Functional fulleropyrrolidine derivatives as acceptors for organic photovoltaics

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Chapter 1

General Introduction

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General Introduction

Harvesting energy from the sun is one of the most important ways to prevent exhaustion of fossil fuels and global warming. The present solar cells are based on silicon wafer technology. Silicon based solar cells, however, have many disadvantages, such as high cost of resource materials, heavy weight, and poor flexibility of devices. Recently, organic solar cells have attracted much attention, due to their advantages of easy fabrication, simple device structure, low cost, light weight, flexibility of preparing devices, transparency, and large-area manufacturing compatibility. Dye sensitized solar cells (DSC) and organic thin-film solar cells (organic photovoltaics, OPV) are recognized as organic solar cells. Graetzel and co-workers reported DSC utilizing ruthenium complex based dye reaching the power conversion efficiency (PCE) of 11.2%. [1] However, since DSC requires expensive Ru metal, development of expensive transition metal free solar cells are strongly desired. The OPV has now been recognized as the most important candidate for the next-generation energy harvesting system. Tang reported two-layered cells consisting of p-type semiconductor (copper phthalocyanine (CuPC)) and n-type semiconductor (perylene tetracarboxylic derivative (Im-PTC)) achieved power conversion efficiency (PCE) of approximately 1% (Figure 1-1). [2] Since then, extensive investigation has been carried out to develop OPV and remarkable enhanced PCE has been accomplished by the use of bulk heterojunction (BHJ) cells comprising mixture of p-type semiconductor and n-type semiconductor as an active layer. [3] Exciton diffusion length in organic semiconductor is reported to be 10 – 14 nm;[4] the domain size of the active layer in the BHJ is small enough that generated exciton can reach to the p-n interface and it is believed that this geometry might contribute to enhance PCE drastically.

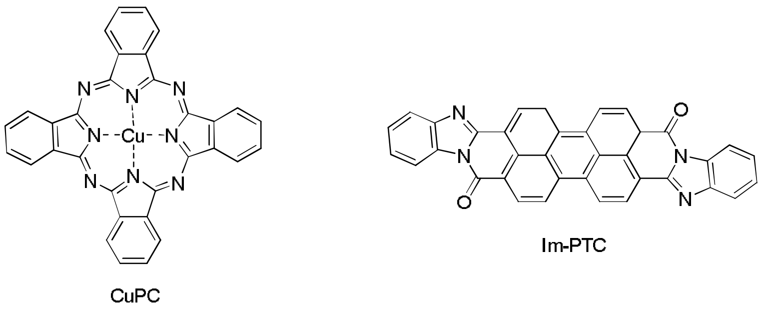

Figure 1-1. Chemical structures of copper phthalocyanine (CuPC) and perylene tetracarboxylic derivative (PV).

The development of new p-type semiconductors has been one of the key drivers of the recent increases in PCE. The best studied p-type semiconductor is poly(3-hexylthiophene) (P3HT); however,P3HT absorbs the light up to only around 650nm. Absorbing wavelengths longer than 650 nm is expected to enhance short circuit current density (J_{sc}); therefore great effort has been made to develop new low band-gap p-type semiconductors in the past decade.[5-8]

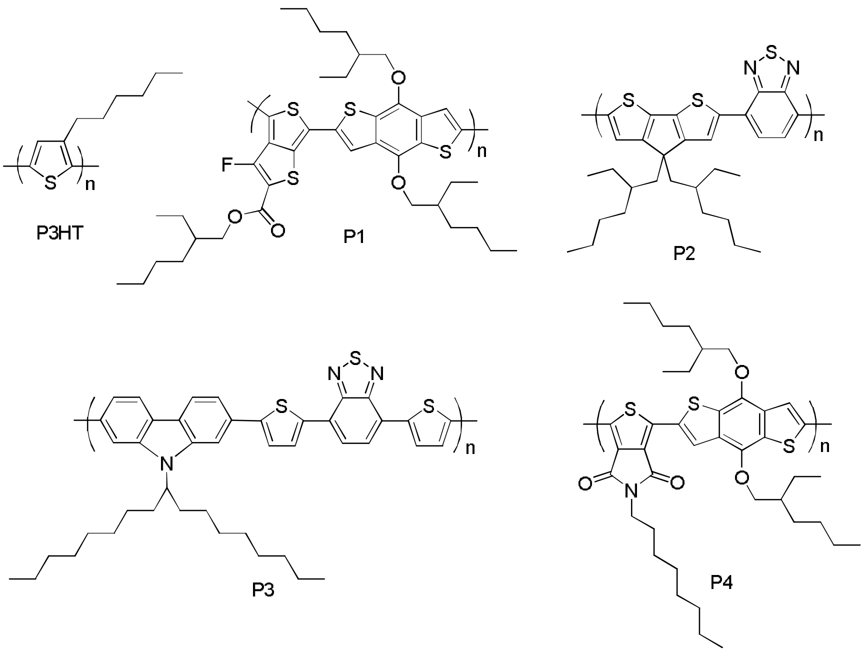

Figure 1-2. Chemical structures of P3HT, P1,[5] P2,[6] P3,[7] and P4[8] as examples for p-type semiconductors.

Changes in the n-type semiconductor are another promising route to increasing PCE. Fullerene derivatives are widely used as n-type materials in OPV devices. Fullerenes show high electron mobilities and suitable LUMO levels for OPV active layer. However, it is well known that the fullerene generally has a poor solubility in conventional organic solvents and this makes it difficult to prepare electric devices based on unsubstituted fullerene using economical techniques such as the spin-coating procedure. Therefore, the development of stable fullerene derivatives with a sufficient affinity toward organic solvents, whilst retaining a high electron mobilities and suitable LUMO level, is desired. Methyl [6,6]-phenyl-C_{61}-butylate ([C_{60}]-PCBM) [9] is known to be one of the best blending material among fullerene derivatives for active layer of OPVs. Hummelen and co-workers synthesised [C_{60}]-PCBM derivatives substituting electron-donating or electron-withdrawing groups on the phenyl ring and revealed that the substituent influenced the LUMO level of the parent fullerene. They found that differences in the LUMO level due to the substituent were enough to cause a change in the open circuit voltage of the resulting solar cell by several tens of mV.[10] Troshin, Hoppe, and co-workers also synthesized various types of methanofullerene derivatives and established that [C_{60}]-PCBM was the best acceptor to use with P3HT polymer in terms of PCE.[11] A further class of fullerene derivatives, the fulleropyrrolidines, are attractive as acceptor materials due to their stability under atmospheric conditions and the ease of synthesising various types of analogues. [12] Several examples have been reported concerning the use of fulleropyrrolidines as the acceptor source of polymer solar cells. However, PCE values of the solar cells using fulleropyrrolidine derivatives have remained at an insufficient level.[13]

In our group, the design of fulleropyrrolidine derivatives with high solubility in various types of organic solvents has been reported.[14] It has been confirmed that fabrication of the film using the spin-coating method is very easy due to this high solubility.[14] Encouraged by the results, we conducted a systematic study on the design of fulleropyrrolidine derivatives as the acceptor in OPV devices using P3HT as the polymer. It was thus established that N-methoxyethoxyethyl-2-(2-methoxyphenyl)fulleropyrrolidine works as a good acceptor partner with P3HT.[15]

In the present study, we focus our effort on the design of novel fulleropyrrolidines as the acceptor in OPV devices using poly(3-hexylthiophene) (P3HT) as the polymer.

In the Chapter 2, we report the results of an investigation into the effect of thiophene derivatives as substituent groups on the fulleropyrrolidine ring: we show five types of thiophene-substituted fulleropyrrolidine which work as a good acceptor partner with P3HT, with the highest power conversion efficiency (PCE) obtained for 1-(2-(2-methoxyethoxy)ethyl)-2-(2-thiophen-2-yl)fulleropyrrolidine (2.99 %). This is superior to the PCE of devices prepared using methyl [C_{60}]-PCBM under the same experimental conditions.

In the Chapter 3, the results of molecular design of fullerene derivatives to prevent adverse chemical reactions with the PEDOT:PSS hole transport layer are reported. Three types of 2,5-diarylfulleropyrrolidine derivatives, i. e. 2,5-diphenyl, 2,5-di(thiophen-2-yl), and 2,5-di(thiophen-3-yl)fulleropyrrolidines were used as acceptor molecules with P3HT in OPV devices using two types of ITO electrodes. We show that their PCE depends on both the stereochemistry and chemical structure of two aryl substituents on the 2 and 5 positions of the pyrrolidine ring. The PCE of the devices using *trans*-diphenyl or either *cis*- or *trans*-di(thiophen-3-yl) compounds was significantly lowered by using an ITO electrode with poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT:PSS), while *cis*-diphenyl isomer was not influenced by PEDOT:PSS. Furthermore, both *cis*- and *trans*-2,5-di(thiophen-2-yl)fulleropyrrolidine displayed a high PCE using PEDOT:PSS.

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Chapter 2

Thiophene-substituted Fulleropyrrolidine Derivatives as Acceptor Molecules in a Thin Film Organic Solar Cell

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Thiophene-substituted Fulleropyrrolidine Derivatives as Acceptor Molecules in a Thin Film Organic Solar Cell

2-1. Introduction

As mentioned in the General Introduction (Chapter 1), fullerene and its derivatives are widely used as n-type materials in the active layer of OPVs due to their high electron mobility and adequate LUMO level.[2,3] Fullerene-based OPV can be fabricated *via* vapor deposition. However, considering the requirement for mass production in order to achieve cost reductions, the application of roll-to-roll processing (i.e., the solvent casting method) is highly desirable. Therefore, development of stable fullerene derivatives that show both a high PCE and a sufficient solubility against organic solvents is strongly desired.[1-3] Various types of fullerene derivatives for use as OPV n-type materials have thus been developed. A [C_{60}]-PCBM[4] is known to be the best blending material among these derivatives as an acceptor with polythiophene which is a donor partner in polymer solar cells.[5-15] Troshin, Hoppe, and co-workers also synthesized various types of methanofullerene derivatives as acceptors for P3HT.[15] Recently Matsuo and co-workers reported OPV devices using silylmethylfullerene (SIMEF) that showed PCE superior to devices using [C_{60}]-PCBM.[16,17] On the other hand, several examples have also been reported concerning the use of fulleropyrrolidines as the acceptor source of polymer solar cells. Reported PCE values of the solar cells derived from fulleropyrrolidine, however, have remained insufficient.[18-25] We were fascinated by the fulleropyrrolidines from the standpoint of their stable nature under atmospheric conditions and the ease of producing various types of analogues,[26] and conducted a systematic study of the design as an acceptor partner in polymer solar cells.[27]

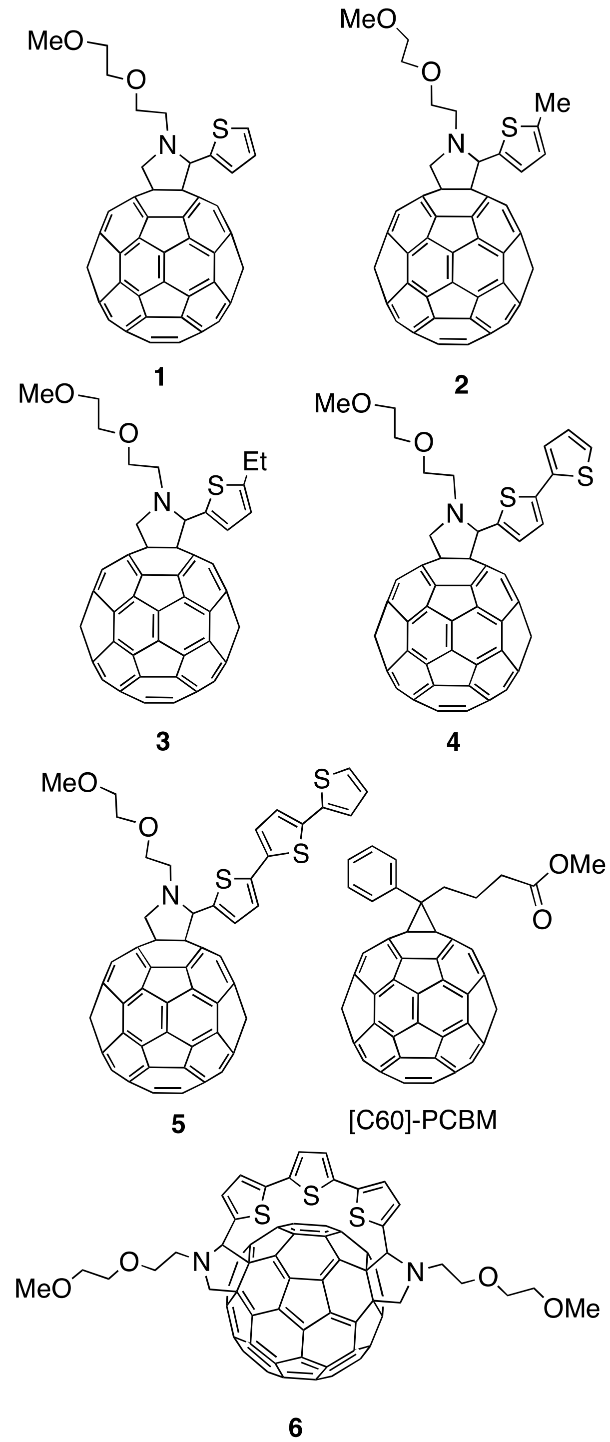

Figure 2-1. Thiophene-substituted fulleropyrrolidine derivatives and [C_{60}]-PCBM

