

## CHEMISTRY

## Isolation of the simplest hydrated acid

Rui Zhang, Michihisa Murata, Atsushi Wakamiya, Takafumi Shimoaka, Takeshi Hasegawa, Yasujiro Murata\*

Dissociation of an acid molecule in aqueous media is one of the most fundamental solvation processes but its details remain poorly understood at the distinct molecular level. Conducting high-pressure treatments of an open-cage fullerene  $C_{70}$  derivative with hydrogen fluoride (HF) in the presence of  $H_2O$ , we achieved an unprecedented encapsulation of  $H_2O\cdot HF$  and  $H_2O$ . Restoration of the opening yielded the endohedral  $C_{70}s$ , that is,  $(H_2O\cdot HF)@C_{70}$ ,  $H_2O@C_{70}$ , and  $HF@C_{70}$  in macroscopic scales. Putting an  $H_2O\cdot HF$  complex into the fullerene cage was a crucial step, and it would proceed by the synergistic effects of “pushing from outside” and “pulling from inside.” The structure of the  $H_2O\cdot HF$  was unambiguously determined by single crystal x-ray diffraction analysis. The nuclear magnetic resonance measurements revealed the formation of a hydrogen bond between the  $H_2O$  and HF molecules without proton transfer even at 140°C.

## INTRODUCTION

One of the most important chemical processes is dissociation of a Brønsted acid in aqueous media accompanied by proton transfer from the acid to  $H_2O$  molecules and solvation of the charged fragments (1). This fundamental event plays a key role in myriad chemical reactions and biological phenomena. However, the detailed mechanism of acid dissociation (2, 3) and the nature of protons in an aqueous environment (4, 5) are rather complex, and still remain to be revealed at the distinct molecular level. Hydrogen fluoride (HF) is the smallest acid and has been studied well, mostly in the gas phase, both theoretically and experimentally (6). One extensively discussed issue on HF is the minimum number of  $H_2O$  molecules that is necessary to solvate an HF molecule resulting in the formation of the solvent-shared ion pair  $[H_3O^+(H_2O)_nF^-]$  (3, 7, 8). However, the central obstacle to resolution of this subject includes the difficulty of preparation of any of the possible  $HF\cdot(H_2O)_n$  complexes in a pure form with definite components. This is because the high reactivity of HF and the strong hydrogen bond affinity of  $H_2O$  often result in the formation of many types of oligomers, which are in equilibrium with others, rendering their separation and isolation almost impossible (9). To understand this fundamental process, it is highly desirable to construct an ideal system that can elucidate the intrinsic nature of the hydrated HF molecule.

To isolate reactive chemical species, the compounds should be located in an inert atmosphere, preventing interaction and/or reaction from the outer environments. These subnano-sized environments can be found inside fullerenes, which are spherical carbon clusters having a hollow cavity. Very reactive chemical species such as metal ions (10, 11), metal clusters (12), and a nitrogen atom (13) have thus far been encapsulated inside fullerenes. These well-defined supramolecular systems have provided opportunities to study the physical and chemical properties of the encapsulated species at the molecular scale and to use them as functional materials (14). However, selectivity in encapsulated species in addition to fullerene cages are difficult to control because of the reliance of most production methods on harsh conditions (12, 14). In contrast, the “molecular surgery” approach can produce molecule-encapsulating fullerenes with almost-perfect selectiv-

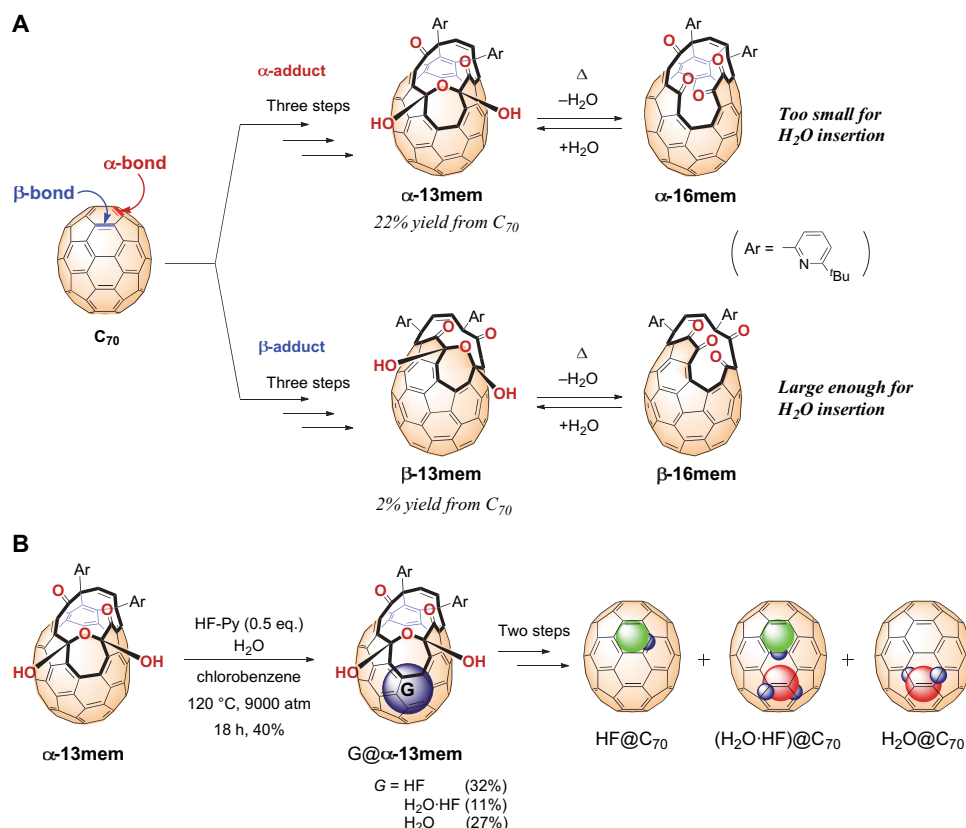
ities under mild conditions in solution (15). Using this method, endohedral  $C_{60}$  encapsulating a single molecule of  $H_2$  (16), He (17),  $H_2O$  (18), and HF (19) was synthesized.

