Solid-State [4 + 2] Cycloaddition of Fullerene C$_{60}$ with Condensed Aromatics Using a High-Speed Vibration Milling Technique

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The solid-state reaction using a high-speed vibration milling (HSVM) technique has been applied to the [4 + 2] cycloaddition of fullerene C$_{60}$ with condensed aromatics such as anthracenes, tetracene, pentacene, and naphtho[2,3-*a*]pyrene. From the reaction with anthracene, [4 + 2] cycloadduct **1** was obtained in better yield than the reaction in solution. Despite such heterogeneous solid-state reaction conditions, an equilibrium state appears to be attained between the reactants (C$_{60}$ and anthracene) and products (mono- and bisadducts) since essentially the same product mixture was obtained starting either from the reactants or from the monoadduct after 30 min of the HSVM reaction. The reaction with pentacene gave double C$_{60}$ adduct **4** with two C$_{60}$ cages attached to a pentacene molecule, which cannot be obtained in the reaction in toluene solution, in addition to symmetrical monoadduct **3**. The HSVM treatment of C$_{60}$ with 9,10-dimethylanthracene, tetracene, or naphtho[2,3-*a*]pyrene also gave the corresponding [4 + 2] cycloadducts in fair yields. The redox properties of these adducts were investigated by the use of cyclic voltammetry.

Introduction

Organic functionalization of fullerene C$_{60}$ has been attracting a great interest in the field of structural and synthetic organic chemistry. It is now well recognized that C$_{60}$ behaves as an electron-deficient olefin with a relatively low-lying LUMO and undergoes various types of addition reactions.[1] One of the most investigated reactions of C$_{60}$ is the [4 + 2] cycloaddition. C$_{60}$ reacts as a dienophile in a [4 + 2] fashion with a large variety of dienes such as 1,3-butadiene derivatives,[2] activated furans,[3,7e] cyclopentadienes,[4,5c] anthracene,[2n,5] cycloheptatrienes,[6] orthoquinodimethanes and their equivalents,[7] and heterodienes[8] under thermal conditions in solution. In these reactions, usually a rather large amount of solvent is required because of the poor solubility of C$_{60}$ in common organic solvents. This results in low concentrations of both C$_{60}$ and the reagent, necessitating a long reaction time and/or high reaction temperatures in many cases. Under such conditions, formation of the monoadduct is often accompanied by formation of the bisadducts in a considerable amount while some amount of C$_{60}$ remains unreacted.

Recently, we have developed a novel method for solid-state reactions using a high-speed vibration milling technique (abbreviated as HSVM) and have applied it to the organic functionalization of C$_{60}$.[9,10] This is a type of a mechanochemical reaction, in which the mechanical energy is utilized as a driving force for the reaction. Here, the generation of local high-pressure spots is presumed

to activate local reaction sites.[11] Furthermore, the absence of any solvent molecule can bring the reacting

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species into the closest contact without any solvation. Such a reaction system is expected to cause novel chemical reactions to occur. Indeed, we have discovered a surprisingly smooth [2 + 2] cyclodimerization of C_{60} to give the fullerene dimer C_{120} under the HSVM conditions.[10] Here, we report the results of a detailed study on the solid-state [4 + 2] cycloaddition of C_{60} with condensed aromatics such as anthracenes, tetracene, pentacene, and naphtho[2,3-*a*]pyrene under the HSVM conditions.

Results and Discussion

Reaction with Anthracene. There have already been three reports[5] for the [4 + 2] cycloaddition of C_{60} with anthracene in solution under conventional thermal conditions: [4 + 2] cycloadduct **1** was obtained in 39% yield
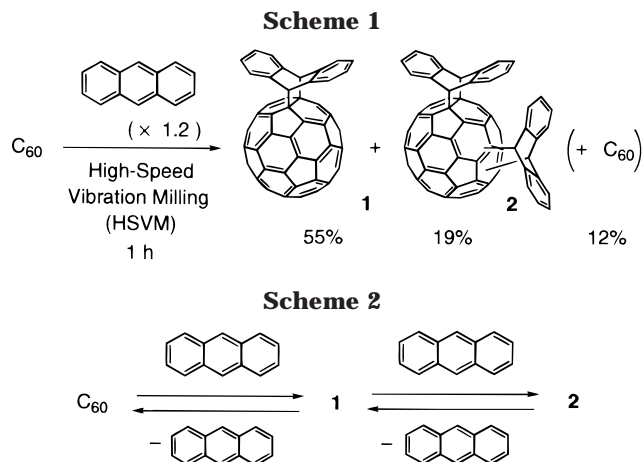
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(11) The temperature of the reacting species is supposed to be lower than 100 °C: ref 10b.

