

Synthesis and Properties of Endohedral C₆₀ Encapsulating Molecular Hydrogen

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Abstract: We report the details of our study to synthesize a new endohedral fullerene, H₂@C₆₀, in more than 100 mg quantities by closure of the 13-membered ring orifice of an open-cage fullerene using four-step organic reactions. The 13-membered ring orifice in a previously synthesized open-cage fullerene incorporating hydrogen in 100% yield was reduced to a 12-membered ring by extrusion of a sulfur atom at the rim of the orifice, and the ring was further reduced into an eight-membered ring by reductive coupling of two carbonyl groups also at the orifice. Final closure of the orifice was completed by a thermal reaction. Purification of H₂@C₆₀ was accomplished by recycle HPLC. A gradual downfield shift of the NMR signal for the encapsulated hydrogen observed upon reduction of the orifice size was interpreted based on the gauge-independent atomic orbital (GIAO) and the nucleus-independent chemical shift (NICS) calculations. The spectral as well as electrochemical examination of the properties of H₂@C₆₀ has shown that the electronic interaction between the encapsulated hydrogen and outer C₆₀ π-system is quite small but becomes appreciable when the outer π-system acquires more than three extra electrons. Four kinds of exohedral derivatives of H₂@C₆₀ were synthesized. The tendency in the shift of the NMR signal of the inner hydrogen was found to be quite similar to that observed for the ³He NMR signal of the corresponding derivatives of ³He@C₆₀.

Introduction

The preparation of endohedral fullerenes, the spherical carbon molecules incorporating atom(s) or a molecule inside the framework,¹ has so far relied on hardly controllable physical processes, such as co-vaporization of carbon and metal atoms^{1b,c} or high-pressure/high-temperature treatment (650 °C/3000 atm) with noble gases,² which yield only limited quantities (e.g., only a few milligrams) of a pure product after laborious isolation procedures. This situation has been a severe obstacle to the development of fundamental as well as application-oriented studies on these molecules of great importance. To bring about a breakthrough to this situation and to make their science developed, an entirely new approach for their production is highly desired. In this regard, a molecular surgery approach to endohedral fullerenes proposed by Rubin³ is quite appealing

because of its great potential and versatility. This method is comprised of steps for opening an orifice on the surface of fullerene, insertion of a small atom or a molecule through the orifice, and closure of the orifice, making use of rational techniques of organic synthesis. In this way, the efficient production of various endohedral fullerenes in a much larger amount is expected.

As the first step of the molecular surgery approach, Wudl and co-workers pioneered an efficient route to open an 11-membered ring orifice on the surface of C₆₀ (**1**).⁴ However, even a small atom, such as helium, was found to be difficult to pass through this orifice.⁵ Subsequently, several open-cage fullerene derivatives with a relatively large orifice have been reported.^{6–11} Rubin and co-workers, for instance, reported the synthesis of cobalt(III) complex **2**, whose cobalt atom was ideally located above a 15-membered ring orifice, but the insertion of this metal atom into the C₆₀ cage through the orifice was not possible even by application of such high pressure as 40 000 atm in a solid state.^{6a,12} A great progress in this research field was brought

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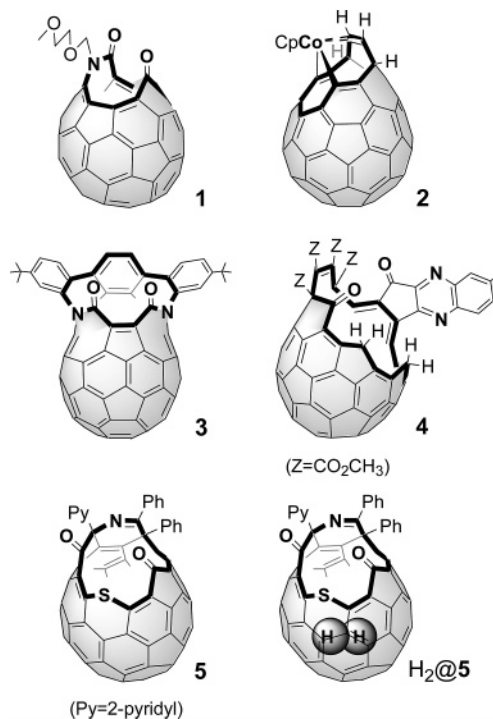
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about again by Rubin's group, who found an elegant strategy to synthesize open-cage fullerene derivative **3** with a 14-membered ring orifice.^{6b} Although the shape of the orifice is rather elliptic, the second step of the molecular surgery was first achieved using **3**, that is, insertion of a helium atom (1.5% yield) or a hydrogen molecule (5% yield) in the hollow cavity of **3** through the orifice under the conditions of 288–305 °C/ca. 475 atm and 400 °C/100 atm, respectively.¹³ Recently, Iwamatsu and co-workers reported a fullerene derivative **4** with a surprisingly huge orifice, with its molecular shape almost looking like a bowl, and showed that a water molecule can get inside the cage even at room temperature under a normal pressure.^{9d}

On the other hand, we synthesized a C₆₀ derivative with a 13-membered ring orifice **5** by thermal reaction of C₆₀ with a 1,2,4-triazine derivative.⁸ In the case of **5**, the shape of the orifice is less elliptic, and the size is slightly larger than that of **3**: a distance between the closest atoms situated at the orifice is 3.9 Å for **5** and 3.3 Å for **3**. Actually, we could achieve insertion of molecular hydrogen into **5** to give H₂@**5** in 100% yield without any decomposition by treating a powder of **5** with high pressure of hydrogen gas (800 atm) at 200 °C in an autoclave.¹⁴ This complete encapsulation made it possible to directly observe a single hydrogen molecule at the center of the fullerene cage by the use of the synchrotron X-ray diffraction technique¹⁵ and also with the solid-state NMR spectroscopy.¹⁶

Now, as the final process of the molecular surgery, we recently succeeded, for the first time, in complete closure of the orifice of H₂@**5** by four-step organic reactions to afford an entirely new endohedral fullerene, H₂@C₆₀, in an amount of more than 100 mg.¹⁷ Here we describe a full account of our research on organic synthesis of H₂@C₆₀ and its properties. So far, the NMR chemical shift of ³He incorporated in fullerenes, albeit in a small amount (0.12% to 1%¹⁸), has been successfully used as a probe sensitive to the structure of fullerenes.^{2a,19} Similarly, the endohedral H₂ chemical shifts should be highly sensitive to the fullerene structure, and this has been also

examined in detail for a series of open-cage fullerene derivatives incorporating H₂ as well as some of the derivatives of H₂@C₆₀.



Results and Discussion

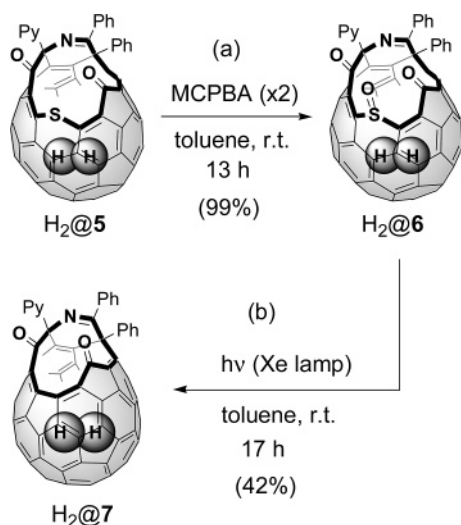
Size Reduction of the 13-Membered Ring Orifice of H₂@**5**.

