

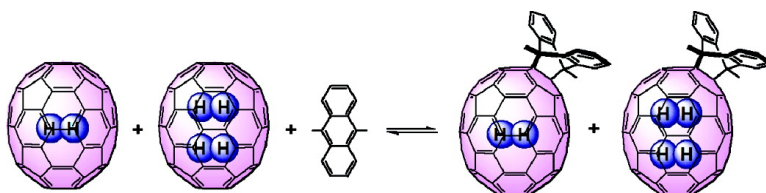
Communication

**Synthesis and Reaction of Fullerene C Encapsulating Two Molecules of H**

Michihisa Murata, Shuhei Maeda, Yuta Morinaka, Yasujiro Murata, and Koichi Komatsu

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## Synthesis and Reaction of Fullerene C<sub>70</sub> Encapsulating Two Molecules of H<sub>2</sub>

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Endohedral fullerene C<sub>60</sub> encapsulating a H<sub>2</sub> molecule (H<sub>2</sub>@C<sub>60</sub>) has become an attractive object for fundamental studies since its organic synthesis<sup>1</sup> by the technique of “molecular surgery”.<sup>2</sup> The encapsulated H<sub>2</sub> has served as a powerful NMR probe to study magnetic properties of ionic C<sub>60</sub> derivatives<sup>3</sup> and to follow chemical reactions taking place at the exterior of the C<sub>60</sub> cage.<sup>4</sup> The synthesis of H<sub>2</sub>@C<sub>60</sub> has also opened up the way to elucidate the intrinsic nature of a single H<sub>2</sub> molecule surrounded by the carbonaceous cage. Thus, Turro and co-workers have disclosed various physical properties of H<sub>2</sub> within C<sub>60</sub> such as an interaction with <sup>1</sup>O<sub>2</sub> outside of the cage,<sup>5</sup> interconversion of ortho-H<sub>2</sub> and para-H<sub>2</sub>,<sup>6</sup> and a spin–lattice relaxation rate.<sup>7</sup> Also an anisotropic rotation of H<sub>2</sub> inside a cage-opened C<sub>60</sub> derivative was studied by the use of solid-state NMR by Levitt and co-workers.<sup>8</sup>

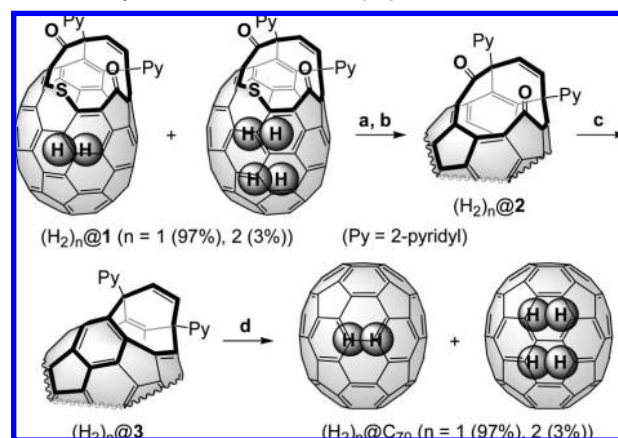
By applying the molecular surgical method to a representative higher fullerene, C<sub>70</sub>, we recently achieved the insertion of one and two molecules of H<sub>2</sub> inside a cage-opened C<sub>70</sub> derivative to provide H<sub>2</sub>@**1** and (H<sub>2</sub>)<sub>2</sub>@**1** and clarified the dynamic behavior of the two molecules of H<sub>2</sub> within the cage.<sup>9</sup> Herein, we report the synthesis of cage-closed C<sub>70</sub> encapsulating one and two H<sub>2</sub> molecules and the reactivity of (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> as compared to H<sub>2</sub>@C<sub>70</sub> in a Diels–Alder reaction with 9,10-dimethylanthracene (DMA).

As shown in Scheme 1, the mixture of H<sub>2</sub>@**1** and (H<sub>2</sub>)<sub>2</sub>@**1** (97:3)<sup>9</sup> was oxidized with *m*-chloroperbenzoic acid (MCPBA) and subjected to subsequent photoelimination of the resulting SO unit to afford 12-membered-ring compounds (H<sub>2</sub>)<sub>n</sub>@**2** (*n* = 1, 2) in 57% yield. Then, two carbonyl groups were coupled by McMurry reaction to give eight-membered-ring compounds (H<sub>2</sub>)<sub>n</sub>@**3** in 61% yield. Finally, thermolysis of (H<sub>2</sub>)<sub>n</sub>@**3** at 400 °C under vacuum for 2 h provided endohedral fullerene (H<sub>2</sub>)<sub>n</sub>@C<sub>70</sub> (*n* = 1, 2) (contaminated with 10% empty C<sub>70</sub>) in 56% as a brown powder.

