Bulk-heterojunction and bilayer polymer solar cells
In this Chapter, the results on the characteristics of P3HT:PCBM bulk-heterojunction solar cells measured as a function of annealing temperature are discussed. In order to investigate the temperature dependent evolution of structural/morphological changes in P3HT:PCBM films, the results of in-situ optical and Raman spectroscopy are presented and a correlation between the morphology and efficiency of P3HT:PCBM solar cells is established. We also present results on the two different types of bilayer solar cells: (i) porphyrin/polyfullerene solar cells fabricated for the first time using electrochemical technique. For this purpose, the growth mechanism of electrodeposited porphyrin and polyfullerene films on ITO substrates are investigated. (ii) porphyrin-modified ZnO-NW/P3HT hybrid solar cells.

3.1 P3HT:PCBM bulk-heterojunction polymer solar cells

As discussed in Chapter 1, BHJ polymer solar cells based on P3HT and PCBM blends are widely studied owing to their low-cost, flexibility, ease of material synthesis and manufacturing advantages[14-18]. In these solar cells, thermal annealing is widely employed as post processing treatment for controlling the morphology of the blend, and hence, the efficiency. Literature survey shows that the best efficiency is obtained when the active layer is annealed at a temperature in the range of 120-150°C[13, 44]. As of now it is not fully understood that how annealing processes affects the ordering of molecules, morphology and domain size of each component in the P3HT:PCBM films. In order to gain an insight into the annealing induced structural and morphological changes, we present In-situ Raman spectroscopy - a powerful inelastic light scattering based technique
that is capable of monitoring the nanoscale changes in the polymer structure through the measurement of vibrational modes[73].

Figure 3.1: Measured (symbol) and fitted (solid line) \( J-V \) characteristics of as-prepared and thermally annealed (at various temperatures) P3HT:PCBM bulk-heterojunction solar cells.

3.1.1 Photovoltaic characteristics

Fig. 3.1 shows the measured current-voltage (\( J-V \)) characteristics of as-prepared and thermally annealed (75°C, 110°C, 130°C, 150°C, and 180°C for 30 min) P3HT:PCBM bulk-heterojunction solar cells, which were measured under AM 1.5G, 1 Sun illumination. From these data, various photovoltaic parameters i.e. open-circuit voltage (\( V_{oc} \)), short-circuit current (\( J_{sc} \)), fill factor (FF), and power conversion efficiency (\( \eta \)) were calculated. The variation of these parameters as a function of annealing temperature is shown in Fig. 3.2. From this figure following inferences can be drawn:

(i) The value of \( V_{oc} \) is \( \sim 0.5 \) V for as fabricated solar cells, which almost remains independent of the annealing temperature up to 130°C. However for higher annealing temperatures it marginally decreases.
(ii) $J_{sc}$ initially remains unaffected up to 75°C, increases rapidly with annealing temperature and attains a maximum of 12.4 mA/cm$^2$ at 130°C. However, at higher annealing temperature the $J_{sc}$ decreases sharply. This behavior is associated with structure/morphological evolution as a function of annealing temperature, and this will be elaborated in the next section.

(iii) Both FF and $\eta$ follow the same trend as that of $J_{sc}$, indicating a critical role played by annealing induced structure/morphology of the P3HT:PCBM films. The maximum values FF and $\eta$ obtained at 130°C are 0.5 and 3.1% respectively. The value of $\eta$ is reasonable considering the fact that we have not employed any electron transport layers. A higher efficiency is normally obtained when calcium is used as top electrode and Lithium fluoride is used as electron transport layer [74].

![Figure 3.2](image-url): Variation of different photovoltaic parameters namely open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiency ($\eta$) of P3HT: PCBM bulk-heterojunction solar cells as a function of annealed temperature.
The measured $J$-$V$ characteristics presented in Figure 3.1 were fitted using the Shockley one diode equation (Eq. 1.6). The initial values of various parameters i.e., ideality factor ($n$), diode saturation current ($I_0$), series resistance ($R_s$), shunt resistance ($R_{sh}$), and photogenerated current ($I_{ph}$) were estimated as follows\[75].

At short circuit condition, $I = I_{sc}$ and $V = 0$, Eq. 1.6 becomes

$$I_{sc} = I_0 \left\{ \exp \left( \frac{qR_sI_{sc}}{nK_BT} \right) - 1 \right\} + \frac{R_sI_{sc}}{R_{sh}} - I_{ph} \quad (3.1)$$

At open circuit condition, $I = 0$, and $V = V_{oc}$, Eq. 1.6 derives as

$$0 = I_0 \left\{ \exp \left( \frac{qI_{sc}}{nK_BT} \right) - 1 \right\} + \frac{V_{oc}}{R_{sh}} - I_{ph} \quad (3.2)$$

Combining Eqs. 3.1 and 3.2, leads to

$$I_0 = \frac{(I_{sc} + \frac{R_sI_{sc}-V_{oc}}{R_{sh}}) \exp \left( \frac{-qV_{oc}}{nK_BT} \right)}{1-\exp \left( \frac{q(R_sI_{sc}-V_{oc})}{nK_BT} \right)} \quad (3.3)$$

and

$$I_{ph} + I_0 = \frac{I_{sc} + \frac{R_sI_{sc}-V_{oc}}{R_{sh}}}{1-\exp \left( \frac{q(R_sI_{sc}-V_{oc})}{nK_BT} \right)} + \frac{V_{oc}}{R_{sh}} \quad (3.4)$$

The above expressions can be simplified if we make the assumption that

$$\exp \left( \frac{q(R_sI_{sc}-V_{oc})}{nK_BT} \right) \ll 1 \quad (3.5)$$

this assumption reduces Eqs. 3.3 and 3.4 to

$$I_0 = \left( I_{sc} + \frac{R_sI_{sc}-V_{oc}}{R_{sh}} \right) \exp \left( \frac{-qV_{oc}}{nK_BT} \right) \quad (3.6)$$

$$I_{ph} + I_0 = I_{sc} + \frac{R_sI_{sc}}{R_{sh}} \quad (3.7)$$

Again from Eq. 1.6, $dV/dI$ is expressed as
\[ \frac{dV}{dl} = \frac{nk_BT/q}{l_{ph}+l_0+l-V-RsI-R_nk_BT/q/Rsh} + R_s \] (3.8)

Substituting Eq. 3.7 into 3.8,

\[ \frac{dV}{dl} = \frac{nk_BT/q}{l_{sc}+l-V/Rsh+R_nk_BT/q/Rsh} + R_s \] (3.9)

At short-circuit condition, \( I = I_{sc} \) and \( V=0 \)

\[ \frac{dV}{dl} \bigg|_{l=I_{sc}, V=0} = R_{sh} + R_s \approx R_{sh} \] (3.10)

And around the open-circuit condition (\( I=0 \) and \( V=V_{oc} \))

\[ \frac{dV}{dl} = \frac{nk_BT/q}{l_{sc}+l-V/Rsh+R_nk_BT/q/Rsh} + R_s \] (3.11)

\[ \approx \frac{nk_BT/q}{l_{sc}+l-V/Rsh} + R_s \] (3.12)

Which can be rewritten as

\[ \frac{dV}{dl} = \left( \frac{V_t}{l_{sc}+l-V/Rsh} \right) \times n + R_s \] (3.13)

Where \( V_t = k_BT/q = 0.0258V \) is thermal voltage.

The initial values of \( n \) and \( R_s \) are calculated by linear fitting of \( dV/dl \) as a function of \( V_t / (I_{sc} + I - V/Rsh) \). The value of y-intercept yields the value of \( R_s \) and the slope gives the value of \( n \). Using these calculated initial values of \( n, R_s, \) and \( R_{sh} \), and experimentally measured values of \( I_{sc} \) and \( V_{oc} \) the initial values of \( I_0 \) and \( I_{ph} \) were calculated using Eqs. (3.6) and (3.7). Using these initial values, the transcendental equation (1.6) is solved using softwares, and the extracted parameters are summarized in Table 3.1.
Table 3.1: Solar cell parameters evaluated from current-voltage characteristics presented in Fig. 3.1.

