# Alkyl substituted [6,6]-thienyl- $C_{61}$ -butyric acid methyl esters: easily accessible acceptor materials for bulk-heterojunction polymer solar cells

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Received 1st December 2009, Accepted 1st February 2010 First published as an Advance Article on the web 1st March 2010 DOI: 10.1039/b925089a

[6,6]-Thienyl-C<sub>61</sub>-butyric acid ester derivatives with methyl, hexyl and 2-ethylhexyl at the 5-position of thiophene ring (**TCBM-C***n*, *n* represents the number of carbon atom in the alkyl chain) were synthesized. Unlike [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (**PCBM**), these methanofullerene derivatives ([6,6] adduct) can be directly obtained from the typical diazo addition under mild conditions, and high temperature isomerization is unnecessary. With a hexyl or 2-ethylhexyl group at the 5-position of thiophene, the solubility of **TCBM-C***n* in chlorobenzene is as high as 180  $\pm$  10 mg ml<sup>-1</sup>. Bulk heterojunction photovoltaic solar cells were fabricated with a device structure of ITO/ poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/poly(3-hexylthiophene) (**P3HT**) : **TCBM-C***n* (1 : 0.8 w/w)/LiF/Al. The device based-on **TCBM-C6** exhibited the best performance with a power conversion efficiency (PCE) of up to 4.26%.

# Introduction

Bulk-heterojunction (BHJ) polymer solar cells (PSCs) have attracted more and more attention as a renewable energy sources due to their easy and cheap processing.<sup>1-5</sup> For this type of device, a blend of electron-donating materials (p-type conjugated polymers) and an electron-accepting material (n-type materials) is used as the active layer, and a derivative of buckminsterfullerene  $(C_{60})$ , *i.e.* [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (**PCBM**), is the most often used electron-accepting material.<sup>6</sup> To further improve the device performance, different C<sub>60</sub> derivatives<sup>7-20,24</sup> have been synthesized. Particularly, many efforts have been devoted to modify the PCBM skeleton by introducing substituents on the phenyl ring,<sup>12,15,16</sup> exchanging methyl groups with long alkyl<sup>17</sup> chains, an ethyleneoxy moiety<sup>18</sup> or a perfloroalkyl chain<sup>19</sup> to tune the miscibility, thermal properties and energy levels, and the resulting C<sub>60</sub> derivatives have been successfully used to control the film morphology, raise the open circuit voltage  $(V_{oc})$ , and improve the device stability.

Although **PCBM** is the most popular acceptor materials so far for BHJ PSCs, it is questionable whether it is the best for polymer donor materials with the huge diversity of chemical structures. Therefore, it is still very important to explore new  $C_{60}$  derivatives, particularly those with ease of synthesis and purification. It is well known that thiophene is an aromatic ring characterized by easy modification. Recently, a **PCBM** analogue, *i.e.* [6,6]-thienyl- $C_{61}$ -butyric acid methyl ester (**TCBM**), has been reported to exhibit device performance close to **PCBM** with regioregular poly(3-hexylthiophene) (**P3HT**) as the donor.<sup>20,24</sup> To further explore the easily made high performance  $C_{60}$ -based acceptors for BHJ PSCs, herein we synthesized a series of **TCBM** analogues with different alkyl chains (methyl, hexyl and ethylhexyl) on the thiophene ring, as shown in Fig. 1. BHJ PSCs based on the blend of **P3HT** and these new  $C_{60}$  derivatives exhibited power conversion efficiencies (PCE) identical to or slightly higher than those prepared from **P3HT** and **PCBM** or **TCBM**. Most importantly, these  $C_{60}$  derivatives can be made directly by the typical diazo addition without high temperature isomerization.

# Experimental

# Materials

Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), *o*-dichlorobenzene (ODCB) and absolute methanol were subject to stirring with CaO and then distilled. **PCBM** with a purity of 99% was purchased from FEM Technology Co. Inc. Compound **1b** with a purity of 99% was purchased from Pacific Chemsource Inc. Compounds **1c** and **1d** were prepared according to ref. 21. **P3HT** was prepared by the McCullough method.<sup>22</sup> Weight-average molecular weight, polydispersity, and regioregularity are 38 600 g mol<sup>-1</sup>, 1.59 and 97%, respectively. Other reagents were used as received without further purification.



