Chapter 5

Two Novel Intense Green Light Emitting Thienylene-Biphenylenevinylene Hybrid Polymers: Synthesis, Characterization and Photophysical Studies

Abstract

Two novel hybrid polymers based on thienylene-biphenylenevinylene have been synthesized through Stille coupling polymerization method. The polymers exhibited complete solubility in common organic solvents such as dichloromethane, tetrahydrofuran, chloroform, toluene etc. Structure of the synthesized polymers was confirmed on the basis of \(^1\)H NMR, \(^1^3\)C NMR, FTIR and elemental analysis data. Gel permeation chromatograph (GPC) indicated that the polymer samples give narrow molecular weight distribution. Thermogravimetric analysis (TGA) demonstrated excellent thermal stability of the polymers. Due to the positional difference in bulky group substitution present in the biphenylene vinylene backbone, the structural and thermal properties of the two synthesized polymers show profound dissimilarities. Structural studies of the polymers were done by using XRD analysis. The polymers showed broad photoluminescence invisible region without any vibronic bands. Both of the polymers provide intense green emission with very high quantum yields. Cyclic voltammetry was used to estimate energy levels of the lowest unoccupied molecular orbit (LUMO), highest occupied molecular orbit (HOMO), and band gap (\(E_{\text{g}}^{\text{EC}}\)) of the polymers. Powder state morphology of the polymers was analyzed by using SEM and surface smoothness of the spin coated films was detected by AFM analysis. Based on cyclic voltammetry studies, Schottky diode has been constructed and these polymers show very low onset voltages. I-V measurements indicated that the two new polymers are promising candidates for fabricating polymer light emitting diodes.

5.1 Introduction and Motivation

Conjugated light emitting polymers (LEPs) have attracted considerable attention due to their dynamic development in electro-optical applications. Optoelectronic devices like polymer light emitting diodes (PLED) have attracted
wide spread research attention owing to superior properties like easy processing, good mechanical properties, flexibility, lower operational power, color tunability, possibility of large area coatings etc. Internal efficiency of the optoelectronic devices is mainly dependent on electroluminescent and photoluminescent efficiency of emissive polymer such as emitted color, quantum efficiency, and balanced injection of electrons and holes. Device life time and luminescent stability are the primary constraints for commercialization of these optoelectronic devices. Many light emitting polymers have poor luminescent efficiency, life times and low color purity due to the presence of interchain interactions such as aggregation, excimer formation, and polaron pair formation. Therefore an effective way of synthesizing conjugated light emitting polymers with reduced π-stacking, high solubility, high thermal stability with high light-emitting efficiency is still a challenge for chemists.

Many organic luminescent polymers are composed of conjugated extended chains of alternating phenyl and vinyl units. The intrachain or interchain interactions (molecular aggregation) within these polymer chains would change their emitted color. One effective approach is to reduce these undesirable effects, by the introduction of structural asymmetry into the polymer backbone that limits its ability to pack effectively in the solid state. Among the approaches attempted to control the undesirable effects such as molecular aggregation, luminescence quenching etc in light emitting polymers, the confinement of conjugation length and increasing interlayer distances are widely reported in literatures. Confine ment in conjugation length was achieved by introducing meta linkages in the main polymer chain backbone that can limit interchain interactions while allowing the polymer backbone to bend and twist more effectively than one with a para-linkage. Recently various research groups have reported the synthesis of poly(phenylenevinylene)s (PPV) containing bulky substituent groups such as
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cyclohexyl, adamantaneethylene, cholestanyl, cyclohexylsilyl etc for controlling the molecular aggregation in the solid state. However some of the bulky group substituted PPVs containing adamantaneethylene and cholestanyl derivatives were not fully soluble in common organic solvents, which limited their processability in optical devices. Another approach is to design a polymer main chain that is structurally constrained to twist in a manner that hinders the effective molecular aggregation (π-π stacking) and also allow fine tuning of the emission wavelength, intensity and lifetime.

A new type of blue light emitting-compounds based on biphenyl units was prepared by Hohnholz et al. The presence of biphenyl moiety in these compounds distorts the molecular backbone while amorphous nature was enhanced by steric hindrance. Such structural constraints induced blue shift of the emission spectrum due to large energy band gap (HOMO-LUMO). Poly(4,4'-biphenylenevinylene) systems are intermediate between the poly(phenylenevinylene)s and poly(p-phenylene)s (PPP)s. Hence it may logically be assumed that poly(4,4'-biphenylenevinylene) would exhibit electro-optical properties intermediate between those of PPV and PPP. Biphenylene polymers with solubilising alkoxy substituent groups were reported by Karaz et al. The band gap of thienylenevinylene was narrower than PPVs so that its absorption spectrum extended to longer wavelength and also the charge carrier mobility could be high. Thienylenevinylene shows very poor film forming property in comparison to PPVs. Thienylene units attached biphenylenevinylene backbone open the possibility to create different aryl-aryl connection and side chain attachment. Recently, synthesis of hybrid PPV/PPE polymers was independently reported by Egbe et al and Chu et al. These hybrid polymers showed high fluorescent quantum efficiency (in solution and in film state) and good electroluminescent properties. Fine tuning of emission wavelength is easier with hybrid polymers.
This chapter describes the synthesis and characterization of a novel class of intense green light emitting thienylene-biphenylenevinylene hybrid polymers with high thermal stability and excellent solubility. Their spectral, electrochemical, structural properties and morphology have been studied. The \textit{Voltage vs. Current} data was collected to confirm the schottkey diode action of the new polymers. To the best of our knowledge, so far polymers having biphenylenevinylene-thienylene units fused together have not been reported in literature. For the synthesis of these polymers, a new type of monomers was designed and they consisted of biphenylenevinylene group linked to two thienylene units through a $\text{trans}$-vinylene double bond. Figure 5.1 shows the molecular structure of \textbf{TBPV1} and \textbf{TBPV2}. Introduction of solubilising side chains enhanced processability. Palladium-catalyzed Stille coupling reaction was the method of our choice for polymerization of the monomer units. This reaction has several advantages including mild reaction conditions and high yields. The Stille reaction encompasses Pd(0)-mediated cross-coupling of organohalides, triflates, and acyl chlorides with organostannanes.\textsuperscript{21} Highly electron rich thiophene containing polymers are easily synthesized using Stille coupling.\textsuperscript{22} The incorporation of thienylene units in the biphenylenevinylene backbone resulted in a modified energy band-gap with strong green PL emission and excellent film forming properties.
5.2 Results and Discussion

