# Design of fulleropyrrolidine derivatives as an acceptor molecule in a thin layer organic solar cell<sup>†</sup>

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A systematic study on the design of fulleropyrrolidine derivatives as the acceptor of photovoltaic cells has been carried out using poly(3-hexylthiophene) (P3HT) as the model base polymer. It was found that *N*-methoxyethoxyethyl-2-(2-methoxyphenyl)fulleropyrrolidine worked as a good acceptor partner with P3HT and a high power conversion efficiency (PCE) (3.44%) was obtained; this is superior to that of the P3HT polymer including methyl [6,6]-phenyl-C61-butylate ([C60]-PCBM) under the same experimental conditions.

## Introduction

Extensive studies have been made regarding the applications of fullerene derivatives in the field of material sciences.<sup>1</sup> Among such studies, the development of fullerene-based polymer solar cells has attracted significant interest in recent years, because fullerenes have become recognized as excellent electron acceptors due to their unique p-electron system, excited state electronic properties, and absorption spectra extending into most of the visible region.<sup>2,3</sup> It is well known that the fullerene generally has a poor solubility in conventional organic solvents and this makes it difficult to prepare fullerene-based electric devices using economical techniques such as the spin-coating procedure. Therefore, the development of stable fullerene derivatives that show a high power conversion efficiency (PCE) with a sufficient affinity toward organic solvents is desired. Methyl [6,6]-phenyl-C61-butylate ([C60]-PCBM)<sup>4</sup> is known to be the best blending material among the fullerene derivatives as the acceptor with polythiophene which is a donor partner in polymer solar cells (Fig. 1).5-15 Hummelen and co-workers synthesised [C60]-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 of the LUMO level due to the substituent were small but caused a significant change of the open circuit voltage of the resulting solar cell.<sup>14</sup> Troshin, Hoppe, and co-workers also synthesized various types of methanofullerene derivatives and established that [C60]-PCBM was the best acceptor towards P3HT polymer.15

We were fascinated by the fulleropyrrolidines from the standpoint of their stable nature under atmospheric conditions and ease of producing various types of analogues.<sup>1a</sup> Several examples have been reported concerning the use of fulleropyrrolidines as the acceptor source of polymer solar cells and reported that PCE values of the solar cells remained at an insufficient level.<sup>16–23</sup> However, we recognized that no systematic study had been carried out on the design of fulleropyrrolidines as an acceptor partner in polymer solar cells to date.

We recently reported the design of fulleropyrrolidine-imidazolium hybrids that have a high solubility in various types of organic solvents and even in water.24 Since the key intermediate of our fulleropyrrolidine-imidazolium hybrid was N-methoxyethoxyethyl-2-(4-(1H-imidazol-1-yl)phenyl)fulleropyrrolidine (FP-PhIm)<sup>24</sup> as shown in Fig. 1, we had a large quantity of this compound on hand. Therefore, we attempted to fabricate a polymer solar cell using FP-PhIm as the acceptor molecule by blending in a thin film composed of poly-3-hexylthiophene (P3HT). Fabrication of the film using the spin-coating method was very easily accomplished due to the highly soluble nature of the FP-PhIm in organic solvents, however, the cell showed no characteristics as a solar cell. Since it was anticipated that the imidazole moiety installed at the para-position of the benzene ring might inhibit the smooth electron transfer between the fullerene molecules, we next prepared the P3HT



Fig. 1 Fullerene derivatives as the acceptor molecule blended in the polymer of poly-3-hexylthiophene (P3HT) for polymer solar cell.

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polymer that included the simple *N*-methoxyethoxyethyl-2phenylfulleropyrrolidine (1a) as an acceptor partner (Fig. 1). To our satisfaction, it was found that the polymer did, in fact, work as a solar cell. Although the solar cell performance of the polymer using 1a was less than 3%, the result strongly encouraged us to investigate the possibility of fulleropyrrolidine derivatives as an acceptor partner with P3HT for the polymer solar cell. We now report that several P3TH polymers blended with a fulleropyrrolidine as acceptor function as effective solar cells that show high PCE values which are superior to those of the combination of [C60]-PCBM and P3HT polymer under the same experimental conditions.

### Experimental

#### General

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 aluminium (100 nm) by evaporation at  $10^{-4}$  Pa at rt. We placed the glass plate on the resulting film and these plates were 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,  $100 \text{ mW cm}^{-2}$ ).

