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Molecular Design, Synthesis, and Characterization of Low Bandgap $\pi$-Conjugated Molecules for Solution-Processed Organic Solar Cells

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Introduction
1. 1. Solar Energy and Solar Cells

The fossil fuels, which include oil, coal, and natural gas, make human life convenience and advance the industrialization. However a naturally occurring gas as well as a by-product of burning fossil fuels, land-use change, and industrial process is the mainly greenhouse gas that affects the Earth’s radiation balance. The greenhouse gas, mainly carbon dioxide (CO₂), caused global warming (Fig. 1-1) and disaster such as El Nino, change of ecosystem and melt of glacier.¹ ² In addition, the finite demand for fossil fuels and the worry about the national energy security arising from the great dependence on imported fossil fuels have made finding sufficient supplies of clean energy urgent and utmost main points in the next half-century.³ Nowadays, there are many alternative energy sources that are both clean and renewable. They are “clean” in the sense that they do not generate the greenhouse gas, mainly CO₂, or any other pollutant sources and “renewable” in the sense that they come from resources which are continually replenished on a human timescale such as sunlight solar, wind, hydro, geothermal, tidal, and bio fuels.⁴ Compared to other renewable clean energy sources, the sun is far and away the most abundant energy source. Solar energy is clean, renewable, safe, and abundant covering 0.1% of the Earth’s surface with 10% efficient solar conversion systems would be enough to power the world. To solve the energy problems, using the solar cells to directly convert clean and renewable solar to electricity is one of the key methods to obtain and convert solar energy. However, current solar technologies only provided a very small part of the world’s electricity, less than 0.1% despite its recent growth of 35-45% per years.⁵ Solar electricity is currently about 5-10 times more expensive than fossil fuel, which is main problem and limiting factor. The expensive solar cell module manufacturing and installation are two dominant cost parameters for solar technologies. Crystalline silicon wafers-based “first-generation” solar cell technologies, a substantial part of module manufacturing cost comes from the materials, most of which are already
made in high volumes and little potential for further reduction of cost. Therefore, amorphous silicon, copper indium gallium diselenide (CIGS), or cadmium telluride (CdTe)-based “second-generation” solar cell technologies have interested in economic point due to advantages of lower material costs than “first-generation” solar cell technologies. However, at least till now, such advantages are somewhat negated by the lower efficiencies of these devices.

**Figure 1-1.** Global annual average temperature (as measured over both land and oceans). Red bars indicate temperatures above and blue bars indicate temperatures below the average temperature. The black line shows atmospheric CO$_2$ concentration in parts per million (ppm). Adapted from [6].
Several different “third-generation” solar cell with ultrahigh efficiencies and ultra-low costs have been proposed, which if successfully demonstrated, would significantly reduce the cost-to-efficiency ratio and make solar electricity competitive against or even cheaper than fossil fuel generated electricity. Cost efficiency analysis for each of the first, second, and third generations are shown in Fig. 1-2. “Third-generation” solar cells could reduce the costs of materials, module manufacturing and installation, by significantly increasing efficiencies but maintaining the economic and environmental cost advantages of thin-film deposition techniques. To increase the efficiency strongly leverages lower costs, such that efficiency values well above 30% could dramatically decrease these costs per Watt.

![Figure 1-2](image)

**Figure 1-2.** Cost efficiency analysis for first (I), second (II), and third (III) generation solar cells. (Wafer-based, thin films, and advanced thin films, respectively.)
1.2. History of Solar Cells

In 1839, the photovoltaic effect was discovered by Becquerel\textsuperscript{8,9} while experimenting with an electrolytic cell composed of two metal electrodes placed in an conducting-electricity solution-electricity-generation increased when exposed to light. Fuller discovered that upon introduction of atoms with different valence electron number, he could convert the silicon from an average to a superior conductor of current. Pearson and Chapin develop the silicon solar cell at Bell Labs-the first solar cell capable of converting enough of solar energy into power to run everyday electrical equipment.\textsuperscript{10,11} The first step of device fabrication was the introduction of a small amount of arsenic into the silicon. Then, boron was introduced only in a very thin layer close to the surface. Boron has one valence electron less than silicon and produces p-doped silicon when used as dopant.\textsuperscript{12} Nowadays, the highest power conversion efficiency (PCE) reported for silicon-based solar cells is 25%.\textsuperscript{13} However, a major problem of this technology is the high costs of solar cell materials, module manufacturing and installation. To absorb the sunlight, the thickness of silicon wafers is required for 200-300 \textmu m, due to weak absorption ability. To solve the problems, many research groups focused on good absorption materials for thin film solar cells. Amorphous silicon-based solar cells with thickness of only 5-8 \textmu m are sufficient to absorb 90% of the solar light. Amorphous silicon, CIGS and CdTe are semiconductors used in thin film solar cells and show PCEs of 10.5, 12.5 and 16.7%, respectively. Even if the use of thin film solar cell technologies reduce the manufacturing cost, the PCEs remain lower than that of crystalline silicon solar cells. High efficient inorganic solar cells can be obtained by stacking multiple thin films, each one absorbing a different part of the solar spectrum. To date, the most efficient solar cell device uses a gallium arsenide (GaAs)/germanium (Ge)/gallium indium phosphide (GaInP\textsubscript{2}) triple configuration and reaches ~32% PCE.\textsuperscript{14} Within the perspective of manufacturing cost reduction and large scale installation, \pi-conjugated organic materials have gained interest.
of research. In 1977, Heeger, McDiarmid, and Shirakawa\textsuperscript{15,16} discovers the conductivity from $\pi$-conjugated polymers, and have enabled the use of $\pi$-conjugated polymers in solar cells and more generally in organic electronics. While inorganic semiconductors produce free electrons and holes upon illumination at room temperature, light absorption in organic semiconductors results in the formation of a tightly bound charge pair called an exciton. The low dielectric constant of organic materials results in a strong Coulombic interaction between the electron and the hole. The binding energy is typically around 0.3-0.4 eV\textsuperscript{17} which is much larger than thermal energy (0.025 eV) and makes the charge separation quite difficult. As a direct consequence, earlier solar cells were exhibiting rather poor performance around 0.3\% PCE.\textsuperscript{18} The breakthrough came in 1986 when Tang\textsuperscript{19} introduced a hetero-junction by evaporating two materials on top of each other in so-called bilayer architecture. The important step is the introduction of a second material with different electron affinity and ionization potential. The resulting electric field across the interface is the driving force for exciton dissociation. The electron is transferred into the material with the lowest reduction potential, also called electron acceptor material, while the hole remains in the material with the highest ionization potential, also called electron donor material. However, PCEs remained below 1\%. The main reason is the rather short lifetime of excitons. They can diffuse 10-20 nm\textsuperscript{20,21} before they decay while the typical thickness of a bilayer solar cell should be ~100 nm to absorb all sunlight. Hence, only the excitons formed close to the interface can be dissociated and contribute to the current. The others will decay before they can reach the junction and are then lost. A step forward in terms of PCE has been made after Sariciftci \textit{et al.} reported evidence for fast photo-induced charge transfer from conducting polymers onto buckminster fullerenes ($C_{60}$).\textsuperscript{22,23,24} In this work, Sariciftci formulated the idea that forming an interpenetrating network by mixing electron donor and acceptor compounds in situ would be ideal. By blending the two materials, the active layer results in a bicontinuous network in which the interface is distributed all over the bulk, allowing for quantitative exciton dissociation.
The first bulk hetero-junction (BHJ) solar cells were manufactured simultaneously in 1995 by Halls\textsuperscript{25} and Yu.\textsuperscript{26} Further improvement has been achieved by Shaheen \textit{et al.} in 2001\textsuperscript{27}, showing that the processing solvent dramatically affects the PCE of a solar cell. Solar cell efficiencies obtained for various materials and technologies are shown in Fig. 1-3.

\textbf{Figure 1-3.} Solar cell efficiencies obtained for various materials and technologies. Adapted from [28].
1.3. Organic Solar Cells

The “third-generation” organic solar cell (OSC) is based on $\pi$-conjugated organic materials, including small-molecules, oligomers, and polymers. $\pi$-Conjugation in organic materials leads to an energy difference between the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs), respectively, somewhere in the range of 1-3 eV, thus exhibiting semiconducting property and strong interactions with visible and near infrared light. OSCs can be easily fabricated into thin films through inexpensive room temperature processes. They are compatible with flexible substrates that can be light weight and inexpensive, which not only makes them suitable for high throughput, low cost roll-to-roll processing, but will greatly reduce the module installation costs. Hence, organic semiconductors are particularly suited for flexible, low cost, light weight, and large area device applications, such as OSCs. Those technological advantages have attracted many researchers to study the physical properties of organic materials and their potential applications in electronic and optoelectronic devices. Many organic devices have been developed over the last two decades, including OSCs, organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs), organic photodetectors, organic lasers, and organic memories. With the introduction of new materials and device structures, the PCE of OSC devices have progressed steadily in the last decade, reaching nearly 9% in state-of-the-art laboratory devices.
1. 4. Operation Principle of Organic Solar Cells

Solar cell devices convert sunlight into electricity from four different photophysical processes in electron donor/acceptor (D/A) between light absorption and exciton generation, exciton diffusion, charge separation and charge transportation and collection at electrodes. Fig. 1-4 illustrates the photon to current conversion processes.

**Figure 1-4.** Schematic representation of the different steps during the photon to current conversion processes of free charges in a donor (D)/acceptor (A) organic solar cell.

1. 4. 1. Light Absorption and Exciton Generation

When electron donor material absorbs the solar energy with larger than energy bandgap of the electron donor materials, electrons in electron donor materials are excited from the HOMO energy level to the LUMO energy level. In this process, electron donor materials in the photoactive layer absorb the incident light depends on the value of the optical absorption coefficient, the thickness of the photoactive layer and the energy band gap of materials. After absorbing the photons, bounded electron and hole pairs, called exciton, are generated rather than creation of free charge carrier. Due to low dielectric constant compared to inorganic semiconductor, strongly bound Frenkel-like localized excitons are generated. 36,37
1. 4. 2. Exciton Diffusion

These excitons can diffuse inside electron donor in the exciton diffusion length which characterizes the effective width of the active area of electron donor film at electron acceptor interface. General exciton diffusion length ($L_D$) of electron donor is around 10-20 nm.\textsuperscript{38,39} The efficiency of exciton diffusion is smaller than 1 in the thick electron donor materials, because various recombination processes can occur in the material.

1. 4. 3. Charge Separation

When an exciton within the exciton diffusion length reaches the interface between an electron donor and acceptor, a fullerene-based material such as PCBM, electron transfer occurs from the LUMO energy level of electron donor to the LUMO energy level of electron acceptor, leaving a hole on the HOMO energy level of electron donor because the electron affinity of electron acceptor is stronger than that of electron donor. Thus excitons are dissociated into free charge carriers which can diffuse in the active materials. This behavior is much faster than any competing relaxation processes. To get efficient charge separation, the HOMO and LUMO energy levels of the electron donor should be 0.3 eV higher than that of the electron acceptor. If the offset is too small, it would be hard to get efficient charge separation. On the other hand, if the offset is too large, much energy loss would occur.\textsuperscript{40}

1. 4. 4. Charge Transport and Collection at Electrodes

Once the charges are dissociated, they have to travel to the respective electrodes (anode contact for the holes and cathode contact for the electrons) to generate electrical current. The first requirement is that the morphology of the materials blend should provide a
pathway for the charges to reach the electrodes. Second, the materials should possess a rather high carrier mobility to efficiently transport the charge carriers. If charge transport is slow or impeded, bimolecular charge recombination may occur which reduces the device performance. To enhance charge collection, the hole collecting electrode should form an Ohmic contact with the HOMO energy level of electron donor and likewise for the electron collecting contact and the LUMO energy level of electron acceptor.

1. 5. Device Structures

The basic structures of solar cells are shown in Fig. 1-5; to create a working solar cell, the photoactive material (D/A) is sandwiched between two dissimilar (metal) electrodes (of which one is transparent), to collect the photogenerated charges. Indium tin oxide (ITO), which fulfills this transparency requirement, is generally used as an electrode. Two metallic electrodes have different work functions, and this creates an electric field across the active material, which may assist to sweep away excited charge carriers generated in the active material. There is no generally consistent understanding within the literature as to how much the device parameters, particularly the open-circuit voltage, are affected by the energy levels of the electrodes and the active material.

1. 5. 1. Bilayer Devices (Planar-Junction Devices)

In a bilayer device, electron donor and acceptor materials are stacked sequentially and sandwiched between two electrodes. Charge separation occurs at the interface between the two active materials, with the HOMO and LUMO energy levels of electron donor higher than those of electron acceptor. After the excitons are dissociated the electron travels within electron acceptor and the hole through electron donor material. Thus the
opposite charges are physically separated from each other and unlikely to recombine.

![Figure 1-5. Solar cells device structures of the (a) planar-junction, (b) bulk hetero-junction, (c) inverted, and (d) tandem devices.](image)

1. 5. 2. Bulk Hetero-Junction Devices

The idea of a bulk hetero-junction (BHJ) device is to blend electron donor and acceptor materials so that an absorbing site is always within an exciton diffusion length of an interface. Electron donor and acceptor phases have to form an interpenetrating and
bicontinuous network in order for the separated charges to have a percolation path to the electrode, as shown in Fig. 1-5b. Whilst this structure has the potential for high efficiency, BHJ devices are very sensitive to morphology changes as isolated domains can trap charges, hence leading to recombination.

1. 5. 3. Inverted Devices

In the normal structure of a solar cell, holes and electrons are injected into transparent ITO and cathode (e.g., Al), respectively. In contrast, in the inverted structure, electrons are injected into ITO while holes are collected by the top electrode (e.g., Ag), which can be less air sensitive, high work function metal electrode such as silver or gold. At the ITO interfaces, electron transporting layer such as ZnO and TiO$_2$, and have been applied as an electron-selective contact. The high electron mobility of ZnO nanoparticles makes it an ideal electron-selective contact layer for inverted device.$^{43,44}$

1. 5. 4. Tandem Devices

The tandem device consists of a front cell with a wide band gap (active layer 1) and a rear cell with a low band gap (active layer 2). The organic molecular band gap for each subcell should be selected carefully to achieve high performance tandem solar cells. The tandem solar cells can address the limitations of single BHJ solar cells because a broader spectrum of solar radiation can be covered. Furthermore, thermal losses are reduced, since high energy photons are converted by the large band gap subcell, providing a high open-circuit voltage ($V_{oc}$), while low energy photons are converted by the low band gap subcell at a lower $V_{oc}$. The $V_{oc}$ of an optimized tandem cell is the sum of $V_{oc}$ of the individual subcells.$^{45,46}$
1.6. Solar Cell Parameters

Solar cell devices convert sunlight into electricity. The power conversion efficiency (PCE) of a cell, \( \eta \), is the ratio of the maximum power generated by the device \( (P_{\text{out}}) \) to the incident power \( (P_{\text{in}}) \), due to sunlight, and is generally expressed as a percentage.

\[
\eta = \frac{P_{\text{out}}}{P_{\text{in}}}
\]

The incident power is a function of the solar spectrum, and is generally given in terms of air-mass (AM) which is defined to be:

\[
\text{AM} = \frac{1}{\cos\theta}
\]

where \( \theta \) is the incident angle of the sun, measured from directly overhead. The AM gives an indication of the amount of atmosphere which the light has passed through to reach the surface of the Earth. The standard for device testing is AM 1.5, which corresponds to an angle of 48.2\(^\circ\), and a total power density of 100 mW/cm\(^2\). The AM 1.5 spectrum is shown in Fig. 1-6. Experimentally, the power generated by a device is calculated from its current density versus voltage \( (J-V) \) curve, an example BHJ OSC device based on poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)car-bonyl]thieno[3,4-b]thiophenediyl] (PTB7) and phenyl-C\(_{71}\)-bupyric acid methyl ester (PC\(_{71}\)BM) of which is shown in Fig. 1-7. The power generated is:

\[
P_{\text{out}} = J_{\text{mp}} \cdot V_{\text{mp}}
\]

where \( P_{\text{out}} \) is given by the product of \( J_{\text{mp}} \) and \( V_{\text{mp}} \) (see Fig. 1-7). Alternatively, \( P_{\text{out}} \) can be expressed as:
\[ P_{\text{out}} = V_{\text{oc}} \cdot J_{\text{sc}} \cdot \text{FF} \]

From the \( J-V \) curve, four important parameters can be deduced. The current density under illumination at zero bias is called the short-circuit current density \( (J_{\text{sc}}) \). The voltage where the current density under illumination is zero is defined as the open-circuit voltage \( (V_{\text{oc}}) \), and the fill factor (FF) is related to the maximum power that can be obtained from the device.

