



Cycloaddition of hexacene and fullerene[60]



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ABSTRACT

The [4+2] cycloaddition of hexacene and C₆₀ yielded 1:1 and 1:2 adducts. The highest yield of 1:1 adduct was 90% by heating hexacene and C₆₀ in toluene. The formation of **2** was achieved by reacting **1** with an excess amount of C₆₀ in the presence of silica gel 60 with a yield up to 69%. The function of silica gel was rationalized by the effect of concentration enhancement inside the pore of silica gel. The reaction was examined systematically by changing the parameters of solvent, temperature, reaction time, and the pore size of silica gel. Both purified compounds **1** and **2** can be used for the fabrication of bulk heterojunction solar cells.

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Introduction

The chemistry of acenes is of fundamental importance for the study of aromaticity, and in recent years it attracts considerable interest in the development of organic semiconductors.¹ Pentacene and tetracene are the most well-known members in the acene family, and their properties have been thoroughly investigated before. The chemistry of higher acenes including hexacene, however, was not clearly known, because they have not been easily accessible until recently. In a previous report, we developed an efficient way to prepare pure hexacene as stable crystals.² With this new method, the semiconducting property of hexacene was examined for the first time.

One of the unique reactions of acenes is their cycloaddition with C₆₀. The reaction of C₆₀ as a dienophile with a variety of dienes has been studied, such as cyclopentadiene, anthracene, tetracene, and pentacene.^{3–5} Most C₆₀ adducts showed a broad absorption range, therefore were useful on opto-electronic applications, such as n-type semiconductor for field effect transistors,^{5j} and organic photo voltaics.^{5k,l} The reaction of dienes with C₆₀ can be promoted either by heat or by light, and proceeds in a highly regioselective manner. The C₆₀ derivative, [6,6]phenyl-C61-butyric acid (PC₆₁BM), is a widely used material on organic photovoltaic cells.⁶ For the reac-

tions with anthracene and tetracene, both the 1:1 adducts of C₆₀ have been reported. The reaction of pentacene with C₆₀ has been explored by Komatsu and co-workers by using a high-speed vibration milling technique, while three kinds of adducts were obtained in 1:1, 1:2, and 2:1 ratios, respectively.⁷ In this Letter we describe our results on the reaction of hexacene with C₆₀. Two products are isolated in good yields. Their potential usage on bulk heterojunction solar cells was also examined (see Table 1).

Results and discussion

The reactions of hexacene with C₆₀ in solutions are shown in Scheme 1. A mixture of hexacene and C₆₀ (1:5 mol ratio) was heated in toluene to reflux for 3 h. The resulted crude product was passed through a flash column chromatograph (silica gel 60) eluted with a mixed solvent of CS₂/hexane (1:1 vol %). Two products were obtained in ca. 2:1 mol ratio, and were identified to be the 1:1 adduct **1** and the 1:2 adduct **2**. In ¹H NMR spectra, the two products can be clearly distinguished by the methine signals, that is, H (c) of **1** at δ 6.00 ppm and H (c,e) of **2** at δ 5.93 and 6.04 ppm.

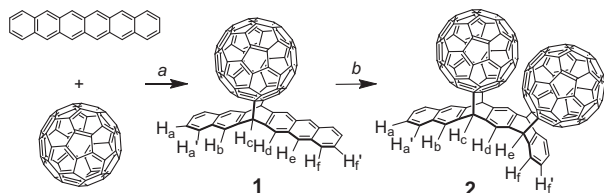
Full spectral assignment was done by examining the ¹H–¹H 2D COSY and NOESY correlation signals (Fig. 1). In the spectrum of **1**, the methine signal (H_c) correlated with two aromatic protons at δ 8.34 (anthracene H_d) and 8.22 (naphthalene H_b) ppm. The H_d signal correlated with the central anthracene signal H_e at δ 8.51. In addition, there are four AA'BB' patterns at δ 7.99 (H_f), 7.96 (H_{a'}), 7.53

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Table 1
BHJ solar cell device parameters^a

Adduct	Weight ratio (P3HT:adduct)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PC ₆₁ BM	1:1 ^b	0.65	9.95	52	3.27
1	1.5:1 ^c	0.72	0.71	31	0.16
1	1.5:1 (DIO) ^d	0.66	1.24	47	0.38
2	2:1	0.61	0.66	45	0.18
2	2:1 (DIO) ^d	0.53	0.42	39	0.09

^a Device structure: glass/ITO/PEDOT:PSS/P3HT:adduct/BCP (7 nm)/Al (100 nm).^b P3HT (17 mg) and PC₆₁BM (17 mg) in dichlorobenzene (1.0 g).^c P3HT (21 mg) and adduct (14 mg) in dichlorobenzene (1.0 g).^d Diiodooctane (DIO) (2 wt %)