#### 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).

# *N*-Methoxyethoxyethyl-2-(2-methoxyphenyl) fulleropyrrolidine (1p)

A solution of C<sub>60</sub> (500 mg, 0.69 mmol), [2-(2-methoxyethoxy)ethylamino]acetic acid<sup>24,25</sup> (177 mg, 1.0 mmol), and 2-methoxybenzaldehyde (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 **1p** (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): <sup>1</sup>H NMR (500 MHz, ppm, CDCl<sub>3</sub>)  $\delta$  2.77–2.82 (1H, m), 3.39 (3H, s), 3.61 (2H, t, J = 4.5 Hz), 3.69 (3H, s), 3.71–3.78 (2H, m), 3.92–4.02 (2H, m), 4.27 (1H, d, J = 9.6 Hz), 5.18 (1H, d, J = 9.6 Hz), 5.73 (1H, s), 6.85 (1H, d, J = 8.2 Hz), 7.01 (2H, t, J = 7.5 Hz), 7.20 (1H, m), 7.94 (1H, d, J = 7.8 Hz); <sup>13</sup>C NMR (125 MHz, ppm, CDCl<sub>3</sub>)  $\delta$  52.19, 54.71, 58.77, 67.45, 69.17, 70.49, 70.57, 71.96, 73.92, 75.24, 76.75, 110.67, 121.10, 125.42, 128.80, 129.74, 134.32, 135.79, 136.21, 136.31, 139.09, 139.17, 139.86, 139.96, 141.27, 141.42, 141.52, 141.69, 141.78, 141.88, 141.96, 142.00, 142.05, 142.27, 142.33, 142.36, 142.71, 142.76, 144.08, 144.13, 144.29, 144.77, 144.94, 144.97, 145.03, 145.28, 145.44, 145.59, 145.74, 145.81, 145.86, 145.90, 145.94, 146.25, 146.47, 146.96, 153.86, 153.91, 154.76, 156.72, 157.79; IR (Neat, cm<sup>-1</sup>) 2864, 2827, 1489, 1460, 1425, 1284, 1244, 1179, 1109, 1048, 1026, 754, 729, 527; MALDI-TOF-MS (matrix: SA) found 971.1526 (calcd for C<sub>74</sub>H<sub>21</sub>NO<sub>3</sub>, exact mass: 971.1521%). For the synthesis of the fulleropyrrolidine derivatives **1b–1z**, see the ESI†.

#### **Computational methodologies**

The DFT calculations of the fulleropyrrolidine derivatives, 1a, 1p, 1q, 1r, 1x, and 2, were performed at the B3LYP/6-31G\* level of theory. All of the calculations were carried out using the Gaussian 03 suite of programs.<sup>26</sup>

#### **Results and discussion**

We focused our investigation on the characterization of the polymers that included the N-methoxyethoxyethyl-2-(2-aryl)fulleropyrrolidine derivatives as the acceptor partner with P3HT, because these types of compounds have a good affinity toward various types of organic solvents. Fulleropyrrolidine derivatives were prepared following the method developed by Prato and Maggini.<sup>1a</sup> N-Methoxyethoxyethyl glycine<sup>24,25</sup> was treated with the C60 fullerene in the presence of an aldehyde in chlorobenzene and the mixture was heated at 130 °C for 3 h. Purification of the desired compounds was easily accomplished by silica-gel flash column chromatography or silica-gel thin layer chromatography; the desired mono adduct 1 was thus obtained in acceptable yields from 40% to 78%. The photovoltaic cells were fabricated by spin-coating the blended film from a dichlorobenzene solution of the fulleropyrrolidine/polymer and the PCE values were obtained using a solar simulator (AM1.5G, 100 mW cm<sup>-2</sup>). The obtained characteristic current-voltage parameters are summarized in Table 1.

We first investigated the characteristic current–voltage parameters of polymer solar cells composed of three isomers **1b**, **1c**, and **1d** (entries 2–4). The power conversion efficiency (PCE) significantly depended on the position of the methyl group on the benzene ring and the best PCE was recorded for compound **1c**, which has a methyl group at the *meta*-position of the phenyl group; the PCE is close to that of [C60]-PCBM.

Since it was anticipated that an electron-withdrawing group may have a favourable effect on the acceptor functionality, we next prepared the chlorine-, bromine-, or fluorine-substituted compounds and tested their PCEs. As can be seen in Table 1 for entries 5–13, the *ortho*-substituted compounds produced better results than the corresponding *meta*- or *para*-substituted compounds; in particular, a slightly better PCE compared to that of [C60]-PCBM was recorded for the fluorine-substituted fulleropyrrolidine **1k** (entry 11). On the other hand, lower PCE values were obtained for compounds **1n** or **10** which have a very strong electron-withdrawing CF<sub>3</sub> group (entries 14 and 15).

