Chapter 3

Probing Molecular Aggregation in Bulky PPVs, OPVs and Their Blends
3.1. Introduction

The photophysics of conjugated polymers especially PPVs, made them promising candidates in the optoelectronic industry soon after the discovery of light emitting phenomena.\textsuperscript{1-6} Although there are a lot of salutary characteristics for PPVs like color-tuning ability,\textsuperscript{7-13} solubility, good processability,\textsuperscript{14-20} etc., one of the cursed problems over many versatile features of them is its lower luminescence quantum efficiency in the solid state. This is mainly due to the very high tendency of conjugated polymer chains towards aromatic \(\pi\)-\(\pi\) interactions, which lead to the formation of weakly emissive aggregated species predominantly in the solid state (in films).\textsuperscript{21-30} However, in some cases these molecular aggregates enhances the cross linking and luminescent properties, which found applications in coating and opto-electronic industry.\textsuperscript{31,32} Recently, Bhongale et al. have reported the enhanced emission from the fluorescent organic nanoparticles of 1,4-di-\([(E)-2\text{-phenyl-1-propenyl}]benzene (PPB) which were prepared by the re-precipitation method.\textsuperscript{31} The fluorescent intensity was found to be enhanced as the size of the nanoparticles increases. This enhancement in the fluorescent emission was explained due to the nearly planar conformation of PPB and the formation of herringbone type aggregates. Very recently, another group also shown gel formation in the well known MEH-PPV by the addition of large amount of alkane solvents.\textsuperscript{32} They describe the gelation phenomena as a result of the interchain cross linking via the interaction between neighboring alkoxy chains with the alkane solvents (see scheme 3.1).

Even though the molecular aggregates show many promising properties as mentioned above, most of them are lower energy non-emissive species in which the excitation energy of the highly luminescent excimers get trapped during the radiative emission processes. Recent studies have shown that the intra- and inter-chain interactions play a major role in the physical origin of molecular aggregation phenomena.\textsuperscript{23-25} In most cases, it acts as luminescent quenching sites, therefore, control of \(\pi\)-stack induced molecular aggregation in the polymer chain is an important task in the development of highly emissive
conjugated polymers and also making the ideal polymer luminescent optoelectronic devices in reality.

Scheme 3.1. Schematic representation of the physical cross linking between MEH-PPV and alkane (nonane) solution (adopted from ref. 32).

Several methods have been adopted to reduce the interchain interactions, which involves the incorporation of cis-vinylene linkages in the polymer backbone \(^{33-36}\), polymer blends \(^{37-40}\) and introduction of bulky anchoring groups \(^{41-45}\) etc. (explained in chapter 1 and chapter 2 in detail). The control of molecular aggregation through inter-chain separation via bulky anchoring groups were found to be very attractive since one can easily control the molecular aggregation through space without disturbing the electronic/device properties of the parent polymer. Reports of PPVs based on the bulky anchoring groups showed additional advantages that they also enhances the glass transition temperature \((T_g)\) of the PPV backbone which is an important parameter for long operating lifetime of devices.\(^{46}\) However, it is surprising to notice that most of the reports on bulky PPVs have focused on the structural parameters and so far not much effort have been paid to trace the aggregation behavior of these emerging bulky conjugated materials. This is partially due to
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the poor solubility of the efficient bulky-PPVs such as adamantane and cholesteryl rings\textsuperscript{47-50} in common organic solvents which hampered the application of spectroscopic techniques to study the aggregation properties in solution. Therefore, it is very important to carry out systematic spectroscopic studies to probe the origin of the molecular aggregates in bulky conducting polymers, which will provide valuable information for the future development of new highly luminescent materials.

The formation of molecular aggregates can be understood by the choice of good/poor solvents, varying the solution concentration or temperature, thermal annealing process etc.\textsuperscript{51-54} By varying the external stimuli, the photophysical properties of the polymer chains found to alter according to the extended and coiled conformation the polymer chains adopt.\textsuperscript{55} This will usually result either in a red shifted peak or an additional peak in the absorption spectra. It was widely noticed that chains in the well-stacked regions exhibits red shifted spectra with low luminescent quantum yield while the chains in the poorly packed region show bluer spectra with high quantum yield.\textsuperscript{22} As already discussed in the second chapter, the introduction of TCD-units into the PPV backbone reduces the molecular aggregation and enhances the solution and solid state photoluminescence characteristics. This chapter mainly deals with the investigation of the molecular aggregation properties of the soluble TCD-substituted bulky-PPVs in combination with the well-studied poly(2-methoxy-5-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV). A random copolymer of MEH-PPV with 60 % of symmetrically TCD substituted polymer was chosen for the above purpose due to its high solubility, good molecular weight and similar photophysical properties as that of its partially soluble bulky-TCD-PPV homo-polymer (BTCD-PPV). Structurally identical two oligo-phenylenevinylene (OPVs) bearing either (methoxy-ethylhexyloxy) (MEH) or TCD units were also utilized as model compounds for the aggregation studies. Absorption and photoluminescence (PL) spectroscopic techniques were employed as tools to trace the aggregation properties of these materials in
solvents such as toluene, tetrahydrofuran (THF), THF+methanol or THF+water combinations as well as in the solid state. Further, the effect of bulky TCD-anchoring units on the luminescence properties of PPV backbone were also investigated by making MEH-PPV and OPV binary blends. The composition of the MEH-PPV and OPVs were varied from 0 to 100%. Through selective PL excitation, both the effect of oligomer-to-polymer energy transfer and luminescent enhancement in MEH-PPV via inter-chain separation were investigated. Time resolved fluorescence decay measurements were also carried out to study the luminescent decay life time of bulky polymers, oligomers and their binary blends.