using naphthalene as a solvent at 200 °C for 48 h,[5a] in 13% yield using toluene at 115 °C for 72 h,[5b] and in 25% yield using benzene at 80 °C for 12 h.[5c] Instead of conventional heating, microwave irradiation of a toluene solution of C_{60} and anthracene has been reported to afford **1** in 35% yield.[12] Photoirradiation with a high-pressure mercury lamp of a mixture of C_{60} and 9-methylanthracene in the solid-state was also reported to give the corresponding cycloadduct in 30% yield.[13]

Solid-state organic reactions have been extensively studied by Toda using a mortar and pestle,[14] but it has not been applied to the organic functionalization of C_{60}. First, we examined the reaction of C_{60} with anthracene by means of grinding a 1:1 mixture of C_{60} and anthracene using a mortar and pestle. HPLC analysis of the reaction mixture (Buckyprep/toluene, detection at 326 nm) showed the formation of [4 + 2] cycloadduct **1** in a 2.3% peak area ratio while 98% of C_{60} was unchanged. Encouraged by this result, we applied the HSVM conditions to the reaction of C_{60} with anthracene. Thus, we placed a 1:1.2 mixture of C_{60} and anthracene in a stainless steel capsule together with a stainless steel milling ball and vigorously shook the capsule at a rate of 3500 cycle per minute for 1 h in a nitrogen glovebox. Monoadduct **1** was isolated in 55% in addition to a positional isomeric mixture of bisadducts **2** in 19% and unchanged C_{60} in 12% by flash chromatography on silica gel (Scheme 1). The yield of monoadduct **1** is the highest among the reported values described above even though the reaction time was the shortest. These results clearly demonstrate the advantage of the present HSVM method in the [4 + 2] cycloaddition reaction.

Equilibrium State in the Solid-State Reaction. Under the thermal conditions in solution, the [4 + 2] reaction of C_{60} and anthracene never reaches completion because the [4 + 2] cycloaddition is in equilibrium with the retro-cycloaddition as shown in Scheme 2. Therefore, unchanged C_{60} and bisadducts **2** are always present together with monoadduct **1**.

To examine whether such an equilibrium exists in the present solid-state reaction using the HSVM technique, the time dependence of the HPLC peak area[15] of the C_{60}