**Figure 1-6.** AM 1.5 solar spectrum. Many of the deep minima in this spectrum are due to absorption within the Earth’s atmosphere.
Figure 1-7. Typical current-voltage characteristics under AM 1.5 G condition from PTB7-based solar cells.

1. 6. 1. Short-Circuit Current Density ($J_{sc}$)

The $J_{sc}$ is determined by the amount of absorbed light and the internal conversion efficiency. The current is delivered by photogenerated free charge carrier and the number of free charge carrier is mainly related to absorption of photon, formation of excitons, and dissociation of excitons. In order to increase the absorption of photon, the absorption spectrum of an electron donor material should be matched to longer wavelength of the solar emission spectrum and hence harvest the maximum photon flux. Absorption of electron donors can increase through narrowing their optical band gap. Thus, low band gap molecules are good candidates as electron donor materials. Also, by replacing PC$_{61}$BM with asymmetrical PC$_{71}$BM which have much higher absorption coefficient, it leads to higher absorption at the shorter wavelength. For efficient dissociation of excitons,
it is known that the energy difference between the LUMO energy levels of electron donor and acceptor should be larger than 0.3 eV for efficient charge separation. Also, the morphology of electron donor-acceptor blend influences the dissociation efficiency of photogenerated excitons and the collection efficiency of the free charge carriers. Finally, the photocurrent is dependent on the charge carrier mobility in the active layer. The charge-carrier mobility of electrons and holes in electron donor-acceptor blend must be high enough to allow efficient charge extraction. The hole mobility in electron donors is lower than electron mobility in PCBM, because holes are conducted via thermally activated intermolecular hopping of highly localized charge carriers. In order to obtain much higher $J_{sc}$, hole mobility in the blend composite must be improved.

1. 6. 2. Open-Circuit Voltage ($V_{oc}$)

The $V_{oc}$ is the difference of electrical potential between two terminals of a device when there is no external load connected, i.e. the circuit is broken or open. It is the maximum voltage available from a solar cell, and this occurs at zero current density. In OSCs, active layer composited with PCBM and electron donors modifies the nature of the thin film devices, compared to those made from electron donor alone. The $V_{oc}$ in OSCs is directly related to electron acceptor strength and the influence of the work function of the cathode on the $V_{oc}$ is considerably weaker. The $V_{oc}$ is directly proportional to energy difference between the HOMO energy level of electron donor materials and the LUMO energy level of electron acceptor materials as shown in Fig. 1-8. Once PCBM is used as an electron acceptor materials, deeper HOMO energy level of electron donor should be employed to achieve higher $V_{oc}$ in OSC performance.
1. 6. 3. Fill Factor (FF)

The FF in solar cells is defined as:

\[ FF = \frac{V_{\text{max}} \cdot J_{\text{max}}}{V_{\text{oc}} \cdot J_{\text{sc}}} \]

where \( V_{\text{max}} \) is the voltage at maximum power, and \( J_{\text{max}} \) is the current density at maximum power. The FF gives a good indication of the performance of the device as shown in Fig. 1-9. FF is influenced by various parameters such as the choice of electrodes, morphology and thickness of active layer, mobility of the active materials and interface between electrodes and the blend layer. It is mainly influenced by the series resistance (\( R_s \)) and the shunt resistance (\( R_{\text{sh}} \)) of the cells as shown in Fig. 1-9. \( R_s \) is related with the intrinsic resistance, morphology, and thickness of the active layer, but \( R_{\text{sh}} \) is related with impurities and defects in the active layer because it causes charge recombination and leakage current.
I. 6. 4. Power Conversion Efficiency (PCE, $\eta$)

The PCE of the solar cells is defined as:

$$\eta = \text{FF} \cdot \frac{V_{oc} \cdot J_{sc}}{P_{in}}$$

The external quantum efficient (EQE) or incident photon to collected electron (IPCE) is determined by the ratio of collected charge carriers per incident photons where is expressed in nanometers.
\[
\eta_{\text{EQE}} = \eta_A \cdot \eta_{\text{ED}} \cdot \eta_{\text{CT}} \cdot \eta_{\text{CC}} = \eta_A \cdot \eta_{\text{IQE}} = \text{IPCE} (\%) = \frac{I_{\text{sc}}(A)}{P(W)} \cdot \frac{1240}{\lambda} \cdot 100
\]

This value can be further corrected by different losses like reflection from the glass surface and absorption by different nonphotoactive layers involved in the device to illustrate the internal quantum efficiency (IQE). Where \( \eta_A, \eta_{\text{ED}}, \eta_{\text{CT}}, \) and \( \eta_{\text{CC}} \) are the efficiency of photon absorption, exciton diffusion to electron donor/acceptor interface, exciton dissociation by charge transfer and charge collection at the electrodes, respectively.

1.7. Electron Donor Materials

The chemical structures of electron donors which are commonly used in BHJ solar cells are shown in Fig. 1-10. Generally, the optical absorption coefficient of electron donors is larger than that of inorganic materials such as silicon. Contrastively, the band gap of electron donors is much larger than that of inorganic counterparts. Thus, the absorption bandwidth of electron donor materials is too narrow to absorb a large fraction of the solar spectrum. Therefore, the band gap of electron donors must be lowered for light harvesting up to longer wavelengths. An increase in PCE does not solely rely upon an improved current density; a high \( V_{\text{oc}} \) and a reasonable FF are also required. Unfortunately, because \( V_{\text{oc}} \) is ultimately limited by the difference between the HOMO energy level of electron donor and the LUMO energy level of electron acceptor, lowering of band gap energy is accompanied by a decrease of \( V_{\text{oc}} \), canceling the benefit of an absorption increase. The LUMO-LUMO offset of electron donor and acceptor is much larger than the 0.3 eV which is necessary for the electron transfer to occur. By reducing this excess of LUMO-LUMO offset, a large increase in device efficiency can be obtained without loss of \( V_{\text{oc}} \). In order to reduce the offset, two strategies can be employed into the energy level of electron donor.
Firstly, the LUMO energy level of electron donor can be lowered resulting in the low band gap electron donors. Alternatively, both the LUMO energy level and the HOMO energy level of electron donor can be lowered. In this case the band gap of electron donor remains constant but the device gains in efficiency due to larger $V_{oc}$.

**Figure 1-10.** Chemical structures of efficient electron donors including $\pi$-conjugated organic molecules.
Also, the inefficient performance of low band-gap electron donor materials is often associated with their lower hole mobility in the blend or poor solubility. The alkyl or alkoxy groups attached on electron donors make the rigid $\pi$-conjugated organic materials soluble in common organic solvents. This allows these $\pi$-conjugated organic materials to be cast via solution process techniques.

1.8. Electron Acceptor Materials

The chemical structures of electron acceptors which are commonly used in BHJ solar cells are shown in Fig. 1-11. Currently, one of the best electron acceptor materials for BHJ OSCs is fullerene compounds. The most widely used electron acceptor, buckminsterfullerene ($C_{60}$), is a good electron acceptor, however, the solubility of $C_{60}$ is limited in common organic solvent. To improve the solubility, Wudl et al. synthesized soluble derivative of $C_{60}$, phenyl-$C_{61}$-boryric acid methyl ester (PC$_{61}$BM). An approach to extend the photocurrent spectrum has been proposed by changing electron acceptor in the BHJ OSC, except utilizing a low band gap polymer. Some improvement of photocurrent was observed when the PC$_{61}$BM is replaced by a less symmetrical fullerene PC$_{71}$BM without loss of $V_{oc}$. This enhancement can be contributed to the broader and higher absorption of PC$_{71}$BM compared with that of PC$_{61}$BM. The low absorption coefficient of PC$_{61}$BM can be attributed to a high degree of symmetry which forbids the lowest energy transition. Therefore, when the PC$_{61}$BM is replaced by a less symmetrical fullerene PC$_{71}$BM, the transition will become apparent and a significant increase in light absorption can be expected. Some improvement of photocurrent was observed when the PC$_{61}$BM is replaced by a less symmetrical fullerene PC$_{71}$BM without loss of $V_{oc}$. This enhancement can be contributed to the broader and higher absorption of PC$_{71}$BM compared with that of PC$_{61}$BM. The low absorption coefficient of PC$_{61}$BM can be
attributed to a high degree of symmetry which forbids the lowest energy transition. Therefore, when the PC$_6$BM is replaced by a less symmetrical fullerene PC$_7$BM, the transition will become apparent and a significant increase in light absorption can be expected. The LUMO energy level of PC$_7$BM is almost same with that of PC$_6$BM, so open-circuit voltage of the cells which used PC$_7$BM is not different compared with that used PC$_6$BM. As well as the donor, LUMO-LUMO offset can be reduced by raising the LUMO energy level of electron acceptor.

**Figure 1-11.** Chemical structures of efficient electron acceptors including fullerenes and non-fullerenes derivatives.
1. 9. Motivation and Outline of This Thesis

Harvesting energy from sunlight directly using solar cell technology is considered as being one of the most important ways to address growing global energy needs using a renewable resource. Organic solar cell (OSC) is the one of alternative for producing clean and renewable energy because it can be fabricated onto large areas of light-weight flexible substrates by solution processing at a low cost. Thus, an important research area is the development of new efficient materials for solar cells. Ideally these materials will lead to devices which are cheaper to fabricate and require less energy to produce than silicon solar cells. Possible alternatives to silicon solar cells include semiconductor thin films, the dye-sensitized solar cell (DSSC), and thin films of organic materials such as π-conjugated polymers, oligomers, or small-molecules.

In this thesis, the author concentrates on the development of new π-conjugated electron donating molecules for solution-processed OSCs. π-Conjugated materials are inherently inexpensive and can be processed using high throughput, low temperature processes such as printing. They have high absorption coefficients, and this allows thin films to be used and hence lowers material costs. The synthesis of such molecules is very flexible and allows electronic parameters and solubility to be controlled. In addition, there is the possibility of using flexible plastic substrates for OSCs, making the structure for more versatile than conventional silicon solar cells. There are several classes of π-conjugated materials which are promising for OSC applications. Nowadays, the potential of soluble diketopyrrolopyrrole (DPP)-based molecules has been explored with promising results in OSCs.\textsuperscript{60,61,62} The electron-withdrawing effect of the aromatic imide units causes the chromophore to have a high electron affinity and thus, it can be used as a strong electron-deficient unit. In addition, strong electron-deficient moiety, DPP unit, for donor/acceptor (D/A) type molecules show a high absorption coefficient because of their strong intramolecular charge transfer (ICT) characteristics.
To improve the OSC performance, the author focuses on the molecular design, synthesis and characterization of DPP-based electron-donating small and oligomeric molecules for efficient solution-processed OSCs. Our intention here is to utilize self-organization of liquid-crystalline (LC) characteristics and high absorption capability of A-π-D-π-A type molecules for the fabrication of bulk hetero-junction (BHJ) structures in OSCs, for achieving high photovoltaic performance.

In chapter 2, self-organization of LC molecules is utilized for the fabrication of well-ordered BHJ architectures in small-molecule OSCs. For the small-molecular system, the important advantages are monodispersity and well-defined structure, easy purification, and less batch-to-batch variation (better reproducibility), but the main problems are inferior film quality and interconnectivity in the active layer due to their intrinsic crystalline nature, which results in low device fill factors. If the scale of the phase-segregated domains in the BHJ layer is smaller than the Coulomb capture radius, it will increase the geminate or bimolecular recombination probability. Therefore, the self-organizing LC DPP-based donor molecules (DPP-TP6 and DPP-TP12) with low bandgap and deep HOMO energy level are synthesized and characterized. DPP-TP6 showed liquid crystalline property, and thus intermolecular orientation can be controlled through thermal annealing. The $J_{sc}$ and FF values have increased significantly for the DPP-TP6-based devices through the LC organization process.

In chapter 3, to further enhance the photovoltaic properties, A-π-D-π-A long π-extended narrow-bandgap oligomers, BDT-DPP, IDT-DPP, and T-DPP, having high absorption coefficient are designed and applied to BHJ structures in OSCs. In addition, the impacts of these different central cores on their photophysical and morphological properties, carrier mobility, and photovoltaic performance are investigated. For oligomeric system, limited photovoltaic performance factor is a relatively low current density, which is
partially due to a poor spectral overlap between the absorption of the active layer and solar irradiation. Therefore, spectral overlap between solar spectrum and absorption range of the electron donor material is very important factor for enhancing the efficiency. The design of A-π-D-π-A structures enable to further lower the optical band gap, by interconnecting electron-donating unit with electron-deficient units, as a result of the strong donor-acceptor ICT. To improve the device performance, the effects of additive on photovoltaic performance are also investigated, in which the molecular packing and film surface morphologies are strongly affected by the central donor units. The $J_{sc}$ and FF values can increase significantly for the BDT-DPP-based devices with use of an additive.
References

(1) “Protect health from climate change”, *World Health Organization*-World Health Day 7th April, 2008.


(6) “Global Climate Change” in the report, *Global Climate Change Impacts in the United States*, page 17 of the chapter.


