NOVEL SEMICONDUCTING POLYMERS FOR HIGHLY EFFICIENT SOLAR ENERGY HARVESTING

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Final Report

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In the past three years, our research project sponsored partially by AFOSR has been focused on developing low bandgap semiconducting polymers as the donor components for BHJ solar cells. We have made very important contributions to the field and have developed a series of new semiconducting polymers with thieno[3,4-b]thiophene and benzodithiophene alternating units. They exhibited superior solar energy PCE to polymers disclosed in literature in BHJ polymer solar cells in combination with fullerene derivatives as acceptors. Solar power conversion efficiency has reached to 9.4%. In addition to those achievements, we have gained deeper insight in understanding design principles for these high efficiency polymers. In the elucidation of structure/property relationship, we uncovered the local dipolar effect for designing highly efficient semiconducting polymers for OPV solar cells, which gives us solid design principle to search better materials.
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Accomplishments:

From the considerations of energy sustainability and environmental protection, solar energy is the largest carbon-neutral energy source to be explored and utilized much more extensively. There are solar cell devices based on inorganic semiconductors current on the market which already efficiently harvest solar energy. These devices are now being installed in solar factories and on rooftops of buildings. However, the cost of these devices is still too high to be economically viable. The urgency of securing sustainable energy resources for the world calls upon the scientific community to develop new materials for the cost-effective harvest of solar energy. This is the major motivation for the development of organic photovoltaic (OPV) materials and devices, which are envisioned to exhibit advantages such as low cost, high device flexibility, and fabrication from highly abundant materials. Although there are skeptics in the solar energy community, the past success in organic light emitting diodes provides scientists with confidence that organic photovoltaic devices will provide vital alternatives to their inorganic counterparts.

So far, the most successful architecture to build organic photovoltaic solar cells is the BHJ structure prepared by mixing donors and acceptor with nanoscale phase separation. The BHJ structure offers a high density of heterojunction interfaces in the device, and the structure can be easily implemented. In addition, it allows for a quick survey of the best composition of materials in the active layer. The composite active layer can be prepared by solution or vacuum deposition techniques. Solution processed BHJ solar cells offer the possibility of manufacturing the composite active layer over a large area in one simple step at room temperature, which can be very effective both in cost and energy.

There are generally two components in the BHJ structure, donor and acceptor. Selection of the materials in both components is very important for the solar cell performance. As donor materials, semiconducting polymers have showed better performance than their small-molecular counterparts due to their ability to more efficiently form films from solution and the higher charge mobility typical of the blend. In the acceptor component, fullerene derivatives are the best candidates so far due to their high electron affinity, superior electron mobility and their three dimensional structure, providing unique packing ability in blend to efficiently form electron transport channels. The original fullerenes do not have enough solubility in organic solvents, so fullerene derivatives with solubilizing groups are usually used, such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). As a result, the most effective composite structure in solution processed BHJ organic solar cells is based on a conjugated polymer/fullerene derivative blend.

The development of new polymers requires careful consideration of several issues including absorption, energy level, hole mobility and miscibility with fullerenes, which are mentioned above. It is difficult to design a polymer to fulfill all these requirements. Current polymer solar cells often suffer from inferior properties in some or all of these parameters due to a variety of
issues related to the nature of the materials and device engineering. So far, besides the P3HT system, there are only a few polymer solar cell systems reported which exceed 5% in power conversion efficiency.\textsuperscript{18}

In the past three years, our research project sponsored partially by AFOSR has been focused on developing low bandgap semiconducting polymers as the donor components for BHJ solar cells. We have made very important contributions to the field. Our group has developed a series of new semiconducting polymers with thieno[3,4-\textit{b}]thiophene and benzodithiophene alternating units. They exhibited superior solar energy PCE to polymers disclosed in literature in BHJ polymer solar cells in combination with fullerene derivatives as acceptors.\textsuperscript{19} Solar power conversion efficiency has reached to 9.4%. In addition to those achievements, we have gained deeper insight in understanding design principles for these high efficiency polymers.

\textbf{2. Synthesis of polymers}

The polymers were designed based on the considerations discussed above. Scheme 1 shows the structures and synthetic scheme of the new polymers. The key monomer contains the thieno[3,4-\textit{b}]thiophene moiety that can support the quinoidal structure and lead to a narrow polymer bandgap, which is crucial to efficiently harvest solar energy.\textsuperscript{20} In our past efforts, we found that incorporation of this monomer into polymers indeed lowered the band gap of the resulting conjugated polymers. Since the thieno[3,4-\textit{b}]thiophene moiety is very electron-rich, an electron-withdrawing ester group is introduced to stabilize the resulting polymers.\textsuperscript{21} The benzo[1,2-\textit{b}:4,5-\textit{b'}]dithiophene monomers are chosen because of their more extended conjugated systems and proper side chain patterns for enhanced solubility.\textsuperscript{22}

\textbf{Scheme 1. Synthetic schemes for polymers PTB1-PTB6.}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{scheme1.png}
\caption{Synthetic schemes for polymers PTB1-PTB6.}
\end{figure}

The Stille polycondensation between the ester substituted 2,5-dibromothieno[3,4-\textit{b}]thiophene and benzodithiophene distannane monomers (Scheme 1) led to the synthesis of these polymers in high yield.\textsuperscript{19} We have found that the Stille polycondensation is an ideal approach to these functionalized semiconducting polymers because it can tolerate functional groups such as esters and the homogeneous reaction conditions can be beneficial for high polymerization degree. These polymers exhibit relatively high molecular weight and are soluble in halogenated solvents.

