Soluble Phenanthrenyl-Imidazole-Presenting Regioregular Poly(3-octylthiophene) Copolymers Having Tunable Bandgaps for Solar Cell Applications**

By Yao-Te Chang, So-Lin Hsu, Ming-Hsin Su, and Kung-Hwa Wei*

1. Introduction

The development of conjugated polymers that possess extended delocalized π-electrons for use in organic optoelectronic devices has advanced dramatically in recent years. In particular, there have been extensive studies into solar cell devices based on bulk heterojunctions formed using conjugated polymers.[1–8] The structures of bulk heterojunction polymer solar cells have been prepared from a thin film of the electron-donating conjugated polymer and an electron-accepting species, which has been either another polymer or a set of nanoparticles. Polythiophene derivatives are recognized as being among the most promising materials for solar cell applications because of their excellent light absorption and electronic conductivity. Polymeric solar cells containing blends of poly(3-hexylthiophene) and the buckminsterfullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) have been studied in depth; recent reports[3] have indicated that power conversion efficiencies of around 1 % ∼2 % under standard solar conditions (AM 1.5G, 100 mW cm−2, 25 °C). There are a number of ways to proceed toward improving the power conversion efficiencies of these polymer solar cells. For example, varying the annealing temperature and time—to lower the electrical resistance of the devices—and introducing a lower-work-function electrode have been reported.[9–13] Alternatively, copolymerization with different conjugated monomers has also been investigated, but with limited success in improving the power conversion efficiency.[10]

We have used Grignard metathesis polymerization to successfully synthesize a series of regioregular polystyrene copolymers that contain electron-withdrawing and conjugated phenanthrenyl-imidazole moieties as side chains. The introduction of the phenanthrenyl-imidazole moieties onto the side chains of the regioregular polystyrenes increased their conjugation lengths and thermal stabilities and altered their bandgap structures. The bandgap energies, determined from the onset of optical absorption, could be tuned from 1.89 eV to 1.77 eV by controlling the number of phenanthrenyl-imidazole moieties in the copolymers. Moreover, the observed quenching in the photoluminescence of these copolymers increases with the number of phenanthrenyl-imidazole moieties in the copolymers, owing to the fast deactivation of the excited state by the electron-transfer reaction. Both the lowered bandgap and fast charge transfer contribute to the much higher external quantum efficiency of the poly(3-octylthiophene)-side-chain-tethered phenanthrenyl-imidazole than that of pure poly(3-octylthiophene), leading to much higher short circuit current density. In particular, the short circuit current densities of the device containing the copolymer having 80 mol % phenanthrenyl-imidazole, P82, improved to 14.2 mA cm−2 from 8.7 mA cm−2 for the device of pure poly(3-octylthiophene), P00, an increase of 62 %. In addition, the maximum power conversion efficiency improves to 2.80 % for P82 from 1.22 % for P00 (pure P3OT). Therefore, these results indicate that our polymers are promising polymer photovoltaic materials.

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Polymer solar cells containing blends of poly(3-hexylthiophene) and the buckminsterfullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) have been studied in depth; recent reports[3] have indicated that power conversion efficiencies of around 1 % ∼2 % under standard solar conditions (AM 1.5G, 100 mW cm−2, 25 °C). There are a number of ways to proceed toward improving the power conversion efficiencies of these polymer solar cells. For example, varying the annealing temperature and time—to lower the electrical resistance of the devices—and introducing a lower-work-function electrode have been reported.[9–13] Alternatively, copolymerization with different conjugated monomers has also been investigated, but with limited success in improving the power conversion efficiency.[10]

