Facile Synthesis of [6,6]-Phenyl-$C_{61/71}$-Butyric Acid Methyl Esters via Sulfur Ylides for Bulk-Heterojunction Solar Cell

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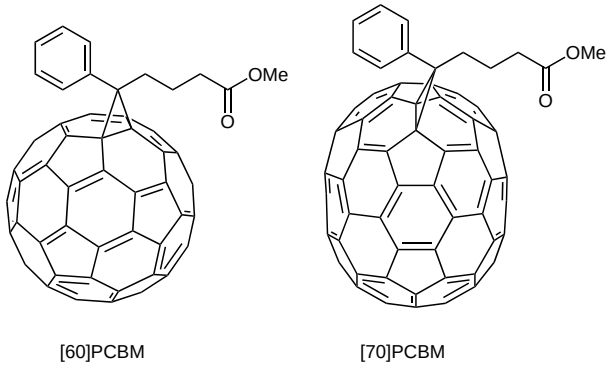
Abstract: A one-step, mild synthesis of methanofullerenes as electron acceptors for solution-processed bulk-heterojunction solar cells was developed. [6,6]-Phenyl-C_{61}-butyric acid methyl ester {[60]PCBM} was directly synthesized in good yields, by the reaction of fullerene with sulfur ylide derivatives in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) at room temperature. This method was also successfully applied to the preparation of [6,6]-phenyl-C_{71}-butyric acid methyl ester {[70]PCBM}.

Key words: methanofullerene, PCBM, photovoltaics, sulfur ylide, addition–elimination reaction

Because of the many potential applications of fullerenes in materials and nanotechnology, numerous fullerene derivatives have been synthesized over the past decade.[1] The excellent electron-accepting capabilities of fullerenes offer promise as materials for organic photovoltaics.[2] In particular, since Sariciftci et al. reported that a conversion efficiency of 2.5–3.0% could be achieved using a polymer solar cell based on a bulk heterojunction (BHJ) of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and methanofullerenes, typically [6,6]-phenyl-C_{61}-butyric acid methyl ester {[60]PCBM} or [6,6]-phenyl-C_{71}-butyric acid methyl ester {[70]PCBM}, the polymer/methanofullerene photovoltaic system has attracted a great deal of attention for its significant promise (Figure 1).[3]



[60]PCBM [70]PCBM

Figure 1

More recently, power conversion efficiencies of 7–8% have been achieved for solution-processed BHJ solar cells through the use of new conjugated polymer donor materials with PCBM.[4] Despite the use of these improved conjugated polymer donors, PCBM are still considered the standard acceptors in organic photovoltaic systems.[5] The development of scalable and efficient methods for the synthesis of PCBM should be further investigated for the purpose of promoting their practical use.

However, PCBM preparative methods have been restricted to the few procedures by Hummelen and Wudl et al.[6] They originally cyclopropanated C_{60} with 1-phenyl-1-[3-(methoxycarbonyl) propyl] diazomethane that was formed in situ through the base-induced decomposition of the sodium salt of methyl 4-benzoylbutyrate *p*-tosylhydrazone. This method always produces isomeric intermediates {primarily the [5,6]-open fulleroids}, which require conversion into the thermodynamically stable [6,6]-closed methanofullerene {[60]PCBM} by tedious thermal or photochemical processing. Although an efficient high-throughput synthesis for PCBM was recently reported using a continuous-flow system, these problems still remained because of the use of tosylhydrazones starting marerials.[7]

Among the various synthetic approaches to methanofullerenes, addition–elimination reactions such as the Bingel reaction,[8] the reactions of stabilized sulfur ylides,[9] the reactions of silylated nucleophiles derived from α-halocarbonyls,[10] and others[11] efficiently afford only [6,6]-closed methanofullerenes without conversion processes. Although these reactions proceed under mild conditions, the resulting methanofullerene cyclopropane rings possess two carbonyl groups or their equivalents in the Bingel reaction, or one carbonyl group in the reaction of sulfur ylides, which limits the preparation of various functionalized methanofullerenes. To the best of our knowledge, the reaction of a sulfur ylide stabilized with a phenyl group (a so-called semistabilized ylide[12]) with a fullerene has never been reported. We herein report an alternative, one-pot, [6,6]-direct, mild, and efficient synthesis of PCBM with a semistabilized sulfur ylide generated in situ from the corresponding novel sulfonium salts (Scheme 1).