The basic electro-optic properties of these polymers are very similar to one other (See Table 1). For example, all of these polymers exhibit identical absorption spectra, with only slight changes in the absorption peak and onset point. The HOMO energy levels of the polymers, as determined by cyclic voltammetry (CV), are very close to one another with the exceptions of those observed for PTB3 and PTB4 (Table 1). From the comparison of PTB2 with PTB3, it is noticed that the HOMO energy level of the polymer is lowered from -4.94 eV to -5.04 eV by the substitution of an alkoxyl side chain for an alkyl side chain. Comparing PTB4 with PTB5, polymers with the same side chain patterns, the introduction of the electron withdrawing fluorine in the polymer backbone
significantly lowers the HOMO level. It shows that the HOMO energy level of the polymer can be lowered by substituting a less electron-rich group in the side chain (i.e. replacement of alkoxyl with an alkyl side chain) or by introduction of electron withdrawing groups (i.e. fluorine) to the backbone.

The hole mobility of these polymers varies according to structures: $4.7 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$, $4.0 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$, $7.1 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$, $7.7 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$, $4.0 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$, $2.6 \times 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ are found for PTB1, PTB2, PTB3, PTB4, PTB5 and PTB6 respectively from the space charge limited current (SCLC) method. The alkyl grafted PTB3 and fluorinated PTB4 exhibit larger hole mobilities than those of the other polymers.

Table 1. Characteristic properties of polymers and their solar cells in PTBx/PC$_{61}$BM composite.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB1</td>
<td>-4.90</td>
<td>-3.20</td>
<td>0.58</td>
<td>12.5</td>
<td>65.4</td>
<td>4.76</td>
</tr>
<tr>
<td>PTB2</td>
<td>-4.94</td>
<td>-3.22</td>
<td>0.60</td>
<td>12.8</td>
<td>66.3</td>
<td>5.10</td>
</tr>
<tr>
<td>PTB3</td>
<td>-5.04</td>
<td>-3.29</td>
<td>0.74</td>
<td>13.1</td>
<td>56.8</td>
<td>5.53</td>
</tr>
<tr>
<td>PTB4</td>
<td>-5.12</td>
<td>-3.31</td>
<td>0.76</td>
<td>9.20</td>
<td>44.5</td>
<td>3.10</td>
</tr>
<tr>
<td>PTB5</td>
<td>-5.01</td>
<td>-3.24</td>
<td>0.68</td>
<td>10.3</td>
<td>43.1</td>
<td>3.02</td>
</tr>
<tr>
<td>PTB6</td>
<td>-5.01</td>
<td>-3.17</td>
<td>0.62</td>
<td>7.74</td>
<td>47.0</td>
<td>2.26</td>
</tr>
<tr>
<td>PTB3$^a$</td>
<td>0.72</td>
<td>13.9</td>
<td>58.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTB4$^a$</td>
<td>0.74</td>
<td>13.0</td>
<td>61.4</td>
<td>5.90 (6.1$^b$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PTB5$^a$</td>
<td>0.66</td>
<td>10.7</td>
<td>58.0</td>
<td></td>
<td></td>
<td>4.10</td>
</tr>
</tbody>
</table>


3. Photovoltaic effect of PTBx/PC$_{61}$BM composites

Photovoltaic properties of all of the polymers were investigated in polymer solar cell devices fabricated in structures of ITO/PEDOT:PSS/polymer:PC$_{61}$BM(1:1, wt ratio)/Ca/Al. Representative characteristics of the solar cells are summarized in Table 1 and Figure 3. The active layer thickness was around 100 – 110 nm, which was shown to be the optimal thickness for this material system.

The solar cells prepared from PTB1/PC$_{61}$BM composites showed a short circuit current, Jsc, of 12.5 mA/cm$^2$, a Voc of 0.58 V and a fill factor of 65.4%. The resulting PCE was thus 4.76%. Those from PTB2 showed enhancement from PTB1. The alkyl substituted PTB3 had an enhanced Voc compared to PTB2. The fluorinated polymer PTB4 devices showed an increase in Voc compared to PTB5. The changes in Voc are well correlated with the HOMO energy levels of
the polymers. With the increase of Voc, the PTB2 solar cell showed a larger PCE than PTB1. Comparing PTB2 and PTB3 with similar side chain patterns, PTB3 had a larger Jsc than PTB2, which is due to the increase of hole mobility in PTB3. With the increase in Jsc and Voc, the PTB3 device showed a PCE of 5.53%. However, with the exceptions of PTB2 and PTB3, the other polymer solar cells suffered a significant decrease in Jsc and FF compared to the PTB1 solar cell.

![Figure 3](image)

**Figure 3.** Current – voltage characteristics of polymer/PC\(_{61}\)BM solar cells under AM 1.5 condition (100mW/cm\(^2\)).

The performances of polymers in solar cell devices were found to be related to the morphology of composite films, which has a large effect on a BHJ polymer solar cell.\(^{21}\) Transmission electron microscopy (TEM) studies revealed fine features in PTB1/PC\(_{61}\)BM blend films, indicating continuous interpenetrating networks with small domains. Large domains were observed from PC\(_{61}\)BM blend films of PTB5 or PTB6 with more bulky side chains and their solar cell performances were significantly reduced. With the same side chain patterns as PTB5, the fluorinated PTB4 also suffered from suboptimal morphology, and large features (over 100 nm) could be observed in the TEM image of the PTB4/PC\(_{61}\)BM blend film (Figure 4). Although PTB4 showed both the lowest HOMO energy level and the largest hole mobility, its photovoltaic performance in simple polymer/PC\(_{61}\)BM solar cells was modest (3.10%).

![Figure 4](image)

**Figure 4.** TEM images of polymer/PC\(_{61}\)BM blend films: (a) PTB1, (b) PTB4 and (c) PTB4/PC\(_{61}\)BM blend films prepared from mixed solvents dichlorobenzene/diodooctance (97/3, v/v). (The scale bar is 200 nm.)