Fig. 1 Chemical structures of TCBM, TCBM-C1, TCBM-C6 and TCBM-C2,6.

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### 5-[5-Alkyl-(2-thienyl)]-5-oxo-pentanoic acids (2a-d)<sup>25</sup>

AlCl<sub>3</sub> (132 mmol) was added in parts to glutaric anhydride (60 mmol) and 2-alkylthiophene (60 mmol) in  $CH_2Cl_2$  (120 ml) with cooling in an ice-water bath. The mixture was allowed to warm to room temperature slowly, stirred for 5 h and then quenched with 2M HCl for extraction with  $CH_2Cl_2$ . The organic extracts were washed with brine, and dried with MgSO<sub>4</sub>. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent.

**2a** (Yield 60%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.71 (dd, J = 0.9 Hz, J = 0.9 Hz, 1H), 7.64 (dd, J = 0.9 Hz, J = 0.9 Hz, 1H), 7.14 (dd, J = 3.9 Hz, J = 3.9 Hz, 1H), 3.02 (t, J = 7.2 Hz, 2H), 2.51 (t, J = 7.2 Hz, 2H), 2.04–2.14 (m, 2H).

**2b** (Yield 72%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.54 (d, J = 3.3 Hz, 1H), 6.79 (d, J = 3.3 Hz, 1H), 2.95 (t, J = 6.9 Hz, 2H), 2.53 (s, 3H), 2.49 (t, J = 6.9 Hz, 2H), 2.02–2.11 (m, 2H).

**2c** (Yield 86%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.56 (d, J = 3.9 Hz, 1H), 6.79 (d, J = 3.9 Hz, 1H), 3.01 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.5 Hz, 2H), 2.06–2.08 (m, 2H), 1.30–1.38 (m, 2H), 1.30–1.38 (m, 8H), 0.87–0.92 (m, 3H).

**2d** (Yield 52%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.56 (d, J = 3.9 Hz, 1H), 6.79 (d, J = 3.9 Hz, 1H), 2.96 (t, J = 6.9 Hz, 2H), 2.77 (d, J = 6.6 Hz, 2H), 2.50 (t, J = 6.9 Hz, 2H), 2.05–2.10 (m, 2H), 1.56–1.66 (m, 1H), 1.27–1.35 (m, 8H), 0.86–0.91 (m, 6H).

### Methyl 5-[5-alkyl-(2-thienyl)]-5-oxo-pentanoate (3a-d)

A solution of **2a–d** (36 mmol) in MeOH (70 ml) with a catalytic amount of hydrochloric acid was refluxed for 5 h. The mixture was extracted with  $CH_2Cl_2$ . The organic extracts were washed with brine, and dried with  $MgSO_4$ . The residue was purified by column chromatography on silica gel with petroleum ether-: ethyl acetate (6 : 1) as eluent.

**3a** (yield 90%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.71 (dd, J = 0.9 Hz, J = 0.9 Hz, 1H), 7.64 (dd, J = 0.9 Hz, J = 0.9 Hz, 1H), 7.14 (dd, J = 3.9 Hz, J = 3.9 Hz, 1H), 3.69 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 2.45 (t, J = 7.2 Hz, 2H), 2.03–2.13 (m, 2H).

**3b** (yield 95%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.54 (d, J = 3.3 Hz, 1H), 6.79 (d, J = 3.3 Hz, 1H), 3.68 (s, 3H), 2.91 (t, J = 3.6 Hz, 2H), 2.53 (s, 3H), 2.43 (t, J = 3.6 Hz, 2H), 2.03–2.08 (m, 2H).

**3c** (yield 96%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.56 (d, J = 3.9 Hz, 1H), 6.79 (d, J = 3.9 Hz, 1H), 3.69 (s, 3H), 2.98 (t, J = 7.5 Hz, 2H), 2.71 (t, J = 7.2 Hz, 2H), 2.50 (t, J = 7.5 Hz, 2H), 2.05–2.07 (m, 2H).