We found that OPV devices using several fulleropyrrolidine derivatives, in particular 1-(2-(2-methoxyethoxy)ethyl)-2-(2-methoxyphenyl) fulleropyrrolidine, showed higher PCE compared to devices using [C_{60}]-PCBM. Further, we established that the open circuit voltage

(V_{oc}) of devices using fulleropyrrolidine derivatives strongly depends on the substituent groups on the pyrrolidine ring.[27]

Heeger and co-workers reported that the V_{oc} of an OPV device is determined by the difference between the HOMO level of the p-type semiconductor and the LUMO level of the n-type conductor.[8] Therefore, it might be expected that appropriate modification of the pyrrolidine ring could enhance the LUMO level, possibly improving the V_{oc}. We hypothesized that introduction of a π-conjugated moiety to the fulleropyrrolidine might affect the HOMO-LUMO level as well as the charge separation process, which could cause significant change in OPV properties. We herein report the synthesis of thiophene-substituted fulleropyrrolidine derivatives **1-6** and results of their evaluation as acceptor materials with P3HT in solar cells. Thus, we have established that the introduction of a thiophene moiety on the pyrrolidine ring of fulleropyrrolidines has a favorable effect on the PCE of a solar cell.

2-2. Development of OPV devises using fulleropyrrolidines having thiophene ring(s) as a substituent group

Synthesis of fulleropyrrolidines having thiophene ring(s).

Thiophene is well known as an electron-releasing substituent group, therefore, it is expected that the thiophene group becomes a π-conjugated moiety and thus influences both the light-absorbing behavior and charge separation process of fullerene molecules. We hypothesized that thiophene-substituted fulleropyrrolidine might become a good candidate as acceptor in polymer solar cells. Synthesis of a thiophene derivative fulleropyrrolidine (**1**) was reported earlier in our previous publication[27]. Fulleropyrrolidine derivatives (**2-6**) were prepared by a similar method[26,27] originally developed by Prato and co-workers.[1a] N-Methoxyethoxyethyl glycine[28] was treated with the [C_{60}]-fullerene in the presence of a thiophene-substituted aldehyde in chlorobenzene and the mixture was heated at 130 °C for 3 h. Purification of the desired compounds was accomplished by silica-gel flash column chromatography or silica-gel thin layer chromatography; the desired mono adducts were thus obtained in acceptable yields from 40% to 78%. We further synthesized bridged type fulleropyrrolidine **6** by the reaction of [2,2’:5’,2”-terthiophene]-5,5”-dicarbaldehyde (**8**) and N-methoxyethoxy glycine in the presence of [C_{60}]-fullerene. The desired bridged type compound **6** was obtained as a single isomer.

Photovoltaic performance.

Using the fulleropyrrolidine derivatives **1-6**, we prepared OPV devices and evaluated their efficiency as follows. Fulleropyrrolidines were mixed with poly(3-hexylthiophene) (1/1 wt/wt) in *o*-dichlorobenzene, and the resulting solution was spin-coated onto ITO or ITO coated with poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT:PSS)[29] as a positive electrode. LiF and aluminum were then deposited as a negative electrode. The PCE values were measured by taking current-voltage measurements with the devices under illumination using a solar simulator (AM1.5G, 100 mW/cm^2). The results are summarized in Table 2-1.

Table 2-1. Photovoltaic performances of the P3HT-based organic photovoltaic devices with various types of fulleropyrrolidine derivatives. [a]

Entry	Fullerene derivative	PCE %	J_{sc} mA/cm^2	V_{oc} Volt	FF
1[b]	**1**	3.0	7.5	0.61	0.66
2	**2**	2.9	7.7	0.62	0.61
3	**3**	2.8	7.9	0.61	0.57
4	**4**	2.8	6.8	0.64	0.64
5	**5**	2.4	6.4	0.65	0.56
6	**6**	0.61	3.1	0.65	0.31
7	[C_{60}]-PCBM	2.5	6.9	0.58	0.63

[a] Under the illumination of AM 1.5G, 100 mW/cm^2. [b] Ref. 27.

The PCE of derivatives **1**-**4** was higher than that of [C_{60}]-PCBM (Entry 7). The PCE of **1** was the highest among the three mono-thiophene derivatives (Entries 1-3) due to a significantly higher fill factor (FF), despite slightly lower open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) (Entry 1). The V_{oc} of all three thiophene-substituted fulleropyrrolidine devices was higher than that of [C_{60}]-PCBM, which we suggest is due to the electron-donating property of thiophene and the resulting higher LUMO. The J_{sc} and FF of terthiophene substituted derivative **5** were lower than devices **1**-**4**, which we propose is a result of its reduced solubility compared to the mono-thiophene and bithiophene derivatives. The distinctive feature of **5** is the high V_{oc} (0.65 V) when compared with **1**-**4** and [C_{60}]-PCBM The reason for that will be discussed below using cyclic voltammograms.

We previously reported that PCE significantly depended on the position of functional group on the benzene ring of the related fulleropyrrolidine derivatives, and high PCE was recorded for compounds which have a methoxy or methyl group at the ortho-position of the phenyl group.[27] Because the alkyl group is believed to be a moderate electron-donating group, we next incorporated an alkyl group to the thiophene ring. As expected, PCE of **2** and **3** was higher than that of [C_{60}]-PCBM. However, little difference in OPV performance was found between derivatives 2 and 3, suggesting that the choice of methyl or ethyl group at the 5-position of the thiophene ring has little influence on the PCE (Entries 2 and 3). Derivative 3, with the ethyl group, showed a slightly reduced FF, possibly due to the effect of steric hindrance on molecular packing (Entry 3).

Bis-[C_{60}]-PCBM was reported to show higher V_{oc} than [C_{60}]-PCBM, because bis-[C_{60}]-PCBM possesses a higher LUMO level due to the additional break in the conjugated fullerene cage.[4] Although the bridged type fulleropyrrolidine **6,** also with an additional break in the conjugation of the fullerene cage, showed higher V_{oc} than [C_{60}]-PCBM, poor PCE was obtained due to its low J_{sc} and FF (Entry 6).

Influences from PEDOT:PSS on device performance.

Recently, an ITO electrode coated with poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT:PSS)[29] has been widely used as the hole transport layer (HTL) for a solar cell. This is explained by the sufficient work function for hole collection. However, we prepared solar cells using a simple ITO electrode without a PEDOT:PSS layer due to concerns that protonation of the nitrogen atom on the pyrrolidine ring by PSS might inhibit the electron transfer pathway between fullerene molecules and P3HT. Although an investigation on the modification of redox properties of fulleropyrrolidine derivatives induced by protonation has been carried out, no detailed report on the photovoltaic performance has been reported. [30] To investigate this, we prepared three types of OPV devices using ITO electrodes: the first without PEDOT:PSS, the second with PEDOT:PSS, and the third having neutral PEDOT. We then evaluated their efficiency using bithiophene substituted fulleropyrrolidine **4** as the acceptor partner with P3HT (Table 2-2).

Table 2-2. Photovoltaic performances of the P3HT-based organic photovoltaic devices with bithiophene-substituted fulleropyrrolidine **4** using three ITO electrodes.

Entry	Acceptor	PCE %	J_{sc} mA/cm^2	V_{oc} Volt	FF	HTL
1	[C_{60}]-PCBM	2.5	6.7	0.56	0.66	bare[a]
2	[C_{60}]-PCBM	2.6	7.0	0.56	0.67	PEDOT:PSS [b]
3	[C_{60}]-PCBM	2.5	7.2	0.55	0.64	neutral PEDOT [c]
4	**4**	2.8	6.8	0.64	0.64	bare
5	**4**	0.10	0.71	0.48	0.29	PEDOT:PSS
6	**4**	1.8	5.9	0.54	0.57	neutral PEDOT
7[d]	**7**	3.0	7.6	0.64	0.63	bare
8	**7**	0.51	6.5	0.52	0.15	PEDOT: PSS

[a] "bare" means a special electrode prepared without HTL. [b] PEDOT:PSS (AI4083 (pH=1.8)): baked at 120°C for 10 min. under air, 44 nm. [c] Neutral PEDOT: 0.4 wt% diethanolamine, 2,4,7,9-tetramethyldec-5-yne-4,7-diol (surfactant) 100 ppm (pH7.5), baked at 120°C for 10 min. under air, 45 nm. [d] Ref. 27.

As shown in Table 2-2, the PCE of [C_{60}]-PCBM devices was independent of the use of electrode (Entries 1-3). However, as anticipated, using PEDOT:PSS in the electrode with isomer **4** caused a significant drop of PCE, mainly due to reduced J_{sc} (Entry 5). A significantly higher PCE was obtained when the cell was prepared with neutral PEDOT (Entry 6), but PCE in this case was still lower than in the devices made using a simple ITO electrode without PEDOT:PSS (Entry 4). It was thus found that it was essential to use an electrode lacking PEDOT:PSS in order to obtain good PCE for thiophene-substituted fulleropyrrolidine based devices. In addition, a similar significant reduction of photovoltaic performance was recorded when 1-(2-(2-methoxyethoxy)ethyl)-2-([1,1'-biphenyl]-2-yl)fulleropyrrolidine (**7**)[27] was used as an acceptor (Entry 8).

It is reported that the protonation of the fulleropyrrolidine by trifluoroacetic acid caused a blue shift on the UV-visible spectrum.[30] Figure 2-2 shows UV-visible spectra of fulleropyrrolidine **4** with and without acids, when trifluoroacetic acid (TFA) and *p*-toluenesulfonic acid (*p*-TsOH) were used as acid. As can be seen, blue shift of the fulleropyrrolidine was observed in the presence of both TFA and *p*-TsOH. Since *p*-TsOH is thought to be a model compound of PSS, it is likely that protonation of the fulleropyrrolidine indeed formed when PEDOT:PSS was used as hole transport layer.