Molecular surgery can also be applied to fullerene  $C_{70}$  despite difficulties in characterization of products due to low symmetry. Reflecting the larger inner space in  $C_{70}$  compared to  $C_{60}$  (20, 21), two small molecules were introduced inside open-cage  $C_{70}$  derivatives to afford the corresponding doubly encapsulating endohedral  $C_{70}s$  after restoration of the cage, that is,  $(H_2)_2@C_{70}$  (22) and  $(H_2O)_2@C_{70}$  (23), respectively. Previously, we reported two open-cage  $C_{70}$  derivatives,  **$\alpha$ -13mem** (24) and  **$\beta$ -13mem** (Fig. 1A) (23), both having a 13-membered ring opening with the same functional groups. These compounds were synthesized by a three-step reaction starting from the addition of a pyridazine derivative to the  $\alpha$ - and  $\beta$ -bonds of  $C_{70}$ , with total yields of 22 and 2%, respectively. Both openings were enlarged in situ into the 16-membered ring as their  $C_{60}$  analog (18). The opening of  **$\alpha$ -16mem** is smaller than that of  **$\beta$ -16mem**, evidenced by the fact that only a trace amount of  $H_2O$  was introduced inside  **$\alpha$ -16mem**, whereas an  $H_2O$  molecule was entrapped almost quantitatively inside  **$\beta$ -16mem**. Density functional theory (DFT) calculations also supported the smaller size of  **$\alpha$ -16mem** (23). Taking advantage of the efficient synthetic yield of  **$\alpha$ -13mem**, we envisioned that  **$\alpha$ -13mem** would be more suitable as a starting material for novel endohedral  $C_{70}s$ . Because the size of HF is smaller than that of  $H_2O$  (25), we studied encapsulation of HF into  **$\alpha$ -13mem** with initial intention to synthesize  $HF@C_{70}$ . Here, we report facile synthesis of  $HF@C_{70}$ , as well as unprecedented formation of  $(H_2O\cdot HF)@C_{70}$  and  $H_2O@C_{70}$ , using  **$\alpha$ -13mem** as a key compound despite the small size of the opening for the insertion of  $H_2O$ .

As shown in Fig. 1B, after optimization of the conditions (vide infra), the high-pressure treatment of  **$\alpha$ -13mem** in the presence of 0.5 equivalence of 70% (w/w) HF in pyridine (HF-Py) (26) and a trace amount of water was conducted in chlorobenzene under 9000 atm at 120°C for 18 hours to afford guest-encapsulating  **$\alpha$ -13mem** ( $G@$ - **$\alpha$ -13mem**;  $G = HF, H_2O\cdot HF,$  and  $H_2O$ ) in 40% isolated yield after purification with column chromatography. The filling factors of the guests inside  **$\alpha$ -13mem** were determined by the proton nuclear magnetic resonance ( $^1H$  NMR) analysis: 32%  $HF@$ - **$\alpha$ -13mem**, 11%  $(H_2O\cdot HF)@$ - **$\alpha$ -13mem**, 27%  $H_2O@$ - **$\alpha$ -13mem**, and 30% empty  **$\alpha$ -13mem**, respectively. After collecting the products from several batches, closing of  $G@$ - **$\alpha$ -13mem** via two-step reactions, without considerable loss of the encapsulated species, gave the corresponding endohedral  $C_{70}s$ , that is, expected

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan.

\*Corresponding author. Email: yasujiro@scl.kyoto-u.ac.jp



**Fig. 1. Molecular surgery for the synthesis of endohedral fullerene  $C_{70}$ s.** (A) Two open-cage  $C_{70}$  derivatives  $\alpha$ -13mem and  $\beta$ -13mem obtained from the initial addition of a pyridazine derivative to the  $\alpha$ -bond and  $\beta$ -bond of  $C_{70}$  followed by stepwise cleavages of the C=C double bonds. The openings of  $\alpha$ -13mem and  $\beta$ -13mem are enlarged in situ by dehydration to afford  $\alpha$ -16mem and  $\beta$ -16mem. The opening size of  $\alpha$ -16mem is too small for  $H_2O$  insertion, whereas that of  $\beta$ -16mem is large enough. (B) Insertion of the guest molecules ( $G = HF, H_2O \cdot HF, \text{ and } H_2O$ ) into  $\alpha$ -13mem and synthesis of  $HF@C_{70}, (H_2O \cdot HF)@C_{70}, \text{ and } H_2O@C_{70}$  by closure of the opening via two-step reactions.