This morphological effect was also demonstrated by studies on thermal annealing of the PTB1/PC\(_{61}\)BM blend film. It is known that thermal annealing of P3HT:PC\(_{61}\)BM films resulted in increased ordering of the P3HT domains and red-shifted optical absorption features, which produced an enhancement in the PCE in solar cells.\(^{26}\) Conversely, annealing PTB1:PC\(_{61}\)BM film reduced device PCE to 1.92% from 4.76% of the pristine film.\(^{27}\) The TEM image of pristine film...
showed very fine, intertwined, fibrous features (i.e. ~5 nm width), suggesting a better donor-acceptor interaction. The annealed film, however, showed large phase-separated PC$_{61}$BM-enriched domains with sizes ranging from 10 to 200 nm. The larger feature size indicates a smaller surface area to volume ratio of the domains, which reduces the interfacial surface area between polymer and PC$_{61}$BM and thereby lowers the exciton splitting efficiency. Ultra-fast spectroscopic studies indicated that the cation yield of the annealed film characterized by the signal at 2.5 ns time delay was only about 43% of that for the pristine film.

The morphological problem could be remedied via use of a mixed solvent in preparing polymer/fullerene spin-coating solution. The PTB4/PC$_{61}$BM blend film prepared by using dichlorobenzene/1,8-diiodooctane (97/3, v/v) as the solvent exhibited improved morphology. There are no large features in the TEM images and the film shows similar morphology to that of PTB1 or PTB2 blend films in their TEM images (Figure 4). Dramatic performance enhancements could be observed both in PTB4 and PTB5 solar cells. (Figure 5a) Besides the increase of Voc, the PTB4 solar cell showed larger Jsc and a slight increase of FF than that observed in PTB5, due to the higher hole mobility found in the fluorinated PTB4. The PCE from the PTB4/PC$_{61}$BM solar cell reached 5.9%. After calibrating with the spectral mismatch factor, the efficiency of PTB4/PC$_{61}$BM solar cell reached 6.1%. Figure 5b shows the EQE spectrum of the PTB4/PC$_{61}$BM solar cell prepared from a mixed solvent system. The device can very efficiently harvest the light in the maximum photon flux region (680 nm), showing over 50% from 550 nm to 750 nm.

Figure 5. (a) Current – voltage characteristics of polymer/PC$_{61}$BM solar cells prepared from mixed solvents dichlorobenzene/diiodooctane (97/3, v/v) under AM 1.5 condition (100mW/cm$^2$). (b) External quantum efficiency of PTB4/PC$_{61}$BM device prepared from mixed solvents.

4. Photovoltaic effect of PTBx/PC$_{71}$BM composites

The PCE of these polymer solar cells can be further enhanced by using PC$_{71}$BM instead of PC$_{61}$BM. The absorption spectra of the PTB1/PC$_{71}$BM film exhibited a stronger absorption in the spectral range between 400-580 nm than the PC$_{61}$BM composite (Figure 6a). This led to a higher Jsc of 15.0 mA/cm$^2$, as indicated by the much higher EQE values. The device exhibited a Voc of 0.56 V and a fill factor of 63.3%, which yielded an impressive PCE of 5.6% after correcting the spectral mismatch factor.

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Most recently, we further developed a new polymer from the PTB family, PTB7 (Figure 7 inset), which exhibited an excellent photovoltaic effect (Figure 7). A power conversion efficiency of about 7.4% has been achieved from PTB7/PC$_{71}$BM solar cell devices, which is the first polymer solar cell system showing power conversion efficiency over 7%. As shown in the structure of PTB7, it seems that the branched side chains in ester and benzodithiophene render the polymer highly soluble organic solvents and highly miscible with fullerenes. Although the side chains are branched, the PTB7 has a relatively high hole mobility of approximately $5.8 \times 10^{-4}$ cm$^2$/v·s measured from the SCLC model.

Table 2 shows the comparison of solar cell performances as a function of solvent composition. The best performances of solar cells based on the PTB7/PC$_{71}$BM blend film were obtained by using a mixed solvent system in preparing the films. Devices prepared from the mixed solvent system consisting of dichlorobenzene (DCB)/1,8-diiodooctane (97%:3% by volume) exhibited a fill factor of 68.9%, an Jsc of 14.09 mA. The PCE of 7.18% was obtained. When chlorobenzene was used as the co-solvent, the solar cell Jsc significantly increased to 14.5 mA/cm$^2$ and the fill factor increased to 69%. The combined effect was power conversion efficiency of 7.40%.
Table 2. Device photovoltaic parameters of (a) DCB only, (b) DCB with 3% DIO; (c) CB and (d) CB with 3% DIO as solvent(s). The Jsc calculated from EQE spectrum is also shown.

<table>
<thead>
<tr>
<th></th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Jsc (Cal.) (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. DCB</td>
<td>0.74</td>
<td>13.95</td>
<td>60.25</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>b. DCB+DIO</td>
<td>0.74</td>
<td>14.09</td>
<td>68.85</td>
<td>7.18</td>
<td>13.99</td>
</tr>
<tr>
<td>c. CB</td>
<td>0.76</td>
<td>10.20</td>
<td>50.52</td>
<td>3.92</td>
<td></td>
</tr>
<tr>
<td>d. CB+DIO</td>
<td>0.74</td>
<td>14.50</td>
<td>68.97</td>
<td>7.40</td>
<td>14.16</td>
</tr>
</tbody>
</table>

Again, the dramatic enhancement of photovoltaic performances is caused by the change in morphology of the blend film. The TEM images (Figure 8) clearly showed that there are large domains (about 100 – 200 nm in diameter) in the blend film prepared from chlorobenzene, which could diminish exciton migration to the donor-acceptor interface and is not favorable for charge separation. The morphology of the blend film prepared from chlorobenzene/diiodooctane was much more uniform and there is no large phase separation, showing good miscibility between PTB7 and PC₇₁BM and the formation of interpenetrating networks.