Semiconducting conjugated polymers that are used presently in light emitting diodes typically absorb in the range between 300 and 500 nm, which is only a small portion of the spectrum of sunlight. Thus, another approach toward higher-efficiency polymer solar cells is the use of conjugated polymers that absorb light more effectively. There are two main ways to tackle this problem. The first involves introducing chromophores that have different energy bandgaps into the conjugated polymers, thereby increasing the bandwidth of absorption. This method usually leads to some synthetic difficulties resulting from the typical bulkiness and low reactivity of functionalized chromophores or dyes. The second way is to incorporate electron-withdrawing moieties into side chains that are in conjugation with
the main polymer chains. In this way, not only the electron transfer efficiency of the excitons of the side-chain-tethered phenanthrenyl-imidazole polymers can be improved but also their bandgaps can be lowered for matching the wavelength of the maximum photon flux of sunlight (700 nm), which is ca. 1.77 eV[14]. The extent of the reduction in the bandgap of the side-chain-tethered phenanthrenyl-imidazole polymers will depend on the effective conjugation length of the system, which are sometimes reduced by steric hindrance. Previously, oxadiazo-, triazole-, quinoxaline-, imidazole-, and triazine-containing moieties are used in semiconducting polymers for other applications[15]. In this present study, we designed an extended conjugated molecular structure in which phenanthrenyl-imidazole moieties were attached covalently to the side chain of thiophene units to form regioregular copolymers that had lowered bandgaps—which were tunable depending on the content of phenanthrenyl-imidazole moieties—and enhanced electron transferring abilities. Because of the poor solubility of the phenanthrenyl-imidazole moiety, we used a thiophene monomer (3-octylthiophene) presenting a long alkyl chain to form copolymers exhibiting improved solubility. Scheme 1 displays our synthetic approaches toward the 2,5-dibromo-3-octylthiophene and the planar phenanthrenyl-imidazole moiety monomer. We expected that the presence of phenanthrenyl-imidazole moieties conjugated to the thiophene units would enhance the electron transfer of polythiophene and alter the energy levels of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of our polymers, thereby decreasing the bandgap and enhancing their photovoltaic properties. Scheme 2 displays the copolymerization of the 2,5-dibromo-3-octylthiophene M1 and 2-(2,5-dibromothiophen-3-yl)-1H-phenanthro[9,10-d]imidazole M2, performed using a Grignard metathesis method.

2. Results and Discussion

Figure 1 presents the $^1$H NMR spectra of M2 and some of the synthesized polymers. The regioregularity of the polymers can be determined from the ratio of the area under the peak at 6.98 ppm to the area under all of the peaks ranging from 6.98 to 7.04 ppm. Because only a signal at 6.98 ppm is present in the spectrum of P00, with no other peaks nearby, we believe that this polymer possesses an almost complete head-to-tail configuration (i.e., the regioregularity close to 100%).[15] In the spectrum of P37, the peak at 6.73 ppm (CH proton of the thiophene ring) is absent, and the broad peaks in the ranges 8.2–9.2 (CH protons of the phenanthrenyl group), 7.2–8.2 (CH protons on the phenyl group), and 0.8–3.0 ppm (octyl chain protons) confirm that the copolymers of M1 and M2 had formed.

Table 1 displays the molecular weight, the degradation temperature and the glass transition temperatures of synthesized copolymers, P00 to P82. The number molecular weight (Mn) of our polymers range from 7.2 kg/mole to 11.6 kg/mole and the polydispersity index (PDI) shows at the range of 1.28 and 1.61. The thermal degradation temperatures of these copolymers increased upon increasing the content of phenanthrenyl-imidazole moieties. For instance, the degradation temperature of P82 improved to 432.2 °C from 370.1 °C for P00, an increase of 62 °C. Whereas, the glass transition temperature of P82 was not detectable as compared to 40 °C for P00.

Figure 2 displays UV-vis spectra of the polymers in the solid state. The small peak at 270 nm is caused by the presence of conjugated phenanthrenyl-imidazole moieties that are not fully coplanar to the polythiophene chain owing to steric hindrance. The π–π* transitions are responsible for the maximum absorb-
tions ($\lambda_{\text{max}}$) that occur at ca. 520 nm for $P00$ and 556 nm for $P82$ thin films. These data indicate that the optical bandgap of the $P82$ copolymer is lower than that of pure $P3OT$. Table 2 lists the absorption maxima, and the optical bandgaps of the synthesized polymers. Optimally, conjugating 80 mol % of phenanthrenyl-imidazole moieties to the polythiophene chains led to the optical bandgap being reduced from 1.89 to 1.77 eV, confirming that the presence of the phenanthrenyl-imidazole moieties increases the effective conjugation length of the polythiophene main chain to some extent. The cyclic voltammogram data also shows the same trend, despite absolute values being different (see Supporting Information Table S1).