As the precursors of the PCBM, the sulfonium salts, dimethyl (5-methoxy-5-oxo-1-phenylpentyl) sulfonium triflate (**2a**) or dimethyl (5-methoxy-5-oxo-1-phenylpentyl) sulfonium tetrafluoroborate (**2b**), were successfully pre-

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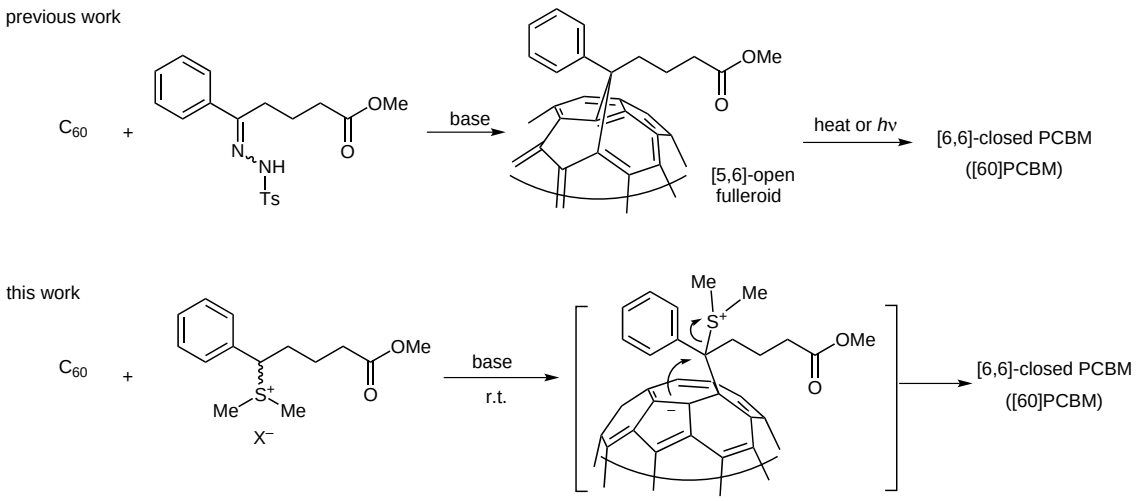
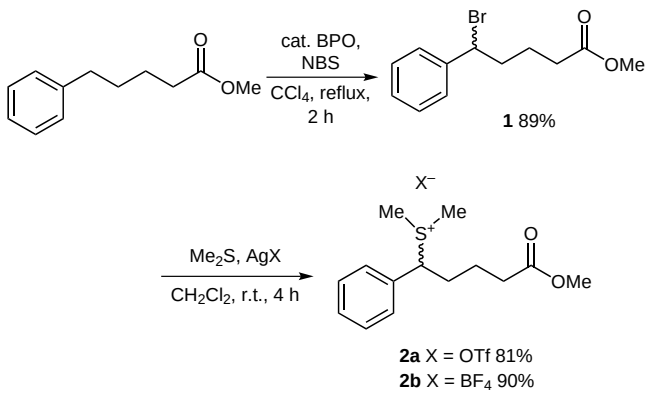


Scheme 1 Synthetic protocols of PCBM

pared in two steps. Facile bromination of methyl 5-phenylpentanoate at the benzyl position generated **1**, followed by nucleophilic substitution of the bromide with dimethyl sulfide (Scheme 2).[13]