3.2. Experimental Methods

3.2.1. Materials: 1,8-Tricyclodecanemethanol (TCD) was donated by Celanese Chemicals & Co, Fluorescence standards Rhodamine-6G and Quinine sulfate were purchased from Aldrich Chemicals and used without further purification. A relatively low molecular weight of poly(2-methoxy-5-(2-ethylhexyloxy))-1,4-phenylenevinylene (MEH-PPV) (M<sub>n</sub> = 20,300 and M<sub>w</sub> = 70,100) was prepared for the present study and the chemical structures of the polymers and OPVs selected for the studies is given in scheme 3.2. Synthesis and structural details were provided in chapter 2. The symmetrically TCD-substituted copolymer of MEH-PPV, poly[(2-methoxy-5-(2-ethylhexyloxy))-1,4-phenylenevinylene-co-(2,5-bis(1,8-tricyclodecanemethyleneoxy)-1,4-phenylenevinylene] (BTCD-60) (with 60 % TCD content, M<sub>n</sub> = 9,300 and M<sub>w</sub> = 23,900) was also used. It possesses high molecular weight, good solubility in common organic solvents and the bulky BTCD-60 has photoluminescent properties similar to that of its bulky homopolymer.

3.2.2. General Procedures: For the photo physical studies, all the solvents were purified according to the standard procedures prior to use. The samples were completely dissolved by ultra sonication and the homogenous solutions thus obtained were used for further studies. The absorption and emission
studies were done by a Perkin-Elmer Lambda 35 UV-Visible spectrophotometer and Spex-Fluorolog DM3000F spectrofluorometer with a double grating 0.22-m Spex 1680 monochromator and a 450-W Xe lamp as the excitation source using the front-face mode. For the solid state spectra, polymers thin films (10-100 µM) were casted from chloroform solution on glass substrates. The quantum yields of the PPVs and OPVs were determined using Rhodamine 6G in water (ϕ=0.95) and quinine sulfate in 0.1 M H₂SO₄ (ϕ=0.546) as standards, respectively. The solvent induced aggregation studies were done using methanol (MeOH) and water as nonsolvents respectively for PPVs and OPVs and by making different solvent/nonsolvent combinations. The absorbance or optical density (O.D) of the solutions was maintained at 0.1 for the photo physical studies. The stock solution was prepared by dissolving the polymer or oligomer in tetrahydrofuran (THF) and various combinations of tetrahydrofuran and methanol/water of the samples were prepared by maintaining the absorbance ≈ 0.1 at the absorption maxima. Temperature dependant absorbance studies were done in THF/methanol or THF/water mixture heating and cooling were done by the help of Perkin Elmer PTP-1 Peltier cooling system. The fluorescence lifetime was measured using an IBH FlouroCube Time-correlated picosecond single photon counting system (TCSPC). Solutions and films were excited with a pulsed diode laser 401nm <100 ps pulse duration with a repetition rate of 1 MHz. The detection system consists of a microchannel plate photomultiplier (5000U-09B, Hamamatsu) with a 38.6 ps response time coupled to a monochromator (5000M) and TCSPC electronics (DataStation Hub including Hub-NL, NanoLED controller and preinstalled Fluorescence Measurement and Analysis Studio (FMAS) software). The fluorescence lifetime values were determined by deconvoluting the data with exponential decay using DAS6 decay analysis software. The quality of the fit has been judged by the fitting parameters such as χ²<1 as well as the visual inspection of the residuals.
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3.2.3. Synthesis of Binary Blends

The polymer-oligomer binary blends were prepared as follows. A filtered stock solution of MEH-PPV (2.8 mg in 10 mL) in tetrahydrofuran (THF) and BTCD-OPV or MEH-OPV (50 mg in 10 mL) in THF were mixed at varjous ratio (see table 3.1) to obtain the OPV-amount as 15, 30, 40, 55, 80, 90, 95 wt % in the blend solution. The blend solution was stirred under ultrasonic for 5-10 minutes prior to drop casting on glass substrates. The films were dried and stored at room temperature to protect from light.

