



## Thiophene-substituted fulleropyrrolidine derivatives as acceptor molecules in a thin film organic solar cell

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### ABSTRACT

A study of the design of thiophene-substituted fulleropyrrolidine derivatives as the acceptor in photovoltaic cells has been carried out using poly(3-hexylthiophene) (P3HT) as the model donor polymer. It was found that five types of thiophene-substituted fulleropyrrolidine worked as a good acceptor partner with P3HT, and the highest power conversion efficiency (*PCE*) was obtained for 1-(2-(2-methoxyethoxy)ethyl)-2-(2-thiophen-2-yl)fulleropyrrolidine (2.99%); this is superior to that of the P3HT polymer including methyl [C60]-PCBM under the same experimental conditions.

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### 1. Introduction

Use of photovoltaic technology is now well recognized as one of the most important ways to prevent the exhaustion of fossil fuels. Organic photovoltaics (OPV) have been attracting much attention as a next-generation photovoltaic system, because of their light weight and shape flexibility, as well as the potential to achieve low cost production.<sup>1</sup>

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.<sup>2,3</sup> Fullerene-based OPV can be fabricated via vapor deposition; however, considering the expected demand for enhancing cost performance by mass production in the near future, application of roll-to-roll processing (i.e., the solvent casting method) appears highly desirable. Therefore, development of stable fullerene derivatives that show both a high power conversion efficiency (*PCE*) and a sufficient solubility against organic solvents is strongly desired.<sup>1–3</sup> Various types of fullerene derivatives for use as OPV n-type materials have thus been developed. Methyl [6,6]-phenyl-C<sub>61</sub>-butylate ([C60]-PCBM)<sup>4</sup> 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.<sup>5–15</sup> Troshin and co-workers also synthesized various types of methanofullerene derivatives as acceptors for P3HT.<sup>15</sup> Recently Matsuo and co-workers reported OPV devices using silylmethylfullerene (SIMEF) that showed *PCE* superior to devices using [C60]-PCBM<sup>16,17</sup>.

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.<sup>18–25</sup> 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,<sup>26</sup> and conducted a systematic study of the design as an acceptor partner in polymer solar cells.<sup>27</sup>

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 [C60]-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.<sup>27</sup>

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.<sup>8</sup> 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  $\pi$ -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** (Fig. 1) 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.

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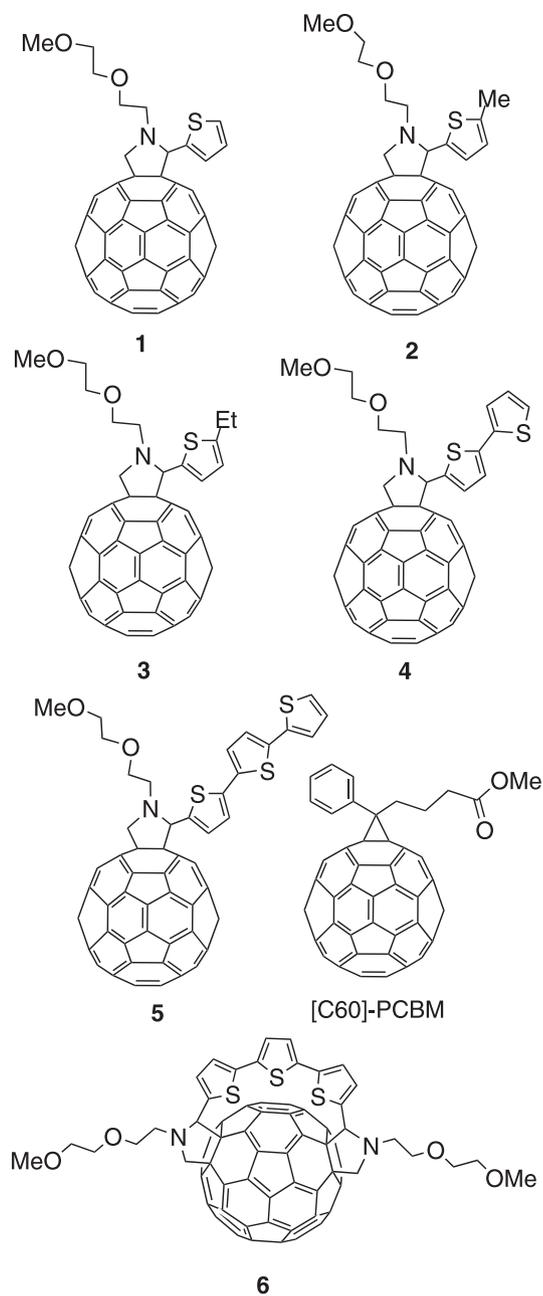


Fig. 1. Thiophene-substituted fulleropyrrolidine derivatives and [C60]-PCBM.