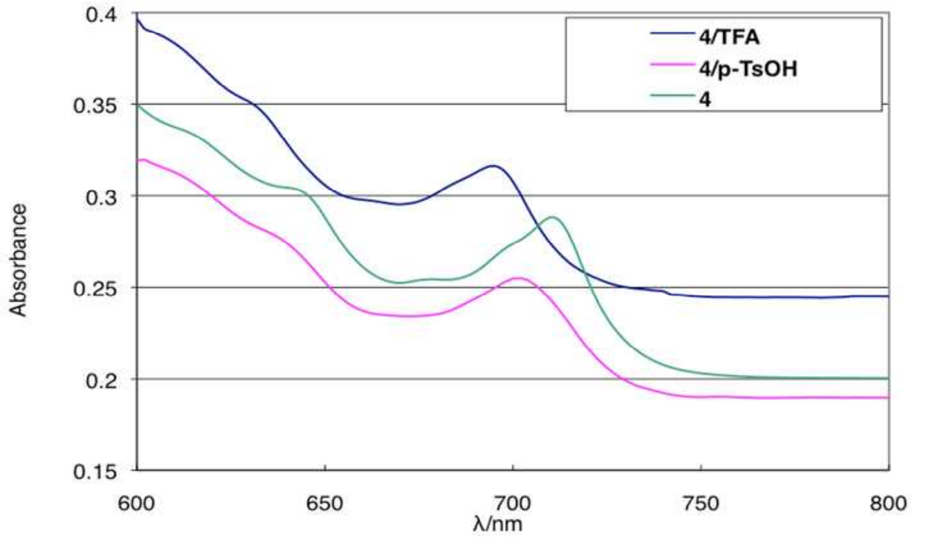

Figure 2-2. UV-visible spectra of fulleropyrrolidine **4** in the presence and absence of TFA or *p*-TsOH in CS_2. (**4** : Acid = 1 : 20 (mol/mol). Concentration of **4** in CS_2 is approximately 0.02mM.)

Effect of substituent group on device performance.

Figure 2-3 shows the UV-visible spectra of the P3HT/**1**, P3HT/**5** and P3HT/[C_{60}]-PCBM. All films show a broad π–π* absorption from 400 to 700 nm and the λ_{max} of the three films is around 500 nm, which is attributable to the P3HT. The P3HT/**5** blend has distinctive broad absorption between 350 and 400 nm, which is assumed to be caused by the terthiophene moiety on the fulleropyrrolidine molecule.

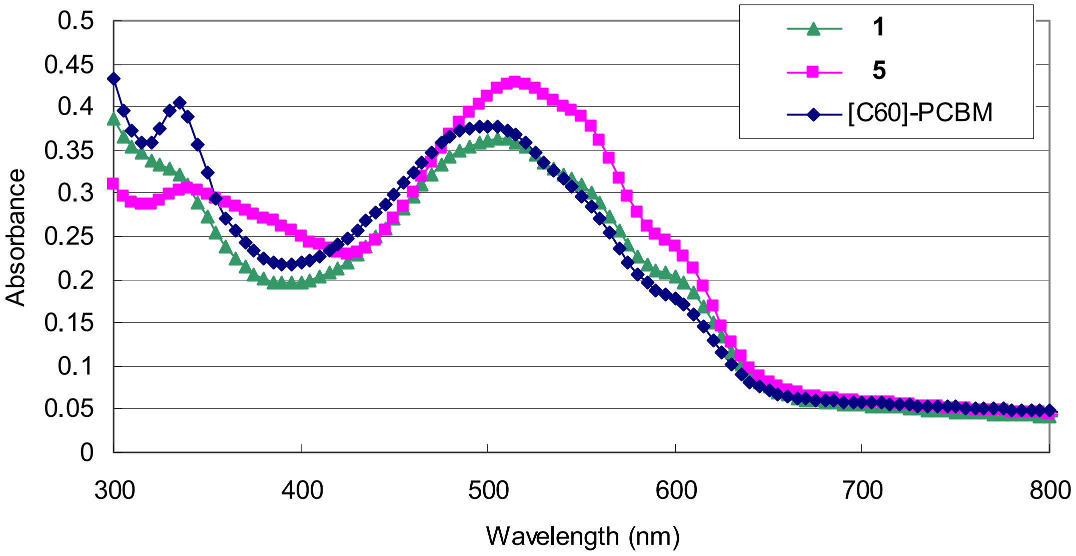

Figure 2-3. UV-visible spectra of **1**, **5** and [C_{60}]-PCBM.

External quantum efficiency (*EQE*) of the P3HT/**5** and P3HT/[C_{60}]-PCBM are shown in Figure 2-4. Since there is less absorption in the range of 350 - 400 nm in the UV-visible spectrum of P3HT/[C_{60}]-PCBM film, the *EQE* of the film in this range stayed low (*EQE* = 0.3 - 0.4). On the other hand, as can be seen on the P3HT/**5**, the *EQE* between 350 – 400 nm reached around 0.5, thus revealing that the terthiophene moiety of **5** not only absorbed the light but also contributed to produce excitons within the range of 350 – 400 nm.

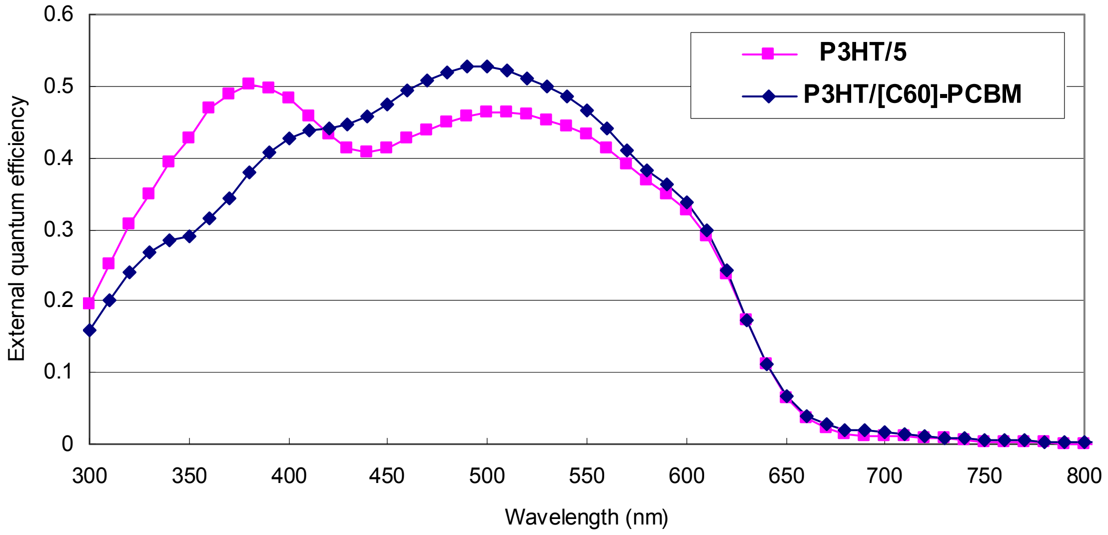

Figure 2-4. External quantum efficiency of terthiophene derivative **5** and [C_{60}]-PCBM

Fulleropyrrolidine **6** has a terthiophene bridge, which should have a similar absorption spectrum to compound **5**. However, the PCE of the device using P3HT/**6** was unexpectedly low as mentioned above, which indicated that bridged-terthiophene moiety showed poor PCE (Entry 6 in Table 2-1). The bridged-terthiophene moiety might be too close to the fullerene ring, preventing charge separation.

Electrochemical study.

The highest V_{oc} was found when mono-thiophene **5** was used as an electron acceptor component in the active layer. To understand the reason for the high V_{oc} of **5** compared to [C_{60}]-PCBM, the electrochemical properties of terthiophene **5** and [C_{60}]-PCBM were studied by cyclic voltammetry. The cyclic voltammograms of the fullerene derivatives in the potential range of 1.0 ~ –2.0 V vs. ferrocene F_c/F_c^+ are shown in Figure 2-5. In the negative potential range, it can be seen that these derivatives showed three apparent reversible reduction waves respectively in the potential range from –0.8 V to –1.8 V. The half-wave potential of the reduction process is defined as E^0 = [E_c + E_a] / 2 (wherein E_c and E_a are the potential of cathodic peak and anodic peak, respectively). The half-wave potentials are summarized in Table 2-3. The first ($E^0{}_1$), second ($E^0{}_2$) and third ($E^0{}_3$) reduction potentials of **5** were shifted negatively when compared to [C_{60}]-PCBM.

The LUMO energy levels of the fullerene derivatives were estimated from their first half-wave potentials ($E^0{}_1$) indicated in the cyclic voltammograms. The $E^0{}_1$ of terthiophene **5** and [C_{60}]-PCBM were –1.09 and –1.15 V vs. Fc/Fc$^+$, respectively. The LUMO energy levels of the fullerene derivatives from the onset reduction potentials were calculated by use of the following equation: LUMO (eV) = –($E^0{}_1$ + 4.80). The LUMO energy levels of [C_{60}]-PCBM and **5** calculated by this method are –3.71 and –3.65 eV, respectively, and are summarized in Table 2-3. The LUMO level of **5** is raised by 0.06 eV in comparison with that of [C_{60}]-PCBM. The higher LUMO level of **5** is desirable for its application as acceptor in the active layer to obtain V_{oc}.

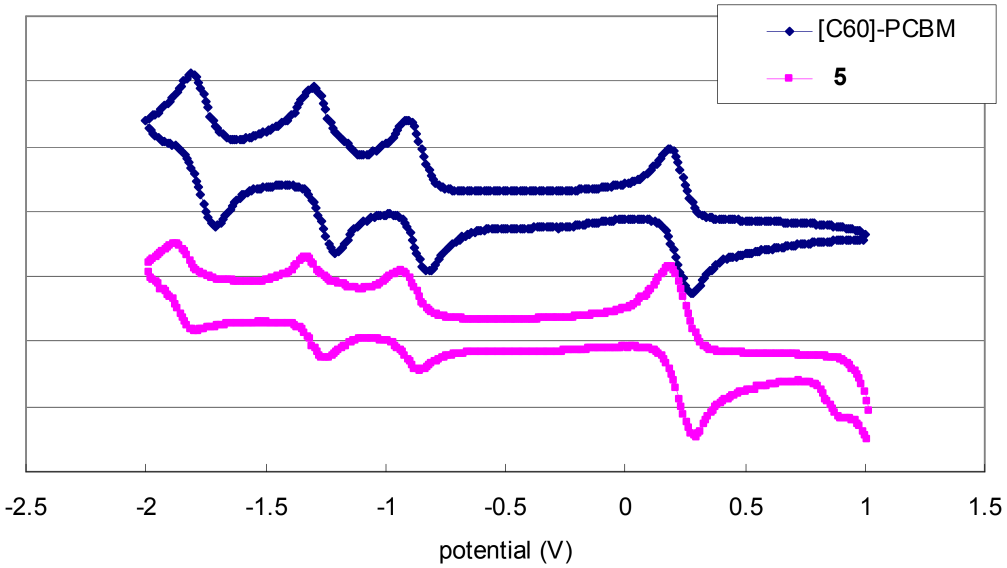

Figure 2-5. Cyclic voltammograms of [C_{60}]-PCBM and **5** in CH_3CN (0.1 mM) with 0.1M n-Bu_4NPF_6 at a scan rate of 10 mV/s.

Table 2-3. Estimated half-wave potentials and LUMO of the fullerene derivatives [a]

Entry		$E^0{}_1$ V	$E^0{}_2$ V	$E^0{}_3$ V	LUMO eV
1	[C_{60}]-PCBM	–1.09	–1.49	–2.00	–3.71
2	**5**	–1.15	–1.53	–2.08	–3.65

[a] The potential values in this table are versus Fc/Fc^+

2-3. Conclusions

In summary, we have carried out the rational design of thiophene-substituted fulleropyrrolidine derivatives (**1**-**5**) as the acceptor partner with poly(3-hexylthiophene) and established that these fulleropyrrolidines work as good acceptor partners with P3HT. A high power conversion efficiency was obtained, superior to that of the P3HT-based devices including [C_{60}]-PCBM under the same experimental conditions. It was also found that using an electrode that lacked PEDOT:PSS was essential to obtain good PCE for fulleropyrrolidine based solar cells. The effect from PEDOT:PSS to the active layer containing fulleropyrrolidines and will be discussed in Chapter 3

2-4. Experimental section

General Procedures.

