

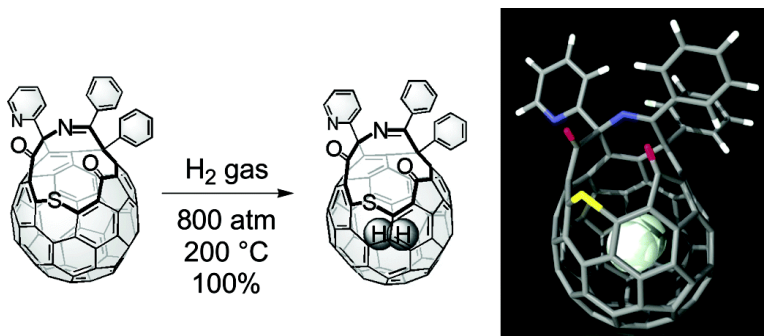
Communication

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100% Encapsulation of a Hydrogen Molecule into an Open-Cage Fullerene Derivative and Gas-Phase Generation of $H_2@C_{60}$

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Endohedral fullerene complexes incorporating noble gases¹ or atomic nitrogen² have been prepared by insertion of these atoms into pristine C_{60} under forced conditions. However, the yields of these materials have been as low as 0.4% to $10^{-5}\%$. If a sufficiently large orifice is opened on a fullerene surface, such atoms would be encapsulated efficiently by insertion through the orifice. In this respect, Rubin et al. prepared an open-cage fullerene derivative **2**³ and succeeded in introducing a He atom and a H_2 molecule in 1.5% and 5% yields, respectively.⁴ To achieve 100% encapsulation of these gas molecules, it is desirable to have a larger orifice on the fullerene surface. We recently synthesized an open-cage fullerene derivative **1**, which has a 13-membered-ring orifice on a C_{60} cage (Figure 1). The derivative **1** has an orifice of 5.64 Å along the long axis and 3.75 Å along the short axis⁵ and is expected to be a better host molecule for small atoms and molecules than **2**. Here we show that encapsulation of a H_2 molecule into **1** does take place to produce the endohedral complex $H_2@1$ in 100% yield, and that $H_2@C_{60}$ can be generated in the gas phase by restoration of the C_{60} cage from $H_2@1$ upon laser irradiation.

To examine the feasibility of insertion of small atoms and molecules through the orifice of **1**, theoretical calculations using hybrid density functional theory (B3LYP/6-31G**//B3LYP/3-21G) were conducted.⁶ The energies required for insertion of He, Ne, H_2 , and Ar into **1** were calculated to be 18.9, 26.2, 30.1, and 97.7 kcal/mol, respectively, considerably lower than the corresponding energies for **2** (24.5, 40.6, 41.4, and 136.3 kcal/mol),⁴ indicating that encapsulation of atoms and molecules as small as He, Ne, and H_2 in **1** is quite promising.

Molecules or molecular systems based on carbon that can freely absorb and eject hydrogen are currently attracting great interest as hydrogen storage materials.⁷ Thus, the encapsulation of H_2 gas into **1** was attempted by treatment of a powder of **1** with a high-pressure of H_2 (800 atm) at 200 °C in an autoclave. After 8 h, formation of the endohedral complex $H_2@1$ without any decomposition of **1** was confirmed by HPLC and ¹H NMR, as described below.

First, the HPLC analysis (Buckyprep/toluene) showed a single peak at exactly the same retention time as that for **1**. Next, the ¹H NMR spectrum of the resulting material showed a new sharp signal at high field, δ -7.25 ppm, in addition to the signals for aromatic protons appearing with exactly the same chemical shifts as those for **1** itself (Figure 2). This new signal is assigned to the resonance of the encapsulated H_2 molecule, which is subjected to the strong shielding effect of the fullerene cage. This signal is 1.82 ppm more upfield-shifted than the H_2 signal of $H_2@2$ (δ -5.43).⁴ The value of δ -7.25 is between the ¹H NMR chemical shifts for H_2 inside of **1** calculated using the gauge-invariant atomic orbital approach⁸ by use of the Hartree-Fock method (GIAO-HF/6-311G**//B3LYP/6-31G**) (δ -9.00) and density functional theory (GIAO-B3PW91/6-311G**//B3LYP/6-31G**) (δ -5.76), confirming the strong shielding effect inside of **1**. The integrated relative intensity of the signal was determined to be 2.00 ± 0.02 H by comparison

