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# An orifice design: water insertion into C<sub>60</sub><sup>†</sup>

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Using an open-cage C<sub>60</sub> derivative possessing an orifice designed on the basis of computational studies, we have experimentally demonstrated the quantitative encapsulation of H<sub>2</sub>O as well as effective conversion into H<sub>2</sub>O@C<sub>60</sub> in an overall yield remarkably higher than the previously reported methods by ca. 2–5 times.

Soon after the discovery of C<sub>60</sub>,<sup>1</sup> the first endohedral fullerene, K<sup>+</sup>@C<sub>59</sub>B, was proven by Saunders and co-workers in 1991 under mass spectrometric conditions.<sup>2</sup> To date, a number of endohedral fullerenes encapsulating metal ions, nitrides, and oxides, which are so-called metallofullerenes, have been produced by physical approaches, *e.g.*, laser ablation and arc discharge methods.<sup>3</sup> While these approaches could provide endohedral fullerenes albeit only in 0.1% yield, their properties have received growing attention from a wide research area owing to their potential applications in photovoltaic cells (Lu<sub>3</sub>N@C<sub>80</sub> (ref. 4) and Li<sup>+</sup>@C<sub>60</sub> (ref. 5)) and MRI (magnetic resonance imaging) contrast agents (Gd@C<sub>60</sub> and Gd@C<sub>82</sub>).<sup>6</sup> Additionally, DNP (dynamic nuclear polarization) was recently demonstrated by utilizing Gd<sub>2</sub>@C<sub>79</sub>N, which resulted in increased nuclear polarization of <sup>1</sup>H and <sup>13</sup>C spins from electron spins by *ca.* 50% at 1.2 K.<sup>7</sup>

In 1997, Rubin advocated an original concept to produce endohedral fullerenes *via* sequential steps: creation of an opening, insertion of small molecules, and closure of the opening.<sup>8</sup> This molecular surgical synthesis based on organic reactions is conceptually different from physical approaches. Of particular importance is to chemically synthesize endohedral fullerenes encapsulating neutral species that cannot be generated by physical approaches. Since the successful synthesis of the first open-cage C<sub>60</sub> derivative in 1995 by Wudl and co-workers,<sup>9</sup> a number of derivatives with different structural motifs on their orifices have been reported.<sup>10</sup> In the present time, a variety of molecules have been found to be encapsulated inside the fullerene cavities, few of which are able to be restored into the pristine caged structures such as C<sub>60</sub>,<sup>11</sup> C<sub>70</sub>,<sup>12</sup> and C<sub>59</sub>N<sup>13</sup> with retaining the molecule inside. Nevertheless, organic syntheses of such endohedral fullerenes still suffer from low

yielding. To overcome this problem, we focused on an orifice structure which is crucial for trapping a guest molecule as well as for controlling the reactivity of open-cage C<sub>60</sub> derivatives. Since the orifice substructure, *i.e.*, <sup>1</sup>ArC–E=C(<sup>2</sup>Ar)–C(<sup>3</sup>Ar), originates from a heterocyclic azine (Fig. 1) which is used for the creation of an opening by a thermal reaction with C<sub>60</sub>,<sup>11c,14</sup> we considered six hypothetical azines including pyridazines and triazines (**1a–f**) so as to design an orifice suitable both for encapsulation of guest molecules and closure of the opening. Herein, we discuss the molecular design toward efficient synthetic methodology for synthesizing endohedral fullerenes based on theoretical studies as well as experimental demonstration.

With regard to the synthesis of endohedral fullerenes, **INT1** (structure in Table 1) is a key material since it can encapsulate guest molecules such as H<sub>2</sub>O,<sup>11c</sup> H<sub>2</sub>,<sup>15</sup> and HF.<sup>16</sup> More importantly, the orifice with a substructure of tetraketone in **INT1** can be zipped up to reduce its orifice size from 16- to 8-membered ring by the reaction with phosphine and/or phosphite.<sup>11c–e</sup> The plausible mechanism on this closing process was depicted in