Photovoltaic devices were prepared by spin-coating the fulleropyrrolidine-polymer blends from chlorobenzene onto an indium tin oxide (ITO) glass electrode as follows: To a P3HT (1.0 wt%) solution of chlorobenzene were added fulleropyrrolidine **1** (equal weight vs. P3HT) and silica gel (1.0 wt % vs. P3HT solution), then the mixture was stirred for 12 h at ambient temperature. It was then filtered through a Teflon (0.2 μm) filter. The resulting solution was applied to the surface of an ITO plate by the spin-coating method at a thickness of ca. 100 nm, and the surface was washed with acetone and irradiated under UV light and ozone gas for 20 min to decompose the impurities. After drying under vacuum for 20 min, the resulting plate was placed in a vacuum chamber and the surface was coated with the electrode layers of lithium fluoride (LiF) (4 nm) and aluminum (100 nm) by evaporation at 10^{-4} Pa at rt. We placed the glass plate on the resulting film and the plate was firmly fixed using a bonding agent under an argon atmosphere to produce the solar cell. The PCE values were obtained using the solar simulator OTENTO-SUN II (AM1.5G, 100 mW/cm^2). Cyclic voltammograms were obtained in acetonitrile with 0.1mM tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte using a glassy carbon (1 mm diameter) as a working electrode, a Pt counter electrode and Ag/AgCl reference electrode. UV-visible spectra were obtained using the spectrophotometer JASCO V-670.

Materials

The [C_{60}]-fullerene was purchased from Frontier Carbon (nanom purple ST-A) and P3HT from Aldrich. The silica gel was purchased from Wako Pure Chemical Industry, Ltd. (Wakogel C-300, 45~75 μm).

1-(2-(2-methoxyethoxy)ethyl)-2-(2-thiophen-2-yl) fulleropyrrolidine (1)[27]

A solution of [C_{60}]-fullerene (500 mg, 0.69 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid[26,28] (177 mg, 1.0 mmol), and thiophene-2-carbaldehyde (188 mg, 1.38 mmol) in chlorobenzene (100 mL) was stirred for 3 h at 130 °C under argon. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (toluene, then CS_2 / ethyl acetate=10:1) affording the product **1** (351 mg, 0.36 mmol) as a dark brown solid in 52% yield, and the unreacted fullerene (174 mg) was recovered in 35% yield.

R_f 0.61 (toluene/methanol=2/1); ^{1}H NMR (400 MHz, $CDCl_3$, J= Hz) δ 2.87-2.93 (1H, m), 3.39 (3H, s), 3.49-3.57 (3H, m), 3.60-3.62 (2H, m), 3.92-3.97 (1H, m), 4.00-4.05 (1H, m), 4.26 (1H, d, J= 9.8 Hz), 5.19 (1H, d, J= 9.8 Hz), 5.47 (1H, s), 6.99 (1H, t, J= 4.9 Hz), 7.31 (1H, d, J= 5.9 Hz), 7.34 (1H, d, J= 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.25, 58.77, 67.60, 68.56, 70.41, 70.51, 71.87, 75.82, 77.68, 126.37, 126.44, 127.83, 127.99, 128.6, 135.27, 135.60, 136.33, 136.74, 139.28, 139.60, 139.84, 139.89, 140.72, 141.28, 141.36, 141.56, 141.66, 141.71, 141.73, 141.81, 141.83, 141.85, 141.92, 141.94, 142.27, 142.37, 142.68, 142.83, 144.03, 144.06, 144.32, 144.40, 144.81, 144.89, 144.91, 144.95,145.01, 145.05, 145.11, 145.17, 145.24, 145.29, 145.45, 145.61, 145.75, 145.78, 145.84, 145.88, 145.96, 146.00, 146.02, 146.55, 146.96, 152.82, 152.96, 153.77, 155.82; IR (KBr, cm^{-1}) 2864, 2812, 1462, 1427, 1180, 1107, 839, 768, 700, 527; MALDI-TOF-MS (matrix: SA) found 947.0978 (calculated for $C_{71}H_{17}NO_2S$, exact mass: 947.0981)

Reaction of 5-methylthiophene-2-carbaldehyde or 5-ethylthiophene-2-carbaldehyde with C_{60}-fullerene gave fulleropyrrolidine **2** or **3** in similar yield in the reaction of **1**.

1-(2-(2-methoxyethoxy)ethyl)-2-(5-methylthiophen-2-yl)fulleropyrrolidine (2)

^{1}H NMR (500 MHz,$CDCl_3$, J= Hz) δ 2.47 (3H, s), 2.89-2.95 (1H, m), 3.44 (3H, s), 3.57-3.59 (1H, m), 3.61-3.70 (2H, m), 3.77-3.84 (2H, m), 3.98-4.02 (1H, m), 4.04-4.08 (1H,m), 4.25 (1H, d, J= 9.7 Hz), 5.16 (1H, s), 5.39 (1H, s), 6.06 (1H, dd, J= 3.5, 1.1 Hz), 7.16 (1H, d, J= 3.5 Hz); ^{13}C NMR (100MHz,$CDCl_3$) δ 15.63, 52.16, 59.14, 67.66, 68.91, 70.50, 70.54, 72.00, 76.15, 78.25, 124.57, 128.36, 135.54, 135.77, 136.60, 138.30, 139.58, 139.84, 140.06, 140.08, 141.25, 141.53, 141.62, 141.90, 141.93, 141.98, 142.08, 142.12, 142.19, 142.51, 142.52, 142.62, 142.91, 143.09, 144.32, 144.59, 144.68, 145.17, 145.21, 145.26, 145.30, 145.45, 145.49, 145.73, 145.87, 145.89, 146.01, 146.05, 146.10, 146.15, 146.24, 146.34, 146.45, 147.25, 153.39, 153.60, 154.24, 156.27; IR (KBr, cm^{-1}) 2853, 1684, 1458, 1425, 1107, 795; MALDI-TOF-MS (matrix: SA) found 961.1138 (calculated for $C_{72}H_{19}NO_2S$, exact mass: 961.1138)

1-(2-(2-methoxyethoxy)ethyl)-2-(5-ethylthiophen-2-yl)fulleropyrrolidine (3)

^{1}H NMR (500 MHz, $CDCl_3$, J= Hz) δ 1.28 (3H, t, J= 7.5 Hz), 2.82 (2H, q, J= 7.5 Hz), 2.90-2.95 (1H, m), 2.88 (3H, s), 3.58-3.62 (1H, m), 3.63-3.70 (2H, m), 3.78-3.84 (2H, m), 3.99-4.04 (1H, m), 4.06-4.09 (1H, m), 4.26 (1H, d, J= 9.7 Hz), 5.16 (1H, d, J= 9.8 Hz), 5.40 (1H, s), 6.68 (1H, d, J= 3.5 Hz), 7.18 (1H, d, J= 3.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.70, 23.60, 52.18, 59.14, 67.66, 68.90, 70.49, 70.54, 72.00, 76.20, 78.31, 122.57, 128.13, 135.55, 136.61, 136.93, 137.80, 139.52, 139.82, 140.05, 141.86, 141.93, 141.98, 142.09, 142.12, 142.19, 142.24, 142.51, 142.62, 142.91, 143.10, 144.32, 144.59, 144.67, 145.07, 145.18, 145.23, 145.29, 145.45, 145.48, 145.73, 145.87, 146.01, 146.04, 146.10, 146.15, 146.23, 146.26, 146.35, 146.44, 146.95, 147.25, 148.89, 153.39, 153.64, 154.25; IR (KBr, cm^{-1}) 2866, 1670, 1508, 1458, 1425, 1107, 802; MALDI-TOF-MS (matrix: SA) found 975.1292 (calculated for $C_{73}H_{21}NO_2S$, exact mass: 975.1294)

1-(2-(2-methoxyethoxy)ethyl)-2-([2,2'-bithiophen]-5-yl)fulleropyrrolidine (4)

A solution of [C_{60}]-fullerene (500 mg, 0.69 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid[26,28] (177 mg, 1.0 mmol), and 5-(thiophen-2-yl)thiophene-2-carbaldehyde[31] (268 mg, 1.40 mmol) in chlorobenzene (100 mL) was stirred for 3 h at 130 °C under argon. The resulting mixture was separated by silica gel flash chromatography to give **2** (298 mg, 0.29 mol) in 42% yield, and the unreacted fullerene (275 mg) was recovered in 55% yield.

^{1}H NMR (500 MHz,$CDCl_3$, J= Hz) δ 2.93-3.01 (1H, m), 3.15 (3H, s), 3.60-3.70 (3H, m), 3.75-3.85 (2H, m), 3.98-4.04 (1H, m), 4.05-4.10 (1H, m), 4.28 (1H, d, J= 9.7 Hz), 5.23 (1H, d, J= 9.6 Hz), 5.44 (1H, s), 6.98 (1H, dd, J= 5.5, 3.7 Hz), 7.07 (1H, d, J= 3.7 Hz), 7.15 (1H, dd, J= 3.7, 1.0 Hz), 7.18 (1H, dd, J= 5.7, 1.0 Hz), 7.28 (1H, d, J=3.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.35, 59.04, 67.74, 68.87, 70.52, 70.55, 71.99, 76.03, 78.01. 122.89, 123.78, 124.50, 127.77, 128.90, 135.82, 136.53, 137.08, 137.31, 139.66, 139.87, 139.94, 140.07, 140.52, 141.59, 141.80, 141.87, 141.95, 142.04, 142.07, 142.14, 142.20, 142.49, 142.60, 142.89, 143.06, 144.29, 144.54, 144.63, 145.06, 145.15, 145.20, 145.24, 145.35, 145.40, 145.43, 145.52, 145.67, 145.84, 145.98, 146.03, 146.08, 146.10, 146.22, 146.73, 147.22, 153.05, 154.01, 156.02; IR (KBr, cm^{-1}) 2864, 1638, 1107, 795; MALDI-TOF-MS (matrix: SA) found 1029.0873 (calculated for $C_{75}H_{19}NO_2S_2$, exact mass: 1029.0859)

1-(2-(2-methoxyethoxy)ethyl)-2-([2,2':5',2''-terthiophen]-5-yl)fulleropyrrolidine (5)

(1) To a solution of terthiophene (250 mg, 1.01 mmol) in dichloromethane (CH_2Cl_2)(5.0 ml) was added N,N-dimethylformaldehyde (DMF) (162 mg, 2.21 mmol) under argon, then 0.21 ml of $POCl_3$ (2.21 mmol) was added at 0°C and the resulting mixture was stirred at 50°C for 2 hr. The reaction was quenched by addition of 1M sodium acetate (NaOAc) aqueous solution then extracted with CH_2Cl_2. After evaporation, silica gel flash coloumn chromatography (CH_2Cl_2/ ethyl acetate= 1:0 to 10:1) to afford [2,2':5',2''-terthiophene]-5-carbaldehyde (**7**)[32] (231 mg, 0.84 mmol, 83 %) and [2,2':5',2''-terthiophene]-5,5''-dicarbaldehyde (**8**)[33] (68.0 mg, 0.22 mmol, 22%), respectively.