Self-Organizing Mesomorphic Diketopyrrolopyrrole Derivatives for Efficient Solution-Processed Organic Solar Cells
2.1. Introduction

Organic solar cells (OSCs) are drawing considerable interest for the great promise as a next-generation clean and renewable energy source.\textsuperscript{1,2} To date, intensive research efforts have focused on developing dye-sensitized solar cells,\textsuperscript{3} low bandgap polymer/fullerene bulk hetero-junction (BHJ) solar cells,\textsuperscript{4} and vacuum-deposited small-molecule solar cells.\textsuperscript{5,6,7} Recently, solution-processed small-molecule OSCs\textsuperscript{8,9,10} have been emerging as an attractive alternative to widely studied polymeric counterparts, offering several promising advantages such as monodispersity and well-defined structure, easy purification, and less batch-to-batch variation (better reproducibility). Indeed, high power conversion efficiencies (PCEs) exceeding 6\% have been accomplished thus far for small-molecule BHJ OSCs,\textsuperscript{11,12} approaching those with conjugated polymers. However, overall performance of solution-processed small-molecule devices still lags behind alternative sources. In most cases, the small molecular system suffers from inferior film quality and interconnectivity in the active layer due to their intrinsic crystallization, which results in low device fill factors. Because of the relatively large exciton binding energy (e.g., 0.3 eV) and short exciton diffusion length (e.g., 10-20 nm) in organic semiconductors, a large donor/acceptor (D/A) interfacial area should be required for efficient exciton dissociation and charge carrier transport in BHJ OSCs.\textsuperscript{13,14} However, if the scale of the phase-segregated domains in the BHJ layer is smaller than the Coulomb capture radius, it will increase the geminate or bimolecular recombination probability.\textsuperscript{15} Therefore, the design of suitable donor molecules, which are capable of forming nanoscale ordered structures and overall optimum film morphologies, is a prerequisite for high-performance BHJ OSCs. Our intention here is to utilize self-organization of liquid-crystalline (LC) molecules\textsuperscript{16,17} for the fabrication of well-ordered BHJ architectures in small-molecule OSCs, to achieve better photovoltaic efficiencies. There has been a few researches conducted on tuning the active layer morphology by using LC donor molecules.\textsuperscript{18,19} As a
platform to explore this approach, diketopyrrolopyrrole (DPP)-based small-molecules, DPP-TP6 and DPP-TP12, have designed and synthesized, since the incorporation of multiple flexible chains into the rigid π-conjugated DPP core can provide highly light-absorbing electron donor materials forming LC ordering. Various DPP-based small-molecules and polymeric materials have been developed to render high charge carrier mobility and photovoltaic properties.

In this chapter, photophysical and self-organizing properties of DPP-TP6 and DPP-TP12 as well as their performance as donor materials in OSCs, are studied. Moreover, the author demonstrates that the formation of well-developed nanostructured domains through LC organization has a drastic impact on the photovoltaic properties.

2.2. Synthesis and Thermal Properties

DPP-TP6 and DPP-TP12 were synthesized from dithienyl-DPP precursor (3), using palladium-catalyzed Suzuki-Miyaura cross-coupling reactions (Scheme 2-1). To make donor molecules with a deeper HOMO energy level suitable for OSC applications, the phenylthiophene-appended DPP was designed as the low bandgap π-conjugated core and was tethered with multiple alkyl chains, which enhance solubility and film-forming properties. As expected, DPP-TP6 and DPP-TP12 are soluble in common organic solvents such as chloroform, THF, toluene, and chlorobenzene.
Thermogravimetric analysis (TGA) indicates that DPP-TP6 and DPP-TP12 possess high thermal stability with a 5% weight loss temperature ($T_d$) greater than 360 °C under N₂ atmosphere (Fig. 2-1a). Thermal behaviors of these compounds have been further studied by differential scanning calorimetry (DSC). As shown in Fig. 2-1b, DPP-TP6 with hexyl terminal chains exhibits two endothermic peaks at 117 and 170 °C upon heating, corresponding to LC mesophase and isotropic phase transitions, respectively.
The crystalline-to-mesomorphic phase transition of DPP-TP6 at 117 °C was accompanied by transformation from $J$-aggregates into the thermodynamically favored $H$-aggregates on heating, with a relatively small enthalpy change ($\Delta H = 3$ kJ/mol). However, upon cooling from the isotropic phase, DPP-TP6 ends to form kinetically favored $J$-aggregates predominantly. Thus, the $H$-aggregation stats can be regarded as a monotropic LC mesophase; so that no clear endothermic transition peak could be observed upon cooling. In DPP-TP12, the introduction of dodecyl chains on both terminals results in a decrease of the isotropization temperature to 128 °C and the LC mesophase disappears.
2. 3. Photophysical Properties

![Figure 2-2](image)

**Figure 2-2.** UV/Vis absorption spectra of (a) DPP-TP6 and (b) DPP-TP12 in CHCl₃ solution and an as-spun thin film.

The UV/Vis absorption spectrum of DPP-TP6 in CHCl₃ solution presents an absorption peak ($
\lambda_{\text{max}}$) at 602 nm (Fig. 2-2a), which corresponds to the $\pi-\pi^*$ (HOMO $\rightarrow$ LUMO) transition. The structured absorption is likely intrinsic to a single molecule with restricted intramolecular motion. Compared with dilute solutions, a spin-coated thin film of DPP-TP6 exhibits a red-shifted $\lambda_{\text{max}}$ at 637 nm with a large maximum absorption coefficient of $4.7 \times 10^4$ cm$^{-1}$, and a distinct subpeak at 581 nm. The red-shift of the lowest vibronic band in the solid state originates from $J$-type aggregation, due to the excitonic coupling between the transition dipoles of adjacent molecules. The absorption bands thus extend from 500 nm to a lower energy level of ~700 nm in the thin films of DPP-TP6 and DPP-TP12, and their optical bandgap is estimated to be 1.8 eV from the absorption edge. The HOMO energy levels of DPP-TP6 and DPP-TP12 in the thin films have been determined to be approximately $-5.5$ eV by photoelectron yield spectroscopy. The low-lying HOMO energy levels and sufficient LUMO offsets (>0.6 eV), allow these materials to serve as electron donors in combination with PC$_{71}$BM as an acceptor material, which has HOMO and LUMO energy levels of $-6.1$ and $-4.3$ eV, respectively. The optical data of DPP-TP6
and DPP-TP12 are summarized in Table 2-1. To clarify how the thermotropic LC behavior can affect the molecular assembly and photophysical properties, the absorption spectra of DPP-TP6:PC\textsubscript{71}BM and DPP-TP12:PC\textsubscript{71}BM (1:1, w/w) blend films have been measured by varying the thermal annealing temperatures (Fig. 2-3). The blend films were deposited by spin-coating from CHCl\textsubscript{3} solutions, with a donor concentration of 7-8\% (w/v). It should be noted that the absorption coefficient of the \textit{J}-aggregation band at ~640 nm observed for the as-cast DPP-TP6:PC\textsubscript{71}BM film steadily decreases and at the same time a new absorption band centered around 540 nm emerges, as the annealing temperature increases to 140 °C (Fig. 2-3a).

**Table 2-1.** Optical properties of DPP-based materials

<table>
<thead>
<tr>
<th>compound</th>
<th>absorption ( \lambda_{\text{max}} ) (nm)</th>
<th>HOMO\textsuperscript{c}</th>
<th>LUMO\textsuperscript{d}</th>
<th>( E_g )\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solution\textsuperscript{a}</td>
<td>film\textsuperscript{b}</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
<td>DPP-TP6</td>
<td>602, 563</td>
<td>637, 581</td>
<td>−5.50</td>
<td>−3.69</td>
</tr>
<tr>
<td>DPP-TP12</td>
<td>603, 563</td>
<td>651, 592</td>
<td>−5.48</td>
<td>−3.68</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In CHCl\textsubscript{3} solution at 10\textsuperscript{−4} M. \textsuperscript{b}Spin-coated thin film (ca. 100 nm). \textsuperscript{c}Determined by photoelectron yield spectroscopy. \textsuperscript{d}LUMO = HOMO + \( E_g \), in which the optical energy gap, \( E_g \), was derived from the absorption onset of the thin film.

**Figure 2-3.** Changes in absorption spectra of (a) DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) and (b) DPP-TP12:PC\textsubscript{71}BM (1:1, w/w) blend thin films upon thermal annealing.
This hypsochromic shift of the absorption band is the defining characteristic of \( H \)-type aggregation.\(^{26} \) Therefore, upon thermal treatment, the \( J \)-aggregates comprised of the DPP-TP6 molecules eventually transform into the thermodynamically favored \( H \)-aggregates, accompanied by specific stacking changes within the thin film. This thermo-responsive reorganization behavior for DPP-TP6 is in accordance with the appearance of the LC state from 117 °C upon heating (Fig. 2-1), in which the DPP-TP6 molecules retain at least some mobility. However, for DPP-TP12:PC\(_{71}\)BM films, the initial peak position and absorption intensity do not change significantly by thermal annealing (Fig. 2-3b), suggesting that the DPP-TP12 molecules with longer dodecyl chains predominantly form slipped-stacking \( J \)-aggregates in the thin films over a wide range of temperatures. The difference in the terminal chain length has a strong impact on the mesomorphism and self-organizing behavior of the donor molecules both in the neat and the BHJ thin films.

2.4. Photovoltaic Properties

Solution-processed BHJ solar cells have been fabricated using DPP-TP6 and DPP-TP12 as an electron donor and PC\(_{71}\)BM as an acceptor with a standard device structure (Fig. 2-4): ITO/PEDOT:PSS (40 nm)/donor:PC\(_{71}\)BM blend (90-120 nm)/LiF (1 nm)/Al (100 nm). Various donor:PC\(_{71}\)BM blend ratios (1:1, 1.5:1, and 2:1, w/w), film thickness, and post-deposition thermal annealing have been examined. Table 2-2 summarizes the photovoltaic parameters of representative BHJ devices obtained under AM 1.5 G illumination at an intensity of 100 mW/cm\(^2\). These devices provide reasonably high open-circuit voltages (\( V_{oc} \)) of \(~0.93 \) V, regardless of the D/A weight ratio, which is attributed to a large difference (\(~1.2 \) eV) between the HOMO energy level of the donors and the LUMO energy level of the PC\(_{71}\)BM acceptor\(^{27} \) (Fig. 2-4).
Fig. 2-5a depicts the current density-voltage (J-V) characteristics of as-cast and annealed DPP-TP6:PC71BM (1:1, w/w) BHJ solar cells. The optimized device based on the DPP-TP6:PC71BM layer with annealing at 140 °C, exhibits a short-circuit current density ($J_{sc}$) of 8.4 mA/cm$^2$, $V_{oc}$ of 0.93 V, and a fill factor (FF) of 0.55, yielding a power conversion efficiency (PCE) of 4.3% (Table 2-2); whereas the as-cast device gives a much lower PCE of 2.6%. It can be found that for DPP-TP6-based devices, thermo-responsive LC molecular organization improves $J_{sc}$ and FF, significantly increasing device efficiencies. The substantial increases in $J_{sc}$ and FF should be attributed to the reduction of series resistance ($R_s$) and the increase of shunt resistance ($R_{sh}$) of the devices, upon the LC phase transition in the active layer. From a physical point of view, $R_s$ is associated with the conductivity of the semiconductors, and thus the carrier mobility in the active layer; while $R_{sh}$ is related to the loss of charge carriers via recombination and leakage. Indeed, the dark J-V curves of the devices (inset of Fig. 2-5a) reveals the effective suppression of the leakage current under low biases after thermal annealing, indicating improved diode

**Figure 2-4.** Energy-level diagram of BHJ solar cells based on DPP-TP:PC71BM layer and the calculated HOMO/LUMO distributions of the $\pi$-conjugated core of the donor molecules.
characteristics. Similar enhancement in the PCEs upon thermal annealing has been attained for other DPP-TP6:PC71BM blend ratios as well (Table 2-2).

To address the origin of the enhanced device performances, the incident photon-to-current conversion efficiency (IPCE) spectra for the DPP-TP6-based BHJ devices (Fig. 2-5b) have measured. With annealing at 140 °C, a pronounced enhancement in photoresponses ranging from 350 to 600 nm, corresponding to the superposition of the absorption of H-aggregated DPP-TP6 and PC71BM molecules, can be observed. The IPCE reaches the maximum value at ~70%, which is considerably high for small-molecule BHJ solar cells, implying highly efficient charge extraction.

Table 2-2. Photovoltaic parameters for solution-processed BHJ solar cells

<table>
<thead>
<tr>
<th>donor</th>
<th>D/A ratio</th>
<th>thickness (nm)</th>
<th>annealing temp. (°C)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Rs (Ω cm²)</th>
<th>Rsh (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPP-1:1</td>
<td>112</td>
<td>as-spun</td>
<td>7.51 ± 0.26</td>
<td>0.92</td>
<td>38 ± 1</td>
<td>2.6 ± 0.1</td>
<td>18.9</td>
<td>566</td>
<td></td>
</tr>
<tr>
<td>TP6 1:1</td>
<td>107</td>
<td>140</td>
<td>8.27 ± 0.10</td>
<td>0.93</td>
<td>54 ± 1</td>
<td>4.2 ± 0.1</td>
<td>9.1</td>
<td>773</td>
<td></td>
</tr>
<tr>
<td>1.5:1</td>
<td>114</td>
<td>as-spun</td>
<td>6.65 ± 0.26</td>
<td>0.91</td>
<td>36 ± 2</td>
<td>2.1 ± 0.2</td>
<td>12.8</td>
<td>238</td>
<td></td>
</tr>
<tr>
<td>1.5:1</td>
<td>94</td>
<td>140</td>
<td>7.28 ± 0.08</td>
<td>0.93</td>
<td>51 ± 1</td>
<td>3.5 ± 0.1</td>
<td>12.1</td>
<td>1426</td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>112</td>
<td>as-spun</td>
<td>7.04 ± 0.47</td>
<td>0.91</td>
<td>32 ± 1</td>
<td>2.0 ± 0.2</td>
<td>36.0</td>
<td>213</td>
<td></td>
</tr>
<tr>
<td>2:1</td>
<td>101</td>
<td>140</td>
<td>6.24 ± 0.10</td>
<td>0.94</td>
<td>50 ± 1</td>
<td>3.0 ± 0.1</td>
<td>17.2</td>
<td>967</td>
<td></td>
</tr>
<tr>
<td>DPP-2:1</td>
<td>97</td>
<td>as-spun</td>
<td>3.86 ± 0.11</td>
<td>0.91</td>
<td>31 ± 2</td>
<td>1.1 ± 0.1</td>
<td>69.4</td>
<td>352</td>
<td></td>
</tr>
<tr>
<td>TP12 1:1</td>
<td>108</td>
<td>120</td>
<td>3.73 ± 0.17</td>
<td>0.93</td>
<td>35 ± 1</td>
<td>1.2 ± 0.1</td>
<td>85.1</td>
<td>451</td>
<td></td>
</tr>
</tbody>
</table>

aDevice structure: ITO/PEDOT:PSS/donor:PC71BM blend/LiF/Al, with 4 mm² illuminated areas. All devices were characterized under the standard AM 1.5 G 1 Sun test conditions. Power conversion efficiencies (PCEs) were derived from the equation: PCE = (Jsc × Voc × FF)/P0, where Jsc = short-circuit current density, Voc = open-circuit voltage, FF = fill factor, and P0 = incident light intensity. Series resistance (Rs) and shunt resistance (Rsh) were estimated from the reverse slopes of the J-V curves at zero current and at zero voltage, respectively.
In contrast, negligible enhancement of the device performances (PCE = 1.1% to 1.2%) has been observed for DPP-TP12:PC$_{71}$BM devices even after annealing (Fig. 2-5d). Despite the similarities in molecular structures and physical properties, the non-LC DPP-TP12 molecules are unable to reorganize into an appropriate chromophore packing structure upon heating, resulting in a relatively low device performance (Table 2-2).

