxy analog **10** have been used to

construct devices capable of emitting either red or green light with modest efficiencies and lifetimes (Table 1).



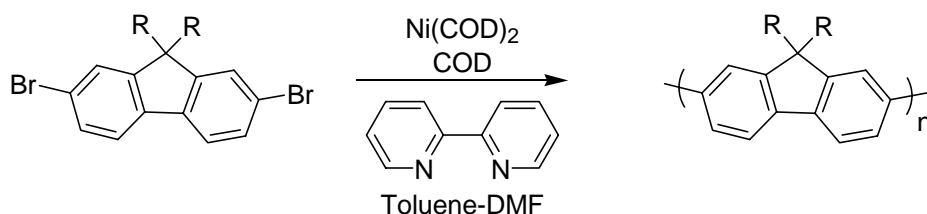
**Polyfluorene based Devices**

PPV-based materials are useful as red and green light emitters in LEDs, but accessing blue light via EL has remained a challenge due to the large band gap required for blue emission. The bulk of initial research in blue-emitting polymers focused on OLEDs containing PPP as the emissive layer.<sup>9</sup> Since PPP is insoluble in most solvents, derivatives containing solubilizing side groups were synthesized to improve processibility. However, the steric demand introduced by the solubilizing groups causes an increase in the torsional angle between the phenyl rings.<sup>10</sup> This lowers the conjugation between rings and causes a blue shift in emission and a reduction in EL efficiency. Ohmori and coworkers first demonstrated blue EL from an LED using poly(9,9-dihexylfluorene) as the emissive layer.<sup>8</sup> Polyfluorene can be considered a structural analog of PPP in which pairs of phenyl rings are joined together by a methylene bridge. The methylene bridge serves to lock the ring pairs into a coplanar arrangement and can be functionalized without distorting the torsional angle between the fluorene units. This feature has made polyfluorene derivatives attractive new targets for use as emissive materials in OLEDs.

### Synthesis of fluorene based polymers

Many polyfluorene derivatives have been prepared by the nickel-mediated Yamamoto polymerization (Scheme 2).<sup>11</sup> One drawback to this procedure is that polymers with a degree of

**Scheme 2.** Yamamoto polymerization of 9,9 substituted fluorene.



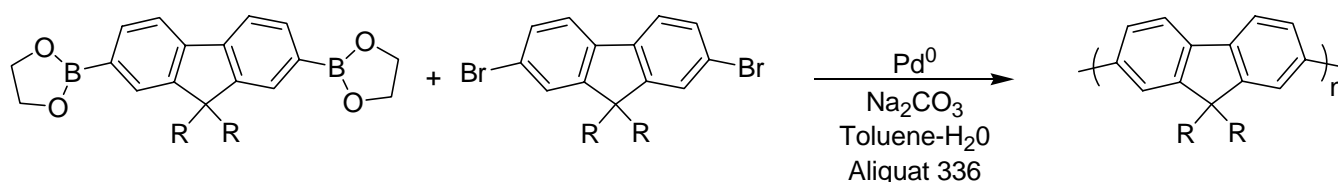
**Table 1. Emissive Properties of PPV and PPV derivatives.**

Polymer	Color ( $\lambda_{\text{max}}$ [nm])	$\eta_{\text{ext}}$ (%) <sup>a</sup>	Lifetime (h)
<b>2</b>	green (550)	0.3	1400
<b>9</b>	red-orange (610)	2.5	2000
<b>10</b>	red-orange (600)	2.5	3000

<sup>a</sup> The external quantum efficiency ( $\eta_{\text{ext}}$ ) is quantified as the number of photons emitted per electrons injected divided by  $2n^2$  ( $n$ =refractive index of polymer).

polymerization (DP) greater than 50 are difficult to obtain due to low solubility in the highly polar aprotic reaction medium.<sup>12</sup> Ordered copolymers are also hard to obtain as the relative reactivities and concentrations of each monomer needs to be precisely balanced. A superior method is based on the palladium-catalyzed reaction of mixed phenylboronic acids and arylbromides to give biphenyls.<sup>13</sup> The polymerization method has been modified such that polymers of molecular weight ranging from 10,000 to 500,000 Da are generated in high yields with good purity (Scheme 3).<sup>14</sup> Both the Yamamoto and Suzuki polymerization have been used to synthesize a variety of 9,9- substituted polyfluorenes with various physical and EL properties.

