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Facile synthesis of a 56 π -electron 1,2-dihydromethano-[60]PCBM and its application for thermally stable polymer solar cells†Chang-Zhi Li,^a Shang-Chieh Chien,^{ab} Hin-Lap Yip,^{ac} Chu-Chen Chueh,^a Fang-Chung Chen,^b Yutaka Matsuo,^d Eiichi Nakamura^d and Alex K.-Y. Jen^{*ace}

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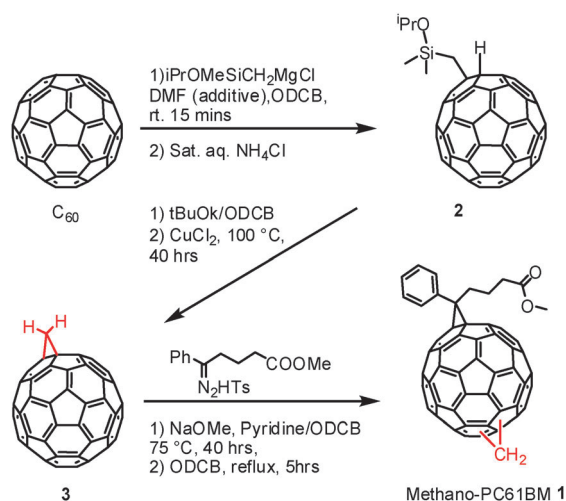
A facile synthesis was employed to make a 56 π -electron methano-PC₆₁BM with a very small 1,2-dihydromethano (CH₂) group. This new fullerene derivative possesses high electron mobility (0.014 cm² V⁻¹ s⁻¹) and higher LUMO energy level (0.15 eV) than PC₆₁BM. Bulk hetero-junction devices based on using poly(3-hexylthiophene) and methano-PC₆₁BM as active layer exhibited better performance and thermal stability than those using the PC₆₁BM analogue.

Fullerene and its derivatives have been widely utilized in organic electronics.^{1,2} Among them, [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and its C₇₀ analogue PC₇₁BM represent the benchmark materials used in bulk heterojunction (BHJ) polymer solar cells (PSCs).³ Although these fullerene derivatives are widely used,⁴ they still need to be further optimized to have a suitable energy level,⁵ electron mobility,⁶ and thermal stability,⁷ 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.⁸ Bis-functionalized 56 π -electron fullerenes with up-shifted LUMO, such as bis-PCBM and bis-indene-C₆₀ 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.⁶ 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.⁹

Here we report the facile synthesis of a 1,2-dihydromethano group (CH₂) functionalized phenyl-C₆₁-butyric acid methyl ester, namely methano-PC₆₁BM **1** (Scheme 1). This 56 π -electron fullerene not only possesses a higher LUMO energy (0.15 eV) than PC₆₁BM but also has the smallest structural alternation¹⁰ to ensure that this new acceptor has similar electron mobility (Fig. 1). BHJ photovoltaic devices derived from the blend of methano-PC₆₁BM **1**/P3HT exhibit superior performance and thermal stability compared to PC₆₁BM-based PSCs (Fig. 2 and 3).

Methano-PC₆₁BM **1** was prepared through a three-step synthesis starting from pristine C₆₀ (Scheme 1 and ESI†). Following the procedure for synthesizing 1,2-dihydromethano fullerene,¹⁰ the silylmethyl-fullerene **2** was first prepared in 85% yield by adding *i*-PrO-Me₂SiCH₂MgCl to C₆₀ in the presence of DMF.¹¹ 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-PC₆₁BM **1** was isolated in 23% yield after refluxing in ODCB for 5 h,

Scheme 1 Synthesis of methano-PC₆₁BM **1** from fullerene.

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to convert the [5,6]-open isomer into the [6,6]-closed isomer. The resulting compound **1** 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 **1**), because of the extraction of two more π -electrons from the fullerene core. As illustrated by cyclic voltammograms, PC₆₁BM shows the first reduction potential, $E_{1/2}^{\text{red1}}$, at -1.07 V. While, the $E_{1/2}^{\text{red1}}$ of **1** is at -1.22 V (Fig. 1 and Table 1). Therefore, the increased energy difference between the LUMO of **1** 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 **1** in PSCs.