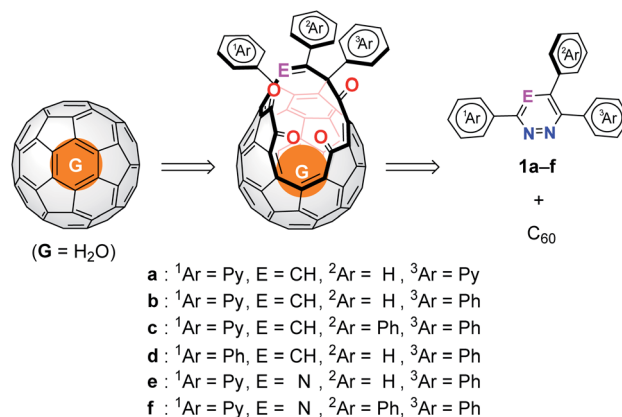
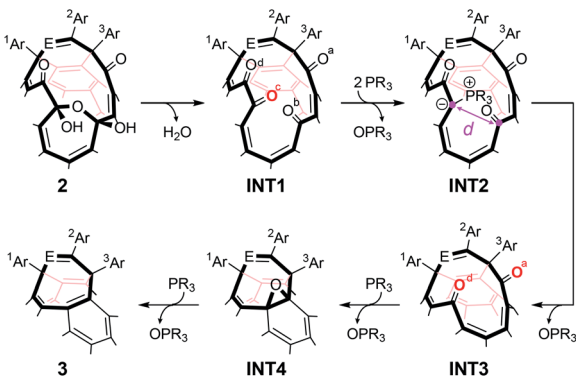


Fig. 1 Retrosynthetic route for endohedral fullerenes (Py: 2-pyridyl group).

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**Table 1** Partial charges  $q_{\text{NPA}}$  obtained by natural population analysis (NPA), stabilization energies  $\Delta\Delta G$ , and interatomic distances  $d$  (B3LYP-D3/6-31G(d) at 298 K)


Addends	$q_{\text{NPA}}$			$\Delta\Delta G(\text{INT2})^a$ (kcal mol <sup>-1</sup> )	$d(\text{INT2})$ (Å)
	O(c)/INT1	O(a)/INT3	O(d)/INT3		
a	-0.465	-0.510	-0.474	0.0	3.35
b	-0.464	-0.502	-0.469	-1.0	3.36
c	-0.467	-0.511	-0.467	+0.1	3.36
d	-0.461	-0.497	-0.469	-1.4	3.34
e	-0.465	-0.501	-0.469	-0.4	3.32
f	-0.464	-0.491	-0.469	-3.3	3.32

<sup>a</sup>  $\Delta\Delta G(\text{INT2}) = \Delta G(\text{INT2}) - \Delta G(\text{INT2a})$  where  $\Delta G(\text{INT2}) = G(\text{INT2}) + G(\text{OPPh}_3) - G(\text{INT1}) - 2G(\text{PPh}_3)$ .

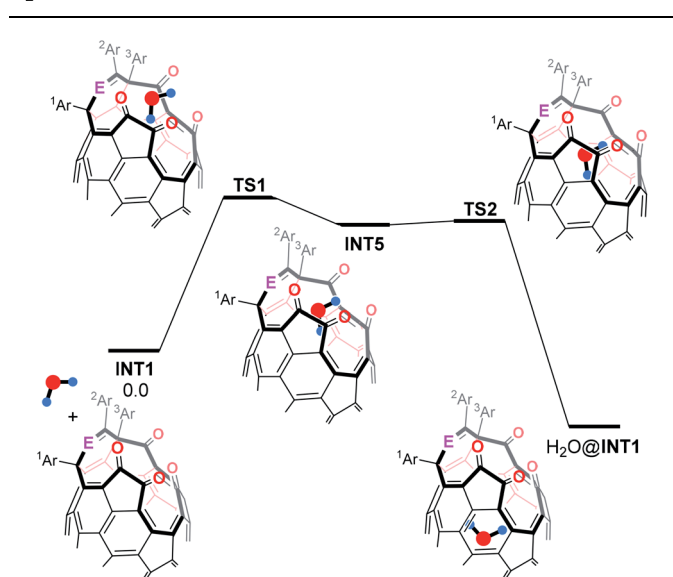
Table 1. Firstly, a water molecule would be eliminated from the 13-membered ring of **2** to afford **INT1**. The ring-closing reaction is then initiated by the nucleophilic attack of  $\text{PR}_3$  to O(c) in **INT1**, leading to the formation of  $\beta$ -oxo-phosphorus ylide **INT2** (ref. 17) which undergoes intramolecular Wittig reaction to give diketo derivative **INT3**.<sup>18</sup> The further nucleophilic attack of another  $\text{PR}_3$  molecule on O(a) and/or O(d) in **INT3** followed by the elimination of  $\text{O}=\text{PR}_3$  furnishes epoxide **INT4**.<sup>19</sup> Finally, deoxygenation of **INT4** by  $\text{PR}_3$  provides **3** possessing an eight-membered-ring opening. Previously, we used **2a'** (which bears 6-*t*-butylpyridin-2-yl groups instead of 2-pyridyl groups) for preparing **INT2a'**. Even though **INT2a'** could be formed at 100 °C for 3 h, **INT2a'** was significantly decomposed during the conversion into **INT3a'** at 120 °C for 8 h, resulting in 52% yield.<sup>20</sup> Thus, open-cage  $\text{C}_{60}$  derivatives should have an orifice which meets criteria including (i) less polarized carbonyl groups in **INT1** and **INT3** to promote nucleophilic attack of  $\text{PR}_3$  to carbonyl O-atoms, (ii) formation of stable ylide **INT2** to suppress undesirable decomposition pathways, and (iii) readily conversion of **INT2** into **INT3**.