**Figure 2-5.** *J*-Ψ characteristics under one sun illumination (inset: dark *J*-Ψ curves) for BHJ solar cells based on (a) DPP-TP6:PC$_{71}$BM (1:1, w/w) blend as-cast and after thermal annealing at 140 °C and (c) DPP-TP12:PC$_{71}$BM (1:1, w/w) blend as-cast and after thermal annealing at 120 °C and IPCE spectra for BHJ solar cells based on (b) DPP-TP6:PC$_{71}$BM (1:1, w/w) blend as-cast and after thermal annealing at 140 °C and (d) DPP-TP12:PC$_{71}$BM (1:1, w/w) blend as-cast and after thermal annealing at 120 °C.
2. 5. Film Morphology and Structures

To gain deeper insight into the variation in the photovoltaic properties of DPP-TP6:PC$_{71}$BM BHJ devices by LC organization, the active layer morphologies have been analyzed using polarizing optical microscopy (POM) and atomic force microscopy (AFM), as shown in Fig. 2-6. The morphology of the active material in the BHJ solar cells significantly affects the device performance. With increasing annealing temperature, the POM images indicate the emergence of highly birefringent LC domains with sizes over several tens of micrometers (Fig. 2-6a-c), implying the spontaneous formation of well-organized crystallites within the blend films. The AFM image of the as-cast DPP-TP6:PC$_{71}$BM blend film exhibits a small-grained (100-200 nm in size) macrophase-separated morphology, with a root-mean-square (RMS) roughness of 12.6 nm (Fig. 2-6d). This coarse surface structure of the blend films is ascribed to the low entropy of mixing between DPP-TP6 and PC$_{71}$BM during the spin-coating process. After thermal annealing at 140 °C, the protruding edges merge into larger homogeneous domains (approximately tens of µm in size), and the surface morphology of the composite blend film becomes smoother with a surface roughness of around 4 nm (Fig. 2-6e, f). The obvious trend of such morphological changes by LC organization is also observed for other blend ratios. The author infers that thermal annealing allows the LC DPP-TP6 and PC$_{71}$BM molecules to diffuse and reorganize into thermodynamically favorable nanoscale interpenetrating networks in the active layer. Since the exciton diffusion length of organic materials is generally about 10-20 nm, the well-developed interpenetrating nanostructures with enlarged interfacial D/A areas should be beneficial to effective exciton dissociation and charge transport in the BHJ layer.
Figure 2-6. Polarizing optical micrographs (POM) (left panels) and atomic force microscopy (AFM) height images (right panels) of DPP-TP6:PC71BM (1:1, w/w) films on ITO-coated glass substrates: (a, d) as-spun and after thermal annealing at (b, e) 120 °C and (c, f) 140 °C for 10 min. The scan size for the AFM images is 5 × 5 μm.
Figure 2-7. POM (left panels) and AFM images (right panels) of DPP-TP12:PC$_{71}$BM (1:1, w/w) films on ITO-coated glass substrates: (a, d) as-spun and after thermal annealing at (b, e) 100 °C and (c, f) 120 °C for 10 min.
In contrast, for the non-LC DPP-TP12:PC\textsubscript{71}BM blends the grains are not interconnected and the surface morphology of the films is coarse even after thermal annealing (Fig. 2-7). There is weaker molecular ordering within the blend films owing to the lack of LC characteristics, which agrees with the lower photovoltaic properties of DPP-TP12, compared with those of DPP-TP6.

X-ray diffraction (XRD) studies clearly manifest the enhancement of molecular ordering within the DPP-TP6:PC\textsubscript{71}BM blend films by LC organization (Fig. 2-8). The as-cast DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) film only shows a weak broad scattering at $2\theta = 5.8^\circ$, corresponding to a $d$-spacing of 1.52 nm, which originates from very small crystalline domains of DPP-TP6. Once the thin film is annealed to 120 °C, an additional reflection peak appears at 6.7° ($d = 1.32$ nm). Further annealing at 140 °C leads to a steep increase of the intensity of the latter peak, as a result of the formation of $H$-aggregates in the LC mesophase. The size of the DPP-TP6 crystallites ($D$) can be estimated from the full width at half-maximum (FWHM) of the respective XRD peaks using Scherrer’s equation\textsuperscript{28}:

$$ D = \frac{(K\lambda)}{(\beta \cos \theta)}, $$

where $K$ is the shape factor (normally assumed to be 0.89), $\lambda$ is the incident X-ray wavelength, $\beta$ is the FWHM in radians of the XRD peak, and $\theta$ is the diffraction angle. Apparently, the average size of the crystallites of DPP-TP6 increases from 1.0 nm for the as-spun to 32 nm for the annealed DPP-TP6:PC\textsubscript{71}BM films. This observation allows us to correlate the morphology of the active layer with the resulting photovoltaic properties. The larger size of the crystallites corresponds to a larger D/A segregation in the composite films. This nanostructured texture provides better percolation pathways for the generated charge carriers, which would be reflected in larger $J_{sc}$ and FF of the annealed DPP-TP6:PC\textsubscript{71}BM device.
**Figure 2-8.** Out-of-plane X-ray diffraction (XRD) patterns of DPP-TP6:PC$_{71}$BM (1:1, w/w) films on ITO-coated glass substrates: (a) as-spun and after thermal annealing at (b) 120 °C and (c) 140 °C for 10 min. The peak with * denotes reflection from ITO.
Molecular dynamics (MD) simulations have been performed on the DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) system with a constant temperature at 140 °C, as displayed in Fig. 2-9. The simulation cell contains 160 molecules of DPP-TP6 and 128 molecules of PC\textsubscript{71}BM, and the cell size is around (x, y, z) = (6.6 nm, 6.6 nm, 8.5 nm) at the equilibrated state. It is observed that the DPP-TP6 molecules repel the PC\textsubscript{71}BM molecules to form a stable phase-segregated structure after proper relaxation. The formation of zigzag layers of PC\textsubscript{71}BM agglomerates can be discerned, which is similar to the single-crystal structure of PC\textsubscript{71}BM.\textsuperscript{29}

![Figure 2-9. Molecular dynamics (MD) snapshot of DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) blend at 140 °C, after 50 ns. Atoms belonging to PC\textsubscript{71}BM, the DPP-TP6 conjugated backbone, and the alkyl chains are colored blue, pink, and gray, respectively.](image-url)
Photoluminescence (PL) spectra and absolute fluorescent quantum yields of pure DPP-TP6 thin films before and after thermal annealing at 140 °C have been measured. (Fig. 2-10) It has been revealed that the non-annealed pristine film (i.e., J-aggregates) is fluorescent more than twice in intensity compared with the annealed film, upon photoexcitation both at 640 nm (J-band) and 540 nm (H-band). The fluorescent quantum yields of the films also obviously decreased from 7 to 3% along the formation of H-aggregates. In general, H-aggregates are almost non-fluorescent whereas J-aggregates are significantly fluorescent, according to Förster and Kasha theories. The relative absorption intensities of J- and H-bands (640 and 540 nm, respectively) shown in Fig. 2-3a indicate that the content of H-aggregates was considerably higher in the annealed DPP-TP6 film compared to pristine one, leading to decreased quantum yields after thermal annealing. Therefore, the PL experimental results concomitantly support our notion of the thermo-responsive J-to-H reorganization in the DPP-TP6 films.

Figure 2-10. Photoluminescence (PL) spectra of pure DPP-TP6 films before and after annealing.
2. 6. Charge Carrier Mobility

As the enhancement in photovoltaic properties can also be related to facile charge transport and collection, the impact of LC organization on charge carrier mobilities of the semiconductor materials has been assessed in organic field-effect transistors (OFETs). Top-contact bottom-gate OFETs have been fabricated by employing pure DPP-TP6 and blended DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) materials. The carrier mobilities are obtained from the source-drain current versus gate voltage (\(I_D\) vs \(V_G\)) plots in well-resolved saturation regions (Fig. 2-11). As-cast films of the pristine DPP-TP6 exhibit a hole mobility of \(7.0 \times 10^{-4}\text{ cm}^2/\text{V s}\). After thermal annealing at 140 °C, the hole mobility of DPP-TP6 increases to \(4.2 \times 10^{-3}\text{ cm}^2/\text{V s}\) (Fig. 2-11a). Thermal annealing results in a higher degree of crystallinity of the DPP-TP6 molecules (cf. Fig. 2-6 and 8), which is manifested in increased hole mobilities.

![Figure 2-11](image)

**Figure 2-11.** Source-drain current (\(I_D\)) and \(I_D^{1/2}\) vs. gate voltage (\(V_G\)) plots of OFETs based on (a) pure DPP-TP6 film with annealing at 140 °C for p-type operation and (b) DPP-TP6:PC\textsubscript{71}BM (1:1, w/w) blend film with annealing at 140 °C for n-type operation. Insets: POM images of each device (scale bar: 100 \(\mu\text{m}\)). Channel length (\(L\)) and width (\(W\)) were 50 \(\mu\text{m}\) and 2000 \(\mu\text{m}\), respectively.
The hole mobility of the annealed DPP-TP6 film have further investigated by means of the space-charge-limited current (SCLC) method.\textsuperscript{30,31} The SCLC hole mobility is \(2-4 \times 10^{-3} \text{ cm}^2/\text{V s}\) (Fig. 2-12), which is coincident well with that obtained with the OFET, in spite of the difference in the charge transport lengths between SCLC (ca. 300 nm) and OFET devices (50 \(\mu\)m). In contrast to the case of the hole mobility, the electron mobility of the DPP-TP6:PC\textsubscript{71}BM films cannot determined by the SCLC method, owing to the lack of clear SCLC region in the \(J-V\) curves. However, it has been found that the hole mobility of DPP-TP6 decreases to approximately \(10^{-5} \text{ cm}^2/\text{V s}\) when mixed with PC\textsubscript{71}BM in a 1:1 (w/w) ratio, which is about 2 orders of magnitude lower with respect to the pristine DPP-TP6 after annealing.

\textbf{Figure 2-12.} Double logarithmic plots of \(J-V\) characteristics of hole-only devices comprising ITO/MoO\textsubscript{3} (0.8 nm)/DPP-TP6 (310 nm, after annealing at 140 °C) or \(\alpha\)-NPD (340 nm, for reference)/MoO\textsubscript{3} (10 nm)/Al (70 nm). The solid lines represent the best fit to the space-charge-limited current (SCLC) model. The inset shows the electric field dependence of the hole mobility (\(\mu\)) for the thin film of DPP-TP6 (red) and \(\alpha\)-NPD (black).
Likewise, the electron mobilities show a pronounced dependence on thermal annealing. The OFETs based on as-spun DPP-TP6:PC$_{71}$BM films without annealing exhibits a low electron mobility of $1.6 \times 10^{-5}$ cm$^2$/V s, and after annealing at 140 °C, the electron mobility abruptly increases to $1.1 \times 10^{-3}$ cm$^2$/V s (Fig. 2-11b). These results suggest that the enhancement of photovoltaic properties for the BHJ DPP-TP6:PC$_{71}$BM films are ascribable in part to the improved hole and electron transport. However, the electron and hole mobilities still differ by approximately 2 orders of magnitude in the DPP-TP6:PC$_{71}$BM BHJ architectures. Therefore, higher photovoltaic performance could be achieved if one can further improve the hole mobility of the LC donor materials.
2. 7. Summary

Diketopyrrolopyrrole-based solution-processable photovoltaic molecules, DPP-TP6 and DPP-TP12, have designed, synthesized, and characterized that show an intense absorption in the visible region from 400 to 700 nm, with a low optical bandgap of 1.8 eV and a deep HOMO level of −5.5 eV. The use of these molecules as electron donors has been demonstrated in solution-processed bulk hetero-junction solar cells with PC71BM as the electron acceptor. The effect of liquid-crystalline properties on photovoltaic performance of the bulk hetero-junction devices based on DPP-TP6:PC71BM and DPP-TP12:PC71BM films have investigated, in which the molecular packing and thin film morphologies are strongly affected by the length of the terminal alkyl chains. The $J_{sc}$ and FF have increased significantly for the DPP-TP6-based devices through the liquid-crystalline organization process, and the best-performing device has generated a high PCE of 4.3% with a $V_{oc}$ of 0.93 V, $J_{sc}$ of 8.4 mA/cm$^2$, and FF of 0.55 without use of any additives. The induction of liquid-crystalline characteristics to direct molecular self-assembly represents an effective strategy for designing donor molecules. It is anticipated that further enhancement of photovoltaic performances could be realized by a combination of fine structural tuning of diketopyrrolopyrrole-based materials and precise control of their liquid-crystalline organization processing.
2. 8. Experimental

2. 8. 1. Materials and Instrumentation

Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under a nitrogen atmosphere in dry solvents using standard Schlenk techniques. 2-Cyanothiophene, 1-bromo-4-hexyl benzene, 1-bromo-4-dodecyl benzene, and 2-isoproxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from Tokyo Chemical Industry (TCI). 2-Ethylhexyl bromide, dibutyl succinate, N-bromosuccinimide, tert-amyl alcohol, and n-butyllithium (1.62 M in hexane) were purchased from Wako Pure Chemical Industries, Ltd.

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts of $^1$H and $^{13}$C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and CDCl$_3$ ($\delta = 77.0$) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were carried out with a Yanaco MT-5 CHN corder. UV/Vis absorption spectra were measured with a Shimadzu UV-2550 spectrometer. The HOMO energy levels were determined using a Riken-Keiki AC-2 ultraviolet photoelectron spectrometer. The LUMO energy levels were estimated by subtracting the optical energy gap ($E_g$) from the measured HOMO energy levels; the $E_g$ values were determined from the onset position of the absorption spectra. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DTG-60AH at a scanning rate of 10 °C/min and an SII DSC6220 calorimeter at a scanning rate of 5 °C/min, respectively, under N$_2$ atmosphere. Atomic force microscopy (AFM) was performed using a JEOL JSPM-5400 scanning probe microscope with tapping-mode in air. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer with Ni-filtered
CuK\textsubscript{\alpha} radiation. The molecular model of Molecular Dynamics (MD) simulations is a detailed atomic model with treating all hydrogen atoms explicitly. The partial atomic charges of both DPP-TP6 and PC\textsubscript{71}BM molecules were obtained by MOPAC-PM7. The optimized potentials were employed for liquid simulations (OPLS) all atom force field mainly. Some parameters of dihedral angle potential functions were modified by fitting those obtained from the molecular orbital calculations. The MD simulations were carried out using GROMACS 4.5.5 simulation package. Initially, the author run the steepest descent energy minimization for the system and start the MD run at the low temperature for the sufficient simulation time under the three-dimensional periodic boundary conditions. The main simulation was performed under the conditions to keep 140 °C by using Nosé-Hoover thermostat and 1 bar by using Parrinello-Rahman barostat with the relaxation time of 0.2 ps and 1 ps, respectively. The equations of motion were integrated by the leap-frog algorithm with a time step of 1 fs. The cut-off distance of 1.4 nm was applied for calculating van der Waals interactions and that for electrostatic interactions was 1 nm. The long-range electrostatic interactions were computed using the particle-mesh Ewald method.