(2) A solution of C_{60} (250 mg, 0.35 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid (92 mg, 0.52 mmol), and [2,2':5',2''-terthiophene]-5-carbaldehyde (**7**) (192 mg, 0.69 mmol) in chlorobenzene (50 mL) was stirred for 3 h at 130 °C under argon. The resulting mixture was separated by silica gel flash chromatography to give **3** (157 mg, 0.14 mol) in 41% yield, and the unreacted fullerene (118 mg) was recovered in 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$, J= Hz) δ 2.87-2.93 (1H, m), 3.39 (3H, s), 3.49-3.57 (4H, m), 3.60-3.62 (2H, m), 3.92-3.97 (1H, m), 4.00-4.05 (1H, m), 4.26 (1H, d, J= 9.8 Hz), 5.19 (1H, d, J= 9.8 Hz), 6.96 (1H, dd, J=5.1 Hz, 3.6 Hz), 7.00 (2H, dd, J=9.2 Hz, 3.6 Hz), 7.03 (d, 1H, J=3.6 Hz), 7.09 (1H, dd, J= 3.4Hz, 1.0Hz), 7.15 (1H, dd, J=5.0 Hz, 0.9 Hz), 7.26 (1H, d, J=3.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.40, 58.81, 67.68, 68.67, 70.49, 71.93, 75.83, 77.94, 122.71, 123.61, 124.17, 124.27, 124.44, 127.69, 128.74, 135.27, 135.65, 135.92, 136.35, 136.84, 136.94, 138.21, 139.54, 139.74, 139.93, 140.03, 141.37, 141.43, 141.62, 141.70, 141.79, 141.88, 141.98, 142.01, 142.33, 142.45, 142.74, 142.90, 144.12, 144.40, 144.46, 144.89, 144.97, 145.03, 145.13, 145.18, 145.21, 145.29, 145.39, 145.50, 145.67, 145.81, 145.87, 145.94, 146.01, 146.08, 146.54, 147.03, 152.71, 152.81, 153.77, 155.79; IR (KBr, cm^{-1}) 2864, 2812, 1462, 1427, 1180, 1107, 839, 768, 700, 527; MALDI-TOF-MS (matrix: SA) found 1111.0753 (calculated for $C_{79}H_{21}NO_2S_3$, exact mass: 1111.0736)

Bridge type terthiophene fullerobipyrrolidine (6)

A solution of [C_{60}]-fullerene (630 mg, 0.88 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid (142 mg, 0.80 mmol), and [2,2':5',2''-terthiophene]-5,5''-dicarbaldehyde (**8**) (43 mg, 0.14 mmol) in chlorobenzene (60 mL) was stirred for 3 h at 130 °C under argon. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (toluene, then CS_2 / ethyl acetate= 10:1) affording the product **6** (196mg, 0.16mmol) as a dark brown solid in 76% yield, and the unreacted fullerene (174 mg) was recovered in 35% yield. R_f 0.61 (toluene/methanol=2/1): ^{1}H NMR (500 MHz, ppm, $CDCl_3$, J= Hz) δ 2.91-2.95 (2H, m), 3.39 (6H, s), 3.56-3.65 (6H, m), 3.72-3.79 (4H, m), 3.94-3.98 (2H, m), 4.01-4.07 (2H, m), 4.25 (2H, d, J= 10.0 Hz), 5.18 (2H, d, J= 10.0 Hz), 5.41 (2H, s), 7.00 (2H, s), 7.03 (2H, d, J= 3.7 Hz), 7.25 (2H, d, J= 4.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.37, 58.86, 67.66, 68.67, 70.49, 70.58, 71.92, 75.85, 77.92, 122.83, 124.35, 128.78, 135.28, 135.68, 136.23, 136.37, 136.94, 138.12, 139.54, 139.84, 139.94, 140.18, 141.38, 141.43, 141.62, 141.72, 141.80, 141.90, 141.99, 142.03, 142.34, 142.46, 142.75, 142.90, 144.11, 144.40, 144.48, 144.90, 144.98, 145.04, 145.11, 145.15, 145.19, 145.31, 145.39, 145.50, 145.68, 145.82, 145.87, 145.95, 146.02, 146.09, 146.53, 147.04, 152.72, 152.79, 153.78, 155.78; IR (KBr, cm^{-1}) 2866, 1460, 1425, 1105, 727; MALDI-TOF-MS (matrix: SA) found 1255.40 (calculated for $C_{86}H_{35}N_2O_4S_3$ (MH$^+$), Exact Mass: 1255.1765).

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Chapter 3

Photovoltaic Properties of OPV Devices using *cis*- and *trans*-2,5-Diarylfulleropyrrolidines as Acceptor Partners with P3HT on an ITO Electrode with PEDOT:PSS

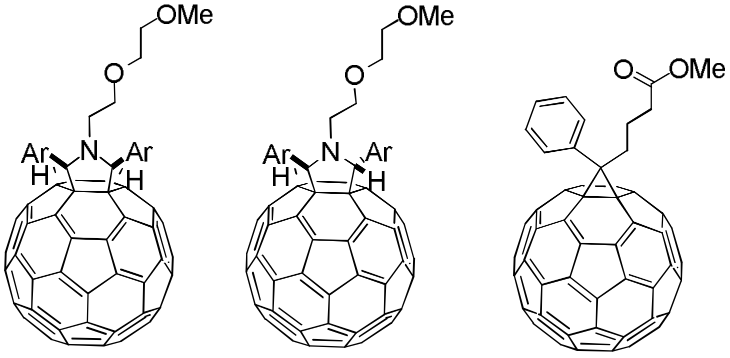
Chapter 3

Photovoltaic Properties of OPV Devices using *cis*- and *trans*-2,5-Diarylfulleropyrrolidines as Acceptor Partners with P3HT on an ITO Electrode with PEDOT:PSS

3-1. Introduction

As described in Chapter 2 and reported earlier [1], fulleropyrrolidines have a certain advantage over [C_{60}]-PCBM from the standpoint of their stable nature under atmospheric conditions and the ease of producing various types of analogues.[2] However, it was essential to use a special electrode without the commonly-used hole transport layer (HTL) poly(3,4-ethylenedioxythiophene) :poly(styrenesulfonate) (PEDOT: PSS)[3] layer to obtain high PCE.[3] The role of the HTL is believed to be to prevent the leak current from the active layer to the ITO electrode, thereby strongly contributing to the enhancement of the OPV performance, especially FF and V_{oc}.[4] Therefore, we have investigated the interaction between the sulfonic acid group of PEDOT:PSS and nitrogen moiety of the fulleropyrrolidine to determine the reason why PEDOT:PSS causes the drop in PCE of fulleropyrrolidine based OPV devices. It was found that a quaternary ammonium salt was formed on the interface of the active layer with PEDOT:PSS and this hindered hole transport.[5] Inspired by the results, we hypothesized that a good OPV device might be produced using fulleropyrrolidine derivatives if we could prevent the formation of such quaternary ammonium salt by PEDOT:PSS. We hypothesized that 2,5-diaryl-substiuted fulleropyrrolidine might become a good acceptor material because it might be difficult for the sulfonic acid group of PSS to access the nitrogen atom on the pyrrolidine ring due to enhanced steric hindrance of the N atom. Formation of the quaternary ammonium salt would thus be avoided. In this communication, we report that the performance of OPV devices using 2,5-diarylfulleropyrrolidines with P3HT and an ITO electrode with

PEDOT:PSS layer significantly depends on the stereochemistry of the two substituents of the pyrrolidine ring.



9: Ar= Ph(*cis*)
11: Ar= 2-Th(*cis*)
13: Ar= 3-Th(*cis*)

10: Ar= Ph(*trans*)
12: Ar= 2-Th (*trans*)
14: Ar= 3-Th (*trans*)

[C_{60}]-PCBM

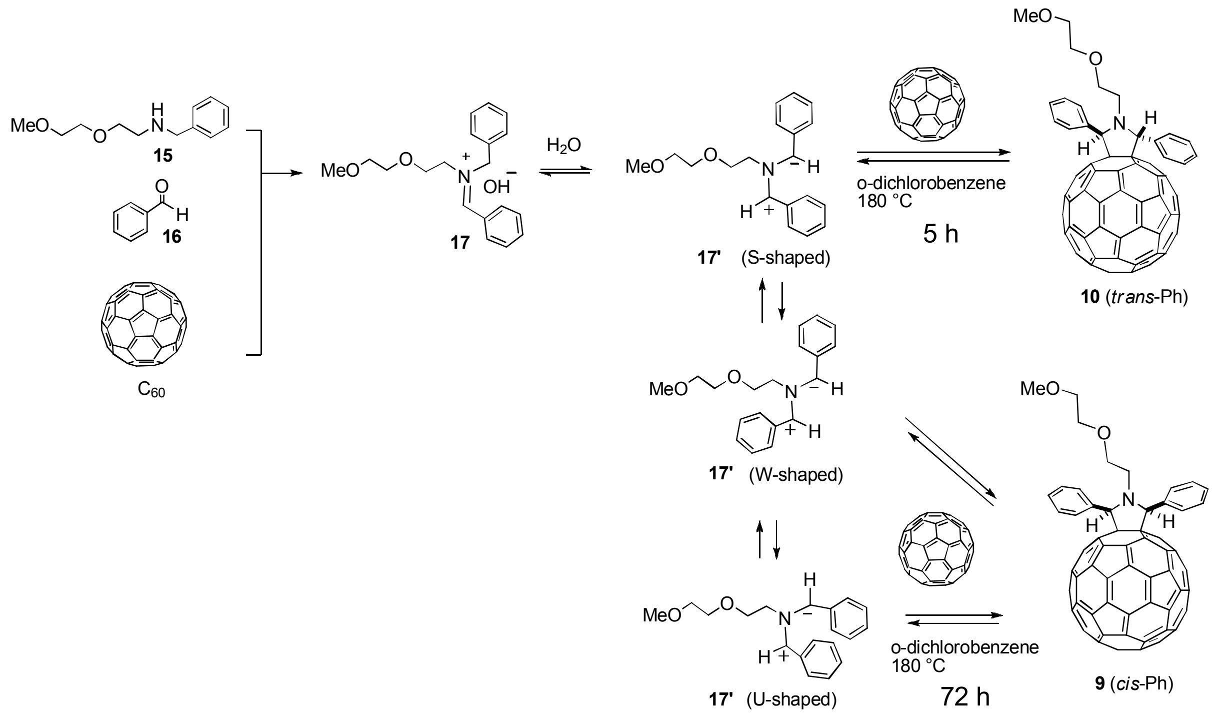
Figure 3-1. Fulleropyrrolidines investigated for their OPV device properties

3-2. Development and study of OPV Devices using *cis*- and *trans*-2,5-Diarylfulleropyrrolidines

Synthesis of *cis*- and *trans*-2,5-Diarylfulleropyrrolidines

We have accomplished stereoselective synthesis of *cis*- and *trans*-2,5-diphenylfulleropyrrolidine *via* the reaction of *N*-benzyl-2-(2-methoxyethoxy)ethanamine (**15**)[6] with benzaldehyde (**16**) in the presence of C_{60} (Scheme 3-1): (*trans)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-diphenylfulleropyrrolidine (**10**) was obtained when the reaction was stopped at 5 h reaction under reflux conditions in *o*-dichlorobenzene. On the other hand, a mixture of **9** and **10** was obtained when the reaction was stopped at 12 h stirring. We found that *cis* isomer **9** was obtained as a sole product after 72 h reaction. Prato and co-workers established that a N-substituted imine formed from an amine and an aldehyde can be tautomerized to azomethine ylide that readily undergo with C_{60} fullerene to yield fulleropyrrolidine.[7] It is reported that tri-substituted ylide **17'** exists in three conformations: S-shaped, W-shaped, and U-shaped:[8] the [2+3]-cycloaddition of the S-shaped ylide is expected to give *trans* isomer **10** (*trans*-Ph), while W- and U-shaped ylide **17'** should yield *cis* isomer **9** (*cis*-Ph) (Scheme 3-1). It has also been reported that the S-shaped conformer is more stable than the W- and U-shaped geometries.[9] In fact, we found that **10** was produced initially and *cis* **9** was gradually formed during the reaction, and *cis* isomer **9** was obtained as a sole product after long time stirring under reflux condition at 180°C. This indicates that *cis* isomer **9** might be more thermodynamically stable than *trans* isomer **10**. This is indeed supported by the DFT calculation of **9** and **10** at the B3LYP/6-31G* level of theory:[10] *cis* isomer **9** is more 23.9 kJ/mol stable than *trans* isomer **10**. We suppose that *trans* isomer might be decomposed during the reactions, while thermodynamically stable *cis* isomer survived under the conditions. Reaction of thiophene-2-carbaldehyde or thiophene-3-carbaldehyde with [C_{60}]-fullerene gave fulleropyrrolidines **11** (*cis*-2-thienyl), **12** (*trans*-2-thienyl), **13** (*cis*-3-thienyl), and **14** (*trans*-3-thienyl) in similar yields, respectively.