**3d** (yield 95%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.56 (d, J = 3.9 Hz, 1H), 6.79 (d, J = 3.9 Hz, 1H), 3.69 (s, 3H), 2.93 (t, J = 6.9 Hz, 2H), 2.71 (t, J = 6.6 Hz, 2H), 2.49 (t, J = 6.9 Hz, 2H), 2.04–2.09 (m, 2H), 1.55–1.65 (m, 1H), 1.28–1.36 (m, 2H), 0.87–0.92 (m, 2H).

### Methyl 5-[5-alkyl-(2-thienyl)]-5-oxo-pentanoate-*p*-tosylhydrazone (4a–d)

A mixture of **3a–d** (30 mmol), *p*-toluene-sulfonyl hydrazide (33 mmol), and MeOH (60 ml) with a catalytic amount of CH<sub>3</sub>COOH was refluxed for 17 h. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic extracts were washed with brine, and dried with MgSO<sub>4</sub>. The residue was purified by column chromatography on silica gel with petroleum ether : ethyl acetate (9:1) as eluent.

**4a** (yield 68%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.98 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 1.2 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 7.18 (dd, J = 1.2 Hz, J = 1.2 Hz, 1H), 6.97 (dd, J = 3.9 Hz, J = 3.6 Hz, 1H), 3.80 (s, 3H), 2.61 (t, J = 7.8 Hz, 2H), 2.40 (s, 3H), 2.31 (t, J = 6.0 Hz, 2H), 1.68–1.78 (m, 2H).

**4b** (yield 70%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.84 (s, 1H), 7.90 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 6.97 (d, J = 2.7 Hz, 1H), 6.61 (d, J = 2.7 Hz, 1H), 3.78 (s, 3H), 2.56 (t, J = 7.5 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 2.30 (t, J = 7.5 Hz, 2H), 1.59–1.71 (m, 2H).

**4c** (yield 56%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.82 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 3.6 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H), 3.78 (s, 3H), 2.75 (t, J = 7.5 Hz, 2H), 2.56 (t, J = 7.5 Hz, 2H), 2.40 (s, 3H), 2.30 (t, J = 6.0 Hz, 2H), 1.63–1.74 (m, 2H), 1.31–1.39 (m, 8H), 0.87–0.92 (m, 3H).

**4d** (yield 75%); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.86 (s, 1H), 7.91 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.99 (d, J = 3.6 Hz, 1H), 6.61 (d, J = 3.6 Hz, 1H), 3.78 (s, 3H), 2.69 (d, J = 6.6 Hz, 2H), 2.56 (t, J = 8.1 Hz, 2H), 2.40 (s, 3H), 2.31 (t, J = 8.1 Hz, 2H), 1.62–1.80 (m, 2H), 1.54–1.64 (m, 1H), 1.28–1.35 (m, 8H), 0.86–0.91 (m, 6H).

### [6,6]-Thienyl-C<sub>61</sub>-butyric acid methyl ester (TCBM)

A mixture of 4a (313 mg, 0.83 mmol), sodium methoxide (49 mg, 0.91 mmol), and dry pyridine (15 ml) was stirred at room temperature for 30 min. Then a solution of C<sub>60</sub> (590 mg, 0.83 mmol) in ODCB (60 ml) was added, and the homogeneous reaction mixture was stirred at 75 °C under argon for 24 h. The solvent was evaporated at reduced pressure, and the residue was purified by column chromatography on silica gel with toluene as eluent. The product was precipitated with MeOH with a yield of 40% (300 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 7.47–7.50 (m, 2H), 7.13-7.15 (m, 1H), 3.69 (s, 3H), 2.96 (t, J = 4.8 Hz, 2H),2.58 (t, J = 7.2 Hz, 2H), 2.22–2.26 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.45 (CO<sub>2</sub>CH<sub>3</sub>), 148.30, 147.49, 145.69, 145.25, 145.22, 145.49, 145.15, 145.08, 144.83, 144.73, 144.67, 144.60, 144.52, 144.18, 143.82, 143.80, 143.12, 143.06, 143.02, 142.95, 142.21, 142.16, 142.14, 140.97, 140.75, 139.45, 138.18, 131.96, 126.24, 126.19, 79.92 (bridgehead C), 51.69, 45.76, 33.98, 33.67, 22.48. Anal. Calcd for C<sub>70</sub>H<sub>12</sub>O<sub>2</sub>S (%): C, 91.69; H, 1.32. Found (%): C, 91.52; H, 1.10.