## 2. Results and discussion

Thiophene is well known as an electron-releasing substituent group, therefore, it is expected that the thiophene group becomes a  $\pi$ -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 literature.<sup>27</sup> Resulting fulleropyrrolidine derivatives (**2–6**) were also prepared by a similar method,<sup>26,27</sup> which was originally developed by Prato and co-workers.<sup>1a</sup> *N*-Methoxyethoxyethyl glycine<sup>28</sup> was treated with the [C<sub>60</sub>]-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 and *N*-methoxyethoxy glycine in the presence of [C<sub>60</sub>]-fullerene. To our delight, the desired bridged type compound **6** was obtained as a single isomer.

Using these fulleropyrrolidine derivatives, we prepared solar cells 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 with poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS)<sup>29</sup> as a positive electrode to make an active layer of organic photovoltaic cells. LiF and aluminum were used as a negative electrode. The *PCE* values were measured using a solar simulator (AM1.5G, 100 mW/cm<sup>2</sup>). The results are summarized in Table 1.

**Table 1**  
Photovoltaic performances of the P3HT-based organic photovoltaic devices with various types of fulleropyrrolidine derivatives<sup>a</sup>

| Entry          | Fullerene derivative | <i>PCE</i> % | <i>J</i> <sub>sc</sub> mA/cm <sup>2</sup> | <i>V</i> <sub>oc</sub> Volt | <i>FF</i> |
|----------------|----------------------|--------------|---|-----------------------------|-----------|
| 1 <sup>b</sup> | <b>1</b>             | 3.0          | 7.5                                       | 0.61                        | 0.66      |
| 2              | <b>2</b>             | 2.9          | 7.7                                       | 0.62                        | 0.61      |
| 3              | <b>3</b>             | 2.8          | 7.9                                       | 0.61                        | 0.57      |
| 4              | <b>4</b>             | 2.8          | 6.8                                       | 0.64                        | 0.64      |
| 5              | <b>5</b>             | 2.4          | 6.4                                       | 0.65                        | 0.56      |
| 6              | <b>6</b>             | 0.61         | 3.1                                       | 0.65                        | 0.31      |
| 7              | [C60]-PCBM           | 2.5          | 6.9                                       | 0.58                        | 0.63      |

<sup>a</sup> Under the illumination of AM 1.5G, 100 mW/cm<sup>2</sup>.

<sup>b</sup> Ref. 27.

The characteristic current–voltage parameters of polymer solar cells composed of six isomers, **1–6** (entries 1–6) were investigated; the *PCE* of isomers **1–4** was higher than that of [C60]-PCBM (entry 7). The *PCE* of **1** was highest among three mono-thiophene derivatives (entries 1–3) due to its having the highest fill factor (*FF*), while it showed the lowest open-circuit voltage (*V*<sub>oc</sub>) and short-circuit current (*J*<sub>sc</sub>) (entry 1). The *V*<sub>oc</sub> of these thiophene-substituted fulleropyrrolidine devices was higher than that of [C60]-PCBM, which was assumed to be due to their electron-donating property of thiophene. The *J*<sub>sc</sub> and *FF* of terthiophene substituted derivative **5** were lower than devices **1–4**, as a result of its reduced solubility compared to mono-thiophene and bithiophene derivatives. The distinctive feature of **5** is among the high *V*<sub>oc</sub> (0.65 V) when compared to **1–4** and [C60]-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.<sup>27</sup> 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** were, in fact, higher than that of [C60]-PCBM, though it was found that introduction of methyl or ethyl group at 5-position of the thiophene ring had no significant influence on the *PCE* (entries 2 and 3). Rather, introduction of ethyl group at the 5-position caused a slight drop of *PCE* due to reduced *FF* by the steric effect (entry 3).