<table>
<thead>
<tr>
<th>Device parameters</th>
<th>P3HT-25</th>
<th>P3HT-75</th>
<th>P3HT-110</th>
<th>P3HT-130</th>
<th>P3HT-150</th>
<th>P3HT-180</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>2.4</td>
<td>2.2</td>
<td>1.69</td>
<td>1.55</td>
<td>1.6</td>
<td>1.78</td>
</tr>
<tr>
<td>$R_s$ (Ω-cm$^2$)</td>
<td>78</td>
<td>70</td>
<td>14.5</td>
<td>6</td>
<td>11.5</td>
<td>21</td>
</tr>
<tr>
<td>$R_{sh}$ (kΩ-cm$^2$)</td>
<td>0.28</td>
<td>0.32</td>
<td>0.11</td>
<td>0.14</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>$I_0$ (nA/cm$^2$)</td>
<td>1100</td>
<td>790</td>
<td>84</td>
<td>33</td>
<td>72</td>
<td>190</td>
</tr>
<tr>
<td>$I_{ph}$ (mA/cm$^2$)</td>
<td>5.25</td>
<td>5.90</td>
<td>10.60</td>
<td>11.96</td>
<td>10.94</td>
<td>8.0</td>
</tr>
<tr>
<td>$I_{sc}$ (mA/cm$^2$)</td>
<td>4.0</td>
<td>4.6</td>
<td>9.5</td>
<td>11.5</td>
<td>9.8</td>
<td>6.8</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.50</td>
<td>0.49</td>
<td>0.49</td>
<td>0.50</td>
<td>0.47</td>
<td>0.46</td>
</tr>
<tr>
<td>FF (%)</td>
<td>0.3</td>
<td>0.32</td>
<td>0.42</td>
<td>0.49</td>
<td>0.4</td>
<td>0.39</td>
</tr>
<tr>
<td>$\eta$ (%)</td>
<td>0.7</td>
<td>0.9</td>
<td>2.1</td>
<td>3.2</td>
<td>2.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

From Table 3.1 it is evident that the active layer annealed at 130ºC, yields highest efficiency of 3.2 %, along with lowest value of $n$, $I_0$, $R_s$ and highest values of $I_{ph}$. These results indicate that there a correlation among the materials and device parameters. Before, we discuss these correlation, it is essential to investigate why an annealing temperature of 130ºC leads to best efficiency. It may be noted that similar annealing temperature variation in $\eta$ has been reported by several groups [76-78], with an optimum temperature in the 110-150ºC range. This relatively wide annealing temperature range could be possibly due to a difference in the temperature calibration of the heating stage. To under this behavior, we have investigated the structure/morphological evolution by conducting the in-situ Raman as well as optical microscopy, which were further supported by ex-situ AFM, SEM,
elemental x-ray imaging and UV-Vis spectroscopic measurements. The results of these studies are discussed below.

![Raman spectra of as-cast P3HT, PCBM and P3HT:PCBM films recorded using 514 nm excitation.](image)

**Figure 3.3:** Raman spectra of as-cast P3HT, PCBM and P3HT:PCBM films recorded using 514 nm excitation. Inset shows the molecular structure of P3HT molecule. Substrate peak is represented by (*).

### 3.1.2 In-situ Raman spectroscopy and optical microscopy

Typical Raman spectra of as-deposited P3HT, PCBM and P3HT:PCBM films reordered at room temperature are shown in Fig. 3.3. The inset of the figure shows the molecular structure of P3HT. Various identified Raman modes observed in the case of P3HT films are 1449 cm\(^{-1}\) (symmetric C=C stretch mode), 1380 cm\(^{-1}\) (C-C intra-ring stretch mode), 723 cm\(^{-1}\) (C-S-C ring deformation), 1204 cm\(^{-1}\) (inter-ring C-C stretch mode) and 1170 cm\(^{-1}\) (C-H bending mode with C-C inter-ring stretch mode)[79, 80]. Among various these modes, symmetric C=C ring stretching (1449 cm\(^{-1}\)) and skeletal C-C stretching (1375 cm\(^{-1}\)) modes are of major concern, as they are sensitive to \(\pi\)-electron
delocalization i.e. conjugation length[80, 81]. In literature, Raman spectra of P3HT and P3HT:PCBM films under both non-resonant (e.g. excitations at 785 and 633 nm) and resonant (e.g. excitations at 514, 488 or 496.5 nm) excitations have been reported[79-81]. It has been shown that the peak position of C-C mode at 1380 cm$^{-1}$ is not only insensitive to degree of molecular order, but also to the excitation wavelength i.e. same for the non-resonant and resonant excitation. On the other hand, for C=C mode, its peak position, linewidth and intensity is found to strongly dependent on the excitation wavelength (i.e. resonant excitation yield better results as compared to non-resonant excitation) and the molecular ordering. Therefore, Raman shift of P3HT C=C mode can be used as a measure of the conjugation length due to its symmetry with respect to the conjugation direction. The blue shift in this mode, therefore, indicates reduced conjugation length which might arise due to disorder occurring in the P3HT chains or PCBM incorporation as reported by Tsoi and Carach[80, 82]. In the case of PCBM films, the major peak observed at 1566 cm$^{-1}$ corresponds to A$_{1'}$ mode[83].

Figure 3.4: Typical normalized Raman spectra with respect to the intensity of the C–C mode for (a) P3HT and (b) P3HT:PCBM films. (1) as-deposited films at room temperature; (2) at 130°C and (3) again at room temperature after cooling from 130°C.
For P3HT:PCBM films, peaks corresponding to both P3HT as well as the predominant peak of PCBM have been observed, indicating presence of both P3HT and PCBM. In order to gain insight into the evolution of P3HT:PCBM structure, the *in-situ* Raman spectra of pristine P3HT and P3HT:PCBM films were recorded during both heating and cooling cycles at an interval of 25-30°C. In different experiments, films were annealed to different temperatures between 75°C and 180°C. Typical Raman spectra normalized with respect to the intensity of C-C stretching mode for P3HT and P3HT:PCBM films during different stages of thermal annealing are shown in Fig. 3.4. It is evident that the symmetric C=C stretching mode ($\nu_\text{C=C}$) undergoes a slight blue shift on heating to 130°C; while cooling back to room temperature it has a red shift. In the literature it has been reported that the P3HT C=C band consists of contributions from ordered (aggregated) and amorphous (un-aggregated) components which appear at 1450 cm$^{-1}$ and 1470 cm$^{-1}$, respectively\cite{80}. The relative ratio of these contributions are dependent on the processing conditions as well as regioregularity of the P3HT\cite{81}. Tsoi *et al.* \cite{80} have carried out detailed analysis of regioregular and regiorandom P3HT, and found high degree of ordered components (1450 cm$^{-1}$) in case of regioregular P3HT having FWHM $\sim$31 cm$^{-1}$. In our case, both P3HT and P3HT:PCBM blend already have significant ordered structure as indicated by relatively narrow FWHM $\sim$26 cm$^{-1}$ of C=C peak. Such differences in the films may arise because of differences is the sample preparation. In our case, high molecular weight P3HT was used and the cast films were left overnight in the glove box. The slow evaporation of the solvent may lead to slightly high molecular ordering in P3HT films than reported by Gao *et al.*\cite{81}. Because of relatively low concentration of amorphous region, the deconvolution of C=C Raman peak does not
provide two Lorentzian curve fitting. Therefore, we have extracted FWHM from the fitted single Lorentzian curve to the C=C Raman mode. When the temperature is raised to 180°C, contributions from the amorphous region (1470 cm\(^{-1}\) peak) is increased, which intrinsically have broader linewidths. This lead to broader FWHM~35 cm\(^{-1}\) owing to linear dependence of the spontaneous Raman scattering on the concentration of scatterers. As temperature decreases, P3HT chains re-assemble into aggregates causing an increase of the crystalline component. The slight blue shift in C=C Raman mode on heating suggest molecular disorder in P3HT which in present case is induced by thermal annealing. During cooling, a red shift in this mode occurs, suggesting that during cooling the P3HT undergoes molecular ordering.