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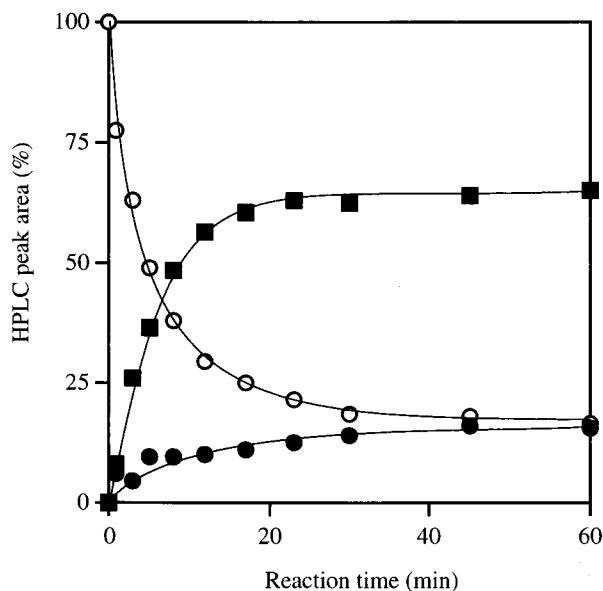
Figure 1. Time dependence of HPLC peak areas for the reaction of C_{60} with 1.2 equiv of anthracene under the HSVM conditions. O: C_{60}. ■: Monoadduct **1**. ●: Bisadduct **2**.
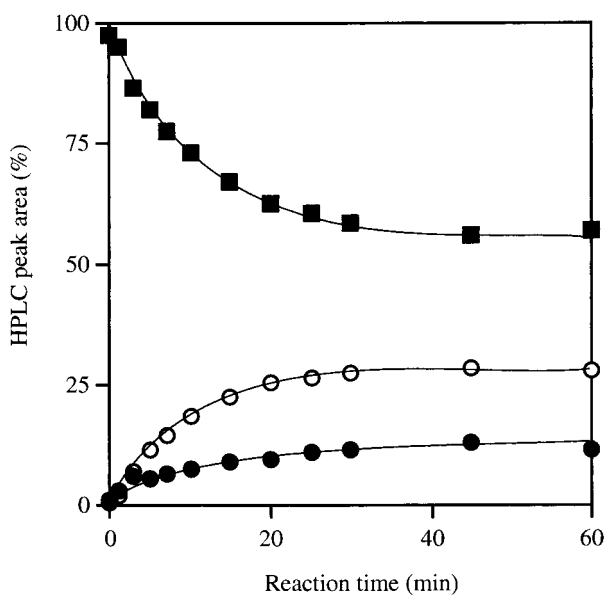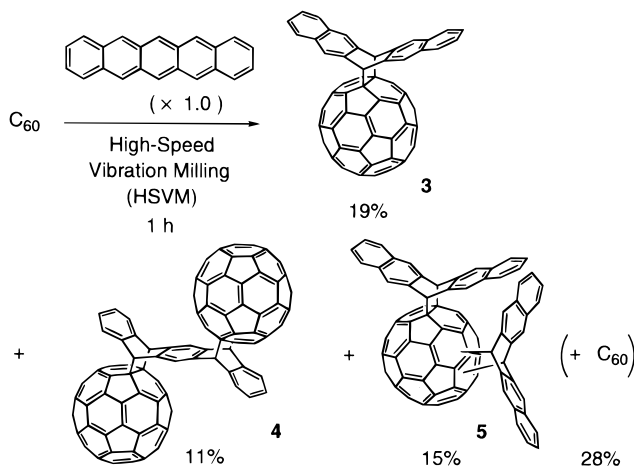

Figure 2. Time dependence of HPLC peak areas for the retro-cycloadditiion of C_{60}-anthracene monoadduct **1** under the HSVM conditions. O: C_{60}. ■: Monoadduct **1**. ●: Bisadduct **2**.

derivatives and of C_{60} was examined for the reaction of C_{60} and 1.2 equiv of anthracene under the HSVM conditions. As shown in Figure 1, the reaction appears to reach equilibrium as shown by the HPLC peak area of monoadduct **1** leveling to nearly 60% intensity after a reaction time of about 30 min.

Next, the possibility of the reverse reaction, i.e., dissociation of monoadduct **1**, was examined by placing **1** under the HSVM conditions. As clearly shown by the time dependence in Figure 2, the amount of **1** gradually decreased with concomitant formation of C_{60} and bisad-

Scheme 3

ducts **2**. Thus, a similar equilibrium state has been attained after a reaction time of about 30 min. Because the molar ratio of the fractions of C_{60} and anthracene in this reverse reaction is exactly 1:1, the HPLC peak area of monoadduct **1** in the equilibrium state is slightly lower, and that of C_{60} is slightly higher, than those in Figure 1 in which the ratio of C_{60} and anthracene was 1:1.2. However, it is to be noted that the final ratio of the HPLC-observable components appears to be essentially the same between the reaction of C_{60} with anthracene and its reverse reaction mentioned above. This suggests that a chemical equilibrium is established even under such heterogeneous solid-state reaction conditions. Since a higher yield of monoadduct **1** was obtained in the solid-state reaction than in solution, the equilibrium in the solid state is considered to lie more in favor of monoadduct **1** than the reaction in solution. The presence of a similar association−dissociation equilibrium has also been observed under the HSVM conditions between C_{60} and the dimer C_{120} in our previous work.[10b]

The crystalline monoadduct **1** has been reported to undergo a regiospecific thermal disproportionation into a solid 1:1 mixture of C_{60} and the *trans-1* isomer[16] of bisadducts **2**.[2n] However, bisadducts **2** obtained by both the solid-state reaction of C_{60} with anthracene and the solid-state dissociation of monoadduct **1** under the HSVM conditions described above were a mixture of positional isomers.