To verify electronic and structural properties of **INT1**, **INT2**, and **INT3**, we performed theoretical calculations at the B3LYP-D3/6-31G(d) level of theory at 298 K (Table 1). From natural charges  $q_{\text{NPA}}$  of O(c) in **INT1**, the substituent effect is predicted to be not so significant in the initial step. Contrastingly, the  $q_{\text{NPA}}$  values of O(a) and O(d) in **INT3** are reflected by the opening substructure. Compared with **INT3a** which is a model that we previously synthesized,<sup>11c</sup> both absolute values of  $q_{\text{NPA}}$ , except

for O(a) in **INT3c**, markedly decreased, suggestive of increased reactivity of **INT3** by replacing one of Py groups with a less electron-withdrawing Ph group at the <sup>3</sup>Ar position. Subsequently, we confirmed thermodynamic properties of  $\beta$ -oxo-phosphorus ylide **INT2**, showing considerable stabilization for **INT2f** ( $\Delta\Delta G$  -3.3 kcal mol<sup>-1</sup>) which is superior to others in preventing decomposition. This is probably due to the better orientation for one of Ph groups on the P-atom in **INT2f** via CH/ $\pi$  interaction with the Ph group at the <sup>2</sup>Ar position which is also tightly fixed via an H-bonding with the imine moiety (Fig. S8†). Furthermore, the replacement of an olefin unit with an imine moiety causes decrease in the C(b)⋯C(c) distance by 0.04 Å, implying the positive effect on the intramolecular Wittig reaction in **INT2e** and **INT2f**.

To gain insight into the orifice size of **INT1**, we summarized an energy profile for the  $\text{H}_2\text{O}$ -insertion as shown in Table 2. Interestingly, the  $\text{H}_2\text{O}$ -insertion is predicted to occur stepwisely. Firstly, the  $\text{H}_2\text{O}$  molecule is trapped at a cross-section of the orifice to form **INT5** via **TS1** which is the rate-determining step. Subsequently, the trapped  $\text{H}_2\text{O}$  molecule is encapsulated inside **INT1** via **TS2** to give  $\text{H}_2\text{O}@\text{INT1}$ . Upon seeing activation barriers, the Ph group at the <sup>2</sup>Ar position seems not to have considerable influence on the  $\text{H}_2\text{O}$ -insertion, showing the similar  $\Delta G^\ddagger$  values of 21–22 kcal mol<sup>-1</sup>. The substantial stabilization of **INT1f** by the  $\text{H}_2\text{O}$  encapsulation ( $\Delta G$  -10.4 kcal mol<sup>-1</sup>) would be an advantage to obstruct the escape of the  $\text{H}_2\text{O}$  molecule from the inside. Consequently, the orifice of **2f**, which consists of one Py and two Ph groups with an imine



**Table 2** Changes in Gibbs energies ( $\Delta G$ , kcal mol<sup>-1</sup>) on a profile for H<sub>2</sub>O-insertion into INT1 (B3LYP-D3/6-31G(d) at 298 K)

Addends	TS1	INT5	TS2	H <sub>2</sub> O@INT1
a	+21.6	+17.1	+17.5	-10.0
b	+21.7	+17.2	+17.6	-9.3
c	+21.4	+16.9	+17.2	-8.9
d	+22.0	+17.5	+18.2	-9.7
e	+21.0	+17.3	+17.8	-8.9
f	+21.0	+17.3	+17.8	-10.4

moiety, should be preferable for the synthesis of H<sub>2</sub>O@C<sub>60</sub> both in terms of reactivity on the closing process and capability of encapsulating a H<sub>2</sub>O molecule.