### 5-Methyl-[6,6]-thienyl-C<sub>61</sub>-butyric acid methyl ester (TCBM-C1)

**TCBM-C1** was synthesized following the procedure for preparation of **TCBM** with a yield of 40% (380 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.26 (d, J = 4.8 Hz, 1H), 6.76 (d, J = 4.8 Hz, 1H), 3.69 (s, 3H), 2.92 (t, J = 7.2 Hz, 2H), 2.59 (s, 3H), 2.57 (t, J = 7.2 Hz, 2H), 2.19–2.29 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.52 (CO<sub>2</sub>CH<sub>3</sub>), 148.47, 147.62, 145.73, 145.24, 145.20, 145.13, 144.82, 144.73 144.65, 144.58, 144.48, 144.16, 143.82, 143.79, 143.10, 143.05, 143.01, 142.93, 142.91, 142.25, 142.17, 142.12, 140.94, 140.82, 140.72, 138.25, 138.17, 136.41, 132.02, 124.24, 80.03 (bridgehead C), 51.67, 46.10, 33.84,

33.70, 22.51. Anal. Calcd for  $C_{71}H_{14}O_2S$  (%): C, 91.60; H, 1.52. Found (%): C, 90.37; H, 1.31.

### 5-Hexyl-[6,6]-thienyl-C<sub>61</sub>-butyric acid methyl ester (TCBM-C6)

**TCBM-C6** was synthesized following the procedure for preparation of **TCBM** with a yield of 46% (490 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.26 (d, J = 4.5 Hz, 1H), 6.76 (d, J = 4.5 Hz, 1H), 3.69 (s, 3H), 2.87–2.95 (m, 4H), 2.58 (t, J = 7.2 Hz, 2H), 2.21–2.29 (m, 2H), 1.72–1.79 (m, 2H), 1.35–1.43 (m, 2H), 0.90 (s, 3H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.53 (CO<sub>2</sub>CH<sub>3</sub>), 148.54, 147.66, 147.03, 145.75, 145.24, 145.20, 145.13, 144.82, 144.73, 144.64, 144.57, 144.48, 144.14, 143.82, 143.79, 143.10, 143.05, 143.00, 142.93, 142.90, 142.26, 142.17, 142.12, 140.93, 140.70, 138.25, 138.11, 136.00, 131.77, 122.83, 80.10 (bridgehead C), 51.66, 46.21, 33.81, 33.70, 31.52, 31.36, 30.40, 28.85, 22.56, 22.52, 14.06. Anal. Calcd for C<sub>76</sub>H<sub>24</sub>O<sub>2</sub>S (%): C, 91.18; H, 2.42. Found (%): C, 91.00; H, 2.19.

# 5-(2-Ethylhexyl)-[6,6]-thienyl-C<sub>61</sub>-butyric acid methyl ester (TC-BM-C2,6)

**TCBM-C2,6** was synthesized following the procedure for preparation of **TCBM** with a yield of 49% (500 mg). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 7.26 (d, J = 4.5 Hz, 1H), 6.76 (d, J = 4.5 Hz, 1H), 3.69 (s, 3H), 2.90–2.95 (m, 2H), 2.80–2.85 (m, 2H), 2.58 (t, J = 4.5 Hz, 2H), 2.22–2.29 (m, 2H), 1.64–1.66 (m, 1H), 1.31–1.43 (m, 8H), 0.88–0.96 (m, 6H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 173.50 (CO<sub>2</sub>CH<sub>3</sub>), 148.58, 147.66, 145.76, 145.24, 145.19, 145.12, 144.74, 144.71, 144.64, 144.57, 144.48, 144.13, 143.82, 143.79, 143.10, 143.07, 143.04, 143.00, 142.92, 142.90, 142.23, 142.20, 142.18, 142.12, 140.93, 140.70, 138.22, 138.13, 136.25, 131.75, 123.96, 80.12, 80.10 (bridgehead C), 51.65, 46.21, 41.55, 34.53, 33.75, 33.70, 31.45, 28.85, 25.93, 22.94, 22.52, 14.11, 11.00. Anal. Calcd for C<sub>71</sub>H<sub>14</sub>O<sub>2</sub>S (%): C, 91.03; H, 2.74. Found (%): C, 90.69; H, 2.54.

### Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 300 spectrometer at 300 MHz and a Bruker AV 600 spectrometer at 600 MHz. Elemental analysis was performed on a varioEL elemental analysis system. UV-Vis-NIR spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrometer. Cyclic voltammetry (CV) was performed on a CHI660a electrochemical analyzer with a three-electrode cell in a solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mV s<sup>-1</sup>. A platinum disc electrode with a diameter of 10 mm, a Pt wire, and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple. The lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations:  $LUMO = -(4.80 + E_{red}^{onset}) \text{ eV.}^{26}$ Transmission electron microscopy (TEM) was performed on a JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV.

### Photovoltaic device fabrication and characterization

The PSCs were fabricated with the device structure of ITO/ poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PED-OT:PSS)/P3HT : TCBM-Cn (1:0.8 w/w)/LiF/Al. The ITO glass was precleaned and modified by a 40 nm PEDOT:PSS (Baytron P4083) layer which was spin-coated from a PEDOT-PSS aqueous solution on the ITO substrate, and was dried subsequently at 120 °C for 30 min. The active layer of the blend of P3HT and TCBM-Cn was prepared by spin-coating the chlorobenzene solution of the P3HT and TCBM-Cn (1:0.8, w/w) with the **P3HT** concentration of 10 mg ml<sup>-1</sup> on the ITO/ PEDOT:PSS electrode. The thickness of the active layer was controlled to ca. 115-125 nm by adjusting the rotating speed of the spin-coater. Then the LiF/Al cathode was deposited at a vacuum level of  $4 \times 10^{-4}$  Pa. The thicknesses of the LiF and Al layers are 1 and 200 nm, respectively. The devices were annealed at 160 °C for 10 min in the glove-box. Eight devices were fabricated per material to ensure the reproducibility of results. The effective area of the unit cell is 12 mm<sup>2</sup>. The current-voltage (I-V) measurement of the devices was conducted on a computercontrolled Keithley 236 Source Measure Unit. A xenon lamp (500 W) was used as the white light source, and the optical power at the sample was 100 mW cm<sup>-2</sup>. The external quantum efficiency (EQE) was measured using a Model SR830 DSP Lock-in Amplifier coupled with a SBP500 monochromator, a DSC102 date acquisition system and a Model SR540 chopper controller. The light intensity at each wavelength was calibrated with a standard single-crystal Si photodiode.

### **Results and discussion**

### Synthesis and characterization

As shown in Scheme 1, TCBM derivatives, i.e. TCBM-C1, TCBM-C6 and TCBM-C2,6 with methyl, hexyl and 2-ethylhexyl groups at the 5-position of the thiophene ring, were synthesized following the procedure for preparation of PCBM and TCBM,<sup>6a,20</sup> but without high temperature isomerization. TCBM was also synthesized for comparison. First, 2a-d were prepared from 1a-d by Friedel-Crafts acylation<sup>25</sup> in yields of 52 to 86%. Compounds 3a-d were prepared from 2a-d by esterification. They were reacted with *p*-toluenesulfonyl hydrazide in methanol under reflux to afford compounds 4a-d. For preparation of the final compounds, C<sub>60</sub> was dissolved in dried ODCB by ultrasonic method, and the resulting solution was added to the solution of 4 and sodium methoxide in pyridine. Unlike the preparation of PCBM, the successive reaction at 75 °C for 24 h directly afforded [6,6] isomers instead of the mixture of [5,6] and [6,6] adducts without further isomerization at high temperature, such as 180 °C typically for PCBM-type compounds as reported in the literature.<sup>6a,12,16–18</sup> The resulting **TCBM-C***n* were purified by column chromatography on silica gel with toluene as eluent to give TCBM, TCBM-C1, TCBM-C6 and TCBM-C2,6 in yields of 40, 40, 46 and 49%, respectively. The enhanced yields for TCBM-C6 and TCBM-C2,6 are attributed to their high solubility, which makes the compounds easily recovered from chromatography. Actually, the solubility of TCBM and TCBM-C1 in chlorobenzene is 50  $\pm$  5 mg ml<sup>-1</sup>, lower than 80  $\pm$  5 mg ml<sup>-1</sup> of **PCBM**. However, the solubility of TCBM-C6 and TCBM-C2,6 is as high



