Facile synthesis of a 56π-electron 1,2-dihydromethano-[60]PCBM and its application for thermally stable polymer solar cells†

Chang-Zhi Li, Chang-Chieh Chien, Hin-Lap Yap, Chu-Chen Chueh, Fang-Chung Chen, Yutaka Matsuo, Eiichi Nakamura and Alex K.-Y. Jen

A facile synthesis was employed to make a 56π-electron methano-PC_{61}BM with a very small 1,2-dihydromethylene (CH_2) group. This new fullerene derivative possesses high electron mobility (0.014 cm^2 V^{-1} s^{-1}) and higher LUMO energy level (0.15 eV) than PC_{61}BM. Bulk hetero-junction devices based on using poly-(3-hexyl thiophene) and methano-PC_{61}BM as active layer exhibited better performance and thermal stability than those using the PC_{61}BM analogue.

Fullerene and its derivatives have been widely utilized in organic electronics. Among them, [6,6]-phenyl-C_61-butyric acid methyl ester (PC_{61}BM) and its C_{70} analogue PC_{71}BM represent the benchmark materials used in bulk heterojunction (BHJ) polymer solar cells (PSCs). Although these fullerene derivatives are widely used, they still need to be further optimized to have a suitable energy level, electron mobility, and thermal stability, to be compatible with the rapidly developed polymer donors. For instance, the open circuit voltage (V_{oc}) of PSCs with good organic/electrode interfacial contact is known to proportionally reflect the energy offset between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor. Bis-functionalized 56π-electron fullerenes with up-shifted LUMO, such as bis-PCBM and bis-indene-C_{60} adducts, have been demonstrated to improve the performance of poly(3-hexyl thiophene) (P3HT) based PSCs. While, significant structural perturbation from two steric-hindered addends may hamper the close contact between fullerene/fullerene and fullerene/polymer, to deteriorate charge separation and transport.

On the other hand, it is well-known that crystalline PCBM tends to form large aggregates in the blends with P3HT under continuous thermal annealing, which is a severe problem for achieving long lifetime for PSCs.

Here we report the facile synthesis of a 1,2-dihydromethano group (CH_2) functionalized phenyl-C_61-butyric acid methyl ester, namely methano-PC_{61}BM 1 (Scheme 1). This 56π-electron fullerene not only possesses a higher LUMO energy (0.15 eV) than PC_{61}BM but also has the smallest structural alternation to ensure that this new acceptor has similar electron mobility (Fig. 1). BHJ photovoltaic devices derived from the blend of methano-PC_{61}BM 1/P3HT exhibit superior performance and thermal stability compared to PC_{61}BM-based PSCs (Fig. 2 and 3).

Methano-PC_{61}BM 1 was prepared through a three-step synthesis starting from pristine C_{60} (Scheme 1 and ESI†). Following the procedure for synthesizing 1,2-dihydromethano fullerene, the silylmethyl-fullerene 2 was first prepared in 85% yield by adding i-PrO-Me_2SiCH_2MgCl to C_{60} in the presence of DMF. It was then converted into 1,2-dihydromethano[60]fullerene 3 in 77% yield, via the Cu(II)-promoted cyclization of γ-silylfullerene anion species. Treating p-tosylhydrazide with sodium methoxide in dry pyridine affords the diazo compounds, which were directly reacted with compound 3 at 75 °C in dry ODCB for 40 h. Methano-PC_{61}BM 1 was isolated in 23% yield after refluxing in ODCB for 5 h,

![Scheme 1](https://example.com/scheme1.png)

**Scheme 1** Synthesis of methano-PC_{61}BM 1 from fullerene.
to convert the [5,6]-open isomer into the [6,6]-closed isomer. The resulting compound I has similar solubility compared to PC61BM, which can be dissolved easily in common organic solvents, such as chloroform, toluene, chlorobenzene, and o-dichlorobenzene. The new fullerene derivative was characterized by MALDI-TOF MS, 1H, and 13C NMR spectroscopy. It consists of a mixture of regioisomers, which are inseparable over a silica gel column.

The addition of a small CH2 group efficiently lifts the LUMO level by 0.15 eV, from −3.73 eV (PC61BM) to −3.58 eV (methano-PC61BM I), because of the extraction of two more π-electrons from the fullerene core. As illustrated by cyclic voltammograms, PC61BM shows the first reduction potential, $E_{1/2}^{\text{red}1}$, at −1.07 V. While, the $E_{1/2}^{\text{red}1}$ of I is at −1.22 V (Fig. 1 and Table 1). Therefore, the increased energy difference between the LUMO of I and the HOMO of P3HT should improve the $V_{oc}$ of PSCs. It is also worthy to note that the high electron mobility (0.014 cm2 V−1 s−1) can be preserved by using this 1,2-disubstitution with a very small group to ensure minimal structural perturbation. The slightly decreased mobility may be due to the intrinsic electronic properties of bisfullerene and the nature of mixed isomers. For comparison, bis-PC61BM with two identical addends exhibits much lower electron mobility (0.002 cm2 V−1 s−1), which is almost two-orders lower than that of parent PC61BM. Therefore, better performance is expected from using this new fullerene I in PSCs.