In our previous work, we found that, upon strong laser irradiation in the MALDI-TOF mass measurement of H₂@**5**, a weak peak at *m/z* 722 corresponding to H₂@C₆₀ is observed, indicating that the orifice of H₂@**5** can be closed by the laser power in a gas phase.¹⁴ However, not only the peak intensity was weak but also about 70% of the originally encapsulated hydrogen was shown to escape from the C₆₀ cage during the process to close the orifice. This result indicated that it is necessary to reduce the size of the orifice in order to produce H₂@C₆₀ without a serious loss of the encapsulated hydrogen.

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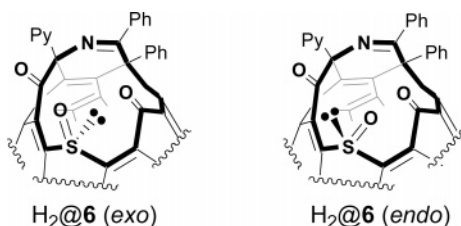
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Scheme 1



Since the hydrogen molecule in H₂@5 was found to be gradually released with the half-life of 54.4 h at 160 °C or 4.2 h at 190 °C,¹⁴ such a high temperature must be avoided in the process to close the orifice.

At a first glance of the molecular structure of **5**, removal of a sulfur atom appeared as the most facile procedure for the orifice size reduction. Thus we first conducted an oxidation of the sulfide unit of H₂@5 by *m*-chloroperbenzoic acid (MCPBA) to make the sulfur atom readily removable.²⁰ The oxidation reaction proceeded at room temperature smoothly to give the corresponding sulfoxide H₂@6 quantitatively (Scheme 1a). The product was easily identified: the FAB mass spectrum exhibited a molecular ion peak at *m/z* 1084 (M⁺) corresponding to H₂@6, and the IR spectrum showed a prominent sulfinyl stretching band at 1073 cm⁻¹, in addition to NMR data (Experimental Section). Between the two possible stereoisomers, H₂@6(*exo*) and H₂@6(*endo*), the *exo*-isomer is considered to be formed since it can avoid steric repulsion between the sulfinyl group and two carbonyl groups. Indeed, theoretical calculations at the B3LYP/6-31G* level of theory²¹ indicated the *exo*-isomer to be more stable than the *endo*-isomer by 8.6 kcal mol⁻¹. The ¹H NMR spectrum of H₂@6 showed a sharp signal for the encapsulated hydrogen at $\delta = -6.33$ ppm in *o*-dichlorobenzene-*d*₄ (ODCB-*d*₄), which is 0.92 ppm downfield shifted compared to that of H₂@5 ($\delta = -7.25$ ppm), with the integrated peak area of 2.0 ± 0.02 H.



As shown in Figure 1, the MALDI-TOF mass spectrum of empty **6** exhibited three strong peaks, that is, a molecular ion

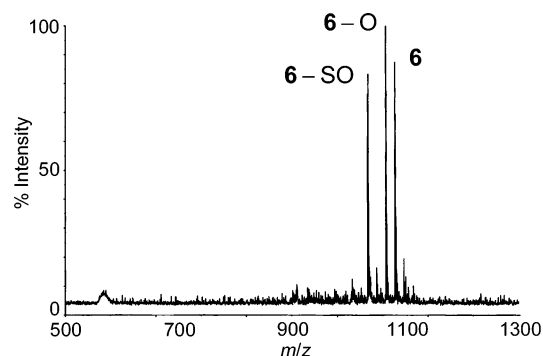


Figure 1. MALDI-TOF mass spectrum of **6** (positive ionization mode, dithranol matrix).

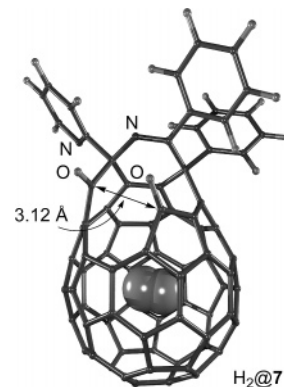


Figure 2. The optimized structure of H₂@7 (B3LYP/6-31G*).

peak and peaks for **5** and for a derivative having a 12-membered ring orifice generated by fragmentation of an SO unit, as expected.²² To chemically remove the SO unit, first we attempted its thermal extrusion by heating H₂@6 in refluxing toluene or at 140 °C in ODCB, but there was practically no reaction. In contrast, simple irradiation of a solution of H₂@6 in benzene with visible light through a Pyrex glass flask by the use of a xenon lamp at room temperature afforded desired product H₂@7 in 42% yield (Scheme 1b), with 38% recovery of unreacted H₂@6.²³ The structure of H₂@7 was confirmed by NMR, FAB mass, IR, and UV–vis spectra, which were identical to those of **7**⁸ except the following. The ¹H NMR spectrum (in ODCB-*d*₄) clearly exhibited a signal for the encapsulated hydrogen at $\delta = -5.80$ ppm, which is 0.53 ppm downfield shifted compared to H₂@6, with the integrated ratio corresponding to 2.0 ± 0.02 H.

As shown by the optimized structure of H₂@7 at the B3LYP/6-31G* level of theory in Figure 2, removal of the sulfur atom from the 13-membered ring orifice of H₂@5 brought about a significant size reduction of the orifice. The distance between two carbonyl carbons across the orifice is reduced from 3.89 Å for H₂@5 to 3.12 Å for H₂@7. Accordingly, the calculated activation energy for the escape of the hydrogen molecule from H₂@7 is estimated as 50.3 kcal mol⁻¹, which is significantly greater than that of 28.7 kcal mol⁻¹ for H₂@5²⁴ (both calculated at the B3LYP/6-31G** level with optimized structures at the B3LYP/3-21G level). In fact, we could not observe any escape of the encapsulated hydrogen at all upon heating an ODCB-*d*₄

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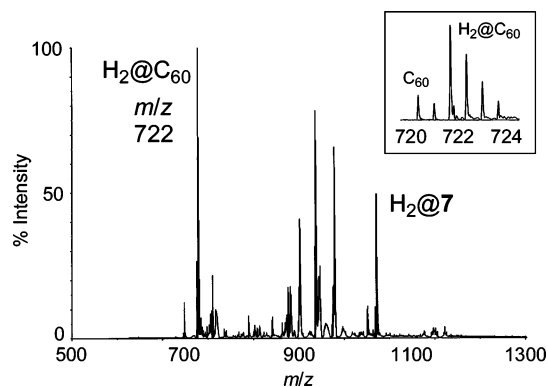
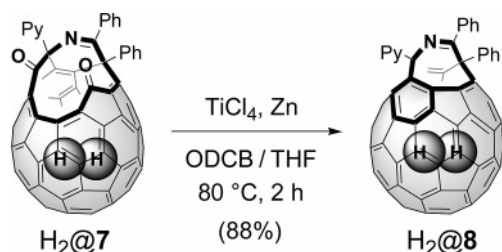


Figure 3. MALDI-TOF mass spectrum of H₂@7 (positive ionization mode, dithranol matrix). Inset shows an expanded spectrum.

Scheme 2



solution of H₂@7 even at 190 °C for 3 days under vacuum, as examined by ¹H NMR. This is in a sharp contrast with the case of H₂@5, from which the hydrogen molecule was gradually released with the half-life period of 4.2 h under the same conditions.¹⁴ The MALDI-TOF mass spectrum of H₂@7 (Figure 3) showed a dramatic change from that of H₂@5.¹⁴ Now a peak for H₂@C₆₀ was observed as a base peak, indicating its highly enhanced accessibility from H₂@7. Unfortunately, however, the spectrum showed that about 20% of the hydrogen molecule escaped during the transformation to C₆₀ upon laser irradiation (see inset of Figure 3). As a preliminary study, the powder of H₂@7 was heated at 350 °C under vacuum (ca. 1 mmHg), but this resulted in the formation of H₂@C₆₀ only in a trace amount. Hence, further reduction of the orifice size was apparently required to produce a macroscopic amount of H₂@C₆₀.