**Figure 3.5:** (a) and (b) are the variation of full-width-half-maximum (FWHM) of symmetric C=C stretching mode for P3HT and P3HT:PCBM films, respectively during heating and cooling cycles upto annealing temperature of 180°C. (c) and (d) are the variation of the C=C/C–C intensity ratios for P3HT and P3HT:PCBM films, respectively during heating and cooling cycles of annealing temperature upto 130°C.
The molecular ordering of P3HT was further supported by the data on full-width half-maximum (FWHM) of symmetric C=C stretching mode (1449 cm\(^{-1}\)) and C=C/C-C intensity ratio \((I_{\text{C=C}}/I_{\text{C-C}})\). The variation of FWHM and \(I_{\text{C=C}}/I_{\text{C-C}}\) (extracted by fitting the data with Lorentzian) as a function of heating as well cooling cycles for P3HT and P3HT:PCBM films (annealed upto a maximum temperature of 130°C) are plotted in Fig. 3.5. The major inference drawn from these results are as follows.

(i) It is well established that smaller values of FWHM is indicative of improved ordering of P3HT chains. As shown in Fig. 3.5 (a) and (b), the lower FWHM value of as-deposited P3HT film (cm\(^{-1}\)) as compared to that of P3HT:PCBM film, suggests that the inclusion of PCBM hampers the ordering of P3HT\([84]\). In both the case, during heating the FWHM increases, which is expected owing to the thermal induced disordering of P3HT chains. On the other hand, during cooling cycle the FWHM decreases sharply at \(~100^\circ C\), indicating thermally induced H-aggregation (or \(\pi\)-stacking) of polymer chains. After annealing, the FWHM’s at room temperature are lower as compared to pre-annealed films, suggesting that the molecular ordering is frozen in the films.

(ii) The intensity of C-C intra-ring stretch mode relative to C=C Raman mode is sensitive to the conjugate backbone planarity of the P3HT. Based on the simulated C=C and C-C Raman modes in oligothiophene, Tsoi et al. [80] have suggested that planarity of the P3HT chains is higher for higher relative intensity of C-C mode and vice versa. This might be because of better electron-phonon coupling of C-C mode and/or increased charge transfer from C=C bonds. More planar backbone conformation favors the \(\pi\)-stacking of the polymer chains and therefore, results in
more molecular ordering. Fig. 3.5 (c) & (d) clearly shows that $I_{C-C}/I_{C=C}$ ratio increases with temperature during heating cycles, which indicates an increase in disorder in the films that is in agreement with the FWHM measurements. A lower value of $I_{C-C}/I_{C-C}$ after completion of the cooling cycle also supports the fact that annealing enhances the molecular ordering owing to an increase of π electron density in C-C bonds resulting from an increase in planarity of P3HT chains[81].

In order to find out how the film morphology evolves as a function of annealing temperature, we have carried out in-situ optical imaging during heating as well as cooling cycles of the annealing. Typical optical images for the films subjected to the annealing of 130 and 180°C are shown in Fig. 3.6. As shown in Fig. 3.6 (a1-a3), the morphology of the films remains uniform when heated upto 130°C and subsequently cooled down to room temperature. However, this situation is not the same when the films are annealed upto 180°C, as shown in Fig. 3.6(b1-b3). It is seen that at 180°C large aggregate of size 2-4 µm forms at the surface, which remains there on the surface even after cooling. This result suggests that a phase segregation occurs when films are annealed to temperatures >130°C [85]. Similar results of P3HT:PCBM blends were observed by Yang et al. [86] and Hoppe et al. [87]. Using transmission electron microscopy (TEM) and SEM results, they have shown that thermal annealing leads to the crystallization of P3HT chains via stacked coplanar conjugated segments and dispersion of PCBM molecules forming large aggregates. A detailed study of the thermal annealing effect on PCBM aggregation was reported by Kiel et al. [88]. On the basis of their neutron reflectivity results, they showed
that upon annealing the PCBM concentration is increased at the sample-air interface and a little change at the buried interface of substrate and blend.

![micrographs](image)

**Figure 3.6:** Real time optical micrographs of P3HT:PCBM films at different temperatures (a1) room temperature, (a2) at 130°C after 30 min of annealing, and (a3) at 25°C after cooling from 130°C. (b1) morphology at 180°C after 30 min of annealing, (b2) morphology at 25°C after cooling from 180°C, and (b3) magnified version of b2 image.

### 3.1.3 Ex-situ Raman and UV-Vis spectroscopy

As discussed above, the *in-situ* Raman spectroscopic and optical microscopic studies clearly show that when P3HT and P3HT:PCBM films are annealed to 130°C, the disorder nature increases in the films due to thermal energy, while molecular ordering of P3HT chains takes place during the cooling cycle. In order to investigate the role of maximum annealing temperature, the Raman spectra were recorded at room temperature after subjecting them to various annealing temperatures i.e. 110, 130, 150, and 180°C. Fig. 3.7(a) shows the recorded Raman spectra in the C=C stretching mode region of
P3HT:PCBM films. The calculated FWHM values as a function of annealing temperature are plotted in Fig. 3.7(b). It is seen that the FWHM decreases with increasing annealing temperature and attains a minimum of 28.9 cm\(^{-1}\) at 130°C, and beyond that the FWHM starts increasing. This clearly indicates that the maximum molecular ordering of P3HT in P3HT:PCBM is attained when the films are annealed to 130°C.

Figure 3.7: (a) Room temperature Raman spectra (in the range of symmetric C=\(C\) stretching mode) of P3HT:PCBM films recorded after annealing them at different temperatures. (b) Variation of corresponding FWHM's of symmetric C=\(C\) stretching mode as a function of annealing temperature.

In order to further confirm our data, we recorded UV/Vis spectra of the films annealed at different temperatures, which are shown in Fig. 3.8 and also provide a clue on the aggregation of PCBM and crystallization of P3HT. For as-deposited films, the peaks at 485 nm correspond to that of \(\pi-\pi^*\) (\(S_0 \rightarrow S_1\)) transition of P3HT chains. On the other hand, 551 and 602 nm peaks are indicative of the inter-chain ordering and intra-chain ordering respectively. This may arise because of increase in conjugation within the polymer chains and the \(\pi-\pi\) stacking. Well-defined peaks for inter-chain ordering and intra-chain ordering in our as-cast films suggest that significant molecular ordering already exist in as-cast films as corroborated by Raman spectrum. In addition to P3HT peaks, a peak at 380 nm
corresponding to the PCBM is also observed. As the films are annealed to temperatures \( \geq 130^\circ C \), the \( \pi-\pi^* \) transition peak exhibits a strong red-shift from 485 to 517 nm, which has been attributed to the crystallization of P3HT \([40, 89]\). Similarly, increase in relative intensity of 551 nm peak on annealing suggests that the inter-chain ordering of P3HT has improved \([84]\). In addition to this, the intensity peak of PCBM decreases at 180°C, which has been attributed to the aggregation of PCBM.

Figure 3.8: UV–Vis spectra of P3HT:PCBM films as-cast, and annealed at 130–180°C for 30min.