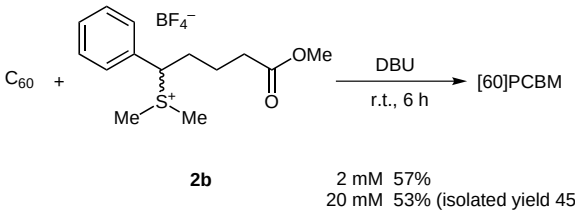


Scheme 2 Preparation of sulfonium salts as precursor of PCBM

Initially, we examined the reactions between the sulfonium salts and fullerene C_{60}. *o*-Dichlorobenzene (ODCB) and 1,2,4-trimethylbenzene (TMB) were chosen as the solvents because of the high solubility of C_{60} therein.[14] A brief, small-scale optimization of the reaction conditions was performed using 1.5 equivalents of sulfonium salt **2a** with C_{60} in the presence of various bases (1.5 equiv) in ODCB at room temperature for six hours. The reactions were monitored by HPLC,[15] which showed the presence of a monoaddition product in conjunction with unreacted C_{60} and small amounts of bisadducts. The results are summarized in Table 1.

In the reactions with inorganic bases such as K_2CO_3 and Cs_2CO_3, the starting material was completely recovered because of the low solubility of the bases in ODCB (Table 1, entries 1 and 2). Various organic bases were then examined. In the cases of pyridine, Et_3N, and 1,4-diazabicyclo[2.2.2]octane (DABCO), no reaction occurred (Table 1, entries 3–5). The use of DBN gave polar compounds with 21% of [60]PCBM (Table 1, entry 6). Among the organic bases, it was found that the relatively strong basicity[16] of DBU promoted the reaction to afford the corresponding PCBM in 55% yield with 28% of recovered C_{60} (Table 1, entry 8). Furthermore, by increasing the quantities of sulfonium salt **2a** and base relative to C_{60},[17] the yield of PCBM was improved to 58% (Table 1, entry 11), together with 7% of the bisadducts and 24% of recovered C_{60}. Equally good results were achieved through the use of sulfonium salt **2b** (Table 1, entry 12). The pure monoadduct could be obtained after a silica gel column chromatography. The ^{1}H NMR and ^{13}C NMR spectra of the product suggested the formation of the [6,6]-closed methanofullerene {[60]PCBM}, which exhibited only one singlet for methyl ester proton at $\delta = 3.68$ ppm, and a bridgehead cyclopropane carbon at $\delta = 79.87$ ppm.[7b] It was important that the desired [6,6] isomer {[60]PCBM} was directly obtained without the corresponding [5,6]-open fulleroid.

To increase throughput in the synthesis of [60]PCBM, a higher concentration would be desirable. The method was also successfully applied at 20 mM C_{60} concentration with similar efficiency (53% yield by HPLC analysis, 45% isolated yield, together with 5% of the bisadducts and 22% of recovered C_{60}, after column chromatography, Scheme 3).[18]



Scheme 3 Preparation of [60]PCBM using sulfonium salt

Next, our attention turned to the preparation of the higher fullerene analogue, [70]PCBM, which exhibits a stronger absorption in the visible-light region than [60]PCBM. Therefore, this material has often been used in photovol-

Table 1 Optimization of the Synthesis of [60]PCBM via Sulfur Ylide[a]

Entry	Sulfonium salt (equiv)	Base (equiv)	Solvent[c]	Yield of [60]PCBM (%)[b]
1	**2a** (1.5)	K_2CO_3 (3.0)	ODCB	0
2	**2a** (1.5)	Cs_2CO_3 (3.0)	ODCB	0
3	**2a** (1.5)	pyridine (3.0)	ODCB	0
4	**2a** (1.5)	Et_3N (3.0)	ODCB	0
5	**2a** (1.5)	DABCO (3.0)	ODCB	0
6	**2a** (1.5)	DBN (3.0)	ODCB	21
7	**2a** (1.5)	DBU (3.0)	TMB	25
8	**2a** (1.5)	DBU (3.0)	ODCB	55
9[d]	**2a** (1.5)	DBU (3.0)	ODCB	16
10	**2a** (1.0)	DBU (2.0)	ODCB	45
11	**2a** (2.0)	DBU (4.0)	ODCB	58
12	**2b** (1.5)	DBU (3.0)	ODCB	57