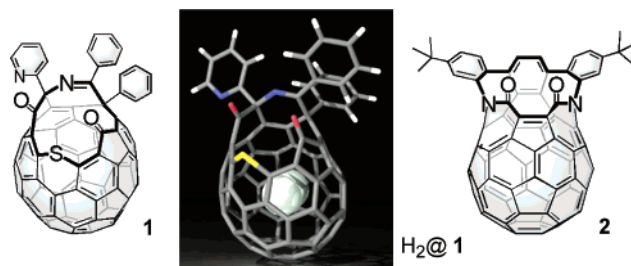


Figure 1. Structures of open-cage fullerene derivatives **1** and **2** and the optimized structure of $H_2@1$ calculated at the B3LYP/6-31G** level of theory. The H_2 molecule is shown as a space-filling model, and the host molecule is shown as a stick model.

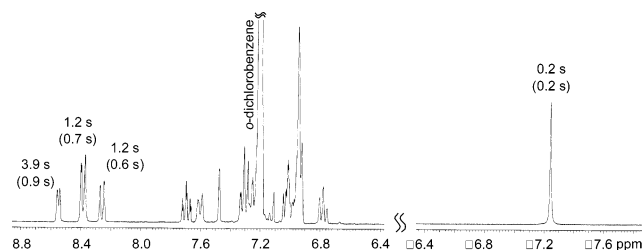


Figure 2. ¹H NMR spectrum (300 MHz, *o*-dichlorobenzene-*d*₄) of $H_2@1$ together with the values of the spin-lattice relaxation time T_1 obtained for a vacuum-sealed sample for some selected signals. In parentheses are shown the T_1 values obtained for the oxygen-saturated sample.

with the intensities of well-resolved aromatic-proton signals at δ 8.55 (1 H), 8.38 (2 H), and 8.26 (1 H), clearly demonstrating that 100% encapsulation was achieved.

The encapsulation rate was highly dependent on the pressure of H_2 : the yield of $H_2@1$ was 90% under 560 atm of H_2 and 51% under 180 atm of H_2 , with all other conditions the same.

To gain insight about the properties of the H_2 molecule inside of **1**, the spin-lattice relaxation time (T_1) of each proton in the ¹H NMR was measured, using both a solution sealed under vacuum ($<10^{-4}$ Torr) and an oxygen-saturated solution of $H_2@1$ in *o*-dichlorobenzene-*d*₄. The T_1 values for the signals at δ 8.55 (6-pyridyl), 8.38 (2,6-phenyl), and 8.26 (3-pyridyl) were 3.9 s (0.9 s), 1.2 s (0.7 s), and 1.2 s (0.6 s), respectively, which are in the range of normal values for aromatic protons. In sharp contrast, a very short T_1 value of 0.2 s (0.2 s) was obtained for the encapsulated H_2 protons. [The values in parentheses are those obtained from the oxygen-saturated solution.] Generally, T_1 values are sensitive to freedom in the motion of the molecule and to an interaction with paramagnetic species such as O_2 .⁹ The T_1 value for the encapsulated H_2 molecule was found to suffer no influence of oxygen at all, confirming that it is completely isolated from the outside by the fullerene cage. The remarkably short T_1 value observed for this encapsulated H_2 molecule might be ascribed to the interaction with the ¹³C atom(s) in the fullerene cage or to its hindered rotation caused by the cage.¹⁰

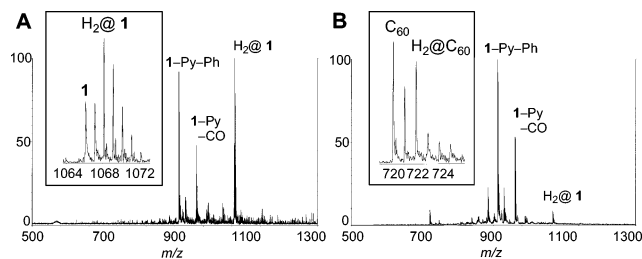


Figure 3. MALDI-TOF mass spectra of $H_2@1$ obtained in the negative ionization mode. (A) Spectrum taken with a laser power slightly above the threshold for ion formation. (B) Spectrum taken with a higher laser power. Insets show the expanded spectra.