Reaction with Pentacene. The next example of the solid-state [4 + 2] cycloaddition using the HSVM technique is the reaction of C_{60} with pentacene. An equimolar mixture of C_{60} and pentacene was vigorously shaken using the HSVM technique described above for 1 h. Upon separation using flash chromatography on silica gel and preparative HPLC over a Cosmosil 5PBB column, monoadduct **3** (19%) and "double C_{60} adduct" **4** (11%) were isolated in addition to a positional isomeric mixture of bisadducts **5** (15%) and unchanged C_{60} (28%) as shown in Scheme 3. When 2 molar equiv of C_{60} was used against pentacene, the yield of double adduct **4** increased to 16%.

The structure of double adduct **4** was determined on the basis of the following spectral data and the considerations discussed below. The atmospheric-pressure chemi-

(15) There is a fairly good agreement between the HPLC peak area and the isolated yield. For example, the HPLC peak areas for C_{60}, monoadduct **1**, and bisadduct **2** were 16, 65, and 15% respectively, whereas the isolated yields for these compounds were 12, 55, and 19%, respectively, after the HSVM reaction for 1 h.

(16) For the nomenclature of bisadducts of C_{60}, see: (a) Hirsch, A.; Lamparth, I.; Karfunkel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437. (b) Hirsch, A.; Lamparth, I.; Grösser, T. *J. Am. Chem. Soc.* **1994**, *116*, 9385.

cal-ionization mass spectrum (APCI MS) operated in the negative-ion mode using MeOH/toluene as an eluent exhibited peaks at m/z 1719, 998, and 720 corresponding to M^-, $M^- - C_{60}$, and C_{60}^-, respectively. The ^1H NMR spectrum showed AA′BB′ multiplets at δ 7.68 and 7.45 in addition to a singlet at δ 5.91 corresponding to the bridgehead proton. These signals are similar to those of C_{60}-anthracene monoadduct **1** (δ 7.73, 7.43, and 5.76).[5a] Another singlet signal that appears at δ 8.14 corresponds to the central phenyl proton, reflecting the deshielding effect of the closely located C_{60} cages.[17] The ^{13}C NMR spectrum displayed three signals for the proton-bearing aromatic carbons at δ 127.86, 126.32, and 124.08, and two signals for the sp^3 carbons at δ 73.13 and 58.63, in addition to 26 signals between δ 156.02 and 137.41 for the sp^2 carbons of the C_{60} cage and the two ipso carbons of the benzene rings. Assuming that seven signals are hidden by incidental overlapping in the sp^2-carbon region, the ^{13}C NMR data are consistent with the structure of the anti adduct having C_{2h} symmetry such as **4**.[18]