<table>
<thead>
<tr>
<th>% of OPV</th>
<th>Volume of OPV (mL)</th>
<th>Volume of PPV (mL)</th>
<th>Amount of OPV (mg)</th>
<th>Amount of PPV (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.05</td>
<td>0.95</td>
<td>0.05</td>
<td>0.266</td>
</tr>
<tr>
<td>30</td>
<td>0.1</td>
<td>0.9</td>
<td>0.1</td>
<td>0.252</td>
</tr>
<tr>
<td>40</td>
<td>0.15</td>
<td>0.85</td>
<td>0.15</td>
<td>0.238</td>
</tr>
<tr>
<td>55</td>
<td>0.25</td>
<td>0.75</td>
<td>0.25</td>
<td>0.210</td>
</tr>
<tr>
<td>65</td>
<td>0.1</td>
<td>0.9</td>
<td>0.50</td>
<td>0.252</td>
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<tr>
<td>80</td>
<td>0.2</td>
<td>0.8</td>
<td>1</td>
<td>0.224</td>
</tr>
<tr>
<td>90</td>
<td>0.3</td>
<td>0.7</td>
<td>1.5</td>
<td>0.196</td>
</tr>
<tr>
<td>95</td>
<td>0.4</td>
<td>0.6</td>
<td>2</td>
<td>0.168</td>
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</table>
3.3. Results and Discussion

The structures of the polymers and oligomers selected for the present study were shown in scheme 3.2. Their detailed structural characterization and thermal studies were given in chapter 2. In the present chapter, more effort has been taken to understand and analyze the molecular aggregation properties of these new classes of bulky \( \pi \)-conjugated materials.

![Scheme 3.2. Structure of the polymers and oligomers.](image)

3.3.1. Solvent Dependant Photophysical Properties

The photophysical properties (absorption and emission) of the polymers were studied in solution as well as in the solid state (in film). The absorption and emission spectra of the polymers were recorded in tetrahydrofuran (THF) and toluene to study the influence of solvents on the polymer structure (see figure 3.1). The absorption spectra of both polymers showed 6-7 nm red shift in toluene compared to that in THF (see table 3.2). It is due to the fact that aromatic hydrocarbon solvents solvate the PPV backbone in such a way to adopt closer chain interactions via \( \pi \)-stacking which account for the red shift.\(^{22}\)
The emission spectra of the polymers were recorded for 0.1 O.D (optical density) solutions in THF and toluene. The emission spectra were almost identical even though there is a slight difference in the absorption maxima for the polymer solutions in THF and toluene.

![Absorption and emission spectra of MEH-PPV and BTCD-60 in solution.](image)

Figure 3.1. Absorption and emission spectra of MEH-PPV and BTCD-60 in solution.

The solution quantum yields were determined using Rhodamine 6G in water as standard ($\phi = 0.95$) and the values were obtained in the range of 0.23-0.28 and 0.24-0.31 for MEH-PPV and BTCD-60, respectively (see table 3.2). It can be clearly noticed that the emission quantum yield was less in toluene compared to that of THF (see table 3.2). This may be due to the partial $\pi$-stacking of the polymer chains in toluene compared to that of THF, as noticed in their absorbance spectra. Thin polymer films were caste on glass substrate from polymer solution and the O.D. of the films were obtained as 0.1 by adjusting the concentration of the polymer solution. The solid state absorbance and emission spectra of films were shown in figure 3.2. The absorbance spectra of MEH-PPV and BTCD-60 films prepared from toluene solution were almost identical and red-shifted compared to that of those films obtained from THF solution. It suggests that the films caste from aromatic hydrocarbon solvents...
such as toluene possess more π-stacking compared to that of the films from good solvent like THF.\textsuperscript{22,56}

![Absorption and emission spectra of MEH-PPV and BTCD-60 in film (caste from THF and Toluene solution) on glass substrate.](image)

**Figure 3.2.** Absorption and emission spectra of MEH-PPV and BTCD-60 in film (caste from THF and Toluene solution) on glass substrate.