We assigned the stereochemistry of the 2,5-diarylfulleropyrrolidines using ^{1}H NMR analysis, because it was report that the signal of methine protons of the *trans* isomer at 2,5-position of the pyrrolidine ring was observed as a singlet peak at lower field ca. 0.6 ppm than the *cis* isomer.[9]



Scheme 3-1. Synthesis of 2,5-diphenylfulleropyrrolidine **9** (*cis*-Ph) and **10** (*trans*-Ph)

Photovoltaic performance

OPV devices were prepared using fulleropyrrolidine as acceptor partner with P3HT . Two types of OPV devices were fabricated: the first with PEDOT:PSS between ITO and the active layer, the second without PEDOT:PSS. Their PCE values were tested according to following process: dispersion of a mix of fulleropyrrolidine (5 mg), P3HT (5 mg) and silica gel (5 mg) in chlorobenzene (1.0 mL) was filtered through a Teflon (0.2 μm) filter to obtain a solution. The solution was then cast onto the ITO substrate (with or without PEDOT:PSS) by the spin-coating method at a thickness of ca. 100 nm. After drying under vacuum for 20 min, the resulting plate was placed in a vacuum chamber and the surface was coated with electrode layers of lithium fluoride (LiF) (4 nm) and aluminum (100 nm) by evaporation at 10^{-4} Pa at rt. The glass plate was firmly encapsulated using a bonding agent under an argon atmosphere to produce a solar cell. PCE values were obtained using a solar simulator at AM1.5G, 100 mW/cm^2. OPV device performance was investigated as summarized in Table 3-1. Current-voltage characteristics of *cis*-Ph (**9**), *trans*-Ph (**10**) and [C_{60}]-PCBM devices with or without PEDOT:PSS were shown in Figure 3-2.

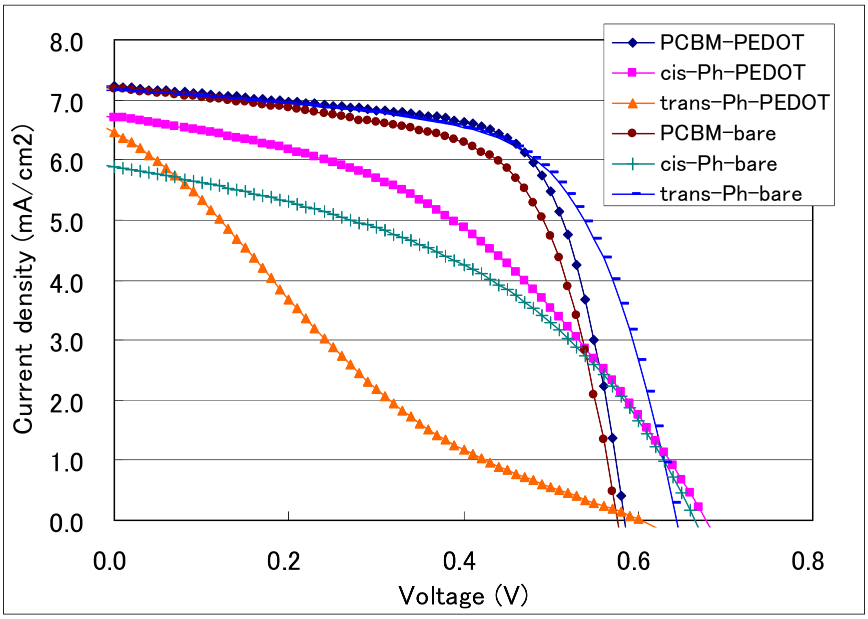
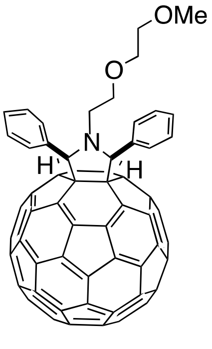
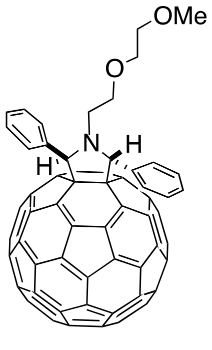


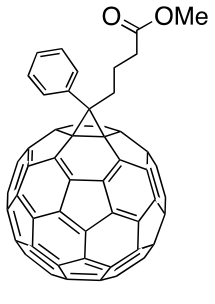
Figure 3-2. Current-voltage characteristics of *cis*-Ph, *trans*-Ph and [C_{60}]-PCBM solar cell devices with or without PEDOT:PSS under illumination by an AM 1.5G solar simulated light (100 mW/cm^2).



cis-Ph



trans-Ph



[C_{60}]-PCBM

Table 3-1. Photovoltaic properties of the devices using P3HT and fulleropyrrolidine derivatives with or without PEDOT:PSS

Entry	Acceptor	PCE (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	ITO electrode [a]
1	**9**: *cis*-Ph	1.73	5.89	0.665	0.441	bare
2	**9**: *cis*-Ph	1.95	6.71	0.679	0.429	PEDOT:PSS
3	**10**: *trans*-Ph	2.90	7.16	0.644	0.628	bare
4	**10**: *trans*-Ph	0.740	6.46	0.602	0.190	PEDOT:PSS
5	**11**: *cis*-2-Th	1.91	6.83	0.590	0.474	bare
6	**11**: *cis*-2-Th	2.04	6.49	0.651	0.482	PEDOT:PSS
7	**12**: *trans*-2-Th	2.48	7.16	0.649	0.535	bare
8	**12**: *trans*-2-Th	2.24	6.11	0.640	0.573	PEDOT:PSS
9	**13**: *cis*-3-Th	2.54	7.14	0.612	0.582	bare
10	**13**: *cis*-3-Th	0.364	4.06	0.563	0.159	PEDOT:PSS
11	**14**: *trans*-3-Th	1.84	6.72	0.566	0.485	bare
12	**14**: *trans*-3-Th	0.092	0.88	0.496	0.210	PEDOT:PSS
13	[C_{60}]-PCBM	2.44	6.79	0.585	0.614	bare
14	[C_{60}]-PCBM	2.77	7.30	0.574	0.660	PEDOT:PSS
15	Ph-FP	2.81	7.32	0.599	0.641	bare
16	Ph-FP	0.523	2.32	0.582	0.387	PEDOT:PSS

[a] "bare" means a special electrode which lacked PEDOT:PSS. "PEDOT:PSS" means ITO electrole with PEDOT:PSS (CLEVIOS^{TM}P VP AI4083).

It was found that the PCE values were significantly dependent on the electrode employed and on the stereochemistry of the substituent. The device using **10** (*trans*-Ph) showed a PCE of 2.90% without the PEDOT:PSS layer (Entry 3), while it dropped significantly when

PEDOT:PSS was used (Entry 4). Especially, FF drastically deteriorated from 0.628 to 0.190. On the other hand, increased PCE was observed for using PEDOT:PSS as reported previously when [C_{60}]-PCBM was employed as acceptor partner (Entry 14) because this had no nitrogen moiety.[11]

Similar results were observed when **13** (*cis*-3-Th) or **14** (*trans*-3-Th) was used as an n-type material in the presence of the PEDOT:PSS layer (Entries 9 - 12). This phenomenon was also seen when mono-substituted fulleropyrrolidine Ph-FP[1] was used (Entries 15 and 16). As we reported earlier, this significant drop was assumed to be caused by quaternization of the pyrrolidine ring and sulfonic acid group of PSS.[5] Therefore, it is likely that **10** (*trans*-Ph), **13** (*cis*-3-Th) and **14** (*trans*-3-Th) form a quaternary ammonium salt which might prevent the transport of charge from PEDOT:PSS to the ITO electrode.

The PCE values of **9** (*cis*-Ph), **11** (*cis*-2-Th), and **12** (*trans*-2-Th) were not influenced by the electrode (Entries 1, 2, 5-8). It is particularly interesting that the FF values of **11** (*cis*-2-Th) and **12** (*trans*-2-Th) increased when OPV devices were prepared using the ITO electrode with PEDOT:PSS (Entries 6 and 8) more than those without PEDOT:PSS (Entries 5 and 7). This would indicate that introduction of the 2-thiophen-2-yl group at 2 and 5-positions of the pyrrolidine ring is effective in protecting nitrogen atom from forming quaternary ammonium salt by PSS.

On the other hand, V_{oc} was independent of the electrode and all devices showed a higher or similar level of V_{oc} compared to the device using [C_{60}]-PCBM, except for Entry 12 (**14**: *trans*-3-Th with PEDOT:PSS). Since P3HT worked as a p-type material in our devices, we assume that the higher V_{oc} might be ascribable to the higher LUMO level of the fulleropyrrolidine than that of [C_{60}]-PCBM.

Electrochemical study.

To learn the LUMO level of these fullerene derivatives, cyclic voltammogram (CV) experiments were conducted (Table 3-2).[12] The CV plots of **9** (*cis*-Ph) and [C_{60}]-PCBM in CH_3CN (0.1 mM) with 0.1 M n-Bu_4NPF_6 are shown in Figure 3-3 and Figure 3-4, respectively. In the negative potential range these derivatives showed three apparently reversible reduction waves in the potential range from –0.8 to –1.8 V (vs. Fc^+/Fc). The half-wave potentials are defined as $E^0 = [\ E_c + E_a\ ] / 2$ (wherein E_c and E_a are the potential of cathodic peak and anodic peak, respectively).[12] The first reduction potentials (E_1^0) of **9** to **14** were shifted negatively when compared to [C_{60}]-PCBM. The LUMO levels of the fullerene derivatives from the onset reduction potentials were determined using the following equation: LUMO(eV) = $-(E_1^0+4.80)$. These levels are slightly higher than those of [C_{60}]-PCBM. Using di-substituted fullerenes with a high LUMO level is expected to achieve high V_{oc}.[4] As expected, we confirmed that there were no significant differences in LUMO levels between isomers. The gap of the LUMO level between **9** (*cis*-Ph) and **14** (*trans*-3-Th) determined by CV was only 0.01 eV (Table 3-2), whereas the gap of V_{oc} using device using **9** and **14** (Entry 1 and 11 in Table 3-1, respectively) was 0.099 V. The reason for this was unclear at the present; we assume that there might be some distinctive interactions with ITO and substrate, because these fulleropyrrolidines have different substitute groups.

Table 3-2. LUMO of fullerene derivatives determined by cyclic voltammograms.

Entry	Acceptor	E_1^0 /V	LUMO / eV
1	**9**: *cis*-Ph	-1.12	-3.68
2	**10**: *trans*-Ph	-1.11	-3.69
3	**11**: *cis*-2-Th	-1.12	-3.68
4	**12**: *cis*-2-Th	-1.13	-3.67
5	**13**: *trans*-2-Th	-1.13	-3.67
6	**14**: *trans*-3-Th	-1.11	-3.69
7	[C_{60}]-PCBM	-1.09	-3.71

[a] in CH_3CN (0.1 mM) with 0.1M n-Bu_4NPF_6 at a scan rate of 10 mV/s.