Apparently, double C_{60} adduct **4** is produced by trapping unsymmetrical monoadduct **7**, which still retains an anthracene moiety, with the second molecule of C_{60}. Figure 3 shows the space-filling models of **7** as well as anti and syn double C_{60} adducts **4** and **6** obtained by PM3 calculations.[19,20] It would be reasonable to assume that the trapping of C_{60} takes place only at the less sterically hindered anti-face to give **4** (solid arrow) rather than at the syn-face to give **6** (dotted arrow).
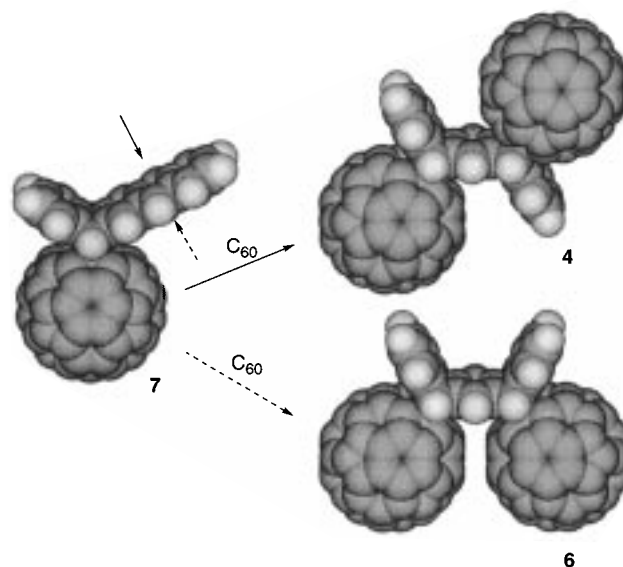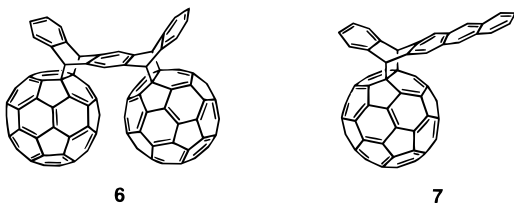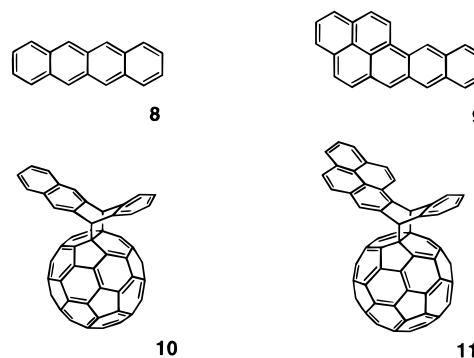

After the present work was completed, an independent paper describing the reaction of C_{60} with pentacene in refluxing toluene reported the formation of only monoadduct **3**.[21] We conducted the same reaction and confirmed the absence of double C_{60} adduct **4** in the product. We believe that the double addition of C_{60} readily proceeds in the solid-state HSVM reaction because of the abundance of C_{60} molecules in close proximity of the reagents without the intervention of any solvent molecules.[22]

Reaction with Other Condensed Aromatics. The solid-state reaction was conducted under the HSVM conditions with tetracene (**8**) (1.0 equiv) and with naphtho[2,3-*a*]pyrene (**9**) (1.6 equiv) for 1 h to give the

(17) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876.

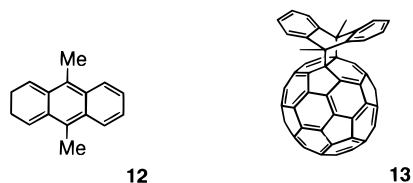(18) The ^{13}C NMR data are also consistent with the syn adduct having C_{2s} symmetry such as **6**.

(19) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221. The PM3 calculations were performed using the standard methods as implemented in the MOPAC 6.0 semiempirical molecular orbital package on a CRAY T94/4128 machine.

(20) The PM3 calculations of ΔH_f values indicated that **4** is only 0.36 kcal mol^{-1} more stable than **6**.

(21) Mack, J.; Miller, G. P. *Fullerene Sci. Technol.* **1997**, *5*, 607.

(22) When 1,2-dichlorobenzene (ODCB) was used as a solvent in this reaction conducted at 150 °C for 17 h, double adduct **4** was isolated in 3% yield in addition to monoadduct **3** in 32% yield while 26% of unchanged C_{60} was recovered. The higher concentration of the reagents in ODCB solution (21 mM) than that in toluene (1.5 mM) seems to have caused the formation of double adduct **4**.

Figure 3. Space-filling models of the calculated structures by PM3 of adduct **7**, anti double C_{60} adduct **4**, and syn double C_{60} adduct **6**.

corresponding [4 + 2] cycloadducts **10** and **11** in 61% and 51% yields, respectively, in an analogous manner.