![Figure 8. TEM images of PTB7/PC₇₁BM blend film prepared from chlorobenzene without (left) and with (right) diiodooctane. (The scale bar is 200 nm.)](image)

These solar cells exhibited high photo conversion efficiency in the range between 400 and 700 nm with EQE values of over 50%. (Figure 9a) A maximum EQE of 68.1% at 630 nm was obtained, which represents one of the highest EQE values in organic solar cells from a low band gap polymer system disclosed in literature. These measurements are rather accurate as further examined by integrating the EQE data with the AM1.5G solar spectrum. The calculated Jsc is 14.2 mA/cm² in the CB:DIO device. Comparing to the experimental Jsc of 14.5 mA/cm², it represents an error of ~2%. The internal quantum efficiency (IQE) of these cells was estimated based on the following simple facts and assumptions: (a) 4% light loss at air (n = 1) /glass (n=1.5) interface; (b) metal as perfect mirror (i.e. film absorbs light twice); (c) ignore the absorption in the glass, ITO and PEDOT:PSS in real device. These solar cells also exhibited a high IQE value over 90% in a wide range of 420 nm to 660 nm, and the maximum IQE reaches 92%. (Figure 9b) The wide and high IQE data unambiguously proves the very high quality of the new polymer system. In this system the exciton dissociation, charge transport in donor and acceptor networks and charge extraction in both organic/electrode interfaces are all very close to 100%. These facts imply that the morphology of blend films is close to an ideal donor and acceptor bi-continuous interpenetrating network in nano-scale.
In collaboration with Solarmer Energy Company, we further modified the polymer structures by using ketone groups to replace the ester groups in polymer PTB4. The resulting polymers exhibited a lower HOMO energy level of 5.22 eV. This slight change did not alter the properties of polymer assembly and charge transport behavior, but further increased the Jsc to 15.2 mA, resulting in a polymer solar cell with a power conversion efficiency as high as 7.7%.

5. Unique features of these polymers

Several factors synergistically combine to make these polymers good materials for polymer solar cells exhibiting high power conversion efficiency. First of all, these polymers possess an optimal bandgap of ~1.6 eV as well as preferred energy levels that match well with PCBM. As shown in Scheme 1, the flexibility in structural modification makes it possible to fine-tune the energy levels of polymers, which has shown significant effect in enhancing the solar PCE. For example, the introduction of fluorine into the thieno[3,4-b]thiophene provides the polymer a relatively low-lying HOMO energy level, which offers enhanced Voc. The high PCE is the direct result of the proper match of energy levels.

Second, the thieno[3,4-b]thiophene unit can stabilize the quinoidal structure in the polymer chain and thus enhance the planarity along the aromatic polymer backbone. The benzodithiophene unit makes the polymer backbone much more rigid than P3HT. For example, the absorption spectrum of P3HT exhibits a large red shift when comparing the solution spectrum with that of solid state films. This is caused by forced planarity in the solid state due to bond twisting. The PTBx series of polymers show minimal shifts in their absorption peaks between solution and solid states. The planarity and conjugation length of the polymer shows little change with the introduction of PC_{61}BM, as illustrated by the small change in the absorption of the blend film at longer wavelengths. The rigidity and planarity of the polymer backbone is directly responsible for the high SCLC mobility of the polymers. The high hole mobility and the capability of forming balanced carrier mobility in the blend lead to a high fill factor. The mobility value reported by us based on SCLC is underestimated due to the limitation in our measurement facility. However, under similar conditions, our polymers always exhibit larger charge carrier mobility than the P3HT system.

Third, the polymer blend systems have a preferred morphology with interpenetrating networks that can benefit not only the charge separation, but also the charge transport, which leads to the high fill factor. Atomic force microscopy (AFM) and TEM studies revealed that the morphology of the PTB1/PC_{61}BM blend film exhibited very fine domains and no large phases can be found. Figure 4a) Other PTBx polymers can form similar morphologies from suitable solvent systems. Small nanofibers (about 5 nm width) are observed in the TEM images and are distributed...
in the entire image field, indicating more effective donor-acceptor interactions. Ultrafast photoluminescence studies revealed that the PTB1/PC$_{61}$BM blend film exhibited a higher degree of PL quenching due to the photoinduced charge transfer from the polymer to PC$_{61}$BM than the corresponding P3HT:PC$_{61}$BM system. All of these results indicated that the polymer and PCBM formed an effective interpenetrating network in the blend film. Our results indicate that control in morphology to form finely mixed composite structures is crucial to obtain high PCE for the solar cell.

The polymer chain was found to be stacked on the substrate in the face-down conformation. This is very different from the polymer alignment in well-studied P3HT solar cell system and favors charge transport. Grazing incidence X-ray scattering (GIXS) revealed a unique lamellae packing structure with both the π-conjugated backbone and the side chains parallel to the substrate, as identified in PTB1/PC$_{61}$BM composite. Figure 10 showed GISAXS images of the PTB1 (a) and PTB1/PC$_{61}$BM (1:1) pristine (b) films. The neat PTB1 film presented two distinctive intermolecular peaks (Figure 10a) with one at $q = 0.226 \text{ Å}^{-1}$ (corresponding to a d-spacing of 27.4 Å), and the other at $q = 1.708 \text{ Å}^{-1}$ (d = 3.68 Å). The latter was due to the interchain π-π stacking between polymer backbones. The 27.4 Å feature was preferentially in-plane, whereas that associated with 3.68 Å was vertically out-of-plane. The results suggest that PTB1 molecules assembled and oriented with the aromatic backbones stacked parallel to the substrate surface and with the stack separation of 27.4 Å defined by the side chains extended parallel to the substrate. This unique molecular packing is one of the reasons behind the higher carrier mobility observed on PTB1 than that of P3HT.