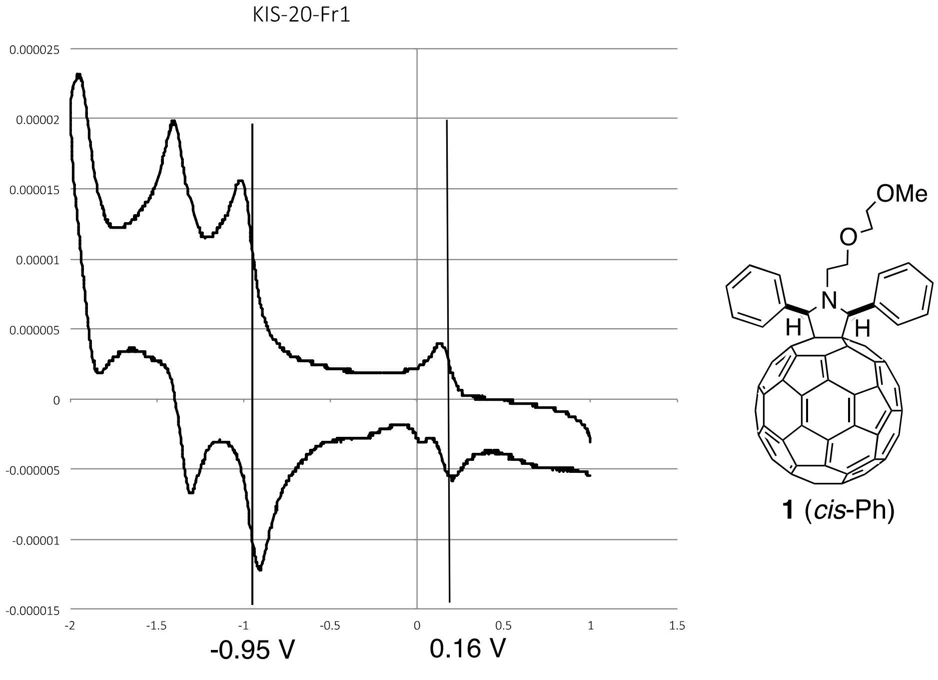


Figure 3-3. Cyclic voltammogram of **9** (*cis*-Ph) in CH_3CN (0.1 mM) with 0.1 M n-Bu_4NPF_6 at a scan rate of 10 mV/s. LUMO (eV)= –[0.16 + 0.95] + 4.80 = –3.69 eV

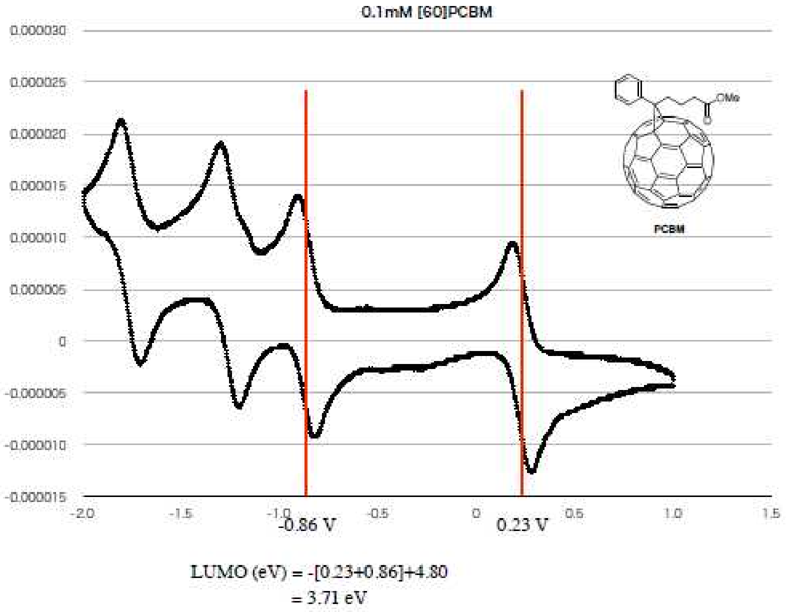


Figure 3-4. Cyclic voltammogram of [C_{60}]-PCBM in CH_3CN (0.1 mM) with 0.1 M n-Bu_4NPF_6 at a scan rate of 10 mV/s. LUMP (eV)= -[0.23 + 0.86] + 4.80 = -3.71 eV

Study of UV-visible spectra

We next measured UV-visible spectra of these fulleropyrrolidines in the presence or absence of *p*-toluene sulfonic acid (PTS) in dichlorobenzene to evaluate the formation of quaternary ammonium salt of fulleropyrrolidine derivatives with PSS (Figure 3-5).[5] No blue shift was observed for **9**, **11** or **12** after addition of PTS. However, it was found that the UV spectra of the *trans* isomer of phenyl substituted fulleropyrrolidine **10** and both isomers of thiophen-3-yl substituted fulleropyrrolidine **13** and **14** were blue shifted. These results clearly indicate that the interaction of fulleropyrrolidine with PSS is determined by the stereochemistry of the substituent on the pyrrolidine ring, but that the mode depends on the nature of substituent.

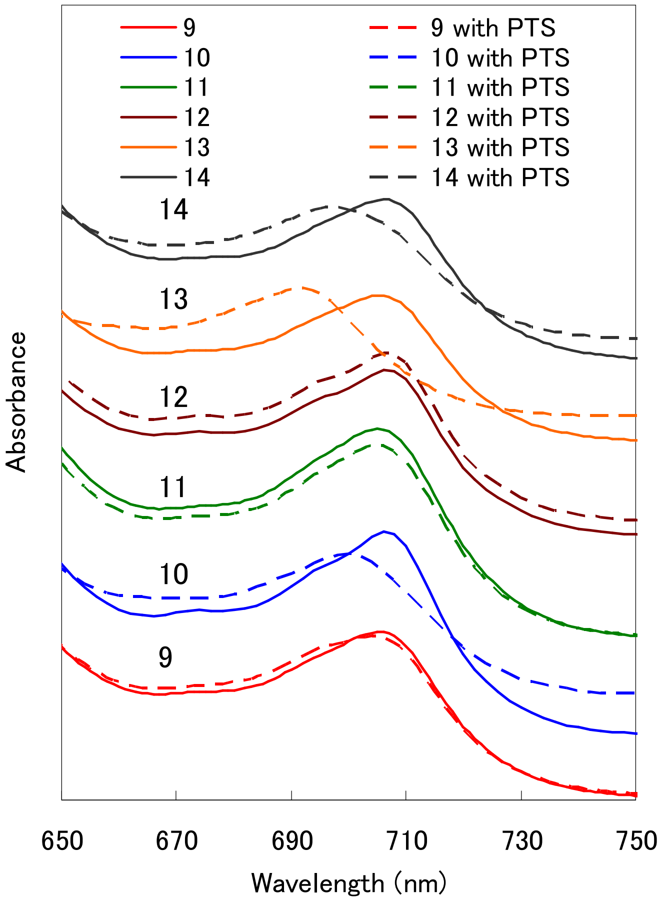


Figure 3-5. UV-visible spectra of fulleropyrrolidine **9** - **14** in the absence (solid line) and presence (dot line) of *p*-toluene sulfonic acid (PTS) in *o*-dichlorobenzene (ODCB) (fulleropyrrolidine / PTS = 1 : 20 (mol/mol). Concentration of fulleropyrrolidine in ODCB is approximately 0.002 mM).

Results of B3LYP/6-31G(d) calculation of 9 and 10

DFT calculation of *cis*-2,5-dipehnylfulleropyrrolidine **9** and *trans*-2,5-dipehnylfulleropyrrolidine **10** were performed with the Gaussian 09 suite of programs.[9] Geometrical optimization and vibrational analysis were performed at the B3LYP/6-31G(d) level of theory.[1-3] The vibrational analyses for the compounds in Table 3-3 shows all of the optimized structures were energetically stable, because all of the calculated Eigen frequencies of molecular vibrations are real.

Table 3-3. Calculated values for 1,5-substituted fulleropyrollidine by B3LYP/6-31G(d) level.

			Optimized molecular energy		Orbital energy
Compound number	Substituent at 2,5-position	Stereo for 2,5-position	*E* (au)	Δ*E* (kJ/mol)	LUMO (eV)
1	phenyl	*cis*	-3229.210996	0.0	-3.0404
2	phenyl	*trans*	-3229.201883	23.9	-3.0499

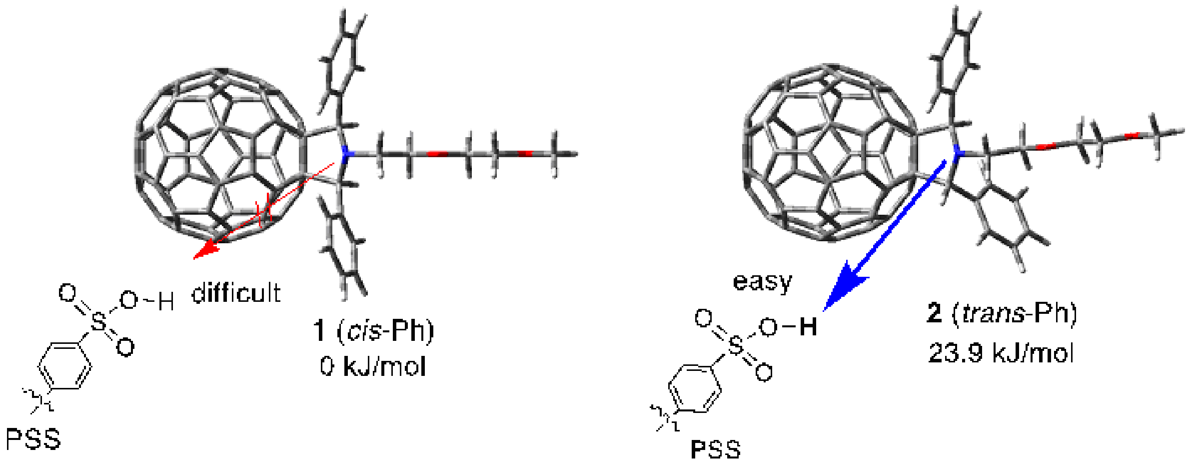


Figure 3-6. Optimized structure of *cis*- and *trans*-2,5-diphenylfulleropyrrolidine using B3LYP/6-31G(d) calculation

To gain insight on the origin of different interactions of pyrrolidine moiety with the PSS group between stereoisomers of 2,5-diphenylfulleropyrrolidine, we investigated the stable structure of **9** (*cis*-Ph) and **10** (*trans*-Ph) by calculating at the B3LYP/6-31G(d) level (Figure 3-6). The calculation suggested that the *cis* isomer **9** was more stable than the *trans* isomer **10**. Interestingly, as seen in Figure 3-6, it looks that PSS access to the nitrogen atom easier for *trans* than that for the *cis* isomer. In fact, PCE of the device using *trans* isomer **10** is strongly influenced by PSS, while that of *cis* isomer **9** is not dependent on the presence or absence of PSS on the electrode. As we hypothesized, due to the protecting effect of the two aryl group, formation of quaternary ammonium salt of **9** (*cis*-Ph) may be avoided.

3-3. Conclusion

We have shown that PCE values of OPV devices prepared using 2,5-diarylfulleropyrrolidines as an acceptor partner with P3HT depend on both the stereochemistry and the chemical structure of the substituent. PCE of the devices using *trans*-2,5-diphenylfulleropyrrolidine **10**, *cis*-2,5-di(thiophen-3-yl)fulleropyrrolidines **13** and *trans*-2,5-di(thiophen-3-yl)fulleropyrrolidines **14** were significantly lowered by PEDOT:PSS. This was found not to be the case for *cis*-2,5-diphenylfulleropyrrolidine **9** and thiophen-2-yl-substituted compounds **11** and **12**, for which high PCE values were obtained with and without PEDOT:PSS. Among the tested compounds, *trans*-2,5-diphenylfulleroppyrrolidine **10** showed the best PCE, superior to that of [C_{60}]-PCBM. These results clearly indicate a rich variety of fulleropyrrolidine type acceptors for OPV devices with the potential to show high PCE values. Fulleropyrrolidine acceptors thus meritfurther investigation.

3-4. Experimental

General Procedures.

Photovoltaic devices were prepared by spin-coating the fulleropyrrolidine-polymer blends from chlorobenzene onto an indium tin oxide (ITO) glass electrode as follows: a mixture of fulleropyrrolidine (5 mg), P3HT (5 mg) and silica gel (5 mg) in chlorobenzene (1.0 mL) was stirred for 12 h at ambient temperature. It was then filtered through a Teflon (0.2 μm) filter. The resulting solution was applied to the surface of an ITO plate, which was previously washed with acetone and irradiated under UV light and ozone gas for 20 min to decompose the impurities, by the spin-coating method at a thickness of ca. 100 nm. After drying under vacuum for 20 min, the resulting plate was placed in a vacuum chamber and the surface was coated with the electrode layers of lithium fluoride (LiF) (4 nm) and aluminum (100 nm) by evaporation at 10^{-4} Pa at rt. We placed the glass plate on the resulting film and the plate was firmly fixed using a bonding agent under an argon atmosphere to produce the solar cell. The PCE values were obtained using the solar simulator OTENTO-SUN II (AM1.5G, 100 mW/cm^2). Cyclic voltammograms were obtained in acetonitrile with 0.1mM tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte using a glassy carbon (1 mm diameter) as a working electrode, a Pt counter electrode and Ag/AgCl reference electrode. UV-visible spectra were obtained using the spectrophotometer JASCO V-670.

Materials

The [C_{60}]-fullerene was purchased from Frontier Carbon (nanom purple ST-A) and P3HT from Aldrich. The silica gel was purchased from Wako Pure Chemical Industry, Ltd. (Wakogel C-300, 45~75 μm).