In order to further investigate the phase segregation in P3HT:PCBM films, we have carried out AFM and SEM studies on the films annealed at different temperatures. Typical AFM images of the bare ITO substrate, as-deposited P3HT:PCBM film, films annealed to different temperatures are shown in Fig. 3.9 (a-f). The AFM images were analyzed and the rms roughness was measured. The obtained results are plotted in Fig. 3.9(g). It is evident that the bare ITO substrate has an rms roughness of 3nm, whereas the as-deposited
P3HT:PCBM film has a reduced rms value of 0.5 nm, indicating a very high uniformity of the film. The film roughness increases marginally up to 1.3 nm after annealing at 130°C. However, for higher annealing temperature, the roughness increases rapidly, which is a consequence of phase segregation (as revealed by AFM image as well as by in-situ optical micrographs. The size of these aggregates is in the range of 2-5 μm with an average height of 250 nm. Similar images were reported in literature by scanning of near-field microscopy (SNOM) and AFM[90].

Figure 3.9: 5 μm × 5 μm AFM images of (a) bare ITO substrate, (b) as-cast P3HT:PCBM film, (c)–(f) are after annealing at 110, 130, 150 and 180°C, respectively. (g) RMS roughness of the films as a function of annealing temperature (inset shows the magnified version of the selective area).
Figure 3.10: (a) and (b) are the SEM images of the P3HT:PCBM films annealed at 130 and 180°C, respectively. (c) and (d) are the carbon X-ray counts across the lines drawn in (a) and (b) respectively.

In order to investigate the composition of the aggregates observed in the P3HT:PCBM films, we have carried out the carbon X-ray elemental imaging of the SEM micrographs for the films annealed at 130 and 180°C. The obtained results are shown in Fig. 3.10. The SEM image of the films annealed at 130°C is featureless and the carbon X-ray imaging is very uniform. This result indicates that the P3HT and PCBM are uniformly distributed. However, for films annealed at 180°C, the SEM image shows aggregates (in
agreement with AFM image shown in Fig. 3.9). The line profile of carbon X-ray imaging across the two such aggregates indicates that they are rich in carbon, suggesting that the aggregates are composed of PCBM because the intense carbon counts are due to presence of C\textsubscript{70}.

3.1.4 Correlation between morphology evolution and photovoltaic parameters

Based on the analyses of in-situ Raman spectra and optical imaging, ex-situ AFM, SEM and UV/Vis results, we envisage a schematic representation of the annealing induced morphological evolution of P3HT:PCBM films, as depicted in Fig. 3.11. In the as-deposited P3HT:PCBM films, both P3HT and PCBM have disordered structure and uniformly distributed across the film. As the temperature is increased to 130°C, P3HT undergoes molecular ordering (i.e. inter-chain and intra-chain ordering) without any phase segregation (i.e. PCBM remains uniformly distributed). Therefore, the Raman intensity corresponding to the PCBM molecules is very low in pristine as well as annealed (~130°C) films. However, as the annealing temperature is raised to 180°C, the segregation of PCBM molecules from the P3HT matrix takes place to form large PCBM aggregates of size 2-4 µm as reflected in our in-situ Raman spectroscopic and optical microscopic images. This induces the phase separation of PCBM from the P3HT matrix and thereby, restrict homogeneous P3HT:PCBM blend. Therefore, in homogeneous region more P3HT chains tend to crystallize (or order), resulting in stronger Raman signals for C=C peaks. The Raman signals, on the other hand, on PCBM aggregates are higher than those observed at the homogeneous part owing to linear relationship between Raman scattering and
concentration of scatterers. This aggregation of the PCBM at the active layer surface may have significant effect on the photovoltaic properties.

![Figure 3.11: (a–c) Schematic depiction of morphology evolution in P3HT:PCBM films as a function of temperature. Typical selective area Raman spectrum in each case is also presented.](image)

Now we discuss the correlation between the photovoltaic parameters (shown in Fig. 3.2) and the morphology of the films, shown in Fig. 3.11 (a-c), which were annealed at different temperatures. The value of $V_{oc}$ (~0.5 V) almost remains independent of the annealing temperature up to 130°C. This is expected because $V_{oc}$ is a measure of the difference between HOMO of donor and LUMO of acceptor, which is not very much affected by the annealing. However, a slight decrease in the $V_{oc}$ is observed, when the annealing temperature is increased beyond 130°C. This is attributed to the significant segregation of PCBM at the sample surface as reflected in the in-situ Raman spectroscopy and optical microscopy. The $J_{sc}$ and $FF$ on the other hand, increases significantly up to an
annealing temperature of 130°C, and then reduce for higher annealing temperature. As schematically presented in Fig. 3.11(d), in as-cast blend films, P3HT can have twisted polymer chains, which can cause a disorder, and as a result, a reduced $J_{sc}$ and $FF$. When the blend films are cooled after annealing at 130°C, during cooling the P3HT chains can get planar, as shown in Fig 3.11(e), which can then induce molecular ordering via $\pi-\pi$ stacking (i.e. H-aggregation), which is supported by a decrease in $I_{C=C}/I_{C-C}$ ratio in in-situ Raman data. This enhanced molecular ordering is responsible for maximum FF and $J_{sc}$ owing to the reduced transport resistance within the blend film. However, when the temperature is increased beyond 130°C, a decrease in the $J_{sc}$ and FF is observed. This decrease $J_{sc}$ and FF is attributed to following facts:

(i) Increase in the annealing temperature higher than 130°C results in growth of molecular ordered P3HT domains which is bigger than the exciton diffusion length within the blend, as indicated by increase in the C=C Raman intensity and shown schematically in Fig. 3.11(c). This, in turn limits, the transport of free electrons and holes towards electrodes upon exciton dissociation

(ii) The PCBM molecules diffuse out of the blend towards sample-air surface, forming large aggregates, in agreement with increase in surface roughness deduced from AFM images, in-situ optical images as well as increased intensity of Raman $A_{1}$ mode of PCBM. In spite of increased ordering of P3HT molecules beyond 130°C, the interfacial area between P3HT and PCBM in the blend films reduces significantly owing to the diffusion of PCBM molecules towards the sample-air surface. The reduced interfacial area in the blend films then results in the reduction of $J_{sc}$. The increased aggregation of the PCBM at
the sample-air interface also damages the metal electrode as shown by Chirvase et al. [91] which leads to poor contact between the active layer (i.e. P3HT:PCBM blend) and the cathode, resulting in decrease in FF.

3.1.5 Correlation between materials parameters and device parameters

As discussed in the previous section the material properties, such as morphology, crystallinity etc. govern the efficiency of the device. Also, as seen from Table 3.1, the device parameters \( (n, I_0, R_s, R_{sh}, \text{ and } I_{ph}) \) are intimately correlated with annealing temperature of the device. It was observed that the values of \( n, I_0, R_s \) initially decreases with annealing temperature upto 130ºC and thereafter increases upon further increase in annealing temperature. On the other hand, \( I_{ph} \) increases upto 130ºC, which however decreases upon increasing the annealing temperature. The lowering of \( n, I_0, R_s \) values and increase in \( I_{ph} \) for device annealed at 130ºC can be attributed to the enhanced ordering or crystallinity of P3HT chains, leading to an improved charge transport. However, at lower and higher annealing temperatures these parameters deteriorate owing to the respectively poor ordering and formation of large PCBM aggregates.

Ideality factor of the device provides an indication on the overall quality of the device, as it describes how closely the \( J-V \) curve follows the theoretical model. Essentially, ideality factor provides an important information on the transport and recombination processes in solar cells. The value of \( n \) changes depending on the type of carrier recombination present in the device. A band-to-band or Schottky contact recombination gives \( n = 1 \) (close to the ideal diode), while \( n = 2 \) may attribute to Shockley-
Read-Hall (SRH) recombination traps, and an intermediate ideality factor (between 1 and 2) would attribute to the presence of a distribution of localized states (traps) [92]. Hence, the ideality factor may reflect more than one recombination mechanism, and the dominant mechanism may depend on the specific material and device condition. As shown in Table 3.1, $n=1.55$ has been obtained for the device annealed at 130°C, whereas for all the other device higher $n$ values have been obtained. As described earlier, device annealed at 130°C has the best ordering/crystallinity among all the devices, and therefore, are expected to have minimum localized states, leading to minimum recombination. For all other devices, the localized states are higher due to the disorder in the system, and therefore, higher $n$ values are obtained.