For this purpose, the McMurry reaction²⁵ worked efficiently for reductive coupling of the two carbonyl groups at the orifice of H₂@7, leading to the formation of open-cage fullerene derivative H₂@8 with an eight-membered ring orifice in 88% yield (Scheme 2). The high efficiency of this reaction is quite reasonable since the two carbonyl groups of H₂@7 are fixed at the parallel orientation in a close proximity, as mentioned above. The structure of H₂@8 was confirmed by ¹H and ¹³C NMR, FAB mass, IR, and UV-vis spectra, which were identical to those of empty 8 except the ¹H NMR (see below). The MALDI-TOF mass spectrum of H₂@8 is quite simple, exhibiting only two peaks over the range of *m/z* > 500, that is, a base peak corresponding to H₂@C₆₀ and a smaller molecular ion peak for H₂@8 (Figure 4). The NMR signal of the encapsulated hydrogen of H₂@8, with integrated area of 2.0 ± 0.02 H, was observed at δ = -2.95 ppm in ODCB-*d*₄, which was 2.85 ppm downfield shifted compared to that of H₂@7.

It is to be noted that the encapsulated hydrogen was completely retained at each step of the process for orifice size

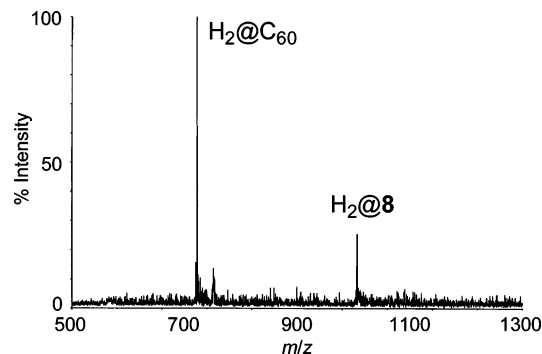


Figure 4. MALDI-TOF mass spectrum of H₂@8 (positive ionization mode, dithranol matrix).

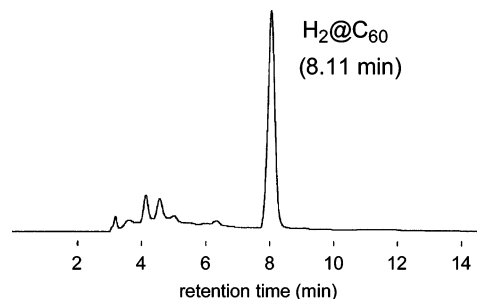


Figure 5. HPLC chart of the crude products obtained by thermal reaction of H₂@8. Column, Cosmosil Buckyrep (4.6 mm × 250 mm); solvent, toluene; flow rate, 1 mL min⁻¹.

reduction, which was confirmed by comparing the integrated peak area for the encapsulated hydrogen with reference to that for the aromatic protons in each ¹H NMR spectrum.

Complete Restoration of the Fullerene Cage: Formation of H₂@C₆₀. The final step to completely eliminate extra organic addends and to close the orifice was accomplished by heating a brown powder of H₂@8 (245 mg) in a vacuum-sealed tube placed in an electric furnace at 340 °C for 2 h. The resulting black material completely dissolved in carbon disulfide (CS₂) and was analyzed by HPLC on a Cosmosil Buckyrep column eluted with toluene. As shown in Figure 5, the chromatogram exhibited one prominent peak at the retention time of 8.11 min, which was exactly the same as that for empty C₆₀, while the peak for H₂@8 at the retention time of 4.52 min disappeared. A preparative-scale separation of the C₆₀ portion was readily made by flash chromatography over silica gel eluted with CS₂ to give a purple solution containing desired H₂@C₆₀ (118 mg, 67%), contaminated by 9% of empty C₆₀, which was proven as described below. Similar results were obtained when H₂@8 was heated at 300 °C for 24 h or at 400 °C for 2 min.

The mechanism for this thermal reaction is considered as shown in Figure 6. An initial [$\pi 2s + \pi 2s + \pi 2s$] electrocyclozation produces intermediate 9 incorporating two cyclopropane rings, which undergo subsequent radical cleavage to give intermediate 10. As to the following step, conceptually the most reasonable one is a retro [$\pi 2s + \pi 2s + \pi 2s$] reaction to give C₆₀ together with 2-cyanopyridine (11) and diphenylacetylene (12) (Figure 6a). Indeed, 11 and 12 were detected in the crude product as described in the Experimental Section. However, the reaction was not so clean, and, to our surprise, benzonitrile (13) and 2-(phenylethynyl)pyridine (14) were also found to be formed together with an unknown compound having a molecular formula of Ph₂PyC₃N. This latter fact indicates that occurrence

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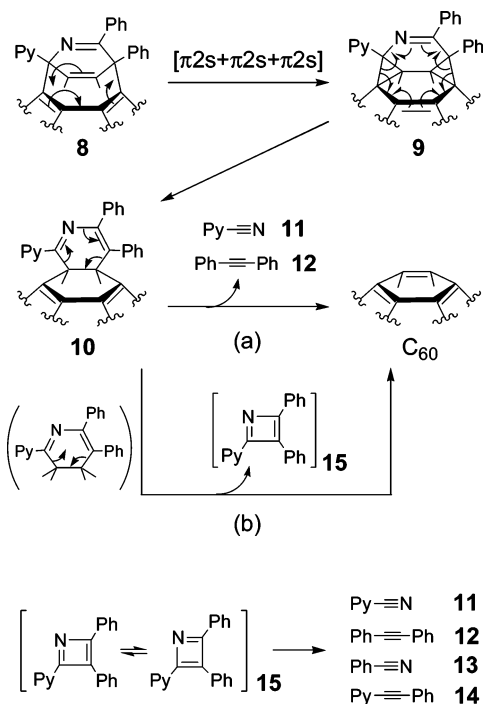


Figure 6. Possible reaction mechanisms for the formation of C_{60} from compound **8**. For the fullerene derivatives, only top parts of the molecules are shown.

of the reaction pathway shown in Figure 6b cannot be rigorously ruled out, although we regrettably do not have a reasonable explanation for the occurrence of this reaction, which has to involve an extrusion of highly unstable byproduct, such as azacyclobutadiene (azete) derivative **15**.²⁶

It was also unexpected that 9% of encapsulated hydrogen molecule had escaped from the cage during this thermal reaction. Theoretical calculations as well as inspection of the molecular model suggest that it is impossible for a hydrogen molecule to pass through the eight-membered ring in compound **8**. We assume that cleavage of some additional single bonds in the fullerene skeleton of $\text{H}_2@8$ (not shown in Figure 6) also takes place at a temperature higher than 300 °C, which instantaneously opens a window to release a small portion of the encapsulated hydrogen.^{2a}

Purification and Characterization of $\text{H}_2@C_{60}$. Although the desired product of the thermal reaction, $\text{H}_2@C_{60}$, was contaminated by 9% of empty C_{60} , the purification of $\text{H}_2@C_{60}$ was achieved by recycling HPLC on a semipreparative Cosmosil Buckyprep column (two directly connected columns; 250 mm length, 10 mm i.d.; mobile phase, toluene; flow rate, 4 mL min^{-1}) as shown in Figure 7. After 20 recycles, $\text{H}_2@C_{60}$ was completely separated, with its total retention time being 399 min, while that of C_{60} was 395 min. The adsorption mechanism of the Buckyprep column is based on a π - π interaction with the pyrenyl groups in the stationary phase. Therefore, a very weak but appreciable van der Waals interaction must be operating between the inner hydrogen molecule and the π -electron cloud of outer C_{60} , and this must have contributed

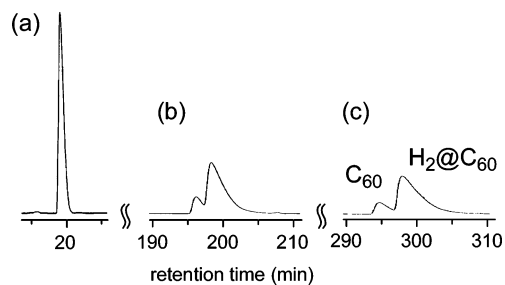


Figure 7. Recycle HPLC chart for the separation of $\text{H}_2@C_{60}$ and empty C_{60} . (a) Before recycle, (b) after 10 recycles, and (c) after 15 recycles.