5.2.1 Monomer Synthesis

The synthesis of two new monomers is shown in Scheme 5.1. Compounds 1a, 1b, 1c, 2a, 2b and 2c were synthesized as per the modified procedure available in literature.\(^{17}\) 4,4’-Dioctyloxy-1,1’-biphenyl (1a) was prepared by O-alkylation of commercially available 4,4’di(hydroxy)-1,1’-biphenyl using two equivalents of 1-bromo-octane in acetone under reflux. Under these conditions 1a was generated as pure white needles in very high yield. Double bromomethylation\(^{23}\) of 1a resulted in the formation of bis(bromomethylene) compound 3,3’-bis(bromomethyl)-4,4’di(octyloxy)-1,1’-biphenyl (1b). Subsequent Michaelis–Arbuzov reaction\(^{24}\) of triethylphosphite with bis(bromomethylene) compound yielded 3,3’bis(diethylphosphonate)-4,4’(dioctyloxy)-1,1’-biphenyl (1c) as a colourless thick oil. The monomer \(M1\) was synthesized by applying well known Wittig-Horner reaction.\(^{25}\) The monomer 5,5’-(1\(E\),1’\(E\))-2,2’-(4,4’-bis(octyloxy)biphenyl-3,3’-diyl)bis(ethene-2,1-diyl)bis(2-bromothiophene) (M1) was prepared by the reaction between 3,3’bis(diethylphosphonate)-4,4’(dioctyloxy)-1,1’-biphenyl (1c) and 5-bromothiophene-2-carboxaldehyde in the presence of potassium tert-butoxide as the base. The yellow coloured waxy liquid formed was then isolated by using column chromatography which afforded bright yellow crystals in 35% yield. Second monomer 5,5’-(1\(E\),1’\(E\))-2,2’-(6,6’-bis(octyloxy)biphenyl-3,3’-diyl)bis(ethene-2,1-diyl)bis(2-bromothiophene) (M2) was also synthesized in a similar manner, starting with 2,2’dihydroxy-1,1’-biphenyl. After Wittig-Horner reaction, monomer M2 was obtained as light brown crystals in 22% yield. The monomers were completely soluble in common organic solvents such as tetrahydrofuran (THF), dichloromethane, hexane, chloroform, toluene etc due to the presence of long chain octyloxy substituents.
Scheme 5.1. Synthesis of monomers M1 and M2 via Wittig-Horner reaction

Monomers M1 and M2 showed remarkable differences in their melting points: 65°C for M1 and 85°C for M2. The average conformational structure in the ground state 4,4’-linked monomer M1 is expected to be more planar than M2, which has steric strain inducing substitution at the 2,2’-positions. Therefore, the 1,1’-bond (meta-meta bond) coupled stilbene units tends to be twisted easily, whereas the linkage in meta position doesn’t interfere with the electronic properties of the biphenyl unit.26 Depending on the positions of the octyloxy substituents present in the biphenyl moiety a distortion can be achieved. Two thiophene rings are linked with a conjugated biphenyl moiety through trans-
vinylene bond by the Wittig–Horner reaction. Consequently the monomer maintains planarity and the conjugated polymer system grows effectively, so that the band gap of the polymer could be reduced. Monomers M1 and M2 were characterized by using $^1$H NMR, $^{13}$C NMR, FT-IR spectroscopic techniques. Figure 5.2 displays the $^1$H NMR spectrum of monomers M1 and M2. The disappearance of aldehyde proton peaks around 10ppm in $^1$HNMR spectra implied successful reaction via Wittig–Horner reaction. Based on our previous experience with the stereochemical outcome of Wittig-Horner reactions and coupling constant information, trans geometry is assigned to the newly generated carbon-carbon double bonds.
5.2.2 Polymer Synthesis

The polymers were synthesized by Stille coupling reaction illustrated in Scheme 5.2. The Stille reaction carried out by using catalytic amount of Pd(PPh₃)₄ added to a mixture of 2,5-bis(tributylstannyl)thiophene and M₁ with freshly distilled toluene as solvent. The mixture was refluxed for 18h and the mixture was poured into methanol and filtered to remove the precipitated metallic palladium. The crude polymers were purified by sequential extraction with methanol, hexane, and THF to remove the oligomers and other impurities. THF fraction was collected and again the polymer was reprecipitated by using methanol. Polymer TBPV₁ was obtained as reddish brown solid in 87% yield. Similarly, polymer TBPV₂ was obtained as a dark brown solid in 77% yield. Polymers TBPV₁ and TBPV₂ possess good solubility in common polar and non-
polar organic solvents such as dichloromethane, toluene, THF, chloroform etc. The polymers were fully characterized on the basis of $^1$H NMR, $^{13}$C NMR, FT-IR spectroscopies and elemental analysis data. $^1$H NMR spectrum of the polymers (Figure 5.3) is in good agreement with its molecular structure. Aromatic and vinylic protons appear in the $\delta$ 7.61–6.85 region. Methylenoxy protons appear at 3.98ppm to 4.01ppm for both polymers. $^{13}$C NMR and FT-IR spectroscopic data were also in agreement with the proposed polymer structures. Due to the complexity of the aromatic/vinylic region, it was not possible to isolate the signal due to vinylic protons. Out-of-plane –CH=CH– bending frequencies of polymer TBPV1 appears at 954cm$^{-1}$ and TBPV2 appears at 952cm$^{-1}$, which is the characteristic absorption peak of trans-vinylene groups.$^{25}$ Therefore it is suggested that the generated double bonds are mainly in trans-configurations. We assume that the trans geometry of alkene linkages present in the monomers is maintained in the polymers generated by Stille coupling.