$HF@C_{70}$ , and unprecedented  $(H_2O \cdot HF)@C_{70}$  and  $H_2O@C_{70}$  (figs. S8 to S15).

We confirmed that HF encapsulation into  $\alpha$ -16mem did not take place in chlorobenzene under ambient pressure at 110°C, in contrast to the case for the open-cage  $C_{60}$  (25). Thus, the high-pressure conditions were found to be critical, where the guest species are forced to be “pushed from outside” of the opening of  $\alpha$ -16mem. The experimental conditions and results are summarized in Table 1. Upon checking the time dependence (entries 1 to 4), the filling factor of HF appeared to almost reach a plateau after 14 hours, whereas that of  $H_2O \cdot HF$  increased slowly and that of  $H_2O$  was developed rapidly at around 14 hours. These observations suggested stepwise formation of  $G@$ - $\alpha$ -16mem, that is,  $HF@$ - $\alpha$ -16mem followed by  $(H_2O \cdot HF)@$ - $\alpha$ -16mem and then  $H_2O@$ - $\alpha$ -16mem. To prevent a high degree of decomposition of the starting materials and the products, a reduced amount of HF-Py at slightly higher temperature gave the better chemical yield of  $G@$ - $\alpha$ -13mem (entry 5). As described previously by Zhang *et al.* (23, 24),  $H_2O$  encapsulation did not occur in the absence of HF (entry 6), showing only that pushing from outside was not an effective method of inserting  $H_2O$  inside  $\alpha$ -16mem. Among the products obtained from entries 1 to 5,  $(HF)_2@$ - $\alpha$ -13mem and  $(H_2O)_2@$ - $\alpha$ -13mem were not detected.

Our experiments considered the insertion mechanisms of HF,  $H_2O \cdot HF$ , and  $H_2O$  (as shown in Fig. 2). Because the size of the opening of  $\alpha$ -16mem, which was generated in situ from  $\alpha$ -13mem by eliminat-

ing a water molecule from the bis(hemiketal) moiety, is not large enough for water to pass through, insertion of a smaller HF initially takes place by pushing from outside to give molecular complex A. In earlier work, Gan *et al.* (27) reported that encapsulated  $H_2O$  inside an open-cage  $C_{60}$  was pulled out by attractive interaction with fluorine atom being present outside the opening, resulting in the release of the  $H_2O$ . Taking into consideration the similar attractive interaction of the encapsulated HF and the  $H_2O$  near the opening, the  $H_2O$  should be introduced into  $\alpha$ -16mem by the assist of “pulling from inside,” shown as B, to yield C. Then, positional exchange of the lower HF and the upper  $H_2O$  occurs to afford D. DFT calculations at the M06-2X/6-31G(d) level showed that the required energy for the positional exchange of the HF and  $H_2O$  in C is 20.8 kcal/mol (tables S3 to S5), which should be possible to occur under the applied conditions. Finally, the resulting HF near the opening escapes to form E. During the cooling process, addition of a water molecule regenerates the  $\alpha$ -13mem cage to furnish  $G@$ - $\alpha$ -13mem.

Because of the complexities in the structures of  $H_2O$  clusters and hydrated HF, it is very difficult to evaluate energy profiles including A, B, D, and E by DFT studies. In the case of the gas-phase stabilization energy calculated at the MP2/6-311++G(3pd,3df) level,  $H_2O \cdot HF$  gains more energy (7.3 kcal/mol) than HF dimer (3.9 kcal/mol) and  $H_2O$  dimer (3.8 kcal/mol) (tables S8 to S15). This stability is considered to play an important role for the formation of C. However, we needed to study another possibility that the presence of an acid would change

the solvated structures of HF and H<sub>2</sub>O before encapsulation to result in facile encapsulation of H<sub>2</sub>O. Although a high-pressure treatment in the presence of HCl-Py, instead of HF-Py, under the same conditions was conducted, the resulting products obtained in 64% isolated yield were found to contain only a small amount of H<sub>2</sub>O@ $\alpha$ -13mem (1.8% filling factor). These results strongly support the hypothesis that both pushing and pulling effects are necessary to achieve encapsulation of H<sub>2</sub>O-HF inside  $\alpha$ -13mem in a remarkably high yield compared with the doubly encapsulating C<sub>70</sub>s reported so far (22, 23).