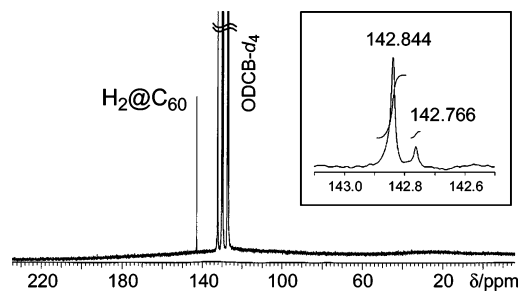


Figure 8. ^{13}C NMR spectrum (75 MHz, ODCB-d_4) of the C_{60} portion of the thermolysis product. Inset shows the expanded spectrum.

to this separation. Also in the case of a mixture of C_{60} and $\text{E}@C_{60}$ ($\text{E} = \text{Ar}$,²⁷ Kr ,²⁸ and Xe ²⁹), $\text{E}@C_{60}$ is known to be more strongly adsorbed than empty C_{60} to the PYE column,³⁰ which also has the pyrenyl groups on the stationary phase. The π -electron distribution of C_{60} is considered to be slightly pushed outward by the encapsulated noble gas atoms.²⁷

The ^{13}C NMR spectrum of the crude C_{60} portion of the thermolysis product readily obtained by passing the CS_2 solution through a silica gel column is shown in Figure 8. Between the two signals at δ 142.844 and 142.766 ppm with an integrated ratio of 10:1, the one at 142.766 ppm is identical to that of empty C_{60} , and the other signal is assigned to that of $\text{H}_2@C_{60}$. The difference in chemical shift is only 0.078 ppm, indicating that an electronic or van der Waals interaction between the inner hydrogen and outer fullerene cage is quite minute. After the HPLC separation, the main product, $\text{H}_2@C_{60}$, exhibited a ^{13}C NMR signal only at δ 142.844 and a ^1H NMR signal for the inside hydrogen as a sharp singlet at $\delta = -1.44$ ppm in ODCB-d_4 , which is 1.51 ppm downfield shifted compared to that of $\text{H}_2@8$. This is also 5.98 ppm upfield shifted from dissolved free hydrogen. This value is comparable to the 6.36 ppm upfield shift of a ^3He NMR signal observed for $^3\text{He}@C_{60}$.^{2a,b} This similarity proves that the total shielding effect of the fullerene cage is nearly constant and indifferent to the paramagnetic species inside the cage. The slight difference in chemical shift ($\Delta\delta$ 0.38 ppm) might be attributed to the geometry of each hydrogen atom in the molecule, which should be off-centered compared to a ^3He atom,³¹ or, otherwise, to the difference of

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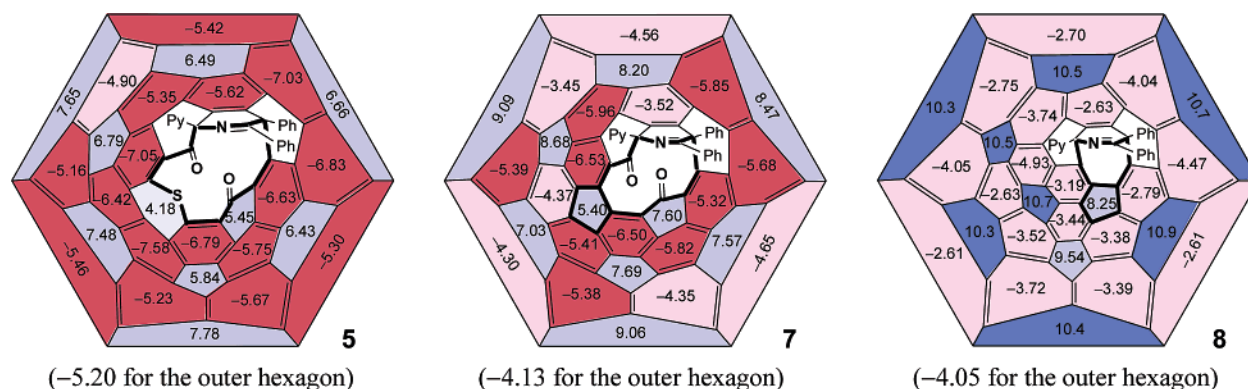


Figure 9. NICS patterns of the open-cage fullerene derivatives **5**, **7**, and **8**, calculated at the B3LYP/6-31G* level of theory: red regions are for $\delta < -5$ ppm, pink for $\delta = 0$ to -5 , pale blue for $\delta = +5$ to $+10$, and blue for $\delta > +10$.

the paramagnetic property of the encapsulated species. In accord with a very minute effect of encapsulated hydrogen, the IR spectrum was almost the same as that of empty C₆₀, exhibiting four absorption bands at 1429.2, 1182.3, 576.7, and 526.5 cm⁻¹ (to be compared with 1429.2, 1182.3, 575.7, and 526.5 cm⁻¹ for empty C₆₀ measured under exactly the same conditions). Only the band at 576.7 cm⁻¹ of H₂@C₆₀, corresponding to an out-of-plane vibration mode,³² is slightly higher in energy than that of empty C₆₀ by 1.0 cm⁻¹. This might be taken as evidence that a slight repulsive interaction with the inner H₂ molecule has caused a very slight deformation of the spherical cage of H₂@C₆₀. The UV-vis spectrum was also the same as that of empty C₆₀. An attempt to measure the Raman spectrum of H₂@C₆₀ was unsuccessful because of strong fluorescence from the outer C₆₀ cage. Further trials are now underway.

The endohedral fullerene H₂@C₆₀ is thermally stable. Upon heating the pure sample of H₂@C₆₀ at 500 °C for 10 min under vacuum, there was no decomposition or release of incorporated hydrogen at all, as judged from the ¹³C NMR and HPLC.