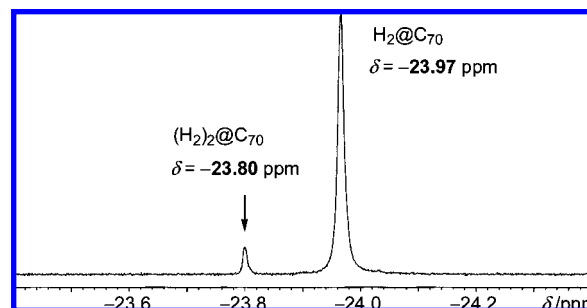
The <sup>1</sup>H NMR spectrum of the crude product from the thermal reaction (Scheme 1, step d) in 1,2-dichlorobenzene-*d*<sub>4</sub> (ODCB-*d*<sub>4</sub>) exhibited a sharp signal for the encapsulated H<sub>2</sub> inside C<sub>70</sub> at such a high field as δ = –23.97 ppm, along with a small signal for (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> at δ = –23.80 ppm with an integrated ratio being 97:6 (Figure 1). This indicates that the molar ratio of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> is the same as that of H<sub>2</sub>@**1** and (H<sub>2</sub>)<sub>2</sub>@**1**. The difference in these chemical shifts (Δδ = 51 Hz) is apparently larger than that between <sup>3</sup>He@C<sub>70</sub> and (<sup>3</sup>He)<sub>2</sub>@C<sub>70</sub> (Δδ = 6 Hz),<sup>10</sup> reported by Saunders and co-workers. The two molecules of H<sub>2</sub> or two atoms of <sup>3</sup>He should be located along the longer axis of the oval cage with a dynamic behavior of the positional exchange. Along this axis there exists a small gradient in the intensity of the magnetic field with the intensity being lower at the center of the C<sub>70</sub> cage.<sup>10</sup> Therefore, the observed difference in Δδ values could be ascribed to the geometry of the two molecules of H<sub>2</sub> of (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub>, which

should be more off-centered than that of the two atoms of <sup>3</sup>He of (<sup>3</sup>He)<sub>2</sub>@C<sub>70</sub> due to the sterics.

### Scheme 1. Synthesis of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub><sup>a</sup>



<sup>a</sup> Reagents and conditions: (a) MCPBA, CS<sub>2</sub>, rt, 10 h, 66%. (b) Visible light, benzene, 40 °C, 5 h, 86%. (c) TiCl<sub>4</sub>, Zn, ODCB/THF, 80 °C, 40 min, 61%. (d) 400 °C, vacuum, 2 h, 56%.



**Figure 1.** <sup>1</sup>H NMR (300 MHz, in ODCB-*d*<sub>4</sub>) signals of the encapsulated H<sub>2</sub> of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub>.

In the <sup>13</sup>C NMR spectrum of H<sub>2</sub>@C<sub>70</sub> in ODCB-*d*<sub>4</sub>, five signals appeared at δ = 150.95, 148.39, 147.71, 145.72, and 131.24 ppm. All of the signals were slightly shifted to downfield as compared to those of empty C<sub>70</sub> in the range Δδ = 0.02–0.07 ppm. It should be noted that these Δδ values are smaller than that between H<sub>2</sub>@C<sub>60</sub> and empty C<sub>60</sub> (Δδ = 0.08 ppm).<sup>1,4a</sup> This indicates that the van der Waals interaction between inner H<sub>2</sub> and outer C<sub>70</sub> is quite minute, as compared to that of H<sub>2</sub>@C<sub>60</sub>, reflecting the larger space inside C<sub>70</sub>. In accord with this, the UV–vis and IR spectra of H<sub>2</sub>@C<sub>70</sub> were almost identical to those of empty C<sub>70</sub>.

We previously reported that H<sub>2</sub>@C<sub>60</sub> and empty C<sub>60</sub> are separable<sup>1,4a</sup> by the use of recycling HPLC on a semipreparative Cosmosil Buckyprep column. Under similar conditions (two directly connected columns; 250 mm length, 20 mm inner diameter; mobile

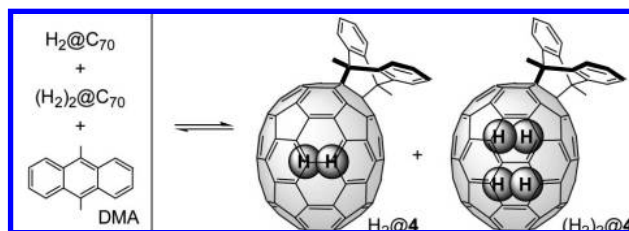
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phase, toluene; flow rate, 6 mL/min; 50 °C), H<sub>2</sub>@C<sub>70</sub> was separated from empty C<sub>70</sub> after 15 recycles with the total retention time being 1081 and 1073 min, respectively. Furthermore, a fraction eluted just after that of H<sub>2</sub>@C<sub>70</sub> was found to contain (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> with increased concentration (18%) together with H<sub>2</sub>@C<sub>70</sub> (82%). By repeating this HPLC purification three times, (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> was completely isolated (<1 mg), which exhibited the correct molecular-ion peak at *m/z* = 844 (C<sub>70</sub>H<sub>4</sub>) upon MALDI-TOF mass spectrometry.