Scheme 5.2 Synthesis of TBPV1 and TBPV2 via Stille coupling polymerization.
Figure 5.3 $^1$H NMR spectrum of polymers TBPV1 and TBPV2
The weight average molecular weight (MW) and the polydispersity index (PDI) were measured by gel-permeation chromatograph (GPC) against polystyrene standards using toluene as mobile phase. Gel permeation chromatograms of the polymers are shown in Figure 5.4. This showed a moderate MW of 4928 g/mol\(^{-1}\) with PDI of 1.66 for TBPV1 and MW of 4549 g/mol\(^{-1}\) with PDI of 1.82 for TBPV2. Such relatively low molecular weights are typical of Stille coupling polymerization. The decrease of polydispersity index value of currently synthesized polymers is due to sequential extraction with different solvents such as methanol, hexane and THF. The polymers TBPV1 and TBPV2 could be spin coated at ambient temperature to give bright yellowish-orange coloured transparent, homogeneous and pin-holes free thin films.

Figure 5.4 Gel permeation chromatograms of TBPV1 and TBPV2 (Waters 2414 column with toluene as eluent, at a flow rate of 0.5 mL/min at 25 °C)
5.2.3 Thermal Properties

Thermal properties of the polymers were investigated by thermogravimetric analysis (TGA) (Figure 5.5) and differential scanning calorimetry (DSC) (Figure 5.6). The thermal and physical properties of copolymers are shown in Table 5.1. From TGA results, the maximum degradation temperature ($T_d$) is at 443°C for TBPV1 and 452°C for TBPV2. Thienylene units present in the conjugated biphenylenevinylene backbone helps to enhance the thermal stability of TBPV1 and TBPV2. This high thermal stability indicates that the polymers are adequate for applications in optoelectronic devices. The onset degradation for TBPV1 and TBPV2 are at 324°C and 361°C respectively. Polymer TBPV2 shows enhanced thermal stability compared to TBPV1 due to the steric strain induced by the bulky substitution at the 2,2’-positions of biphenyl backbone which reduces its coplanarity.

![Figure 5.5 Thermal gravimetric curve (TGA) of TBPV1 (solid line) and TBPV2 (dashed line) at a heating rate of 10°C/min in nitrogen.](image)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_w$ (g/mol$^1$)</th>
<th>PDI</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBPV1</td>
<td>87%</td>
<td>4928</td>
<td>1.66</td>
<td>54</td>
<td>102</td>
<td>443</td>
</tr>
<tr>
<td>TBPV2</td>
<td>77%</td>
<td>4549</td>
<td>1.82</td>
<td>55</td>
<td>110</td>
<td>452</td>
</tr>
</tbody>
</table>

Table 5.1 Physical and thermal properties of polymers TBPV1 and TBPV2
Differential scanning calorimetry (DSC) (Figure 5.6) of the polymers TBPV1 and TBPV2 show Glass transition temperature ($T_g$) at $54^{0}C$ and $55^{0}C$ respectively. Both polymers show moderate and comparatively similar $T_g$ values, due to the influence of long octyloxy substituent chain present in the rigid biphenyl polymer backbone. DSC profile of TBPV1 shows a melting temperature at $102^{0}C$ but TBPV2 do not have a well defined melting peak, it shows a weak melting temperature at $110^{0}C$. Therefore TBPV1 and TBPV2 have both glass transition temperature and melting temperature ($T_m$) suggesting their semicrystalline nature. From the DSC results TBPV1 shows more crystalline characteristics than TBPV2 because it is expected to be more planar. TBPV2 shows less crystalline characteristics due to strain induced by 2,2’ linkge.

![Figure 5.6 Differential scanning calorimetry (DSC) thermogram TBPV1 and TBPV2 in nitrogen atmosphere at a heating rate of 10 °C/min](image)
5.2.4 X-ray diffraction analysis (XRD)

Powder X-ray diffraction (XRD) (Rigaku X-ray diffractometer, Cu-Kα radiation (1.542Å) was used to investigate the crystalline nature and molecular organization of the polymers. The XRD pattern is shown in Figure 5.7. **TBPV1** shows two main peaks, with d-values 7.64Å, 4.02Å. **TBPV2** also shows similar peaks with d values 7.53Å, 4.17Å. The d₁ values of **TBPV1** and **TBPV2** are observed corresponds to the number of carbons in the octyloxy side chain and the distance between the π- conjugated main chains separated by the octyloxy group.³⁰ Due to the presence of octyloxy side chains present in the biphenylene backbone, both polymers show side chain crystallinity. It was previously reported that the octyloxy substituted PPV layers show side chain induced semicrystalline nature.³¹ The diffraction peaks at 2θ values of **TBPV1** at 22.6° (d₂= 4.02Å) for and **TBPV2** at 21° (d₂= 4.17Å) corresponds to the interlayer distance between the π-π stacks of the polymer.³² If it is observed that slightly larger π-π distance which denote that the coplanarity of these two polymers is lesser in their solid state.³³

![Figure 5.7 Powder XRD patterns of TBPV1 and TBPV2.](image)

5.2.5 Scanning electron microscopy (SEM)

The morphology of the polymers in powder form was studied by using scanning electron microscopy (Hitachi FESEM SU6600). Figure 5.8 shows the
SEM images of TBPV1 and TBPV2 respectively. From these figures, both of the polymers appeared to be circular plate like morphology. Therefore these morphologically similar polymers particularly differentiated by their dissimilar positions such as 4,4’ or 2,2’ linked substitution of long octyloxy side chain in the rigid biphenylenevinylene backbone.