After closure of the openings (Fig. 1B), the high-performance liquid chromatography (HPLC) analysis of the products displayed three peaks corresponding to empty C<sub>70</sub>, a mixture of HF@C<sub>70</sub> and H<sub>2</sub>O@C<sub>70</sub>, and (H<sub>2</sub>O-HF)@C<sub>70</sub> (as shown in Fig. 3A). The mono-encapsulating HF@C<sub>70</sub> and H<sub>2</sub>O@C<sub>70</sub> appeared at almost the same

retention time regardless of the encapsulated species. In contrast, facile separation of (H<sub>2</sub>O-HF)@C<sub>70</sub> as a pure form was achieved in a preparative scale, showing clear differences caused by the double encapsulation. By the atmospheric pressure chemical ionization mass analysis (APCI MS), we detected (HF)<sub>2</sub>@C<sub>70</sub> before elution of (H<sub>2</sub>O-HF)@C<sub>70</sub>, albeit in only a trace amount (fig. S16).

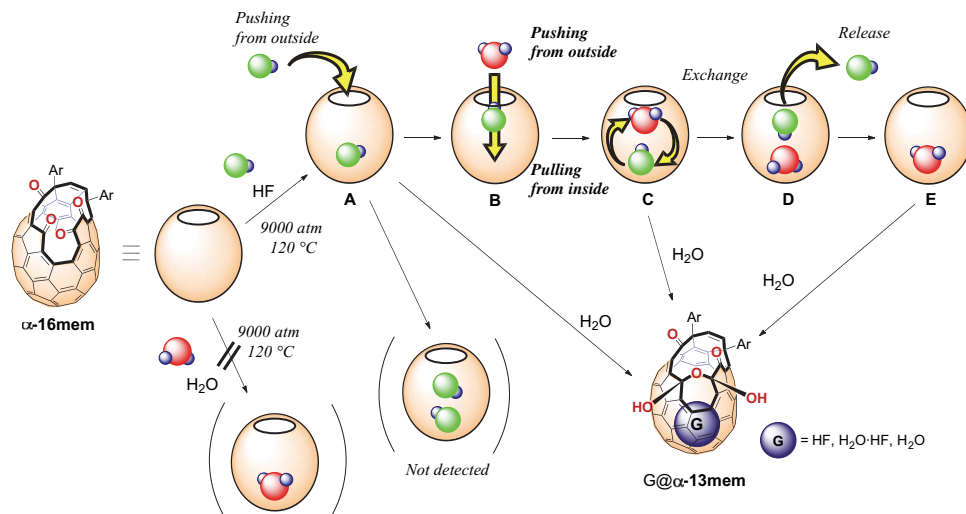
The <sup>1</sup>H NMR analysis is a powerful tool to study the structure and dynamics of the isolated H<sub>2</sub>O-HF. As shown in Fig. 3B, a signal of the singly encapsulated H<sub>2</sub>O at -27.1 parts per million (ppm) [500 MHz; CDCl<sub>3</sub>/CS<sub>2</sub> (1:1), 25°C] coincides with that of our previous report for H<sub>2</sub>O@C<sub>70</sub> synthesized from different synthetic routes (23), showing strong shielding effects due to C<sub>70</sub> cage (22, 23). A doublet corresponding to the singly encapsulated HF was observed at -25.0 ppm with a coupling constant  $J_{\text{HF}} = 507$  Hz, whose value is almost the same as that of HF@C<sub>60</sub> (19). The <sup>1</sup>H NMR of (H<sub>2</sub>O-HF)@C<sub>70</sub> displayed a singlet at -25.3 ppm corresponding to the H<sub>2</sub>O in addition to a doublet at -17.5 ppm corresponding to the HF. It is noteworthy that both chemical shifts are downfield-shifted compared with those of H<sub>2</sub>O@C<sub>70</sub> and HF@C<sub>70</sub>, indicating more positive charges on the protons due to the formation of a hydrogen bond. The shifted value for the HF ( $\Delta\delta +7.5$ ) is larger than that of the H<sub>2</sub>O ( $\Delta\delta +1.8$ ), demonstrating that this molecular complex adopts the structure H<sub>2</sub>O-HF, in which the oxygen works as a hydrogen bond acceptor, rather than HF-H<sub>2</sub>O, in which the fluorine works as the acceptor. In addition, the smaller value of the coupling constant  $J_{\text{HF}} = 443$  Hz also supports the structure H<sub>2</sub>O-HF, the value being close to those of HF in diethyl ether and dimethyl sulfoxide solutions,  $J_{\text{HF}} = 464$  and 410 Hz, respectively (28). Hence, we concluded that this is the simplest hydrated acid. Upon heating the solution in *ortho*-dichlorobenzene-*d*<sub>4</sub> (ODCB-*d*<sub>4</sub>), no change in the spectral shape was observed even at 140°C, revealing that no proton transfer takes place between the H<sub>2</sub>O and HF on the NMR time scale.