Synthesis of *(cis)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-diphenylfulleropyrrolidine (9)

A solution of [C_{60}]-fullerene (133 mg, 0.21 mmol), *N*-benzyl-2-(2-methoxyethoxy)ethanamine (133 mg, 0.633 mmol), acetic acid (0.5 ml) and benzaldehyde (72 mg, 0.678 mmol) in *o*-dichlorobenzene (35 mL) was stirred for 72 h at 180 °C under argon. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (toluene, then CS_2 / ethyl acetate=10:1) affording the product **9** (*cis*-Ph) (45 mg, 0.0437 mmol) as a dark brown solid in 21% yield. Fulleropyrrolidine derivatives showed no clear melting point and only caused decomposition. Decomposition point was shown as "dp".

dp >300°C; ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 3.37 (2H, t, J = 5.7Hz, 5.7Hz), 3.41 (3H, s), 3.48-3.50 (2H, m), 3.52-3.53 (2H, m), 3.70 (2H, t, J = 5.7Hz, 5.7Hz), 5.81 (2H, s, proton at 2,5-position), 7.32-7.35 (4H, m), 7.47 (2H, t, J = 6.9Hz, 6.9Hz), 7.64 (2H, d, J = 6.9Hz), 8.20 (2H, d, J = 8.0Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 46.80, 58.88, 67.68, 70.11, 71.97, 74.91, 79.48, 128.13, 128.78, 129.21, 130.23, 136.51, 136.82, 139.12, 141.26, 141.75, 141.81, 141.97, 142.30, 142.40, 144.87, 144.99, 145.63, 145.89, 145.98, 147.08, 153.65, 154.01; IR (KBr, cm^{-1}) 2917.1, 2879.6, 1455.7, 1260.2, 1186.1, 1104.9, 737.1, 698.4, 526.9; MALDI-TOF-MS (matrix: SA) found 1017.1726 (calcd for $C_{79}H_{23}NO_2$, exact mass: 1017.1729).

Synthesis of *(trans)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-diphenylfulleropyrrolidine (10)

A solution of [C_{60}]-fullerene (204 mg, 0.28 mmol), *N*-benzyl-2-(2-methoxyethoxy)ethanamine (178 mg, 0.85 mmol), acetic acid (0.5 ml) and benzaldehyde (93 mg, 0.88 mmol) in *o*-dichlorobenzene (40 mL) was stirred for 5 h at 180 °C under argon. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (toluene, then CS_2 / ethyl acetate=10:1) affording the product **10** (*trans*-Ph) (54 mg, 0.053 mmol) as a dark brown solid in 19% yield and the unreacted fullerene (89 mg) was recovered in 44% yield.

dp >300°C; ^{1}H NMR (400 MHz, ppm, $CDCl_3$) δ 2.91-2.94 (1H, m), 3.21-3.24 (1H, m), 3.40 (3H, s), 3.58-3.60 (2H, m), 3.66-3.68 (2H, m), 3.89 (2H, t, J = 6.8Hz), 6.38 (2H, s, proton at 2,5-position), 7.35 (2H, t, J = 7.8Hz), 7.46 (4H, t, J = 7.8Hz), 7.95 (4H, d, J = 6.8Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 45.55, 59.09, 70.34, 70.50, 72.05, 74.49, 77.88, 128.35, 128.67, 130.17, 135.64, 136.54, 138.69, 139.45, 139.88, 141.53, 141.57, 141.84, 141.94, 141.97, 142.36, 142.50, 142.98, 144.39, 144.41, 144.97, 145.08, 145.16, 145.32, 145.42, 145.82, 145.87, 145.97, 146.06, 146.12, 147.24, 153.89, 155.85; IR (KBr, cm^{-1}) 2851.0, 1452.7, 1428.6, 1187.7, 1106.1, 1027.8, 745.9, 709.5, 527.0; MALDI-TOF-MS (matrix: SA) found 1017.1719 (calcd for $C_{79}H_{23}NO_2$, exact mass: 1017.1729).

(*cis)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-di(thiophen-2-yl)fulleropyrrolidine (11)

dp >300°C; ^{1}H NMR (400 MHz, ppm, $CDCl_3$) δ 3.40 (3H, s), 3.51 (2H, t, J= 5.8 Hz), 3.52 (4H, s), 3.76 (2H, t, J= 5.8 Hz), 6.16 (2H, brs, proton at 2,5-position), 7.00 (2H, brs), 7.32 (4H, brs); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 59.06, 68.06, 72.21, 72.04, 74.62, 135.48, 139.33, 139.76, 141.41, 141.81, 141.93, 141.97, 142.07, 142.45, 142.52, 142.81, 144.24, 144.55, 145.00, 145.14, 145.24, 145.39, 145.48, 145.76, 145.98, 146.10, 146.22; IR (KBr, cm^{-1}) 2865.2, 1430.0, 1182.7, 1103.7, 699.3, 526.6; MALDI-TOF-MS (matrix: SA) found 1029.0862 (calcd for $C_{75}H_{19}NO_2S_2$ exact mass: 1029.0927).

(*trans)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-di(thiophen-2-yl)fulleropyrrolidine (12)

dp >300°C; ^{1}H NMR (400 MHz, ppm, $CDCl_3$) δ 2.99-3.00 (1H, m), 3.27-3.28 (1H, m), 3.37 (3H, s), 3.59 (2H, brs), 3.71 (2H, brs), 3.87-3.88 (1H, m), 3.95-3.96 (1H, m), 6.62 (2H, s, proton at 2,5-position), 7.06 (2H, s), 7.40 (2H, d, J = 4.9 Hz), 7.44 (2H, d, J = 4.9 Hz); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 45.85, 58.91, 70.44, 71.43, 72.03, 73.26, 74.30, 126.54, 126.92, 129.49, 136.29, 136.86, 139.51, 139.80, 141.01, 141.55, 141.70, 141.99, 142.38, 142.53, 142.93, 144.42, 144.99, 145.15, 145.87, 146.06, 146.11, 146.12, 147.24, 153.17; IR (KBr, cm^{-1}) 2858.0, 1512.6, 1429.6, 1187.70, 1036.9, 698.9, 526.8; MALDI-TOF-MS (matrix: SA) found 1029.0864 (calcd for $C_{75}H_{19}NO_2S_2$ exact mass: 1029.0927).

***(cis)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-di(thiophen-3-yl)fulleropyrrolidine (13)**

dp >300°C; ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 3.35-3.36(1H, m), 3.42(3H, s), 3.53-3.56(4H, m), 3.68(2H, t, J= 5.5 Hz), 5.85(2H, s, proton at 2,5-position), 7.34 (2H, s), 7.58-7.65(2H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 47.69, 58.90, 67.85, 67.99, 70.09, 71.98, 74.49, 99.67, 125.00, 130.98, 135.44, 136.36, 139.27, 139.14, 141.33, 141.73, 141.78, 141.82, 141.90, 141.95, 142.34, 142.43, 142.74, 142.95, 144.46, 144.88, 145.06, 145.28, 145.34, 145.42, 145.66, 145.80, 145.90, 145.99, 146.09, 147.10; IR (KBr, cm^{-1}) 2856.2, 1462.0, 1420.7, 1182.1, 1104.0, 771.3, 526.3; MALDI-TOF-MS (matrix: SA) found 1029.0867 (calcd for $C_{75}H_{19}NO_2S_2$ exact mass: 1029.0927).

***(trans)*-1-(2-(2-methoxyethoxy)ethyl)-2,5-di(thiophen-3-yl)fulleropyrrolidine (14)**

dp >300°C; ^{1}H NMR (500 MHz, ppm, $CDCl_3$) δ 2.80-2.85(1H, m), 3.12-3.17(1H, m), 3.40(3H, s), 3.61-3.62(2H, m), 3.71-3.72(2H, m), 3.84-3.88(1H,m), 3.89-3.94(1H, m), 6.37(2H, s, proton at 2,5-position), 7.40-7.42(2H, m), 7.66-7.67(4H, m); ^{13}C NMR (125 MHz, ppm, $CDCl_3$) δ 45.84, 58.86, 70.51, 71.01, 72.09, 72.72, 74.04, 125.84, 126.30, 128.52, 135.88, 136.40, 139.32, 139.51, 139.85, 141.58, 141.77, 141.91, 141.93, 141.98, 142.36, 142.49, 142.93, 144.34, 144.94, 145.08, 145.32, 145.79, 145.84, 146.02, 147.18, 153.78, 155.39; IR (KBr, cm^{-1}) 2847.8, 1462.0, 1419.8, 1180.3, 1103.9, 776.0, 7, 526.0; MALDI-TOF-MS (matrix: SA) found 1029.0865 (calcd for $C_{75}H_{19}NO_2S_2$ exact mass: 1029.0927).

Computational Methodologies

The DFT calculations of the fulleropyrrolidine derivatives were performed at the B3LYP/6-31G* level of theory. All of the calculations were carried out using the Gaussian 03 suite of programs.[10] The computations were performed at the Research Center for Computational Science in Okazaki (Japan).

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General Summary

In this study, we focused our attention on the fulleropyrrolidine as an n-type semiconductor for organic photovoltaic (OPV) cell and discussed the effect of the substituent groups on pyrrolidine ring in terms of photovoltaic performance and influence from PEDOT:PSS.

In Chapter 2, we reported the results of an investigation into the effect of thiophene derivatives as substituent groups on the fulleropyrrolidine ring. We have synthesized fulleropyrrolidine derivatives that have thiophene rings and discovered that thiophene groups worked to enhance LUMO level of the fulleropyrrolidine and increase the V_{oc} of the device. However, it was found that the devices prepared using PEDOT:PSS as HTL showed considerably lower PCE values than devices prepared without PEDOT:PSS. Our modeling has revealed that this results from protonation of the fulleropyrrolidine with sulfonic acid in PSS In the Chapter 3, we reported the results of a molecular design strategy for fullerropyrrolidine derivatives to prevent the adverse effect of PEDOT:PSS. We have designed novel fulleropyrrolidine derivatives having two aryl substituent groups at the 2,5- positions on the pyrrolidine ring. We accomplished stereoselective synthesis of *cis*- and *trans*-2,5-diarylfulleropyrrolidines. Three types of 2,5-diarylfulleropyrrolidine derivatives, i. e. 2,5-diphenyl, 2,5-di(thiophen-2-yl), and 2,5-di(thiophen-3-yl)fulleropyrrolidines have thus prepared and were used as an acceptor partner with P3HT in OPV devices with and without PEDOT:PSS.. Their PCE depended on both the stereochemistry and nature of two aryl substituents on 2,5-position of the pyrrolidine ring: PCE of the devices using *trans*-diphenyl or both *cis*- and *trans*-di(thiophen-3-yl) compounds was significantly lowered using PEDOT:PSS, while *cis*-diphenyl isomer was not influenced by PEDOT:PSS. In addition, both *cis*- and *trans*-2,5-di(thiophen-2-yl)fulleropyrrolidine displayed high PCE with PEDOT:PSS. Among the tested compounds, *trans*-2,5-diphenylfulleropyrrolidine showed the best PCE,superior to that of [C_{60}]-PCBM. These results indicate the rich possibility of fulleropyrrolidine type acceptors for OPV devices with the potential to show high PCE values. Fulleropyrrolidine acceptors thus meritfurther investigation.

List of publications

Chapter 1.

Thiophene-Substituted Fulleropyrrolidine Derivatives as Acceptor Molecules in a Thin Film Organic Solar Cell

Ken Yoshimura, Kei Matsumoto, Yasunori Uetani, Shigeki Sakumichi, Shuichi Hayase, Motoi Kawatsura, Toshiyuki Itoh

Tetrahedron, **2012**, *68*, 3605-3610.

Chapter 2.

Photovoltaic Properties of OPV Devices using *cis*- and *trans*-2,5-Diarylfulleropyrrolidines as Acceptor Partners with P3HT on an ITO Electrode with PEDOT:PSS,

Ken Yoshimura, Kiyotaka Sugawara, Shigeki Sakumichi, Kei Matsumoto, Yasunori Uetani, Shuichi Hayase, Toshiki Nokami, Toshiyuki Itoh

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