**Scheme 2.** Diels–Alder Reaction of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> with DMA in ODCB-*d*<sub>4</sub>



**Table 1.** Equilibrium Constants  $K_1$  and  $K_2$  and Free Energy Differences  $\Delta G_1$  and  $\Delta G_2$  for Addition of DMA to H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> in ODCB-*d*<sub>4</sub> at 30, 40, and 50 °C

		<i>T</i> (°C)	30	40	50
H <sub>2</sub> @C <sub>70</sub>	$K_1$ (M <sup>-1</sup> )		364	177	88.4
	$\Delta G_1$ (kcal/mol)		-3.55	-3.22	-2.88
(H <sub>2</sub> ) <sub>2</sub> @C <sub>70</sub>	$K_2$ (M <sup>-1</sup> )		296	143	74.7
	$\Delta G_2$ (kcal/mol)		-3.43	-3.09	-2.77

Although the interaction between the encapsulated H<sub>2</sub> and C<sub>70</sub> cage is quite minute for H<sub>2</sub>@C<sub>70</sub>, there is still a possibility that a difference in chemical reactivity of the outer cage becomes appreciable when two molecules of H<sub>2</sub> are incorporated inside the cage. To clarify this, we investigated the Diels–Alder reaction of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> with DMA: the addition of DMA to C<sub>70</sub> is known to occur reversibly at room temperature (Scheme 2).<sup>11</sup> Thus, a solution of a mixture of H<sub>2</sub>@C<sub>70</sub>, (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub>, and C<sub>70</sub> (molar ratio, 70:2:28; total concentration, 13.8 mM) and DMA (6.11 mM) in ODCB-*d*<sub>4</sub> was prepared.<sup>12</sup> The NMR spectrum exhibited new signals for the encapsulated H<sub>2</sub> of monoadducts H<sub>2</sub>@4 and (H<sub>2</sub>)<sub>2</sub>@4 at  $\delta$  = -22.22 and -21.80 ppm, respectively,<sup>13</sup> in addition to the H<sub>2</sub> signals of unreacted H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub>. The equilibrium constants at 30, 40, and 50 °C were determined based on the intensity of the NMR signals of the encapsulated H<sub>2</sub> and the concentration of unreacted DMA.<sup>13</sup> Table 1 summarizes the equilibrium constants  $K_1$  and free-energy difference  $\Delta G_1$  for the addition of DMA to H<sub>2</sub>@C<sub>70</sub>, together with  $K_2$  and  $\Delta G_2$  for that to (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub>. As shown, the  $K_2$  value is smaller than the  $K_1$  value by more than 15% at each temperature, demonstrating the “apparently” decreased reactivity of (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> toward DMA. The van’t Hoff plot of  $\ln K_1$  or  $\ln K_2$  versus  $1/T$  gave excellent linear fits and provided  $\Delta H_1$  and  $\Delta H_2$  as  $-13.8 \pm 0.1$  and  $-13.4 \pm 0.2$  kcal/mol, respectively, and  $\Delta S_1$  and  $\Delta S_2$  as  $-33.7 \pm 0.3$  and  $-32.9 \pm 0.6$  cal/mol·K, respectively.<sup>14</sup>

As a related study, Saunders and co-workers reported the decreased reactivity of <sup>129</sup>Xe@C<sub>60</sub> to the addition of DMA as compared to that of <sup>3</sup>He@C<sub>60</sub>.<sup>15</sup> The encapsulated Xe atom was

suggested to have substantial interaction with C<sub>60</sub> and change the electron distribution of C<sub>60</sub>.<sup>15</sup> Thus, we conducted theoretical calculations for H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> using the MPWB1K functional with the 6-31G(d,p) basis set.<sup>16,17</sup> It was shown that the long axis of the C<sub>70</sub> cage of (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> is elongated only by 0.02 Å, while the short axis is shortened by 0.02 Å, as compared to those of H<sub>2</sub>@C<sub>70</sub>. Also, the energy levels of the frontier orbitals of H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> are almost identical. However, the encapsulation of two molecules of H<sub>2</sub> into C<sub>70</sub> is shown to be exothermic by -9.3 kcal/mol after BSSE correction. This stabilization energy of (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> is higher than that of H<sub>2</sub>@C<sub>70</sub> (-6.9 kcal/mol), indicating more interaction is present between two molecules of H<sub>2</sub> and the C<sub>70</sub> cage. Hence, it would be also reasonable to ascribe the observed difference in reactivity between H<sub>2</sub>@C<sub>70</sub> and (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> to the increased electron density on the exterior of the cage.

In conclusion, we have synthesized and characterized new endohedral fullerene C<sub>70</sub> encapsulating one and two molecules of H<sub>2</sub> by the molecular surgical method. Although the interaction between H<sub>2</sub> and C<sub>70</sub> is minute, (H<sub>2</sub>)<sub>2</sub>@C<sub>70</sub> showed smaller  $\Delta G$  values concerning the Diels–Alder reaction with DMA as compared to that to H<sub>2</sub>@C<sub>70</sub>.

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**Supporting Information Available:** Experimental procedures, spectroscopic data, optimized geometries of new compounds, and data for monitoring the equilibrium reaction. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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