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### Letter

# Facile Synthesis of Methanofullerenes in an Aqueous Two-Phase System under Photoirradiation Conditions

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**Abstract** Methanofullerenes, such as [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester [[6,6]PC<sub>61</sub>BM (**1a**)], were synthesized in good yields from the corresponding tosylhydrazones in an aqueous two-phase (o-dichlorobenzene–H<sub>2</sub>O) system under photoirradiation conditions. This simple and convenient procedure was adopted for the synthesis of thienyl analogues of PC<sub>61</sub>BM and its C<sub>70</sub> analogue, PC<sub>71</sub>BM.

**Key words** photovoltaics, fullerenes, hydrazones, methanofullerenes, PCBM

Organic thin-film photovoltaics are a promising alternative to silicon-based solar cells owing to their considerable advantages, such as light weight, flexibility, and low fabrication cost. The power-conversion efficiency of organic photovoltaics is still lower than that of silicon-based solar cells; however, numerous studies have achieved improvements in the performance of organic photovoltaics during the past decade.<sup>1</sup> Following the report of a power-conversion efficiency of 2.5% by Sariciftci and coworkers for a polymer solar cell based on a bulk heterojunction of [6,6]phenyl- $C_{61}$ -butyric acid methyl ester {[6,6]PC<sub>61</sub>BM (1a), Figure 1<sup>2</sup> and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV),<sup>3</sup> improvement of the power-conversion efficiency sped up and has now reached more than 9%.<sup>4</sup> These achievements were based on the development of polymer donor materials, such as poly(3-hexylthiophene) (P3HT),<sup>5</sup> some other low-band-gap polymers,6 and also the development of fullerene-based acceptor molecules.<sup>7-9</sup> In spite of these developments, [6,6]PC<sub>61</sub>BM (1a) is still widely recognized as a standard acceptor molecule,<sup>5</sup> and numerous studies have continued to develop novel acceptor materials based on the modification of PCBM, including our previous work.8b-d



Syntheses of PC<sub>61</sub>BM and its analogues are carried out following the procedure reported by Hummelen et al.<sup>2</sup> In their procedure<sup>3</sup>  $C_{60}$  reacts with tosylhydrazone **3a** in the presence of NaOMe in pyridine and o-dichlorobenzene (ODCB) to give derivative of [6,6]PC<sub>61</sub>BM (**1a**, Scheme 1). In general, this procedure is performed under severe anhydrous conditions and [6,6]PC<sub>61</sub>BM (1a) is obtained in relatively low yield (ca. 40%) together with unreacted  $C_{60}$  and higher adducts, such as bisadducts. This reaction is very sensitive to moisture; in our group, we have found the reproducibility of this method problematic and also found that the selectivity and yield of PC<sub>61</sub>BM depends on the degree of anhydrous conditions.<sup>10</sup> To improve the selectivity for PC<sub>61</sub>BM, excess amounts of C<sub>60</sub> are sometimes used to prevent the formation of higher adducts. Additionally, during this procedure, open-cage [5,6]PC<sub>61</sub>BM (2a) is obtained first and then converted into the thermally stable closed-cage [6,6]PC<sub>61</sub>BM (1a) under thermal or photoirradiation conditions.<sup>2,11</sup> Recently, the synthesis of [6,6]PC<sub>61</sub>BM derivatives via photoirradiation conditions has gained popularity,<sup>7d,e,h,11</sup> but the yields and selectivity of the PCBM are still low. Separation of PC<sub>61</sub>BM from the reaction mixture



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and purification are laborious and costly; therefore, a cost-effective and convenient preparation of  $PC_{61}BM$  is desired for practical use.

During our research on the development of fullerene derivatives for acceptor molecules in photovoltaics,<sup>8</sup> we have also focused on efficient, convenient, and cost-effective synthetic methods for PCBM. Herein, we report a facile synthesis of  $[6,6]PC_{61}BM$  (**1a**) with a good yield using an aqueous two-phase system in the presence of quaternary ammonium hydroxide under photoirradiation conditions.