**Scheme 3.** Modified Suzuki Coupling of 9,9-substituted fluorenes.



### Origin of Unwanted Green Emission of Polyfluorenes

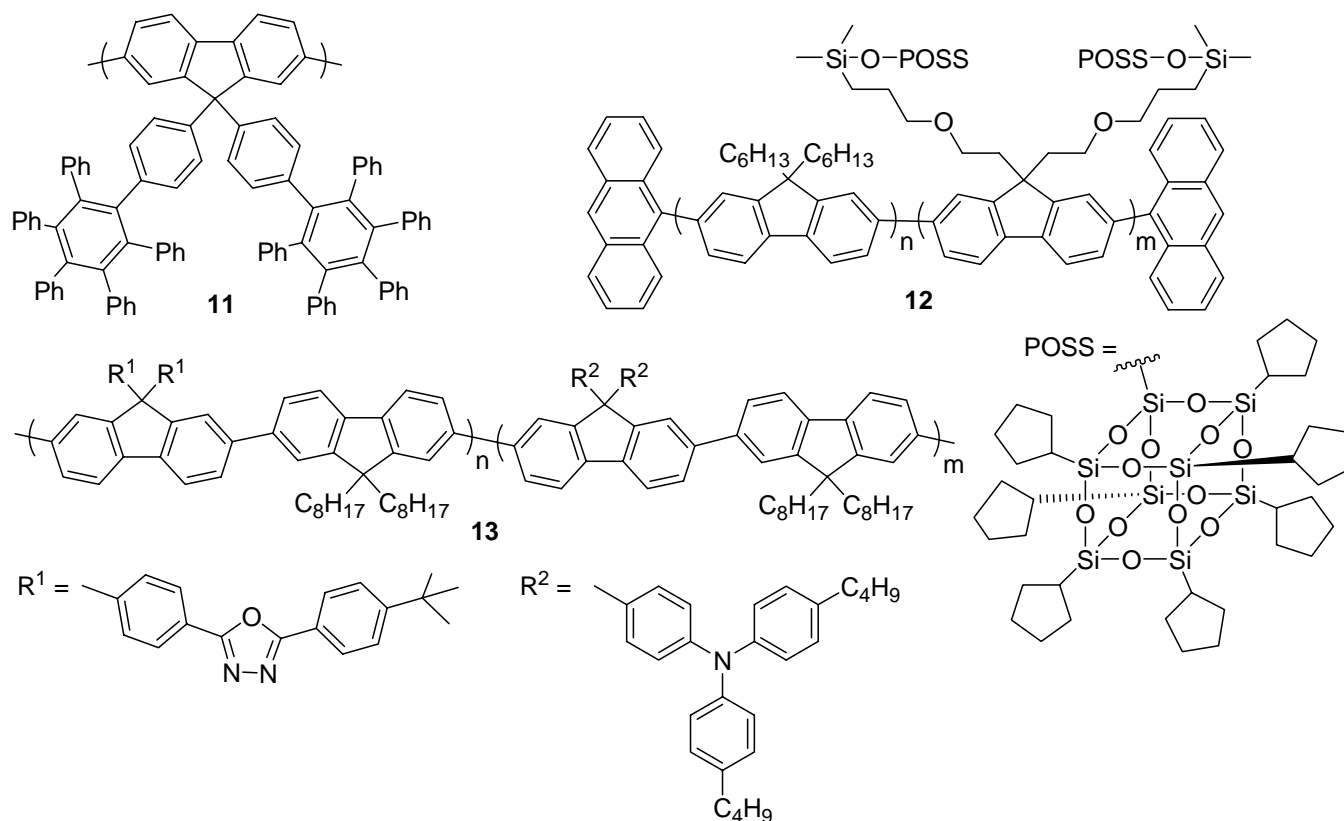
Although polyfluorenes show great promise as blue emitting materials in LEDs due to their solution processibility, high photoluminescence (PL) efficiencies, and ease of functionalization, many of the polymers developed have suffered from an unwanted green emission band (535 nm) along with the desired blue emission. The origin of the green emission was initially attributed to intermolecular excimer formation between polyfluorene chains.<sup>15</sup> An excimer is defined as a complex between an excited state of a molecule and a ground state of the same molecule which typically results in the emission of light at a lower frequency than that of the isolated molecule without affecting ground state spectral features.<sup>16</sup> Bliznyuk and coworkers showed that the intensity of the green emission band in thin films of poly(9,9-di-*n*-hexylfluorene) increased over time when irradiated with UV light in air and during LED device operation.<sup>15</sup> They did not observe a change in the absorbance band linked with growth of the green emission and found a common excitation band for both the blue and green emission. Thus, they believed the green emission resulted from excimer formation. In the same study, it was also demonstrated that poly(9,9-di-*n*-hexylfluorene) photodegrades in the presence of oxygen to form 9-fluorenone units in the polymer backbone. Additional experimental evidence suggests that the origin of the green emission is related to the presence of fluorenone defects in the polymer backbone and not from fluorene-fluorene excimer emission.<sup>17,18</sup> The intensity of the green band has also been demonstrated to increase with increasing concentration of fluorenone containing polymers. This suggests that there is a