¹H NMR Chemical Shift of Hydrogen Inside the Open-Cage Fullerenes. At each step in the chemical transformation to reduce the orifice size, gradual downfield shifts were observed for the ¹H NMR signal of encapsulated hydrogen: H₂@**5**, δ -7.25 ppm; H₂@**6**, δ -6.33 ppm; H₂@**7**, δ -5.80 ppm; H₂@**8**, δ -2.95 ppm; H₂@C₆₀, δ -1.45 ppm. To examine if theoretical calculations can reproduce this tendency, we first conducted the GIAO (gauge-independent atomic orbital) calculations at the B3LYP/6-311G** level of theory for the structures optimized at the B3LYP/6-31G* level, on a series of the open-cage and closed-cage fullerenes containing H₂.³³ All chemical shifts are expressed as the values with reference to tetramethylsilane also calculated using the same level. As shown in Table 1, the GIAO calculations were found to reproduce the trend of gradual downfield shifts, although there was a tendency to underestimate the magnetic shielding effects of the fullerene cage in the extent which gradually increased in the order of H₂@**5** ($\Delta\delta$ 1.38) to H₂@C₆₀ ($\Delta\delta$ 3.24). A similar tendency of underestimation of the NMR chemical shift of encapsulated species in the GIAO-DFT method has been reported and discussed in detail.^{33,34}

Table 1. Experimental and Calculated NMR Chemical Shifts for Encapsulated Hydrogen of a Series of Open-Cage Fullerene Derivatives and H₂@C₆₀

	H ₂ @ 5	H ₂ @ 6	H ₂ @ 7	H ₂ @ 8	H ₂ @C ₆₀
exp ^a	-7.25	-6.33	-5.80	-2.95	-1.45
calcd ^b	-5.87	-4.72	-3.85	-0.17	+1.79
Δ	1.38	1.61	1.95	2.78	3.24

^a At 300 MHz, in ODCB-*d*₄. ^b Calculated at the GIAO-B3LYP/6-311G**//B3LYP/6-31G* level of theory.

The observed gradual downfield shift must be due to the change in magnetic environment of this hydrogen, resulting from the change in diamagnetic and paramagnetic ring currents of hexagons and pentagons, and the consequent total ring currents, of the fullerene cage. To prove this, the diamagnetism and paramagnetism of all the π -conjugated five- and six-membered rings in the open-cage fullerenes **5–8** and of C₆₀ were assessed by the NICS (nucleus-independent chemical shifts) calculations.^{33,35,36} The obtained NICS values for each pentagon and hexagon are shown in the Schlegel diagrams of Figure 9. Upon removal of the sulfur atom from the orifice of **5**, which caused a 1.45 ppm downfield shift, the aromatic character of most of the hexagons (14 out of 18) decreased (decrease in absolute NICS value, 0.5–2.2 ppm) with the exception of two rings (increase in absolute NICS value, 0.1–0.6 ppm), whereas the antiaromatic character of most pentagons (8 out of 9) increased by 1.1–2.2. A similar trend is also seen in the case of the chemical transformation of **7** to **8**,³⁷ which caused further downfield shift by 2.85 ppm (calculated value, 3.68 ppm). In this way, the size reduction of the orifice in each step is shown to lower the aromatic character of the fullerene cage as a whole. A series of these orifice size reduction processes should also be accompanied by very slight but gradual increase in strain of the fullerene's σ -frameworks, which should gradually weaken the extent of the total π -conjugation on the fullerene surface.^{19m} These are all taken together as the reason for observed downfield shifts upon the reduction of the orifice size.

In the final step, in which the organic addends were completely removed and the original C₆₀ structure was restored

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(37) The aromatic character in all hexagons decreased (by the absolute value, 0.7–3.1 ppm), and the antiaromatic character of all pentagons increased (by the absolute value, 0.7–5.3 ppm).

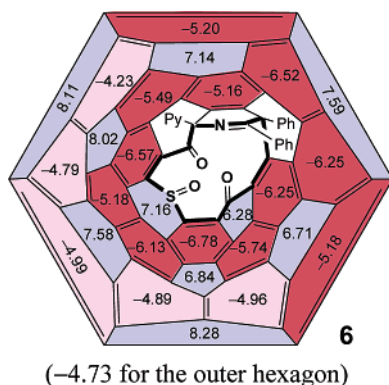


Figure 10. NICS pattern of the open-cage fullerene derivatives **6**, calculated at the B3LYP/6-31G* level of theory.

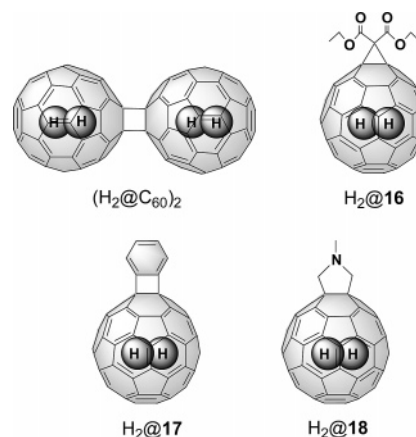
from H₂@**8**, 1.50 ppm downfield shift was observed. The NICS values for C₆₀, calculated in the same way as above, are -2.4 for the hexagon and $+11.8$ for the pentagon,^{36a} clearly indicating that the aromaticity of the hexagon is considerably decreased and the antiaromaticity of pentagons is increased, despite the formation of a completely π -conjugated system. Again, the pyramidalization of all 60 carbons and the resulting increase of strain should be related to the lowering of the overall aromaticity. In addition, this last step is accompanied by the formation of two fully π -conjugated antiaromatic pentagons compared to **8**. All these effects are assumed to be added together to cause the downfield shift of the H₂ NMR signal.

Upon oxidation of the sulfur atom of H₂@**5**, a 0.92 ppm downfield shift was observed, even though the structure of the fullerene skeleton itself was not affected. The NICS values of sulfoxide **6** indicated that the oxidation of S to SO influenced not only the carbocycles in its vicinity but also almost all of the cyclic systems of the fullerene cage (Figure 10): the magnetic characteristics of most hexagons and pentagons are changed to make the overall aromaticity of **6** lower than that of **5**. This is presumably due to an electronegative characteristic of the S=O group. As a related example, it has been reported by Taylor and co-workers that the ³He NMR signal of ³He@C₆₀-Cl₆ ($\delta = -12.3$ ppm) is 2.8 ppm downfield shifted compared to that of ³He@C₆₀Ph₃Cl ($\delta = -15.1$ ppm) due to the electronegative chloro addends.^{19m}

To examine the effect of encapsulated hydrogen upon the reactivity of the outer fullerene cage, the solid-state mechanochemical dimerization of H₂@C₆₀ was conducted under the same conditions as we previously reported.³⁸ It was found that the dumbbell-shaped dimer, (H₂@C₆₀)₂, was obtained in 30% isolated yield similarly to the reaction of empty C₆₀. Apparently, the inside hydrogen does not affect the reactivity of the outer C₆₀ cage. The NMR signal for the inside hydrogen was observed as a singlet at $\delta = -4.04$ ppm,³⁹ which is 8.58 ppm upfield shifted from free hydrogen, similar to the case for ³He@C₆₀ (8.81 ppm upfield shift from free ³He).^{38b}

Three additional fullerene derivatives, H₂@**16**, H₂@**17**, and H₂@**18**, were synthesized by the Bingel reaction,⁴⁰ benzyne addition,⁴¹ and Prato reaction in order to further investigate this

issue.⁴² The NMR signal for encapsulated hydrogen was observed in ODCB-*d*₄ at $\delta = -3.27$ ppm for H₂@**16** (upfield shifted from dissolved free hydrogen by $\Delta\delta$, 7.81 ppm), -4.30 ppm for H₂@**17** ($\Delta\delta$, 8.84 ppm), and -4.64 ppm for H₂@**18** ($\Delta\delta$, 9.18 ppm). These upfield shifts are quite similar to those reported for the NMR signal of ³He encapsulated in the corresponding derivatives for ³He@C₆₀ ($\Delta\delta$, 8.06, 9.11, and 9.45 ppm, respectively) being constantly less shielded by 0.23–0.27 ppm.^{2a} Thus, the inside molecular hydrogen of C₆₀ can also be used as a good probe to investigate the chemical reactions at the exterior of the fullerene cage, just as the ³He atom inside the fullerene cage has been utilized.¹⁹