Table 1 Characteristic current-voltage parameters under Standard AM 1.5G conditions<sup>a</sup>

Entry	Fullerene derivative Ar	PCE (%)	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	FF
1	$C_{6}H_{5}$ -(1a)	2.81	7.32	0.599	0.641
2	$2 - Me - C_6 H_4 - (1b)$	3.12	7.56	0.633	0.653
3	$3-Me-C_6H_4-(1c)$	3.20	7.54	0.649	0.654
4	$4-Me-C_6H_4-(1d)$	2.97	7.32	0.634	0.639
5	$2-Cl-C_6H_4-(1e)$	3.03	7.54	0.627	0.642
6	$3-Cl-C_6H_4-(1f)$	2.95	7.65	0.600	0.642
7	$4-Cl-C_{6}H_{4}-(1g)$	2.94	7.68	0.591	0.647
8	$2-Br-C_6H_4-(1h)$	3.03	7.55	0.626	0.640
9	$3-Br-C_6H_4-(1i)$	2.95	7.74	0.607	0.627
10	$4-Br-C_{6}H_{4}-(1j)$	2.87	7.66	0.597	0.627
11	$2 - F - C_6 H_4 - (1k)$	3.13	7.77	0.620	0.651
12	$3 - F - C_6 H_4 - (11)$	3.02	7.84	0.607	0.635
13	$4-F-C_{6}H_{4}-(1m)$	2.98	7.86	0.581	0.654
14	$2-CF_{3}-C_{6}H_{4}-(1n)$	2.59	7.43	0.600	0.580
15	$4-CF_{3}-C_{6}H_{4}-(10)$	2.25	6.79	0.550	0.602
16	$2-MeO-C_6H_4-(1p)$	3.44	7.85	0.660	0.662
17	$3-MeO-C_6H_4-(1q)$	3.09	7.49	0.635	0.650
18	$4-MeOC_{6}H_{4}-(1r)$	3.02	7.34	0.639	0.645
19	$2,6-Di(MeO)-C_6H_3-(1s)$	0.093	2.18	0.190	0.225
20	$2,4,6$ -Tri(MeO)– $C_6H_2$ – (1t)	0.174	2.70	0.244	0.264
21	$2-(n-\text{HexylO})-C_6H_4-(1\mathbf{u})$	2.56	7.71	0.644	0.516
22	$3-(n-\text{HexylO})-C_6H_4-(1v)$	2.64	7.59	0.605	0.574
23	$4-(n-\text{HexylO})-C_6H_4-(1w)$	1.38	5.28	0.599	0.437
24	2-Naphthyl-(1x)	3.21	7.95	0.659	0.613
25	1-Naphthyl– (1y)	2.70	7.21	0.637	0.588
26	Thienyl– (1z)	2.99	7.51	0.606	0.658
27	[C60]-PCBM	2.53	6.85	0.583	0.633
28	2	0.849	2.88	0.562	0.525

<sup>a</sup> Since it was known that PCE values were slightly dependent on the lot of P3HT, we prepared these solar cells using the P3HT polymer having the same lot number (Aldrich #08510JJ).

The best PCE value (3.44%) with a high  $J_{sc}$  (7.85 mA cm<sup>-2</sup>) was obtained when the polymer solar cell was prepared using the 2methoxyphenyl-substituted fulleropyrrolidine **1p** as the acceptor (entry 16). A significant reduction in the PCE was recorded using the di-methoxy or tri-methoxy substituted compounds (entries 19 and 20). The PCEs of the hexyloxy-substituted compounds were inferior to those of the methoxy-substituted compounds (entries 21–23); we speculated that the long alkyl chain may disturb the favourable arrangement of these compounds in the P3HT polymer.

For the naphthyl substituted compounds, 1x and 1y, the 2-naphthyl-substituted fulleropyrrolidine (1x) acts as a better acceptor (entries 24 and 25).

Lastly, we tested the thiophene substituted fulleropyrrolidine (1z) in anticipation of a good affinity of 1z with P3HT. However, the resulting power was not impressive; although a moderate PCE was obtained, the polymer showed a low  $J_{sc}$  value (entry 26). It was also confirmed that the presence of an aromatic substituent on the pyrrolidine ring is essential for the acceptor functionality because the *N*-methoxyethoxyethylfulleropyrrolidine (2)<sup>24,25</sup> showed a very poor PCE (0.849%) along with a low  $J_{sc}$  value (2.88 mA cm<sup>-2</sup>) (entry 28).

Fig. 2 shows that the **1p** cell has the highest AM 1.5G power conversion efficiency (PCE) of 3.44%, a short circuit current density ( $J_{sc}$ ) of 7.85 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{oc}$ ) of 0.660 V, and a fill factor (FF) of 0.662.

We prepared five sets of samples of the solar cell using two P3HT polymers with different lot numbers blended with **1p** or [C60]-PCBM. The average PCE value of the former five cells was  $3.38 \pm 0.066\%$  and that of the latter was  $2.66 \pm 0.13\%$ . Although the performance of the solar cells was somewhat dependent on the lot of P3HT polymer, the PCE of the P3HT/1p system was very reproducible and the values were always superior to those of the P3HT/[C60]-PCBM system under the same experimental conditions (see Table S1 in ESI†). It should also be noted that <sup>1</sup>H



Fig. 2 Current density–potential characteristics of 1p and [C60]-PCBM solar cell devices under illumination by an AM 1.5G solar simulated light (100 mW cm<sup>-2</sup>).