The structure of (H<sub>2</sub>O-HF)@C<sub>70</sub> was unambiguously determined by the single-crystal x-ray diffraction analysis for the crystals containing nickel(II) octaethylporphyrin and solvent molecules, with almost the same unit cell constants as those of empty C<sub>70</sub> (29) and H<sub>2</sub>O@C<sub>70</sub> (23). As shown in Fig. 3D, the O and F atoms of the H<sub>2</sub>O-HF were observed inside the C<sub>70</sub> located on the porphyrin. It is the first example of the x-ray structure for doubly encapsulating C<sub>70</sub>. Here, in contrast to

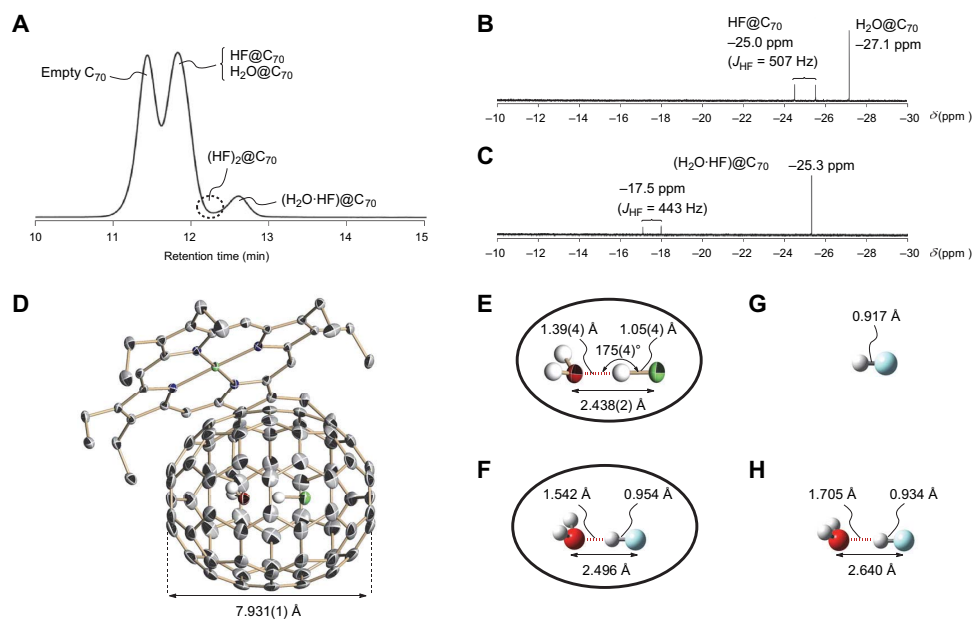
**Table 1. Encapsulation of HF, H<sub>2</sub>O-HF, and H<sub>2</sub>O inside  $\alpha$ -13mem under the high-pressure conditions of 9000 atm in the chlorobenzene solution.**

| Entry | HF-Py (eq.) | Temperature (°C) | Time (hours) | Yield (%) <sup>*</sup> | Filling factor (%) <sup>†</sup> |                     |                  |
|-------|-------------|------------------|--------------|------------------------|---------------------------------|---------------------|------------------|
|       |             |                  |              |                        | HF                              | H <sub>2</sub> O-HF | H <sub>2</sub> O |
| 1     | 1           | 110              | 3            | 34                     | 1.8                             | 0.9                 | 1.2              |
| 2     | 1           | 110              | 6            | 23                     | 24                              | 15                  | 5                |
| 3     | 1           | 110              | 14           | 29                     | 32                              | 16                  | 22               |
| 4     | 1           | 110              | 18           | 20                     | 32                              | 20                  | 33               |
| 5     | 0.5         | 120              | 18           | 40                     | 32                              | 11                  | 27               |
| 6     | 0           | 120              | 18           | 87                     | 0                               | 0                   | 4.4              |

<sup>\*</sup>Isolated yields of the sum of recovered  $\alpha$ -13mem and G@ $\alpha$ -13mem (G = HF, H<sub>2</sub>O-HF, and H<sub>2</sub>O) after purification with a column chromatography on silica gel. <sup>†</sup>The filling factors were determined by comparison of the integral values of the encapsulated species ( $\delta = -18.2$  ppm for HF, -15.6 ppm for H<sub>2</sub>O-HF, and -11.8 ppm for H<sub>2</sub>O) with that of the organic addends ( $\delta = 6.7$  ppm for the olefinic proton at the opening) in the <sup>1</sup>H NMR [500 MHz; CDCl<sub>3</sub>/CS<sub>2</sub> (1:1)] spectra.



**Fig. 2. Insertion mechanism of HF, H<sub>2</sub>O-HF, and H<sub>2</sub>O into  $\alpha$ -16mem with the synergistic effects of pushing from outside by high-pressure conditions and pulling from inside by attractive interaction of HF with the outer H<sub>2</sub>O.**



**Fig. 3. Properties of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$ .** (A) HPLC trace of reaction products after the complete closure of the opening. The HPLC was equipped with the Cosmosil Buckyprep column ( $4.6\phi \times 250$  mm) eluted with toluene at  $50^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz) spectra in  $\text{CDCl}_3/\text{CS}_2$  (1:1) at  $25^\circ\text{C}$  of (B) a mixture of  $\text{HF}@C_{70}$  and  $\text{H}_2\text{O}@C_{70}$ , and (C) pure  $(\text{H}_2\text{O}-\text{HF})@C_{70}$ . (D) Single crystal x-ray structure of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  with thermal ellipsoids at the 50% level, with cocrystallized nickel(II)octaethylporphyrin. Solvent molecules and hydrogen atoms were omitted for clarity. (E) Detailed x-ray structure of the encapsulated  $\text{H}_2\text{O}-\text{HF}$  complex. The H atom between O and F was refined, whereas the other two H atoms were geometrically fixed. (F) Calculated structure of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  at the ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)). Only the encapsulated species were shown. Calculated structures at the MP2/6-311++G(3df,3pd) of (G) a free HF and (H) a free  $\text{H}_2\text{O}-\text{HF}$ .