Among the films produced from THF solution, the absorption spectra of BTCD-60 film is blue shifted by 15-20 nm compared to MEH-PPV films (compare plots a and b in figure 3.2). It indicates that inter (or intra) chain interactions (π-stacking) are relatively weak in BTCD-60 compared to MEH-PPV. It may be due to the strong steric hindrance induced by the TCD-bulky unit. The solid state emission spectra of the polymers have shown an interesting trend that the spectra of BTCD-60 showed almost 5-6 times enhancement in PL intensity than that of MEH-PPV. The emission intensity of MEH-PPV films were very low for both films caste from toluene and THF (see emission plots a and a’ in figure 3.2) compared to the BTCD-60 films. Among the two BTCD-60 films, the film obtained from THF solution showed twice the PL intensity compared to that of films obtained toluene solution (see emission plots b and b’ in figure 3.2). The comparison of absorbance and emission spectra of the films of BTCD-60 revealed that the less π-aggregated film (plot-b) showed higher luminescence intensity compared to that of more π-aggregated chains (plot b’).
Table 3.2. Photo physical, thermal and electrochemical properties of the polymers and oligomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>In soln. (nm)</th>
<th>In film (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{Abs}}$</td>
<td>$\lambda_{\text{Em}}$</td>
</tr>
<tr>
<td>MEH-PPV(THF)</td>
<td>489</td>
<td>549</td>
</tr>
<tr>
<td>MEH-PPV(Toluene)</td>
<td>495</td>
<td>553</td>
</tr>
<tr>
<td>BTCD-60(THF)</td>
<td>486</td>
<td>550</td>
</tr>
<tr>
<td>BTCD-60(Toluene)</td>
<td>493</td>
<td>554</td>
</tr>
<tr>
<td>MEH-OPV</td>
<td>389</td>
<td>433-475</td>
</tr>
<tr>
<td>BTCD-OPV</td>
<td>386</td>
<td>432-481</td>
</tr>
</tbody>
</table>

(a) Excitation wave length used is 480 nm for the polymers and 380 nm for the oligomers.
(b) Determined using Rhodamine 6G as standard for the polymers ($\lambda_{ex}=480$ nm) and Quinine sulfate as the standard for the oligomers ($\lambda_{ex}=380$ nm), the absorbance of solutions were maintained as 0.1 at the excitation wavelength.
(c) Excitation wavelength is 500 nm for polymers and 390nm for the model compounds.
(d) The emission intensity of the polymers at the emission maxima.
(e) Determined from the diffuse reflectance measurements.

It evident that the molecular aggregation is a very strong phenomenon in PPV chains for reduction in emission characteristics in both solutions as well as in the films caste from their solution. The presence of TCD-bulky unit significantly hinders the $\pi$-stacking of polymer backbone and enhances the solution quantum yield and PL intensity almost 5-6 times in BTCD-60 compared to that of MEH-PPV. In order to trace the aggregated species at the excited state, the excitation spectra of the polymers were recorded at two different concentrations in THF ($10^{-4}$ and $10^{-5}$ M$^{-1}$). The concentration dependent experiment was chosen since the polymer chains are closely packed at higher concentration which resembles the chain arrangements in the film.$^{52}$ The excitation spectra of MEH-PPV and BTCD-60 were collected at three different emission wavelengths ($\lambda_{em}= 550, 590, 660$ nm) and shown in figure 3.3.

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At lower concentration, the excitation spectra of MEH-PPV showed maxima at 470 nm with a shoulder at 340 nm at all three collected emission wavelengths. At higher concentration, the intense peak was blue-shifted by 70 nm and centered at ~ 405 nm corresponding to strong inter chain interaction and π-stacking in concentrated solution. Additionally, the excitation spectra was collected at higher emission wavelengths (collection at 590 and 660 nm) of the concentrated solution of MEH-PPV showed a new peak at 545 nm which was assigned to the aggregated polymer chains.57 Interestingly, the BTCD-60 showed almost identical excitation spectra irrespective of the concentration of the solution and collected emission wavelengths. It confirmed that the MEH-PPV polymer chain undergo more π-stacking at higher concentration (similar to film) which results in quenching of the luminescence properties. From chapter 2, we have also seen that the solid state luminescence quantum yield of the model compounds (MEH-OPV and BTCD-OPV) determined using diffuse reflectance technique according to the reported procedure58-60 was obtained as 0.64 for BTCD-OPV which was two times higher than that of MEH-OPV (φ=0.27). It clearly demonstrates that the bulky TCD unit is very efficient structure directing unit for highly luminescent π-conjugated materials. From the above photo physical studies, it is evident that the bulky-TCD unit increases the inter-chain distance in the polymer backbone leading to the reduction in the
molecular aggregation for enhanced luminescence. In poly(phenylenevinylene)s, the polymer chains have very strong affinity towards π-stacking and the resultant π-aggregates in solution or solid state strongly quenches the luminescent intensity.\textsuperscript{29, 30} In the present investigation, we have noticed that the introduction of bulky units enhances the solution quantum yield as well as the solid state PL intensity for both polymers as well as oligomers. Therefore, tracing the π-stacking properties of conjugated polymers, especially in the case of bulky systems, it is very important to understand their luminescent properties. There are different methods to probe the molecular aggregation in π-conjugated systems and among them solvent and temperature dependant aggregation studies are very important.

### 3.3.2. Solvent Induced π-Aggregation Studies

Solvent induced self-organization in conjugated chains is an attractive approach, since the isolation or aggregation of polymer chains can be easily controlled by choosing the appropriate combination of good or non-solvent (or bad solvent).\textsuperscript{36} In good solvent the polymer chains exist as isolated chains and subsequent addition of bad solvent forces the polymer chains to undergo collapsed stage which is similar to that of in the film (see figure 3.4).