**Fig. 3** UV-vis spectra of P3HT film blended with [C60]-PCBM and that blended with **1p** (2-MeO).

and <sup>13</sup>C NMR analyses confirmed that no decomposition of **1p** took place after storing it for one year under atmospheric conditions at rt on the bench in the laboratory; fulleropyrrolidine was indeed a very stable compound.

Fig. 3 shows the UV-vis absorption spectra of the **1p** film as well as the [C60]-PCBM film for comparison. As can be seen, both films showed a broad  $\pi$ - $\pi$ \* absorption from 300 to 700 nm, and the  $l_{\text{max}}$  of **1p** is around 500 nm. In addition, very similar spectra were obtained from films including compounds **1a** to **1z**.

Based on a comparison with the devices prepared from [C60]-PCBM, the open circuit voltage of the **1p** polymer increased by *ca.* 0.076 V. It is recognized that  $V_{oc}$  is generally related to the difference between the HOMO of the donor (P3HT polymer) and LUMO of the acceptor (**1p**).<sup>12,14</sup> Therefore, the higher  $V_{oc}$  of the **1p** film is consistent with the higher LUMO energy levels of the **1p**, since the LUMO of **PCBM** in P3HT is reported to be 4.3 eV and the LUMO of **1p** has been estimated to be 4.25 eV.

We have shown that several fulleropyrrolidine derivatives work as good acceptor partners with P3HT. Furthermore, it was found that the PCE of the solar cells depended on the position of substituent installed on the benzene ring of the blending materials (Table 1).

It is well recognized that the acceptor function depends on the LUMO energy level of the acceptor materials.<sup>12</sup> Since *ortho*substituted compounds generally showed higher PCE values compared to those of the *meta-* or *para-substituted* ones, we conducted DFT calculations of three isomers of (methoxyphenyl)fulleropyrrolidines, such as **1p**, **1q**, **1r**, and the reference compound **2**. With the objective of investigating what factor determines the PCE of the polymer in the structural differences of the acceptor molecules, calculations were also carried out for **1a**, **1x** and **1y**. The typical optimized structures based on the DFT calculation of **1p** and **2** are shown in Fig. 4. We have compared  $V_{oc}$  versus  $\Delta E_{LUMO}$  (eV) that shows the difference in the LUMO energy between the reference compound **2** and that of each material (see Fig. 5 and Table S2 in ESI†). Hummelen *et al.* reported that *ortho-*methoxy(2-MeO)-substituted [C60]-PCBM



**Fig. 4** Optimized structure of fulleropyrrolidine derivatives **2** and **1p** by DFT calculation at the B3LYP/6-31G\* level of theory.<sup>26</sup>

showed higher LUMO with higher  $V_{oc}$  compared to that of *para*methoxy(4-MeO)-substituted [C60]-PCBM.<sup>14</sup> Like the PCBM derivatives, **1p** (2-MeO) showed higher LUMO level than did **1r** (4-MeO), and it was found that the  $V_{oc}$  of the solar cell is directly proportional to the LUMO energy of the four blending materials, **1p**, **1q**, **1r**, and **1a** (Fig. 5). On the contrary, no relationship was found for  $V_{oc}$  versus  $\Delta E_{LUMO}$  among **1x**, **1y** and **1a**: these three compounds showed similar  $\Delta E_{LUMO}$  values with different  $V_{oc}$  values.

We conclude that the PCE of the polymer solar cells is determined by multiple factors, such as the LUMO energy level of the acceptor material and structural interaction of the functional group on the fullerene ring between the donor polymers.



Fig. 5 Relationship between  $V_{\rm oc}$  and  $\Delta E_{\rm LUMO}$  among seven compounds.

#### Conclusion

In summary, we have carried out the rational design of fulleropyrrolidine derivatives as the acceptor partner with poly-3-hexylthiophene (P3HT) and established that *N*-methoxyethoxyethyl-2-(2-methoxyphenyl)fulleropyrrolidine (**1p**) might take the position of [C60]-PCBM. The important advantages of the use of the fulleropyrrolidine **1p** are in its stable nature under ambient conditions and its ease of preparation; these characteristics make it possible to reduce the production cost of large-area polymer solar cells.

It has been established that the band gap of the acceptor between the LUMO and HOMO strongly depends on the donor polymer; in fact, several more efficient polymers superior to P3HT have been developed using [C60]-PCBM as the acceptor.<sup>10–15</sup> Therefore, we expect that we will 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.

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