For practical devices, thermal properties of the fullerene acceptors strongly affect their performance and lifetime. Fullerene **1** is amorphous in nature as inferred from the thermal analysis

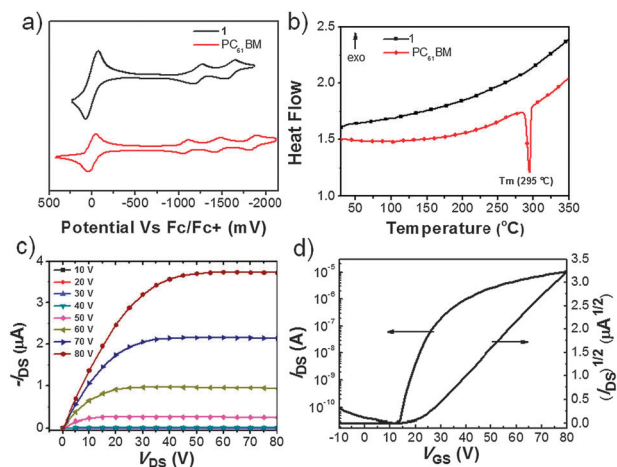


Fig. 1 Material properties of methano-PC₆₁BM **1**. (a) Cyclic voltammograms of **1** (black), and PC₆₁BM (red) in ODCB/MeCN (5/1) containing tetrabutylammonium perchlorate as a supporting electrolyte (vs. Fc/Fc⁺). (b) Second heating trace of DSC analysis (10 °C min⁻¹) for **1** (black), and PC₆₁BM (red).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

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

Compound	$E_{1/2}^{\text{red1}}$ /V	LUMO ^a /eV	T_m /°C	FET μ_e /cm ² V ⁻¹ s ⁻¹
1	-1.22	-3.58	ND	0.014
PCBM	-1.07	-3.73	295	0.104

^a The LUMO level: LUMO = -(4.8 + $E_{1/2}^{\text{red1}}$).

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.^{7a} 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 **1** as acceptor showed improved PCEs compared to those using PC₆₁BM and bisPC₆₁BM as acceptors (Fig. 2 and ESI†). 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 **1** BHJ (J_{sc} = 8.03 mA cm⁻²; V_{oc} = 0.69 V and FF = 0.69), 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 **1** with a very compact structure inherited similar electron-transporting properties in BHJ as PCBM. Importantly, the enhanced V_{oc}

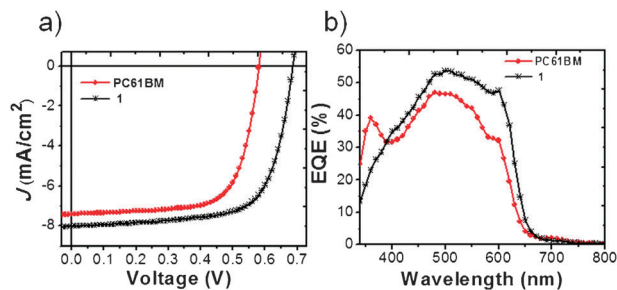


Fig. 2 (a) The current density-voltage (J - V) characteristics of devices under illumination of AM 1.5G at 100 mW cm⁻² and (b) their corresponding external quantum efficiency spectra.

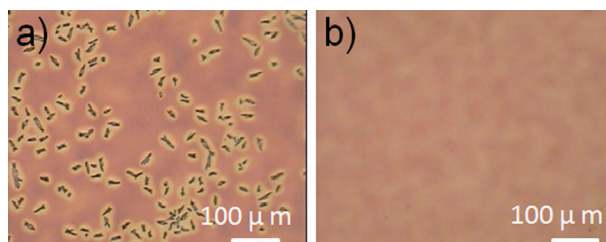


Fig. 3 Optical microscope images of (a) the P3HT:PCBM, and (b) P3HT:methano-PCBM **1** blends after annealing at 150 °C for 1 h.

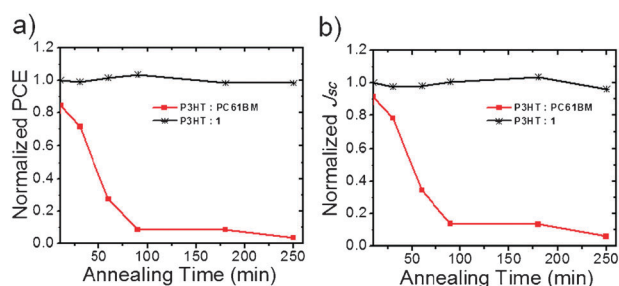


Fig. 4 The normalized PCE (a) and J_{sc} (b) of PSCs based on the P3HT:PCBM (red), and P3HT:methano-PCBM **1** (black) BHJs as functions of annealing time at 150 °C (normalized according to the optimal PCE and J_{sc} of P3HT:methano-PCBM **1** annealed at 150 °C for 10 min).

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 bisfunctional 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 V_{oc} of 0.71 V, and the dramatically decreased J_{sc} (5.86 mA cm⁻²) and FF (0.54), which correlated to the lower electron mobility of the bis-adduct (see ESI†). Therefore, the 1,2-dihydromethano functionalized PCBM gives an ideal example for simultaneous tuning of the LUMO energy level while preserving high electron-transporting properties.

The external quantum efficiency (EQE) spectra of PSCs based on P3HT/PC₆₁BM and P3HT/methano-PC₆₁BM **1** 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-PC₆₁BM remains homogenous with no obvious phase segregation observed (Fig. 3b). The μ m-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 J_{sc} 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 J_{sc} 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 56 π -electron methano-PC₆₁BM using a very small and stable 1,2-dihydromethano (CH₂) group. This new bis-functionalized

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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