On the other hand, it is known that 9,10-dimethylanthracene (**12**) undergoes facile cycloaddition−dissociation equilibrium with C_{60} at room temperature in solution. Such high lability of **12** has been demonstrated by its use as a template for the synthesis of the hexaadduct of bis(ethoxycarbonyl)methylene with I_h symmetry in the Bingel reaction.[23] It has not been possible to isolate the cycloadduct of C_{60} and **12** from the reaction in solution due to the facile retro-cycloaddition. However, we have found that when an equimolar mixture of C_{60} and **12** is subjected to the HSVM reaction for 30 min and the reaction mixture is immediately separated by flash chromatography on silica gel, monoadduct **13** can be isolated in 62% yield in addition to unchanged C_{60} in 16%. The ^1H NMR shows AA′BB′ multiplets at δ 7.76 and 7.50 and a singlet for the methyl group at δ 2.85 in agreement with the structure **13**. Although monoadduct **13** is stable in the solid state, it undergoes facile dissociation into C_{60} and **12** in solution at room temperature, with a half-life of about 2 h. This result clearly demonstrates the advantage of the present solid-state reaction in the formation of a thermodynamically unfavorable product.

(23) Lamparth, I.; Maichle, C.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1607.

12   **13**

Electrochemistry. The redox behavior of the newly obtained C_{60} derivatives **3**, **4**, **10**, and **11** was investigated by the use of cyclic voltammetry in 1,2-dichlorobenzene with $Bu_4N^+BF_4^-$ as a supporting electrolyte, and the results were compared with that of C_{60}. As has been observed in the case of 1,2-dihydrofullerene derivatives,[24] the adducts **3**, **4**, **10**, and **11** were reduced at more negative potentials than C_{60} by about 0.1−0.2 V (Table 1). In the double C_{60} adduct of pentacene (**4**) the two C_{60} cages were reduced simultaneously at each step of the three-step reduction with two-electron transfers at each step, revealing the absence of any appreciable electronic interactions between the two C_{60} cages (Figure 4).

Conclusion

The solid-state reaction using a high-speed vibration milling technique has been applied to the [4 + 2] cycloaddition of fullerene C_{60} with condensed aromatics such as anthracene, tetracene, pentacene, and naphtho-[2,3-a]pyrene to give the monoadducts in good yields. The equilibrium state was shown to be established in a cycloaddition with anthracene, and it has been clarified that the present heterogeneous solid-state reaction is particularly advantageous for the reaction of C_{60} with reactants that are hardly soluble in organic solvents. Further study on the application of this technique is in progress.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in CS_2-acetone-d_6 (7:1).

All the solid-state reactions were performed using a mill that consisted of a capsule and a milling ball made of stainless steel.[10b] The capsule containing the milling ball was fixed in a home-built vibrating machine, which was shaken vigorously at a rate of 3500 cycles per min.

HPLC analysis was conducted using a Cosmosil Buckyprep column (4.6 mm × 250 mm) with toluene as an eluent for analytical purposes and a Cosmosil 5PBB column (10 mm × 250 mm) with 1,2-dichlorobenzene (ODCB) as an eluent for preparative purposes, detected at 326 nm. Cyclic voltammetry was conducted using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01 M AgNO$_3$ reference electrode. The potentials were corrected against ferrocene used as an internal standard added after each measurement.

Fullerene C_{60} was commercial material (>99.5%) purchased from Term Co. All the other reagents were commercial materials of reagent grade and were used as received.

General Procedure for the [4 + 2] Cycloadditions. A mixture of C_{60} (30 mg, 0.042 mmol) and 1 equiv of diene was vigorously shaken together with a milling ball in a stainless steel capsule for 1 h by the use of a high-speed vibration mill under an atmosphere of nitrogen at room temperature. The reaction mixture was dissolved in 20 mL of CS_2 to give a dark brown solution, which was filtered and evaporated to dryness to give a black residue. The residue was separated by flash chromatography on silica gel eluted with hexane−CS_2 (1:1).

(24) For example, see: Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.