![Figure 3.4. Behavior of polymer chains in good and bad solvents](image)

The solvent induced aggregation studies of the oligomers (MEH-OPV and BTCD-OPV) and polymers (BTCD-60 and MEH-PPV) will provide more insight into the effect of π-aggregation on the luminescent properties. For the
solvent induced aggregation studies, the photo physical properties of polymers were studied in THF (good solvent) and methanol (poor solvent) solvent mixture. For the molecular aggregation studies of the model compounds THF+water was chosen as the solvent combination. The absorption and emission spectra of MEH-PPV and BTCD-60 in THF/methanol mixture (from 0-100 % v/v) are shown in figure 3.5.

**Figure 3.5. Absorption and emission spectra of polymers in THF/MeOH with varying solvent combination at 30 °C. Color change from orange to red with the addition of methanol into the polymer solution (from left to right – increasing methanol content)**
The addition of methanol into the polymer solutions in THF, drastically affect both the absorption maxima as well as luminescent intensity. The color of the polymer solution gradually changed from orange to red with the addition of methanol and the transition point was noticed at 40-50 % of methanol in THF (see figure 3.5). It can be clearly noticed that MEH-PPV was more drastically affected by the MeOH addition compared to that of BTCD-60 ((see absorption and emission spectra in figure 3.5). The quantum yields for the different solvent/non-solvent combinations were calculated using Rhodamine 6G in water as the standard. Since the MeOH addition reflects both on the absorption maxima and quantum yield, these two parameters can be used to trace the extent of molecular aggregation in polymer chains.

The plots of absorption maxima (Figure 3.6a) indicate the existence of two types of species depending upon the amount of methanol in polymer solution. The polymer chains are free and isolated below 30-40 % of methanol whereas they are fully aggregated above 50-60 % of methanol. The extent of absorption maxima shift (Y-axis) revealed that the MEH-PPV chains showed strong aggregation with 25 nm red-shift compared to that of bulky BTCD-60 which showed only 16 nm red-shift. The quantum yield plots (Figure 3.6 b) also support the existence of the aggregated chains and the values are lower for MEH-PPV compared to that of BTCD-60 (above 50 % methanol concentration). It reveals that polymer chains in MEH-PPV chains experience more π-aggregation compared to that of the bulky PPY chains in BTCD-60.

The solvent induced aggregation studies of the model compounds (OPVs) also reflect on the molecular aggregation in absorption and emission properties (see figure 3.7). As expected, the extent of aggregation relatively weak in model compounds compared to their polymer counterparts since long range of π-stack is not possible in simple OPVs compared to that of high molecular weight polymer chains. The shift in the absorption spectra is not very significant; however, the emission properties are affected at high amount of non-solvent addition (figure 3.7a).
Figure 3.6. Plot of absorption maxima and quantum yield versus the percentage of MeOH in the THF/MeOH mixture.

The fluorescence quantum yields of the model compounds (figure 3.7b) almost unaffected up to 80 % of water in THF. However, at higher water content, a significant decrease in quantum yield can be noticed for MEH-OPV compared to that of BTCD-OPV.

Figure 3.7. (a) Emission spectra of BTCD-OPV in THF/H₂O with varying solvent combination at 30 °C. (b) Plot quantum yield versus the percentage of H₂O in the THF/ H₂O mixture.
Based on the solvent induced aggregation studies it can be concluded that bulky TCD-unit is very efficient anchoring groups for PPV backbone (also for OPVs) in preventing the molecular aggregation for enhanced emission properties.

3.3.3. Temperature Dependent \(\pi\)-Aggregation Studies

The aggregation of the polymer chains in solution are also sensitive to the temperature which can also be used as another stimuli for tracing the molecular aggregation properties.\textsuperscript{36} To study the influence of temperature on the nature and reversibility of the molecular aggregation in PPV chains, the polymers at the aggregated stage was subjected to temperature dependant absorption studies. There are two ways one can design the temperature dependent studies: (i) start from the non-aggregated stage at room temperature and force the chains to undergo aggregation and isolation by cooling/heating at sub-ambient region\textsuperscript{36} or (ii) start from the pre-aggregated stage at room temperature and carryout the aggregation and isolation by heating/cooling at elevated temperatures. We adapted the second method, because it is more relevant to the practical purpose.

For the temperature dependent studies 40 \% methanol in THF solvent combination was selected because at this stage the polymers show a transition from the isolated to the aggregated state (see Figure 3.8a). The polymer solution (40 \% methanol in THF) were taken in a screw capped cuvette and subjected to absorption studies by heating or cooling the solution from 30 to 80 °C. The UV-visible spectra of BTCD-60 in the heating and cooling cycles are shown in figure 8. As the solution temperature gradually increases, the absorption spectra found to be blue shifted corresponding to the isolation of polymer chains from the pre-aggregated state (see figure 8a). While cooling, the absorbance spectra were red-shifted corresponding to the aggregation of polymer chains (see figure 8b). This experiment was found completely reversible for many more heating/cooling cycles (see figure 3.8c) which confirmed the reversibility of molecular aggregation in PPV chains. Similar
observation was shown by MEH-PPV also; in the heating/cooling cycles (see figure 3.8d, 3.8e, and 3.8f).