![GISAXS images](image)

**Figure 10.** GISAXS images of (a) polymer PTB1 film, and (b) pristine PTB1/PC$_{61}$BM (1:1) film.

Efficient charge separation was observed in ultrafast spectroscopic studies of PTB1 and PTB1/PC$_{61}$BM (1:1 in weight ratio) films in the NIR spectral region of 850 - 1700 nm. A peak centered at 1150 nm appears at 100 ps after the excitation in pure polymer films, which is assigned to the PTB1 cation due to the interchain charge transfer. This assignment of the 1150-nm peak to the PTB1 cation is supported by the optical absorption spectra of the same film undergoing the electro-spectrochemical oxidation. This 1150-nm peak had a lifetime much longer than a few nano-seconds, suggesting the formation of a new cationic species in the composite film. An increased absorption with time was also observed for the feature above 1500 nm, which could be assigned to free carrier absorption. The appearance of the free PTB1 cation...
after CS is also consistent with the fluorescence quenching mentioned above.\(^{19a}\)

**Figure 11.** TA spectra of (a) PTB1 and (b) PTB1/PC\(_{61}\)BM (1:1) film in the NIR region with 600 nm excitation wavelength. (c) Kinetic traces of pristine and annealed PTB1/PC\(_{61}\)BM films monitored at 1150 nm. The traces are normalized by the number of photons absorbed at 600 nm. The inset shows the same kinetic traces at early delay time. (d) Fitting coefficient of PTB1 cation at different time delay for PTB1/PC\(_{61}\)BM pristine and annealed PTB1/PC\(_{61}\)BM 1:1 film by using equation S1.

It was found that the average CS rate for the pristine PTB1:PC\(_{61}\)BM film was 1.5 ps, which is more than twice as fast as that of 4 ps observed for the annealed P3HT/PC\(_{61}\)BM film.\(^{35}\) This faster CS rate, combined with higher charge carrier mobility contributes to the high device efficiency of PTB1:PC\(_{61}\)BM solar cell in addition to more effective light harvesting in the NIR region.

**Investigation of the effect of fluorination of PCEs of solar cells.**

In the previous work, we have shown that the introduction of one fluorine atom into the thieno[3,4-b]thiophene ring substantially improves the \(V_{oc}\) value and achieves the highest power conversion efficiency. We attributed this to the lowering in HOMO energy level. Motivated by these results, we decided to further investigate the effect of fluorination on properties of PTB polymers. Two new polymers PTBF2 and PTBF3 are designed and synthesized. Their utilization as active layers in BHJ photovoltaic devices and their comparison with previous polymers are discussed in this work.

**Scheme 2. Polymer Synthesis**

\[ \text{PTBF0} : X_1 = H, X_2 = H, R_1 = \text{n-octyl}, R_2 = 2\text{-ethylhexyl} \]
\[ \text{PTBF1} : X_1 = F, X_2 = H, R_1 = 2\text{-ethylhexyl}, R_2 = 2\text{-ethylhexyl} \]
\[ \text{PTBF2} : X_1 = H, X_2 = F, R_1 = 2\text{-ethylhexyl}, R_2 = 2\text{-ethylhexyl} \]
\[ \text{PTBF3} : X_1 = F, X_2 = F, R_1 = 2\text{-ethylhexyl}, R_2 = 2\text{-ethylhexyl} \]
Table 3. Solar Cell Performance

<table>
<thead>
<tr>
<th>polymer</th>
<th>Polymer/PCBM (w/w ratio)</th>
<th>Solvent</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTBF0</td>
<td>1:1</td>
<td>DCB</td>
<td>14.1</td>
<td>0.58</td>
<td>62.4</td>
<td>5.1</td>
</tr>
<tr>
<td>PTBF1</td>
<td>1:1.5</td>
<td>DCB</td>
<td>14.0</td>
<td>0.74</td>
<td>60.3</td>
<td>6.2</td>
</tr>
<tr>
<td>PTBF1</td>
<td>1:1.5</td>
<td>DCB/DIO</td>
<td>14.1</td>
<td>0.74</td>
<td>68.9</td>
<td>7.2</td>
</tr>
<tr>
<td>PTBF2</td>
<td>1:1.5</td>
<td>DCB</td>
<td>11.0</td>
<td>0.68</td>
<td>43.4</td>
<td>3.2</td>
</tr>
<tr>
<td>PTBF2</td>
<td>1:1.5</td>
<td>DCB/DIO</td>
<td>11.1</td>
<td>0.68</td>
<td>42.2</td>
<td>3.2</td>
</tr>
<tr>
<td>PTBF3</td>
<td>1:1.5</td>
<td>DCB</td>
<td>9.1</td>
<td>0.75</td>
<td>39.4</td>
<td>2.7</td>
</tr>
<tr>
<td>PTBF3</td>
<td>1:1.5</td>
<td>DCB/DIO</td>
<td>8.8</td>
<td>0.68</td>
<td>39.0</td>
<td>2.3</td>
</tr>
</tbody>
</table>

It is found that the dramatic decrease of the FF found for PTBF2/PC70BM and PTBF3/PC70BM photovoltaic devices is mostly due to the morphology problem coming from poor miscibility of the polymers with PC$_{70}$BM. Figure 1a-d shows TEM images of polymer/PC70BM blend films prepared by using the same conditions used for the formation of the solar cell active layers. Both TEM images of PTBF0 and PTBF1 blend films possess uniform and fine features, suggesting nanoscale phase-separation. However, the TEM images of PTBF2 and PTBF3 blend films clearly show 50-200 nm, indicating large scale phase separation and no bicontinuous networks.

Figure 12. TEM images of polymer/PC$_{70}$BM blend films prepared from DCB solvent, PTBF0 (a), PTBF1 (b), PTBF2 (c), PTBF3 (d), Scale bar = 200μm.