For practical devices, thermal properties of the fullerene acceptors strongly affect their performance and lifetime. Fullerene I is amorphous in nature as inferred from the thermal analysis using Differential Scanning Calorimetry (DSC), with no endothermic peak detected during the second heating. In contrast, PCBM exhibits an obvious melting peak at 295 °C, which indicates its crystalline nature. It is well known that the morphology of PCBM/P3HT BHJ is not thermodynamically stable. Small and crystalline molecules like PCBM tend to diffuse and aggregate into larger clusters or crystals during the thermal annealing. This will significantly affect the optimal morphology and deteriorate device performance.

Previously, we have demonstrated that amorphous fullerenes can be used to overcome this crystallization-driven phase separation between a polymer donor and fullerene to achieve thermally stable PSCs.7 In this study, we have also observed very good thermal stability for methano-PCBM based PSC upon thermal annealing at 150 °C, which is sharply different from the fast decay performance of PCBM-based devices (Fig. 3 and 4).

The fullerene derivatives were further studied in PSC devices with the configuration of ITO/PEDOT:PSS(45 nm)/P3HT: fullerene (w/w = 1:1)/Ca(30 nm):Al (100 nm). The devices based on using I as acceptor showed improved PCEs compared to those using PC61BM and bisPC61BM as acceptors (Fig. 2 and ES1†). The reference P3HT/PC61BM device fabricated from chlorobenzene (with a thickness of 110 nm) showed a PCE of 3.02% ($V_{oc}$ = 0.58 V, $J_{sc}$ = 7.42 mA cm−2, and FF = 70%). Under the same fabrication conditions, higher PCE of 3.81% was achieved from the P3HT/methano-PC61BM I BHJ ($J_{sc}$ = 8.03 mA cm−2, $V_{oc}$ = 0.69 V and FF = 69%), which accounts for 26% improvement compared to the reference device.

Similar FF and $J_{sc}$ were observed compared to the devices using PC61BM. This suggests that compound I with a very compact structure inherited similar electron-transporting properties in BHJ as PCBM. Importantly, the enhanced $V_{oc}$

![Fig. 1](image1)

**Fig. 1** Material properties of methano-PC61BM I. (a) Cyclic voltammograms of I (black), and PC61BM (red) in ODCB/MeCN (5/1) containing tetraethylammonium perchlorate as a supporting electrolyte (vs. Fe/FeCl3). (b) Second heating trace of DSC analysis (10 °C min−1) for I (black), and PC61BM (red). (c) Output current–voltage characteristics of I. (d) Transfer characteristics of I.

**Table 1** LUMO, thermal properties and OTFT mobility of compound I and PCBM

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}^{\text{red}1}$/V</th>
<th>LUMO/eV</th>
<th>$T_{mi}$/°C</th>
<th>$FET_{m}$/cm2 V−1 s−1</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td>−1.22</td>
<td>−3.58</td>
<td>ND</td>
<td>0.014</td>
</tr>
<tr>
<td>PCBM</td>
<td>−1.07</td>
<td>−3.73</td>
<td>295</td>
<td>0.104</td>
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</tbody>
</table>

*a* The LUMO level: LUMO = −(4.8 + $E_{1/2}^{\text{red}1}$).

![Fig. 2](image2)

**Fig. 2** (a) The current density–voltage ($J$–$V$) characteristics of devices under illumination of AM 1.5G at 100 mW cm−2 and (b) their corresponding external quantum efficiency spectra.

![Fig. 3](image3)

**Fig. 3** Optical microscope images of (a) the P3HT:PCBM, and (b) P3HT:methano-PCBM I blends after annealing at 150 °C for 1 h.
resulting from the higher LUMO of compound 1 was the key for devices to achieve better performance. To further evaluate the effect of the methano group on bifunctional PCBM, we also fabricated a device with the P3HT/bisPC61BM as the active layer. The resulting device only exhibited a moderate PCE of 2.26%, with a
active layer. The resulting device only exhibited a moderate

The external quantum efficiency (EQE) spectra of PSCs based on P3HT/PC61BM and P3HT/methano-PC61BM are shown in Fig. 2b. The higher EQE in the region from 400 to 650 nm correlates well with the results of higher photocurrents. It is probably because an optimal D–A domain size in BHJ was achieved from this amorphous fullerene to facilitate excitons dissociation.

To understand how PCBM and methano-PCBM affect device stability, we compared the BHJs annealed at 150 °C for various heating times using optical microscopy. P3HT/PCBM (Fig. 3a) after heating at 150 °C for 1 h exhibited several micrometre-sized aggregates. In contrast, the active layer of P3HT/methano-PCBM remains homogenous with no obvious phase segregation observed (Fig. 3b). The μm-scale PCBM aggregates dramatically reduce the D–A interfacial contact, resulting in decreased efficiency for exciton dissociation.

The size of the PCBM domain became even larger with longer annealing time. As a result, the PCE and Jsc of PCBM-based devices showed continuous decay as a function of annealing time (Fig. 4). In contrast, the methano-PC61BM-based PSCs show very good thermal stability with no obvious decay of PCE and Jsc that could be observed under annealing. This may be ascribed to the amorphous nature of the new fullerene derivative that remarkably suppresses the continuous growth of phase segregation in BHJ to enhance device thermal stability.

In conclusion, we have designed and synthesized a new
fullerene derivative possesses higher LUMO energy level (0.15 eV) and good electron-transporting properties (0.014 cm² V⁻¹ s⁻¹) compared to parent PCBM. The BHJ devices that incorporate methano-PC61BM exhibited much improved performance and thermal stability than those using the PC61BM/P3HT active layer. This study provides a simple and generally applicable method to improve the performance and long-term stability of PSCs.

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Notes and references