### 3.2 Porphyrin/polyfullerene diffuse bilayer solar cells

In this Section, we present the results on porphyrin/diffuse bilayer solar cells. As discussed in Chapter 1, in diffuse bilayer solar cells, the donor and acceptor layers interpenetrate. The diffused interface results in high interfacial area and improved charge transport, and therefore, are potential candidate for further investigation. The fabrication process of porphyrin-polyfullerene diffuse bilayer solar cells is described in Chapter 2, which is based on a sequential electrodeposition of porphyrin and polyfullerene films. Porphyrin-polyfullerene are selected because porphyrin is strongly light absorbing chromophores and fullerene has high electron affinity. Before we present the photovoltaic characteristics of diffuse bilayer solar cell, we discuss the results on the optimization of the electrodeposition of individual porphyrin and polyfullerene layers.
3.2.1 Electrodeposition of porphyrin films

As discussed in Section 2.2.2, the porphyrin films were deposited on ITO substrates by electrodeposition[93, 94]. Fig. 3.12 shows the typical cyclic voltammograms of first 5 scans recorded between 0 and 1 V at a scan rate of 50 mVs$^{-1}$. It is evident from the figure that porphyrin undergoes an electrochemical oxidation at a potential ($E_{ox}$) of ~0.4 V. This peak is irreversible, which indicates that the molecule is covalently grafted to the working ITO electrode. The intensity of this peak decreases monotonically and vanishes after 5 scans, indicating a complete coverage of the molecules onto ITO substrate.

![Cyclic voltammograms of electrodeposition of porphyrin on ITO substrates](image)

**Figure 3.12:** First 5 cyclic voltammograms of electrodeposition of porphyrin on ITO substrates.

**Characterization of electrodeposited porphyrin films**

Typical UV-Vis spectra of the electrodeposited porphyrin films on ITO substrates after different scans (recorded at scan rate 50 mV/s) are shown in Fig. 3.13 (a). In the inset, we show the absorption spectra of porphyrin monomer in methanol. The absorption spectrum of porphyrin monomer in methanol solution has a strong Soret band at 417 nm.
and four weak Q bands at 515, 553, 592, and 650 nm [95-97]. The absorption spectrum of the porphyrin films is shown in Fig. 3.13 (a), which is broader as compared to that of monomer in solution. This indicates that the porphyrin molecules do not decompose during electrodeposition. The Soret band is broadened and red-shifted from 417 nm (for porphyrin in methanol) to 432 nm (for the electrodeposited film), which is consistent with excitonic interactions between densely packed porphyrins owing to the J-type aggregation. This result suggests that electrodeposited porphyrin films are well packed. The absorbance of the Soret band increases with increasing number of scans, which indicates that the thickness of the film is increasing. The typical thickness of the films after 10 and 75 scans measured using profilometer was respectively 20±3nm and 75±3nm.

**Figure 3.13**: UV-Vis spectra of (a) porphyrin films deposited on ITO substrates after different number of scans and (b) porphyrin monomer in methanol.
The typical SEM images of the electrodeposited porphyrin films deposited for different number of scans are shown in Fig. 3.14. It is seen that up to 5 scans, a uniform porphyrin film is deposited onto the ITO substrate. However, at higher scans, the multilayers grow that has a random granular interpenetrated network, leading to a morphology similar to gyroid structure. Typical AFM image of porphyrin film electrodeposited for 5 scans is shown in Fig. 3.15. The height profile analysis show that the film has a rms roughness of ~7 nm for 2µm x 2µm area. The morphology consists of elongated grains, which is consistent with UV/Vis data that porphyrin molecules arrange in the form of J-aggregate. This type of morphology is appropriate for the fabrication of diffuse bilayer solar cells.
Figure 3.15: AFM image of porphyrin film deposited for 3 CV scans, a height profile showing formation of granular morphology.

Figure 3.16: The Raman spectra of (a) electrodeposited porphyrin film and (b) drop-casted porphyrin film.

The Raman spectrum of an electrodeposited porphyrin film is shown in Fig. 3.16(a). For comparison the Raman spectrum of the drop-casted film of porphyrin monomer is shown in Fig. 3.16(b). It is seen that the characteristics bands at 1375 cm\(^{-1}\), 1477 cm\(^{-1}\), 1536 cm\(^{-1}\), 1603 cm\(^{-1}\) of porphyrin film are similar to that observed for the
drop-cast porphyrin film i.e. 1378 cm$^{-1}$, 1471 cm$^{-1}$, 1538 cm$^{-1}$, 1594 cm$^{-1}$[97]. The shifts in the electrodeposited films can be attributed to the J-aggregation of porphyrin molecules.

### 3.2.2 Electrodeposition of polyfullerene films

As discussed in Chapter 2, the polyfullerene films were deposited onto ITO in two steps: (i) preparation of C$_{60}^{2-}$ solution in dichloromethane (DCM) by electroreduction method, and (ii) electrodeposition of polyfullerene films on ITO by oxidation of C$_{60}^{2-}$ using linear sweep voltammetry (LSV)[98].

First we describe the method for the preparation of a homogeneous C$_{60}^{2-}$ solution by electroreduction process. It may be noted that the electrochemistry of C$_{60}$ normally exhibits three to six chemically-reversible one-electron reductions corresponding to the C$_{60}^{0/1-}$, C$_{60}^{1-/-2}$, C$_{60}^{2-/-3}$, C$_{60}^{3-/-4}$, C$_{60}^{4-/-5}$, and C$_{60}^{5-/-6}$ couples in which the three-fold degenerate lowest unoccupied molecular orbital (LUMO) of C$_{60}$ is populated[99-101]. By contrast, the oxidation of C$_{60}$ is generally irreversible in most solvents, which is attributed to the C$_{60}$/solvent interactions i.e. hydrogen bonding and electrostatic interactions[102]. Experimental and theoretical studies show that among various C$_{60}$ species, C$_{60}^{2-}$ is most stable, and therefore, has widely been used in different reactions[100]. Fig. 3.17(a) shows the CV recorded for C$_{60}$ in DCM and TBAP as electrolyte and Pt foil as working electrode. The CV exhibits two reduction peaks at −0.66 and −1.14 V, corresponding to C$_{60}^{-}$ and C$_{60}^{2-}$, respectively. Similar to the reported literature[102], we do not find the oxidation peaks possibly due to the C$_{60}$/DCM or TBAP interactions. However, some fraction of oxidized C$_{60}^{1-}$ and C$_{60}$ are inevitable. Therefore, in order to obtain a solution of C$_{60}^{2-}$, a potential of −1.5 V was applied until the violet colour (characteristic of C$_{60}$ solution)
turned into light brown colour (characteristic of dianion C\textsubscript{60} solution[103]), as shown in the inset of Fig. 3.17(b). The UV-Vis spectra of C\textsubscript{60} solution recorded before and after electroreduction processes are shown in Fig. 3.17(b). Presence of a characteristics peak at 975 nm confirms the formation of C\textsubscript{60}\textsuperscript{2−} after electroreduction[104]. It was found that the C\textsubscript{60}\textsuperscript{2−} solution remains stable for several hours under inert atmosphere. Once a C\textsubscript{60}\textsuperscript{2−} solution in DCM is formed, which also consists of TBAP electrolyte, the Pt foil working electrode was replaced by ITO substrate.

**Figure 3.17:** (a) Cyclic voltammogram recorded for C\textsubscript{60} solution prepared in DCM and TBAP as a supporting electrolyte. (b) UV-Vis spectra recorded for C\textsubscript{60} and C\textsubscript{60}\textsuperscript{2−} solutions. Inset shows photographs of C\textsubscript{60} (violet) and C\textsubscript{60}\textsuperscript{2−} (light brown) solutions.