First, we reinvestigated the procedure to generate the diazo compound from the corresponding tosylhydrazone 3a. Hummelen et al. used the aprotic Bamford-Stevens conditions<sup>12</sup> in pyridine using NaOMe as a base. This aprotic conditions require severe anhydrous conditions; however, in general the diazo compound can also be prepared in protic solvents, such as alcohols, though these conditions are rarely used for the synthesis of fullerene derivatives owing to the poor solubility of the fullerenes.<sup>13</sup> In our preliminary experiment, a methanol solution of *n*-Bu₄NOH (TBAH) was used as a base and caused precipitation of C<sub>60</sub> from the ODCB solution, which would affect the proportion of the products. On the other hand, Jończyk et al. reported the reaction of cycloalkenes with in situ generated diazo compounds from tosylhydrazones in an aqueous basic twophase system.<sup>14</sup> This result encouraged us to perform the synthesis of PCBM under similar conditions. In the ODCB-H<sub>2</sub>O two-phase system, the reactants, tosylhydrazone and  $C_{60}$  are soluble in ODCB, and  $H_2O$ , which is immiscible with ODCB would not cause precipitation of fullerene. Therefore, we expected an aqueous basic two-phase system would be effective to generate diazo compounds that can subsequently react with C<sub>60</sub> to obtain PC<sub>61</sub>BM derivatives. Jończyk et al. used an excess amount of sodium hydroxide (50% aqueous solution) to generate diazocompounds;<sup>14</sup> however, theoretically only one equivalent of base is needed for the formation of the tosylhydrazone anion and the diazotization. In addition, an excess amount of hydroxide ions may result in hydroxylation of fullerenes,<sup>15</sup> thus the use of one equivalent of base should be adequate for this reaction.





R = (CH<sub>2</sub>)<sub>3</sub>COOMe

5a

2a

				LC yield (%)		
Entry	<b>3a</b> (equiv)	TBAH (equiv)	Temp (°C)	4	2a	5a
1	0.8	0.8	110	36	49	14
2	1.0	1.0	110	24	49	19
3	1.2	1.2	110	16	48	26
4	1.5	1.5	110	8	42	36
5	1.0	1.0	70	41	47	11
6	1.0	1.0	90	26	52	20
7	1.0	1.0	110	28ª	52ª	18ª

<sup>a</sup> Isolated yields.

The optimization of the reaction is summarized in Table 1. An ODCB solution of tosylhydrazone **3a** was vigorously stirred with aqueous TBAH at room temperature for 0.5 hours, and then an ODCB solution of  $C_{60}$  (**4**) was added and

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heated to reflux (Table 1, entries 1-4). The reactions were completed within two hours, and the yields of [5,6]PC<sub>61</sub>BM (2a) reached 48-49% when 0.8-1.2 equivalents of tosylhydrazone **3a** were used (Table 1, entries 1–3). The use of an excess amount of tosylhydrazone 3a decreased the yield of monoadduct 2a and increased the ratio of bisadduct 5a and higher adducts (Table 1, entry 4). During the reaction, tosylhydrazone 3a was consumed almost quantitatively, and the diazo compound was generated and reacted to  $C_{60}$  (4) with high efficiency.<sup>16</sup> A lower reaction temperature did not result in completion of the reaction within two hours, and the vields were slightly decreased. However, at 90 °C the reaction was completed, and the yields were quite similar to those obtained at 110 °C (Table 1, entries 5 and 6). A higher selectivity for monoadducts over bisadducts was observed at 70 °C but the conditions of entry 7 (Table 1) were selected as the optimized conditions owing to the high isolated vield and short reaction time.

Using these optimized reaction conditions, the obtained PC<sub>61</sub>BM was open-cage [5,6]fulleroid with small amounts of closed-cage [6,6]methanofullerene. It is well-known that [5,6]fulleroid has a lower solubility than [6,6]methanofullerene and is thermodynamically unstable; therefore, [6,6]methanofullerene is used in photovoltaic devices. The conversion of [5,6]fulleroid to [6,6]methanofullerene could be performed under thermal heating or photoirradiation conditions.

The direct preparation of [6,6]methanofullerene from tosylhydrazone and  $C_{60}$  was then examined. After treatment of tosylhydrazone with TBAH at room temperature for 0.5 hours,  $C_{60}$  was added and the mixture was heated to reflux under irradiation of a 375 W incandescent lamp for two hours (Scheme 2).<sup>17</sup> The obtained PC<sub>61</sub>BM was predominantly [6,6]methanofullerene **1a** and [5,6]fulleroid **2a** was not detected by <sup>1</sup>H NMR spectroscopy or HPLC.

To evaluate the versatility of this reaction, thienyl analogues of  $PC_{61}BM$ ,<sup>7c,8b-d</sup> which are prominent acceptor candidates owing to their expected higher compatibility with P3HT, were examined, and the results are summarized in Table 2. The thienyl analogues of  $PC_{61}BM$  **1b**-**d** were syn-

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C<sub>60</sub> (4)

∆, 2 h



n-Bu₄NOH

ODCB-H<sub>2</sub>O

3b 20 3ł 22 1b 43 (32)d **6b** 20 3 30 30 1c 50 (33)d 6c 18 3d 30 1d 44 (42)d 6d 19 EtOO

Table 2 Synthesis of Thienyl Analogues of [6,6]PC<sub>61</sub>BM

COOMe

II NNHTs

3h-d

<sup>a</sup> Isolated yield.