the x-ray structure of  $\text{H}_2\text{O}@C_{70}$  with dynamic disorder on the position of the O, the O and F in this study did not show any dynamic or positional disorder, demonstrating the perfect alignment of the  $\text{H}_2\text{O}-\text{HF}$ . Reflecting its dense encapsulation, the averaged longer axis of the  $C_{70}$  cage [7.931(1) Å] was elongated by 0.20% compared with that of  $\text{H}_2\text{O}@C_{70}$  [7.915(1) Å]. The distance between the O and F was 2.438(2) Å (Fig. 3E). It should be mentioned that the position of H between O and F was experimentally determined and refined, showing a distance of 1.39(4) and 1.05(4) Å, respectively. Thus,  $\text{H}_2\text{O}-\text{HF}$  was found to adopt such structure as the proton of HF forms a liner hydrogen bond to the oxygen of  $\text{H}_2\text{O}$ , which is in good agreement with the  $^1\text{H}$  NMR results.

To obtain deeper insights, the structure of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  was optimized at the ONIOM (our own n-layered integrated molecular orbital and molecular mechanics)-(MP2/6-311++G(3pd,3df):M06-2X/6-31G(d)) level (Fig. 3F). The calculated structure was found to reproduce well the x-ray structure, showing a distance of 2.496 Å between O and F as well as 0.15% elongation of the cage. Then, an HF molecule and a molecular complex  $\text{H}_2\text{O}-\text{HF}$ , in free forms in a gas phase, were calculated at the MP2/6-311++G(3pd,3df) level (Fig. 3, G and H). Comparison of the calculated structures of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  with free  $\text{H}_2\text{O}-\text{HF}$  demonstrated that the O-F (2.496 Å) and O-H (1.542 Å) distances are shorter by 5.5 and 9.6%, respectively, whereas the H-F bond is longer by 2.1%. These data supported the hypothesis that a contact ion character described as  $\text{H}_3\text{O}^+\cdot\text{F}^-$  slightly appears by compression of the  $\text{H}_2\text{O}$  and HF inside the limited space. The positional exchange of the  $\text{H}_2\text{O}$  and HF was not detected at room temperature because the  $^{13}\text{C}$  NMR of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  displayed nine signals due to its  $C_{5v}$  symmetry (fig. S14), in contrast to the averaged  $D_{5h}$  symmetry of  $\text{H}_2\text{O}@C_{70}$  and  $\text{HF}@C_{70}$  with dynamic motion of the encapsulated species.

The molecular complex  $\text{H}_2\text{O}-\text{HF}$  should have a polarity, which could affect the properties of the outer  $C_{70}$  cage. In the  $^{13}\text{C}$  NMR spectra,

the chemical shifts of the cage carbons near the  $\text{H}_2\text{O}$  are smaller than those near the HF, indicating the polarity of  $(\text{H}_2\text{O}-\text{HF})@C_{70}$ , which was shown by the gauge-independent atomic orbital (GIAO) calculations (fig. S17). However, this polarity was not obvious on reduction potentials determined by cyclic voltammetry (CV) in ODCB, the first reduction potentials for  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  and empty  $C_{70}$  being  $-1.04$  and  $-1.06$  V versus a ferrocene/ferrocenium couple (fig. S18). The ultraviolet-visible (UV-vis) absorption in toluene is almost superimposable with that of empty  $C_{70}$  (fig. S19). The infrared (IR) bands for the HO-H and F-H bonds were not observed, probably due to the shielding effects of the cage, which was the same for  $\text{H}_2\text{O}@C_{60}$  (18),  $\text{HF}@C_{60}$  (19), and  $\text{H}_2\text{O}@C_{70}$  (23). However, interesting suppression of the characteristic IR bands of  $C_{70}$  was observed for  $\text{HF}@C_{70}$  and  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  (fig. S20).

In summary, the simplest hydrated HF was isolated in a confined subnano space by the use of molecular surgical methods. Compared with the doubly encapsulating  $C_{70}$ s reported so far, a high efficiency of the encapsulation was achieved because of the synergetic effects of pushing from outside by the high-pressure conditions and pulling from inside with an attractive interaction of the encapsulated HF with the outer  $\text{H}_2\text{O}$ , which was supported by the stepwise formation of  $\text{HF}@C_{70}$ , followed by  $(\text{H}_2\text{O}-\text{HF})@C_{70}$  and then  $\text{H}_2\text{O}@C_{70}$ . The NMR studies revealed the rigid structure of the  $\text{H}_2\text{O}-\text{HF}$  without hydrogen exchange. The single crystal x-ray analysis and theoretical calculations showed the closer contact of the oxygen with the hydrogen of HF compared with that of free  $\text{H}_2\text{O}-\text{HF}$ .