Table 1. Results of Cyclic Voltammetry[a]

compd	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
		$E_{1/2}$[b]		
C_{60}	−1.11	−1.51	−1.97	−2.45
3	−1.22	−1.66	−2.23	c
4	−1.24	−1.66	−2.18	c
8	−1.24	−1.63	−2.18	c
9	−1.21	−1.60	−2.14	c

[a] Potential in V vs ferrocene/ferrocenium measured in 1,2-dichlorobenzene with Bu_4NBF_4 (0.05 M) as a supporting electrolyte; scan rate, 0.02 V s^{-1}. [b] The half wave potential for the reversible wave. [c] Not observed.
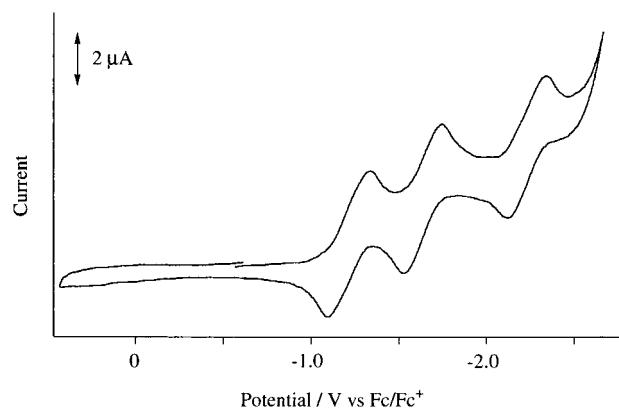
Figure 4. Cyclic voltammogram of double C_{60} adduct **4** (V vs ferrocene/ferrocenium (Fc/Fc$^+$), 0.05 M Bu_4NBF_4 in 1,2-dichlorobenzene, 0.02 V s^{-1}).

C_{60}−tetracene adduct 10: mp > 300 °C; ^1H NMR δ 8.11 (s, 2H), 7.89 (AA'BB', 2H), 7.75 (AA'BB', 2H), 7.48 (AA'BB', 2H), 7.44 (AA'BB', 2H), 5.89 (s, 2H); ^{13}C NMR δ 155.92, 155.62, 147.88, 146.78, 146.54, 146.52, 145.82, 145.79, 145.77, 145.75, 144.98, 143.35, 142.92, 142.60, 142.50, 142.41, 142.40, 142.02, 141.61, 140.39, 140.34, 139.40, 137.51, 137.47, 133.26 (nine signals are supposed to be overlapped between δ 148 and 132), 128.69, 128.07, 126.89, 126.44, 124.82, 72.65, 58.69; UV−vis (CHCl$_3$) λ_{max} (log ϵ) 258 nm (4.90), 312 (4.52), 436 (3.44), 704 (2.53); MS (−APCI) m/z 948 (M$^-$), 720 (C_{60}^-). Anal. Calcd for $C_{78}H_{12}$: C, 98.73; H, 1.27. Found: C, 98.62; H, 1.46.

C_{60}−naphtho[2,3-a]pyrene adduct 11: mp > 300 °C; ^1H NMR δ 8.62 (d, 1H), 8.47 (s, 1H), 8.12−8.01 (m, 5H), 7.89 (t, 1H), 7.82−7.74 (m, 2H), 7.37 (m, 2H), 6.78 (s, 1H), 6.13 (s, 1H); ^{13}C NMR δ 156.06, 156.03, 155.92, 155.79, 148.17, 147.89, 147.91, 146.88, 146.86, 146.79, 146.73, 146.57, 146.53, 146.11, 145.98, 145.89, 145.88, 145.84, 145.82, 145.79, 145.66, 145.65, 145.08, 145.05, 144.98, 144.95, 143.53, 143.41, 143.18, 142.96, 142.95, 142.73, 142.57, 142.49, 142.46, 142.41, 142.12, 142.05, 140.39, 140.34, 140.20, 137.71, 137.67, 137.41, 137.19, 135.90, 131.87, 131.33, 130.79, 129.42, 128.47, 128.33, 127.97, 127.90, 127.71, 126.64, 126.58, 126.50, 126.31, 125.96, 125.70, 124.61, 122.90, 122.87 (17 signals are supposed to be overlapped between δ 148 and 123), 73.45, 73.36, 59.72, 54.31; UV−vis (CHCl$_3$) λ_{max} (log ϵ) 255 nm (5.17), 336 (4.77), 352 (4.72), 433 (3.67), 459 (3.52), 705 (2.60); MS (−APCI) m/z 1325 (M$^-$), 720 (C_{60}^-). Anal. Calcd for $C_{84}H_{14}$: C, 98.62; H, 1.38. Found: C, 98.48; H, 1.39.