![SEM images of TBPV1 and TBPV2](image)

Figure 5.8 SEM micrographs of TBPV1 and TBPV2 in powder form

5.2.6 Photophysical studies

5.2.6.1 Absorption and photoluminescence (PL) studies of monomers

Two new monomers 5,5’-(1E,1’E)-2,2’-(4,4’-bis(octyloxy)biphenyl-3,3’-diyl)bis(ethene-2,1-diyl)bis(2-bromothiophene) (M1) and 5,5’-(1E,1’E)-2,2’-(6,6’-bis(octyloxy)biphenyl-3,3’-diyl)bis(ethene-2,1-diyl)bis(2-bromothiophene) (M2) were synthesized and characterized and are described in Section 5.2.1. Figure 5.9 (A & B) shows normalized UV-Vis absorption spectra and PL spectra of monomer M1 and M2 in dichloromethane. Monomer M1 shows absorption at 343nm and the corresponding band gap was determined as 3.11eV and M2 shows absorption at 347nm and its band gap is estimated at 3.19eV. Major emission peak appears at 428 nm for M1 and 419nm for M2. Therefore monomers show their emission at UV-Vis wavelength region.
5.2.6.2 Absorption and photoluminescence (PL) studies of polymers

The UV-Vis absorption spectra and PL spectra provide information on the electronic structures of the synthesized polymers. The absorption and photoluminescence (PL) spectra of the polymers TBPV1 and TBPV2 in dichloromethane solution and spin casted film are depicted in Figure 5.10. In solution state, the absorption peaks of TBPV1 and TBPV2 appear at 444nm and 442nm respectively which can be attributed to π-π* transitions. The optical band-gap energies of TBPV1 and TBPV2 solutions calculated from the onset of the UV-Vis absorption spectra are 2.31eV and 2.32eV respectively. The longest wavelength absorption peaks of TBPV1 and TBPV2 films were 456nm and 455nm respectively. Compared to the corresponding monomers be have observed
a red-shift of about 12nm and 13nm in \textbf{TBPV1} and \textbf{TBPV2} polymers. Therefore, it can be assumed that the ground state interaction such as aggregation between the chains in the polymers is very low and does not interfere with the electronic properties of these polymers. Polymers with long octyloxy chains were selected in order to decrease the interchain interactions between the polymer backbones and to enhance the quantum efficiencies.

![Normalized UV–Vis absorption spectra (UV) and photoluminescence (PL) of TBPV1 and TBPV2 in dichloromethane solution and in the solid state (film).](image)

The PL maxima of \textbf{TBPV1} and \textbf{TBPV2} in dilute dichloromethane solutions appeared at 536nm and 538nm on excitation at 444nm and 442nm respectively. In \textbf{TBPV1} and \textbf{TBPV2} films, the PL maxima appear at 576nm and
571nm respectively. This small variation of emission wavelength of these polymers may be due to the difference of positional substitution of long octyloxy side chains present in the biphenylenevinylene backbone. Absorption maxima of copolymers in the film state bathochromically shifted with respect to their spectra in the solution state. Figure 5.11 shows that the light emissions of TBPV1 and TBPV2 under UV irradiation at 365nm. Both polymers show powerful green emission in their solution state as well as in their film forms. Previous section revealed that monomer M1 and M2 have emission in blue region but after polymerization of these monomers its emission spectrum shifted from blue to green region. In the case of both polymers their emission wavelength have shifted to higher wavelength region due to increased number of attached thienylene units present in the biphenylenevinylene backbone which leads to decrease in band gap.

![Figure 5.11 Light emissions of TBPV1 and TBPV2 under UV irradiation with light at 365nm](image)

5.2.6.3 Fluorescence quantum yield of polymers

Photophysical data of TBPV1 and TBPV2 are shown in Table 5.2. Method for estimating fluorescence quantum yield ($\Phi_F$)\textsuperscript{34} is described elsewhere in this thesis (Section 3.2.6.1 in Chapter 3). The comparative fluorescence quantum yield for polymers TBPV1 and TBPV2 was determined by using fluorescein as the standard. Fluorescein has remarkably good photostability and high quantum yield of 0.79 in ethanol having excitation wavelength was used as 453nm (Kellogg, 1964).\textsuperscript{35} The fluorescence quantum yield ($\Phi_F$) of TBPV1 was found to be 0.93 and TBPV2 was obtained as 0.39 in dichloromethane solution.
Polymer **TBPV1** has higher fluorescence quantum yield than fluorescein. But **TBPV2** shows lower quantum yield due to the steric strain induced by 2,2’ linked substitution present in its polymer backbone. We attribute the sharp decrease in quantum yield to geometric constraints imposed by substituents at 2,2’-positions in the biphenyl residue that is likely to tilt the two aryl rings out of planarity whereby effective conjugation is decreased. The fluorescence quantum yield ($\Phi_F$) of **TBPV1** and **TBPV2** indicates that both the polymers are very attractive for application in optoelectronics.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>UV-Vis (nm)</th>
<th>PL (nm)</th>
<th>$E_g^{\text{OP}}$ (eV)</th>
<th>Fluorescence Quantum Yield ($\Phi_F$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solution</td>
<td>Film</td>
<td>Solution</td>
<td>Film</td>
</tr>
<tr>
<td><strong>TBPV1</strong></td>
<td>444</td>
<td>456</td>
<td>536</td>
<td>576</td>
</tr>
<tr>
<td><strong>TBPV2</strong></td>
<td>442</td>
<td>455</td>
<td>538</td>
<td>571</td>
</tr>
</tbody>
</table>