Entry Ar

<sup>b</sup> [5.6]-Isomers were obtained.

<sup>c</sup> Irradiated with an incandescent lamp (375 W).

<sup>d</sup> Yields reported by Matsumoto et al. using the Hummelen procedure.<sup>8d</sup>



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thesized from the corresponding tosylhydrazones **3b–d**. Without photoirradiation, the benzothiophene derivative was obtained as the [5,6]fulleroid **2b** (Table 2, entry 1), similar to the synthesis of  $PC_{61}BM$ . However, under photoirradiation conditions, [6,6]methanofullerene **1b** was directly synthesized (Table 2, entry 2). On the other hand, thieno-thiophene derivatives **1c** and **1d** were directly converted into the [6,6]methanofullerene without photoirradiation, as reported by Matsumoto et al. (Table 2, entries 3 and 4).<sup>8d</sup>

Hummelen et al. also synthesized PC<sub>71</sub>BM (**8**),<sup>7h</sup> the higher fullerene analogue of PC<sub>61</sub>BM. C<sub>70</sub> (**7**) has a higher absorption coefficient in the visible region of the spectrum; therefore, C<sub>70</sub> derivatives are regarded as some of the most promising acceptor molecules for organic photovoltaics. PC<sub>71</sub>BM (**8**) was synthesized using the optimized reaction conditions and irradiation with a 375 W incandescent lamp for two hours and was obtained in 49% isolated yield with 17% of bisadducts **9** and 20% of unreacted C<sub>70</sub> (**7**) (Scheme 3). The obtained monoadducts **8** consisted of the three inseparable isomers ( $\alpha$ -type and two kinds of  $\beta$ -type) in a ratio similar to that previously reported.<sup>7h</sup>

In conclusion, we have developed a facile synthetic method to obtain methanofullerenes, such as  $PC_{61}BM$ . This aqueous two-phase system with quaternary ammonium hydroxide under photoirradiation conditions gave reproducible results and avoids the need for laborious anhydrous conditions and excess amount of reagents.  $PC_{61}BM$ ,  $PC_{71}BM$ , and some thienyl analogues could be obtained in good yields. Further exploration to improve the yield and selectivity for the monoadducts are now in progress, including the utilization of flow synthesis.<sup>18</sup>

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- (16) When an excess amount of tosylhydrazone was used, higher adducts, such as trisadducts, were detected.
- (17) General Procedure for the Synthesis of Methanofullerenes under Photoirradiation Conditions Under Ar atmosphere, to a solution of tosylhydrazone (18.7 mg, 0.050 mmol) in ODCB (2.0 mL) was added a solution of TBAH

(1.0 M in H<sub>2</sub>O, 0.05 mL, 0.050 mmol) in H<sub>2</sub>O (1.95 mL), and the mixture was stirred at r.t. for 0.5 h. A solution of  $C_{60}$  (36.0 mg, 0.050 mmol) in ODCB was added to the mixture, and the mixture was stirred (800-1000 rpm by magnetic stirrer), heated in an oil bath, and irradiated with a 375 W incandescent lamp for 2 h. During the irradiation, the oil bath temperature was kept at 105–115 °C by adjusting the distance between the light source and the flask was approximately 15 cm. After the reaction, the layers were separated and the aqueous phase was extracted with toluene (2 × 5 mL). The combined organic phase was dried over MgSO<sub>4</sub>, filtered, and concentrated to 1 mL under reduced pressure. The residue was purified by silica gel column chromatography [silica gel; 20 g, eluent; toluene for C<sub>60</sub> and monoadduct, toluene-CH<sub>2</sub>Cl<sub>2</sub> (1:2) for bisadducts], and the obtained [6,6]PC<sub>61</sub>BM (1a) was dissolved in a small amount of toluene and transferred to a 50 mL centrifuge tube. MeOH (ca. 30 mL) was added, and the mixture was immersed in an ultrasound bath for 1 min, the suspension was centrifuged (4000 rpm, 30 min), the supernatant was decanted, and the residue was treated with MeOH in the same manner. The product was dried in vacuo at 60 °C. [6,6]PC<sub>61</sub>BM (1a, 23.5 mg, 0.026 mmol, 52%) was obtained as brown powder. Unreacted  $C_{60}$  (7.8 mg, 0.011 mmol, 22%) and bisadducts (10.9 mg, 0.010 mmol, 20%) were isolated in the same manner.

#### Analytical Data for 1a

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 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). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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<sup>-1</sup>. MS (MALDI): *m/z* calcd for  $C_{72}H_{14}O_2$ : 910.1; found: 910.1 [M]<sup>-</sup>.

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