Figure 3 displays photoluminescence (PL) spectra of polymer films recorded at excitation wavelengths of 450 nm, respectively. The PL of the phenanthrenyl-imidazole-containing copolymers films was dramatically quenched relative to that of pure $P3OT$, with the degree of quenching increasing upon increasing the content of phenanthrenyl-imidazole units in the copolymer. This finding suggests that photoinduced charge transfer occurred from the photoexcited polythiophene backbone to the electron-withdrawing phenanthrenyl-imidazole side chains, and that this charge transfer was sufficiently rapid to compete with radiative recombination of the excitons.

Figure 4 displays the photocurrents of diodes having the structure ITO/PEDOT:PSS/polymer: [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM):PC$_{61}$B. The optical bandgap of the copolymer was found to be 1.77 eV, which is lower than that of pure $P3OT$. This indicates that the copolymer has a lower recombination rate and a higher photocurrent compared to the pristine polymer.

Table 1. Molecular weights and thermal properties of the synthesized polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n [10^3]$</th>
<th>$M_w [10^3]$</th>
<th>PDI</th>
<th>$T_d [^\circ C]$</th>
<th>$T_g [^\circ C]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P00</td>
<td>11.6</td>
<td>15.6</td>
<td>1.34</td>
<td>370.1</td>
<td>40.0</td>
</tr>
<tr>
<td>P55</td>
<td>11.2</td>
<td>17.8</td>
<td>1.61</td>
<td>404.5</td>
<td>[b]</td>
</tr>
<tr>
<td>P73</td>
<td>7.2</td>
<td>12.2</td>
<td>1.58</td>
<td>430.2</td>
<td>[b]</td>
</tr>
<tr>
<td>P82</td>
<td>7.7</td>
<td>9.9</td>
<td>1.28</td>
<td>432.2</td>
<td>[b]</td>
</tr>
</tbody>
</table>

[a] The temperature at which 5 % weight loss occurred based on the initial weight. [b] The glass transition temperature cannot be observed.

Table 2. UV-Vis absorption peaks and optical bandgaps of synthesized polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption $\lambda_{\text{max}}$ [nm]</th>
<th>Optical bandgap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P00</td>
<td>439 [549, 603]</td>
<td>1.89</td>
</tr>
<tr>
<td>P55</td>
<td>470 [540, 628]</td>
<td>1.82</td>
</tr>
<tr>
<td>P73</td>
<td>476 [548, 631]</td>
<td>1.81</td>
</tr>
<tr>
<td>P82</td>
<td>478 [556, 638]</td>
<td>1.77</td>
</tr>
</tbody>
</table>
acid methyl ester (PCBM) (1:2, w/w)/Ca/Al that were illuminated at AM 1.5 G and 100 mW cm\(^{-2}\). In Figure 4, the short circuit current density \((J_{sc})\) increased upon increasing the content of the phenanthrenyl-imidazole moieties, probably as a consequence of enhanced light absorption at longer wavelength due to the extended conjugation and the fast charge transfer of the copolymers.\(^{[19]}\) For all efficiency values reported in this paper we used a spectral mismatch factor of 0.8 to account for deviations in the spectral output of the solar simulator with respect to the standard AM 1.5 spectrum and deviations in the spectral response of the device with respect to that of the reference cell. Table 3 lists the detailed photovoltaic properties of these polymer solar cells. In particular, the short circuit current densities of the device containing the copolymer having 80 mol % phenanthrenyl-imidazole, \(P82\), improved to 14.2 mA cm\(^{-2}\) from 8.7 mA cm\(^{-2}\) for the device of pure poly(3-octylthiophene), \(P00\), an increase of 62\%. Because of the increased degree of the short circuit current density that occurred when the phenanthrenyl-imidazole content increased, the current density-voltage characteristics of our solar cell devices suggest that charge transfer occurred from the photoexcited polythiophene backbone through the phenanthrenyl-imidazole moieties and PCBM to the electrode. The open circuit voltages \((V_{oc})\) of the \(P82\) heterojunction device increased to 0.69 V from 0.59 V for the \(P00\) device. The open circuit voltages of polymer heterojunction cell is usually proportional to the difference between the lowest unoccupied molecular orbital (LUMO) of the electron acceptor and the highest occupied molecular orbital (HOMO) of the electron donor\(^{[20]}\) but are influenced by many other factors, for example, solvent effects.\(^{[21]}\) In the \(P82\) device case, it appears that the fact that the copolymers became less soluble and less miscible with PCBM at higher phenanthrenyl-imidazole moieties contents\(^{[21]}\) dominates over the decrease between the LUMO of the electron acceptor and the HOMO of the electron donor, resulting in a slightly higher \(V_{oc}\) than that of the \(P00\) device. Nevertheless, the filled factors remained low as a result of the devices maintaining large series resistances and low shunt resistances.\(^{[22]}\) Even with the disadvantage of low filled factors, the power conversion efficiency increased dramatically to 2.8\% for \(P82\) from 1.22\% for \(P00\), presumably due to the lowered bandgap and the enhanced electron transfer for the former polymer. The photophysics of the devices using the synthesized copolymers can be manifested by examining their external quantum efficiency and light absorption data. Figure 5a and b show the external quantum efficiency (EQE) of the polythiophene side-chain-tethered phenanthrenyl-imidazole/PCBM devices and the UV-vis absorption of the copolymer/PCBM blends experienced the same annealing condition as that of the device, respectively. The EQE values of \(P82\) device is at least 19\% larger than that of the \(P00\) device at wavelength from 400 to 600 nm. In a detailed comparison, the EQE value of the \(P82\) device improved to 50\% from 29\% for the \(P00\) device at 450 nm incident light, almost 100\% increase. The maximum EQE value of the \(P82\) and \(P00\) devices reaches 69\% and 29\%, respectively, at 480 nm, with a 1.5 times increase. Even at a much longer wavelength of 600 nm, the EQE of \(P82\) device improved to 33\% from 11\% for \(P00\) device, a two-fold increase. The relative light absorption intensity of \(P82\)/PCBM blend is about 20\% higher than that of \(P00\)/PCBM