Table 5.2 Photophysical data of **TBPV1** and **TBPV2**

**5.2.7 Electrochemical studies**

Redox potentials of the polymers were recorded using a BAS CV50W voltammetric analyzer. Figure 5.12 shows the current-voltage curve for **TBPV1** and **TBPV2** from the cyclic voltammetry measurements. Polymers were dissolved in dichloromethane containing 0.1M tetra-$n$-butyl ammonium hexafluoro-phosphate as supporting electrolyte. A platinum disc electrode was used as working electrode and a platinum wire was used as counter electrode and the potentials were referred to Ag/AgCl (calibrated against the FC/FC$^+$ redox system) was 4.8eV below vacuum levels. Ferrocene was used as external standard. The estimations were done with the empirical relation was used:  

$$E_{\text{HOMO}} = (IP) \text{ eV} = -e (E_{\text{ox}, \text{on}} - E_{\text{Foc}}) - 4.8$$  

$$E_{\text{LUMO}} = (EA) \text{ eV} = -e (E_{\text{red}, \text{on}} - E_{\text{Foc}}) - 4.8$$
The *p*-doping and *n*-doping processes occur under the anodic and cathodic scans. Electrochemical data of TBPV1 and TBPV2 are displayed in Table 3. On sweeping TBPV1 and TBPV2 in anodic direction, onset oxidation potentials ($E_{\text{ox,on}}$) are 0.52V for TBPV1, 0.50V for TBPV2 or in cathodic direction, onset reduction potentials ($E_{\text{re,on}}$) are `1.49V for TBPV1, `1.72V for TBPV2 respectively. On the base of the measured oxidation potentials, HOMO (IP) levels of TBPV1 and TBPV2 have been estimated to be `4.869eV, `4.844eV. Similarly, the LUMO (EA) levels of TBPV1 and TBPV2 have been calculated to be `2.841eV, `2.619eV, respectively. From the equation $E_g = E_{\text{ox,on}} - E_{\text{re,on}}$ the electrochemical band gaps were also calculated to be 2.21eV and 2.22eV for TBPV1 and TBPV2. The positional difference of the 2,2’ or 4,4’ linked long octyloxy side chain substitution is the main reason for the small difference of band gap energies of the two polymers. Ding et al have reported that, alkoxy-substituted biphenyl compounds have band gap above 2.91eV.37 The band-gap of TBPV1 and TBPV2 was engineered to the green region by the incorporating thiylene units into the biphenylenevinylene backbone. The optical band gap and electrochemical band gap calculated from the HOMO and LUMO are within the range of 0.2-0.5 eV.38

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>$E_{\text{ox,on}}$ (V)</th>
<th>$E_{\text{re,on}}$ (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBPV1</td>
<td>0.52</td>
<td>`1.49</td>
<td>`4.86</td>
<td>2.84</td>
<td>2.21</td>
</tr>
<tr>
<td>TBPV2</td>
<td>0.50</td>
<td>`1.72</td>
<td>`4.84</td>
<td>2.61</td>
<td>2.22</td>
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</table>

Table 5.3 Electrochemical data of TBPV1 and TBPV2
Figure 5.12 Cyclic voltammograms of TBPV1 and TBPV2 with solution of 0.1M tetra-n-butyl ammonium hexafluoro-phosphate as supporting electrolyte in dichloromethane at the scan rate of 10mV/s

5.2.8 Measurement of Schottky diode characteristics

Schottky diode (metal-semiconductor) junction has been constructed from currently synthesized polymers TBPV1 and TBPV2. The device fabrication is simple because of direct casting of the polymers from the dichloromethane solution. Figure 5.13 shows three dimensional atomic Force Microscopy (AFM) image of the spin coated film of polymers TBPV1 and TBPV2 from

* The device fabrication and related characterizations are carried out in collaboration with Department of Physics, Cochin University of Science and Technology
dichloromethane solution. The thickness of the films thus obtained was measured using Dektak 6M stylus profilometer and films with thickness 50nm (±5nm). AFM analysis reveals that polymers have smooth surface with the root mean square (RMS) value of TBPV1 gives 1.53nm and TBPV2 gives 1.80nm.

Thin films of TBPV1 and TBPV2 made from dichloromethane were spin cast (SPS Spin wafer 150, 2000 rpm, 30s) from solutions on top of Indium Tin Oxide coated glass plates which is the anode. Aluminium contacts (top-electrode as cathode) were made on top of the spin coated polymer layers by thermal evaporation to form a Schottky junction. The current-voltage characteristics were analyzed using Keithley 2400 source meter (2-point probe method) for the two diode configurations to confirm the formation of metal-semiconductor junction which is mandatory for the fabrication of polymer light emitting diodes (PLEDs) as well as polymer photovoltaic devices. Figure 5.14 shows the Current Vs Voltage graph of TBPV1 and TBPV2 polymers respectively. From the two graphs, one can easily confirm that the polymers TBPV1 and TBPV2 show the formation of a Schottky diode. Both of the polymers exhibit very low onset voltage i.e. TBPV1 shows 1.93V and TBPV2 gives 2.38V. This indicates that TBPV1 and TBPV2 are very attractive for polymer light emitting diode applications.
Figure 5.14 I–V characteristics of ITO/polymer/Al devices of TBPV1 and TBPV2

The energy band diagrams of ITO/polymer/Al device configuration by using TBPV1 and TBPV2 are shown in Figure 5.15. The barrier heights of the polymers were found to be 0.16eV and 0.14eV at the interface of ITO (4.7eV)/HOMO state for holes and 1.35eV and 1.58eV at the interface of Al (4.2eV)/LUMO for electrons. The HOMO level of both polymers is very close to the work function of ITO which enables the effective supply of holes through ITO. Hence an intermediate layer between the emissive polymer and ITO can also be avoided. From the energy band diagram, one can assume that both polymers easily injected holes from the ITO electrode than of electron from the Al electrode. We can conclude that the required energy levels, excellent film
smoothness, high thermal stability of these two polymers are fulfilled for fabricating polymer light emitting diodes.