The electrodeposition of C\textsubscript{60} on ITO was carried out by oxidizing C\textsubscript{60}\textsuperscript{2−} in two modes: (i) by applying a constant potential and (ii) by linear sweeping of potential from −1 to 0 V. The first mode did not yield good films, whereas LSV resulted in uniform C\textsubscript{60} films. Typical LSV curves recorded for different number of scans are shown in the Fig. 3.18(a). In these curves, two peaks at −0.65 (I) and −0.83 (II) are identified. The peak I is identified as the first oxidation peak i.e. conversion of C\textsubscript{60}\textsuperscript{2−} into C\textsubscript{60}−, whereas the peak II corresponds to second one electron oxidation i.e. conversion of C\textsubscript{60}− into neutral C\textsubscript{60}. As
the numbers of LSV scans were increased, an increasing film thickness was visibly observed. The mechanism underlying the growth of C\textsubscript{60} films on ITO is not very clear. However, as we demonstrate latter that the HRTEM images show formation of a series of 1-dimensional (1D) “pearl-chain” structures, indicating the presence of covalent cross-linking bonds. This prompted speculation that polymerization had occurred between C\textsubscript{60} molecules via [2+2] cycloaddition reaction, as schematically shown in Fig. 3.18(b). Since the current studies were carried out under inert atmosphere, therefore oxygen anion induced polymerization, as reported in the literature\[105\], is ruled out. In the present case, oxidation of C\textsubscript{60}\textsuperscript{2−} takes place at ITO substrate, leading to the formation of C\textsubscript{60}\textsuperscript{−} and neutral C\textsubscript{60}. It is therefore anticipated that C\textsubscript{60}\textsuperscript{−} ions induce [2+2] cycloaddition re-actions at room temperature, leading to the formation of dimers and 1D polymer chain. Such cycloaddition reaction between neutral C\textsubscript{60} and C\textsubscript{60}\textsuperscript{−1} has previously been reported for polymerized LiC\textsubscript{60} film\[106\]. The mechanism proposed above also explains why good films are not obtained under the constant potential mode. This is because under this mode, it is not possible to obtain both C\textsubscript{60} and C\textsubscript{60}\textsuperscript{−1} species required for the cycloaddition reaction.

**Figure 3.18:** (a) Typical linear sweep voltammograms (LSV) recorded using ITO as working electrode and C\textsubscript{60}\textsuperscript{2+} + TBAP solution after different numbers of scans. Peaks (I) and (II) correspond to C\textsubscript{60}\textsuperscript{2−} to C\textsubscript{60}\textsuperscript{−} and C\textsubscript{60}\textsuperscript{−} to C\textsubscript{60} oxidations, respectively, which occur at ITO surface. (b) Schematic of the proposed pathways of polymerization of C\textsubscript{60}. 

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Characterization of poly-fullerene films

First we confirm the formation of polyfullerene films on ITO substrates using the results of electrochemical characterization, FTIR and UV/Vis measurements. A unique advantage of electrochemical process is that it can be used for the film deposition as well as its characterization. Typical cyclic voltammetry curve, which was recorded using “films deposited on ITO” (deposited for 200 LSV scans) as working-electrode and pure TBAP as electrolyte, is shown in Fig. 3.19(a). It is apparent that the film undergoes a reduction at $-0.55 \text{ V}$, which is slightly lower than that of $C_{60}$ monomer in the solution (see Fig. 3.19(a)). This characteristics reduction peak indicates presence of polymerized $C_{60}$ in the films. Fig. 3.19(b) shows the FTIR spectra recorded for the polyfullerene films deposited for 200 LSV scans. Presence of peaks at 527, 548, 554, 576, 606, 721, 753, 1091, 1122, 1171, 1287, 1336 and 1423 cm$^{-1}$ confirms the presence of polymeric $C_{60}$ [107, 108]. The four IR modes observed for $C_{60}$ monomer at 527, 576, 1182, 1429 cm$^{-1}$ are also observed in the films. However, these peaks were found to be quite broad and their relative intensities were quite different, indicating that vibrational modes found in $C_{60}$ are also active in polyfullerene and that there are different degrees of shifts in the IR peaks upon the cycloaddition of $C_{60}$ cages. The polyfullerene films have many more IR-active modes than $C_{60}$, which is attributed to the lowering of molecular symmetry upon the polymerization of $C_{60}$[109].
Figure 3.19: (a) Cyclic voltammogram recorded using electrodeposited polyfullerene film as working electrode and 0.1 M TBAP as electrolyte. (b) Typical FTIR spectrum of polyfullerene film in the wavenumber range 500 – 800 cm\(^{-1}\). Inset shows the FTIR spectrum in the range 800–1500 cm\(^{-1}\).

Figure 3.20: (a) Typical UV-Vis spectra recorded for C60 solution (i) and electrodeposited polyfullerene films on ITO after different numbers of LSV scans: (ii) 50, (iii) 100, (iv) 150, (v) 200 and (vi) 300. (b) Energy band gap of polyfullerene films as a function on numbers of LSV scans used for deposition. Inset shows a typical Tauc plot used for determination of band gap.

The UV/Vis spectra recorded for films deposited using different numbers of LSV scans are shown in Fig. 3.20(a). It is seen that for C\textsubscript{60} solution (prepared in DCM) a sharp absorption peak is observed at 329 nm. However, this peak broadens for polyfullerene
films deposited using increasing numbers of LSV scan. In polyfullerene, C₆₀ loses its symmetry and consequently degeneracy of energy levels is lifted up, resulting in broadening of the absorption peak[104]. Fig. 3.20(b) shows the optical energy band gap of the films plotted against the number of LSV scans used for their preparation. The energy gap values were deduced as the energy ($h\nu$)-axis intersections of the linear extrapolations of $(\alpha h\nu)\frac{1}{2}$ versus $h\nu$ plots, known as Tauc plot. A typical Tauc plot for polyfullerene film electrodeposited for 300 LSV scans is shown in the inset of Fig. 3.20(b). The value of band gap for films prepared using 50 LSV scans is 2.6 eV, which is similar to that evaluated for vacuum evaporated C₆₀ films as well as the values determined for C₆₀ single crystals using photoemission and inverse photoemission experiments[110]. The value of band gap monotonically reduced for the films prepared using increased numbers of LSV scans, and a value of 1.78 eV was deduced for the film prepared using 300 scans, indicating polymerization of C₆₀ leading to long polyfullerene chains.

Figure 3.21: SEM images of bare ITO surface (a), and polyfullerene films deposited after 50 (b) and 100 (c) LSV scans.