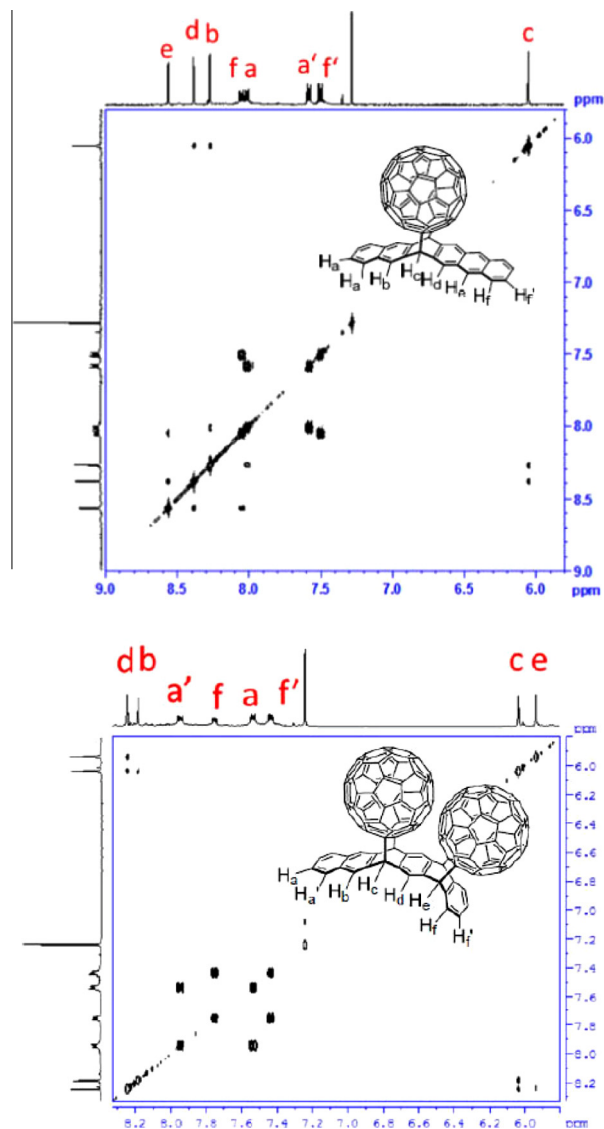
Scheme 1. Synthesis of **1** and **2**. Reagents and conditions: (a) hexacene and C₆₀ (1:5 mol ratio), toluene reflux under N₂, 3 h, 90% isolated yield. (b) Compound **1** and C₆₀ (1:4 mol ratio), stirred with silica gel 60 in CS₂/hexane (1:3) at room temperature for 5 d under N₂, 50–69% yield depending on the purification process.

(H_a), and 7.45 ppm (H_f), which are assigned to the hydrogen atoms on the outer rim. It is clear that the fullerene was attached to one of the internal rings of hexacene. In the spectrum of compound **2**, the hydrogen on the middle benzene ring (H_d at δ 8.25) correlated with both of the methine signals (H_c and H_e). The methine H_e is located next to the outer benzene ring (H_f at δ 7.75), and the other methane H_c is adjacent to the naphthalene moiety (H_b at δ 8.19). There are also four AA'BB' patterns at δ 7.95 (H_{a'}), 7.75 (H_f), 7.54 (H_a), and 7.43 (H_f) ppm. The second fullerene unit in **2** was attached to the center of an anthracene moiety of **1**. In the ¹³C NMR, the sp² carbons of C₆₀ overlap with each other in the region of δ 155–130 ppm, while those of hexacene at δ 130–120 ppm (seven peaks for **1**, six peaks for **2**). In the region of 80–50 ppm, there were two methine peaks for **1** and four for **2**.

The thermal stability of **1** was examined by both DSC (differential scanning calorimetry) and TGA (thermogravimetric analysis). No sign of decomposition was observed below 400 °C (Fig. S12). When a solution of **1** in toluene-*d*₈ was heated to 180 °C in a sealed tube for 3 h, the ¹H NMR spectrum did not exhibit any observable change. These experiments revealed a very good thermal stability of **1**. For compound **2**, there are two possible diastereomers, that is, the two fullerenes may be located either on the same face of hexacene (the *syn*-isomer) or on the opposite faces of hexacene (the *anti*-isomer). Although the *anti*-isomer seems able to avoid a steric hindrance between two fullerenes, the *syn*-isomer is suggested due to the presence of a significant π – π attractive interaction. The *syn*-diastereoselectivity has been established in a previous report.^{5a,b} In the present study, however, a direct evidence confirming the *syn*-diastereomer is still in demand.

During the isolation process, we have observed an unusual phenomenon. The ratio of compounds **1** and **2** collected from the silica gel chromatograph varied with operational conditions. When pressure was applied onto the column, as normally performed on a flash column chromatograph, the ratio of **1** to **2** was about 2:1. In case no pressure was applied onto the column, such as a gravity column, the amount of **2** obtained became minimal (<5%).

The reaction details were examined in a more systematic manner by changing the effects of solvent, temperature, time, and silica gel. The progress of heating in toluene-*d*₈ was monitored by ¹H

**Figure 1.** 2D ¹H–¹H COSY NMR (400 MHz) spectra of **1** and **2** in CS₂/CDCl₃ (1:1 vol %).

NMR in a period of 0–24 h, while compound **1** was the only observable product. A yield of 90% was achieved after heating for 3 h. Compound **1** was purified by washing the crude product with THF to remove the excess C₆₀. An attempt of purification by using silica gel flash chromatographic column revealed that the formation of **2** can be promoted in the presence of silica gel 60. A mixture of **1**, C₆₀ (4 equiv), and silica gel in CS₂/hexane (1:3 vol %) was stirred at room temperature for 5 d (Table S2). Compound **1** completely disappeared, while **2** was isolated in 50–69% yield depending on the purification process (Table S2). However, if the same reaction was done in pure CS₂ (without hexane), the yield of **2** was reduced to less than 5%. It is clear that the product ratio was significantly influenced by both the solvent and silica gel.

Murata et al. have used a solid state ball-milling method for synthesizing the C₆₀-pentacene and (C₆₀)₂-pentacene adducts.^{7a} A similar method was also examined in this reaction. In a stainless steel vial, a mixture of hexacene and C₆₀ (1 equiv) was shaken with a stainless steel ball at 30 Hz for 1 h in air. Compounds **1** and **2** were obtained in about 85:15 ratio. However, the ratio of **1**/**2** was increased to ca. 2:1 as the crude product mixture was passed through a silica gel flash column chromatograph under pressure.

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