![Energy band diagram of TBPV1 and TBPV2](image)

**Figure 5.15 Energy band diagram of TBPV1 and TBPV2**

### 5.3 Conclusions

Two novel, highly soluble, thermally stable, highly luminescent, intense green-light emitting thienylene-biphenylenevinylene hybrid polymers synthesized using Stille coupling polymerization reaction. The Stille coupling reaction is superior to the conventional cross-coupling reactions like Suzuki and Kumada polycondensation reactions because of its simpler reaction conditions. The introduction of thienylene groups to the biphenylenevinylene backbone alters the emission spectrum of the polymers from lower wavelength region to higher wavelength region. Changing the substituent positions of the long chain octyloxy groups attached to the polymer backbone leads to some structural changes in both of the polymers. **TBPV1** is structurally more planar compared to **TBPV2** due to its 4,4’ linkage of the substituent groups present in the biphenylenevinylene backbone. Photophysical studies confirm that both polymers give intense green emission in their solution state. Both polymers show excellent fluorescence quantum yield ($\Phi_F$) in dichloromethane solution. The polymers show $\pi$-stacked structure in their solid state, which was confirmed by XRD analysis. The electrochemical band gap (E$_g^{EC}$) of the polymers analyzed by cyclic voltammetry analysis. Schottky diode formation has been confirmed from the I-V characteristics of the two polymers. Both of the hybrid polymers find prospects of application in the field of optoelectronics, mainly for Polymer LEDs.
5.4 Experimental Section

5.4.1 General Techniques

All reactions were performed in oven-dried glassware under a nitrogen atmosphere with magnetic stirring unless otherwise noted. Reagents and solvents were purchased from commercial suppliers and were used without further purification. Solvents used for experiments were distilled and dried according to procedures given in standard manuals. For all palladium-catalyzed reactions, the solvents were carefully degassed. All reactions were followed by TLC to completion. TLC analysis was performed by illumination with a UV lamp (254nm) or staining with Iodine. All Column chromatography was performed with 60-120 mesh silica gel purchased from SD Fine-Chem. limited, as the stationary phase. $^1$H NMR spectra were measured on a Bruker Avance III 400 MHz instrument in CDCl$_3$, and chemical shifts were measured relative to residual solvent peak ($\delta$ 7.26). The following abbreviations were used to describe coupling: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. $^{13}$C NMR spectra were measured on Bruker Avance III instruments at 100MHz with chemical shifts relative to residual solvent peak ($\delta$ 77.0). FTIR spectra were recorded using KBr pellet technique on a Thermo Nicolet, Avatar 370spectrometer. Melting points were recorded on a Fisher-Johns melting point apparatus. The percentage of elements C, H, S was analyzed by Elementar Vario EL III analyzer. The absorption and fluorescence spectra were recorded using UV-Visible spectrophotometer (JASCO V-570) and fluoromax-3fluorimeter was used to record the fluorescence spectra of the samples, respectively. The electrochemical cyclic voltammetry (CV) was conducted on a BAS CV50W voltammetric analyzer. Polymers were dissolved in dichloromethane containing 0.1M tetra-n- butyl ammonium hexafluoro-phosphate as supporting electrolyte, at a scanning rate of 10 mV/s at room temperature under the protection of argon. The Powder X-ray diffraction (XRD) patterns were obtained using a (Rigaku X-ray diffractometer with Cu Ka radiation (1.542Å). The molecular weight of the
synthesized polymers was determined by GPC, (Waters 2414) using a column packed with polystyrene gel beads. The polymer was analyzed using toluene as eluent, at a flow rate of 0.5 mL/min at 25°C. The molecular weight was calibrated using polystyrene standards. Glass transition temperature was determined from differential scanning calorimeter (DSC), (Q-100, TA Instruments) under nitrogen at heating rate of 10°C/min. Thermal stability was determined from thermo gravimetric analyzer (TGA), (Q-50, TA Instruments) under nitrogen at a heating rate of 10°C/min. Homogeneous and good quality thin films in nanometer thickness scales were obtained by spin coating (SPS Spin wafer 150) the solution at different spin speeds in different durations on ultra-sonically cleaned glass substrates. The thickness of the films was measured using Dektak 6M stylus profiler. The morphology of the polymers was determined by scanning electron microscopy Scanning Electron Microscopy (SEM) (Hitachi FESEM SU6600). Atomic force microscopy image of copolymer film was analyzed by Park systems XEI 100 AFM. The current-voltage characteristics were analyzed using Keithley 2400 source meter (2-point probe method).

5.4.2 Materials

Compounds such as 4,4’-dihydroxy-1,1’-biphenyl, 1-bromooctane, Pd(PPh)$_3$, 2,5-bis(tributylstannyl)thiophene, 2,2’-dihydroxy-1,1’-biphenyl, and 5-bromo thiophene-2-carboxaldehyde, were purchased from Sigma-Aldrich and used as received. HBr (31%) in glacial acetic acid, triethylphosphite and potassium tert-butoxide were purchased from Merck. Solvents were distilled and used in the reaction. Toluene used in the Stille coupling polymerization was dried using calcium chloride followed by distillation over sodium wire.

5.4.3 Synthesis of monomers M1 and M2

5.4.3.1: Synthesis of 4,4’-Dioctyloxy-1,1’-biphenyl (1a)

To a solution of 4,4’-dihydroxy-1,1’-biphenyl (2g, 10mmol) in 25mL of dry acetone was added anhydrous potassium carbonate (6g, 43mmol), 1-
bromooctane (5mL, 25mmol), and a catalytic amount of sodium iodide. The mixture was refluxed for 48h under nitrogen atmosphere. The reaction mixture was poured into ice water. The product was filtered, washed with water, and dried. After recrystallization from acetone, product 1a was obtained as white crystalline plates (yield: 90%).

\[ ^1H-NMR \ (400MHz, CDCl_3): \delta 7.46-7.40 \ (4H, d), 6.95-6.92 \ (4H, d), 3.99-3.96 \ (4H, t), 1.81-1.77 \ (4H, t), 1.48-1.29 \ (20H, m), 0.90 \ (6H, s). \]

5.4.3.2: Synthesis of 2,2'-Dioctyloxy-1,1'-biphenyl (2a)

To a solution of 2,2'-dihydroxy-1,1'-biphenyl (2g, 10mmol) in 50mL of dry acetonitrile was added anhydrous potassium carbonate (6g, 43mmol), 1-bromooctane (5mL, 25mmol), and a catalytic amount of sodium iodide. The mixture was refluxed for 72h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and filtered. Solvent was evaporated under vacuum. The liquid product was purified by silica gel column chromatography (elution with hexane/dichloromethane). Compound 2a was obtained as clear colourless oil. (Yield: 85%).

\[ ^1H-NMR \ (400MHz, CDCl_3): \delta 7.32-7.28 \ (4H, m), 7.02-6.95 \ (4H, m), 3.94-3.91 \ (4H, t), 1.68-1.61 \ (4H, m), 1.32-1.26 \ (22H, m), 0.94-0.92 \ (6H, t). \]