3. Photochemical Stability of the polymers

It was found that the PTBF2 and PTBF3 polymers are photochemically much less stable than PTBF0 and PTBF1 in an ambient condition. With UV light exposure to the spin-coated polymer films in the air condition, the maximum absorption peaks of the PTBF2 and PTBF3 polymers decreased rapidly in intensity and shifted to the blue. The decomposition caused in the polymers is proved due to photooxidation, which significantly occurs to PTBF2 and PTBF3. In order to gain more insight into this process, we monitored the photochemical reaction of the PTBF3 film by using the FT-IR spectrometer and $^{19}$F NMR spectroscopy. It is concluded that, in the thienothiophene of the polymer, the thienyl ring directly linked to the polymer main chain is most likely to be the reaction site. The photooxidation mechanism of the polymers, PTBF2 and
PTBF3 is proposed. The process involves energy transfer from the photoexcited polymer to the triplet oxygen to generate the singlet oxygen ($^{1}A_g$ state : 0.9 eV) and the subsequent reaction of the singlet oxygen with the thienyl moieties by [2+4] cycloaddition. PTBF1, which has a similar $M_w$ value and the same structure as PTBF3 except unfluorination of benzodithiophene, also undergoes photooxidation. However, it is much more stable from photooxidation compared to PTBF3. It is postulated that the rapid photodegradation of PTBF3 is due to larger singlet oxygen quantum yield of PTBF3 compared to that of PTBF1. The large singlet oxygen quantum yield may reflect a large quantum yield of triplet polymer. We expect that the structural change of fluorine substitution on 3 and 7 positions of benzodithiophene in the polymer backbone enhance the quantum yield of triplet polymer followed by the increased singlet oxygen quantum yield, resulting in the decrease of photochemical stability of the polymer.

Figure 13. (a) Absorption spectra of PTBF3 film recorded as a function of irradiation time under air. (b) Decrease in the optical density ($\lambda_{\text{max}}$) of polymer films

**Effect of extended conjugation.**

Another strategy to enhance solar performances is to develop new polymers with more extended conjugation systems because more extended conjugation will enhance p-p stacking. Better p-p stacking favors charge transport and diminish charge density. The new polymer structures are shown in scheme 3.

Scheme 3. Polymer Structures and Synthesis

As the first attempt, we synthesized the tetrathienoanthrancene with relatively short branch alkyl side chain (2-ethylhexyl). Because of the poor solubility of the extended π-conjugated monomer, the final polymer PTTATT-1 showed very poor solubility and hardly processible in the
organic solvents tested for solar cell application. In order to improve the solubility of this polymer, a series of polymers with more branched alkyl side chain had been synthesized to target better processibility during solar cell device fabrication. As shown above, four new polymers (PTTATT-2-4) showed a number-average molecular weight more than 18 kDa with PDI from 1.6 to 2.6. It was found that long linear side chain, n-hexyldedocyl in PTTATT-5, led to low molecular weight polymer (less than 10 kDa) with limited processibility and widened optical band gap. PTTATT-5 shows an optical band gap about 2.04 eV while the other three polymers with branched side chain show lower optical gap around 1.65 eV. In addition to fluorothieno[3,4-b]thiophene monomer, we also polymerized the tetraphthioanthracene monomer with thieno[3,4-c]pyrrole-4,6-dione, a well known electron-deficient monomer, to obtain the new copolymer PTTATPD-1 for comparison in physical properties. The number average molecular weight of PTTATPD-1 is 26.9 kDa with a PDI about 1.79. The optical band gap had been found around 1.98 eV, which was much bigger than the PTTATT family polymers with good solubility (PTTATT2-4).

Transmission electron microscopy (TEM) was used to study the morphology of the polymer/PC$_{61}$BM blend films as shown in Figure 1. All of these films were spin-coated from chloroform/DIO (98/2, v/v) co-solvent except the first one without DIO. These polymers with different alkyl chains exhibited very fine domains and no large phases can be found for PTTATT-3-4 and PTTATPD-1 from the TEM images. As shown in Figure 1A, without adding of DIO, PTTATT-3 film from chloroform showed very tiny aggregation, which indicated that the tetraphthioanthracene-based polymer had good compatibility with fullerene due to its extended 2D π-system. After DIO was added as a co-solvent, the film became more uniform as shown in Figure 1B. As demonstrated as other reports, here DIO will also improve the morphology of tetraphthioanthrance-based polymers and enhance the PCEs of solar cells at some level.

![Figure 14](image_url) TEM images of polymer/PC$_{61}$BM blend films. A) PTTATT-3 from chloroform; B) PTTATT-3 from chloroform/DIO (98/2, v/v); C) PTTATT-4 from chloroform DIO (98/2, v/v); D) PTTATPD-1 from chloroform DIO (98/2, v/v), the scale bar is 200 nm.
Table 4. Characteristic properties of polymer solar cells.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
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<tbody>
<tr>
<td>PTTATT-2*</td>
<td>0.73</td>
<td>1.7</td>
<td>0.52</td>
<td>0.63</td>
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<tr>
<td>PTTATT-3</td>
<td>0.66</td>
<td>15.0</td>
<td>0.58</td>
<td>5.62</td>
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<tr>
<td>PTTATT-4</td>
<td>0.62</td>
<td>9.6</td>
<td>0.50</td>
<td>2.98</td>
</tr>
<tr>
<td>PTTATPD-1</td>
<td>0.70</td>
<td>6.0</td>
<td>0.55</td>
<td>2.30</td>
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</table>

*Chlorobenzene/DIO (98/2, v/v), 1000 rpm; others: chloroform/DIO (98/2, v/v), 2500 rpm

Photovoltaic properties of the polymers were investigated in solar cell structures of ITO/PEDOT:PSS/polymer:PC$_{61}$BM (1:1, w/w)/Ca/Al. The polymer active layers were spin-coated from a chloroform or chlorobenzene solution. The PTTATT-3/PC$_{61}$BM systems spin-coated from different solvents, chlorobenzene (CB), o-dichlorobenzene (DCB) and chloroform (CF), were investigated. The devices fabricated from CB and DCB showed low $J_{sc}$ and FF, 12.3 mA cm$^{-2}$, 32% (CB) and 10.5 mA cm$^{-2}$, 27% (DCB) with PCEs about 2.65% (CB) and 1.91% (DCB), respectively. PTTATT-3 showed better solubility and film-forming ability in CF. The resulting thin films were very uniform for PTTATT-3/PC$_{61}$BM blend. Upon using CF as a solvent, the solar cell $J_{sc}$ was significantly increased to 15.0 mA cm$^{-2}$ and the fill factor, at the same time, increased to 58%. The combined effect leads to the PCE up to 5.6%. As the comparison, PTTATT-2 with much more bulk side chain showed a PCE about 0.6%; PTTATT-4 with 2-ethyldecylic side chain showed a PCE about 3.0% and the copolymer with thieno[3,4-c]pyrrol-4,6-dione unit, PTTATPD-1, showed a PCE of 2.3% with a high $V_{oc}$ of 0.70 V.