Bis-[C60]-PCBM was reported to show higher *V*<sub>oc</sub> than [C60]-PCBM, because bis-[C60]-PCBM possesses a higher LUMO level due to a break in the conjugated bond.<sup>4</sup> Although the bridged type fulleropyrrolidine **6** showed higher *V*<sub>oc</sub> than that of [C60]-PCBM, poor *PCE* was obtained due to its low *J*<sub>sc</sub> and *FF* (entry 6).

Recently, an ITO electrode coated with poly(3,4-ethylene dioxothiophene)/poly(styrenesulfonate) (PEDOT:PSS)<sup>29</sup> has been

widely used as the hole transport layer for a solar cell. This is explained by the layer working as an antistatic agent and preventing electrostatic discharges during the film production. However, we prepared solar cells using a simple ITO electrode, which lacked the PEDOT:PSS layer, because we were concerned that protonation of the nitrogen atom on the pyrrolidine ring by PSS might inhibit the electron transfer pathway between fullerene molecules and P3HT. Although investigation on modification of redox properties of fulleropyrrolidine derivatives induced by protonation has been carried out, no detailed report on the photovoltaic performances has been reported.<sup>30</sup> To investigate this, we prepared three types of solar cells using ITO electrodes: those that lacked PEDOT:PSS, those having PEDOT:PSS, and those having neutral PEDOT, and evaluated their efficiency using bithiophene-substituted fulleropyrrolidine **4** as acceptor partner with P3HT (Table 2).

**Table 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 <sup>2</sup> ) | $V_{oc}$ (V) | FF   | Antistatic agent           |
|----------------|------------|---------|--------------------------------|--------------|------|----------------------------|
| 1              | [C60]-PCBM | 2.5     | 6.7                            | 0.56         | 0.66 | No                         |
| 2              | [C60]-PCBM | 2.6     | 7.0                            | 0.56         | 0.67 | PEDOT:PSS <sup>a</sup>     |
| 3              | [C60]-PCBM | 2.5     | 7.2                            | 0.55         | 0.64 | Neutral PEDOT <sup>b</sup> |
| 4              | <b>4</b>   | 2.8     | 6.8                            | 0.64         | 0.64 | No                         |
| 5              | <b>4</b>   | 0.10    | 0.71                           | 0.48         | 0.29 | PEDOT:PSS                  |
| 6              | <b>4</b>   | 1.8     | 5.9                            | 0.54         | 0.57 | Neutral PEDOT              |
| 7 <sup>c</sup> | <b>7</b>   | 3.0     | 7.6                            | 0.64         | 0.63 | No                         |
| 8              | <b>7</b>   | 0.51    | 6.5                            | 0.52         | 0.15 | PEDOT:PSS                  |

<sup>a</sup> PEDOT:PSS (AI4083 (pH=1.8)); baked at 120 °C for 10 min under air, 44 nm.

<sup>b</sup> 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.

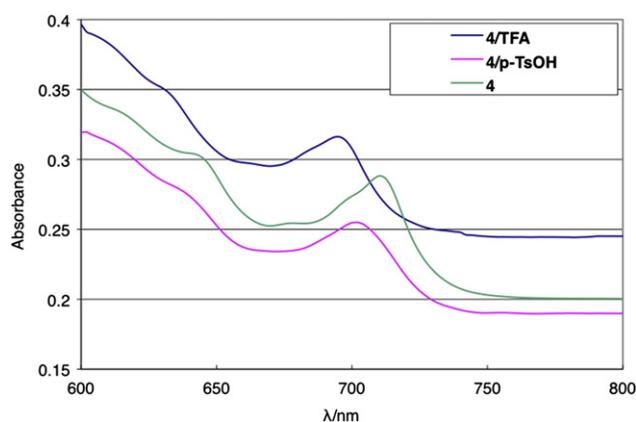
<sup>c</sup> Ref. 27.

As shown in Table 2, the PCE of [C60]-PCBM solar cells was independent of the use of electrode (entries 1–3). On the contrary, as anticipated, using acidic PSS in the electrode with isomer **4** caused a significant drop of PCE, mainly due to reduced  $J_{sc}$  (entry 5). In fact, a slight improvement of PCE was obtained when the cell was prepared by neutral PEDOT (entry 6), but PCE was still lower than the devices made using a simple ITO electrode that lacked PEDOT:PSS (entry 4). It was thus found that it was essential to obtain good PCE for thiophene-substituted fulleropyrrolidine based solar cells in order to use an electrode lacking PEDOT:PSS. 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**)<sup>27</sup> was used as an acceptor (entry 8).