Scheme 1 Synthesis of fullerene derivatives. (i) glutaric anhydride,  $AlCl_3$ ,  $CH_2Cl_2$ , 0 °C; (ii)  $CH_3OH$ , HCl, reflux; (iii) *p*-toluenesulfonyl hydrazide (TsNHNH<sub>2</sub>),  $CH_3OH$ ,  $CH_3COOH$ , 75 °C; (iv)  $C_{60}$ ,  $CH_3ONa$ , ODCB, pyridine, 75 °C.

as  $180 \pm 10$  mg ml<sup>-1</sup>. This high solubility of **TCBM-C6** and **TCBM-C2,6** is promising for the device fabrication.

The structures of **TCBM-Cn** were validated by NMR spectroscopy and elemental analysis. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra indicate their [6,6] structural features. Fig. 2 shows the <sup>1</sup>H NMR spectra of **TCBM-C1** and <sup>13</sup>C NMR spectra of **TCBM-C2,6** as an example. As reported in the literature,<sup>6a,23</sup> the <sup>1</sup>H NMR signals of ArC( $CH_2$ )<sub>3</sub>COOMe are different for [5,6] and [6,6] isomers in terms of chemical shift. The presence of three sets of signals at ~2.9, 2.6 and 2.2 ppm assigned to the aforementioned methylene groups in <sup>1</sup>H NMR spectrum (Fig. 2a) together with the <sup>13</sup>C signals at ~80 ppm attributed to the bridgehead carbons in <sup>13</sup>C NMR spectrum (Fig. 2b) clearly indicate the formation of the neat methanofullerene structure, that is the [6,6] isomer.



Fig. 2 <sup>1</sup>H NMR spectrum of TCBM-C1 and <sup>13</sup>C NMR spectrum of TCBM-C2,6 in CDCl<sub>3</sub> at room temperature.

### **Electrochemical properties**

Electrochemical properties of **TCBM-C***n* were studied by cyclic voltammetry (CV) at a scan rate of 100 mV s<sup>-1</sup> with CH<sub>2</sub>Cl<sub>2</sub> and Bu<sub>4</sub>NPF<sub>6</sub> as the solvent and supporting electrolyte, respectively. As shown in Fig. 3 and Table 1, all C<sub>60</sub> derivatives including **TCBM** and **PCBM** have a similar CV scans with three quasireversible redox waves in the potential ranging from 0 to -2.0 V. The first half-wave potentials for all C<sub>60</sub> derivatives ( $E_{22}^{red1}$ ) are around -1.07 V vs. Fc/Fc<sup>+</sup>, corresponding to the lowest unoccupied molecular orbital (LUMO) level of -3.77 eV (Table 1). This indicates that the introduction of an alkyl chain onto the thiophene ring does not affect the LUMO level of **TCBM** derivatives.

### Photovoltaic properties

BHJ PSCs with the device structure of ITO/PEDOT:PSS/ P3HT : TCBM-Cn (1 : 0.8, w/w)/LiF/Al were fabricated for evaluation of the properties of the new acceptors. Control devices based-on P3HT/PCBM or TCBM were also prepared under identical conditions for comparison. As shown in Table 2 and Fig. 4, the performance of the control devices are well



Fig. 3 Cyclic voltammogram scans of PCBM, TCBM and TCBM-Cn.

 Table 1
 Electrochemical data of TCBM-Cn and PCBM<sup>a</sup>

Compound	$E^{\rm red1}_{\nu_2}/{ m V}$	$E^{\rm red2}_{\nu_2}/{ m V}$	$E^{\rm red3}_{\nu_2}/{ m V}$	LUMO/eV
РСВМ	-1.07	-1.46	-1.96	-3.75
ТСВМ	-1.07	-1.46	-1.96	-3.76
TCBM-C1	-1.07	-1.45	-1.95	-3.77
TCBM-C6	-1.07	-1.44	-1.95	-3.77
TCBM-C2,6	-1.06	-1.44	-1.95	-3.77

<sup>*a*</sup> Experiments were carried out in CH<sub>2</sub>Cl<sub>2</sub> solutions (10<sup>-3</sup> M) with Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as the supporting electrolyte at a scan rate of 100 mV s<sup>-1</sup>. Pt disc, Pt wire and SCE were used as working, counter and reference electrodes, respectively. Half-wave potentials were reported in V vs. Fc/Fc<sup>+</sup>.