Effect of heteroatoms-Selenium replacing sulfur atoms.

In the past year, this project has flourished in many aspects. In the synthetic effort, we have developed a series of copolymers (PSeBx) containing selenopheno[3,4-b]selenophene and benzodiselenophene. In comparison with their thiophene counterpart polymer, PTB9, the new poly(selenopheno[3,4-b]selenophene-co-benzodiselenophene (PSeB2) showed a lower band gap and improved charge carrier transportation with the hole mobility up to 1.35 x 10-3 cm2 V$^{-1}$·s$^{-1}$. The bulk heterojunction (BHJ) solar cells based on PSeB2/PC$_{71}$BM exhibited a power conversion efficiency of 6.87%, which was about 21% higher than that of its sulfur version polymer.

In the elucidation of structure/property relationship, we uncovered the local dipolar effect for designing highly efficient semiconducting polymers for OPV solar cells.

![Figure 15. Structures of polymers with different local dipole moments.](image-url)
Dipolar effect on solar cell performances:
We studied four polymers with structural differences as marked in Figure 15. Numerous physical properties of these polymers are comparable, such as the optical absorption, energy gap, energy level and morphological feature. Especially, polymer PBB3 shown in Figure 15 exhibits ideal properties necessary for a high efficiency in solar cells made of PBB3/fullerene composite. But the PCE of PBB3 is very poor as shown in Table 5.

Table 5. Properties of solar cells.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF (%)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E_{g, elec} (eV)</th>
<th>PCE (%)</th>
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<tr>
<td>PTB2</td>
<td>0.58</td>
<td>14.1</td>
<td>62.4</td>
<td>-4.94</td>
<td>-3.22</td>
<td>1.72</td>
<td>5.10</td>
</tr>
<tr>
<td>PTB7</td>
<td>0.74</td>
<td>14.5</td>
<td>68.97</td>
<td>-5.15</td>
<td>-3.31</td>
<td>1.84</td>
<td>7.40</td>
</tr>
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<td>PTBF2</td>
<td>0.68</td>
<td>11.1</td>
<td>42.2</td>
<td>-5.41</td>
<td>-3.60</td>
<td>1.81</td>
<td>3.20</td>
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<td>PBB3:C60</td>
<td>0.57</td>
<td>6.51</td>
<td>38.6</td>
<td>-4.95</td>
<td>-3.28</td>
<td>1.67</td>
<td>1.44</td>
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<tr>
<td>PBB3:C70</td>
<td>0.63</td>
<td>6.37</td>
<td>51.0</td>
<td>-4.95</td>
<td>-3.28</td>
<td>1.67</td>
<td>2.04</td>
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Table 6. Ground state, excited state dipole moments and the differences.

<table>
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<tr>
<th>Polymer</th>
<th>μg (D)</th>
<th>μe (D)</th>
<th>μtr (D)</th>
<th>Δμ_{ge} (D)</th>
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<tbody>
<tr>
<td>PTB2</td>
<td>3.60</td>
<td>6.37</td>
<td>8.50</td>
<td>2.96</td>
</tr>
<tr>
<td>PTB7</td>
<td>3.76</td>
<td>7.13</td>
<td>8.23</td>
<td>3.92</td>
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<tr>
<td>PTBF2</td>
<td>3.35</td>
<td>5.45</td>
<td>9.19</td>
<td>2.41</td>
</tr>
<tr>
<td>PBB3</td>
<td>0.61</td>
<td>0.82</td>
<td>10.62</td>
<td>0.47</td>
</tr>
<tr>
<td>P3HT</td>
<td>0.19</td>
<td>0.43</td>
<td>6.64</td>
<td>0.42</td>
</tr>
</tbody>
</table>

Detailed studies, both experimental and theoretical calculations indicated that the solar cell PCEs and calculated dipolar changes in the thienothiophene monomer units between excited state and group state correlate very well, (see Tables 5 and 6). The EQE curves for the four polymers are also consistent with local dipolar changes in the thienothiophene monomer units. The dipolar changes also explain the ultrafast spectroscopic data (Figure 15) based on the model shown Figure 16.