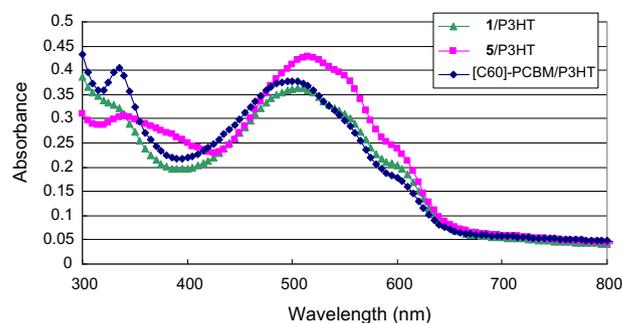
It is reported that the protonation of the fulleropyrrolidine by trifluoroacetic acid caused a blue shift on the UV–visible spectrum.<sup>30</sup> Fig. 2 shows UV–visible spectra of fulleropyrrolidine **4** with and without acids, when trifluoroacetic acid (TFA) and *p*-toluenesulfonic acid (*p*-TsOH) 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.

Fig. 3 shows the UV–visible spectra of the P3HT/**1**, P3HT/**5**, and P3HT/[C60]-PCBM. All films showed a broad  $\pi$ – $\pi^*$  absorption from 400 to 700 nm and the  $\lambda_{max}$  of the three films was around 500 nm, which was attributable to the P3HT. The P3HT/**5** blend has distinctive broad absorption between 350 and 400 nm, which was assumed to be caused by terthiophene moiety on the fulleropyrrolidine molecule.

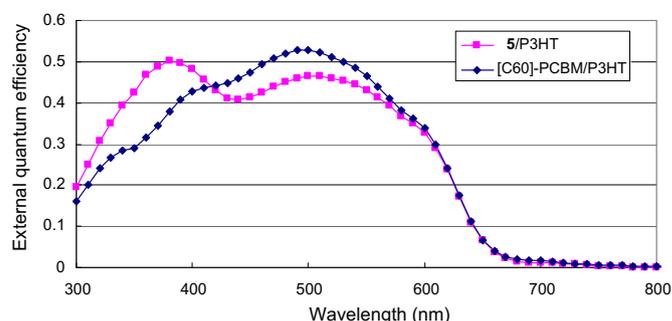
External quantum efficiency (EQE) of the P3HT/**5** and P3HT/[C60]-PCBM are shown in Fig. 4. Since there is less absorption in the range of 350–400 nm in the UV–visible spectrum of P3HT/[C60]-PCBM film, the EQE of the film in this range stayed low (EQE=0.3–0.4). On the other hand, as can be seen on the P3HT/**5**,



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



**Fig. 3.** UV–visible spectra of **1**/P3HT, **5**/P3HT, and [C60]-PCBM/P3HT.



**Fig. 4.** External quantum efficiency of terthiophene derivative **5**/P3HT and [C60]-PCBM/P3HT.

the EQE between 350 and 400 nm reached around 0.5, thus revealing that the terthiophene moiety of **5** not only absorbed the light but also contributed to produce exciton within the range of 350–400 nm.

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 1). The bridged-terthiophene moiety might be too close to the fullerene ring, preventing charge separation.

The highest  $V_{oc}$  was found when mono-thiophene **5** was used as an electron acceptor component in the active layer. To learn the reason for the high  $V_{oc}$  of **5** compared to [C60]-PCBM, the electrochemical properties of terthiophene **5** and [C60]-PCBM were studied by cyclic voltammetry. The cyclic voltammograms of the fullerene derivatives in the potential range of 1.0 to –2.0 V versus