Electrochemical Behavior of H₂@C₆₀. To clarify the electronic properties of H₂@C₆₀ in more detail, we conducted cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Upon measurements at room temperature for the range of 0.0 to -2.0 V (vs Fc/Fc⁺) in ODCB and for the range of 0.0 to $+1.0$ V in 1,1,2,2-tetrachloroethane, three reversible reduction waves ($E_{1/2} = -1.13, -1.54, -1.99$ V vs Fc/Fc⁺) and one irreversible oxidation peak ($E_{pa} = +1.62$ V) were observed, respectively, virtually at the same potentials as those for empty C₆₀. However, when we applied more negative potential using the conditions reported by Echegoyen in toluene–acetonitrile (5.4:1) at -10 °C under vacuum,⁴³ the reduction of H₂@C₆₀ was found to become slightly but gradually more difficult than empty C₆₀ as the fullerene cage acquires more numbers of electrons up to six. As shown in Figure 11, the reduction potentials estimated from the differential pulse voltammogram were $-0.95, -1.37, -1.89, -2.39, -2.95$, and ca. -3.5 V for H₂@C₆₀ to be compared with $-0.95, -1.37, -1.88, -2.35, -2.88$, and -3.35 V for empty C₆₀. Thus the difference in reduction potential reaches nearly 0.15 V at the stage of six-electron reduction. Although the extent is so minute, this result is taken as clear evidence that hydrogen, as a slightly electro-positive molecule, exerts an appreciable electronic repulsion with the outer C₆₀ cage when the π -system of the latter is charged with more than four electrons.

Summary

In the present study, we have demonstrated that an entirely new endohedral fullerene encapsulating molecular hydrogen,

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(39) No magnetic interaction was observed between two hydrogen molecules in the two fullerene cages.

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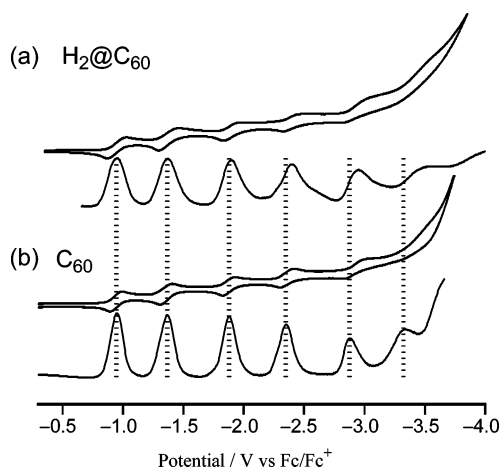


Figure 11. CV and DPV of (a) H₂@C₆₀ and (b) C₆₀ in toluene–CH₃CN (5.4:1) at –10 °C.

H₂@C₆₀, can be synthesized in a macroscopic amount by chemically closing the 13-membered ring orifice of open-cage fullerene **5** incorporating hydrogen. The endohedral chemical shift for the molecular hydrogen in a series of open-cage fullerenes is particularly sensitive to the transformation of the outer cage, and the GIAO and NICS calculations are helpful to rationalize the chemical shift change even for such highly derivatized fullerenes. The endohedral hydrogen's NMR signal of representative derivatives of H₂@C₆₀ has indicated that it can serve as a sensitive probe for the exohedral transformation of the fullerene cage. Although the ¹³C NMR, IR, and UV–vis spectra of H₂@C₆₀ are virtually the same as those of empty C₆₀, the existence of repulsive interaction between the inside hydrogen and the outer π-electron system of C₆₀ in its highly reduced states has been confirmed by electrochemical measurements. The new endohedral fullerene, H₂@C₆₀, can be taken as an ideal model to examine specific characteristics of a hydrogen molecule placed in a totally isolated state. A conversion between ortho- and para-hydrogen is certainly one of such issues. On the other hand, the critical temperature for the appearance of superconductivity upon alkali-metal doping should undergo a change. These studies are now under investigation in collaboration with teams in the areas of physical chemistry and physics. It is evidently possible to apply the present molecular surgery method to synthesize endohedral fullerenes, such as D₂@C₆₀, HD@C₆₀, He@C₆₀, as well as a homologous series with C₇₀. Investigations along these lines are now in progress in our group.

Experimental Section

General. ¹H and ¹³C NMR measurements were carried out on a Varian Mercury 300 instrument, and chemical shifts are reported in parts per million with reference to tetramethylsilane. In some cases, the signal of *o*-dichlorobenzene (ODCB) in the ODCB-*d*₄ solvent was used as internal standard ($\delta = 7.20$ ppm in ¹H NMR). UV–vis spectra were recorded on a Shimadzu UV-3150 spectrometer. IR spectra were taken with a Shimadzu FTIR-8600 spectrometer. MALDI-TOF mass spectra were measured with an Applied Biosystem Voyager-DE STR spectrometer. FAB mass spectra were recorded on a JEOL MStation JMS-700. APCI mass spectra were measured on a Finnigan-MAT TSO 7000 spectrometer. GC/MS analyses were conducted on a Shimadzu GCMS-QP5050A spectrometer. The high-pressure liquid chromatography (HPLC) was performed by the use of a Cosmosil Buckyprep column (4.6 mm × 250 mm) for analytical purpose and wider columns

of the same kind (two directly connected Buckyprep columns, 10 mm × 250 mm) for preparative purpose. Fullerene C₆₀ was purchased from Matsubo Co. *m*-Chloroperbenzoic acid was purchased from Aldrich Co. Zinc (sandy) and titanium(IV) chloride were purchased from Wako Co.

Computational Method. All calculations were conducted using the Gaussian 98 series of electronic structure program. The geometries were fully optimized with the restricted Becke hybrid (B3LYP) method for all calculations. The GIAO calculations were performed at the B3LYP/6-311G** level of theory using the optimized structures at the B3LYP/6-31G* level of theory. NICS calculations were performed at the B3LYP/6-31G* level of theory using the optimized structures at the B3LYP/6-31G* level.

Cyclic Voltammetry and Differential Pulse Voltammetry of H₂@C₆₀. The measurements were conducted on a BAS electrochemical analyzer ALS600A using a four-necked flask equipped with three platinum wires serving as reference, counter, and working electrodes. About 2 × 10^{−4} M solutions of H₂@C₆₀ and C₆₀ were used. TBAPF₆ (0.1 M) was used as supporting electrolyte. For a low-temperature measurement, toluene and acetonitrile (5.4:1 by volume) were dried over P₂O₅, degassed by repeated freeze–pump–thaw cycles under 10^{−4} mmHg, and vapor transferred into an electrochemical cell connected to a vacuum line (10^{−4} mmHg). The voltammograms were recorded at –10 °C at the scan rates of 100 mV s^{−1} for CV and 25 mV s^{−1} for DPV. The potentials were corrected against ferrocene used as an internal standard which was added after each measurement.

Oxidation of H₂@5. A mixture of H₂@**5** (107 mg, 0.0988 mmol) and *m*-chloroperbenzoic acid (34 mg, 0.20 mmol) in 200 mL of toluene was stirred at room temperature for 13 h under nitrogen atmosphere. The solvent was evaporated under reduced pressure, and the residual brown solid was washed twice with 50 mL of methanol and dried under vacuum to give H₂@**6** (106 mg, 0.0977 mmol, 99%) as a brown solid.