2. 8. 2. Synthesis of Compound 1

To a stirred solution of sodium-tert-pentoxide (t-\textit{NaOPe}, 18.2 g, 0.165 mmol) in tert-amyl alcohol (300 mL) was stirred for 1 h while the temperature was slowly increased to 120 °C. 2-Cyanothiophene (18.0 g, 0.165 mmol) was added to the reaction and then dibutyl succinate (13.3 g, 0.058 mmol) was added dropwise to the reaction mixture over 1 h. The reaction mixture was stirred for 3 h at 120 °C. After cooling to room temperature, the reaction mixture was poured into acidic MeOH (400 mL MeOH and 20 mL conc. HCl). The precipitate was collected by filtration and washed with several portions of hot water and methanol, and dried under vacuum to afford 1 as a dark red solid (13.2 g, 76%). Compound 1 was used in subsequent reactions without further purification.
2. 8. 3. Synthesis of Compound 2

A mixture of 1 (10.0 g, 33.3 mmol), 2-ethylhexyl bromide (19.3 g, 99.9 mmol), and K₂CO₃ (18.4 g, 133 mmol) in dry DMF (300 mL) was stirred for 24 h at 120 °C. After cooling to room temperature, the reaction mixture was poured into a large amount of ice water to form a precipitate. The precipitate was collected by filtration and washed with water and methanol. The product was purified by silica gel column chromatography (eluent: CHCl₃/hexane = 1:1, v/v), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 2 as a red brown solid (yield = 8.89 g, 51%). ¹H NMR (500 MHz, CDCl₃): δ 8.89 (dd, J = 4.0 Hz, 1.5 Hz, 2H), 7.63 (dd, J = 5.0 Hz, 1.5 Hz, 2H), 7.27 (dd, J = 5.0 Hz, 4.0 Hz, 2H), 4.07-3.98 (m, 4H), 1.89-1.84 (m, 2H), 1.40-1.20 (m, 16H), 0.89-0.84 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 161.78, 140.45, 135.25, 130.49, 129.87, 128.42, 107.98, 45.89, 39.11, 30.24, 28.39, 23.58, 23.06, 14.01, 10.50. MS (MALDI-TOF): m/z 525.12 [M]+.

2. 8. 4. Synthesis of Compound 3

To a stirred solution of 2 (6.00 g, 11.4 mmol) in dry CHCl₃ (300 mL) was added slowly N-bromosuccinimide (NBS, 4.07 g, 22.9 mmol) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: toluene/hexane = 4:1, v/v), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 3 as a dark brown solid (yield = 7.13 g, 91%) ¹H NMR (500 MHz, CDCl₃): δ 8.65 (d, J = 4.50 Hz, 2H), 7.23 (d, J = 4.00 Hz, 2H), 3.98-3.89 (m, 4H), 1.86-1.81 (m, 2H), 1.39-1.22 (m, 16H), 0.90-0.87 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 161.43, 139.43, 135.37, 131.48, 131.20, 119.00, 108.06, 46.04, 39.13, 30.20, 28.34, 23.60, 23.03, 14.01, 10.48.
2. 8. 5. Synthesis of Compound 4a

To a stirred solution of 1-bromo-4-hexyl benzene (5.00 g, 20.7 mmol) in dry THF (200 mL) was added dropwise n-butyllithium (1.62 M in hexane, 15.4 mL, 24.9 mmol) at −78 °C. The mixture was allowed to react for 1 h at that temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.63 g, 24.9 mmol) was then added, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into water, and extracted with diethyl ether. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford to 4a as a colorless oil (4.09 g, 68%). ¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.60 (t, J = 8.0 Hz, 2H), 1.63-1.57 (m, 2H), 1.33 (s, 12H), 1.30-1.27 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 146.39, 134.91, 127.93, 83.58, 36.26, 31.79, 31.37, 29.03, 24.91, 22.66, 14.14.

2. 8. 6. Synthesis of Compound 4b

To a stirred solution of 1-bromo-4-dodecyl benzene (5.00 g, 15.4 mmol) in dry THF (150 mL) was added dropwise n-butyllithium (1.62 M in hexane, 11.4 mL, 18.4 mmol) at −78 °C. The mixture was allowed to react for 1 h at that temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.43 g, 18.4 mmol) was then added, and the mixture was stirred overnight at room temperature. The reaction mixture was poured into water, and extracted with diethyl ether. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: hexane), and dried under vacuum to afford to 4b as a colorless oil (4.22 g, 74%). ¹H NMR (500 MHz, CDCl₃): δ 7.72 (d, J
= 8.00 Hz, 2H), 7.18 (d, J = 4.00 Hz, 2H), 2.61 (t, J = 7.75 Hz, 2H), 1.63-1.56 (m, 2H),
1.33 (s, 12H), 1.30-1.24 (m, 18H), 0.88 (t, J = 7.00 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$):
δ 146.39, 134.90, 127.92, 83.57, 36.27, 32.01, 31.42, 29.75, 29.74, 29.72, 29.67, 29.59,

2. 8. 7. Synthesis of DPP-TP6 (5)

To a mixture of 3 (1.10 g, 1.61 mmol) and 4a (0.98 g, 3.38 mmol) in dry THF (80 mL)
were added Pd(PPh$_3$)$_4$ (0.08 g, 0.06 mmol) and aqueous K$_2$CO$_3$ (2.0 M, 20 mL; N$_2$
bubbled before use). The mixture was stirred for 24 h at 60 °C. After cooling to room
temperature, the reaction mixture was poured into water, and then extracted with CHCl$_3$.
The combined organic layers were washed with water, and dried over anhydrous MgSO$_4$.
After filtration and evaporation, the product was purified by silica gel column
chromatography (eluent: CHCl$_3$), recrystallized from CHCl$_3$/methanol, and
dried under vacuum to afford 5 as a dark violet solid. This compound was further purified by recycling
preparative gel permeation chromatography (GPC) prior to use (yield = 0.71 g, 52%). $^1$H
NMR (500 MHz, CDCl$_3$): δ 8.97 (d, J = 4.50 Hz, 2H), 7.59 (d, J = 8.00 Hz, 4H), 7.43 (d,
J = 4.00 Hz, 2H), 7.24 (d, J = 8.00 Hz, 4H), 4.13-4.04 (m, 4H), 2.64 (t, J = 7.75 Hz, 4H),
1.97-1.93 (m, 2H), 1.67-1.61 (m, 4H), 1.41-1.26 (m, 30H), 0.93-0.89 (m, 18H). $^{13}$C NMR
(125 MHz, CDCl$_3$): δ 161.80, 150.00, 144.14, 139.90, 136.85, 130.70, 129.22, 128.40,
126.08, 124.03, 108.11, 46.02, 39.27, 35.77, 31.73, 31.30, 30.40, 28.97, 28.61, 23.75,
for C$_{54}$H$_{72}$N$_2$O$_2$S$_2$: C, 76.73; H, 8.59; N, 3.31; found: C, 76.65; H, 8.63; N, 3.32.

2. 8. 8. Synthesis of DPP-TP12 (6)

To a mixture of 3 (0.97 g, 1.42 mmol) and 4b (1.11 g, 2.98 mmol) in dry THF (70 mL)
were added Pd(PPh$_3$)$_4$ (0.07 g, 0.06 mmol) and aqueous K$_2$CO$_3$ (2.0 M, 15 mL; N$_2$
bubbled before use). The mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl₃), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 6 as a dark violet solid. This compound was further purified by recycling preparative GPC prior to use (yield = 1.23 g, 85). ¹H NMR (500 MHz, CDCl₃): δ 8.97 (d, J = 4.00 Hz, 2H), 7.59 (d, J = 8.50 Hz, 4H), 7.43 (d, J = 4.00 Hz, 2H), 7.23 (d, J = 8.00 Hz, 4H), 4.13-4.04 (m, 4H), 2.64 (t, J = 7.75 Hz, 4H), 1.97-1.93 (m, 2H), 1.67-1.60 (m, 4H), 1.66-1.26 (m, 52H), 0.93-0.86 (m, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 161.78, 149.98, 144.13, 139.87, 136.85, 130.68, 129.21, 128.39, 126.07, 124.02, 108.09, 46.01, 39.27, 35.77, 31.93, 31.34, 30.41, 29.67, 29.65, 29.60, 29.51, 29.36, 29.30, 28.60, 23.74, 23.13, 22.70, 14.11, 14.07, 10.61. MS (MALDI-TOF): m/z 1013.65 [M]+. Anal. Calcd (%)
for C₁₉H₁₂N₂S: C, 78.21; H, 9.55; N, 2.76; found: C, 78.20; H, 9.45; N, 2.71.

2. 8. 9. Fabrication of Organic Solar Cells (OSCs)

Prepatterned ITO-coated glass substrates were cleansed sequentially by sonicating in detergent solution, deionized water, acetone, and isopropanol for 10 min each, and were then subjected to UV/ozone treatment for 15 min. A thin layer (~40 nm) of PEDOT:PSS (Clevios P VP Al 4083) was spin-coated onto the precleaned ITO substrate at 3000 rpm for 60 s, and then baked at 150 °C for 10 min under air. The photoactive layer was deposited by spin-cast (1000 rpm for 60 s) from a CHCl₃ solution containing 7-8 mg/mL of a donor and a respective amount of PC₇₁BM, after passing through a 0.45 μm poly(tetrafluoroethylene) filter. The thickness of the active layers was 90-120 nm, measured with a Dektak profilometer. Finally, a 1-nm thick LiF and 100-nm thick Al layers were thermally evaporated on top of the active layer under high vacuum, through
a shadow mask defining an active device area of 4 mm$^2$. The current density-voltage ($J-V$) curves of photovoltaic devices were measured using a Keithley 2400 source measure unit in air under AM 1.5 G solar illumination at 100 mW/cm$^2$ (1 sun) using a Bunko-keiki SRO-25 GD solar simulator and IPEC measurement system, calibrated with a standard Si solar cell.

2. 8. 10. Fabrication of Organic Field-Effect Transistors (OFETs)

OFET devices were fabricated in a top-contact configuration on heavily doped n-type Si wafers with 300-nm thick thermally grown SiO$_2$. The SiO$_2$/Si substrates were pretreated with a piranha solution at 90 °C for 0.5 h, and then copiously cleaned with sonication in deionized water, acetone, and isopropanol for 10 min each, followed by UV/ozone treatment for 15 min. An organic semiconductor layer was spin-coated onto the substrate from a CHCl$_3$ solution with a donor concentration of 4% (w/v), at 1000 rpm for 60 s under N$_2$ atmosphere. The devices were completed by evaporating 50-nm thick Au (or Al) source and drain electrodes through a shadow mask, where the source-drain channel length ($L$) and width ($W$) were 50 μm and 2000 μm, respectively. Current-voltage characteristics of the OFETs were measured using an Agilent B1500A semiconductor parameter analyzer under an inert atmosphere at room temperature. Field-effect mobilities ($\mu$) were calculated in the saturation regime of the $I_D$ using the following equation:

$$I_D = \frac{W}{2L}\mu C_i(V_G - V_{th})^2,$$

where $I_D$ is the source-drain current, $C_i$ is the capacitance per unit area of the gate dielectric (11.5 nF/cm$^2$), $V_G$ is the gate voltage, and $V_{th}$ is the threshold voltage.
2. 8. 11. Space-Charge-Limited Current (SCLC) Measurements

Hole mobility was measured by the space-charge-limited current (SCLC) method, using a device structure of ITO/MoO\textsubscript{3} (0.8 nm)/DPP-TP6 (310 nm, after annealing at 140 °C)/MoO\textsubscript{3} (10 nm)/Al (70 nm), by taking current-voltage current in the range of 0-8 V and fitting the results to a space charge limited form, where the SCLC is described by:

\[ J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8L^3, \]

where \( J \) is the current density, \( L \) is the film thickness of active layer, \( \mu_h \) is the hole mobility, \( \varepsilon_r \) is the relative dielectric constant of the transport medium, \( \varepsilon_0 \) is the permittivity of free space (8.85 × 10\textsuperscript{-12} F/m), \( V \) is the internal voltage in the device and \( V = V_{\text{appl}} - V_t - V_{\text{bi}} \), where \( V_{\text{appl}} \) is the applied voltage to the device, \( V_t \) is the voltage drop due to contact resistance and series resistance across the electrodes, and \( V_{\text{bi}} \) is the built-in voltage due to the relative work function difference of the two electrodes.
References


π-Extended Narrow-Bandgap Diketopyrrolopyrrole-based Oligomers for Solution-Processed Inverted Organic Solar Cells
3. 1. Introduction

Solar energy is the most abundant renewable energy source, and solar cells are currently the most promising technology for converting sunlight directly into electricity. Even though high-cost, brittle silicon-based solar cells are widely used, great research efforts are being devoted to produce cost-effective and high-efficiency solar cells as next-generation ubiquitous energy-harvesting devices.\textsuperscript{1,2} Solution-processed organic solar cells (OSCs) based on bulk hetero-junction (BHJ) structures incorporating narrow-bandgap $\pi$-conjugated molecules as a donor and fullerene derivatives as an acceptor have been intensively investigated thus far because of their advantages such as light weight, flexibility, potential for mass production and low energy consumption during manufacturing.\textsuperscript{3,4,5} As a result of rapid advancements in both semiconducting materials and device architectures, high power conversion efficiencies (PCEs) surpassing 9\% have been reported recently for polymer BHJ OSCs.\textsuperscript{6-11} Over the past few years, solution-processable narrow-bandgap small-molecules have gained increasing attention because of their advantages, such as defined molecular structure, intrinsic monodispersity, high purity, negligible batch-to-batch variations, and reproducible performance, compared to conventional polymer counterparts. The PCEs of state-of-the-art small-molecule BHJ OSCs have exceeded 7\%,\textsuperscript{12,13} approaching those of the best-performing polymer OSCs. Despite the foregoing potential benefits, the typical backbone structures for small-molecule donors that can afford high photovoltaic efficiencies are still rather few, including dithienosilole-benzothiadiazole derivatives\textsuperscript{14-18} and oligothiophene derivatives end-capped with electron-withdrawing units.\textsuperscript{19-23} To effectively absorb solar irradiation, chromophoric structures should be incorporated preferably in the $\pi$-conjugated backbones of donor materials. Diketopyrrolopyrrole (DPP) is a promising building block on account of its high optical density and electron affinity, and various DPP-based small-molecules have been developed as photovoltaic materials.\textsuperscript{24,25}
In chapter 2, liquid-crystalline DPP-based small-molecule electron donor materials, 3,6-bis[5-(4-alkylphenyl)thiophen-2-yl]-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-diones (DPP-TP), were synthesized and applied to OSC, which yielded a PCE of 4.3% when combined with [6,6]-phenyl-C\textsubscript{71}-butyric acid methyl ester (PC\textsubscript{71}BM) as an electron acceptor. Although the possibilities for combinations of different chromophoric structures within a molecule are vast, systematic studies on how specific chemical structures can affect material and device properties remain limited. In addition to the design of new molecular backbone structures with efficient light harvesting and high carrier mobility, understanding the structure-property-function relationships is essential to enhance the overall performance of solution-processed small-molecule OSCs.