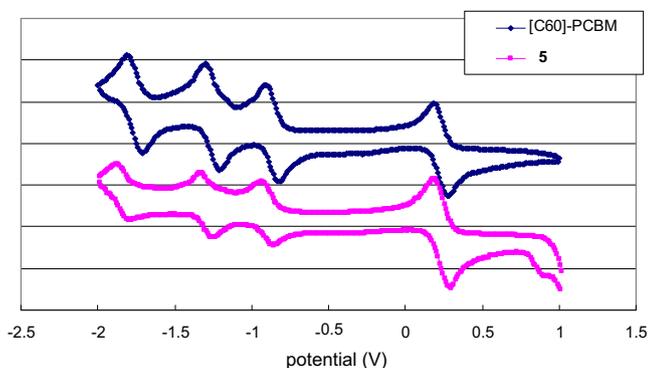


Fig. 5. Cyclic voltammograms of [C60]-PCBM and **5** in CH<sub>3</sub>CN (0.1 mM) with 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> at a scan rate of 10 mV/s.

ferrocene (Fc)/Fc<sup>+</sup> are shown in Fig. 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 to -1.8 V. The half-wave potentials of which 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) of the reduction process are summarized in Table 3. The first ( $E_1^0$ ), second ( $E_2^0$ ), and third ( $E_3^0$ ) reduction potentials of **5** were shifted negatively when compared to [C60]-PCBM.

Table 3  
Estimated half-wave potentials and LUMO of the fullerene derivatives<sup>a</sup>

| Entry |            | $E_1^0$ V | $E_2^0$ V | $E_3^0$ V | LUMO eV |
|-------|------------|-----------|-----------|-----------|---------|
| 1     | [C60]-PCBM | -1.09     | -1.49     | -2.00     | -3.71   |
| 2     | <b>5</b>   | -1.15     | -1.53     | -2.08     | -3.65   |

<sup>a</sup> The potential values in this table versus Fc/Fc<sup>+</sup>.

The LUMO energy levels of the fullerene derivatives were estimated from their first half-wave potentials ( $E_1^0$ ) indicated in the cyclic voltammograms. The  $E_1^0$  of terthiophene **5** and [C60]-PCBM were -1.09 and -1.15 V versus Fc/Fc<sup>+</sup>, respectively. The LUMO energy levels of the fullerene derivatives from the onset reduction potentials were calculated by use of the following equation: LUMO (eV) =  $-(E_1^0 + 4.80)$ . The LUMO energy levels of [C60]-PCBM and **5** calculated by this method are -3.71 and -3.65 eV, respectively, and are summarized in Table 3. The LUMO level of **5** is raised by 0.06 eV in comparison with that of [C60]-PCBM. The higher LUMO level of **5** is desirable for its application as acceptor in the active layer to obtain  $V_{oc}$ .

### 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 worked as good acceptor partners with P3HT. A high power conversion efficiency was obtained, superior to that of the P3HT-based devices including [C60]-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.

We expect to be able to develop efficient donor polymers, which are appropriate for our fulleropyrrolidine derivatives. Further investigation into the development of novel donor polymers as a partner of our fulleropyrrolidine will allow the creation of even more efficient solar cells in the near future.

## 4. Experimental section

### 4.1. 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 mm) 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<sup>2</sup>). Cyclic voltammograms were obtained in acetonitrile with 0.1 mM tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) 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.

### 4.2. Materials

The [C60]-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 mm).

4.2.1. 1-(2-(2-Methoxyethoxy)ethyl)-2-(2-thiophen-2-yl) fulleropyrrolidine (**1**):<sup>27</sup> A solution of [C60]-fullerene (500 mg, 0.69 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid<sup>26,28</sup> (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<sub>2</sub>/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. Fulleropyrrolidines showed no clear melting point and only caused decomposition. Decomposition point was shown as 'dp'.

$R_f$  0.61 (toluene/methanol=2/1); dp >300 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $J$ =Hz)  $\delta$  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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  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<sup>-1</sup>) 2864, 2812, 1462, 1427, 1180, 1107, 839, 768, 700, 527; MALDI-TOF-MS (matrix: SA) found 947.0978 (calculated for C<sub>71</sub>H<sub>17</sub>NO<sub>2</sub>S, exact mass: 947.0981).

Reaction of 5-methylthiophene-2-carbaldehyde or 5-ethylthiophene-2-carbaldehyde with C60-fullerene gave fulleropyrrolidine **2** or **3** in similar yield in the reaction of **1**.