Finally, we discuss morphology evolution of the polyfullerene films as a function of number of LSV scans. Fig. 3.21 shows typical SEM images of the bare ITO-coated
glass substrates, (see Fig. 3.21(a)) and electrodeposited polyfullerene films after different numbers of LSV scans (Figs. 3.21(b) and 3.21(c)). It is evident that as polyfullerene grows on ITO in the form of globular islands. As the numbers of LSV scans are increased, the size as well as density of polyfullerene globular increases and a dense polyfullerene film covering entire ITO substrate is formed after 100 LSV scans. This has been independently confirmed by AFM images, as shown in Fig. 3.22. The analysis of the height profile of the AFM image show that the polyfullerene grain size is \( \sim 0.3 \mu \text{m} \) dia., whereas the average surface roughness is only \( \sim 56 \text{ nm} \). A very small surface roughness and absence of pinholes confirm deposition of uniform high-quality films. Further confirmation on the uniformity of the films was obtained by Kelvin probe microscopy. The scanning work function plots for bare ITO and polyfullerene films (deposited for 50, 100, and 200 LSV scans), measured in the area of 15 mm \( \times \) 15 mm, are shown in Fig. 3.23. The 2D work function of ITO has been modified from 5.01 eV to 4.7 eV after deposition of polyfullerene. The 2D work function plots measured for polyfullerene films deposited at various scans 50, 100, and 200 LSV scan show \( \sim 4.78 \text{ eV} \), indicating a uniform film deposited on ITO substrates. In addition, it was confirmed again by measuring the work function at the interface of the ITO and polyfullerene films (as shown in Fig. 3.24). A clear distinction of work functions from 5.1 eV to 4.7 eV is clearly observed. Also, a 3D work function plot of an interface is shown in Fig. 3.24(b) for reference. In literature, the work function for polymerized \( \text{C}_{60} \) has been measured using ultra-violet photoelectron spectroscopy and was found to be 4.7 eV[111]. Therefore, the average work function of 4.76 eV measured using Kelvin probe microscopy is in agreement with literature value.
Interestingly, as shown in Fig. 3.25, as the numbers of LSV scans are further increased, formation of second polyfullerene layer on top of the first layer was found to grow. However, the second layer grows in the form of small chains, which possibly occurs due to the fusion of C_{60} globules; see Fig. 3.25. These small chains grow in the form of long whiskers with increasing numbers of LSV scans. At 300 LSV scans, a network of polyfullerene whiskers was found to grow, see Fig. 3.25(b). The length and diameter of these whiskers were found to be in the ranges of 100–200 µm and 0.1–0.4 µm, respectively. The magnified SEM images shown in Fig. 3.25(c), clearly indicate that the whiskers are continuous and formed due to the fusion of C_{60} globules. These whiskers could be easily transferred (by mechanically scrubbing) onto the carbon grid for HRTEM measurements.

Figure 3.22: AFM image of polyfullerene films deposited after 100 LSV scans.
**Figure 3.23:** Workfunction mappings of (a) ITO substrate; (b) electrodeposited polyfullerene on ITO substrates for 200 LSV scans.

**Figure 3.24:** (a) Work function mapping of ITO-C$_{60}$ interface (Blue indicates C$_{60}$ region, Red indicates ITO region); (b) 3D work function mapping of ITO-C$_{60}$ interface
A typical HRTEM image of the polyfullerene whisker, isolated from substrate is shown in Fig. 3.26. It may be noted that identical images were obtained for the first polyfullerene layer, indicating that the nucleation and growth mechanism is identical for first and subsequent layers. It is evident that C\textsubscript{60} are polymerized in the 1-dimensional “pearl-structure,” which confirms our preposition that polymerization is based on [2+2] cycloaddition mechanism. The C\textsubscript{60}–C\textsubscript{60} periodicity along the chain is found to be 1.02 nm, whereas the inter-chain distance was found to be around 0.87 nm. In literature, the theoretical calculations based on total-energy pseudo-potential density functional theory showed that a fully polymerized C\textsubscript{60} chain is more stable than nonpolymerized C\textsubscript{60} [112].

**Figure 3.25**: SEM images of (a) polyfullerene films deposited on ITO substrate for (a) 200 LSV scans, (b) 300 LSV scans, and (c) magnified view of single polyfullerene nano whisker.
Assuming [2+2] cycloaddition as the preferred linking mechanism, in the equilibrium structure of the polymer chain the center to-center distance between two adjacent molecules was predicted to in the range of 0.97–0.84 and the structure is expected to be a cylindrically symmetrical ellipsoid with eccentricity 0.933. The reduction in the number of double bonds following [2+2] cycloaddition reduces the strain energy in the C$_{60}$ structure, allowing molecules to elongate in directions parallel to the new cross-links. However, the lateral bonding between individual 1D pearl-chain is assumed to be through Van der Waals interactions, as no indication of chemical bonding was observed in other directions. It may be noted that there are few reports in literature on the assembly of 1D molecular chains of C$_{60}$ with long-range ordering[113]. However, they were fabricated using α-sexithiophene (6T) monolayer nanostripes on Ag (111) surface. Highly ordered arrays of 1D molecular systems represent prototypes for 2D or 1D quantum confinement of surface electronic states and are of technological importance in the realization of molecular nanodevices[114].

Figure 3.26: HREM micrographs of C$_{60}$ on ITO (300 scan) showing avg. roughness of 30nm, The C$_{60}$ – C$_{60}$ periodicity along the chain is 10Å$^\circ$-11Å$^\circ$ and the interchain distance observed is around 8 Å$^\circ$ – 9Å$^\circ$. 
3.2.3 Photovoltaic characteristics of porphyrin/polyfullerene diffuse bilayer solar cells

The energy level diagram of the bilayer device ITO/PEDOT:PSS/porphyrin/polyfullerene/Al is shown in Fig. 3.27(a). Theoretically a maximum $V_{oc}$ of $\sim$1.5V can be generated using this device. The energetics of porphyrin and polyfullerene clearly indicates a facile charge transport of photogenerated carriers through donor and acceptor materials towards respective electrodes. The fabrication process of such a bilayer solar cells is described in Section 2.2.2, for which first a porphyrin layer was electrodeposited onto PEDOT:PSS coated ITO substrate and followed by electrodeposition of poly-fullerene layer.

The UV-Vis spectra of porphyrin/polyfullerene bilayer films are shown in Fig. 3.27(b), which is typically superimposition of porphyrin (431nm) and polyfullerene (325nm) individual films. The results show that in the bilayer heterojunction porphyrin and polyfullerene do not react.

![Energy level diagram and UV-Vis spectra](image)

**Figure 3.27:** (a) Energy level diagram of porphyrin-polyfullerene bilayer solar cell, (b) UV-Vis spectra showing absorbance of porphyrin, polyfullerene, and porphyrin/polyfullerene bilayer.
For photovoltaic characterization, several bilayer devices were fabricated by varying the thicknesses of porphyrin and polyfullerene films. The devices fabricated using thicknesses <25 nm were found to be short-circuited, possibly due to the penetration of top Al electrode. On the other hand, devices fabricated using thicker (>100 nm) porphyrin and/or polyfullerene layer didn’t show any photoresponse characteristics, which is attributed to poor charge collection properties as the generated charge carriers may get recombine before reaching to the respective electrodes.

![Figure 3.28: J-V characteristics of (a) porphyrin/fullerene bilayer solar and (b) porphyrin/PCBM bilayer solar cells under 5 mW/cm² white light illumination.](image)

**Table 3.2:** Solar cell parameters evaluated from current-voltage characteristics presented in Fig. 3.28.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{sc}$ ($\mu$A/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$n$</th>
<th>$R_s$ (k$\Omega$–cm²)</th>
<th>$R_{sh}$ (k$\Omega$–cm²)</th>
<th>$I_0$ (nA/cm²)</th>
<th>$I_{ph}$ ($\mu$A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porphyrin/fullerene</td>
<td>6.5</td>
<td>0.15</td>
<td>0.25</td>
<td>0.005</td>
<td>&gt;3.5</td>
<td>&gt;15</td>
<td>&gt;15</td>
<td>&gt;5000</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Porphyrin/PCBM</td>
<td>4.2</td>
<td>0.18</td>
<td>0.25</td>
<td>0.004</td>
<td>&gt;3.5</td>
<td>&gt;15</td>
<td>&gt;15</td>
<td>&gt;5000</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>
Typical $J-V$ characteristic of diffuse bilayer solar cells fabricated using porphyrin and polyfullerene layer thickness of ~50 nm each is shown in Fig. 3.28 (a). For comparison, $J-V$ characteristic of bilayer solar cells fabricated by spin-coating PCBM solution on electrodeposited porphyrin is shown in Fig. 3.28(b). The diffuse bilayer devices with polyfullerene and PCBM exhibits similar device characteristics, the photovoltaic parameters are shown in Table 3.2. The device exhibited $J_{sc}$ of 2-7 µA/cm$^2$ and $V_{oc}$ of ~180-200 mV with power conversion efficiency ~0.002-0.005% under white light illumination of 5 mW/cm$^2$. The $V_{oc}$ of these solar cell is quite low as compared to the theoretical value of 1.5 V. Despite of low efficiency, our results are quite encouraging from the view point that they are fabricated for the first time. However, there is a good future scope of improving $V_{oc}$ as well as $J_{sc}$, which can be achieved by an optimization of various device parameters i.e. thicknesses of porphyrin and polyfullerene layers, morphology of the layers by appropriate post annealing, etc. The fitting of $J-V$ characteristics using equation 1.6 was not very good, as the device exhibited very high series and shunt resistances, high dark saturation currents, and very low photogenerated currents. The various estimated device parameters are summarized in Table 3.2. Very high value of $n$ (>3.5) indicates that the device consists of high disorder. This is expected as, unlike P3HT, porphyrin does not crystallize. In the absence of large range ordering of porphyrin, the disorder act as traps for the charge carriers and as a result the recombination increases. This leads to overall poor efficiency of the device.
3.3 **Porphyrin-modified ZnO-nanowire/P3HT hybrid solar cells**