## MATERIALS AND METHODS

### General

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR measurements were performed with the JEOL JNM-ECA 500 and JNE-ECA 600 instruments. The NMR chemical



shifts were reported in parts per million with reference to residual protons, carbons, and fluorine of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm in  $^1\text{H}$  NMR,  $\delta$  77.0 ppm in  $^{13}\text{C}$  NMR), tetrahydrofuran (THF- $d_8$ ) ( $\delta$  67.57 ppm in  $^{13}\text{C}$  NMR), and hexafluorobenzene ( $\text{C}_6\text{F}_6$ ) ( $\delta$  164.90 ppm in  $^{19}\text{F}$  NMR). The APCI MS spectra were measured on a Bruker micrOTOF-Q II. High-pressure experiments were conducted by using the Hikari Koatsu high-pressure apparatus HR15-B3. The HPLC was performed with a Cosmosil Buckyrep column (4.6 $\phi$   $\times$  250 mm) for analytical purpose and the same columns (two directly connected columns; 20 $\phi$   $\times$  250 mm) for preparative purpose. CV was conducted in an ALS Electrochemical Analyzer Model 620C using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01 M  $\text{AgNO}_3$  reference electrode. UV-vis spectra were recorded with a Shimadzu UV-3150 spectrometer. The IR spectra were collected by using a Thermo Fisher Scientific Magna 550 FT-IR spectrometer equipped with a Harrick Scientific VRA reflection attachment (30). The detector was a liquid nitrogen-cooled mercury-cadmium-telluride detector with a modulation frequency of 60 kHz. The number of accumulation was 1000, and the wavenumber resolution was 4  $\text{cm}^{-1}$ . Fullerene  $\text{C}_{70}$  was purchased from SES Research Co. Triisopropyl phosphite was purchased from Tokyo Chemical Industry Co. Ltd. Hydrogen fluoride pyridine was purchased from Sigma-Aldrich. The open-cage  $\text{C}_{70}$  derivative  $\alpha$ -13mem was prepared according to a previous report (24).

## Computational methods

All calculations were conducted with Gaussian 09 packages (31). The structures were optimized at the M06-2X/6-31G(d), MP2/6-311++G(3df,3pd), and ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)) levels without any symmetry assumptions (32). For the ONIOM method, the MP2 method was applied for the endohedral species and the M06-2X method was used for the fullerene cage. All structures including the stationary states and the transition states were confirmed by the frequency calculations at the same level. The calculated  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts were obtained at the GIAO-B3LYP/6-311G(d,p) level using the optimized structures at the ONIOM or M06-2X methods with a reference of tetramethylsilane calculated at the GIAO-B3LYP/6-311G(d,p)//M06-2X/6-31G(d) level. The isotropic chemical shifts were calculated for protons (32.3196 ppm) and carbons (185.7282 ppm).

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/4/e1602833/DC1>

Supplementary Text

- fig. S1.  $^1\text{H}$  NMR [500 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of a mixture of HF@ $\alpha$ -13mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem,  $\text{H}_2\text{O}$ @ $\alpha$ -13mem, and empty  $\alpha$ -13mem.
- fig. S2.  $^{13}\text{C}$  NMR (151 MHz; THF- $d_8$ ) spectrum of a mixture of HF@ $\alpha$ -13mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem,  $\text{H}_2\text{O}$ @ $\alpha$ -13mem, and empty  $\alpha$ -13mem.
- fig. S3.  $^{19}\text{F}$  NMR [470 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of a mixture of HF@ $\alpha$ -13mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem,  $\text{H}_2\text{O}$ @ $\alpha$ -13mem, and empty  $\alpha$ -13mem.
- fig. S4.  $^1\text{H}$  NMR [500 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of a mixture of HF@ $\alpha$ -13mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem,  $\text{H}_2\text{O}$ @ $\alpha$ -13mem, and empty  $\alpha$ -13mem obtained under the optimized conditions (Table 1, entry 5).
- fig. S5.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ) spectrum of a mixture of HF@ $\alpha$ -8mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -8mem,  $\text{H}_2\text{O}$ @ $\alpha$ -8mem, and empty  $\alpha$ -8mem.
- fig. S6.  $^{13}\text{C}$  NMR (151 MHz;  $\text{CDCl}_3$ ) spectrum of a mixture of HF@ $\alpha$ -8mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -8mem,  $\text{H}_2\text{O}$ @ $\alpha$ -8mem, and empty  $\alpha$ -8mem.
- fig. S7.  $^{19}\text{F}$  NMR (470 MHz;  $\text{CDCl}_3$ ) spectrum of a mixture of HF@ $\alpha$ -8mem, ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -8mem,  $\text{H}_2\text{O}$ @ $\alpha$ -8mem, and empty  $\alpha$ -8mem.
- fig. S8.  $^1\text{H}$  NMR [500 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of a mixture of HF@ $\text{C}_{70}$  and  $\text{H}_2\text{O}$ @ $\text{C}_{70}$  (1:1).
- fig. S9.  $^{19}\text{F}$  NMR [470 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of a mixture of HF@ $\text{C}_{70}$  and  $\text{H}_2\text{O}$ @ $\text{C}_{70}$  (1:1).