dependence on the interaction between polymer chains/segments containing polyfluorene defects. The nature of this interaction remains a source of controversy in the literature.

### Functionalization of Polyfluorene

The ability to functionalize polyfluorene at the methylene bridge without distorting the conjugation between monomer units has been utilized as a method to help control the undesirable green emission, to modify charge injection and mobility in the emissive layer and to improve thermal properties of the polymer. Most approaches are based on limiting interchain interactions without reducing charge mobility. However, the nature of the green emission remains controversial, so the mechanism by which the modifications stabilize the blue emission is not fully understood.

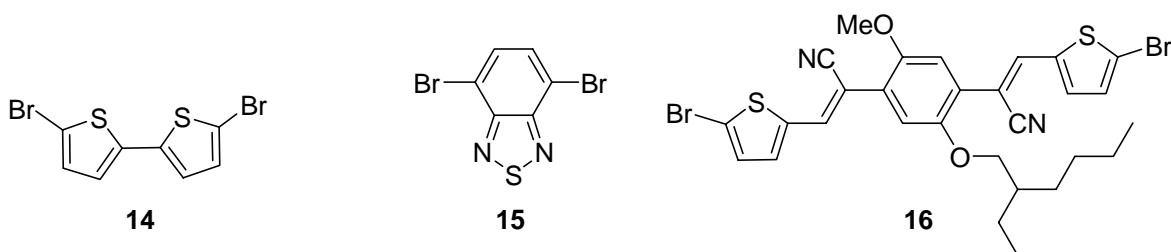
First generation phenylene dendrons **11** effectively stabilize the blue emission without affecting charge mobility.<sup>19</sup> Incorporation of a polyhedral oligomeric silsesquioxane (POSS) as an end group<sup>20</sup> or at the methylene bridge as in the case of **12**<sup>21</sup> improves the thermal properties of the polymers as well as the EL quantum efficiency. Attachment of a hole-transporting triphenylamine and an electron-transporting oxadiazole at the methylene bridge as in the case of copolymer **13** resulted in a stable blue emission with improved charge injection.<sup>22</sup>



**Figure 4.** Functionalized polyfluorene derivatives.

## Polyfluorene copolymers

Due to their high thermal stability and high PL yields, polyfluorene-based polymers have been developed as luminescent materials that emit across the entire visible spectrum. Copolymerization of fluorene monomer derivatives with different aromatic moieties allows for color tuning through modification of the band gap. Copolymers consisting of 9,9-substituted fluorenes and low band gap monomers such as 5,5'-dibromo-2,2'-bithiophene **14** and 2,1,3-benzothiadiazole **15** produce yellow and yellow-green light respectively.<sup>23</sup> Shim and coworkers prepared copolymers spanning the full color range from blue to red by varying the monomer feed ratio of 2,5-bis(5'-bromothiophen-2-yl)-1-cyanovinyl)-1-(2''-ethylhexyl)-4-methoxybenzene **16**.<sup>24</sup>



## CONCLUSION

Conjugated polymers have been studied in great detail as electroluminescent materials for use in organic light emitting diodes. Significant progress has been made in understanding the fundamental working processes involved in generating efficient, reliable light across the entire visible spectrum. Polyfluorene-based materials have been investigated extensively because of the many attractive properties they possess. Additional experimental results are needed to discern the nature of the unwanted green emission that often appears during device operation and quantum efficiencies need to be significantly improved. A more complete understanding of the primary factors that govern device performance and lifetime will aid in these discoveries. Significant progress is required before OLEDs can be created for use in a broad range of consumer applications in a cost-effective manner. However, limited commercial applications are already being developed as OLED displays have been used in digital cameras, cell phones and car stereos. The possibility of creating flexible, ultra-thin displays with high information content remains a novelty but may be realized in the future.

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