![Figure 3. Photoluminescence (PL) spectra, normalized to the number of absorbed photons, of synthesized polymers in the solid state.](image)

![Figure 4. Current density-voltage characteristics of illuminated (AM 1.5G, 100 mW cm\(^{-2}\)) polymer solar cells incorporating \(P00\), \(P55\), \(P73\), and \(P82\) and PCBM.](image)

<table>
<thead>
<tr>
<th>Weight ratio of polymer to PCBM</th>
<th>(V_{oc} ) [V]</th>
<th>(J_{sc} ) [mA/cm(^2)]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P00)/PCBM = 1:2</td>
<td>0.59</td>
<td>8.7</td>
<td>23.6</td>
<td>1.22</td>
</tr>
<tr>
<td>(P55)/PCBM = 1:2</td>
<td>0.64</td>
<td>9.4</td>
<td>30.2</td>
<td>1.68</td>
</tr>
<tr>
<td>(P73)/PCBM = 1:2</td>
<td>0.62</td>
<td>12.4</td>
<td>28.0</td>
<td>2.15</td>
</tr>
<tr>
<td>(P82)/PCBM = 1:2</td>
<td>0.69</td>
<td>14.2</td>
<td>31.1</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Table 3. Photovoltaic properties of the polymer solar cells.
blend at 400 nm and 600 nm, respectively. The similarity between the shape of the EQE curves of these copolymers and their corresponding UV-vis absorption spectra indicated that the enhanced photocurrent current densities, $J_{sc}$, are mainly generated by the rapid electron transfer of the dissociated excitons in polythiophene backbone to the conjugated phenanthrenyl-imidazole side chain and lowered bandgap of the copolymer.

The large increase in the short-circuit current density of the polythiophene-side-chain tethered phenanthrenyl-imidazole device in turn accounts for the large increase in the power conversion efficiency of poly(3-octylthiophene). Due to the high short circuit current density obtained in the phenanthrenyl-imidazole presenting regioregular poly(3-octylthiophene), the power conversion efficiency improved dramatically to 2.80% for the copolymer containing 80 mol% phenanthrenyl-imidazole from 1.22% for pure poly(3-octylthiophene).

### 3. Conclusions

We have prepared a new family of regioregular thiophene copolymers presenting phenanthrenyl-imidazole side chains in conjugation with the main polymeric chain, leading to lowered bandgaps. The reduction in the bandgap energy in conjunction with the observed photoluminescence quenching indicates that rapid charge transfer occurred from the photoexcited polythiophene backbone through the phenanthrenyl-imidazole moieties to PCBM in the device. The much higher external quantum efficiency of the polythiophene-side-chain-tethered phenanthrenyl-imidazole device than that of pure poly(3-octylthiophene) device results in much higher short circuit current density.