No escape of the encapsulated H_2 molecule in $H_2@1$ was observed for the sample solution in *o*-dichlorobenzene- d_4 prepared under vacuum after being kept at room temperature for more than 3 months. However, the H_2 molecule was slowly ejected when the solution was heated above 160 °C, which was monitored as a gradual decrease in the relative intensity of the NMR signal of the encapsulated H_2 with reference to the aromatic proton signals. The rate of ejection monitored at 160, 170, 180, and 190 °C followed first-order kinetics. The Arrhenius plot gave an excellent linear fit, with the pre-exponential factor (A) and the activation energy (E_a) for the escape of H_2 from the cage being $10^{11.8 \pm 0.3}$ and 34.3 ± 0.7 kcal mol $^{-1}$, respectively. The activation parameters at 25 °C were determined as $\Delta G^\ddagger = 35.5 \pm 0.9$ kcal mol $^{-1}$, $\Delta H^\ddagger = 33.4 \pm 0.4$ kcal mol $^{-1}$, and $\Delta S^\ddagger = -7 \pm 2$ cal K $^{-1}$ mol $^{-1}$. Compared with the ΔS^\ddagger value (-17 cal K $^{-1}$ mol $^{-1}$)⁴ reported for the release of He from He@2, the ΔS^\ddagger value in the present work is less negative, although the H_2 molecule is expected to have a more highly ordered arrangement in the transition state upon ejection from **1**. As such, the H_2 molecule inside of **1** is apparently already restricted in motion by the interaction with the cage in the ground state.

Finally, we conducted MALDI-TOF mass spectroscopy on $H_2@1$ using dithranol as a matrix. At a laser power adjusted slightly above the threshold for the ionization of **1**, the molecular ion peak of $H_2@1$ (m/z 1068) was clearly observed, along with a peak for vacant **1** (m/z 1066) formed by escape of the H_2 molecule upon laser irradiation (Figure 3A). In addition, a fragment ion peak due to elimination of pyridyl and carbonyl groups (m/z 960) and a peak due to elimination of pyridyl and phenyl groups (m/z 911) were observed. When a higher laser power was used (Figure 3B), the peak height for the molecular ion decreased and, instead, the formation of C_{60} (m/z 720) was clearly observed. This result demonstrates that a highly modified C_{60} derivative such as **1**, having a large orifice, can regenerate the pristine C_{60} cage by self-restoration through the cleavage of organic addends and through closing of the orifice by itself.

More remarkable is the appearance of a peak at m/z 722, corresponding to $C_{60}H_2$. The intensity of this peak was approximately one-third of that for C_{60} , taking the isotope distribution of C_{60} into consideration. Because exohedral hydrogenated fullerene $C_{60}H_2^{11}$ gave the molecular ion peak not at m/z 722 but at m/z 721 and 720 under the same conditions in a separate experiment, this peak at m/z 722 is assigned to the endohedral complex of C_{60} encapsulating the H_2 molecule, i.e., $H_2@C_{60}$. Thus, it was shown that, upon laser irradiation, generation of $H_2@C_{60}$ is possible in the gas phase by self-restoration of $H_2@1$.

Considering the history of C_{60} , with its discovery by mass spectrometry,¹² macroscopic isolation,¹³ and organic synthesis,¹⁴ the present result can be taken as a promising start for the macroscopic synthesis of $H_2@C_{60}$. The encapsulated H_2 molecule will be an excellent probe to investigate the chemical events taking place at the exterior of the cage and might replace highly expensive 3He , which has been used in NMR studies thus far.^{1c}

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Supporting Information Available: Detailed results of the DFT calculations and procedure for the high-pressure experiments (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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