Thereby, we synthesized **2f** by gram-scale reactions including the thermal reaction of C<sub>60</sub> with 5,6-diphenyl-3-(pyridin-2-yl)-1,2,4-triazine (**1f**), photooxygenation,<sup>14</sup> and nucleophilic oxygenation using *N*-methylmorpholine *N*-oxide.<sup>11c</sup> Recently, we found that  $\beta$ -oxo-phosphorus ylide **INT2a'** bearing a PR<sub>3</sub> unit with a cone angle smaller than 140° is significantly hydrolysed in the presence of water.<sup>17</sup> As to the conversion from **INT3a'** to **3a'**, P(O*i*Pr)<sub>3</sub> was previously found to exhibit high performance.<sup>18</sup> For the efficient synthesis of H<sub>2</sub>O@C<sub>60</sub>, we designed one-pot reaction from **2f** to H<sub>2</sub>O@**3f** via three steps commenced with the H<sub>2</sub>O-insertion under high-pressure conditions followed by stepwise conversion of the thus formed H<sub>2</sub>O@**2f** into H<sub>2</sub>O@**INT3f** and then H<sub>2</sub>O@**3f**. The results were summarized in Table 3. The H<sub>2</sub>O-insertion was conducted using 20 mg of **2f** in a mixed solvent system of 1-chloronaphthalene (1-ClNp) and toluene under 9000 atm for 24 h. For the closure of the opening, we used PPh<sub>3</sub> with a cone angle of 145° (entry 1). Different from **2a'** that required totally 11 h for the conversion into **INT3a'**,<sup>20</sup> **2f** was transformed into **INT3f** within 1.5 to 2 h, meeting the criteria (i)–(iii) owing to stable ylide **INT2f** with a shorter C(b)⋯C(c) distance. The further reaction with P(O*i*Pr)<sub>3</sub> at 120 °C for 0.5 h gave desired H<sub>2</sub>O@**3f** in 48% isolated yield with the encapsulation ratio of 98%. Whereas electron-deficient

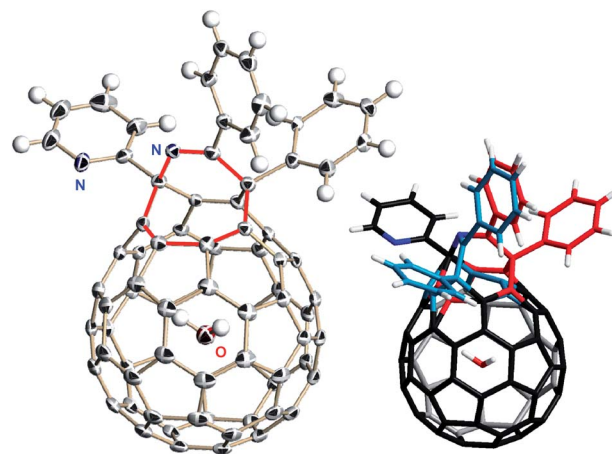
**Table 3** One-pot synthesis of H<sub>2</sub>O@**3f** from **2f**<sup>a</sup>

Entry	Step 1	Step 2	Yield <sup>b</sup>
1	160 °C	PPh <sub>3</sub>	48% (H <sub>2</sub> O: 98%)
2	160 °C	P(2-furyl) <sub>3</sub>	21% (H <sub>2</sub> O: 99%)
3	160 °C	P( <i>p</i> -tolyl) <sub>3</sub>	69% (H <sub>2</sub> O: 98%)
4	140 °C	P( <i>p</i> -tolyl) <sub>3</sub>	67% (H <sub>2</sub> O: 65%)
5	120 °C	P( <i>p</i> -tolyl) <sub>3</sub>	68% (H <sub>2</sub> O: 4%)

<sup>a</sup> Conducted using 20 mg of **2f** in a mixed solvent system of 1-chloronaphthalene (1-ClNp) and toluene. <sup>b</sup> Encapsulation ratio was determined by <sup>1</sup>H NMR or mass spectrum.

phosphine P(2-furyl)<sub>3</sub> gave H<sub>2</sub>O@**3f** in lower yield (21%, entry 2), the reaction employing electron-rich P(*p*-tolyl)<sub>3</sub> resulted in higher yield (69%) with keeping the 98% encapsulation ratio of H<sub>2</sub>O (entry 3). It should be noted that the decreased temperature at the first step drastically influenced on the encapsulation ratio of H<sub>2</sub>O: 98% (160 °C, entry 3), 65% (140 °C, entry 4), and 4% (120 °C, entry 5).