### 4. Experimental

**Materials:** Chemicals were purchased from Aldrich, TCI, or Lancaster. [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) was purchased from Nano-C. Poly(thiophene-2,5-dicarboxaldehyde)poly(styrene sulfonate) (PEIOT/PSS) was purchased from Baytron (PVP A1 4083).

**Preparation of Monomers:** Scheme 1 illustrates the synthetic route used for the preparation of the monomers 2,5-dibromo-3-octylthiophene (M1) and 2-(2,5-dibromothiophene-3-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (M2). 1-Phenyl-2-(3-thienyl)-1H-phenanthro[9,10-d]imidazole (2), which was prepared from the reaction of 3-thiophene-carboxaldehyde, phenanthrenequinone, aniline, ammonium acetate, and acetic acid, was isolated in 92% yield.

**Preparation of Polythiophene Derivatives:** All polymers were synthesized through Grignard metathesis polymerizations in THF, according to procedures similar to those described in the literature [15b, 15c]. The Grignard metathesis polymerizations of 2,5-dibromo-3-octylthiophene (M1) and 2-(2,5-dibromothiophene-3-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (M2) are illustrated in Scheme 2. Detailed synthetic procedures and characterization data are provided in the Supporting Information.

**Preparation of Polymers:** The copolymers were synthesized by the free radical polymerization of the mixed monomers in benzene at 60 °C, using AIBN as the initiator.

**Characterization:**
- **UV-vis Spectroscopy:**
- **Cyclic Voltammetry:**
- **Differential Scanning Calorimetry (DSC):**
- **X-ray Diffraction (XRD):**
- **TGA:**
- **Photoluminescence:**

**Device Fabrication:**
- For the photovoltaic device, the active layer of polythiophene-blocked copolymers was spin-casted onto a PEDOT/PSS-coated FTO substrate. Then, a layer of 60 nm of lithium doped PCBM was thermally evaporated at 2 × 10$^{-4}$ Torr under a nitrogen atmosphere.

**Device Testing:**
- The performance of the devices was evaluated under 1 sun illumination (AM 1.5, 100 mW/cm$^2$).

**Results:**
- The devices exhibited quantum efficiencies of 10% and 15% at 400 nm and 600 nm, respectively.
- The EQE curves showed a sharp increase in the power conversion efficiency for the copolymer containing 80 mol% phenanthrenyl-imidazole.
- The devices achieved a power conversion efficiency of 2.80% under 1 sun illumination.

**Discussion:**
- The improved performance can be attributed to the enhanced charge extraction and transport properties of the copolymers.

**Conclusion:**
- The copolymers present promising potential for applications in solar cells.
trode coated with a thin layer of the polymer was used as the working electrode. A platinum wire was used as the counter electrode and a silver wire was used as the quasi-reference electrode. All of the potentials quoted herein are referenced to the Ag as the quasi-reference electrode; the electrochemical potential of Ag is \(-0.20 \text{ V versus SCE}\). \(E_{\text{HOMO}} = E_{\text{ox}} - 4.4 \text{ eV}\) and \(E_{\text{LUMO}} = E_{\text{red}} + 4.4 \text{ eV}\), where \(E_{\text{ox}}\) and \(E_{\text{red}}\) are the onset potentials of the oxidation and reduction peaks (versus saturated calomel electrode, SCE), respectively, and the value of 4.4 eV relates the SCE reference to a vacuum [16].

UV-vis spectra were measured using an HP 8453 diode array spectrophotometer. PL spectra were recorded using a Hitachi F-4500 luminescence spectrometer. The molecular weights of the polythiophene derivatives were measured through gel permeation chromatography (GPC) using a Waters styragel columns were connected in series in decreasing order of pore size (104, 103, and 102 Å); THF was the eluent and standard polystyrene samples were used for calibration.

Device Fabrication: The current density-voltage (J–V) measurements of our polymers were performed using devices having a sandwich structure (ITO/PEDOT:PSS/polymer:PCBM (1:2, w/w)/Ca/Al). An ITO-coated glass substrate was pre-cleaned and treated with oxygen plasma. Three 5-μm Waters styragel columns were connected in series and standard polystyrene samples were used for calibration.

Testing of the devices was performed under simulated AM1.5 irradiation (100 mW cm\(^{-2}\)) using a xenon lamp-based Newport 66902 white light source, and the optical power at the sample was measured through a Newport 67141 optical power meter. Three 5-μm Waters styragel columns were connected in series.

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