![Absorbance vs Wavelength](image)

Figure 3.8. Temperature dependent absorption spectra of BTCD-60 [(a) and (b)] and MEH-PPV [(d) and (e)] in the heating and cooling cycles respectively. Plots (c) and (f) shows the reversibility of molecular aggregates of BTCD-60 and MEH-PPV.

The shift in the absorption maxima for the cooling and heating experiments are plotted and shown in figure 3.9a and 3.9b, respectively. The absorption maxima plots indicated that the MEH-PPV chains undergo 10 nm blue shift on heating while 15 nm red-shift in the cooling cycle. The polymer
chains in BTCD-60 followed just opposite trend in the extent of absorption maxima shift: it showed 14 nm blue-shifts while heating and 10 nm red-shifts in the cooling cycle. This trend suggests that both the polymers undergo isolation from the aggregated state while heating, however, the degree of interchain separation is more for BTCD-60 (14 nm) compared to MEH-PPV (10 nm). In the cooling cycle, the trend was found just opposite in which the MEH-PPV chains undergo more aggregation (15 nm) compared to that of BTCD-60 (10 nm).

Figure 3. 9. Plots of absorption maxima versus temperature for MEH-PPV and BTCD-60 in the cooling and heating cycles.

The difference in the extent of aggregation from the isolated stage (in cooling cycle) revealed that the bulky TCD-units in the PPV-chains strongly hinder the polymer chain alignment and reduces the molecular aggregation. This can be better explained by the following cartoonic representation (see...
figure 3.10). On heating the polymer chains undergo a conformational change from the pre-aggregated stage to more expanded form, which upon cooling will again undergo coiling. However, the extent of coiling in the cooling process is completely different for MEH-PPV and the bulky PPVs. MEH-PPV undergoes more aggregated state (than it was first) (see figure 3.10, top), while in the case of bulky PPV it is not regaining the initial aggregated stage (see figure 3.10, bottom). This is because the bulky TCD-units do not allow the polymer chains to come closer due to steric effects.

![Figure 3.10. Representation of temperature dependence of polymer chains](image)

The results of temperature dependant studies are in accordance with the solvent induced aggregation studies that the inter-chain separations in the bulky systems reduce the molecular aggregation and enhanced the luminescent properties.

3.3.4. Polymer -Oligomer Binary Blends

The effect of bulky units on the inter-chain separation of PPV backbone was further studied by blending MEH-PPV polymer with MEH-OPV and BTCD-OPV through solution blending techniques. The two series of the blends were named as MEH-blend and BTCD-blend, depending upon the types of OPV used in the blend preparation. The weight % of the oligomer was varied
as 15, 30, 40, 55, 65, 80, 90, and 95% in the blend by varying the amount of the components. The blend solution was caste on a glass substrate in such a way to maintain the optical density of the resultant film ~0.1.

![Diagram](https://via.placeholder.com/150)

**Figure 3.11.** Polymer-oligomer binary blend and possible selective excitation processes in the blend.

Two types of selective photo-physical experiments can be carried out in the polymer-oligomer binary blend, which is explained in figure 3.11 (i). Selectively excite the oligomer and transfer the excitation energy to the polymer, subsequently monitor the emission of the polymer (energy transfer mechanism, path-1) or (ii) directly excite the polymer chains and monitor the polymer emission (path-2). In the case of path-1, the excitation of the OPV may also show self-emission, if the energy transfer process is failed. The efficiency of the energy transfer process in such binary blends is highly dependent on the energy levels of the molecules. The energy levels of the polymer and oligomers and the processes of path-1 and 2 are shown in figure 3.11. The absorption and emission spectra of the MEH- and BTCD-binary blends were shown in figure 3.12.
Figure 3.12. Absorption spectra of MEH-blend (a) and BTCD-blend (b). Emission spectra of MEH-blend for excitation wavelengths 390 nm (c) and 500 nm (e); Emission spectra of BTCD-blend for excitation wavelengths 390 nm (d) and 500 nm (f).

The absorption maxima of the OPV and PPV chains appeared 390 and 500 nm, respectively. It is very clear from the plots that the optical densities of the PPV part increase with the increase in the MEH-PPV content in the blend. The emission spectra for 390 nm excitation (corresponds to the absorption maximum of the oligomer) are given in figure 3.12 (c and d) for MEH and BTCD-blends, respectively. In both blends, the emission spectra showed two peaks at 495 and 570 nm corresponding to the self-emission and polymer chain...
emission followed by energy transfer process, respectively. Though the pure MEH-PPV possess small absorption at 390 nm (O.D. = 0.05, see figure 3.12a and 3.12b), but failed to show any significant luminescence at 450-550 nm for excitation at 390 nm, which suggested that the pure MEH-PPV chains are not contributing to the emission characteristics of blends in this region. The relative intensities of these emission peaks were highly influenced by the compositions and types of the OPVs in the blend. The emission intensity of the peaks at 495 and 570 nm were plotted with respect to their composition and shown in figure 3.13.