In this chapter, \(\pi\)-conjugated oligomers based on the DPP chromophoric units coupled with the benzodithiophene, indacenodithiophene, and thiophene cores, are designed and synthesized for the application as donor materials in solution-processed BHJ OSCs. The impacts of these different central cores on their photophysical and morphological properties, carrier mobility, and photovoltaic performance are investigated. These \(\pi\)-extended oligomers possess broad and intense optical absorption covering the range of 500-750 nm, narrow optical bandgap of 1.52-1.69 eV, and relatively low-lying HOMO energy levels ranging from \(-5.32\) to \(-5.46\) eV in their thin films. A high PCE of 5.9% under AM 1.5 G illumination is achieved for inverted OSCs based on a BHJ system consisting of a benzodithiophene-DPP-containing oligomer as a donor and PC\textsubscript{71}BM as an acceptor. Transmission electron microscopy and energy-dispersive X-ray spectroscopy analyses reveal that the interpenetrating and interconnected donor/acceptor domains with pronounced mesoscopic phase segregation are indeed formed within the photoactive binary blends, which is ideal for efficient exciton dissociation and charge transport in the BHJ devices.
Figure 3-1. Chemical structures of DPP-based oligomers with different central bridging units: benzodithiophene (BDT) for BDT-DPP, indacenodithiophene (IDT) for IDT-DPP, and thiophene (T) for T-DPP.

3.2. Synthesis and Thermal Properties

An effective strategy for designing donor materials with high photoabsorptivity and narrow-bandgap, is to incorporate electron-rich donor (D) and electron-deficient acceptor (A) constituents into \( \pi \)-conjugated frameworks, facilitating intramolecular charge transfer and electronic delocalization.\textsuperscript{26-30} To address this need, \( \pi \)-extended oligomers, BDT-DPP, IDT-DPP, and T-DPP (Fig. 3-1), based on an A-\( \pi \)-D-\( \pi \)-A core framework have designed. Two DPP-based acceptor units are linked through a central weak-donor, benzodithiophene (BDT), indacenodithiophene (IDT), and thiophene (T) unit, respectively.
Hexyl-substituted phenylthiophene end-capping groups are introduced at both extremities to expand the \( \pi \)-conjugated structure and to facilitate film-forming ability. The synthetic procedures for these oligomers are described in Scheme 3-1. Syntheses of these oligomers were achieved via palladium-catalyzed Stille cross-coupling reaction. All of these oligomers are soluble in common organic solvents such as chloroform, toluene, and chlorobenzene, owing to multiple solubilizing alkyl chains.

Scheme 3-1. Synthetic routes of monomers and oligomers (BDT-DPP, IDT-DPP, and T-DPP).
Thermogravimetric analysis (TGA) indicated that BDT-DPP, IDT-DPP, and T-DPP possess good thermal stability with a 5% weight-loss temperature ($T_d$) of 385, 332, and 388 °C, respectively, under N$_2$ atmosphere (Fig. 3-2). For IDT-DPP, attached bulky 4-hexylphenyl substituents on the central IDT core results in a decrease of the $T_d$ to 332 °C.

![Thermogravimetric analysis (TGA) of BDT-DPP, IDT-DPP, and T-DPP.](image)

**Figure 3-2.** Thermogravimetric analysis (TGA) of BDT-DPP, IDT-DPP, and T-DPP.

To understand how variation of the $\pi$-conjugated backbone structures (in particular, central bridging units) affect photophysical properties, time-dependent density functional theory (TD-DFT) calculations were carried out for these designed oligomers. The calculated energy levels of the HOMO and the lowest unoccupied molecular orbital (LUMO) and the respective frontier orbital distributions for the oligomers are presented in Fig. 3-3. It is apparent that for BDT-DPP, IDT-DPP, and T-DPP, the HOMOs are well delocalized along the A-$\pi$-D-$\pi$-A backbone, while the LUMOs involve a strong contribution of the electron-accepting dithieno-DPP units. The first singlet excited-state ($S_1$) transition in these oligomers is dominated by the HOMO→LUMO electronic transition with considerably large oscillator strengths ($f = 2.1-2.9$),$^{31}$ implying enhanced photoabsorption properties desirable for photovoltaic application.
Figure 3-3. Frontier molecular orbital distributions, calculated energy levels, and associated oscillator strengths ($f$), characterized by TD-DFT calculations at the B3LYP/6-31G (d,p) level. The alkyl chains are modified to methyl groups to simplify the calculations. The arrows indicate the first singlet excited-state ($S_1$) transition.

3.3. Photophysical Properties

The UV/Vis absorption spectra of the oligomers in chloroform solution and as thin films are depicted in Fig. 3-4, and the relevant optical data are summarized in Table 3-1. Overall, dilute solutions of the oligomers show similar broad absorption with the lowest-energy absorption peaks ($\lambda_{\text{max}}$) at 640-670 nm and extinction coefficients ($\varepsilon$) of greater than $1.5 \times 10^5$ M$^{-1}$ cm$^{-1}$. Note that such large $\varepsilon$ values for all oligomers are comparable to those of DPP-based $\pi$-conjugated polymers. The optical bandgap energy ($E_g$) derived from the absorption edge of the solution UV/Vis spectra decreases in the order of BDT-DPP > IDT-DPP > T-DPP (Table 3-1), which stands in good agreement with the $S_1$ vertical transition energies estimated from the TD-DFT calculations (Fig. 3-3). Whilst the
absorption spectra in dilute solutions reflect intrinsic electronic properties at the molecular level, the absorption behavior is strongly influenced by intermolecular interactions as well as molecular packing in aggregated solid states. In as-spun thin films, the main absorption peak of BDT-DPP ($\lambda_{\text{max}} = 712$ nm) and T-DPP (675 nm) show an obvious red-shift by ca. 20-60 nm in comparison with their solutions, accompanied by a decrease in $E_g$ (by ca. 0.1-0.2 eV), presumably because of intermolecular $\pi-\pi$ interactions and $J$-aggregation in the solid states. Specifically, the BDT-DPP and T-DPP thin films exhibit photoabsorption throughout the region of largest photon flux in the solar spectrum (ca. 500-750 nm), with the peak absorption coefficients over $10^5$ cm$^{-1}$.

**Figure 3-4.** UV/Vis absorption spectra of BDT-DPP, IDT-DPP, and T-DPP in (a) CHCl$_3$ solutions and (b) as-spun thin films.

As for the IDT-DPP thin film, smaller shifts in both $\lambda_{\text{max}}$ and $E_g$ should originate from the attached 4-hexylphenyl substituents on the central IDT core, which can prevent intermolecular electronic interactions and close molecular packing within the solid thin films. The HOMO energy levels of the oligomers as thin films have been determined to be $-5.32 \sim -5.46$ eV by photoelectron yield spectroscopy (Fig. 3-5), as listed in Table 3-1.
The LUMO energy levels of the oligomers are located within the range of \(~ -3.8 \text{ eV}\), which are sufficiently higher than that of an electron acceptor PC\textsubscript{71}BM (ca. \(-4.3 \text{ eV}\)) to enable directed photoinduced charge transfer.

### Table 3-1. Optical properties of oligomers

<table>
<thead>
<tr>
<th>compound</th>
<th>absorption $\lambda_{\text{max}}$ (nm)</th>
<th>HOMO\textsuperscript{c}</th>
<th>LUMO\textsuperscript{d}</th>
<th>$E_g$\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>solution\textsuperscript{a}</td>
<td>film\textsuperscript{b}</td>
<td>(eV)</td>
<td>(eV)</td>
</tr>
<tr>
<td>BDT-DPP</td>
<td>654</td>
<td>712, 648</td>
<td>(-5.36)</td>
<td>(-3.77)</td>
</tr>
<tr>
<td>IDT-DPP</td>
<td>663</td>
<td>675, 628</td>
<td>(-5.46)</td>
<td>(-3.76)</td>
</tr>
<tr>
<td>T-DPP</td>
<td>646</td>
<td>675</td>
<td>(-5.32)</td>
<td>(-3.80)</td>
</tr>
</tbody>
</table>

\textsuperscript{a}In CHCl\textsubscript{3} solution at 10\textsuperscript{-6} M. \textsuperscript{b}Spin-coated thin film (ca. 100 nm). \textsuperscript{c}Determined by photoelectron yield spectroscopy.

\textsuperscript{d}LUMO = HOMO + $E_g$, in which the optical energy gap, $E_g$, was derived from the absorption onset of the thin film.

**Figure 3-5.** Photoelectron yield spectra of (a) BDT-DPP, (b) IDT-DPP, and (c) T-DPP thin film.
3. 4. Photovoltaic Properties

The BHJ solar cells were fabricated with an inverted device configuration,\textsuperscript{31-34} using the DPP-based narrow-bandgap oligomers as the electron donor material and PC\textsubscript{71}BM as the acceptor material. Fig. 3-6a illustrates the energy level diagram of the fabricated inverted solar cells. A 30-nm-thick ZnO layer was deposited using sol-gel techniques as the electron extraction layer, which gives rise to a suitable energy level alignment with the LUMO of PC\textsubscript{71}BM for electron extraction.

![Energy level diagram](image)

**Figure 3-6.** (a) Energy level diagram of the components for the inverted BHJ solar cells. (b) Cross-sectional transmission electron microscopy (TEM) image and (c) TEM-energy-dispersive X-ray spectroscopy (EDS) element mapping for an optimized inverted device with the configuration of ITO/ZnO (30 nm)/BDT-DPP:PC\textsubscript{71}BM blend (1:1, w/w) with 1-vol\% DIO additive (118 nm)/MoO\textsubscript{x} (10 nm)/Ag (100 nm).
The donor:PC$_{71}$BM (1:1, w/w) blend solution in a mixed solvent of chloroform/1,8-diiodooctane (99:1, v/v) was spin-coated on top of the ZnO layer to form an active layer with a thickness of 90-120 nm. 1,8-Diiodooctane (DIO) was used as a processing additive to optimize the film morphology and induce suitable phase segregation in the BHJ structure.$^{35,36,37}$ A 10-nm-thick MoO$_x$ layer as a hole extraction layer and a 100-nm-thick Ag anode were subsequently vacuum-deposited on the active layer. Apparently, the band alignment in MoO$_x$ and the oligomer donors is also energetically favorable for hole extraction. In the cross-sectional transmission electron microscopy (TEM) image for an inverted solar cell based on an as-cast BDT-DPP:PC$_{71}$BM blend film (Fig. 3-6b), the component multi-stack layers are clearly distinguishable from each other, and their interfaces appear sharp. However, distinct nanoscale morphology within the active layer could not be resolved well in the TEM observation under both focused and defocused conditions. Hence, energy-dispersive X-ray spectroscopy (EDS) element mapping has been performed (Fig. 3-6c). The element mapping of S and C in the cross section reveals that regions containing a high S density appear near the MoO$_x$ overlayer, whereas a low S density (or C-rich) regions are mainly located around the ZnO surface within the active layer. As sulfur is exclusively present in the BDT-DPP donor molecules, the TEM-EDS result demonstrates the spontaneous formation of donor/acceptor interpenetrating network with pronounced phase segregation, involving donor enrichment around the blend/MoO$_x$ interface. This mesoscopic phase segregation is most likely caused by a lower surface energy of BDT-DPP than PC$_{71}$BM, due to the attached alkyl chains. Moreover, DIO seems to have a tendency to accumulate at the surface of the BHJ layer, to lower the overall energy of the free surface in this solution-processed blend system. Similar surface enrichment (i.e., spontaneous vertical phase segregation) phenomena have been reported for some polymer-based systems,$^{38,39,40}$ but has not seen for solution-processed small-molecule OSCs. Given the typical exciton diffusion lengths of organic semiconductors, morphologies consisting of interpenetrating and interconnected
donor/acceptor agglomerates with the size of several tens of nanometers would be suitable for efficient solar cell operation. Fig. 3-7a shows the current density-voltage (J-V) characteristics of the fabricated BHJ OSCs under AM 1.5 G illumination at an intensity of 100 mW/cm². The photovoltaic parameters are summarized in Table 3-2. The device based on the as-cast BDT-DPP:PC₇₁BM (1:1, w/w) blend active layer, processed with 1-vol% DIO additive, presents the best photovoltaic performance with a high short-circuit current density (Jₛₛ) of 12.2 mA/cm², an open-circuit voltage (Vₒₒ) of 0.76 V, and a fill factor (FF) of 62%, leading to a rather high PCE of 5.8 ± 0.1%.

![Figure 3-7. (a) J-V characteristics under one sun illumination and (b) IPCE spectra for BHJ solar cells based on BDT-DPP, IDT-DPP, and T-DPP:PC₇₁BM (1:1, w/w) blend as-cast and with 1% v/v DIO.](image)

As shown in Fig. 3-7b, the incident photon-to-current conversion efficiency (IPCE) of the BDT-DPP-based device exceeds 70%, and the integrated current from the IPCE spectrum is 12.4 mA/cm², which is agreed well with the Jₛₛ value obtained from the J-V curve. Meanwhile, the comparable BDT-DPP-based device without DIO afforded a lower PCE of 3.6 ± 0.1% with an inferior FF of 49% (Table 3-2). It is obvious that the enhancement of PCE in the BDT-DPP-based devices is mainly a result of improvements
in $J_{sc}$ and FF. From the equivalent circuit of a solar cell, a lower series resistance ($R_s$) and higher shunt resistance ($R_{sh}$) should be beneficial to attain a higher FF.\textsuperscript{41} By incorporating 1-vol% DIO additive, the $R_s$ decreases to 0.48 $\Omega$ cm$^2$ and the $R_{sh}$ increases to 0.35 k$\Omega$ cm$^2$ in the BDT-DPP-based device, compared to the corresponding device without DIO, which has $R_s$ and $R_{sh}$ of 3.6 $\Omega$ cm$^2$ and 0.20 k$\Omega$ cm$^2$, respectively. It is noteworthy that the BDT-DPP-enriched and PC$_{71}$BM-enriched agglomerates observed through the TEM-EDS analysis (Fig. 3-6) may function partially as carrier-blocking layers for suppressing the electron leakage to the MoO$_x$-covered anode and hole leakage to the ZnO-coated cathode. In contrast, the inverted solar cells based on IDT-DPP and T-DPP with the same fabrication process delivered inferior photovoltaic properties, yielding average PCEs of 1.8% and 2.3%, respectively (Table 3-2).