[a] All reactions were carried out by using C_{60} (2.0 μmol), bases, and sulfonium salts in organic solvents (1 mL) for 6 h at r.t.
[b] Yields were determined by HPLC analysis.[15]
[c] ODCB: *o*-dichlorobenzene, TMB: 1,2,4-trimethylbenzene.
[d] Reaction was carried out at 0 °C.

taic cells instead of [60]PCBM, and higher current densities have been achieved.[19] In general, [70]PCBM has been synthesized via the conventional method used for [60]PCBM, starting from methyl 4-benzoylbutyrate tosylhydrazone.[3b]

The synthesis of [70]PCBM was performed analogously to the procedure described above for [60]PCBM; the corresponding [6,6]-closed [70]PCBM was successfully obtained in good yield (45% isolated yield, Scheme 4).[20] The products consisted of a mixture of three regioisomers, with a similar component ratio (ca. 85:15) to that observed with the conventional method. Additionally, the use of excess sulfonium salt afforded bisadducts (bis[70]PCBM), in 64% yield, as well as 24% of the monoadducts (Figure 2).[21]

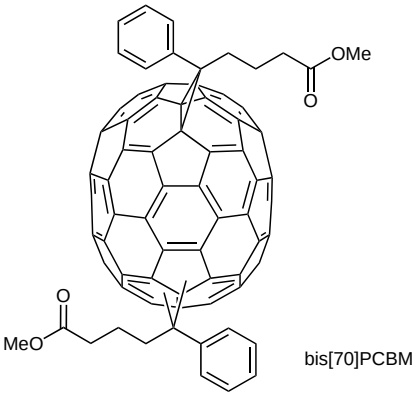
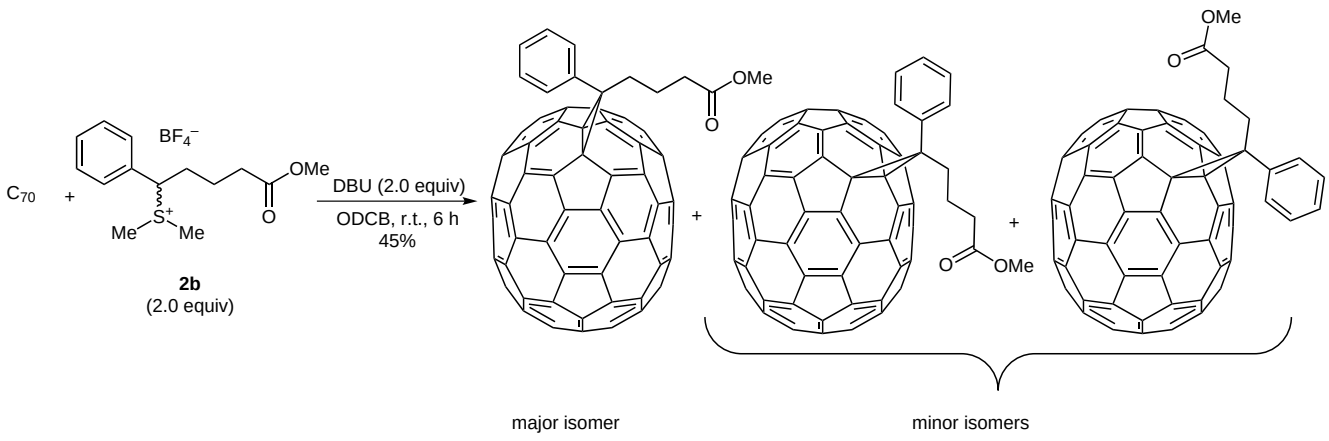


Figure 2



Scheme 4 Preparation of [70]PCBM using sulfonium salt

In conclusion, we demonstrated an alternative method for the preparation of PCBM which provided [6,6]-closed PCBM under simple, mild conditions. The novel sulfonium salts **2a** and **2b** were obtained as useful synthetic precursors and the direct syntheses of [60] and [70]PCBM, via the in situ generated semistabilized sulfur ylide were successfully demonstrateed.