The structure of H<sub>2</sub>O@**3f** was determined spectroscopically. The molecular ion peak was observed at *m/z* 1020.1255 ([H<sub>2</sub>O@**3f**]<sup>-</sup>) in the negative ionization mode by the APCI (atmospheric-pressure chemical ionization) method. The <sup>1</sup>H NMR spectrum of H<sub>2</sub>O@**3f** (CDCl<sub>3</sub>, 500 MHz) clearly showed a singlet signal at  $\delta$  -6.11 ppm corresponding to the



**Fig. 2** Single crystal X-ray structure of H<sub>2</sub>O@**3f** with showing thermal ellipsoids in 50% probability (left) and disordered structures coloured with pink and light blue for major and minor parts, respectively (right). The benzene molecules co-crystallized with H<sub>2</sub>O@**3f** are omitted for clarity.



encapsulated H<sub>2</sub>O molecule, bearing the striking resemblance with that for H<sub>2</sub>O@3a' ( $\delta$  –6.09 ppm<sup>11c,18</sup>). Using H<sub>2</sub>O@3f with an occupation level of 60%, single crystals were grown from the benzene/hexane solution by slow evaporation at 5 °C. The solid-state structure was shown in Fig. 2. The water molecule locates at the centre of the cage and its occupancy was refined to be 0.593(8), being in accordance with the ratio determined by <sup>1</sup>H NMR. A crystallographic disorder was seen in the orifice structure which is identical to two parts with sharing the Py group. Their occupancies were refined to be 0.854(2) for the major part and 0.146(2) for the minor part, respectively.

Based on our previous approach to synthesize H<sub>2</sub>O@C<sub>60</sub> using 2a' in the solid state, the final step has the scale restriction up to 50 mg. Otherwise, the conversion is considerably decreased. For the scalable synthesis of H<sub>2</sub>O@C<sub>60</sub>, we examined one-pot synthesis of H<sub>2</sub>O@C<sub>60</sub> using 160 mg of 2f. As represented in Scheme 1, 2f was firstly subjected to the optimal reaction conditions as entry 3 in Table 3. To the resultant mixture, methanol was added to obtain the crude precipitate containing H<sub>2</sub>O@3f which was further heated at 400 °C under 5 Pa for 2 h, giving H<sub>2</sub>O@C<sub>60</sub> in 6% isolated yield. Considering the high conversion of 2f into H<sub>2</sub>O@3f (Table 3), H<sub>2</sub>O@3f should be mostly decomposed during the final step. To avoid undesirable decomposition pathways, the crude mixture was purified, prior to step 4, by silica gel column chromatography which gave H<sub>2</sub>O@3f (80% yield) together with complex mixture having higher polarity. Since this complex mixture changed into insoluble solid without formation of H<sub>2</sub>O@C<sub>60</sub> under the same conditions as step 4, it might hamper the conversion of H<sub>2</sub>O@3f into H<sub>2</sub>O@C<sub>60</sub>. With H<sub>2</sub>O@3f as a pure form in hand, it was subjected to pyrolytic conditions (Scheme 1). As the results, H<sub>2</sub>O@C<sub>60</sub> was obtained up to 87% yield and the overall yield from 2f reaches to 70% which is remarkably higher than that obtained by our previous approach (15% from 2a')<sup>11c</sup> even when compared with Whitby's variant (40% from 2a').<sup>15</sup>

In summary, we designed the orifice substructure suitable for the synthesis of endohedral fullerenes on the basis of reactivity toward closing processes and encapsulation properties. Among six candidates, the orifice possessing a phenyl imine moiety (f) was expected to have high affinity to phosphines as well as interaction with the encapsulated H<sub>2</sub>O molecule, which is strong enough to prevent its escape from the inside. The thus synthesized open-cage C<sub>60</sub> derivative 2f

demonstrated the effective conversion into H<sub>2</sub>O@3f via one-pot process, showing high yield up to 80% with nearly quantitative encapsulation of H<sub>2</sub>O. The further conversion of H<sub>2</sub>O@3f into H<sub>2</sub>O@C<sub>60</sub> proceeded quite well when H<sub>2</sub>O@3f was used in a pure form. The method demonstrated herein could be applied for a variety of endohedral fullerenes in a practical scale.

## Conflicts of interest

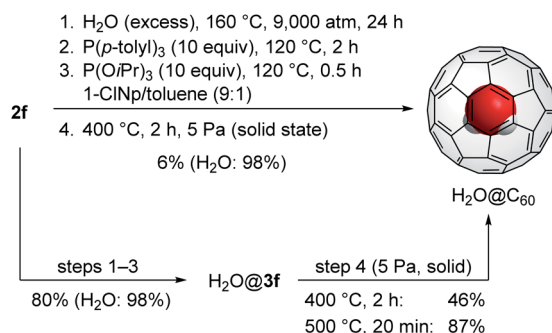
There are no conflicts to declare.

## Acknowledgements

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Scheme 1 Synthesis of H<sub>2</sub>O@C<sub>60</sub> from 2f (160 mg).



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