In hybrid solar cells, the fullerene acceptors are replaced by the inorganic semiconductor nanostructures, such as ZnO nanoparticles (NP), nanowires (NW) etc., as discussed in Chapter 1. Here we describe the results on porphyrin-modified ZnO-nanowire/P3HT hybrid solar cells. The fabrication of these solar cell is described in Section 2.2).

![Figure 3.29: SEM Images of ZnO seed layer deposited on ITO substrate by using (a) 5 µl, (b) 10 µl, (c) 15 µl, and (d) 20 µl of ZnO NP solution.](image)

**Figure 3.29:** SEM Images of ZnO seed layer deposited on ITO substrate by using (a) 5 µl, (b) 10 µl, (c) 15 µl, and (d) 20 µl of ZnO NP solution.

### 3.3.1 Porphyrin-modified ZnO-nanowire

The growth of vertically aligned one dimensional (1D) ZnO NWs onto ITO substrates is described in Section 2.3.2. Figure 3.29 shows the SEM images of the ZnO NPs seed layers on ITO substrates, which were prepared by drop-casting varied volumes of ZnO NPs solution (i.e. 5, 10, 15, and 20µl). It is clear from this images that the seed layers are
uniform and pinhole free until one uses a solution of 15 µl. At higher concentrations, seed layer develop cracks.

**Figure 3.30:** SEM Images of ZnO NW grown on ITO substrate by using (a) 5 µl, (b) 10 µl, (c) 15 µl, and (d) 20 µl of ZnO NP solution as seed layers.

Fig. 3.30 shows the SEM images of ZnO NWs array grown on different seed layered substrates (i.e. 5, 10, 15, and 20µl). It is evident from the images that seed layer prepared using 10 µl volume of the ZnO NP solution (i.e. seed layer b) results in highly packed, well aligned and vertically oriented ZnO NWs array among a series of seed layers. For seed layer using 20 µl volume of the ZnO NP solution, nanowires are found to be disoriented and over grown at some places. Therefore, the optimized seed layer (Fig. 3.29 b) was further used for ZnO NW film preparation, and for fabrication of hybrid solar cells.
Figure 3.31: (a) X-ray diffraction pattern and (b) Raman spectrum of ZnO NW array grown onto ITO substrate.

The XRD pattern and Raman spectrum of the ZnO NW array is presented in Fig. 3.31. A prominent peak is observed at $2\theta = 34.5^\circ$, which suggests that ZnO nanowires grow along c-direction (002) perpendicular to the substrate plane. The Raman spectrum of ZnO NW recorded at room temperature show a sharp and dominant $E_2$ (high) mode at 439 cm$^{-1}$, which corresponds to the intrinsic mode of wurtzite hexagonal ZnO structure associated with oxygen displacement[115]. The two weak peaks at 334 and 382 cm$^{-1}$ may correspond to multi-phonon scattering process of ($E_2$ (high)-$E_2$ (low)) and $A_1$ (TO), respectively[116]. The presence of high intense $E_2$ (high) mode and suppressed $E_1$ (LO) mode suggests high crystalline nature of ZnO NWs.
As described in Chapter 2, hybrid bilayer heterojunction solar cells were fabricated using ZnO-NW as well as porphyrin-modified ZnO-NW. The porphyrin was electrodeposited onto ZnO-NW and the recorded cyclic voltammograms are shown in Fig. 3.32(a). These cyclic voltammograms are almost identical to that of electrodeposition of porphyrin onto ITO electrodes (see Fig. 3.12), indicating almost identical deposition mechanism. The UV-Vis spectra of porphyrin-modified ZnO-NW as well as ZnO-NW are shown in in Fig. 3.32(b), where the absorption peaks at 350nm and 431 nm correspond to ZnO-NW and porphyrin respectively. The high absorbance in ZnO-NW films clearly reveal high opacity of ZnO films.
Figure 3.33: Energy level diagram of (a) ITO/ZnO-NW/P3HT/Au and (b) ITO/porphyrin-modified ZnO-NW/P3HT/Au hybrid bilayer solar cells.

3.3.2 Photovoltaic characteristics of hybrid solar cells

The energy level diagrams of ITO/ZnO-NW/P3HT/Au and ITO/porphyrin-modified ZnO-NW/P3HT/Au solar cells are schematically shown in Fig. 3.33. It is evident that addition of intermittent porphyrin layer is advantageous as it lowers the band-offset for electron/hole dissociation, which facilitates the charge transport. The photoresponse characteristics of these hybrid solar cells were measured under white light (5 mW/cm²)
illumination. It may be noted that no photoresponse was observed for ITO/ZnO-NW/P3HT/Au solar cells. This can be explained on the basis of large band offset between ZnO and P3HT, which results in recombination of photogenerated carriers. In the case of ITO/porphyrin-modified ZnO-NW/P3HT/Au a good photoresponse was observed. The measured values of $I_{sc}$ and $V_{oc}$ were respectively, $\sim 100\mu A/cm^2$ and $\sim 50$mV. The obtained efficiency of the devices was <0.001%. A very low efficiency is attributed to several factors, such as, large phase separation between donor and acceptor (i.e. leading to the poor charge collection), high disorder present at the interfaces (i.e. high recombination) etc. The typical time decay of $I_{sc}$ and $V_{oc}$ is shown in Fig. 3.34. A fast decay of these parameters indicates the presence of localized states at the interface. Clearly there is a need to optimize the device parameters to improve the device efficiency.

**Figure 3.35:** A plot of (a) ideality factor, saturation current obtained by fitting $J$-$V$ curves vs. efficiency of the respective devices obtained experimentally; (b) $R/R_{sh}$, photogenerated current obtained by fitting $J$-$V$ curves vs. experimentally obtained efficiency of bilayer and bulk-heterojunction solar cells.
3.4 Conclusions

We have fabricated three types of polymer solar cells namely, P3HT:PCBM bulk-heterojunction solar cells, porphyrin/polyfullerene diffuse bilayer solar cells and porphyrin-modified ZnO nanowires based hybrid solar cells. Among these, P3HT:PCBM exhibited highest efficiency of 3.2% when annealed at 130°C for 30 min, and the hybrid solar cells exhibited the least efficiency. The $J$-$V$ curves of the devices were analyzed using a diode model. Plots of device parameters with experimentally obtained efficiency are plotted in Fig. 3.35. It is clearly seen that as the for devices with higher efficiency, the ideality factor and saturation current decreases, while $R_{sh}/R_s$ ratio and photogenerated current increases. In the case of P3HT:PCBM devices, temperature dependent in-situ Raman spectroscopy and optical microscopic studies have shown that the highest ordering/crystallinity is obtained at 130°C. Improved ordering implies less recombination (i.e. low $n$ value) and improved charge transport (low $R_s$ and high $J_{sc}$), and therefore high efficiency. In the case of porphyrin/polyfullerene diffuse bilayer solar cells and porphyrin-modified ZnO nanowires based hybrid solar cells, large phase separation between donor and acceptor and high disorder at the interfaces lead to high $n$ values and low efficiencies.