- fig. S10. Recycling HPLC profiles for separation of HF@ $\text{C}_{70}$  and  $\text{H}_2\text{O}$ @ $\text{C}_{70}$ .
- fig. S11.  $^1\text{H}$  NMR [151 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of the purified HF@ $\text{C}_{70}$ .
- fig. S12.  $^{13}\text{C}$  NMR [151 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of the purified HF@ $\text{C}_{70}$ .
- fig. S13.  $^1\text{H}$  NMR [500 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of the purified ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- fig. S14.  $^{13}\text{C}$  NMR [151 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of the purified ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- fig. S15.  $^{19}\text{F}$  NMR [470 MHz;  $\text{CDCl}_3/\text{CS}_2$  (1:1)] spectrum of the purified ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- fig. S16. APCI MS spectra (negative ionization mode) of ( $\text{HF}$ ) $_2$ @ $\text{C}_{70}$  and its theoretical isotopic patterns.
- fig. S17. CV of ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$  and empty  $\text{C}_{70}$  in ODCB with 0.1 M *n*-Bu $_4$ NBF $_4$  at a scan rate of 20  $\text{mV s}^{-1}$ .
- fig. S18. UV-vis spectra of ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$  and empty  $\text{C}_{70}$  in toluene.
- fig. S19. IR reflection-absorption spectra on a gold substrate of empty  $\text{C}_{70}$ , HF@ $\text{C}_{70}$ , and ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- fig. S20. The calculated  $^1\text{H}$  NMR for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem' and ( $\text{HF}\text{-H}_2\text{O}$ )@ $\alpha$ -13mem' obtained at the GIAO-B3LYP/6-311G(d,p)//M06-2X/6-31G(d).
- fig. S21. The calculated  $^1\text{H}$  and  $^{13}\text{C}$  NMR for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ , HF@ $\text{C}_{70}$ , and  $\text{H}_2\text{O}$ @ $\text{C}_{70}$ , at the GIAO-B3LYP/6-311G(d,p)//ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)).
- fig. S22. X-ray structure of ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- table S1. Optimized geometry for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem' at the M06-2X/6-31G(d).
- table S2. Calculated  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -13mem' obtained at the GIAO-B3LYP/6-311G(d,p)//M06-2X/6-31G(d).
- table S3. Optimized geometry for ( $\text{HF}\text{-H}_2\text{O}$ )@ $\alpha$ -13mem' at the M06-2X/6-31G(d).
- table S4. Calculated  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for ( $\text{HF}\text{-H}_2\text{O}$ )@ $\alpha$ -13mem' obtained at the GIAO-B3LYP/6-311G(d,p)//M06-2X/6-31G(d).
- table S5. Optimized geometry for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\alpha$ -16mem' at the M06-2X/6-31G(d).
- table S6. Optimized geometry for ( $\text{HF}\text{-H}_2\text{O}$ )@ $\alpha$ -16mem' at the M06-2X/6-31G(d).
- table S7. Transition state for the positional exchange of the inner HF and  $\text{H}_2\text{O}$  inside  $\alpha$ -16mem' at the M06-2X/6-31G(d).
- table S8. Optimized geometry for HF@ $\text{C}_{70}$  at the ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)).
- table S9. Calculated  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for HF@ $\text{C}_{70}$  obtained at the GIAO-B3LYP/6-311G(d,p)//ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)).
- table S10. Optimized geometry for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$  at the ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)).
- table S11. Calculated  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$  obtained at the GIAO-B3LYP/6-311G(d,p)//ONIOM-(MP2/6-311++G(3df,3pd):M06-2X/6-31G(d)).
- table S12. Optimized geometry for HF at the M06-2X/6-31G(d).
- table S13. Optimized geometry for HF at the MP2/6-311++G(3pd,3df).
- table S14. Optimized geometry for HF dimer at the MP2/6-311++G(3pd,3df).
- table S15. Optimized geometry for  $\text{H}_2\text{O}$  at the M06-2X/6-31G(d).
- table S16. Optimized geometry for  $\text{H}_2\text{O}$  at the MP2/6-311++G(3pd,3df).
- table S17. Optimized geometry for  $\text{H}_2\text{O}$  dimer at the MP2/6-311++G(3pd,3df).
- table S18. Optimized geometry for  $\text{H}_2\text{O}\text{-HF}$  at the M06-2X/6-31G(d).
- table S19. Optimized geometry for  $\text{H}_2\text{O}\text{-HF}$  at the MP2/6-311++G(3pd,3df).
- table S20. Transition state for the proton exchange between HF and  $\text{H}_2\text{O}$  at the M06-2X/6-31G(d).
- table S21. Transition state for the proton exchange between HF and  $\text{H}_2\text{O}$  at the MP2/6-311++G(3pd,3df).
- table S22. Crystal data and structure refinement for ( $\text{H}_2\text{O}\text{-HF}$ )@ $\text{C}_{70}$ .
- table S23. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).
- table S24. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ).
- table S25. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).
- table S26. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).
- table S27. Torsion angles ( $^\circ$ ).
- References (33, 34)

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