### Table 3-2. Photovoltaic parameters for solution-processed BHJ solar cells\textsuperscript{a}

<table>
<thead>
<tr>
<th>donor</th>
<th>D/A ratio</th>
<th>thickness (nm)</th>
<th>DIO (v/v)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ ($\Omega$ cm$^2$)</th>
<th>$R_{sh}$ ($\Omega$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDT-DPP</td>
<td>1:1</td>
<td>114</td>
<td>(-)</td>
<td>10.2 ± 0.20</td>
<td>0.73</td>
<td>49 ± 3</td>
<td>3.6 ± 0.1</td>
<td>3.63</td>
<td>203</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>118</td>
<td>1</td>
<td>12.2 ± 0.10</td>
<td>0.76</td>
<td>62 ± 1</td>
<td>5.8 ± 0.1</td>
<td>0.48</td>
<td>351</td>
</tr>
<tr>
<td>IDT-DPP</td>
<td>1:1</td>
<td>119</td>
<td>(-)</td>
<td>4.18 ± 0.01</td>
<td>0.80</td>
<td>50 ± 1</td>
<td>1.7 ± 0.1</td>
<td>4.06</td>
<td>484</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>99</td>
<td>1</td>
<td>4.10 ± 0.02</td>
<td>0.84</td>
<td>54 ± 2</td>
<td>1.9 ± 0.1</td>
<td>40.2</td>
<td>1133</td>
</tr>
<tr>
<td>T-DPP</td>
<td>1:1</td>
<td>97</td>
<td>(-)</td>
<td>1.85 ± 0.01</td>
<td>0.64</td>
<td>62 ± 1</td>
<td>0.7 ± 0.1</td>
<td>9.68</td>
<td>3698</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>97</td>
<td>1</td>
<td>8.16 ± 0.01</td>
<td>0.66</td>
<td>43 ± 1</td>
<td>2.3 ± 0.1</td>
<td>9.14</td>
<td>390</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Device structure: ITO/ZnO/donor:PC$_{71}$BM blend/MoO$_x$/Ag, with 4 mm$^2$ illuminated areas. All devices were characterized under the standard AM 1.5 G 1 Sun test conditions. Power conversion efficiencies (PCEs) were derived from the equation: PCE = ($J_{sc}$ × $V_{oc}$ × FF)/$P_0$, where $J_{sc}$ = short-circuit current density, $V_{oc}$ = open-circuit voltage, FF = fill factor, and $P_0$ = incident light intensity. Series resistance ($R_s$) and shunt resistance ($R_{sh}$) were estimated from the reverse slopes of the $J$-$V$ curves at zero current and at zero voltage, respectively.
For IDT-DPP, the addition of up to 1-vol% DIO indeed had minimal impact on their photovoltaic properties. Under these conditions, the IDT-DPP molecules are unable to self-organize into suitable well-ordered BHJ morphologies, presumably because of their intrinsic amorphous nature. Because the $V_{oc}$ of BHJ solar cell is commonly determined by the energy difference between the LUMO of acceptor and the HOMO of donor, the higher $V_{oc}$ obtained with the IDT-DPP-based device (0.86 V) is consistent with its relatively deeper-lying HOMO level (−5.46 eV).

3. 5. Film Morphology and Structures

In BHJ OSCs, the morphology of the photoactive layer is of critical importance to their efficient operation. Fig. 3-9 shows atomic force microscopy (AFM) height images of the blend films of the oligomers and PC$_{71}$BM (1:1, w/w) with or without 1-vol% DIO, which have been prepared in the same procedures as the photoactive layers for the OSC devices. Despite their structural similarity, significant differences in the surface morphologies can be seen between the four blends. After adding 1% v/v DIO, the protruding edges of BDT-DPP and T-DPP blend films merge into larger homogeneous domains. The BDT-DPP:PC$_{71}$BM blend film prepared with DIO appears to have rather large cluster-like domains (Fig. 3-9b). In contrast, the IDT-DPP:PC$_{71}$BM blend film shows coarse granular surface morphology with a RMS roughness over 12 nm (Fig. 3-9d), suggestive of strong macroscopic phase separation of the two components. The higher alkyl chain density of IDT-DPP in comparison with other oligomers may result in poorer intermixing with PC$_{71}$BM. Such a coarsely macrophase-separated morphology should limit efficient exciton diffusion to the donor/acceptor interfaces, in turn causing a low photocurrent. In the case of the T-DPP:PC$_{71}$BM blend film with DIO, relatively smooth surface morphologies with an RMS surface roughness of ~5 nm have been obtained (Fig. 3-9f),
which implies that the T-DPP molecules with the central thiophene core have better miscibility (or finer intermixing) with PC71BM within the blend films.

Figure 3-9. Atomic force microscopy (AFM) height images of (a) BDT-DPP:PC71BM (1:1, w/w), (c) IDT-DPP:PC71BM (1:1, w/w), and (e) T-DPP:PC71BM (1:1, w/w) films and (b) BDT-DPP:PC71BM (1:1, w/w), (d) IDT-DPP:PC71BM (1:1, w/w), and (f) T-DPP:PC71BM (1:1, w/w) with 1% v/v DIO films on ITO-coated glass substrates. The scan size for the AFM images is 5 × 5 μm.
X-ray diffraction (XRD) analysis clearly manifests the enhancement of molecular ordering by incorporating DIO in the both BDT-DPP and T-DPP films, as shown in Fig. 3-10. The as-cast pristine BDT-DPP and T-DPP films only show a very weak broad scattering at $2\theta = \sim5.4^\circ$ and $6.4^\circ$, respectively. After adding DIO, an obvious increase of the reflection intensity, together with a peak shift can be observed for both BDT-DPP ($2\theta = 5.1^\circ; d = 1.72$ nm) and T-DPP ($2\theta = 5.8^\circ; d = 1.52$ nm) films. The crystallite size ($D$) of each oligomer can be estimated from the full width at half-maximum (FWHM) using Scherrer’s equation:

$$D = \frac{(K \lambda)}{(\beta \cos \theta)},$$

where $K$ is the shape factor (assumed to be 0.89), $\lambda$ is the incident X-ray wavelength, $\beta$ is the FWHM in radians of the respective XRD peak, and $\theta$ is the diffraction angle. The crystallite sizes of the BDT-DPP and T-DPP molecular agglomerates within the films are found to increase to approximately 20 nm by adding DIO.

Figure 3-10. Out-of-plane X-ray diffraction (XRD) patterns of oligomer films on ITO-coated glass substrates: (a) BDT-DPP, (b) IDT-DPP, T-DPP with (red-line) or without (blue-line) 1% v/v DIO.
This result is consistent with the observation of phase-segregated hierarchical structures in the TEM-EDS analysis. It is widely accepted that the ideal domain size in the active layer for optimized BHJ OSCs is on the order of tens of nanometers because of the relatively short exciton diffusion length.\textsuperscript{43}

3. 6. Charge Carrier Mobility

In OSC devices, hole mobility is an important parameter for donor materials to ensure efficient charge-carrier transport to the electrodes and to suppress photocurrent loss by competing charge recombination. Using the steady-state space-charge-limited current (SCLC) technique,\textsuperscript{44,45,46} hole mobilities ($\mu_h$) of these oligomers were evaluated in vertical hole-only devices. Fig. 3-11 shows the $J$-$V$ curves of the hole-only devices with structures of ITO/MoOx/oligomer (~200 nm with 1-vol\% DIO)/MoOx/Al. At higher voltages (in the SCLC region), the $J$-$V$ characteristics can be fitted by the Mott-Gurney equation:\textsuperscript{47,48}

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h E^2 / L^3,
\]

where $\varepsilon_0$ is the free-space permittivity ($8.85 \times 10^{-14}$ C/V cm), $\varepsilon_r$ is the relative dielectric constant (3.0), $E$ is the electric field, and $L$ is the film thickness. The hole mobility of the BDT-DPP film is determined to be $1.8 \times 10^{-3}$ cm$^2$/V s, indicating good hole-transporting properties. It is thus clear that the mobility of the BDT-DPP film has been enhanced by incorporating the DIO processing additive, compared to its pristine film without DIO ($\mu_h$ = $1.4 \times 10^{-5}$ cm$^2$/V s). The T-DPP and IDT-DPP films exhibit much lower $\mu_h$ values. (IDT-DPP = $2.4 \times 10^{-7}$ cm$^2$/V s and T-DPP = $3.7 \times 10^{-4}$ cm$^2$/V s). These much lower hole-transporting properties are mainly ascribed to poorer packing order of the IDT-DPP molecules in the films.
Figure 3-11. Double logarithmic plots of $J$-$V$ characteristics of hole-only devices with the structure of ITO/MoOx (0.8 nm)/oligomer with 1-vol% DIO/MoOx (10 nm)/Al (70 nm). The solid lines represent the best fits to the space-charge-limited current (SCLC) model (the slope of log $(J)$ vs. log $(V)$ is ~2). Inset: electric-field dependence of hole mobility ($\mu_h$) for the oligomer films.
3. 7. Summary

To establish a rational molecular engineering of solution-processable donor materials for high-efficiency organic solar cells, a new series of narrow-bandgap oligomers based on the diketopyrrolopyrrole units coupled with the π-conjugated benzodithiophene, indacenodithiophene, and thiophene cores have designed and synthesized. Combination studies based on TD-DFT calculations, UV/Vis spectroscopy, TEM-EDS analysis, AFM, XRD, and SCLC measurements have been performed to reveal the structure-property-function relationships, especially the photophysical and morphological properties, for the oligomers. By changing the central π-conjugated segments of only the donor component in binary blends with PC71BM, significant divergences in the overall materials and device properties are observed in this modular structural material set. Among the oligomers, BDT-DPP with the benzodithiophene core possesses excellent nanostructured film-forming ability and a much higher hole mobility over $10^{-3}$ cm$^2$/V s. The optimized inverted solar cell devices based on a BDT-DPP:PC71BM photoactive layer having continuous interpenetrating nanostructures have been fabricated, demonstrating outstanding PCEs of up to 5.9%. This PCE value is the highest level reported to date for the diketopyrrolopyrrole-based small-molecules, thus suggesting the A-π-D-π-A-structured BDT-DPP backbone is a sophisticated building block for developing high-performance donor materials. The judicious molecular design employing suitable combinations of π-conjugated building blocks and control of the phase-segregated morphology of the photovoltaic binary blends are thus crucial to further enhance the overall performance of solution-processed solar cells. The author are investigating the effect of both core and end-cap chemical modifications on the photophysical and morphological properties of the resulting donor materials, and also exploring whether the design guideline can be adopted to other chromophoric molecular scaffolds.
3.8. Experimental

3.8.1. Materials and Instrumentation

Commercially available reagents and solvents were used without further purification unless otherwise noted. All of the reactions were performed under a nitrogen atmosphere in dry solvents using standard Schlenk techniques. Zinc acetate, ethanolamine, 2-methoxyethanol, and 2,5-bis(trimethylstannanyl)thiophene (6) were purchased from Sigma-Aldrich. 2,6-Bis(trimethylstannanyl)-4,8-bis(5-(2-ethylhexyl)-thiophen-2-yl)benzo [1,2-b:4,5-b]dithiophene (4), and 4,4,9,9-tetrakis-(4-hexylphenyl)-2,7-bis(trimethylstannyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b]dithiophene (5) were purchased from Suna Tech. 

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III 500 spectrometer. Chemical shifts of $^1$H and $^{13}$C NMR signals were quoted to tetramethylsilane ($\delta = 0.00$) and CDCl$_3$ ($\delta = 77.0$) as internal standards. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were collected on a Bruker Daltonics Autoflex III spectrometer using dithranol as the matrix. Elemental analyses were carried out with a Yanaco MT-5 CHN corder. UV/Vis absorption spectra were measured with a Shimadzu UV-2550 spectrometer. The HOMO energy levels were determined using a Riken-Keiki AC-3 ultraviolet photoelectron spectrometer. The LUMO energy levels were estimated by subtracting the optical energy gap ($E_g$) from the measured HOMO energy levels; the $E_g$ values were determined from the onset position of the absorption spectra. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60AH at a scanning rate of 10°C/min under N$_2$ atmosphere. Transmission electron microscopy (TEM) measurements were performed using a JEOL JEM-2100F instrument. For cross-sectional observations, samples were prepared as for actual devices. TEM specimens were prepared using focused ion beam (FIB) techniques, and transferred to a TEM grid. The final thinning was carried out with a 15 kV ion beam to a final thickness of ~100 nm.
Atomic force microscopy (AFM) was performed using a JEOL JSPM-5400 scanning probe microscope with tapping-mode in air. X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer with Ni-filtered CuKα radiation.

3. 8. 2. Synthesis of Compound 1

To a stirred solution of 2,5-bis-(2-ethylhexyl)-3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5.00 g, 9.52 mmol) in dry CHCl₃ (300 mL) was added slowly N-bromosuccinimide (NBS, 1.69 g, 9.52 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: toluene/hexane = 4:1, v/v), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 1 as a dark brown solid (yield = 2.59 g, 45%). ¹H NMR (500 MHz, CDCl₃): δ 8.90 (dd, J = 4.0 Hz, 1.0 Hz, 1H), 8.63 (d, J = 4.0 Hz, 1H), 7.64 (dd, J = 5.0 Hz, 1.0 Hz, 1H), 7.28-7.26 (m, 1H), 7.22 (d, J = 4.5 Hz, 1H), 4.03-3.99 (m, 2H), 3.98-3.92 (m, 2H), 1.88-1.80 (m, 2H), 1.38-1.23 (m, 16H), 0.90-0.84 (m, 12H). ¹³C NMR (125 MHz, CDCl₃): δ 161.69, 161.52, 140.92, 138.98, 135.53, 135.09, 131.40, 131.29, 130.82, 129.78, 128.51, 118.62, 108.20, 107.84, 45.98, 45.95, 39.15, 39.09, 30.22, 28.36, 23.60, 23.57, 23.05, 23.04, 14.01, 10.49. MS (MALDI-TOF): m/z 604.84 [M]+.

3. 8. 3. Synthesis of Compound 2

To a mixture of 1 (2.50 g, 4.14 mmol) and 2-(4-hexylphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.70 g, 4.55 mmol) in dry THF (40 mL) were added Pd(PPh₃)₄ (0.24 g, 0.21 mmol) and aqueous K₂CO₃ (2.0 M, 20 mL; N₂ bubbled before use). The
mixture was stirred for 24 h at 60 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl₃), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 2 as a dark violet solid (yield = 2.75 g, 96%). ¹H NMR (500 MHz, CDCl₃): δ 8.98 (d, J = 4.0 Hz, 1H), 8.87 (dd, J = 4.0 Hz, 1.0 Hz, 1H), 7.61 (dd, J = 5.0 Hz, 1.0 Hz, 1H), 7.59 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 4.0 Hz, 1H), 7.28-7.26 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 4.10-4.00 (m, 4H), 2.64 (t, J = 7.5 Hz, 2H), 1.97-1.92 (m, 1H), 1.90-1.85 (m, 1H), 1.67-1.60 (m, 2H), 1.42-1.23 (m, 22H), 0.92-0.84 (m, 15H). ¹³C NMR (125 MHz, CDCl₃): δ 161.91, 161.68, 150.31, 144.22, 140.63, 139.74, 137.10, 135.00, 130.62, 130.28, 129.97, 129.23, 128.40, 128.23, 126.10, 124.04, 108.21, 107.83, 45.98, 45.93, 39.24, 39.12, 35.76, 31.71, 31.29, 30.28, 30.26, 28.95, 28.59, 28.40, 23.71, 23.60, 23.12, 23.07, 22.61, 14.09, 14.06, 14.02, 10.58, 10.53. MS (MALDI-TOF): m/z 686.36 [M]+.