5.4.3.3: Synthesis of 3,3'-bis(bromomethyl)-4,4'di(octyloxy)-1,1'-biphenyl (1b)

To a suspension of 4,4'-dioctyloxy-1,1'-biphenyl (2g, 4mmol) and paraformaldehyde (0.5g, 15mmol) in 30mL of acetic acid was added 7mL of 31% HBr in glacial acetic acid in one portion at 80 °C under nitrogen atmosphere. The reaction mixture became clear immediately. The mixture was stirred for 4h at this temperature. It was then cooled to room temperature. The solid product was
filtered and washed with water. The organic layer was taken in dichloromethane, neutralized with aqueous sodium bicarbonate solution, and dried. Solvent was evaporated and the residue recrystallized from acetone/hexane. The product was obtained as white crystals (yield: 80%).

$^1$H-NMR (400MHz, CDCl$_3$): $\delta$ 7.50-7.41 (4H, m), 6.91-6.89 (2H, d), 4.61 (4H, s), 4.06-4.04 (4H, t), 1.87-1.81 (4H, m), 1.36-1.30 (20H, m), 0.92-0.82 (6H, t).

5.4.3.4: Synthesis of 5,5'-bis(bromomethyl)-2,2'di(octyloxy)-1,1'-biphenyl (2b)

To a mixture of 4,4'-dioctyloxy-1,1'-biphenyl (3g, 7mmol) and paraformaldehyde (1g, 31mmol) in 30mL of acetic acid was added 7mL of 31% HBr in glacial acetic acid in one portion at 80°C. The mixture was heated at this temperature for 4h under nitrogen atmosphere. It was then cooled to room temperature, and 100mL of cold water was added with constant stirring. The precipitate was filtered and washed with water. The solid was dissolved in dichloromethane, neutralized with aqueous sodium bicarbonate solution, and finally washed with brine. After drying over magnesium sulphate, solvent was evaporated from the organic layer. After recrystallization from dichloromethane, the product was obtained as a white solid (yield: 70%).

$^1$H-NMR (400MHz, CDCl$_3$): $\delta$ 7.32-7.29 (4H, m), 6.89-6.86 (2H, d), 4.52 (4H, s), 3.91-3.88 (4H, t), 1.66-1.59 (4H, m), 1.27-1.22 (22H, t), 0.88-0.85 (6H, t).

5.4.3.5: Synthesis of 3,3’bis(diethylphosphonate)-4,4’(dioctyloxy)-1,1’-biphenyl (1c)

A mixture of 3,3’-bis(bromomethyl)-4,4’-dioctyloxy-1,1’-biphenyl (1.0g, 1.68mmol) and triethylphosphite (1mL, 6mmol) was heated to 90°C for 2h under nitrogen atmosphere. Excess triethylphosphite was separated by vacuum
distillation. The product 1c was obtained as thick oil (90%). It was used without further purification.

$$\text{H-NMR} \quad \delta \quad 7.53-7.36 \quad (4H, m), \quad 6.88-6.86 \quad (2H, m), \quad 4.13-3.97 \quad (8H, m), \quad 3.33-3.27 \quad (4H, d), \quad 1.83-1.7 \quad (4H, t), \quad 1.48-1.46 \quad (4H, d), \quad 1.34-1.30 \quad (m, 16H), \quad 1.24-0.87 \quad (12H, m).$$

5.4.3.6: Synthesis of 5,5’-bis(diethyl phosphonate)-2,2’-(dioctyloxy)-1,1’-biphenyl (2c)

A mixture of 5,5’-bis(bromomethyl)-2,2’-dioctyloxy-1,1’-biphenyl (3.0g, 5.75mmol) and triethylphosphate (12mL, 72mmol) was heated to 90°C for 2h under nitrogen atmosphere. Excess triethylphosphite was separated by vacuum distillation. The product 2c was obtained as thick oil (82%). It was used without further purification.

$$\text{H-NMR} \quad \delta \quad 6.94-6.55 \quad (6H, m), \quad 3.84-3.55 \quad (12H, m), \quad 2.83-2.77 \quad (4H, m), \quad 1.50-1.34 \quad (20H, m), \quad 1.26-1 \quad (12H, m), \quad 0.60-0.56 \quad (6H, t).$$

5.4.3.7: Synthesis of monomer 5,5’-(1E,1’E)-2,2’-(4,4’-bis(octyloxy)biphenyl-3,3’-diyl)bis(ethene-2,1-diyl)bis(2-bromothiophene) (M1)

To a stirred solution of 1c (5.5g, 7mmol) in dry DMF (15mL) was added to 5-bromothiophene-2-carboxaldehyde (2.5g, 13mmol) at room temperature under nitrogen atmosphere. After stirring for 10 minutes, 3 eqv of powdered potassium tert-butoxide (2.35g, 21mmol) was added slowly. The reaction was carried out at 48h after which the resultant mixture was poured into water and extracted with dichloromethane. Solvent was evaporated under reduced pressure to obtain the product as yellow waxy liquid. It was further purified by column chromatography.
over silica gel using CH$_2$Cl$_2$ in hexane (1:19) as eluent. Solvent was evaporated to obtain the product as bright yellow crystals. Yield: 35%. mp: 65°C.

$^1$H-NMR (400MHz, CDCl$_3$): $\delta$ 7.64-6.70(14H, m), 4.07(4H, t), 1.89-1.85(2H, t), 1.33-1.25(19H, m), 0.89-0.85(9H, m).

$^{13}$C-NMR (100MHz, CDCl$_3$): $\delta$ 154.8, 144.4, 132.3, 129.3, 126.1, 124.8, 124.8, 124.0, 123.2, 120.9, 111.4, 109.7, 67.7, 30.9, 30.8, 28.6, 28.2, 25.2, 21.6, 13.0;

IR (KBr) $\nu$ 3028, 2920, 2949, 1603, 1519, 1427, 1376, 1304, 1236, 1127, 1062, 1004, 952, 832, 788, 715, 653, 614 cm$^{-1}$;

Anal. Calcd. For C$_{40}$H$_{48}$Br$_2$O$_2$S$_2$: C 61.22, H 6.17, Br 20.36, O 4.08, S 8.17; Found: C 60.88, S 7.69, H 6.10.