Figure 3.13. Plot of PL Intensity versus % of OPV in the blend for MEH-blend and BTCD-blend at different excitation wavelengths.
It is very clear from the plots in figure 3.13a that the MEH-blend did not show self-luminescence up to 80% of the MEH-OPV content, which indicates the strong excitation energy transfer from the OPVs to MEH-PPV chains. On the other hand, BTCD-OPV showed a self-emission even for 30% of its presence in the BTCD-blend. Figure 3.13b represents the luminescence intensities of the blend at 570 nm, followed by the energy transfer process from oligomer to polymers for 390 nm excitation. The energy transfer to the polymer chains lead to the luminescence of the MEH-PPV at 570 nm. The increase in the PL-intensity of MEH-PPV chain was very high for BTCD-blend series throughout the entire composition (see figure 3.13b); it suggests that the bulky OPV molecule showed enhanced energy transfer process compared to that of the normal OPV molecules. The emission spectra of the blends excited at 500 nm (with respect to the absorbance of MEH-PPV, path-2) are shown in figure 3.12e and 3.12f and the PL intensity data are plotted in figure 3.13c. For 500 nm excitation, the blends showed emission peak at 570 nm and the intensity of this emission peak significantly increases with the amount of OPV in the blend (see figure 3.13c) compared to that of pure MEH-PPV film. Since the OPV molecules do not have any luminescence behavior for excitation at 500 nm, the enhanced emission at 570 nm in the MEH-PPV chains is the result of the reduction of molecular aggregation in the solid state. The larger PL intensities of BTCD-blend at the entire composition indicate that the MEH-PPV polymer chains are separated apart very effectively by the BTCD-OPV molecules in the blend compared to the MEH-OPVs. The well separated polymer chains in the blend experience less π-stack induced molecular aggregation. Therefore, it is directly evident from the selective excitation studies of the blends that the BTCD-units are an efficient bulky group for controlling the molecular aggregation for enhanced luminescence properties.

3.3.5. Time Resolved Fluorescence Life-time Measurements

Time resolved fluorescence decay profiles of the polymers, oligomers and polymer-oligomer blends were carried out in solution (THF) and in the...
film at room temperature and are given in figure 3.14. The decay dynamics were carried out at an excitation wavelength of 401 nm and the decays were monitored at respective emission maxima (see table 3.3 and Figure 3.14).

**Figure 3.14. Fluorescence lifetime decay curves of OPVs, PPVs and their blends in solution and film.**

The OPVs in THF show a single exponential fit and they possess similar decay life times, 1.86 ns (MEHOPV) and 1.89 ns (BTCDOPV) indicating that they are having similar excimer species.\textsuperscript{22, 57} The decay profiles of the MEH-OPV and BTCDOPV in film were found to be similar to that in the solution. MEH-PPV and BTCD-60 showed a single exponential decay in THF with life time 0.56-0.60 ns. The aggregated polymer solution (40 % methanol in THF) showed bi-exponential decay with two life times in the range of 0.50-0.60 (98
% and 0.81-1.04 (2 %) confirming the existence of two types of luminescent species corresponding to the aggregated and isolated chains. The polymers in film were also showed a bi-exponential decay and their lifetimes are given in table 3.3. The observed fast decay in the aggregated solution and in the films may be due to the increased extent of non-radiative processes and efficient energy transfer to the aggregated species. The decay lifetime measurements of the polymer-oligomer binary blends were also carried out in films and they showed bi-exponential fit (Figure 3.14d). It was clear from the fitting results that more than 90 % fraction of components undergoes fast decay and only less than 10 % show delayed emission.