Acknowledgment

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(13) **Methyl 5-Bromo-5-phenylpentanoate (1)**
Commercially available methyl 5-phenylpentanoate (3.65 g, 19.0 mmol) was dissolved in CCl_4 (50 mL) and treated with NBS (3.68 g, 20.7 mmol) and a trace amount of dibenzoyl peroxide. The mixture was refluxed for 2 h and then cooled and filtered, followed by solvent removal in vacuo. After the residue was purified by silica gel chromatography, product **1** was obtained in 89% yield (4.61 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 5 H), 4.95 (t, *J* = 6.9 Hz, 1 H), 3.65 (s, 3 H), 2.37–2.14 (m, 4 H), 1.92–1.56 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.42, 141.80, 128.71, 128.40, 127.20, 54.72, 51.57, 39.20, 33.12, 23.60. IR (neat): 2951, 1737, 1455, 1436, 1204, 1174, 759, 697 cm^{-1}. ESI-MS: *m/z* calcd for $C_{12}H_{15}BrO_2Na$: 293.0; found: 292.8 [M + Na]$^+$.
Dimethyl (5-Methoxy-5-oxo-1-phenylpentyl) Sulfonium Triflate (2a)
To a solution of methyl 5-bromo-5-phenylpentanoate (**1**, 271 mg, 1.0 mmol) and Me_2S (186 mg, 3.0 mmol) in CH_2Cl_2 (1 mL) was added AgOTf (257 mg, 1.0 mmol) at 0 °C. The reaction mixture was stirred and gradually warmed to r.t. for 4 h. After filtration through Celite to remove the precipitate, the filtrate was concentrated under reduced pressure. The residue was then washed twice by decantation with hexane (10 mL). The solvent was removed in vacuo and the sulfonium salt **2a** was obtained in 81% yield (324 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 5 H), 4.94 (t, *J* = 7.8 Hz, 1 H), 3.63 (s, 3 H), 3.03 (s, 3 H), 2.64 (s, 3 H), 2.36 (dt, *J* = 6.9, 2.1 Hz, 2 H), 2.25 (sext, *J* = 7.5 Hz, 2 H), 1.73–1.50 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.05, 130.50, 130.10, 129.74, 129.11, 120.44 (q, J_{C-F} = 317 Hz) 59.82, 51.43, 32.45, 29.52, 23.64, 22.30, 21.53. IR (neat): 3021, 2935, 1731, 1436, 1258, 757, 712, 638 cm^{-1}. ESI-MS: *m/z* calcd for $C_{14}H_{21}O_2S$: 253.1; found: 253.0 [M – CF_3SO_3]$^+$.
Dimethyl (5-Methoxy-5-oxo-1-phenylpentyl) Sulfonium Tetrafluoroborate (2b)
The procedure was similar to that described above, except for the use of $AgBF_4$ (195 mg, 1.0 mmol). The sulfonium salt **2b** was obtained in 90% yield (306 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.44 (m, 5 H), 4.83 (t, *J* = 8.4 Hz, 1 H), 3.63 (s, 3 H), 3.01 (s, 3 H), 2.62 (s, 3 H), 2.38 (dt, *J* = 7.2, 3.2 Hz, 2 H), 2.26 (sext, *J* = 7.6 Hz, 2 H), 1.72–1.52 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.19, 130.74, 130.20, 129.99, 129.26, 60.38, 51.63, 32.56, 29.78, 23.70, 22.39, 21.69. IR (neat): 3030, 2951, 1734, 1456, 1437, 1203, 1177, 1061, 701 cm^{-1}. ESI-MS: *m/z* calcd for $C_{14}H_{21}O_2S$: 253.1; found: 252.9 [M – BF_4]$^+$.