3. 8. 4. Synthesis of Compound 3

To a stirred solution of 2 (2.50 g, 3.65 mmol) in dry CHCl₃ (50 mL) was added slowly NBS (0.71 g, 4.01 mmol) at 0 °C. The mixture was allowed to warm up to room temperature and stirred overnight. The reaction mixture was poured into water, and then extracted with CHCl₃. The combined organic layers were washed with water, and dried over anhydrous MgSO₄. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl₃), recrystallized from CHCl₃/methanol, and dried under vacuum to afford 3 as a dark brown solid. (yield = 2.70 g, 97%) ¹H NMR (500 MHz, CDCl₃): δ 8.99 (d, J = 4.0 Hz, 1H), 8.61 (d, J = 4.0 Hz, 1H), 7.58 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 4.5 Hz, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 4.0 Hz, 1H), 4.10-4.01 (m, 2H), 4.00-3.90 (m, 2H), 2.64 (t, J = 8.0 Hz, 2H), 1.96-1.90 (m, 1H), 1.87-1.82
(m, 1H), 1.66-1.60 (m, 2H), 1.41-1.23 (m, 22H), 0.92-0.89 (m, 15H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.80, 161.39, 150.65, 144.31, 141.04, 138.19, 137.41, 134.81, 131.42, 131.36, 130.55, 129.24, 128.13, 126.10, 124.09, 118.28, 108.43, 107.67, 46.02, 39.23, 39.15, 35.77, 31.71, 31.28, 30.36, 30.24, 28.95, 28.57, 28.37, 23.70, 23.62, 23.11, 23.05, 22.97, 22.61, 14.08, 14.06, 14.02, 10.57, 10.52. MS (MALDI-TOF): $m/z$ 766.78 [$M^+$.]

3. 8. 5. Synthesis of BDT-DPP

To a mixture of 3 (0.80 g, 0.88 mmol) and 5 (1.42 g, 1.86 mmol) in dry DMF (20 mL) was added Pd(PPh$_3$)$_4$ (0.05 g, 0.04 mmol). The mixture was stirred for 24 h at 85 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl$_3$. The combined organic layers were washed with water, and dried over anhydrous MgSO$_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl$_3$), recrystallized from CHCl$_3$/methanol, and dried under vacuum to afford BDT-DPP as a dark brown solid. This compound was further purified by recycling preparative gel permeation chromatography (GPC) prior to use (yield = 1.39 g, 81%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 9.02 (d, $J = 4.0$ Hz, 2H), 9.00 (d, $J = 4.0$ Hz, 2H), 7.62 (s, 2H), 7.48 (d, $J = 7.5$ Hz, 4H), 7.39 (d, $J = 3.5$ Hz, 2H), 7.34 (d, $J = 4.0$ Hz, 2H), 7.25 (d, $J = 4.0$ Hz, 2H), 7.12 (d, $J = 7.5$ Hz, 4H), 6.99 (d, $J = 3.5$ Hz, 2H) 4.00-3.94 (m, 8H), 2.96 (d, $J = 6.5$ Hz, 4H), 2.54-2.50 (m, 4H), 1.91-1.85 (m, 4H), 1.82-1.77 (m, 2H), 1.57-1.28 (m, 64H), 1.03 (t, $J = 7.5$ Hz, 6H), 0.97 (t, $J = 6.8$ Hz, 6H), 0.95-0.87 (m, 30H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 161.41, 161.36, 149.97, 146.26, 144.03, 141.79, 139.77, 138.96, 138.52, 137.36, 136.75, 136.65, 136.52, 130.42, 129.07, 128.99, 128.18, 128.08, 125.74, 125.54, 123.74, 120.56, 120.29, 108.41, 107.89, 45.88, 41.43, 39.45, 39.34, 35.72, 34.50, 32.67, 31.69, 31.15, 30.40, 29.03, 29.01, 28.61, 25.78, 23.66, 23.20, 23.16, 23.13, 22.62, 14.24, 14.14, 14.09, 10.93, 10.68, 10.58. MS (MALDI-TOF): $m/z$ 1942.87 [$M^+$.] Anal. Calcd (%) for C$_{118}$H$_{150}$N$_4$O$_4$S$_8$: C, 72.87; H, 7.77; N, 2.88; O,
3.29; S, 13.19; found: C, 72.75; H, 7.70; N, 2.80.

3. 8. 6. Synthesis of IDT-DPP

To a mixture of 3 (0.86 g, 0.70 mmol) and 6 (1.12 g, 1.47 mmol) in dry DMF (15 mL) was added Pd(PPh$_3$)$_4$ (0.05 g, 0.04 mmol). The mixture was stirred for 24 h at 85 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl$_3$. The combined organic layers were washed with water, and dried over anhydrous MgSO$_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl$_3$), recrystallized from CHCl$_3$/methanol, and dried under vacuum to afford IDT-DPP as a brown solid. This compound was further purified by recycling preparative GPC prior to use (yield = 1.31 g, 82%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.97 (d, $J$ = 4.0 Hz, 2H), 8.88 (d, $J$ = 4.5 Hz, 2H), 7.58 (d, $J$ = 8.0 Hz, 4H), 7.43-7.42 (m, 4H), 7.28 (d, $J$ = 4.0 Hz, 2H), 7.22 (m, 6H), 7.19 (d, $J$ = 8.5 Hz, 8H), 7.10 (d, $J$ = 7.5 Hz, 2H), 4.06-3.98 (m, 8H), 2.64 (t, $J$ = 7.5 Hz, 4H), 2.58 (t, $J$ = 7.5 Hz, 8H), 1.97-1.89 (m, 4H), 1.64-1.57 (m, 16H), 1.41-1.28 (m, 64H), 0.92-0.87 (m, 42H). $^{13}$C NMR (125 MHz, CDCl$_3$): 161.71, 157.26, 153.80, 150.08, 144.16, 143.37, 142.12, 141.82, 141.31, 139.84, 139.17, 138.85, 136.93, 136.49, 135.23, 130.65, 129.22, 128.51, 128.36, 127.87, 126.44, 126.06, 124.27, 124.04, 120.67, 117.55, 108.40, 108.16, 63.15, 53.42, 50.89, 46.01, 39.24, 35.76, 35.60, 31.73, 31.34, 31.30, 30.37, 29.16, 28.95, 28.58, 23.72, 23.13, 23.01, 22.60, 14.10, 10.61. MS (MALDI-TOF): $m/z$ 2270.85 [$M^+$]. Anal. Calcd (%) for C$_{148}$H$_{182}$N$_4$O$_4$S$_6$: C, 78.19; H, 8.07; N, 2.46; O, 2.82; S, 8.46; found: C, 78.03; H, 8.05; N, 2.49.
3. 8. 7. Synthesis of T-DPP

To a mixture of 3 (0.41 g, 1.00 mmol) and 4 (1.61 g, 2.10 mmol) in dry DMF (20 mL) was added Pd(PPh$_3$)$_4$ (0.06 g, 0.05 mmol). The mixture was stirred for 24 h at 85 °C. After cooling to room temperature, the reaction mixture was poured into water, and then extracted with CHCl$_3$. The combined organic layers were washed with water, and dried over anhydrous MgSO$_4$. After filtration and evaporation, the product was purified by silica gel column chromatography (eluent: CHCl$_3$), recrystallized from CHCl$_3$/methanol, and dried under vacuum to afford T-DPP as a dark violet solid. This compound was further purified by recycling preparative GPC prior to use (yield = 1.18 g, 81%). $^1$H NMR (500 MHz, CDCl$_3$): $^\delta$ 8.98 (d, $J$ = 4.0 Hz, 2H), 8.87 (dd, $J$ = 3.0 Hz, 1.0 Hz, 2H), 7.61 (dd, $J$ = 4.0 Hz, 1.0 Hz, 2H), 7.59 (d, $J$ = 8.5 Hz, 4H), 7.43 (d, $J$ = 4.0 Hz, 2H), 7.27 (t, $J$ = 4.0 Hz, 2H), 7.24 (d, $J$ = 8.0 Hz, 4H), 4.11-4.00 (m, 8H), 2.64 (t, $J$ = 7.5 Hz, 4H), 1.97-1.92 (m, 2H), 1.90-1.85 (m, 2H), 1.66-1.60 (m, 4H), 1.42-1.23 (m, 44H), 0.92-0.84 (m, 30H). $^{13}$C NMR (125 MHz, CDCl$_3$): $^\delta$ 161.91, 161.68, 150.31, 144.22, 140.63, 139.74, 137.10, 135.00, 130.62, 130.28, 129.97, 129.23, 128.40, 128.23, 126.10, 124.04, 108.21, 107.83, 45.98, 45.93, 39.24, 39.12, 35.76, 31.71, 31.29, 30.28, 30.26, 28.95, 28.59, 28.40, 23.71, 23.60, 23.12, 23.07, 22.61, 14.09, 14.06, 14.02, 10.58, 10.53. MS (MALDI-TOF): $m/z$ 1449.07 [M]$^+$.

Anal. Calcd (%) for C$_{88}$H$_{112}$N$_4$O$_4$S$_5$: C, 72.88; H, 7.78; N, 3.86; O, 4.41; S, 11.06; found: C, 72.67; H, 7.75; N, 3.80.
3. 8. 8. Fabrication of Inverted Organic Solar Cells (OSCs)

Prepatterned ITO-coated glass substrates were cleansed sequentially by sonicating in detergent solution, deionized water, acetone, and isopropanol for 10 min each, and were then subjected to UV/ozone treatment for 15 min. A thin layer (~30 nm) of ZnO was prepared by spin-coating (at 5000 rpm for 60 s) a precursor solution of zinc acetate (1.00 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 mL), followed by baking at 200 °C for 10 min under air. The photoactive layer was then deposited by spin-coating (at 1000 rpm for 60 s) from a chloroform solution containing a donor oligomer (7 mg/mL) and PC71BM (7 mg/mL), after passing through a 0.45 μm poly(tetrafluoroethylene) filter. The thickness of the respective photoactive layer was 90-120 nm, measured with a Dektak profilometer. Finally, a 10-nm thick MoOx and 100-nm thick Ag layers were thermally evaporated on top of the active layer under high vacuum, through a shadow mask defining a each active device area of 4 mm². The current density-voltage (J-V) measurements for the fabricated OSCs were conducted on a computer-controlled Keithley 2400 source measure unit in air under AM 1.5 G solar illumination at 100 mW/cm² (1 sun) using a Xe lamp-based Bunko-keiki SRO-25 GD solar simulator and IPCE measurement system, calibrated with a standard Si photodiode.
References


Summary and Perspective
In this thesis, the molecular design, synthesis and characterization of electron donating small-molecules and oligomers based on diketopyrrolopyrrole (DPP) were described to improve the solution-processed organic solar cell (OSC) performance.

The first strategy (Chapter 2) dealt with utilizing the self-organization of liquid-crystalline (LC) molecules for the fabrication of well-ordered bulk hetero-junction (BHJ) architectures in small-molecule OSCs. DPP-based solution-processable photovoltaic molecules, DPP-TP6 and DPP-TP12, have designed, synthesized, and characterized that show an intense absorption in the visible region from 400 to 700 nm, with a low optical bandgap of 1.8 eV and a deep HOMO level of −5.5 eV. The effect of LC properties on photovoltaic performance of the BHJ devices based on DPP-TP6:PC$_{71}$BM and DPP-TP12:PC$_{71}$BM films have investigated, in which the molecular packing and thin film morphologies are strongly affected by the length of the terminal alkyl chains. The $J_{sc}$ and FF have increased significantly for the DPP-TP6-based devices through the LC organization process, and the best-performing device has generated a high PCE of 4.3% with a $V_{oc}$ of 0.93 V, $J_{sc}$ of 8.4 mA/cm$^2$, and FF of 0.55 without use of any additives. The induction of LC characteristics to direct molecular self-assembly represents an effective strategy for designing donor molecules. It is anticipated that further enhancement of photovoltaic performances could be realized by a combination of fine structural tuning of DPP-based materials and precise control of their LC organization processing.

Chapter 3 dealt with π-extended narrow-bandgap oligomers, BDT-DPP, IDT-DPP, and T-DPP, based on DPP chromophoric units coupled with benzodithiophene (BDT), indacenodithiophene (IDT), and thiophene (T) cores for the application as donor materials in solution-processed OSCs. The impacts of these different central cores on the photophysical and morphological properties, carrier mobility, and photovoltaic performance are investigated. In addition, the effect of 1,8-diiodooctane (DIO) as a
processing additive on photovoltaic performance of the BHJ devices based on donor:PC$_{71}$BM films have been investigated, in which the molecular packing and thin film morphologies are strongly influenced by the central donor units. These π-extended oligomers possess broad and intense optical absorption covering the range of 500-750 nm, narrow optical bandgaps of 1.52-1.69 eV, and relatively low-lying HOMO energy levels ranging from −5.32 to −5.46 eV in their thin films. The $J_{sc}$ and FF have increased significantly for the BDT-DPP-based devices with use of additive. A high PCE of 5.9% is achieved for inverted OSCs based on a BHJ system consisting of a BDT-DPP-containing oligomer. Transmission electron microscopy and energy-dispersive X-ray spectroscopy analyses reveal that interpenetrating and interconnected donor/acceptor domains with pronounced mesoscopic phase segregation are formed within the photoactive binary blends, which is ideal for efficient exciton dissociation and charge transport in the BHJ devices. Meanwhile, the morphology of BDT-DPP:PC$_{71}$BM interpenetration network can be largely optimized by using DIO as a processing additive, which results in improvement of the PCE.

This thesis has investigated the photophysical, morphological, and self-organizing properties of π-conjugated donor molecules for efficient solution-processable OSCs. Experimental results revealed that the efficiency of new designed molecules-based OSCs increased with self-organization by thermal annealing or additive process. This was attributed to changes in the morphologies of active layer which were likely to due to increase of crystallinity and donor/acceptor (D/A) interactions. Future works are to develop the well-developed nanostructured electron donor molecules for OSCs. Nanocrystals are attractive for OSCs because semiconductor nanocrystals can lead to improved charge separation when blended with π-conjugated molecules. Further investigations are needed on the charge separation characteristics of the nanocrystal blends. Charge transport also needs to be addressed in the charge separation, and shape
control of nanocrystals is likely to enhance PCEs in the nanocomposites. The techniques used and developed in this thesis should continue to contribute to a greater understanding of the underlying photovoltaic properties of materials for efficient OSCs.
List of Publications

Original papers

(1) Self-Organizing Mesomorphic Diketopyrrolopyrrole Derivatives for Efficient Solution-Processed Organic Solar Cells

(2) $\pi$-Extended Narrow-Bandgap Diketopyrrolopyrrole-based Oligomers for Solution-Processed Inverted Organic Solar Cells

Symposium

(1) Development of Organic Solar Cells Based on Low Bandgap Liquid Crystalline Conjugated Molecules

(2) Self-Assembling Mesomorphic Materials Based on Diketopyrrolopyrrole for Highly Efficient Organic Solar Cell
Shin, W.; Yasuda, T.; Adachi, C. “The 21st Joint Seminar of the Kyushu Branch of the Chemical Society of Japan and the Pusan Branch of the Korean Chemical Society.”, Busan, Korea (June 12, 2013)
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