**Table 3.3. Fluorescent decay lifetime measurements of the oligomers, polymers and polymer-oligomer blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Medium $^a$</th>
<th>$\lambda_{\text{monitor}}$ (nm) $^b$</th>
<th>$\tau_1$ (ns) $^c$ (99 %)</th>
<th>$\tau_2$ (ns) $^c$ (1 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEH-OPV</td>
<td>THF</td>
<td>470</td>
<td>1.86</td>
<td>-</td>
</tr>
<tr>
<td>BTCD-OPV</td>
<td>THF</td>
<td>470</td>
<td>1.89</td>
<td>-</td>
</tr>
<tr>
<td>MEH-OPV</td>
<td>Film</td>
<td>525</td>
<td>1.70</td>
<td>-</td>
</tr>
<tr>
<td>BTCD-OPV</td>
<td>Film</td>
<td>525</td>
<td>2.04</td>
<td>-</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>THF</td>
<td>555</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>BTCD-60</td>
<td>THF</td>
<td>555</td>
<td>0.60</td>
<td>-</td>
</tr>
<tr>
<td>MEHPPV-Agg</td>
<td>THF/CH$_3$OH</td>
<td>550</td>
<td>0.50</td>
<td>1.04</td>
</tr>
<tr>
<td>BTCD60-Agg</td>
<td>THF/CH$_3$OH</td>
<td>550</td>
<td>0.61</td>
<td>0.81</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Film</td>
<td>585</td>
<td>0.46</td>
<td>0.62</td>
</tr>
<tr>
<td>BTCD-60</td>
<td>Film</td>
<td>585</td>
<td>0.35</td>
<td>0.56</td>
</tr>
<tr>
<td>MEHBlend-30</td>
<td>Film</td>
<td>585</td>
<td>0.52</td>
<td>1.17</td>
</tr>
<tr>
<td>MEHBlend-90</td>
<td>Film</td>
<td>585</td>
<td>0.34</td>
<td>0.81</td>
</tr>
<tr>
<td>BTCDBlend-30</td>
<td>Film</td>
<td>575</td>
<td>0.32</td>
<td>1.33</td>
</tr>
<tr>
<td>BTCDBlend-90</td>
<td>Film</td>
<td>575</td>
<td>0.36</td>
<td>1.69</td>
</tr>
<tr>
<td>BTCDBlend-30</td>
<td>Film</td>
<td>495</td>
<td>0.63</td>
<td>2.46</td>
</tr>
<tr>
<td>BTCDBlend-90</td>
<td>Film</td>
<td>495</td>
<td>0.51</td>
<td>2.35</td>
</tr>
</tbody>
</table>

(a) The optical density of the solutions and films were maintained at $\approx 0.1$ for the lifetime measurements
(b) Emission wavelengths for which the decay was monitored ($\lambda_{\text{exc}} = 401$ nm).
(c) Lifetimes obtained from the exponential decay fitting.
In MEH-blend, as the percentage of OPV in the blend increases the decay lifetime becomes fast because of the high rate of energy transfer process from the oligomer to the polymer chain. This observation in the MEH-blend demonstrated the complete energy transfer from the oligomer which results in the increase in emission intensity of the polymer. However, the decay lifetime of BTCD-blend shows no difference for the emission wavelength collected at 575 nm which corresponds to the polymer emission. But a small difference was observed for the BTCD-blend films when collected at 495 nm which correspond to the oligomer emission. It supports the observation for the polymer-oligomer binary blends that in BTCD-blend two significant processes occur (i) the self-luminescence of the oligomer and (ii) the emission of the polymer chains as a result of the enhanced energy transfer.

It is evident that the bulky OPV sterically hinder the inter-chain interactions preventing the molecular aggregation in the solid state. Therefore, from the photophysical studies and decay lifetime measurements it can be concluded that the bulky TCD- unit is an important anchoring group, which can control the molecular aggregation by increasing the inter-chain distances in the polymer chains as well as in the polymer-oligomer blend for the enhanced luminescent properties.
3.4. Conclusion

In this chapter, systematic spectroscopic studies was carried to probe the origin of the molecular aggregates in bulky conducting polymers and demonstrated the importance of the bulky TCD-anchoring group in controlling the molecular aggregation for improved photo luminescent properties. The absorption, excitation and emission studies of the polymers in solution and solid state were carried out and they demonstrated the following facts: (i) Apart from the solvent effects, the structural configuration of the polymeric backbone plays an important role in enhancing the solid state luminescent intensity, (ii) The solvent induced aggregation studies have proven that the addition of methanol (poor solvent) into the polymer solutions in THF (good solvent), drastically affect both the absorption maxima as well as luminescent intensity. However, the comparative studies suggested that the MEH-PPV chains experience more π-aggregation compared to that of the bulky PPV chains in BTCD-60, (iii) Temperature dependant studies have demonstrated that MEH-PPV chains undergo more aggregation (15 nm) in the cooling cycle compared to that of BTCD-60 (10 nm), (iv) The solvent and temperature dependant studies were further confirmed with the studies done on the OPVs which suggest that the bulky unit separates the interchain distance for the enhanced luminescence properties, (v) Synthesis of polymer-oligomer binary blends revealed that the bulky OPV (BTCD-OPV) increases the emission of the PPV chain via both energy transfer and inter chain separation processes and, (vi) Decay lifetime measurements of the binary blends further support the efficient energy transfer from the OPV to the PPV backbone resulting in the enhanced emission properties.

Therefore, from the present studies it is clearly evident that the bulky substitution in the PPV or in the oligomer separates inter-chain or inter-molecular distance more efficiently leading to the improved photo-luminescent properties which can be explored for the futuristic applications of opto-electronic devices.

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3.5. References

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36. (a) Chu, Q.; Pang, Y. Macromolecules 2003, 36, 4614. (b) Chu, Q.; Pang, Y. Macromolecules 2005, 38, 517.


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