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(15) HPLC conditions were as follows: column, CHEMCOSORB5-ODS-UH (4.6 × 150 mm); column temperature, 40 °C; flow rate, 1.2 mL/min; detection, UV at λ = 340 nm; eluent toluene–MeOH (60:40, v/v). The

absolute calibration method was used for the quantification of analytes.

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(18) **Preparation of [6,6]-Phenyl-C_{61}-butyric Acid Methyl Ester {[60]PCBM}[7b]**
To a stirred mixture of sulfonium salt **2b** (85 mg, 0.25 mmol) and fullerene C_{60} (100 mg, 0.14 mmol) in ODCB (7 mL) was added DBU (46 mg, 0.30 mmol) in one portion at r.t. After stirring for 6 h, AcOH (ca. 3 equiv) was added. The reaction mixture was concentrated to ca. 3 mL under reduced pressure. The residue was purified by silica gel column chromatography {eluent, stepwise gradient of CH_2Cl_2 (0–80%) in toluene}. The obtained product was dissolved in a small amount of toluene and poured into MeOH. The resulting suspension was centrifuged, and the supernatant was decanted. The product was dried in vacuo at 60 °C. [60]PCBM was obtained in 45% isolated yield (57 mg). Unreacted C_{60} (22 mg, 22%) and bisadducts (8 mg, 5%) were isolated in the same manner. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.7 Hz, 2 H), 7.60–7.44 (m, 3 H), 3.68 (s, 3 H), 2.94–2.88 (m, 2 H), 2.52 (t, *J* = 7.5 Hz, 2 H), 2.23–2.13 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.40, 148.79–136.71, 132.06, 128.43, 128.24, 79.87, 51.85, 51.64, 33.87, 33.67, 22.37. IR (KBr): 2921, 2849, 1735, 699, 573, 550, 526, 482, 453 cm^{-1}. MS (MALDI): *m/z* calcd for $C_{72}H_{14}O_2$: 910.1; found: 910.1 $[M]^+$.

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(20) **[6,6]-Phenyl-C_{71}-butyric Acid Methyl Ester {[70]PCBM}[7b]**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.40 (m, 5 H), 3.74 (minor isomer, s, 0.26 H), 3.67 (major isomer, s, 2.55 H), 3.51 (minor isomer, s, 0.19 H), 2.53–2.42 (m, 4 H), 2.25–1.99 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.38, 149.43–128.20, 69.82, 51.68, 33.80, 21.70. IR (KBr): 2941, 2923, 1737, 1429, 795, 726, 699, 674, 643, 579, 534, 459 cm^{-1}. MS (MALDI): *m/z* calcd for $C_{72}H_{14}O_2$: 1030.1; 1030.2 $[M]^+$.

(21) **Bis[70]PCBM**
To a stirred mixture of sulfonium salt **2b** (51 mg, 0.15 mmol) and fullerene C_{70} (25 mg, 0.030 mmol) in ODCB (12 mL) was added DBU (23 mg, 0.15 mmol) in one portion at r.t. After stirring for 7 h, AcOH (ca. 3 equiv) was added and treatments in the same manner of ref. 18, bis[70]PCBM was obtained in 64% isolated yield (23 mg). Unreacted C_{70} (0.6 mg, 2%) and monoadducts (7.5 mg, 24%) were isolated.^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.37 (m, 5 H), 3.67–3.65 (m, 3 H), 2.50–2.10 (m, 6 H). MS (MALDI): *m/z* calcd for $C_{72}H_{14}O_2$: 1220.2; found: 1220.2 $[M]^+$. Spectroscopic data were in good agreement with the literature: Lenes, M.; Shelton, S. W.; Sieval, A. B.; Kronholm, D. F.; Hummelen, J. C.; Blom, P. W. M. *Adv. Funct. Mater.* **2009**, *19*, 3002.