**Table 2** PSC performance of **TCBM-C***n* and **PCBM** under illumination of 100 mW cm<sup>-2</sup> white light.<sup>*a*</sup>

Active layer	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	FF (%)	PCE (%)
РЗНТ/ТСВМ	10.33	0.62	0.62	4.00
P3HT/TCBM-C1	10.51	0.60	0.63	3.95
P3HT/TCBM-C6	10.61	0.63	0.64	4.26
P3HT/TCBM-C2.6	10.53	0.64	0.57	3.84
P3HT/PCBM	10.40	0.62	0.61	3.90

<sup>*a*</sup> The thickness of the active layer is in the range of 115 to 125 nm and the performance data were average values calculated from eight devices for each material.



**Fig. 4** (a) J-V curves and (b) EQE spectra of PSCs with **P3HT** : **TCBM-Cn** (1 : 0.8, w/w) as the active layer. J-V curves were in the dark and under illumination of 100 mW cm<sup>-2</sup> white light.



Fig. 5 Transmission electron micrographs of P3HT/PCBM (a), P3HT/TCBM-C6 (b) and P3HT/TCBM-C2,6 (c) films with a thickness of 30 nm. The films were annealed at 160  $^{\circ}$ C for 10 min.

comparable to the reference report with average PCEs of 3.90 and 4.00% for **PCBM** and **TCBM**, respectively.<sup>24,27</sup> The devices of **TCBM-C1** show an average PCE of 3.95%. The devices of **TCBM-C2,6** exhibit a slightly lower fill factor (FF) of 0.57, leading to the lowest PCE of 3.84%. **TCBM-C6** shows the best device performance with a  $V_{\rm oc}$  of 0.63 V, a short circuit current density ( $J_{\rm sc}$ ) of 10.61 mA cm<sup>-2</sup>, and a FF of 0.64, leading to a PCE of 4.26%. This is different from the results reported by Troshin *et al.*,<sup>24</sup> who reported that the device efficiencies were related to the solubilities of C<sub>60</sub> derivatives, and the better device performance was achieved with solubilities of C<sub>60</sub> derivatives in the range of 30 to 80 mg ml<sup>-1</sup>.

The films of **P3HT/TCBM-C***n* with a thickness of  $\sim$ 30 nm were prepared under conditions identical to the device fabrication for TEM observation. TEM images of **P3HT/PCBM**, **P3HT/TCBM-C6** and **P3HT/TCBM-C2,6** films are shown in Fig. 5. All films are uniform with absence of large aggregates, which is consistent with the good device performance of these materials.

In conclusion, we have demonstrated that [6,6]-thienyl-C<sub>61</sub>butyric acid methyl ester (**TCBM**) and its alkyl-substituted derivatives (**TCBM-C***n*) can be synthesized directly from the typical diazo addition, and that the additional isomerization at high temperature is unnecessary. The yields of the **TCBM-C6** and **TCBM-C2,6** are as high as 46% and 49%, respectively. Meanwhile, these two C<sub>60</sub> derivatives are highly soluble with a solubility of up to 180 mg ml<sup>-1</sup> in chlorobenzene. PSCs of **TCBM-C6** exhibit the best device performance with a PCE of 4.26% ( $J_{sc} = 10.61$  mA cm<sup>-2</sup>,  $V_{oc} = 0.63$  V, FF = 0.64). Easy synthesis, high solubility and excellent device performance qualify thienyl substituted C<sub>60</sub> derivatives as promising alternatives to **PCBM**, the well known electron-accepting materials for BHJ PSCs.

### Acknowledgements

This work is supported by the NSFC (no. 20921061, 20525415 and 50703041), MOST of China (2009CB939702) and Chinese Academy of Sciences (KJCX2-YW-M11).

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