H₂@6: IR (KBr) ν 1746 (C=O), 1073 (S=O) cm^{−1}; UV–vis (CHCl₃) λ_{max} (log ϵ) 258 (5.14), 320 (4.70) nm; ¹H NMR (300 MHz, CS₂–CD₂Cl₂ (5:1)) δ 8.63 (m, 1H), 8.32 (m, 1H), 8.26–8.23 (m, 2H), 8.05 (m, 1H), 7.68 (m, 1H), 7.42–7.34 (m, 4H), 7.17–7.03 (m, 4H), –6.18 (s, 2H); ¹³C NMR (75 MHz, ODCB-*d*₄) δ 193.61, 187.54, 167.08, 163.54, 155.72, 154.97, 150.41, 149.06, 148.94, 148.21, 148.00, 147.99, 147.96, 147.79, 147.71, 147.68, 147.40, 147.34, 147.32, 147.14, 147.03, 146.96, 146.89, 146.71, 146.44, 146.29, 146.14, 145.35, 144.27, 143.79, 142.89, 142.54, 142.06, 141.82, 141.79, 141.69, 140.86, 140.81, 140.80, 140.62, 140.46, 140.25, 139.94, 139.79, 139.41, 139.11, 139.05, 138.85, 138.59, 138.58, 138.46, 137.46, 136.01, 135.68, 133.56, 133.08 (132.15, 131.36, 131.29, 131.02, 130.80, 128.87, 128.76), 125.84, 125.09, 122.81, 122.75, 75.10, 52.60 (the signals at the range of δ 132.4–126.8 were overlapped with the signals of ODCB-*d*₄); HRMS (+FAB) calcd for C₈₀H₁₆O₃N₂S (M⁺), 1084.0882, found 1084.0929.

Photochemical Desulfurization of H₂@6. A stirred solution of H₂@**6** (52 mg, 0.048 mmol) in 150 mL of toluene in a Pyrex glass flask was irradiated with a xenon lamp (500 W) placed at the distance of 20 cm at room temperature for 17 h under argon atmosphere. After removal of the solvent under reduced pressure, the residual brown solid was subjected to flash column chromatography over silica gel. Elution with CS₂–ethyl acetate (30:1) gave H₂@**7** (21 mg, 0.020 mmol, 42%) as a brown solid, and following elution with CS₂–ethyl acetate (10:1) gave unreacted H₂@**6** (20 mg, 0.018 mmol, 38%).

H₂@7: IR (KBr) ν 1747 (C=O) cm^{−1}; UV–vis (CHCl₃) λ_{max} (log ϵ) 257 (5.09), 324 (4.67) nm; ¹H NMR (300 MHz, CS₂–CD₂Cl₂ (5:1)) δ 8.57 (m, 1H), 8.40 (m, 1H), 8.10–7.99 (m, 3H), 7.82 (m, 1H), 7.40–7.35 (m, 4H), 7.27–7.07 (m, 4H), –5.69 (s, 2H); ¹³C NMR (75 MHz, ODCB-*d*₄) δ 196.45, 189.88, 168.35, 163.06, 149.82, 148.75, 148.62, 148.42, 147.66, 147.52, 147.17, 146.88, 146.51, 146.08, 145.92, 145.59, 145.56, 145.55, 145.50, 145.43, 145.38, 145.16, 145.08, 144.95, 144.92, 144.59, 144.47, 143.95, 143.89, 143.73, 142.98, 142.60, 142.41, 142.15, 141.82, 141.72, 141.33, 140.93, 140.64, 140.33, 140.11, 139.96, 139.94, 139.70, 139.66, 139.61, 139.15, 138.43, 137.55, 137.43, 137.25, 136.28,

136.14, 135.72, 133.56, 133.17 (131.46, 131.01, 130.77), 123.31, 122.79, 75.67, 53.01 (the signals at the range of δ 132.4–126.8 were overlapped with the signals of ODCB-*d*₄); HRMS (+FAB) calcd for C₈₀H₁₇O₂N₂ (MH⁺), 1037.1290, found 1037.1290.

Reductive Coupling of the Two Carbonyl Groups in H₂@7. To a stirred suspension of zinc powder (299 mg, 4.57 mmol) in 10 mL of dry tetrahydrofuran was added titanium(IV) tetrachloride (250 μ L, 2.28 mmol) drop by drop at 0 °C under argon atmosphere, and the mixture was refluxed for 2 h. A 1 mL portion of the resulting black slurry was added to a stirred solution of H₂@7 (49 mg, 0.048 mmol) in 7 mL of ODCB at room temperature under argon atmosphere. After heating at 80 °C for 2 h, the resulting brownish purple solution was cooled to room temperature. Then the solution was diluted with 20 mL of CS₂, and the solution was washed with 50 mL of saturated aqueous solution of NaHCO₃. The organic layer was dried over MgSO₄ and evaporated under reduced pressure to give a residual brown solid, which was then subjected to flash column chromatography over silica gel. Elution with CS₂–ethyl acetate (20:1 by volume) gave H₂@8 (42 mg, 0.042 mmol, 88%) as a brown solid.

H₂@8: IR (KBr) ν 1748 (C=N) cm⁻¹; UV–vis (CHCl₃) λ_{\max} (log ϵ) 262 (5.08), 328 (4.66), 431 (3.33), 532 (3.11) nm; ¹H NMR (300 MHz, CS₂–CD₂Cl₂ (5:1)) δ 8.74 (m, 1H), 8.04–7.92 (m, 2H), 7.80 (m, 1H), 7.72 (m, 1H), 7.48–7.39 (m, 2H), 7.29–7.12 (m, 7H), –2.93 (s, 2H); ¹³C NMR (100 MHz, ODCB-*d*₄) δ 168.39, 165.87, 149.48, 148.76, 148.41, 145.57, 145.55, 145.48, 145.44, 145.26, 144.69, 144.64, 144.57, 144.53, 144.44, 144.30, 144.28, 144.13, 144.12, 144.10, 144.01, 143.97, 143.92, 143.86, 143.75, 143.69, 143.61, 143.55, 143.52, 143.49, 143.47, 143.45, 143.38, 141.63, 141.12, 141.09, 140.98, 140.84, 140.62, 140.49, 140.26, 139.84, 139.25, 138.95, 138.37, 138.31, 137.26, 137.01, 136.89, 136.78, 136.64, 136.63, 135.68, 135.65, 135.46, 135.23, 134.98 (131.46, 131.02, 128.76, 128.68, 128.66, 127.69, 127.64), 125.55, 125.51, 122.86, 73.70, 56.69 (the signals at the range of δ 132.4–126.8 were overlapped with the signals of ODCB-*d*₄); HRMS (+FAB) calcd for C₈₀H₁₇N₂ (MH⁺), 1005.1392, found 1005.1381.

Synthesis of H₂@C₆₀. A powder of H₂@8 (245 mg, 0.244 mmol) lightly wrapped with a piece of aluminum foil was placed in a glass tube (inner diameter 20 mm), which was sealed under vacuum (1 mmHg) and heated with an electric furnace at 340 °C for 2 h. The resulting black solid was completely soluble in CS₂, and the solution was passed through a glass tube packed with silica gel to afford H₂@C₆₀ contaminated with 9% of empty C₆₀ (total weight 118 mg (calculated H₂@C₆₀ 107 mg), 67%) as a brown solid. Analytically pure H₂@C₆₀ was obtained by separation of this product by the use of HPLC on a preparative Cosmosil Buckyprep column (two directly connected columns, 10 mm \times 250 mm, with toluene as a mobile phase; flow rate, 4 mL min⁻¹) after recycling for 20 times (total retention time, 399 min).