C_{60}−1,9-dimethylanthracene adduct: ^1H NMR (CS_2−CDCl$_3$ (1:1)) δ 7.76 (AA'BB', 2H), 7.50 (AA'BB', 2H), 2.85 (s, 6H); MS (−APCI) m/z 720 (C_{60}^-); measurements of the ^{13}C NMR spectrum was not successful owing to facile dissociation to C_{60} and 1,9-dimethylanthracene.

Reaction of C_{60} with Pentacene. According to the procedure described above, C_{60} (30.3 mg, 0.042 mmol) and pentacene (11.7 mg, 0.042 mmol) were shaken by the use of a high-speed vibration mill. The reaction mixture was dissolved in 20 mL of ODCB to give a dark brown solution, which was filtered and evaporated to dryness to give a black residue. The

residue was separated by flash chromatography on silica gel eluted with hexane−CS$_2$ (1:1) to afford a mixture of monoadduct **3** and double C$_{60}$ adduct **4** as a dark brown solid (18.2 mg). The mixture was then subjected to preparative HPLC (5PBB, 10 mm × 250 mm) eluted with ODCB to afford monoadduct **3** (8.0 mg, 19%) and double C$_{60}$ adduct **4** (4.3 mg, 11%) as black powders.

C$_{60}$−pentacene adduct 3: mp > 300 °C; ^{1}H NMR δ 8.17 (s, 4H), 7.91 (AA′BB′, 4H), 7.48 (AA′BB′, 4H), 6.01 (s, 2H); ^{13}C NMR δ 155.60, 147.91, 146.77, 146.54, 145.85, 145.81, 145.79, 145.75, 144.99, 143.28, 142.93, 142.52, 142.43, 142.05, 140.43, 139.18, 137.49, 133.44, 128.70, 126.93, 125.06, 72.44, 58.66; UV−vis (CHCl$_3$) λ_{max} (log ϵ) 247 nm (5.16), 312 (4.60), 435 (3.81), 703 (3.00); MS (−APCI) *m/z* 999 (M$^-$), 720 (C$_{60}^-$). Anal. Calcd for C$_{82}$H$_{14}$: C, 98.59; H, 1.41. Found: C, 98.44; H, 1.40.

C$_{60}$−pentacene double adduct 4: mp > 300 °C; ^{1}H NMR δ 8.21 (s, 2H), 7.75 (AA′BB′, 4H), 7.41 (AA′BB′, 4H), 5.98 (s, 4H); ^{13}C NMR δ 156.02, 155.87, 147.88, 146.83, 146.78, 146.54, 146.52, 145.98, 145.82, 145.81, 145.74, 145.04, 144.98, 143.03, 142.96, 142.90, 142.64, 142.41, 142.12, 141.97, 141.94, 141.44, 140.40, 140.27, 137.75, 137.41 (seven signals are supposed to be overlapped between δ 148 and 133), 127.86, 126.32, 124.08, 73.13, 58.63; UV−vis (CHCl$_3$) λ_{max} (log ϵ) 258 (5.33), 312 (4.86), 434 (3.87), 705 (2.82); MS (−APCI) *m/z* 1751 (M$^-$ + OMe), 1719 (M$^-$), 1029 (M$^-$ − C$_{60}$ + OMe), 998 (M$^-$ − C$_{60}$), 751 (C$_{60}^-$ + OMe), 720 (C$_{60}^-$). Anal. Calcd for C$_{142}$H$_{14}$: C, 99.18; H, 0.82. Found: C, 99.31; H, 1.12.

Pentacene bisadducts 5: mp > 300 °C; ^{1}H NMR δ 8.4−7.3 (m), 6.30 (s), 6.15 (s), 6.05 (s), 5.94 (s), 5.85 (s), 5.67 (s), 5.64 (s), 5.63 (s), 5.60 (s), 4.85 (s); MS (−APCI) *m/z* 1277 (M$^-$), 999 (M$^-$ − C$_{22}$H$_{14}$), 720 (C$_{60}^-$).