5.4.3.8: Synthesis of monomer 5,5'-{(1E,1'E)-2,2'-(6,6'-bis(octyloxy)biphenyl-3,3'-diyl)bis(ethane-2,1-diyl)bis(2-bromothiophene)}(M2)

To a stirred solution of 1c (4g, 5mmol) in dry DMF (10mL) was added 5-bromothiophene-2-carboxaldehyde (2.2g, 11mmol) at room temperature under nitrogen atmosphere. After 10 minutes for stirring 3 eqv of powdered potassium tert-butoxide (1.68g, 15mmol) was added slowly. The reaction was carried out at 48h; the resultant mixture was poured into water, extracted with dichloromethane. The solvent was evaporated under reduced pressure to obtain the product as brown waxy liquid. It was further purified by column chromatography over silica gel using CH$_2$Cl$_2$ in hexane (1:19) as eluent. Solvent was evaporated to obtain the product as light brown crystals. Yield: 22%. mp: 85°C.
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$^1$H-NMR (400MHz, CDCl$_3$): $\delta$ 7.39-6.71(14H, m), 3.93-3.90(4H, t), 1.63-1.60 (3H, t), 1.25-1.19(16H, m), 0.86-0.85(5H, d).

$^{13}$C-NMR (100MHz, CDCl$_3$): $\delta$ 155.6, 144.0, 129.3, 128.2, 127.6, 127.5, 127.2, 125.9, 124.2, 117.9, 111.1, 109.1, 67.5, 30.7, 28.3, 28.2, 28.2, 25.0, 21.6, 13.0;

IR (KBr) $\nu$ 2952, 2922, 2848, 1604, 1468, 1432, 1385, 1259, 1150, 1051, 1014, 947, 806 cm$^{-1}$;

Anal. Calcd. For C$_{40}$H$_{48}$Br$_2$O$_2$S$_2$: C 61.22, H 6.17, Br 20.36, O 4.08, S 8.17; Found: C 60.12, S 7.21, H 5.81.

5.4.4 Synthesis of polymers Using Stille Coupling Reaction

5.4.4.1 Synthesis of polymer TBPV1

Pd(PPh)$_3$ (50mg, 0.043mmol), monomer M1 (0.15g, 0.19mmol), and 2,5-bis(tributylstannyl)thiophene (0.12g, 0.18mmol) were taken in a three-necked flask. The mixture was flushed with nitrogen for 10min, and then 5mL of freshly distilled toluene was added. Under a positive pressure of nitrogen, the reactants were heated to reflux until the black metallic palladium precipitated. The mixture was then cooled to room temperature and poured into 50mL methanol and filtered into a thimble to remove metallic palladium. Sequential extraction was performed with methanol, hexane and THF. The polymer was recovered from the THF fraction by rotary evaporation. The resultant reddish brown solid was dried under vacuum overnight. Yield: 0.22g (87%).

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\(^1\)H-NMR (400MHz, CDCl\(_3\)): \(\delta\) 7.61-6.85 (16H, m), 3.99-3.98 (4H, d), 1.82-1.80 (8H, d), 1.48-1.29 (16H, m), 0.81 (6H, s).

\(^{13}\)C-NMR (100MHz, CDCl\(_3\)): \(\delta\) 154.84, 142.86, 135.42, 132.42, 126.51, 125.89, 125.22, 124.65, 124.12, 123.26, 123.04, 122.83, 121.58, 121.37, 111.54, 67.80, 30.85, 28.43, 28.34, 25.30, 25.25, 21.69, 13.10.

IR (KBr) \(\nu\) 2923, 2853, 1616, 1486, 1464, 1384, 1243, 1113, 1023, 954, 793, 692 cm\(^{-1}\)

Anal. Calcd. For C\(_{44}\)H\(_{50}\)O\(_2\)S\(_3\): C 74.80, S 13.61, H 7.07; Found: C 73.44, S 13.24, H 6.37.

5.4.4.2 Synthesis of polymer TBPV2

Pd(PPh\(_3\)) (50mg, 0.043mmol), monomer M\(_2\) (0.3g, 0.38mmol), and 2,5-bis(tributylstannyl)thiophene (0.21g, 0.32mmol), were taken in a three-necked flask. The mixture was flushed with nitrogen for 10min, and then 5mL of freshly distilled toluene was added. Under nitrogen atmosphere, the reactants were heated to reflux until the black metallic palladium precipitated. The mixture was then cooled to room temperature and poured into 80mL methanol and filtered into a thimble to remove the metallic palladium. Sequential extraction was performed with methanol, hexane and THF. The polymer was recovered from the THF fraction by rotary evaporation. The resultant dark brown solid was dried under vacuum over night. Yield: 0.21g (77%).
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$^{1}$H-NMR (400MHz, CDCl₃): $\delta$ 7.61-6.83(17H, m), 4.01-4.00(4H, m), 1.83-1.81(2H, d), 1.50-1.13(24H, m), 0.82-0.75(8H, m).

$^{13}$C-NMR (100MHz, CDCl₃): $\delta$ 154.85, 126.85, 125.96, 125.20, 124.68, 124.13, 123.41, 123.23, 123.06, 122.51, 121.61, 121.44, 111.55, 111.24, 110.34, 67.81, 67.55, 30.85, 29.87, 28.43, 28.34, 28.27, 25.30, 25.05, 21.69, 13.09;

IR (KBr) $\nu$ 2924, 2853, 1599, 1550, 1487, 1465, 1383, 1244, 1119, 1022, 952, 793, 723, 692 cm$^{-1}$

Anal. Calcd. For C₄₄H₅₀O₂S₃: C 74.80, S 13.61, H 7.07; Found: C 73.32, S 13.02, H 6.03.

5.5 References