H₂@C₆₀: mp > 300 °C; IR (KBr) ν 1429, 1182, 577, 527 cm⁻¹; UV–vis (cyclohexane) λ_{\max} (log ϵ) 212 (5.14), 258 (5.17), 330 (4.67), 405 (3.42), 543 (2.84), 600 (2.80), 622 (2.52) nm; ¹H NMR (300 MHz, ODCB-*d*₄) δ –1.44 (s); ¹³C NMR (75 MHz, ODCB-*d*₄) δ 142.844; HRMS (+FAB) calcd for C₆₀H₂ (M⁺), 722.0157, found 722.0163. Anal. Calcd for C₆₀H₂: C, 99.72; H, 0.28. Found: C, 99.04; H, 0.24.

In a similar way, empty **8** (296 mg) wrapped with aluminum foil was heated in a vacuum-sealed glass tube (1 mmHg) in an electric furnace at 350 °C for 2 h. In the course of the reaction, a yellow-colored oil (10 mg, 3 wt % of **8**) gradually appeared, together with a slight amount of colorless oil (ca. 1 mg, ca. 0.3 wt % of **8**). The yellow oil was a complex mixture containing at least nine components based on the GC analysis, one of which exhibited a peak on mass spectral analyses at *m/z* 282 corresponding to molecular formula Ph₂PyC₃N. The colorless oil consisted of mainly four components based on the GC analysis, and each component exhibited a peak on mass spectral analyses corresponding to 2-cyanopyridine (**11**), diphenylacetylene (**12**), benzonitrile (**13**), and phenyl-(2-pyridyl)acetylene (**14**). The black solid

(277 mg, 94 wt % of the weight of **8**) remained inside the aluminum foil and exhibited an HPLC chart shown in Figure 5.

Solid-State Mechanochemical [2 + 2] Dimerization Reaction of H₂@C₆₀. H₂@C₆₀ (10 mg, 0.014 mmol) and 4-aminopyridine (1.5 mg, 0.016 mmol) were placed in a stainless steel capsule together with a stainless steel milling ball. The capsule was sealed under nitrogen and was vigorously shaken at the speed of 3500 rpm for 30 min by the use of a high-speed vibration mill at room temperature.³⁸ The reaction mixture was dissolved in 4 mL of ODCB, and the solution was subjected to HPLC on a preparative Cosmosil 5PBB column (two directly connected columns, 10 mm \times 250 mm, with ODCB as a mobile phase; flow rate, 3 mL min⁻¹) to give unreacted H₂@C₆₀ (6.9 mg, 0.0095 mmol, 69%) and [2 + 2] dimer (H₂@C₆₀)₂ (3.0 mg, 0.0021 mmol, 30%) as a brown solid.

(H₂@C₆₀)₂: IR (KBr) ν 1463.9, 1425.3, 1187.1, 796.5, 770.5, 762.8, 746.4, 710.7, 706.9, 612.4, 574.7, 561.2, 550.6, 544.9, 526.5, 480.2, 450.3, 417.6 cm⁻¹; ¹H NMR (300 MHz, ODCB-*d*₄) δ –4.04 (s). Reported values for (C₆₀)₂:^{38b} IR (KBr) ν 1463.9, 1425.3, 1188.1, 796.5, 769.5, 761.8, 746.4, 710.7, 705.9, 612.4, 573.8, 560.3, 550.6, 544.9, 526.5, 479.3, 449.4, 418.5. HPLC analysis on a Cosmosil Buckyprep column exhibited a single peak at exactly the same retention time as authentic [2 + 2] dimer (C₆₀)₂, 18.7 min.

Synthesis of Methanofullerene H₂@16. To a solution of H₂@C₆₀ (H₂ content: 2%) (21 mg, 0.029 mmol) and CBr₄ (38 mg, 0.11 mmol) in 20 mL of dry toluene were added diethyl malonate (13 mg, 0.083 mmol) and diazabicyclo[5.4.0]undec-7-ene (DBU) (26 mg, 0.17 mmol), and the mixture was stirred for 1 h at room temperature under argon atmosphere. After removal of the solvent under reduced pressure, the residual brown solid was subjected to flash column chromatography over silica gel. Elution with CS₂ gave unreacted H₂@C₆₀ (2.9 mg, 0.0040 mmol, 14%) and elution with toluene gave H₂@16 (10 mg, 0.012 mmol, 41%) as a brown solid.

H₂@16: IR (KBr) ν 2978, 1745 (C=O), 1429, 1294, 1267, 1236, 1207, 1184, 1095, 1061 cm⁻¹; ¹H NMR (300 MHz, ODCB-*d*₄) δ 4.49 (q, *J* = 6.9 Hz, 2H), 1.37 (t, *J* = 6.9 Hz, 3H), –3.27 (s, 0.02H); HRMS (+FAB) calcd for C₆₇H₁₂O₄ (M⁺), 880.0736, found 880.0720. Reported data for **16**: IR ν 2979, 1745 (C=O), 1428, 1295, 1266, 1234, 1206, 1186, 1095, 1061 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 4.57 (q, *J* = 7.1 Hz, 4H), 1.49 (t, *J* = 7.1 Hz, 6H).⁴⁴

Synthesis of Benzyne Adduct H₂@17. To a solution of H₂@C₆₀ (H₂ content: 7%) (23 mg, 0.032 mmol) and isoamyl nitrite (17 mg, 0.15 mmol) in 40 mL of dry benzene was added anthranilic acid (43 mg, 0.31 mmol), and the mixture was stirred at room temperature under argon atmosphere. After 2 h, the solution was passed through a glass tube packed with silica gel, and the solvent was removed under reduced pressure. The resulting brown solid was then separated by HPLC on the preparative Cosmosil 5PBB column to give unreacted H₂@C₆₀ (7.8 mg, 0.011 mmol, 34%) and H₂@17 (6.8 mg, 0.0085 mmol, 27%) as a brown solid.

H₂@17: IR (KBr) ν 2920, 2849, 1458, 1024 cm⁻¹; ¹H NMR (300 MHz, ODCB-*d*₄) δ 7.91 (m, 2H), 7.65 (m, 2H), –4.30 (s, 0.07H); HRMS (+FAB) calcd for C₆₆H₆ (M⁺), 798.0470, found 798.0499. Reported data for **17**: IR (KBr) ν 2924, 2854, 1458, 1278, 1024 cm⁻¹; ¹H NMR (500 MHz, CD₂Cl₂) δ 8.02 (m, 4H), 7.78 (m, 4H).⁴¹

Synthesis of Pyrrolidinofullerene H₂@18. A solution of H₂@C₆₀ (H₂ content: 8%) (23 mg, 0.032 mmol), *N*-methylglycine (2.8 mg, 0.0032 mmol), and paraformaldehyde (5.0 mg, 0.17 mmol) in 30 mL of dry toluene was refluxed for 15 min. After removal of the solvent under reduced pressure, the residual brown solid was subjected to flash column chromatography over silica gel. Elution with toluene gave unreacted H₂@C₆₀ (8.7 mg, 0.012 mmol, 38%) and H₂@17 (8.9 mg, 0.011 mmol, 36%) as a brown solid.

H₂@18: IR (KBr) ν 2937, 2835, 2779, 1466, 1443, 1427, 1340, 1184, 1163, 1115 cm⁻¹; ¹H NMR (300 MHz, ODCB-*d*₄) δ 4.16 (s,

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4H), 2.84 (s, 3H), -4.64 (s, 0.08H); HRMS (+FAB) calcd for $C_{63}H_9N$ (M^+), 779.0735, found 779.0743. Reported data for **18**: 1H NMR (200 MHz, CS_2-CDCl_3) δ 4.38 (s, 4H), 2.98 (s, 3H).⁴²

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Supporting Information Available: Complete ref 21 and 1H and ^{13}C NMR spectra of $H_2@4$, $H_2@5$, $H_2@6$, and $H_2@7$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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