4.2.2. 1-(2-(2-Methoxyethoxy)ethyl)-2-(5-methylthiophen-2-yl)fulleropyrrolidine (**2**). Dp >300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2853, 1684, 1458, 1425, 1107, 795; MALDI-TOF-MS (matrix: SA) found 961.1138 (calculated for C<sub>72</sub>H<sub>19</sub>NO<sub>2</sub>S, exact mass: 961.1138).

4.2.3. 1-(2-(2-Methoxyethoxy)ethyl)-2-(5-ethylthiophen-2-yl)fulleropyrrolidine (**3**). Dp 290 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2866, 1670, 1508, 1458, 1425, 1107, 802; MALDI-TOF-MS (matrix: SA) found 975.1292 (calculated for C<sub>73</sub>H<sub>21</sub>NO<sub>2</sub>S, exact mass: 975.1294).

4.2.4. 1-(2-(2-Methoxyethoxy)ethyl)-2-([2,2'-bithiophen]-5-yl)fulleropyrrolidine (**4**). A solution of [C<sub>60</sub>]-fullerene (500 mg, 0.69 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid<sup>26,28</sup> (177 mg, 1.0 mmol), and 5-(thiophen-2-yl)thiophene-2-carbaldehyde<sup>31</sup> (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.

Dp >300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2864, 1638, 1107, 795; MALDI-TOF-MS (matrix: SA) found 1029.0873 (calculated for C<sub>75</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>2</sub>, exact mass: 1029.0859).

4.2.5. 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<sub>2</sub>Cl<sub>2</sub>) (5.0 mL) was added *N,N*-dimethylformaldehyde (DMF) (162 mg, 2.21 mmol) under argon, then 0.21 mL of POCl<sub>3</sub> (2.21 mmol) was added at 0 °C and the resulting mixture was stirred at 50 °C for 2 h. The reaction was quenched by addition of 1 M sodium acetate (NaOAc) aqueous solution then extracted with CH<sub>2</sub>Cl<sub>2</sub>. After evaporation, silica-gel flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate=1/0 to 10/1) to afford [2,2':5',2''-terthiophen]-5-carbaldehyde (**8**)<sup>32</sup> (231 mg,

0.84 mmol, 83%) and [2,2':5',2''-terthiophen]-5,5''-dicarbaldehyde (**9**)<sup>33</sup> (68.0 mg, 0.22 mmol, 22%), respectively.

(2) A solution of C<sub>60</sub> (250 mg, 0.35 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid (92 mg, 0.52 mmol), and [2,2':5',2''-terthiophen]-5-carbaldehyde (**8**) (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.

Dp >300 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 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, 3.6 Hz), 7.00 (2H, dd, J=9.2, 3.6 Hz), 7.03 (d, 1H, J=3.6 Hz), 7.09 (1H, dd, J=3.4, 1.0 Hz), 7.15 (1H, dd, J=5.0, 0.9 Hz), 7.26 (1H, d, J=3.7 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2864, 2812, 1462, 1427, 1180, 1107, 839, 768, 700, 527; MALDI-TOF-MS (matrix: SA) found 1111.0753 (calculated for C<sub>79</sub>H<sub>21</sub>NO<sub>2</sub>S<sub>3</sub>, exact mass: 1111.0736).

### 4.3. Bridge type terthiophene fulleropyrrolidine (**6**)

A solution of [C<sub>60</sub>]-fullerene (630 mg, 0.88 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid (142 mg, 0.80 mmol), and [2,2':5',2''-terthiophen]-5,5''-dicarbaldehyde (**9**) (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<sub>2</sub>/ethyl acetate=10/1) affording the product **6** (196 mg, 0.16 mmol) as a dark brown solid in 76% yield, and the unreacted fullerene (174 mg) was recovered in 35% yield. *R*<sub>f</sub> 0.61 (toluene/methanol=2/1); dp >300 °C; <sup>1</sup>H NMR (500 MHz, ppm, CDCl<sub>3</sub>, 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>) 2866, 1460, 1425, 1105, 727; MALDI-TOF-MS (matrix: SA) found 1255.40 (calculated for C<sub>86</sub>H<sub>35</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub> (MH<sup>+</sup>), exact mass: 1255.1765).

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### Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.02.080. These data includes MOL files and InChIKeys of the most important compounds described in this article.

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