Figure 15. Dynamics of exciton and charge decay and EQE spectra of the four polymers.
The large local dipole change (Δµge (D) in the single thienothiophene unit in the PTB polymers renders the excited state largely polarized. The negative charge will be concentrated on the electron-deficient TT unit. When one of the monomer units bears large dipole moment change, the large negative density in excited state is concentrated on ester group where charge transfer to PCBM will occur (curved red arrow in Fig. 16). The negative charge will be transferred to PCBM and the positive charge will left on benzodithiophene unit (red cross). That explains the fast decay component of the excitonic state shown in Figure 15a, in which PTB7 and PTB2 showed the fastest electron transfer rates. After the negative charge transferred to the PCBM molecule in close contact with the TT unit, the positive charge will be likely to distribute over the electron-rich benzodithiophene (BDT) unit to avoid the dipolar field in the TT unit. This is consistent with the longer lifetime of the cationic species in PTB7 and PTB2, which makes further charge dissociation/transport easier. However, for PTBF2 polymers, the introduction of two fluorine atoms in the BDT unit makes the BDT unit more electron deficient and less compatible with positive charge. The more positive charge distribution will be forced into the TT units, which will increase the binding energy of the charge transfer complex formed. This leads to enhancement in its recombination decay rate constant, consistent with the faster recombination rate of the charge separated species in PTBF2 as shown in Figure 3b. For PBB3 polymers, a similar reason exists except that the BTT unit has an almost cancelled dipole moment and thus the electron density in the BTT conjugated system remains very high, (the BTT moiety contains 20 π-electrons over 16 atoms). Thus, it will be more accommodative to positive charge, resulting in strong binding force with negative charge in the neighboring PCBM molecule. The charge recombination rate is the highest among all of the polymers discussed. Thus, the solar cells from this polymer have the smallest Jsc, lowest EQE, and lowest PCE although all of the materials characteristics are seemingly optimal. Notably, our modeling studies of the dipole moment of monomer units as shown in Table 6 indicate that PBB3 shows a dipole moment very similar to that of P3HT. Significantly, while PCE’s of close to 5% have been achieved from P3HT,[1] the efficiencies of optimally-processed P3HT are still much lower than those of the PTB series, as well as several recent examples from the literature.[2-4] All of these polymers exhibit high efficiencies (~7%) and include comonomers bearing a substantial net dipole moment in the polymer backbone. A possible explanation for this is that P3HT displays a much greater degree of crystallinity,[5] improving efficiency due to increased exciton diffusion length. Our recent work showed that the crystallinity of PTB7 is only about ~18%, much smaller than P3HT, yet their solar cell efficiency is much higher.[6] Of course, it is important to emphasize that while a dipolar effect seems to be consistent with the evidence presented herein, it is not the only effect present in OPV polymers, and a number of parameters must be synergistically optimized in order to achieve high PCE.

In the effort of OPV device investigation, we have developed an effective approach to enhance PCE and achieved an unprecedented high PCE value around 9.4%.

Figure 16. Model that explain the dipolar effect in charge separation dynamics.
Archival publications (published) during reporting period:


8. Szarko, Jodi Michelle; Rolczynski, Brian Sano; Lee, Byeongdu; Strzalka, Joe; Guo, Jianchang; Liang, Yongye; Yu, Luping; Chen, Lin X, “When Function Follows Form: Effects of Donor Copolymer Side-Chains on Film Morphology and BHJ Solar Cell Performance”, Advanced Materials (Weinheim, Germany) (2010), 22(48), 5468-5472.


11. He, Feng; Wang, Wei; Chen, Wei; Xu, Tao; Darling, Seth; Strzalka, Joseph; Liu, Yun; Yu, Luping, Tetrathienoanthracene-based Copolymers for Efficient Solar Cells, J. Am. Chem. Soc., (2011), 133(10), 3284-3287.


Changes in research objectives, if any: None
Change in AFOSR program manager, if any: None
Extensions granted or milestones slipped, if any: None
Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none): 1
Luping Yu and Haejung Son, “SEMICONDUCTING POLYMERS”, PCT Application Pending.
1. **Report Type**
   - Final Report

**Primary Contact E-mail**  
Contact email if there is a problem with the report.  
lupingyu@uchicago.edu

**Primary Contact Phone Number**  
Contact phone number if there is a problem with the report  
773-702-8698

**Organization / Institution name**  
The University of Chicago

**Grant/Contract Title**  
The full title of the funded effort.  
NOVEL SEMICONDUCTING POLYMERS FOR HIGHLY EFFICIENT SOLAR ENERGY HARVESTING

**Grant/Contract Number**  
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".  
FA9550-09-1-0220

**Principal Investigator Name**  
The full name of the principal investigator on the grant or contract.  
Luping Yu

**Program Manager**  
The AFOSR Program Manager currently assigned to the award  
Dr. Charles Lee

**Reporting Period Start Date**  
04/01/2009

**Reporting Period End Date**  
03/31/2012

**Abstract**  
In the past three years, our research project sponsored partially by AFOSR has been focused on developing low bandgap semiconducting polymers as the donor components for BHJ solar cells. We have made very important contributions to the field and has developed a series of new semiconducting polymers with thieno[3,4-b]thiophene and benzodithiophene alternating units. They exhibited superior solar energy PCE to polymers disclosed in literature in BHJ polymer solar cells in combination with fullerene derivatives as acceptors. Solar power conversion efficiency has reached to 9.4%. In addition to those achievements, we have gained deeper insight in understanding design principles for these high efficiency polymers. In the elucidation
of structure/property relationship, we uncovered the local dipolar effect for designing highly efficient semiconducting polymers for OPV solar cells, which gives us solid design principle to search better materials.

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**Archival Publications (published) during reporting period:**


9. He, Feng; Wang, Wei; Chen, Wei; Xu, Tao; Darling, Seth; Strzalka, Joseph; Liu, Yun; Yu, Luping, Tetrathienoanthracene-based Copolymers for Efficient Solar Cells, J. Am. Chem. Soc., (2011), 133(10), 3284-3287. DOI: 10.1021/ja1110915


**DISTRIBUTION A: Distribution approved for public release.**


22. You, Jingbi; Chen, Chun-Chao; Dou, Letian; Murase, Seiichiro; Duan, Hsin-Sheng; Hawks, Steve; Xu, Tao; Son, Hae Jung; Yu, Luping; Li, Gang; Yang, Yang, “Metal Oxide Nanoparticles as an Electron-Transport Layer in High-Performance and Stable Inverted Polymer Solar Cells”, Adv. Mater., (2012), 24(38), 5267-5272, DOI:10.1002/adma.201201958, OCT 2, 2012.

Changes in research objectives (if any):

None

Change in AFOSR Program Manager, if any:

None

Extensions granted or milestones slipped, if any:

No

AFOSR LRIR Number

DISTRIBUTION A: Distribution approved for public release.
Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

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Report Document

Appendix Documents

2. Thank You

E-mail user
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Response ID: 3404

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